# AN INVESTIGATION OF THE STRUCTURE OF DIAZO KETONES BY INFRARED SPECTRA

by
Henry Nelson Beck

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Doctoral Committee:

Professor Leigh C. Anderson, Chairman
Instructor James D. O'Rourke
Associate Professor Peter A. S. Smith
Assistant Professor Robert C. Taylor
Professor Ralph A. Wolfe

To my parents and Diane, whose help, encouragement, understanding, and patience have contributed immensely to the successful completion of this thesis.

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# I. INTRODUCTION

The preparation of the first diazo compound in Marburg, Germany, by Peter Griess in the year 1858 opened up one of the largest of the fields of modern organic chemistry. The amount of work that since has been expended in the preparation of new diazo compounds and in the investigation of their uses in organic syntheses and in the field of industrial chemistry is phenomenal. Paralleling this work, and equally amazing, is the very large amount of effort that has been expended in trying to elucidate the structure of the various members of this class of compounds.

The second edition of Webster's New International Dictionary defines the word "diazo" as "a combining form denoting the presence of a group of two nitrogen atoms, $N_2$, in direct union with one hydrocarbon radical and also (usually) with some other group or atom." A chemist might readily foresee the large number of formulations which, all agreeing with the above definition, might be used to designate the structure of a given diazo compound. The problem, of course, is to determine which of the many possible structures is the correct one. The literature reveals many examples of this struggle: the geometric isomeric formulations of Hantzsch for the diazotates versus the structural isomeric formulations of Bamberger and Hodgson and Marsden; the Angeli-Thiele formulation versus the Curtius formulation for the structure of the diazo group; the oxadiazole formulation of Kekule versus the quinone diazide formulation of Wolff for the compounds now called diazo oxides; and the "diazo anhydrides" of Wolff and Nierenstein, the diazo esters of Staudinger, and the diazo ketones of Arndt and Eistert. In addition to the usual problems encountered in structure proof work the diazo chemist must cope with the general instability and, therefore, impurity of the diazo compounds. The optical activity exhibited by the diazo compounds of Noyes was shown by Weissburger to be due to impurities and not to the diazo compounds themselves.

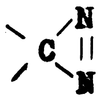
Some of the structure problems of diazo chemistry have been solved and many have not. Our present ideas concerning the structure of diazo compounds have come about not from the results of any one large experiment, but from the accumulation of the data and conclusions of a great many smaller investigations. The following pages present an investigation on diazo ketones which, it is hoped, will be helpful in elucidating their structure. The work consists essentially of two parts: (a) the synthesis of a series of selected diazo ketones and the necessary related compounds, and (b) the recording and interpretation of their infrared spectra in the "triple-bond" and the "carbonyl" regions of the spectrum.

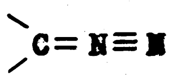
## II. HISTORICAL

### A. Simple Diazo Compounds

The preparation and properties of simple diazo compounds are well known (1,2). Their syntheses have been accomplished by four general preparative methods, the most common of which is the action of base (as potassium hydroxide, sodium isopropoxide, or sodium cyclohexoxide) on a compound of general formula, $RR'CHN(NO)Y$, where Y has been $-C(CH_3)_2CH_2COCH_3$, $-SO_2C_7H_7$, $-CONH_2$, $-COOC_2H_5$, $-COCH_3$, $-COC_6H_5$, and $-C(NH)NHNO_2$, and R and R' have been alkyl or hydrogen. Bis-diazoalkanes have been prepared from compounds with general formula, $(CH_2)_n-[N(NO)-Y]_2$, where n has been 2 to 8 (3). The preparation of diazo compounds of higher molecular weight by the oxidation of the corresponding hydrazone is illustrated by the preparation of diazodiphenylmethane from benzophenone hydrazone. If the diazo compound is sufficiently stable (as is 2-diazo-1,1,1-trifluoroethane) it may be prepared directly from the corresponding amine with nitrous acid. The miscellaneous methods comprising the fourth general preparative method are illustrated by the preparation of diazomethane from chloroform, hydrazine, and base, and by the preparation of diazocyclopentadiene from p-toluenesulfonazide and cyclopentadienyllithium (4).

However, the structure of the diazo group in diazo compounds was in question for many years, and only comparatively recently, after the development of improved physical methods and the introduction of the theory of resonance, has a satisfactory correlation been obtained between the observed data and a suitable structure. Two formulations presented for the diazo group were the Curtius (5) structure in which the carbon and two nitrogen atoms of the diazo group (and of the corresponding hydrazone group as well) formed a ring, I, and


I


II

the straight-chain Angeli-Thiele structure containing pentacovalent nitrogen (6,7), II. Over a period of time preferences were shown for both the Curtius (8-14) and the Angeli-Thiele (13,15-18) formulations as well as for an equilibrium mixture of both forms (19).[a] Langmuir (21) suggested a structure consistent with the Lewis octet theory by replacing the triple bond in the Angeli-Thiele formulation by a double bond. The low dipole moment exhibited by diazo compounds led Sidgwick (22) to the conclusion that either the Curtius formulation was correct or the diazo group existed as a tautomeric mixture of two linear forms, $C=N\rightarrow N$ and $C\leftarrow N\equiv N$; calculations on the known heats of combustion favored the latter hypothesis. These dipole moment measurements together with subsequent electron diffraction (23), ultraviolet (24) and infrared spectral (25-27), and parachor (28) studies are consistent with the now accepted planar, straight-chain, resonance-hybrid structure, III. Mills and Thompson (27) suggest that diazo-

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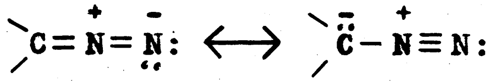
[a] Vid. reference 20.

methane may exist in a tautomeric form which is an isoelectronic analog of hydrazoic acid, $H-\overset{-}{\ddot{C}}=\overset{+}{N}=\ddot{N}-H \leftrightarrow H-C\equiv\overset{+}{N}-\overset{-}{\underset{\cdot\cdot}{\ddot{N}}}-H$.

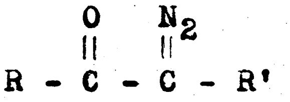


III

## B. Diazocarbonyl Compounds

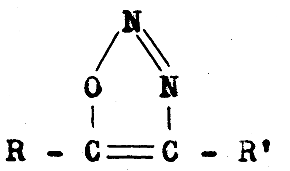
### 1. "Diazo Anhydrides" and Diazo Esters

The introduction of a carbonyl group adjacent to a diazo group in a compound results in a new compound of still greater structural complexity whose physical and chemical properties are radically different from the parent diazo compound. The structures of these diazocarbonyl compounds have been formulated by the 1,2-diazoketone structure, IV, in



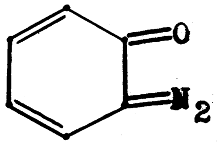
$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{N_2}{\|}}{C}-R'$

IV

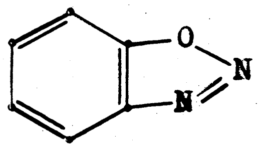


V

which the $N_2$ group has been represented variously by the Angeli-Thiele formulation, the Curtius formulation, and the resonance-hybrid structure; and by the 4,5-disubstituted-1,2,3-oxadiazole structure ("anhydride"), V. The doubts that have existed concerning the structures of these compounds are reflected by the varied nomenclature found in the literature: furodiazoles (29), diazo esters and "diazo anhydrides" (R = alkyl, aryl, and alkoxy; R' = acyl, aroyl, carbalkoxy, carbaryloxy, and hydrogen), and diazo ketones (R = alkyl, aryl; R' = usually hydrogen, also alkyl and aryl). When the diazocarbonyl unit is a part of a carbocyclic ring, VI and VII, the compounds have been called benzo-1,2,3-oxa-



VI



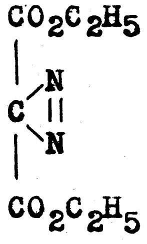
VII

diazoles, diazophenols, quinonediazides, and diazo oxides.

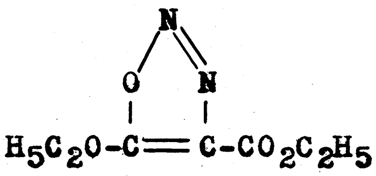
The first diazocarbonyl compound, ethyl diazoacetate, was prepared by Curtius (30) by the reaction of nitrous acid on glycine ethyl ester hydrochloride. The method was extended by Wolff (31-33) for the preparation of "diazo anhydrides" by the action of nitrous acid on the α-amino derivatives of β-ketoesters and β-diketones. Simple diazo compounds are decomposed readily by acids, but diazocarbonyl compounds are much more stable. For instance, ethyl diazoacetate is prepared in weak mineral acid (provided that it is extracted very soon from the acid solution), and the "diazo anhydrides" in which the diazo group is flanked by two carbonyl groups can be prepared in 15-40% sulfuric acid (34, p. 440). A more convenient preparation of diazocarbonyl compounds was the method discovered by Staudinger and coworkers (35,36) in which an acid chloride was added to two moles of a diazoacetic ester, (a).

$$\text{(a)}\quad RCOCl + 2\,N_2CHCO_2R' \longrightarrow RCOCN_2CO_2R' + ClCH_2CO_2R' + N_2$$

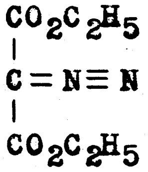
The fact that these diazocarbonyl compounds lacked the characteristic properties of other diazo compounds such as bright color and reactivity towards iodine and especially towards acids induced Wolff to propose the "anhydride" or cyclic formulation, V. The "anhydride" formulation has received but little support (37) and was criticized by Schroeter (14, p. 2348) and by Dimroth (10) who favored an open structure, VIII, rather than a ring structure, IX, for diazomalonic ester.



VIII



IX



$$\begin{array}{c} CO_2C_2H_5 \\ | \\ C=N\equiv N \\ | \\ CO_2C_2H_5 \end{array}$$

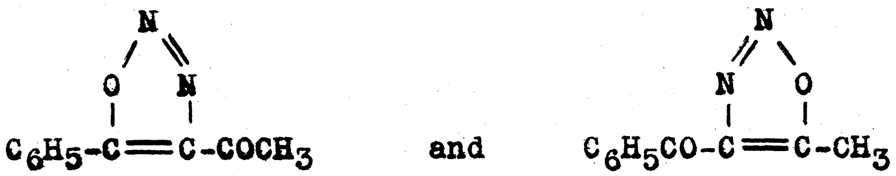
X

Perhaps the greatest opponent of the "anhydride" structure was Staudinger (13,36,38,39) who favored the open structure, X, in which the Angeli-Thiele formulation represented the diazo group. The first of four pieces of evidence that Staudinger (20,38) used against an "anhydride" formulation was a comparison of the observed effect of sodium ethoxide on diazo esters, (b), with the effect observed by Dieckmann (40) on β-ketoesters, (c).

(b) $RCOCN_2CO_2C_2H_5 \xrightarrow{NaOC_2H_5} RCO_2C_2H_5 + CHN_2CO_2C_2H_5$

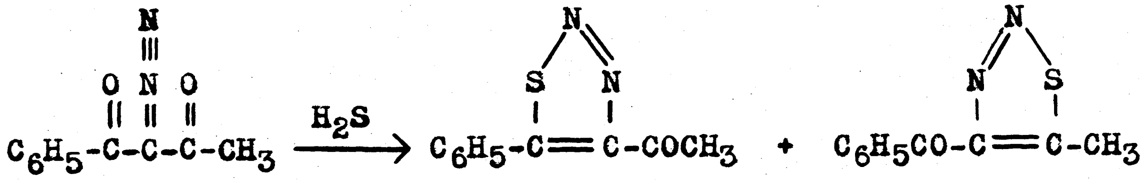
(c) $CH_3COC(CH_3)_2CO_2C_2H_5 \xrightarrow{NaOC_2H_5} CH_3CO_2C_2H_5 + CH(CH_3)_2CO_2C_2H_5$

Second, Wolff (33,41) isolated only one compound and not the two isomers, XI, that might be expected from a compound with structure V in which R is $C_6H_5$- and R' is acetyl; the open chain form, XII, would account for the absence of the unobserved isomers. Third, the fact that Wolff (41,42) had observed the formation of two isomeric 4,5-disubstituted-



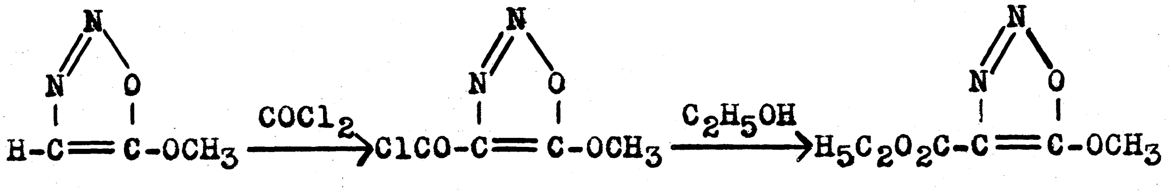
XI

1,2,3-thiadiazoles by the action of hydrogen sulfide on his "diazo anhydrides" could be more readily accounted for by a compound with structure XII than with an "anhydride" structure. Finally, Mächling (13) had sought to prepare two iso-

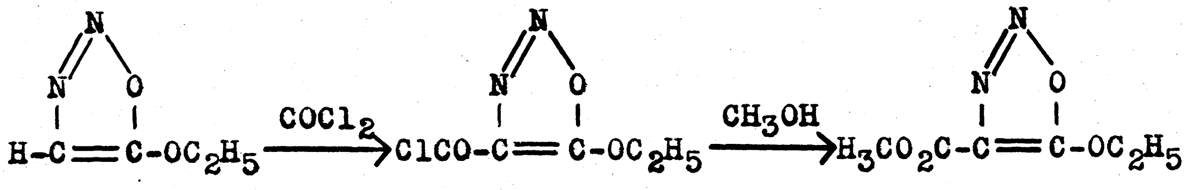


XII

meric "diazo anhydrides" by adding phosgene, respectively, to ethyl diazoacetate and methyl diazoacetate and then esterifying the compounds formed as shown below:

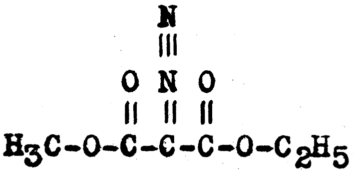


XIII



XIV

Compounds XIII and XIV were identical, thus indicating an open chain formulation, XV, to be more representative of the structure of the product as well as of the starting materials and intermediates.

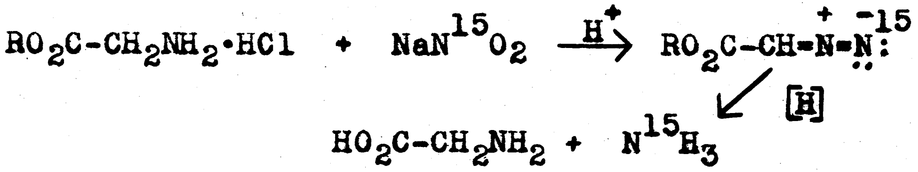


$$H_3C-O-\overset{O}{\overset{\|}{C}}-\overset{\overset{N}{|||}}{\overset{N}{\overset{\|}{C}}}-\overset{O}{\overset{\|}{C}}-O-C_2H_5$$

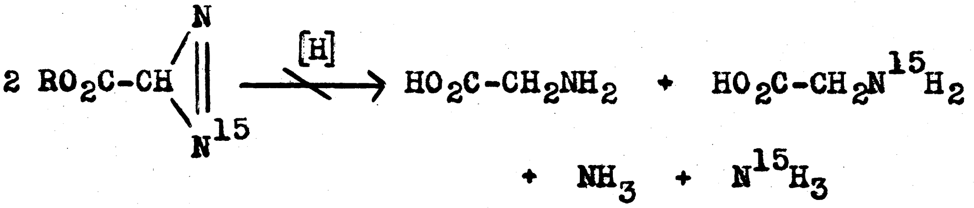
XV

Experiments using isotopic $N^{15}$ have indicated that the diazo group in ethyl diazoacetate has a chain rather than a ring structure, (43). After the diazo ester had been prepared by the action of labeled sodium nitrite on glycine ester hydrochloride it was reduced to glycine and heavy ammonia, (d), the isotopic distribution thus favoring a chain structure. If a ring had existed, a different isotopic distribution would have been found among the products, (e).

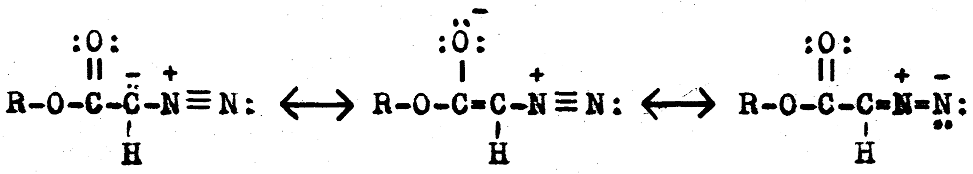
(d)



(e)



Lindemann (12) and von Auwers (18) agreed upon the basis of ultraviolet absorption spectra that the "diazo anhydride" structure was incorrect even though they disagreed upon the structure of the diazo group itself. More recent interpretations in terms of the resonance theory (24,34, p. 440) yield a hybrid structure, XVI.

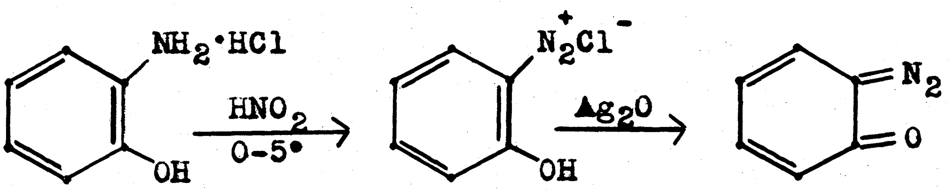


XVI

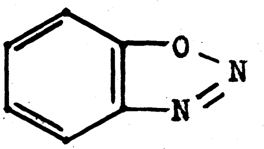
## 2. Diazo Oxides

Another class of diazocarbonyl compounds is the diazo oxides, VI and VII, that are formed when the anion and the hydrogen atom from a hydroxyl group are removed from the diazonium salts of compounds containing a hydroxyl group either ortho or para to the diazonium group. An example is the diazo oxide obtained from o-aminophenol hydrochloride, (f).

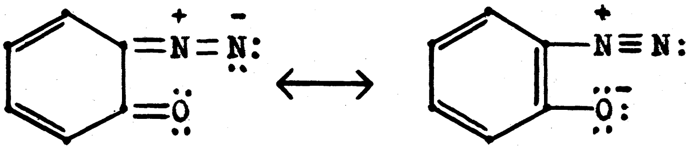
(f)



The structures of the diazo oxides have been in dispute since they were first discovered, five different structures having been proposed (44). The most reasonable structures suggested were the benzo-1,2,3-oxadiazole ring structure, VII, and the quinonediazide resonance hybrid structure,



VII



XVII XVIII

XVII and XVIII. Those that accepted the oxadiazole structure supported it by chemical evidence, the color and absence of the diazonium ion reactions being attributed to the azo link and the easily opened ring (44). Although the ring structure, VII, is a reasonable one to propose for an ortho compound, it is difficult to visualize the long bonds necessary for a similar formulation of the diazo oxides derived from para-hydroxy diazonium compounds. The quinonediazide structure is supported by absorption spectra in that the ultraviolet spectra (45,46) of the diazo oxides resemble those of o- and p-quinones and differ from those of benzo- and naphtho-1,2,3-thiadiazoles and benzo- and naphtho-1,2,3-triazoles which are reported to have ring structures. The resonance hybrid structure is also supported by infrared spectra (47) which shows that the NN bond is between a double and triple bond in character and that the CO bond is somewhat ionic in character. Dipole moment studies (46) were interpreted to indicate that XVII is the principal contributing resonance form.

## 3. Diazo Ketones

Perhaps the most important class of diazocarbonyl compounds from the standpoint of preparative organic chemistry is the one including the diazo ketones (48-50). The preparation, properties, and reactions of diazo ketones were known to Wolff (33,41) who prepared them by the action of cold, dilute base on some of his "diazo anhydrides". However, the practical use of diazo ketones in synthetic work awaited the convenient and efficient method of preparing them that was discovered by Arndt, Eistert, and Partale (51). The preparation, which was similar to the one used by Staudinger (35,36) for making diazo esters, consisted of slowly adding one mole of acid chloride to two moles of stirred diazomethane (51-55) and is represented by equation (g). An acid anhydride has been used instead of the acid chloride (56). This

$$\text{(g)}\quad RCOCl + 2\,CH_2N_2 \longrightarrow RCOCHN_2 + CH_3Cl + N_2$$

method has been used in the preparation of diazo ketones from diazo alkanes other than diazomethane (57-60). A newer method consists of adding a mixture of the acid chloride and the nitroso compound (which is the source of the diazomethane) to a basic solution (61). Although these methods give very high yields of the diazo ketones, they are wasteful of the diazo alkane for one extra mole is needed to absorb the hydrogen halide that is liberated during the preparation. An improved method that requires only one-half as much diazoalkane is one which uses triethylamine to absorb the liberated acid (62,63, also cf. experimental section).

The disputes concerning the mechanism of formation and the structure of the diazo ketones owe their origin to the ease with which Wolff's disputed "diazo anhydride" structure could be applied to them and to the work of Nierenstein and coworkers. Nierenstein studied the reactions of diazomethane with acid chlorides and always obtained phenacyl halides instead of diazo ketones (64-66). For this reason Nierenstein proposed that reaction (h) was the

(h) $RCOCl + CH_2N_2 \longrightarrow RCOCH_2Cl + N_2$

primary reaction taking place. However, a closer examination (67) showed that different products could be obtained depending upon the experimental techniques employed and indicated that the following reactions occur in the order given (48,49,68,69):

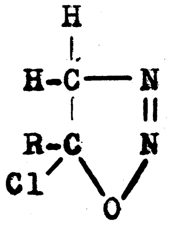
(i) $RCOX + CH_2N_2 \longrightarrow RCOCHN_2 + HX$

(j) $CH_2N_2 + HX \longrightarrow CH_3X + N_2$

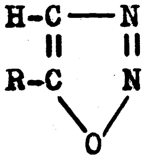
(k)[a] $RCOCHN_2 + HX \longrightarrow RCOCH_2X + N_2$

The initial reaction, (i), is the one between the acid chloride and diazomethane to produce the diazo ketone and the hydrogen halide. The liberated hydrogen halide reacts with any excess diazomethane to give a methyl halide and nitrogen, (j). When no excess diazomethane is present the hydrogen halide reacts with the diazo ketone to give a phenacyl halide and nitrogen, (k). Nierenstein always obtained the phenacyl halide for he added one mole of diazomethane solution to one mole of acid chloride (so no excess diazomethane was ever present) at slightly elevated temperatures, while Arndt, Eistert, Bradley, and Robinson added one mole of acid chloride to two moles of cold diazomethane solution.

Nierenstein (64-66) formulated the reaction between acid chlorides and diazomethane as an extension of the Schlotterbeck reaction (1,2,29,71) between carbonyl compounds and diazomethane and proposed a chlorodihydrofurodiazole, XIX, as initial product and intermediate. Compound XIX then split out hydrogen chloride (instead of



XIX



XX

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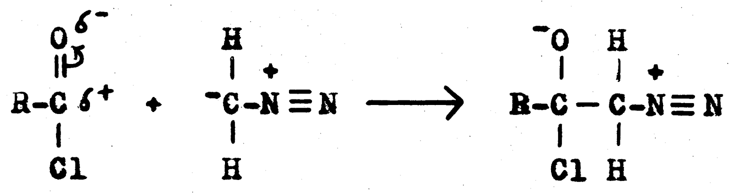
[a] It has been shown that no reaction occurs between the acid chloride and any diazo ketone that is present (70): $RCOCHN_2 + RCOCl \not\rightarrow (RCO)_2CN_2$, where R = $C_6H_5$- and $CH_3$-.

nitrogen as in the Schlotterbeck reaction) and gave a diazo ketone with a "diazo anhydride" ring structure, **XX.** This mechanism and the "anhydride" structure was opposed by Arndt, Eistert, and Scholz (69,72) and Bradley and Robinson (54,56) who proposed that the initial reaction was a carbonyl reaction between diazomethane and the acid chloride,

(1) 

$$R\text{-}\overset{O^{\delta-}}{\underset{Cl}{C}}{}^{\delta+} + {}^{-}\overset{H}{\underset{H}{C}}\text{-}\overset{+}{N}\equiv N \longrightarrow R\text{-}\overset{{}^{-}O}{\underset{Cl}{C}}-\overset{H}{\underset{H}{C}}\text{-}\overset{+}{N}\equiv N$$

**XXI**

(1), to form an intermediate diazonium betaine structure, **XXI.**[a] The fact that sulfonic acid halides, such as p-toluenesulfonyl chloride and methylsulfonyl chloride, in which no such electronic displacement occurs, fail to react with diazomethane is cited as evidence for this mechanism (69). They proposed that the inductive effect of the diazonium group and the COCl group loosens the methylene hydrogens so that one of them can form a hydrogen bridge with a second molecule of diazomethane, (m); after nitrogen separates from the second molecule of diazomethane the remainder splits into methyl chloride and the diazo ketone. A similar

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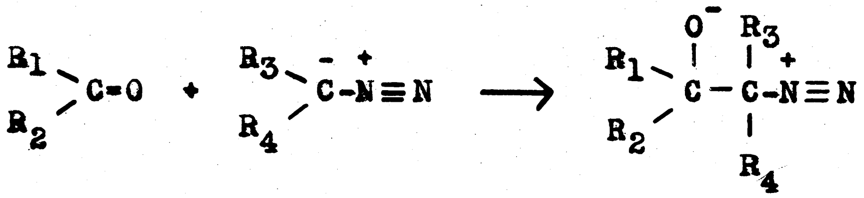
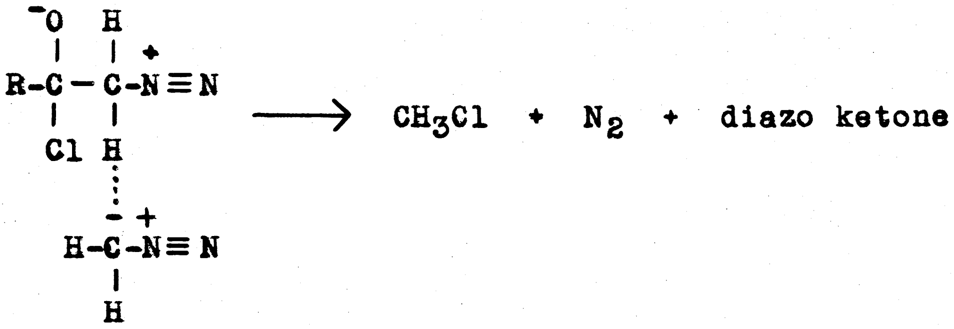
[a] The present accepted mechanism for the Schlotterbeck reaction also is a carbonyl reaction that initially gives a diazonium betaine (1, p. 368):

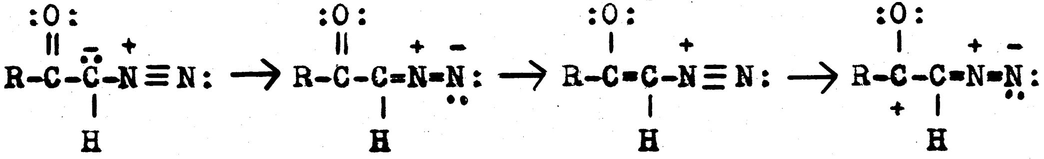


mechanism is possible for reactions employing triethylamine

(m)



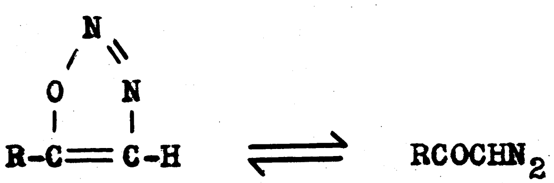
as the base instead of diazomethane. The structure of the diazo ketone was proposed as a resonance hybrid, XXII, rather


(a) (b) (c) (d)

XXII

than the "anhydride" ring, XX (49,72, also cf. 56,73). Noyes and Meitzner (74) proposed a formula similar to XXIIc for diazocamphor and diethyl diazosuccinate, but excluded formulas similar to XXIIa on the basis of the then supposed optical activity of diazo compounds. In a comparison of the different mechanisms proposed for diazo ketone formation Smith (2) shows an equilibrium between the "anhydride" and the open-chain forms, (n), immediately after hydrogen halide

(n)



is split out of a dihydrogenated furodiazole, XIX.

Since excellent summaries have been presented elsewhere by Bachmann and Struve (48) and Eistert (49), only a brief outline and discussion of the reactions of diazo ketones will be presented here. Diazo ketone reactions can be divided roughly into three general classes: a) decomposition by halogens, acids, heat, and/or catalysts without rearrangement; b) decomposition by heat, light, and/or catalysts with rearrangement; and c) miscellaneous reactions.

The halogens, bromine and iodine, react with diazo ketones in acetic acid to give α,α-dihaloketones, (o).

$$\text{(o)}\quad \begin{aligned} &RCOCHN_2 + Br_2 \longrightarrow RCOCHBr_2 + N_2 \\ &RCOCHN_2 + I_2 \longrightarrow RCOCHI_2 + N_2 \end{aligned}$$

Hydrogen bromide, hydrogen iodide, and acetic acid react with diazo ketones to produce the corresponding halomethyl-

$$\text{(p)}\quad \begin{aligned} &RCOCHN_2 + HBr \longrightarrow RCOCH_2Br + N_2 \\ &RCOCHN_2 + HCl \longrightarrow RCOCH_2Cl + N_2 \\ &RCOCHN_2 + HOAc \longrightarrow RCOCH_2OAc + N_2 \end{aligned}$$

and acetoxymethyl ketones, (p), but hydrogen iodide acts as a reducing agent to give methyl ketones, (q). The acetoxy-

$$\text{(q)}\quad RCOCHN_2 + 2\ HI \longrightarrow RCOCH_3 + N_2 + I_2$$

methyl ketones can be reduced with sodium amalgam or by the Meerwein-Ponndorf-Verley method to glycols that can then be oxidized to aldehydes corresponding to the original acid used in preparing the diazo ketone, (r), (75). Although

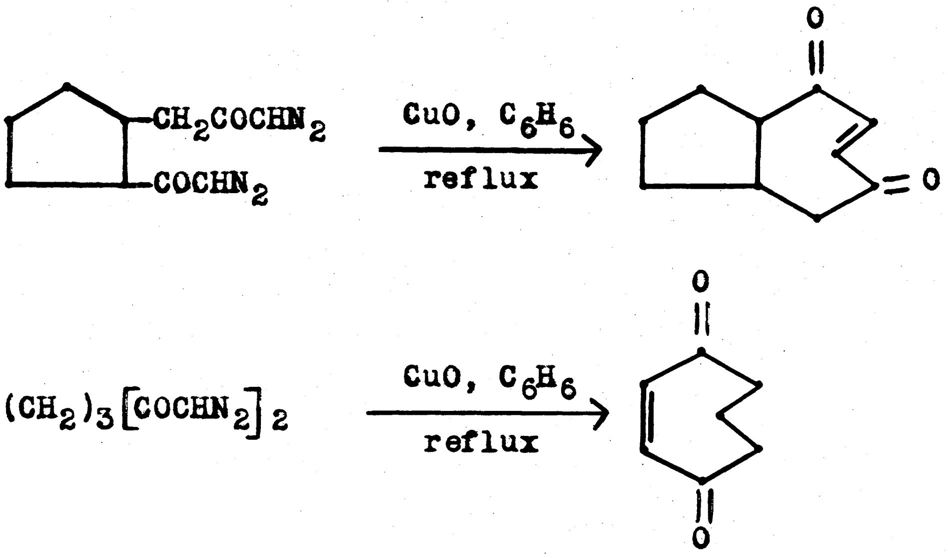
$$\text{(r)}\quad \begin{tikzcd} RCO_2H \arrow[r] & RCOCl \arrow[r] & RCOCHN_2 \arrow[r] & RCOCH_2OAc \arrow[d] \\ & & RCHO + HCHO & RCH(OH)CH_2OH \arrow[l] \end{tikzcd}$$

thermal decomposition of diazo ketones usually gives rearranged products (cf. below), at least one case is reported in which no rearrangement occurs; 2-diazoacetophenone is reported to undergo thermal decomposition in the absence of catalysts or solvent to yield cis-1,2,3-tribenzoylcyclopropane (76). The thermal decomposition of diazo ketones in the presence of copper or cupric oxide in solvents containing no active hydrogen such as benzene, toluene, or xylene yields unsaturated diketones, (s), (76,77) and has

$$(s)\quad C_6H_5COCHN_2 \xrightarrow[C_6H_6]{Cu} \underset{\text{trans}}{C_6H_5COCH{=}CHCOC_6H_5}$$

been applied to the preparation of unsaturated, cyclic diketones from bis-diazoketones, (t), (78). If the decomposition is carried out in a solvent with active hydrogen, the corresponding α-alkoxyketone is formed, (u), (77),

(t)



$$(u)\quad RCOCHN_2 + YH \xrightarrow[50\text{-}70°]{Cu} RCOCH_2Y + N_2$$

where Y has been alkoxy, $C_6H_5O-$, $C_6H_5S-$, $C_6H_5NH-$, and $C_5H_{10}N-$. The reaction, (u), in which Y is alkoxy is catalyzed by non-protonic acids such as boron trifluoride, aluminum chloride, and stannic chloride (79); if Y is hydroxyl, the reaction is catalyzed by dilute sulfuric or formic acids (49,73). Mechanism studies of this reaction

(80,81) indicate a preliminary reversible proton transfer from the solvent to the diazo ketone forming a diazonium ion that subsequently undergoes decomposition.

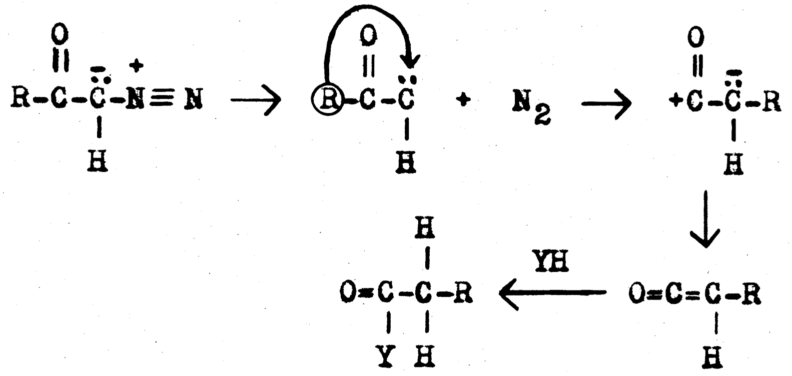
The best known reactions of diazo ketones are those accompanied by rearrangement of the molecular skeleton and bear the name of Wolff who first observed them (33,41, p. 144). The general reaction is represented by equation (v), where Y is alkoxy, $NH_2$-, R'NH-, $C_6H_5NHNH$-, $C_6H_5CH_2O$-,

(v) $RCOCHN_2 + YH \longrightarrow RCH_2COY + N_2$

and HO-, and comprises the last step of the Arndt-Eistert synthesis (48,82) for converting an organic acid to its next higher homolog or to a derivative of the homologous acid. Ortho diazo oxides and ortho-hydroxy diazonium salts undergo a very similar type of rearrangement (83). The rearrangement has been accomplished by metallic catalysts such as silver (copper and platinum have been used, but the yields were poor and the conditions were abnormally forced; cf. 77) (48,49,84), heat (11,14,57,59,60,70,84-87), and ultraviolet light (88,89). Higher and more reproducible yields have been obtained in a homogeneous medium by treating an alcoholic solution of the diazo ketone with a solution of silver benzoate in triethylamine (90). Attempts by Wiberg and Hutton (91) to affect a Wolff rearrangement on 1-diazo-3,3-dimethylbutanone-2 by ultraviolet light resulted in an anomolous reaction yielding $\alpha,\gamma$-di-t-butyl-$\Delta^{\beta\gamma}$-butenolide as the chief product. The rearrangement has been successfully applied to diazo ketones prepared from higher diazo alkanes, but the conditions are somewhat more drastic and the yields poorer (57-60).

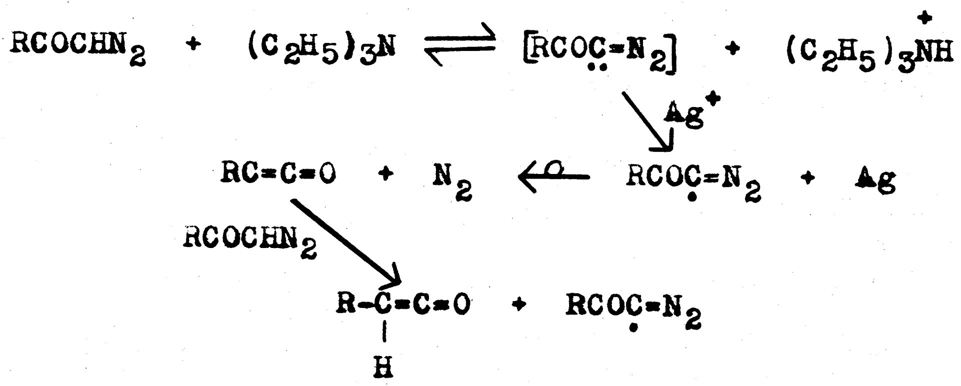
It has been suggested that the Wolff rearrangement proceeds in a manner similar to that postulated for the Curtius rearrangement by the splitting off of nitrogen by heat, light, or catalyst, followed by anionic migration, and subsequent ketene formation; this ketene may then be isolated or may react further with the solvent, (w), (34,69,73,82). This mechanism is supported by the fact that ketenes frequently have been isolated from reaction mixtures originally containing diazo ketones (11,14,85,88,89). Baddeley, Holt, and Kenner (59) doubt that the Wolff rearrangement involves a ketene intermediate, because they obtained 3-anilino-4'-nitropropiophenone instead of the expected 2-(p-nitrophenyl)-propionanilide when they attempted a Wolff rearrangement on 2-diazo-4'-nitropropiophenone; Eistert, however, obtained the expected anilide by using somewhat more drastic conditions (61).

(w)



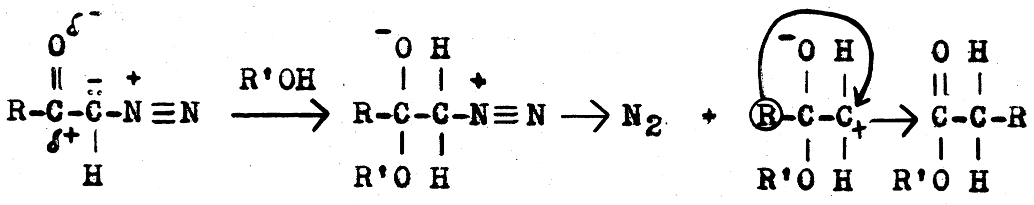
For rearrangements run in homogeneous media Newman and Beal (90) have suggested a ketene intermediate that is formed via a free radical mechanism, (x).

(x)



Another mechanism suggested by Eistert (49,72) avoids the ketene formation by using a diazonium betaine intermediate, XXIII, from which nitrogen separates followed by anionic migration, (y).

(y)



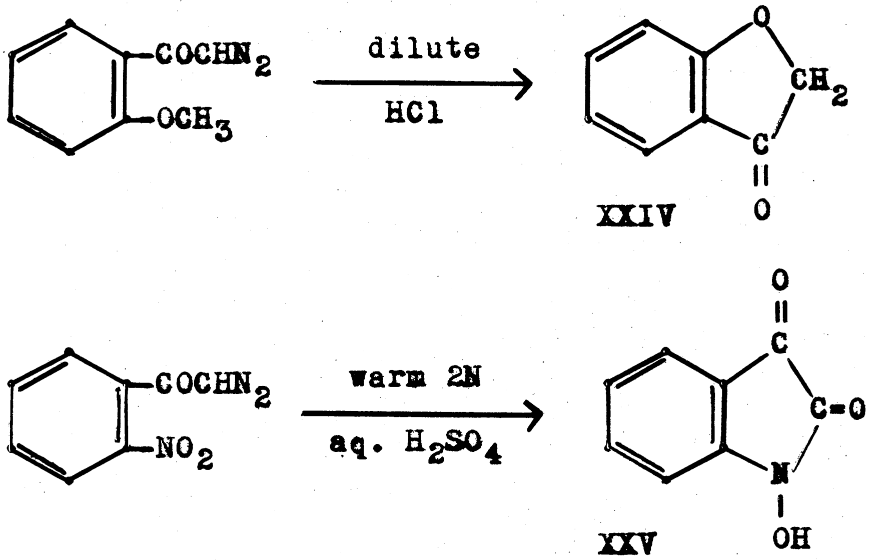
XXIII

Evidence against a mechanism involving an intramolecular oxidation and reduction with no rearrangement was shown by studies using $C^{13}$ isotopes in which it was definitely proven that the carbonyl group of the diazo ketone becomes the carbonyl group of the resulting acid (92).

Studies with optically active diazo ketones have shown that the Wolff rearrangement proceeds with retention of configuration of the migrating group (93). Racemization was observed at high rearrangement temperatures on diazo ketones such as $RR'CHCOCHN_2$ which have an optically active group that contains an enolizable hydrogen.

Among the miscellaneous reactions of diazo ketones are the ring closures of the ortho-substituted aromatic compounds which occurs upon their treatment with acid (49, p.550,51,53,94-96). This reaction is illustrated by the formation of coumaranone, XXIV, from 2-diazo-2'-methoxyacetophenone and of N-hydroxyisatine, XXV, from 2-diazo-2'-nitroacetophenone, (z).

(z)

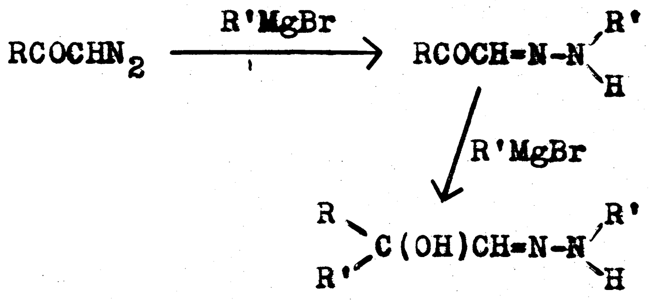


The reduction of diazo ketones, $RCOCHN_2$, has been attempted with many different reagents (33,97) such as hydrogen sulfide, lithium aluminum hydride, zinc and acids, sodium amalgams, aluminum amalgams, and catalytically using CuO, PdO, Pd, Pt, and $PtO_2$. The products obtained depend greatly upon the method of reduction and the nature of R and have included methyl ketones, substituted pyrazines, α-aminoketones, α-ketohydrazones, and α-aminoalcohols. The action of hydrogen sulfide on azibenzil (98) has yielded a reduced product (an α-aminoketone), a rearranged product, and a substituted 1,2,3-thiadiazole.

Diazo ketones have been made to react with thiourea and other thioamide derivatives forming substituted thiazoles (99) and with heterocyclic amine salts to form N-substituted pyridinium salts (100).

Grignard reagents form substituted hydrazones with diazo ketones (17,101), (aa), in a manner similar to their

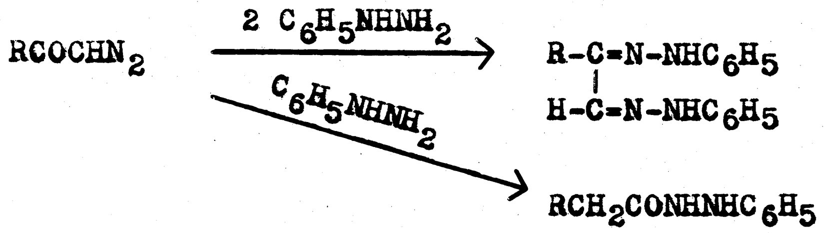
(aa)



reaction with diazo compounds (1).

Phenylhydrazine reacts with diazo ketones (70) to give either phenylosazones or β-phenylhydrazides, (bb),

(bb)



depending upon the nature of R.

### C. Previous Infrared Spectral Work

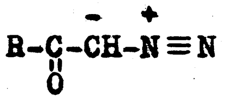
Although the ultraviolet absorption spectra of a number of diazo compounds (4,102,103) including several diazocarbonyl compounds (12,18,24,103, cf. section IIB) and a few diazo ketones (84,104,105) have been reported, the information that can be obtained from them concerning their structure is very limited, because the spectra of no "standard" or "model" compounds, whose structures are known for certain, are available for comparison in these cases. On the other hand the infrared spectra of these compounds should be expected to yield more specific information about the vibrations of individual groups of atoms (as well as of the entire molecule) without requiring the use of "model" compounds. Although the complexity of the diazocarbonyl compounds virtually prohibits a detailed mathematical treatment of the spectra, one might be expected to be able to make a reasonably satisfactory correlation of structure and spectra by making use of the wealth of literature information on the infrared spectra of compounds of known structure.

A literature survey reveals little published information on the infrared spectra of diazo and diazocarbonyl compounds. The precision of most of the spectral data that have been published should not be given too much weight, because the authors were only interested in the gross spectrum either as a means of establishing the purity or identity of their compounds, or else they wanted to use individual bands for special purposes (cf. 91).

The infrared spectra of three simple diazo compounds have been published. The structure of diazomethane has been thoroughly studied by infrared spectra (25-27), while the spectrum of diazocyclopentadiene in carbon tetrachloride and as a vapor has been published (4) only as evidence substantiating the presence of a diazo group. The frequency of the diazo band in diazodiphenylmethane has been published (106) with no experimental details or references given.

Yates (94) mentioned in a footnote in an article in the Journal of the American Chemical Society that a band at 2070 cm.$^{-1}$ (4.83$\mu$) and the displacement of the carbonyl band from about 1724-1695 cm.$^{-1}$ (5.8-5.9$\mu$) to about 1613 cm.$^{-1}$ (6.2$\mu$) were characteristic of aliphatic diazo ketones; he added that details were to follow, but these have not yet appeared. A small spectrum of 2-diazo-2'-methoxyacetophenone in chloroform from 5000-714 cm.$^{-1}$ (2-14$\mu$) was included to give evidence for the absence of chloroketone impurities [band at 1681 cm.$^{-1}$ (5.95$\mu$)] in the compound which was subsequently used for the preparation of coumaranone.

Moore and coworkers (103,107,108) have published the infrared spectra of O-diazoacetyl-DL-serine and O-diazoacetyl-L-serine (azaserine), $N_2CHCO_2CH_2CH(NH_2)CO_2H$, from 3333-714 cm.$^{-1}$ (3-14$\mu$) in Nujol as evidence for the identity of their synthetic compound with the naturally occurring antibiotic. Bands at 2146 cm.$^{-1}$ (4.66$\mu$), 1698 cm.$^{-1}$ (5.89$\mu$), and 1678 cm.$^{-1}$ (5.96$\mu$) were reported for the diazo and carbonyl frequencies.

Moore (105), who has reported the preparation and infrared spectra of three substituted diazoacetyl pyrazolines, mentions diazo bands at 2146-2132 cm.$^{-1}$ (4.66-4.69$\mu$) and says that "the strong sharp band in the 6.05-6.15$\mu$ region of diazoketones (6.15-6.25$\mu$ for conjugated diazoketones) must be associated with the diazocarbonyl system . . . is clear evidence that the simple representation  $R-\underset{\overset{\|}{O}}{C}-\overset{-}{C}H-\overset{+}{N}\equiv N$ is inadequate."

Wotiz and Buco (109) mention a characteristic infrared absorption band of diazo ketones near 2083 cm.$^{-1}$ (4.80$\mu$). They were using the spectra of 3-diazoacetyl-4-phenyl-$\Delta^1$-

pyrazoline and 4-diazo-1-phenylbuten-1-one-3 in chloroform from 5000-769 cm.$^{-1}$ (2-13$\mu$) to partially identify intermediates while studying the Arndt-Eistert synthesis of unsaturated acids.

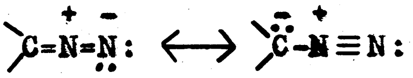
Wiberg and Hutton state in a footnote (91) that the infrared spectra of six aliphatic diazo ketones prepared by them (110) showed a strong diazo band at 2083-2075 cm.$^{-1}$ (4.80-4.82$\mu$) and a strong carbonyl band at 1639-1613 cm.$^{-1}$ (6.1-6.2$\mu$). They were irradiating diazo ketones with ultraviolet light and were determining the reaction termination by the disappearance of the diazo band in the spectrum.

A more careful study of diazocarbonyl compounds is found in a recent paper by LeFevre, Sousa, and Werner (47) who published the infrared stretching frequencies for the diazo and the carbonyl groups in seven diazo oxides and in one diazo ketone (azibenzil). The values for the NN stretching frequency in the diazo oxides varied between 2014 cm.$^{-1}$ and 2173 cm.$^{-1}$; the values for the carbonyl stretching frequency in the same compounds varied between 1562 cm.$^{-1}$ and 1642 cm.$^{-1}$. These results substantiated earlier conclusions from the ultraviolet absorption spectra (45,46), for no band common to azo (-N=N-) absorption was reported (as would be expected if the 1,2,3-oxadiazole ring were present) while the diazo and carbonyl bands were present (as might be expected from a quinonediazide structure). The interpretation of these results also favored the resonance-hybrid structure, for the authors concluded that the NN bond in the diazo oxides was in between a double and triple bond in character, and that the carbonyl group was modified in the sense $C\overset{\curvearrowright}{=}O$, i.e. polarized or somewhat ionic in character.

LeFevre, Sousa, and Werner also reported the NN stretching frequency for benzo-1,2,3-thiadiazole (1542 cm.$^{-1}$) and for benzenediazonium fluoborate (2296 cm.$^{-1}$). Benzo-1,2,3-thiadiazole, which is isoelectronic with the diazo oxides, was assigned a ring structure rather than a diazo sulfide structure for it exhibited no characteristic $>C=S$ frequency, but showed only a band in the region of -N=N- absorption commonly assigned to the azo linkage (111-113). The diazonium salt showed no carbonyl frequency and had an NN stretching frequency in a spectral region common to nitriles (114,115, chapter 15), since shown to be characteristic for diazonium compounds (116-118).

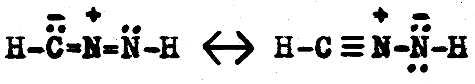
These few papers reveal that, in general, the infrared spectrum of a diazocarbonyl compound might be expected to exhibit: (a) a diazo band in the "triple-bond" region of the spectrum, and (b) a carbonyl band whose position is somewhat displaced to lower frequencies compared to those exhibited by simple carbonyl compounds. In addition, the positions of both the carbonyl band and the diazo band (especially in the diazo oxides) appear to be sensitive to neighboring substitution.

The "triple-bond" region of the infrared spectrum lies approximately between 2500-1887 cm.$^{-1}$ (4-5.3$\mu$) and is characterized by absorption due to vibrations of both triple bonds such as are found in alkynes and nitriles, and accumulated double bonds such as are found in allenes. The fact that diazo compounds show an absorption in this spectral region can be readily correlated with a resonance hybrid, III, as well as with a tautomeric form for diazomethane, XXVI, in which one extreme form contains a triple



$$\rangle C=\overset{+}{N}=\underset{\cdot\cdot}{\overset{-}{N}}: \longleftrightarrow \rangle\overset{-}{\ddot{C}}-\overset{+}{N}\equiv N:$$

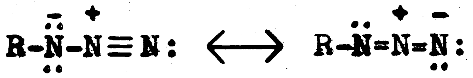
III



$$H-\overset{-}{\ddot{C}}=\overset{+}{N}=\ddot{N}-H \longleftrightarrow H-C\equiv\overset{+}{N}-\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}-H$$

XXVI

bond while the other has a 1,2-dienoid type system (22,25,27). A similar resonance-hybrid system, XXVII, has been postulated for azides (22,119) which also absorb in the "triple-



$$R-\underset{\cdot\cdot}{\overset{-}{\ddot{N}}}-\overset{+}{N}\equiv N: \longleftrightarrow R-\ddot{N}=\overset{+}{N}=\underset{\cdot\cdot}{\overset{-}{N}}:$$

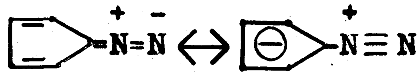
XXVII

bond" region. Table I contains a list of the types of compounds that absorb in the 2500-1887 cm.$^{-1}$ (4-5.3$\mu$) region with the reported limits of absorption in both wave numbers and microns. (Also cf. Figure 5, Appendix)

The infrared absorption band arising from the CO stretching vibration is found at approximately 1700-1760 cm.$^{-1}$ for saturated, open-chain, carbonyl compounds (Table II), but its exact position varies and is governed by a number of factors that affect the nature of the immediate environment of the carbonyl group. Among such governing factors are ring strain, conjugation with double bonds, aryl conjugation, electronegative and electropositive groups, chelation, and hydrogen bonding as well as the particular phase of the compound (i.e. liquid, solid, or gas) and the medium in which it is placed for measurement. An increase in ring strain (in the case of a cyclic ketone for instance) and the pres-

## TABLE I

## TYPICAL ABSORPTIONS IN THE "TRIPLE-BOND" REGION

| COMPOUNDS | WAVE NUMBERS IN $CM.^{-1}$ | WAVE LENGTH IN MICRONS | REFERENCES |
|---|---|---|---|
| Ketenimines<br>$C=C=N$ | 2000-2045 | 4.89-5.00 | 120,121 |
| Allenes (1,2-dienoids)<br>$C=C=C$ | 1930-2200 | 4.55-5.18 | 115,120<br>122 |
| Diazocyclopentadiene<br> | 2082 | 4.80 | 4 |
| Isothiocyanates<br>$N=C=S$ | ca. 2100 | ca. 4.76 | 122 |
| Carbodiimides<br>$N=C=N$ | 2096-2105 | 4.75-4.77 | 120,122 |
| Diazomethane<br>$H_2C=\underset{+}{N}=\underset{-}{N} \leftrightarrow H_2\underset{-}{C}-\underset{+}{N}\equiv N$ | 2101, 2103 | 4.76 | 25,26 |
| Azides<br>$R-\underset{-}{N}-\underset{+}{N}\equiv N \leftrightarrow R-N=\underset{+}{N}=\underset{-}{N}$ | 2080-2169 | 4.61-4.81 | 115,119<br>123,124 |
| Ketenes<br>$C=C=O$ | 2130-2160 | 4.63-4.70 | 25,115 |
| Isonitriles<br>$N\equiv C$ | 2100-2200 | 4.55-4.76 | 115,122 |
| Alkynes<br>$C\equiv C$ | 2100-2260 | 4.42-4.76 | 115,122 |
| Diazonium compounds<br>$R-\underset{+}{N}\equiv N$ | 2110-2310 | 4.33-4.74 | 116-118<br>125 |
| Nitriles<br>$C\equiv N$ | 2160-2260 | 4.42-4.63 | 114,115<br>122 |
| Nitrous oxide<br>$N\equiv\underset{+}{N}-\underset{-}{O} \leftrightarrow \underset{-}{N}=\underset{+}{N}=O$ | 2224 | 4.50 | 126 |
| Isocyanates<br>$N=C=O$ | 2232-2275 | 4.40-448 | 115,124<br>127 |
| Carbon dioxide<br>$O=C=O$ | 2336, 2367 | 4.28, 4.23 | 122 |

ence of electronegative groups on the carbon atom adjacent to the carbonyl group are known to increase the carbonyl frequency. Increasing the distance between the molecules by affecting a suitable change of state or by dissolving the substance in a solvent often will increase the carbonyl frequency, presumably by decreasing interactions between neighboring molecules. Conjugation, chelation, and hydrogen bonding usually tend to decrease the carbonyl frequency.

### TABLE II[a]

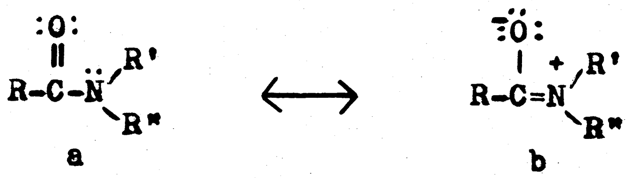
### INFRARED ABSORPTION FREQUENCIES FOR CO STRETCHING VIBRATION IN SATURATED OPEN-CHAIN CARBONYL COMPOUNDS

| COMPOUNDS | CM.$^{-1}$ |
|---|---|
| Esters | 1720-1760 |
| Aldehydes | 1720-1740 |
| Ketones | 1705-1725 |
| Acids | 1700-1725 |

[a] References 115, 122, and 125

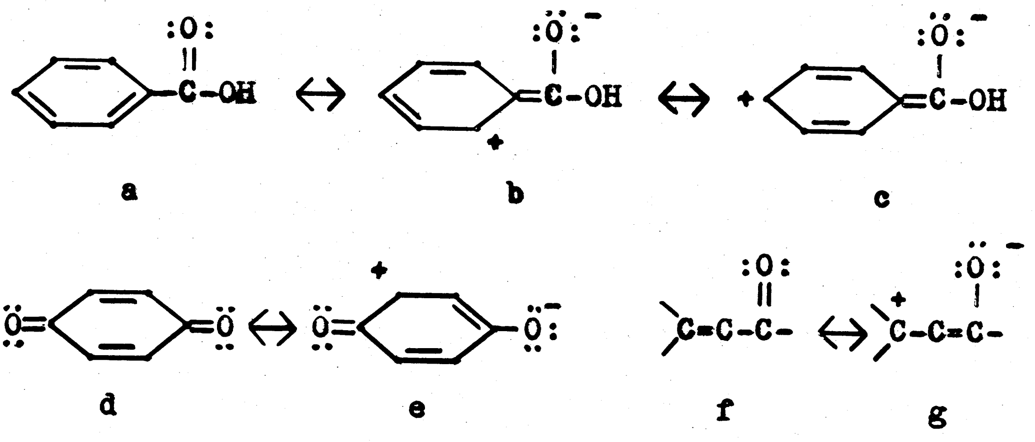
The bathochromic shift in carbonyl frequency that is reported for diazocarbonyl compounds would most likely result when a carbonyl group becomes more highly polarized than "normal", i.e. becomes more ionic in nature as the CO double bond approaches a CO single bond in character. As might be expected, carboxylate ions (absorption at 1630-1550 cm.$^{-1}$), (115,122), and zwitterions (absorption at 1650-1567 cm.$^{-1}$), (115,125), show a markedly lower carbonyl absorption frequency than "normal" carbonyl compounds (cf. Table II).

Amides also exhibit a somewhat ionic carbonyl bond which shows an absorption band (Amide I) at about 1690-1613 cm.$^{-1}$ (115,122,125), the exact position being determined by the nature of R, R', and R" (XXVIII). The shift in frequency



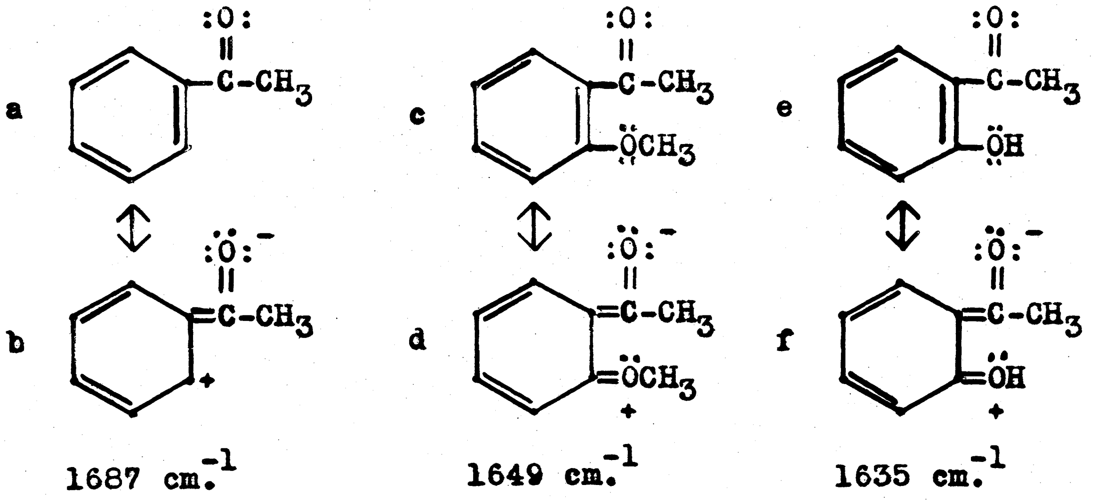
XXVIII

has been explained by assuming an appreciable contribution of form XXVIIIb to the ground state of the resonance hybrid. Substituents on the ring of aryl carbonyl compounds have been reported to affect the position of the carbonyl band (115,128,129), the direction of the shift depending upon the nature of the particular substituent. Conjugation, either aryl conjugation (benzoic acid), conjugation within the ring (quinones), or with a double bond (α,β-unsaturated carbonyl compounds) is known to cause a bathochromic shift in carbonyl frequency and is explained by the greater contribution of forms similar to XXIXb,c,e,g to the ground state (115, 122,125).



XXIX

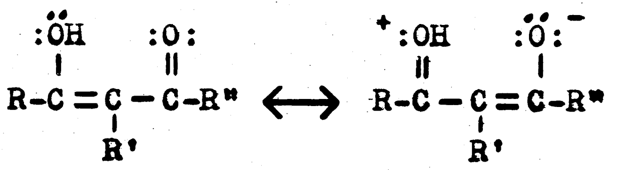
The effect of simple hydrogen bonding on the carbonyl frequency may vary considerably (115), but its combined effect with α,β-unsaturation (conjugation) causes a remarkable bathochromic shift (130,142,235). The fact that 1-hydroxy-2-acyl aromatic compounds, such as salicylaldehyde and 2'-hydroxyacetophenone, show anomolous carbonyl frequencies (1655-1635 $cm.^{-1}$), (115), has been explained by assuming that one of the ring "double bonds" functions as part of an α,β-unsaturated unit, XXX. The difference in



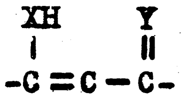
XXX

frequency observed for 2'-hydroxyacetophenone, XXXe,f and 2'-methoxyacetophenone, XXXc,d (130) can be explained by the increased hydrogen bonding (as well as by an increased positive inductive effect) in the former.

A very large decrease in the carbonyl frequency accompanied by an enhancement of its intensity in enolizable β-diketones has been noted by Rasmussen, Tunnicliff, and Brattain (131) who call this effect "conjugate chelation" in order to differentiate it from ordinary hydrogen bonding, XXXI. Such a phenomenon is shown by acetylacetone (carbonyl absorption at 1639-1587 cm.$^{-1}$) and dibenzoylmethane (carbonyl absorption at 1639-1538 cm.$^{-1}$), both of which



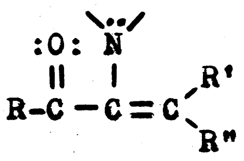
XXXI



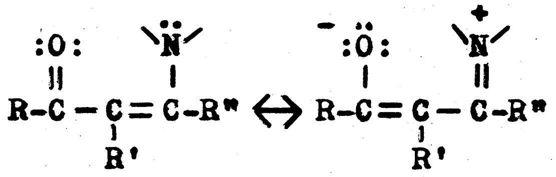
XXXII

exist largely in the mono-enol form, but not by diacetone alcohol (carbonyl absorption at 1712 cm.$^{-1}$) which shows only normal hydrogen bonding. This effect is said to arise from any structure similar to XXXII in which X and Y act as electron donors or acceptors.

Another interesting bathochromic carbonyl shift was noticed by Cromwell, et al. (132) in the spectra of amino-substituted α,β-unsaturated ketones. Upon examining fifteen compounds they found that the presence of an amino group (either substituted or unsubstituted) on the β-carbon atom of an α,β-unsaturated ketone lowered the carbonyl frequency by 20-80 cm.$^{-1}$, while isomeric α-aminoketones, XXXIII, showed no such anomolous carbonyl frequency. They considered the



XXXIII



a XXXIV b

resonance hybrid XXXIV and concluded that form "b" must contribute appreciably to the ground state of the molecule.

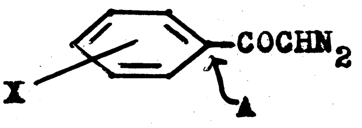
The diazo and the carbonyl frequencies of diazocarbonyl compounds, especially in the diazo oxides, appear to be sensitive to neighboring substituents. Because the spectra of only a small number (seven) of diazo oxides were recorded by LeFevre, Sousa, and Werner (47), and since they made no orderly variation of substituents on the ring, it is virtually impossible to make any correlation between spectra and ring substitution.

# III. PURPOSE AND OUTLINE OF PRESENT INVESTIGATION

The purpose of the present investigation has been to prepare a series of representative diazo ketones and the necessary related compounds, and to study their structure by examining their infrared spectra, especially in the "triple-bond" and in the "carbonyl" region of the spectrum. Since the few reported spectra of diazo ketones, plus the work on similar compounds such as the diazo oxides, indicate that a resonance hybrid, XXII, describes the structure better than a 1,2,3-oxadiazole formulation, it is reasonable to assume that a variation in the electron-attracting or -repelling properties of R, XXXV, should produce a variation in the structure of the molecule that would show up in its infrared spectrum, especially in the position of the bands due to the NN and the CO stretching vibrations. Since a phenyl group with various electron-attracting or -repelling groups placed in any of the three ring positions offers a convenient means of changing the electron density in the vicinity of carbon atom A, XXXVI, a series of ten substituted 2-diazoacetophenones was prepared with X representing methyl, bromo, nitro, and hydrogen in each of the ortho, meta, and para positions. In order to observe the effect of a more complicated ring system on the structure, two diazo ketones

$R\text{-}COCHN_2$

XXXV



XXXVI

$C_6H_5COCR'N_2$

XXXVII

were prepared in which R was represented by α-naphthyl and β-naphthyl groups. The nature of R was varied still further by the preparation of a series of four aliphatic diazo ketones and one diazo ester in which R was t-butyl, methyl, trichloromethyl, trifluoromethyl, and ethoxy. Azibenzil and 2-diazopropiophenone (XXXVII, R' = $C_6H_5$- and -$CH_3$) were prepared, and their spectra compared with 2-diazoacetophenone (XXXV, R = $C_6H_5$-) in order to ascertain the effect on the structure by varying group R' while keeping R constant. New compounds or compounds whose identity could be questioned were subjected to reactions characteristic of diazo ketones (cf. Historical section) that would give compounds which could be identified readily.

Since the diazo frequency had been reported for only two diazo compounds, diazomethane and diazocyclopentadiene, the spectra of diazodiphenylmethane and 9-diazofluorene were recorded in order to give a larger basis for the comparison of the spectra of simple diazo compounds with those of diazocarbonyl compounds. At the completion of this research the position of the diazo band in the spectrum of diazodiphenylmethane was reported by Shriner, Fuson, and Curtin (106), and their value is in agreement with that reported here.

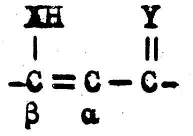
The detection of the diazo spectral band is easier than some other bands, because it lies in a spectral region relatively free from common bands that might interfere with identification, while the reverse is true for the carbonyl frequency. The carbonyl frequency as found in diazo ketones lies in a spectral region common to $>C=N-$, $>C=C<$, and aromatic ring vibrations, so there might be some question as to the actual identity of this band, especially in aromatic diazo ketones. A possible procedure for the identification of this band would be to form a derivative of the ketone, record its infrared spectrum, and hope to observe a disappearance of the characteristic ketonic carbonyl frequency and the appearance of a new C=N band as would be expected, for instance, if the derivative were a hydrazone, phenyl- or other substituted hydrazone, or semicarbazide. Such a procedure would be of little or no value in the case of the diazo ketones for (a) it would be extremely difficult or impossible to prepare such a derivative (cf. 70), and (b) the new C=N frequency would lie in approximately the same spectral position as the original carbonyl frequency. The method selected to help identify the carbonyl frequency consisted of following the gradual bathochromic shift of the carbonyl band in a selected series of benzil derivatives.

## IV. DISCUSSION OF RESULTS AND CONCLUSIONS

### A. Benzil Derivatives

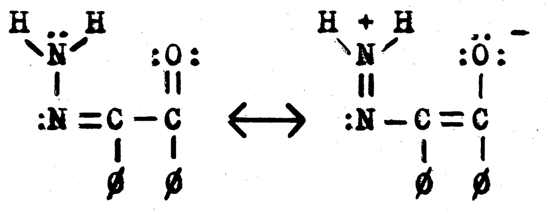
The few reports concerning the position of the carbonyl frequency in the infrared spectra of diazo ketones (1653-1600 $cm.^{-1}$) and of diazo oxides (1642-1562 $cm.^{-1}$), (cf. section IIC), have included specific values, but reasons for the assignment of these frequencies to a CO stretching vibration and values for other neighboring frequencies have not always been included. The assignment of these values to a CO stretching vibration can be subject, therefore, to considerable question for the carbonyl band appears in a spectral region common to vibrations attributed to carbon-carbon double bonds, aromatic rings, NH deformations, C=N, and even nitro groups. Evidence for the correct assignment for the frequency of a carbonyl bond in at least one diazo ketone, azibenzil, is shown here by following the interesting bathochromic shift in the carbonyl frequency for a series of selected benzil derivatives.

The spectra of benzil monohydrazone and the diazo ketone obtained from it by mild oxidation, azibenzil, are strikingly similar in the "carbonyl" and "double-bond" regions, the major difference being, as might be expected, the absence of the NH deformation band in the latter at 1542 $cm.^{-1}$. More surprising is the fact that <u>both</u> compounds exhibit carbonyl frequencies (within 8 $cm.^{-1}$ of one another) that are shifted to frequencies about 40 $cm.^{-1}$ lower than those of the parent compound, benzil, whose carbonyl frequencies show only the effect of normal conjugation. The anomalous carbonyl frequency for benzil monohydrazone might be explained by considering it as a special case of "conjugate chelation". Rasmussen claims that this effect should be shown by compounds of structure XXXII in which XH and Y



$$-\overset{XH}{\overset{|}{C}}=C-\overset{Y}{\overset{\|}{C}}-$$

XXXII



XXXVIII[a]

participate as a hydrogen bond donor-acceptor system and results in a large bathochromic carbonyl band shift accompanied by enhancement of the band intensity. The effect is shown by enolizable β-diketones, (X,Y = O), (131), and β-amino-α,β-unsaturated ketones, (X = NH, Y = O), (132). Benzil monohydrazone, in which the β carbon atom of XXXII is replaced by a nitrogen atom and X is NH, might be expected to show a similar behavior and to possess the resonance-hybrid structure XXXVIII.[b] That such a "conjugate chelate" system is indeed present is shown by comparing the

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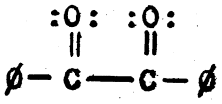
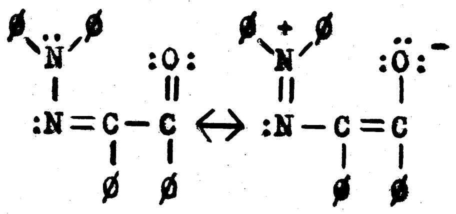
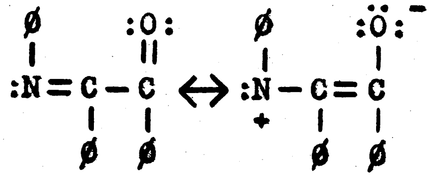
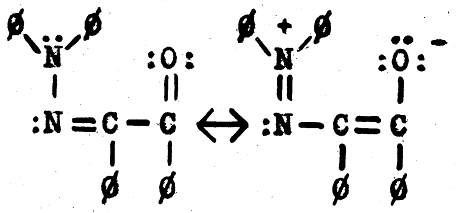
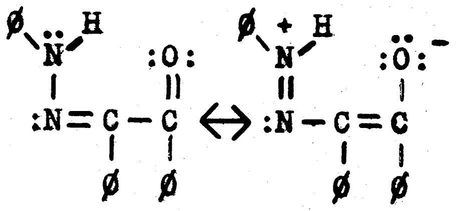
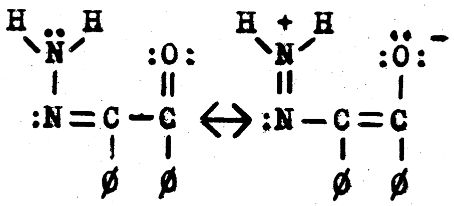
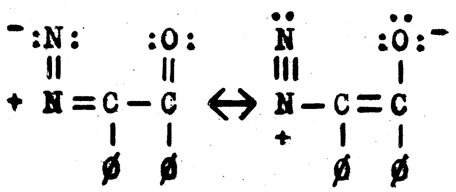
[a] ø represents phenyl, $C_6H_5$-.

[b] Hydrazones may possess either an anti (β) or syn (α) structure depending upon the nature of the parent carbonyl compound. The structure in figure XXXVIII is not intended to represent the true geometric configuration of the compound, but is written in this manner only to show the similarity of its structure to the structure written by Rasmussen, XXXII. With the exception of the α form of benzil mono-diphenylhydrazone, which will be discussed in some detail later on, all the hydrazones prepared are the reported stable, anti (β) forms.

carbonyl frequencies found for the compounds in figure XXXIX.

Two strong carbonyl frequencies were found in the spectrum of solid benzil at 1675 cm.$^{-1}$ and 1660 cm.$^{-1}$ and are those that might be expected from a diaryl ketone showing only normal conjugation (115). Mann and Thompson (133) report that the carbonyl band near 1670 cm.$^{-1}$ shown by solid benzil appeared to be a doublet, while only single bands have been reported previously at 1681 cm.$^{-1}$ (131) and 1680 cm.$^{-1}$ (134) in chloroform and carbon tetrachloride solutions, respectively. The appearance of only a single carbonyl band in the solution spectra is attributed to the trans configuration of the benzil molecule (131). However, the carbonyl band at 1628 cm.$^{-1}$ by the monohydrazone indicates a more highly polarized and ionic carbonyl group, and could arise from a considerable contribution of form XXXIX2 to the ground state. The monophenylhydrazone likewise exhibits a bathochromic shift in carbonyl frequency, but its exact position is doubtful for its spectrum shows two bands at 1638 cm.$^{-1}$ and 1649 cm.$^{-1}$. The former band shows a somewhat more intense absorption and, therefore, perhaps should be assigned to the carbonyl stretching, for carbonyl band intensities are almost always stronger than those of C=N. The spectrum of benzil β-osazone offers no help in making a correct assignment for no band due to C=N stretching could be found, the absence perhaps being due to the high symmetry of the compound. The fact that the carbonyl band of the monophenylhydrazone is shifted less to lower frequencies than that of the mono-

$CM.^{-1}$

| | | C=N | CO |
|---|---|---|---|
| Benzil |  | ---- | 1675 s<br>1660 S |
| Benzil Mono-diphenylhydrazone, β form |  | 1656 mw | 1676 s |
| Benzil Monoanil |  | 1622 s/sm | 1665.5 s |
| Benzil Mono-diphenylhydrazone, α form |  | masked? | 1640 s |
| Benzil Monophenylhydrazone |  | 1649 sm? | 1638 s? |
| Benzil Monohydrazone |  | masked? | 1628 S |
| Azibenzil |  | ---- | 1620 s |

form 1 form 2

XXXIX[a]

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[a] ø represents phenyl, $C_6H_5$-.

hydrazone can be explained by assuming that the phenyl group is electron attracting (phenylacetic acid, log K = -4.3, is a stronger acid than acetic acid, log K = -4.75) and may therefore inhibit electron release from the terminal nitrogen to the adjacent one. Also, any hydrogen bond formed between the oxygen and hydrogen on the terminal nitrogen may be weakened both due to a steric effect of the bulky phenyl group and because only one-half as many hydrogen atoms are present for chelation as are in the monohydrazone. When the possibility of hydrogen bonding is removed and the electron release from the terminal nitrogen is inhibited still more as in the β form of benzil mono-diphenylhydrazone, the carbonyl frequency shows no appreciable shift from that of benzil and occurs at 1676 cm.$^{-1}$; form XXXIX2 can be expected, therefore, to contribute only very little to the structure of the molecule. The α form of benzil mono-diphenylhydrazone has a carbonyl band at 1640 cm.$^{-1}$ and can not be compared properly with the other compounds in the series which are β forms. Palm and Werbin (135) have shown that benzil β-oximes have higher carbonyl and C=N frequencies than the corresponding α-oximes. The C=N frequency in the β form of benzil mono-diphenylhydrazone appears as a medium-weak band at 1656 cm.$^{-1}$, but is absent in the α form, and may be masked by the strong carbonyl absorption at 1640 cm.$^{-1}$.

Benzil monoanil, which would not be expected to show the "conjugate chelate" phenomenon, has a carbonyl band very near to those of benzil at 1665.5 cm.$^{-1}$. The only resonance form for the monoanil similar to those illustrated for the other compounds would be XXXIX2, which violates the Lewis octet rule, and which would be expected to contribute practically nothing to the ground state.

Compounds which exhibit "conjugate chelation" effects might also be expected to have a C=N bond somewhat more like a C-N single bond in character (i.e. modified in the sense $\overset{\curvearrowleft}{\mathrm{C{=}N}}$) and thus show a C=N bond shifted somewhat to lower frequencies from those that do not, the magnitude of the shift being dependent upon the "amount" of form XXXIX2 that contributes to the ground state. Some evidence supporting this proposition is shown by the benzil derivatives, for the β form of benzil mono-diphenylhydrazone shows a C=N band at 1656 $\mathrm{cm.}^{-1}$, and the monophenylhydrazone has one at 1649 $\mathrm{cm.}^{-1}$ (or 1638 $\mathrm{cm.}^{-1}$, cf. discussion on CO band). The C=N band in the monohydrazone is either absent or, more likely, masked by the strong CO band at 1628 $\mathrm{cm.}^{-1}$.

The diazo ketone related to these benzil derivatives, azibenzil, has a carbonyl band at 1620 $\mathrm{cm.}^{-1}$ (reported, 1619 $\mathrm{cm.}^{-1}$, reference 47), (data in Table V). The structure of the diazo ketone can not be explained completely by a similar "conjugate chelate" type formula, for there is no possibility of hydrogen bonding and the positive charge must be placed on the nitrogen atom bonded to the carbon atom rather than on the terminal nitrogen as in the other benzil derivatives, XXXIX. However, it is possible that the separate charges in XXXIX2 are closer to one another than they are in form XXXIX2 of the benzil derivatives, and thus tend to increase the probability of this resonance form's contributing to the true structure of the molecule. The increased stability due to the increased proximity of these charges might be more than sufficient to make up for the effect of hydrogen bonding present in the monohydrazone but lacking in the diazo ketone.

As expected, azibenzil (and all the other diazo ketones) shows no band attributable to C=N stretching. Diazodiphenylmethane and 9-diazofluorene show aromatic bands in approximately the same positions as in the parent hydrazones, benzophenone hydrazone and 9-fluorenone hydrazone, but lack the C=N stretching band as well as the band due to NH deformation (data in Tables V and VI). The exact assignment of the bands due to the NH deformation and to the aromatic band at 1525-1475 $cm.^{-1}$ (115) in both hydrazones is impossible here, for the two bands occur very close together. The exact assignment of the C=N stretching vibration in benzophenone hydrazone also is impossible for two bands of medium-weak intensity at 1623 $cm.^{-1}$ and 1614.5 $cm.^{-1}$ are present.

## B. Simple Diazo Compounds

The previously reported infrared spectra of simple diazo compounds together with the spectra of those simple diazo compounds reported here show that this class of compounds shows absorption between 2101 $cm.^{-1}$ and 2045 $cm.^{-1}$. This absorption is attributable to an NN stretching vibration and indicates that the NN bond is between a double and a triple bond in character.

The reported frequency of the NN stretching vibration in diazocyclopentadiene is 2082 $cm.^{-1}$ (4) and illustrates the effect of normal conjugation in decreasing the frequency of 2101 cm.$^{-1}$ and 2103 cm.$^{-1}$ reported for diazomethane (25,26). Increasing the conjugation (and the number of possible resonance structures) still more results in a further decrease in the NN stretching frequency as shown by the values found for 9-diazofluorene, 2068 cm.$^{-1}$, and for diazodiphenylmethane, 2052 cm.$^{-1}$. A value of 2045 cm.$^{-1}$ is reported for diazodiphenylmethane by Shriner, Fuson, and Curtin (106) who give no references to the source of the information or to the experimental details. The increase in NN frequency in 9-diazofluorene over that in diazodiphenylmethane can be attributed to the increase in the strain of bond angles at the diazo carbon atom caused by the formation of a five membered ring by joining the phenyl groups of diazodiphenylmethane at the ortho positions. The ring strain present in five and four membered cyclic ketones causes a similar hypsochromic shift in the carbonyl frequency, the amount of the shift increasing with decreasing ring size (115, page 128).

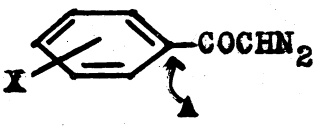
## C. Diazo Ketones

The spectra of the fourteen aromatic diazo ketones examined reveal absorption bands of medium to very strong intensity between 2138 cm.$^{-1}$ and 2078 cm.$^{-1}$ which can be attributed to an NN stretching vibration. These compounds also show bands of strong-medium to very strong intensity between 1622 cm.$^{-1}$ and 1594 cm.$^{-1}$. The lower limit of 1594 cm.$^{-1}$ is in some doubt and will be discussed detail further on. The four aliphatic diazo ketones show strong to very strong NN bands between 2116 cm.$^{-1}$ and 2142 cm.$^{-1}$ and medium to strong carbonyl bands between 1630 cm.$^{-1}$ and 1668 cm.$^{-1}$. The diazo ester, ethyl diazoacetate, absorbs very strongly at 2121 cm.$^{-1}$ (NN) and strongly at 1693 cm.$^{-1}$ (CO). In the spectra of many of the compounds weaker bands of unknown origin flanked the main strong NN stretching band and are probably overtone or combination bands. Characteristic absorption bands assigned to an NN symmetric stretching vibration have been reported between 1180 cm.$^{-1}$ and 1343 cm.$^{-1}$ for azides (115,119,123,124). The spectra of the diazo ketones contain many bands of variable intensity in this region, but the spectra are too complex to make any certain assignments possible. The data found indicate that, in general, the NN band in the diazo ketones lies between a double and a triple bond in character and that the carbonyl group is polarized somewhat, i.e. modified in the sense $C\overset{\curvearrowright}{=}O$.

Any correlations between the diazo band frequency or the carbonyl band frequency and the nature of R (XXXV)

$R\text{-}COCHN_2$

XXXV



XXXVI

or X (XXXVI) are somewhat difficult to make, because (a) differences in the corresponding band frequencies for two different compounds are usually small and quite close to the assigned probable error; (b) three compounds have two diazo bands of approximately equal intensity; and (c) the carbonyl band in several compounds can not be assigned with certainty for the band is either unresolved or falls so close to the aromatic band near 1600 cm.$^{-1}$ so as to be indistinguishable from it both in frequency and in intensity. 2-Diazo-2'-nitroacetophenone, 2-diazo-3'-nitroacetophenone, and 2-diazo-3'-methylacetophenone each exhibited two NN stretching bands of equal intensity and quite close together (within 11 to 16 cm.$^{-1}$). The reason for this particular splitting is not known.

The carbonyl band was detected by its intensity, relative position, and by a process of elimination. In every case the intensity of the carbonyl band varied from strong-medium to very strong. Its shifted position (i.e. to lower frequencies) was expected from previous literature information and the spectra of the benzil derivatives. The process of elimination made use of the literature of accumulated spectral data (115,122,125). The only infrared absorption expected in the compounds examined in the "carbonyl" and "double-bond" regions might be due to carbonyl, C=N, aromatic, and nitro groupings. The spectral results of the benzil derivatives and the simple diazo compounds indicate that the C=N band is absent or, less likely, masked by the carbonyl absorption. Aromatic compounds are reported to show three bands at approximately 1600 cm.$^{-1}$, 1600-1560 cm.$^{-1}$, and 1525-1475 cm.$^{-1}$ (115, chapter 5), the exact band positions and intensities depending upon the nature of the particular aromatic compound. Nitro compounds also absorb strongly in the "double-bond" region at 1560-1500 cm.$^{-1}$ (115, chapter 17). In most cases the assignment of the aromatic and nitro bands was relatively easy, and the only strong band remaining was most likely due to carbonyl stretching. The aliphatic compounds showed only a strong carbonyl band in the "carbonyl" and "double-bond" regions.

The greatest doubt in the assignment of the carbonyl band occurs in the cases of the three diazonitroacetophenones and 2-diazo-4'-methylacetophenone. The 2'-nitro, 3'-nitro, and 4'-methyl compounds have a strong band with a strong shoulder in the region of 1600 $cm.^{-1}$. Even if the bands had been suitably resolved it probably would have been difficult to make an assignment with any certainty for they lie so close together. The 4'-nitro compound has two bands at 1620 $cm.^{-1}$ and 1594 $cm.^{-1}$. In most cases the carbonyl band is stronger and lies at somewhat higher frequencies than the 1600 $cm.^{-1}$ aromatic band. However, the correct assignment of the carbonyl frequency in the 4'-nitro compound can be questioned, for the 1594 $cm.^{-1}$ band is the strongest band in the spectrum. Also, para substitution has been reported to cause a hypsochromic shift in the 1600 $cm.^{-1}$ band (115, page 60) when compared to ortho and meta substitution, and such an effect might be present in this case.

The carbonyl band in each of the two 2-diazoacetonaphthones is the strongest band in each spectrum and falls between two aromatic bands. The double nature of the 1600 $cm.^{-1}$ band in naphthalenes has been reported previously (115, page 61, 136) and was verified also by the derivative spectra of 2-bromo-2'-acetonaphthone and 2-chloro-2'-acetonaphthone.

Certain miscellaneous features observed in the spectra of the aromatic diazo ketones also deserve mention. Only one very strong band appears near 1600 cm.$^{-1}$ in the spectrum of 3'-bromo-2-diazoacetophenone. This band at 1602 cm.$^{-1}$ is most likely a carbonyl stretching band and probably masks the relatively weaker 1600 cm.$^{-1}$ aromatic band. The three nitro-substituted diazoacetophenones show strong bands due to the nitro group between 1520 cm.$^{-1}$ and 1534 cm.$^{-1}$. The 4'-nitro compound shows the lowest nitro band frequency of the three at 1520 cm.$^{-1}$, and this is in agreement with the observation that this band is displaced to lower frequencies in compounds which contain a strongly electronegative group in the para position to the nitro group (115, page 250). The 2'-nitro compound has two equally strong nitro bands at 1525 cm.$^{-1}$ and 1533 cm.$^{-1}$. In general the aromatic band found near 1500 cm.$^{-1}$ is weaker than the other two medium to strong aromatic bands. This observation is in agreement with Bellamy's (115, page 62) that conjugation of the ring with any double bond such as found in C=O, C=C, $NO_2$, etc. generally produces a very marked enhancement of the intensities of all three aromatic bands, and sometimes the enhancement of the first two is at the expense of the weaker 1500 cm.$^{-1}$ band. In some cases bands of medium to weak intensity were found in the "double-bond" region; their origin is unknown, although they possibly may be overtones or combination bands, and their assignments were designated in the tables with a question mark.

It was suggested earlier (cf. section III) that the positions of the bands due to NN and CO stretching vibrations might be dependent upon the electron-attracting and-repelling nature of R (XXXV), and that various substituted phenyl groups offered a convenient way to change the electron density in the vicinity of carbon atom A (XXXVI). In monosubstituted benzenes, except biphenyl, the electron pair forming the bond between the benzene nucleus and the substituent does not lie exactly halfway between the substituent and the ring carbon atom to which it is attached, but is displaced either toward the ring carbon atom or toward the substituent group, the amount of the displacement depending upon the relative electronegativities determined by the nature of the group and the ring. The relative amount and the direction of the displacement can be determined from the measured dipole moments of mono- and disubstituted benzenes. Since benzene is symmetrical, it has no dipole moment, and the dipole moment of the monosubstituted benzene thus can be attributed to the substituent (group moment).[a] Since the electrons in a benzene ring are easily moved about (resonance), the relative abundance of electrons at all the carbon atoms of a monosubstituted benzene should be dependent upon the magnitude of the dipole moment and, therefore, the group moment of the substituent. Therefore, it is reasonable to assume that in a given ortho, meta, or para

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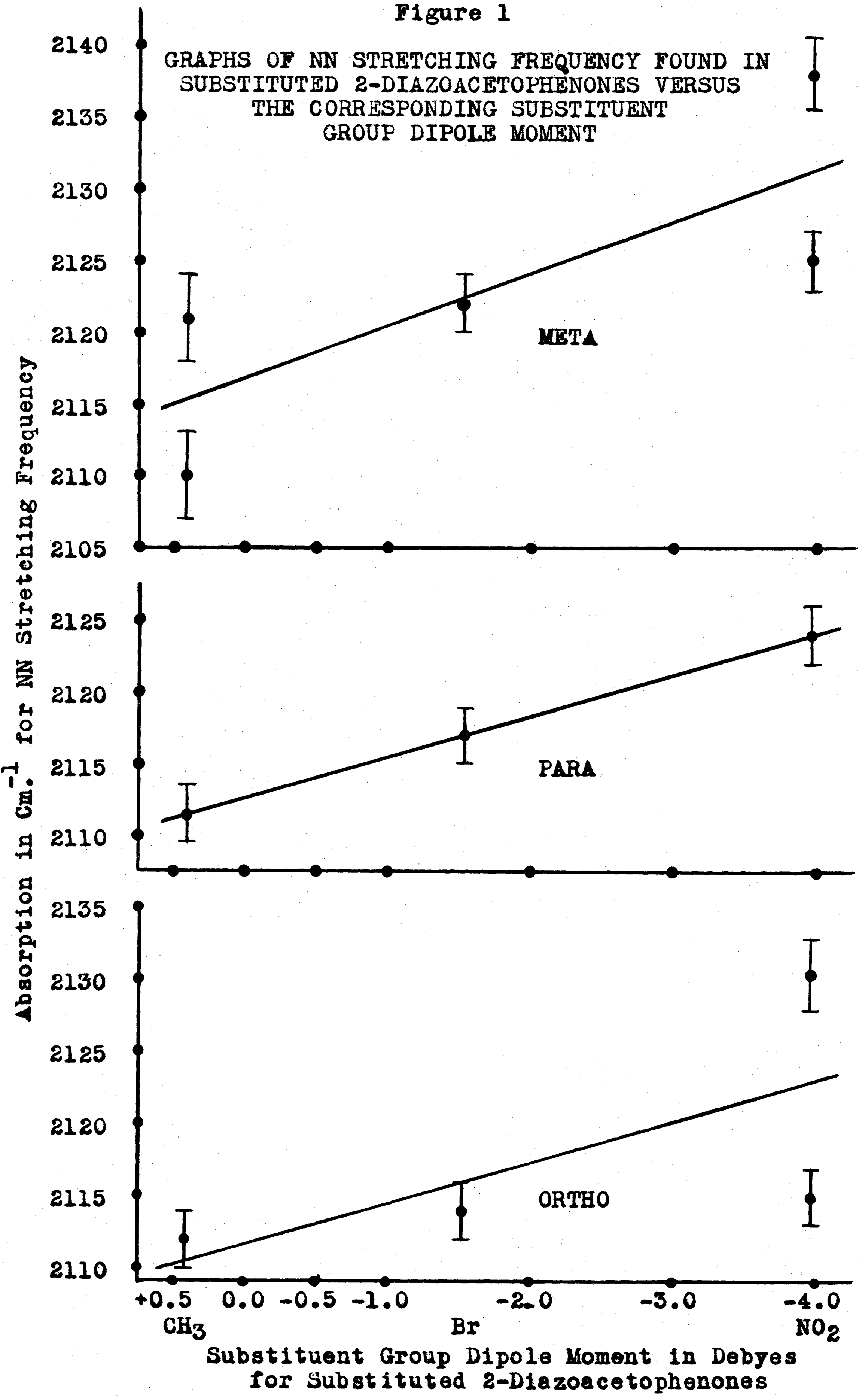
[a] Actually the group moment is a vector sum of the moment of the C-H bond and the "true" moment of the C-substituent bond.

substituted series of a monosubstituted diazoacetophenone (XXXVI) the electron density in the region of carbon atom A is dependent upon the group moment of the substituent provided that (a) the carbon-substituent bond angle and the bond angle between carbon atom A (XXXVI) and the carbonyl carbon are always the same, and (b) the geometry of the diazocarbonyl unit remains the same. It is assumed here that the group moments for meta and para substituents will always be the same, while those of ortho substituents are expected to vary somewhat depending upon the amount of interaction with neighboring groups such as the carbonyl group.

Figure 1 shows a plot of the absorption in wave numbers found for the diazo NN stretching band versus the corresponding ring-substituent group moment in Debyes for each of the three ortho, meta, and para substituted diazoacetophenones (XXXVI). The values used for the group moments are in Table VII (Appendix). Since the 2'- and 3'-nitro and the 3'-methyl compounds showed two NN bands, both values were plotted and the curve drawn between them. The vertical line through each point represents the assigned probable error. It should be emphasized that Figure 1 (as well as Figures 2-4) represents only a semiquantitative relationship at best because of the assumptions necessary in using the group moments. The figure shows that the NN stretching frequency in a given ortho, meta, or para substituted series of 2-diazoacetophenones is dependent upon the relative electron-attracting or -repelling ability of

Figure 1

GRAPHS OF NN STRETCHING FREQUENCY FOUND IN SUBSTITUTED 2-DIAZOACETOPHENONES VERSUS THE CORRESPONDING SUBSTITUENT GROUP DIPOLE MOMENT



the substituent. The more electronegative the substituent is, the higher is the NN stretching frequency. Also, for a given substituent in each of the three ring positions, meta substitution produces a significantly higher NN frequency than does either para or ortho substitution. According to Figure 1 para substitution produces a higher NN frequency than does ortho, but the difference is not significant for it lies within the experimental error. Generally nitro substitution produces a hypsochromic effect in the NN frequency when compared to the unsubstituted compound, 2-diazoacetophenone (2119 $cm.^{-1}$); bromo substitution apparently produces a small effect, but it lies very close to or within the experimental error; and methyl substitution produces a bathochromic effect.

All of the substituted diazoacetophenones were solids except the 2'-methyl compound which was a liquid at room temperature. Since the corresponding absorption bands shown by a compound in a liquid state are usually at higher frequencies than in the solid state, NN frequency values all of which are obtained from solid ortho-substituted compounds might fit a straight line somewhat better.

A reasonable check on the above conclusions might be made using Hammett's substitution (sigma) constants. A correlation of spectral data with Hammett's sigma constants has been mentioned before by Soloway and Friess (128) whose data shows an almost linear relationship between sigma constants and the carbonyl stretching frequency found for a series of meta and para substituted acetophenones. When plotted the carbonyl stretching frequencies found for ten substituted acetophenones by Tanaka, Nagakura, and Kobayashi (129) also exhibit an almost linear relationship with the corresponding Hammett sigma constants.[a]

The sigma constant is obtained from Hammett's equation, $\text{Log } k_{\sigma} = \text{Log } k_{\mu} + \sigma\rho$ , where $k_{\mu}$ is the rate or equilibrium constant of a general reaction for the unsubstituted member of a class of compounds (such a class would be those of monosubstituted benzoic acids); $k_{\sigma}$ is the rate or equilibrium constant of a general reaction for the substituted member of a class; $\sigma$ is a substituent constant; and $\rho$ is a constant for the general type of reaction. Hammett arbitrarily chose $\rho = 1$ for the equilibrium constants for the dissociation of substituted benzoic acids. The equation is considered to be a good approximation when the effect of the substitution is due chiefly to a change of the electric charge on the aromatic carbon atom to which the reacting group is attached. Hammett's equation generally is not considered to be applicable to ortho-substituted compounds where steric interactions, directly transmitted polar effects, and important resonances other than those between the substituent group and the aromatic resonances can cause appreciable error (137,138). Taft (139) has attempted to obtain two ortho substituent constants, one being a measure of the substituent polarities, and the other a measure of

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[a] It is interesting to note that the carbonyl frequencies obtained by both sets of workers also show a similar relationship to the corresponding substituent group moment.

the steric factors involved. Mamalis and Rydon (140) also have attempted to evaluate ortho sigma constants from data obtained by the alkaline fission of ortho-substituted aroyloxyethyldimethylsulphonium iodides.

Figure 2 shows a plot of the NN stretching frequency in wave numbers for substituted 2-diazoacetophenones versus the corresponding Hammett sigma constant. The values used for the sigma constants are given in Table VIII (Appendix). The points for the two ortho constants were included in the graph, but they were not used in drawing the line because of their questionable value (cf. reference 140 for a brief comparison of the ortho sigma values of Mamalis and those of Taft). Although the graph does not indicate a completely linear correlation, it does show, however, that a rough parallelism does exist between the NN frequency and the corresponding sigma constant, the NN frequency increasing as the sigma value becomes more positive.

A sigma value of +0.170 has been reported for β-naphthalene derivatives (137,141), but the NN frequency in 2-diazo-2'-acetonaphthone (2094 cm.$^{-1}$) is found far off the curve in Figure 2. It is somewhat surprising to find that 2-diazo-1'-acetonaphthone has its NN frequency at 2112 cm.$^{-1}$, since Hunsberger (142) has shown that in 0.02 molal carbon tetrachloride solution α- and β-naphthyl carbonyl compounds have carbonyl bands very close to one another.[a] However,

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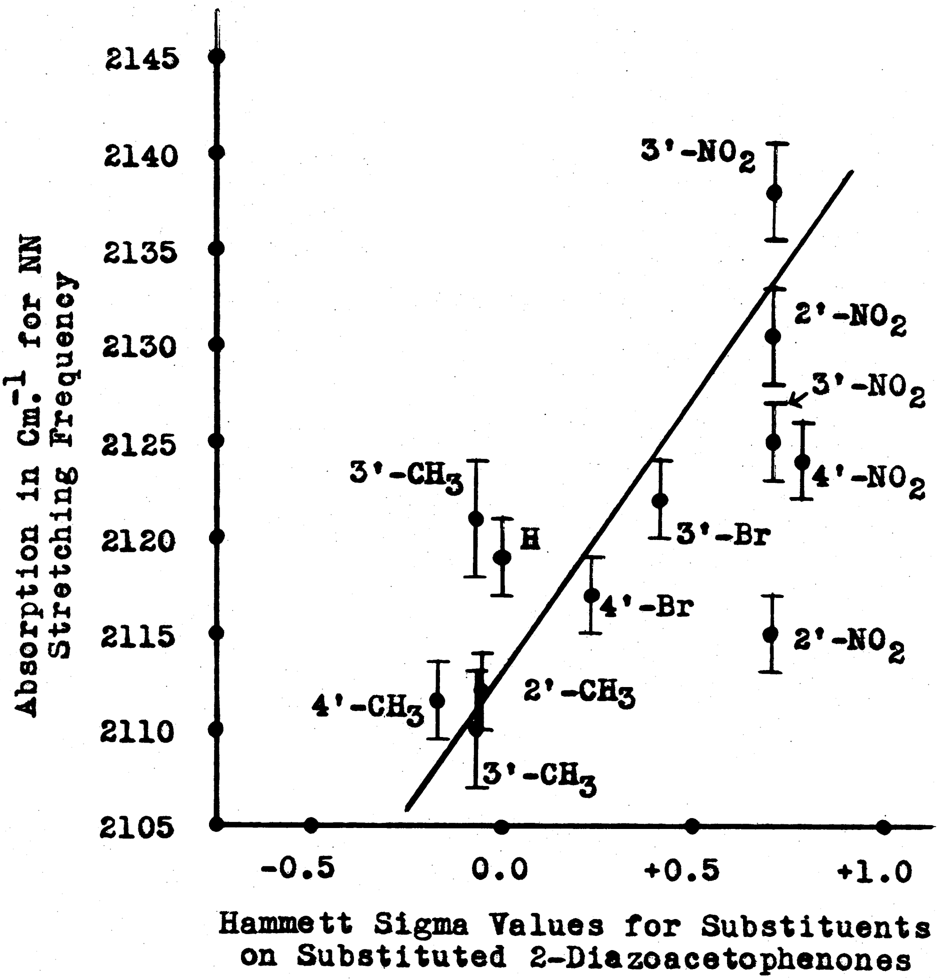
[a] α-naphthaldehyde, 1700 cm.$^{-1}$; β-naphthaldehyde, 1702 cm.$^{-1}$; α-acetonaphthone, 1685 cm.$^{-1}$; β-acetonaphthone, 1685 cm.$^{-1}$; methyl α-naphthoate, 1724 cm.$^{-1}$; methyl β-naphthoate, 1726 cm.$^{-1}$.

## Figure 2

## GRAPH OF NN STRETCHING FREQUENCY FOUND IN SUBSTITUTED 2-DIAZOACETOPHENONES VERSUS THE CORRESPONDING HAMMETT SIGMA VALUE FOR SUBSTITUENTS[a]

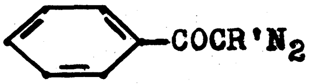


[a] 2'-Points not used in plotting graph.

since the measurements on the two diazoacetonaphthones were made on the solid phase, it is quite possible that internal crystal forces were much more active in one compound than the other.

Unfortunately the doubt concerning the correct assignment of the carbonyl frequency in four of the substituted 2-diazoacetophenones makes any significant and complete correlations virtually impossible. The only certain correlation observed is that bromo substitution produces a significant bathochromic shift in the carbonyl frequency compared to that in 2-diazoacetophenone with meta bromo substitution giving the largest shift. 2-Diazo-2'-acetonaphthone also exhibits a lower carbonyl frequency (1607 $cm.^{-1}$) than 2-diazo-1'-acetonaphthone (1613 $cm.^{-1}$) as well as a lower NN frequency.

A comparison of the carbonyl and NN frequencies in 2-diazoacetophenone (R' = H, 1618.5 $cm.^{-1}$ and 2119 $cm.^{-1}$), 2-diazopropiophenone (R' = $CH_3$, 1621 $cm.^{-1}$ and 2085 $cm.^{-1}$), and 2-diazo-2-phenylacetophenone (R' = $C_6H_5$, 1620 $cm.^{-1}$ and 2078 $cm.^{-1}$) indicates that variation in the nature of R' (XXXVII) has very little effect upon the carbonyl frequency,



**XXXVII**

but does reduce significantly the NN stretching frequency. Since the spectrum of 2-diazopropiophenone was obtained from the liquid and those of the other two compounds from solids, it would be presumptuous to attempt any further correlations.

The values of 1619 $cm.^{-1}$ and 2073 $cm.^{-1}$ which have been reported for azibenzil ($R' = C_6H_5$), (47), compare favorably with the above values.

The positions of the NN and CO stretching bands in the spectra of the four aliphatic diazo ketones also are dependent upon the electron-attracting or -repelling nature of group R (XXXV). Figure 3 and figure 4 show a plot of

$R-COCHN_2$

XXXV

the CO stretching frequency and the NN stretching frequency in wave numbers, respectively, found for the aliphatic diazo ketones versus the group dipole moment for R in $RCOCHN_2$. Though the relationship is not completely linear, it is apparent that as group R becomes more strongly electron-attracting in nature the positions of both the NN and the CO stretching bands shift progressively to higher frequencies. The value previously reported for the NN frequency for 1-diazo-3,3-dimethylbutanone-2, 2079 $cm.^{-1}$, by Wiberg and Hutton (91) is quite low compared to the value 2116 $cm.^{-1}$ reported here. However, their value can be questioned, because they were using the disappearance of the NN band only as a check on a reaction termination.

The values found for the NN and the CO frequency, especially the latter, for ethyl diazoacetate (2121 $cm.^{-1}$ and 1693 $cm.^{-1}$) are quite out of line with those for the aliphatic diazo ketones. The values used for the group moments in the figures are those obtained from the corresponding monosubstituted benzenes (cf. previous discussion)

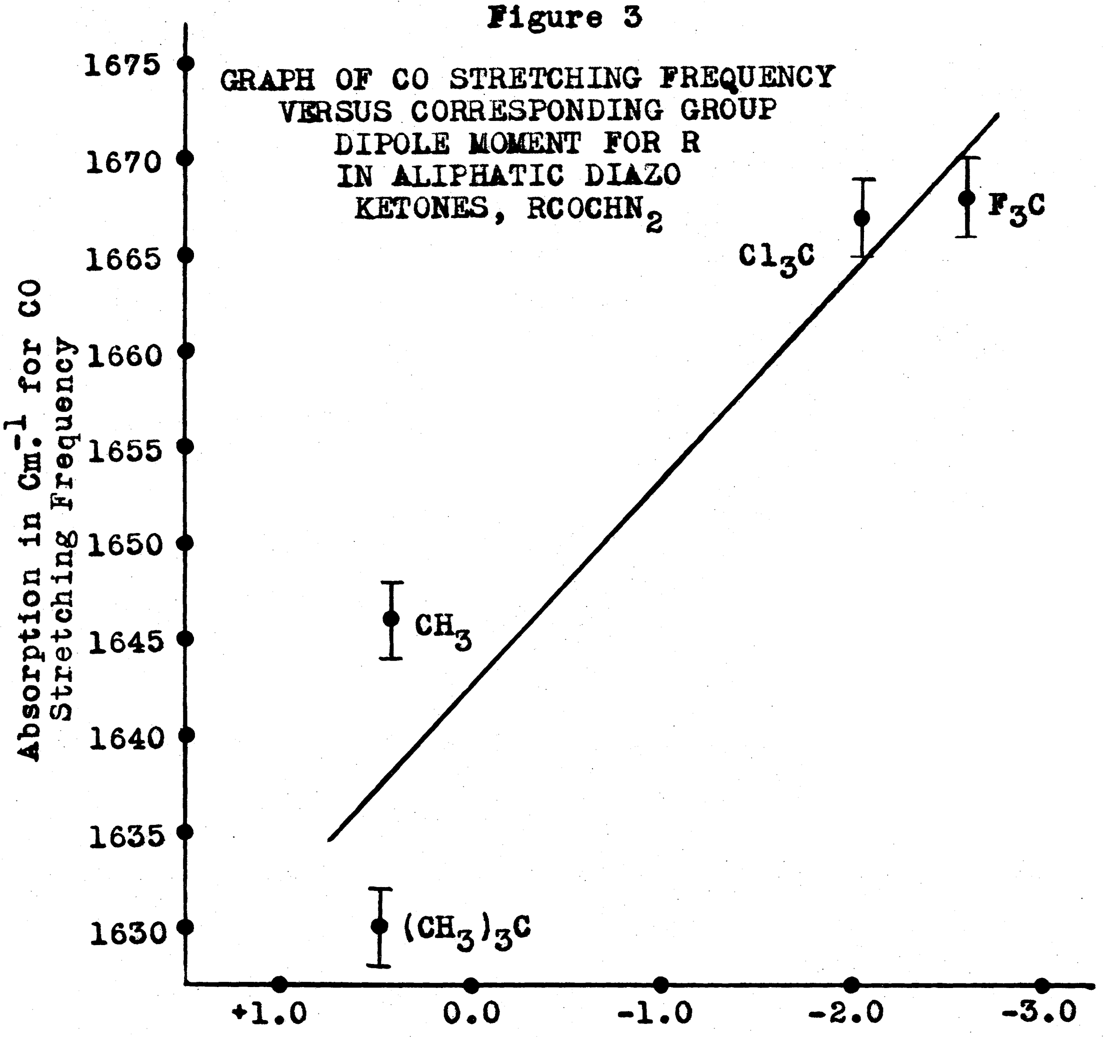


**Figure 3**

GRAPH OF CO STRETCHING FREQUENCY VERSUS CORRESPONDING GROUP DIPOLE MOMENT FOR R IN ALIPHATIC DIAZO KETONES, $RCOCHN_2$

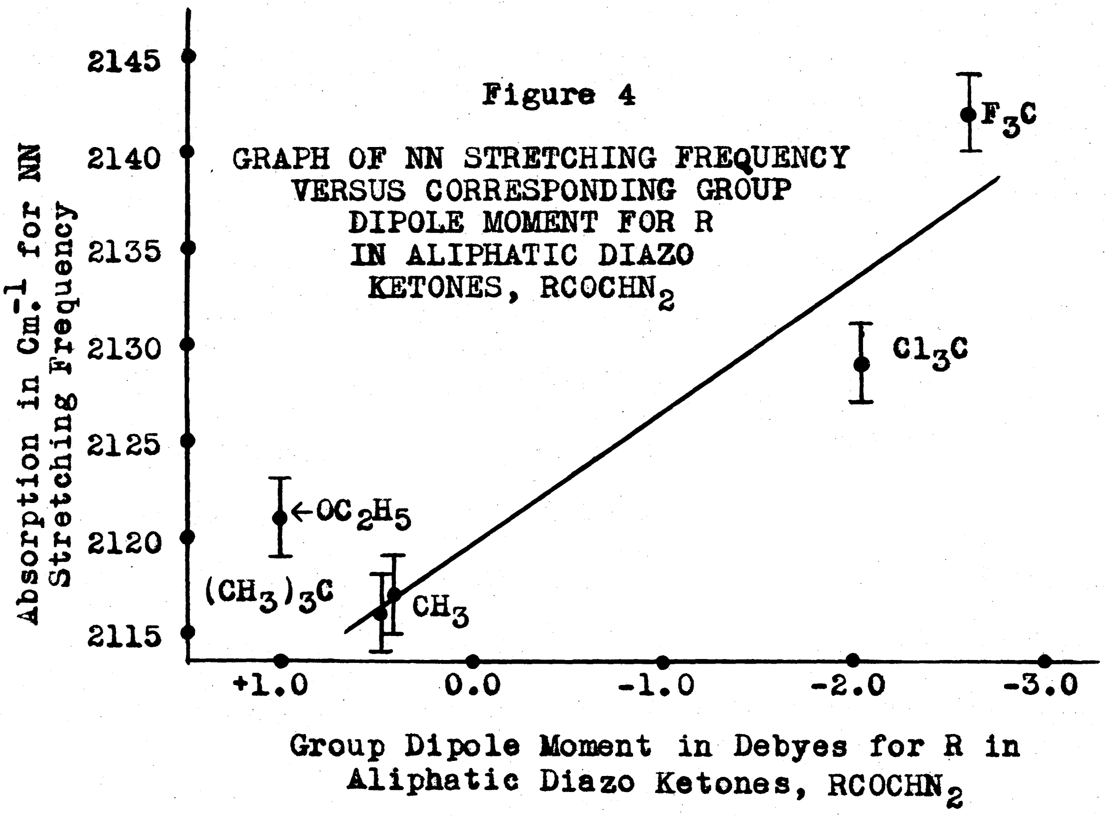
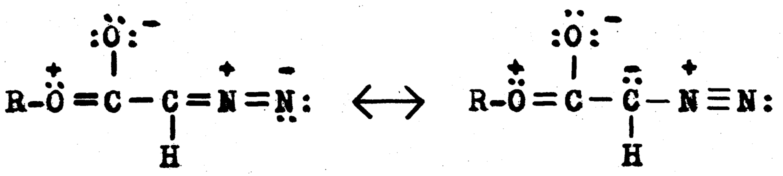


**Figure 4**

GRAPH OF NN STRETCHING FREQUENCY VERSUS CORRESPONDING GROUP DIPOLE MOMENT FOR R IN ALIPHATIC DIAZO KETONES, $RCOCHN_2$

in which the substituents may undergo some, though not appreciable, resonance with the ring. However, the ethoxy group in ethyl diazoacetate is free to form structures of the type **XL** (similar to those usually assumed for esters) in addition to those of the nature shown in XXII (page 15) and which may contribute appreciably to the ground state



$$R-\overset{+}{\ddot{O}}=\overset{:\ddot{O}:^{-}}{C}-\underset{H}{C}=\overset{+}{N}=\overset{-}{\underset{\cdot\cdot}{N}}: \longleftrightarrow R-\overset{+}{\ddot{O}}=\overset{:\ddot{O}:^{-}}{C}-\underset{H}{\overset{-}{\ddot{C}}}-\overset{+}{N}\equiv N:$$

**XL**

of the diazo ester. Similar structures can not be assumed to contribute appreciably to the ground state of the other aliphatic diazo ketones. The carbonyl values of 1698 cm.$^{-1}$ and 1678 cm.$^{-1}$ that have been reported for the diazo ester azaserine (103,108) and the values found here for ethyl diazoacetate indicate that diazo esters may, in general, show carbonyl bands at higher frequencies than do other diazocarbonyl compounds.

# V. SUMMARY

A series of benzil derivatives was prepared and their infrared spectra in the "carbonyl" and "double-bond" regions carefully recorded. The gradual bathochromic shift in the carbonyl band from its position in the spectrum of benzil through the spectra of the derivatives to that in the corresponding diazo ketone was observed. The shift can be explained by "conjugate-chelation", ordinarily exhibited by compounds of the structure -C(XH)=C-C(=Y)-, which is shown here also to include compounds of the general type :N(XH)=C-C(=Y)-.

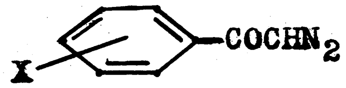
The preparation and physical properties of eighteen aromatic and aliphatic diazo ketones, two simple diazo compounds, a diazo ester, and the necessary intermediates and derivatives have been described. The following seven compounds are those prepared whose properties have not been previously reported:

a) 3'-bromo-2-diazoacetophenone
b) 2-diazo-3'-nitroacetophenone
c) 2-diazo-2'-methylacetophenone
d) 2-diazo-3'-methylacetophenone
e) 2-diazo-2'-acetonaphthone
f) 2-o-tolylacetanilide
g) benzil α(syn)-mono-diphenylhydrazone

The infrared spectra of all the simple diazo compounds and the diazocarbonyl compounds were carefully recorded in the "triple-bond" and in the "carbonyl" and "double-bond" regions. The characteristic absorption frequencies at 2068 $cm.^{-1}$ and 2052 $cm.^{-1}$ due to an NN stretching vibration shown by the simple diazo compounds extends the range of reported absorption for this type of compound from 2103 cm.$^{-1}$ to 2052 cm.$^{-1}$. The exact position of the NN band appears to be dependent upon conjugation and the ring strain at the carbon atom to which the diazo group is attached.

The aromatic diazo ketones show characteristic NN stretching frequencies between 2138 cm.$^{-1}$ and 2078 cm.$^{-1}$ and CO stretching frequencies between 1622 cm.$^{-1}$ and 1594 cm.$^{-1}$. The aliphatic diazo ketones show similar absorptions between 2116 cm.$^{-1}$ and 2142 cm.$^{-1}$, and 1630 cm.$^{-1}$ and 1668 cm.$^{-1}$; the ester, ethyl diazoacetate, absorbs at 2121 cm.$^{-1}$ and 1693 cm.$^{-1}$. The NN band appears to be between a double and a triple bond in nature, and the CO bond appears to be somewhat ionic in character, i.e. modified in the sense $C\overset{\curvearrowright}{=}O$.

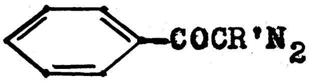
The NN frequency in the substituted diazoacetophenones, XXXVI, is shown to be dependent upon the position and electron-attracting or -repelling power of the substituent, the frequency increasing with meta substitution and increased electron-withdrawing ability of X. Doubts arising from several instances of uncertain assignments prohibit similar correlations of the CO frequency. Both the NN and CO frequency in aliphatic diazo ketones, XXXV, are observed to be dependent upon the electron-attracting or -repelling nature of R, both frequencies increasing as R becomes more electron-attracting. Changing the nature of R' (XXXVII) from hydrogen to methyl and phenyl has no



XXXVI

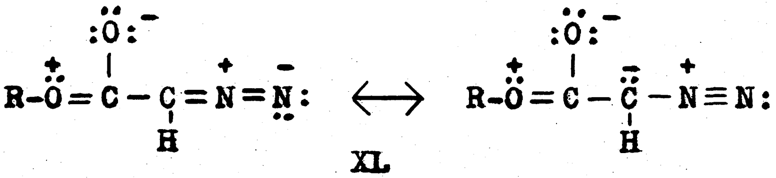
$R-COCHN_2$

XXXV



XXXVII

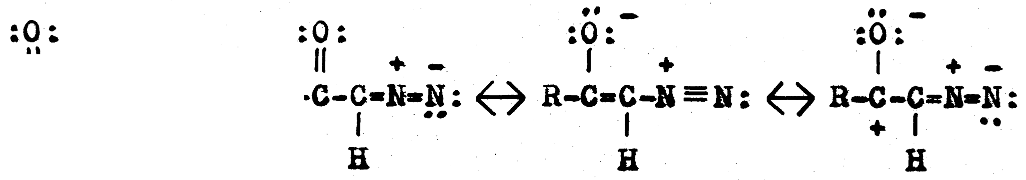
effect on the CO frequency but considerably reduces the NN frequency. From the data obtained from ethyl diazoacetate it is suggested that resonance forms of the kind in XL may



$$R-\overset{+}{O}=\overset{\overset{O^{-}}{|}}{C}-\underset{H}{C}=\overset{+}{N}=\overset{-}{N}: \longleftrightarrow R-\overset{+}{O}=\overset{\overset{O^{-}}{|}}{C}-\underset{H}{\overset{-}{C}}-\overset{+}{N}\equiv N:$$

XL

contribute appreciably to the ground state in addition to forms of the nature shown in XXII.



$$-\overset{\overset{O}{\|}}{C}-\underset{H}{C}=\overset{+}{N}=\overset{-}{N}: \longleftrightarrow R-\overset{\overset{O^{-}}{|}}{C}=\underset{H}{C}-\overset{+}{N}\equiv N: \longleftrightarrow R-\overset{\overset{O^{-}}{|}}{C}-\underset{H}{\overset{+}{C}}=\overset{+}{N}=\overset{-}{N}:$$

(b) (c) (d)

XXII

# VI. EXPERIMENTAL

## A. Spectral Techniques

All infrared spectra were obtained by the use of a Perkin-Elmer Double Beam Recording Infrared Spectrophotometer, Model 21, manufactured by the Perkin-Elmer Corporation, Norwalk, Connecticut. The instrument is equipped with sodium chloride optics and is located in a room with controlled temperature and humidity. The instrument records a spectrum linear in frequency in wave numbers from 4000 $cm.^{-1}$ to 600 $cm.^{-1}$. The manufacturer claims a resolving power of 1.5 $cm.^{-1}$ at 850 $cm.^{-1}$. The instrument's dispersion can be widely varied by selective interchange of scale change gears; a solonoid operated scale changer, effective at 2000 $cm.^{-1}$, compresses the spectrum between 2000-4000 $cm.^{-1}$ to four times that from 2000-600 $cm.^{-1}$.

The following is a tabulation of the operating conditions used:

Nernst glower source --- 0.3 amperes

Response setting --- 1

Automatic suppression setting --- 0-2

Gain setting --- 5 1/4

Scattered light filter --- out

Scanning speed --- variable (see text below)

Resolution setting --- 927. A resolution setting of 927 gives the following approximate slit widths:

33.5$\mu$ at 2200 cm.$^{-1}$
36 at 2100
38.5 at 2000
40.5 at 1900
46.7$\mu$ at 1700 cm.$^{-1}$
53 at 1600
60 at 1500

No compensating cell was placed in the reference beam at any time.

Most of the samples investigated were solids, and the spectra of these materials were determined as Nujol mulls; liquids were determined both as thin films and mixed with Nujol. At the beginning of this investigation the spectra of approximately 0.2-0.5 molar solutions of each sample in chloroform and in diethyl ether, as well as in Nujol, were recorded on a calibrated Baird infrared recording spectrophotometer, Model B, manufactured by Baird Associates, Inc., Cambridge, Massachusetts. The instrument was equipped with sodium chloride optics and recorded a spectrum linear in wave length at a dispersion of 1$\mu$/3.2 centimeters. These preliminary studies revealed significant differences in the positions of the diazo and the carbonyl bands of a given compound in the three substances. The use of solvents was consequently abandoned, because it would be virtually impossible to correlate spectral data obtained in solution with data obtained on solids; the relative insolubility of several of the compounds also made the use of solvents undesirable. The diazo bands of four liquid diazo ketones and ethyl diazoacetate were recorded by the Perkin-Elmer instrument both in Nujol and as thin liquid films; the Nujol was found to have a negligible effect upon the bands, because the differences in frequency for a diazo band of a given compound in Nujol and as a film were never more than 1 $cm.^{-1}$.

All compounds were purified until their spectra and physical properties (melting points of solids and boiling points and refractive indicies of liquids) were constant. The spectra of the compounds were recorded as soon as possible after their purification. Many of the solid compounds were repurified by crystallization several times after their spectra and physical properties appeared to be constant, and the spectra again were recorded. The compounds were always stored in a refrigerator coil at -4° to -7° and were allowed to reach room temperature only when the spectra were being recorded.

The infrared spectrum of each compound was recorded three times using a different dispersion each time. To check on purity and reproducibility of the spectrum (purification to constant spectra) as well as to obtain a complete and compact spectrum of each sample, the spectrum was recorded from 4000-600 $cm.^{-1}$ with a maximum instrument scanning speed of ten; this yielded a spectrum that could be recorded on an 8 1/2 by 11 inch piece of paper. The dispersion was 400 $cm.^{-1}$ per one centimeter between 4000 $cm.^{-1}$ and 2000 $cm.^{-1}$, and 100 $cm.^{-1}$ per one centimeter between 2000 $cm.^{-1}$ and 600 $cm.^{-1}$. No calibrations were run for these small spectra.

For the accurate determination of all bands below 2000 $cm.^{-1}$ the spectrum of each compound was run from 3200 $cm.^{-1}$ to 600 $cm.^{-1}$ at an instrument scanning speed from between three to four; this yielded an expanded spectrum with a dispersion of 100 cm.$^{-1}$ per one centimeter for bands greater than 2000 cm.$^{-1}$, and 25 cm.$^{-1}$ per one centimeter for bands between 2000 cm.$^{-1}$ and 600 cm.$^{-1}$. Either immediately before or after the recording of this spectrum the instrument was carefully calibrated by recording the spectrum of a 0.07 mm. thick film of polystyrene. These calibrations always substantially agreed with periodic departmental calibrations obtained with polystyrene, atmospheric water vapor, and carbon dioxide. The values reported for bands between 2000 cm.$^{-1}$ and 600 cm.$^{-1}$ are the result of from one to five such determinations.

For the determination of the diazo NN stretching frequency the spectrum of each compound was recorded between 2200 cm.$^{-1}$ and 2050 cm.$^{-1}$ with a dispersion of 8 cm.$^{-1}$ per one centimeter and an instrument scanning speed between two and four. Either immediately before or after (or at both times) the recording of this spectrum the instrument was carefully calibrated with the 1946 cm.$^{-1}$ band from a piece of 0.07 mm. thick polystyrene film. All values reported between 2200 cm.$^{-1}$ and 2050 cm.$^{-1}$ are the average obtained from four to fifteen such determinations on each compound.

An experimental error is reported with each band recorded. This error should be looked upon as a "confidence limit" or "probability limit" and is the result of several estimations rather than the result of rigid mathematical determinations. A calibration error was assigned to each calibration band depending upon its particular sharpness and resolution in each spectrum. The instrument error was assumed to vary linearly between calibration bands. A probable error was similarly assigned to each band measured, the magnitude of this error depending upon the sharpness and resolution of the band as well as upon the ease with which the band center could be estimated. When an average value was reported for a band, the reported error was always slightly greater than the maximum deviation of any single measurement from the average value. The final plus and minus error reported for each band is the sum of the error in the band and the error in the calibration.

A relative band intensity also is reported along with each band position reported, the small letter accompanying it representing the relative intensity. This system for reporting band intensities is an arbitrary one; the use of Nujol mulls makes the calculation of accurate extinction coefficients impossible, since cell thickness, particle size, and concentration of the mull can not be conveniently measured or reproduced. On each spectrum a base line was drawn parallel to the base of the paper and tangent to the spectrum at the point of maximum transmittancy; this base line was used in a region where the solid particle size has little effect on the base line (essentially from 2200 $cm.^{-1}$ to 600 $cm.^{-1}$ in all spectra run). After selecting the base line the most intense band in each spectrum was selected, given an arbitrary intensity value of 100, and its height measured in some convenient unit (as millimeters). The relative height of each band measured was then determined in the same units, and the ratio of its height to the height of the strongest band was calculated and multiplied by one hundred. The following assignments were made:

S -- strongest band in the spectrum.

s -- strong intensity -- intensity is 80-100% that of S.

sm -- strong-medium intensity -- intensity is 70-80% that of S.

m -- medium intensity -- intensity is 30-70% that of S.

mw -- medium-weak intensity -- intensity is 20-30% that of S.

w -- weak intensity -- intensity is less than 20% that of S.

If a Nujol band were the strongest band in the spectrum then the next strongest band was chosen as the reference band (S), and the Nujol band labeled with an intensity of S'. Many bands contained "shoulders" resulting from unresolved bands; the position and the intensity of the "shoulders" were estimated and reported.

## B. Preparation of Organic Compounds

All the melting points reported in the following experimental work are corrected unless specified to the contrary; all boiling points are uncorrected. With two exceptions all analyses were performed by Mrs. Anna Griffin, Department of Chemistry, University of Michigan. The bromine analysis on 2'-bromo-2-diazoacetophenone was performed by the author. The analysis of benzil mono-diphenylhydrazone was carried out by Spang Microanalytical Laboratory, Plymouth, Michigan. In a few cases the nitrogen analysis (by the Dumas method) varied considerably from the calculated value even though the carbon and hydrogen analysis was quite acceptable. This variation is presumably due to the instability of the particular compounds toward heat and the method of analysis rather than impure samples. The difficulties in analyzing diazo ketones for nitrogen by the Dumas method have been noted previously by Roth (143).

The names of compounds unreported up to this time are preceded by a double asterisk (**). The infrared spectral curves of compounds whose names are followed by an asterisk (*) are included in section VIII. The nomenclature used is consistent with that used by Chemical Abstracts, 1954; the compound names enclosed in parentheses are those consistent with older nomenclature.

## 1. Preparation of Benzil Derivatives

Benzil*--Eastman Kodak #35 was recrystallized four times from methanol. m.p. 94.2-95.1°C.

Benzil Monohydrazone*--Hydrazine hydrate, 12.4 ml. (0.255 moles), was added slowly with stirring over a one-half hour period to a solution of 52.5 g. (0.25 moles) of benzil in 130 ml. of hot 95% ethanol. The solution was refluxed for two hours and then cooled to 0°C. The white solid which precipitated was filtered, washed with cold

95% ethanol, and air dried. Yield 54.2 g. (96.8%), m.p. 142-147°. After three recrystallizations from 95% ethanol and drying over $CaCl_2$ at 15 mm. Hg the white granular crystals melted at 149.2-150.0°C with decomposition after being inserted in the melting point bath at 146°. Reported m.p. 151°, 151-152°C (85). In another identical run a 96.0% yield of product was obtained.

<u>Benzil Dihydrazone</u>*--A mixture of 30.0 g. (0.143 moles) of benzil, 17.5 ml. (0.361 moles) of hydrazine hydrate, and 85 ml. of isopropanol was gently refluxed for 138 hours. A white precipitate which appeared after several minutes heating disappeared after about one day's refluxing. The yellow solution was cooled, the resulting solid white mass filtered, washed with cold absolute ethanol, and the needles dried overnight at 15 mm. Hg over $CaCl_2$. Yield 27.3 g. (80.3%). After four recrystallizations from 95% ethanol the white needles melted at 148.0-148.4°C with decomposition. Reported m.p. 147° (144) and 152-153°C (145).

<u>Benzil Monophenylhydrazone</u>*--A mixture of 5.0 g. (0.024 moles) of benzil and 2.4 ml. (0.024 moles) of phenylhydrazine was heated on a steam bath for one hour. The orange-yellow oil solidified upon the addition of a small amount of methanol and cooling. Yield 3.3 g. (46.4%). After five recrystallizations from methanol and drying overnight at 15 mm. Hg over $P_2O_5$ the canary-yellow crystals melted at 135.0-135.5°C. Reported m.p. 134°, uncorrected (146), 128-129° (147), 135° (148).

Benzil Di-monophenylhydrazone (Benzil β-Osazone)*--A mixture of 5.0 g. (0.024 moles) of benzil and 5.9 ml. (0.060 moles) of phenylhydrazine was refluxed for one hour. An additional 3.2 ml. (0.032 moles) of phenylhydrazine was then added and the refluxing continued for another hour. The reaction mixture was cooled, and the dark crystals which immediately precipitated were filtered off and dissolved in hot chloroform. Ethanol, 95%, was added dropwise until a slight precipitate appeared, and the solution was then heated to boiling and allowed to cool slowly. The crystals which appeared were filtered and washed with cold ethanol. Yield 8.3 g. (89.0%). After five more such recrystallizations from chloroform-ethanol mixture and drying over $CaCl_2$ at 15 mm. Hg the fine pale-yellow needles melted at 238.0-238.4°C. The samples were placed in the melting point bath at 236°, because the melting point was quite sensitive to the rate of heating. Reported m.p. 235-236°, uncorrected (146), 234-235° (148); both references reported that the melting point was very dependent upon the rate of heating.

**Benzil Mono-diphenylhydrazone*--A mixture of 1.90 g. (0.00905 moles) of benzil, 2.00 g. (0.00907 moles) of 1,1-diphenylhydrazine hydrochloride, 1.10 g. of anhydrous sodium acetate, and 50 ml. of absolute ethanol was gently refluxed for 307 hours. After cooling the reaction mixture in a refrigerator overnight 0.68 g. of sodium acetate was filtered off and washed with absolute ethanol. The very impure yellow solid that remained after the solvent from the combined filtrates had been removed under reduced pressure was dissolved in a small amount of hot absolute ethanol and the solution allowed to cool slowly. The crystals that appeared in the warm solution were quickly filtered off, yield 2.26 g., m.p. 105-118°. After dissolving this material in excess, hot, absolute ethanol and cooling the solution slowly, the yellow-green compact crystals that appeared in the warm solution were quickly filtered off and dried, yield 0.29 g. (8.5%) of yellow-green powder, m.p. 132-138°. (Refluxing similar amounts of the above starting materials for 19 1/2 hours resulted in a 2.8% yield of product.) Further cooling of the filtrate yielded 1.24 g. (36.4%) of bright yellow-orange crystals, m.p. 106.5-113°.

After the yellow-green powder had been recrystallized three more times from absolute ethanol and dried over $P_2O_5$ at 9 mm. Hg the clusters of greenish-yellow needles melted at 139.7-140.2°C. The compound melted quite quickly to a deep red clear liquid with no apparent decomposition. All samples were placed in the melting point bath at 136.5°, since the melting point appeared to be very sensitive to the amount of prior heating of the sample. The compound showed a strong infrared carbonyl band at 1640 ± 2 $cm.^{-1}$.

After the yellow-orange crystals had been recrystallized three more times from absolute ethanol and dried over $P_2O_5$ at 10 mm. Hg the deep yellow crystals melted at 108.8-109.9°C to a deep red liquid. Reported melting point for benzil mono-diphenylhydrazone, 108° (149). The crystals slowly assumed an orange coloration after a week's standing in the light but remained bright yellow in a black desiccator. The compound showed a strong infrared carbonyl band at 1676 ± 2 $cm.^{-1}$.

Palm and Werbin (135) have shown that the infrared carbonyl and C=N bands of benzil β(anti)-monoxime occur at considerably longer frequencies than those of benzil α(syn)-monoxime. The spectra of the benzil mono-diphenylhydrazones indicate that the high melting form (139.7-140.2°) is the α or syn form while the low melting form (108.8-109.9°) is the β or anti form.

Anal. Calcd. for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44. Found for α form: C, 82.96; H, 5.43; N, 7.50. Found for β form: C, 83.00; H, 5.36; N, 7.43.

Benzil Monoanil*--This compound was prepared six different times under a variety of experimental conditions; the two procedures given below represent those giving the best yields.

Five grams (0.0238 moles) of benzil, 5.0 ml. (0.05 moles) of aniline, and 0.05 g. of iodine (reference 100) were heated together for fifteen minutes at 130° ± 5°. Absolute ethanol was added to the mixture until the total volume was approximately 45 ml., and the material was cooled for several days in the refrigerator. Yield 5.08 g. (74.9%), m.p. 94-102°C.

Five grams (0.0238 moles) of benzil, 5.0 ml. (0.05 moles) of aniline, and two drops of concentrated hydrochloric acid were heated together for four and one-third hours at 125-130°. Absolute ethanol was added to the mixture until the total volume was approximately 45 ml. and the material cooled for several days in the refrigerator. Yield 4.89 g. (72.1%), m.p. 93-103°C.

Five recrystallizations of the above crude compounds from 95% ethanol did not appreciably change the melting points. Three grams of this crude material was placed in 50 ml. of 95% ethanol and stirred at room temperature until all soluble material had dissolved. The insoluble material was filtered off and then recrystallized six times from 95% ethanol. After drying overnight over $P_2O_5$ at 15 mm. Hg the yellow crystals melted at 104.8-105.7°C. Reported m.p. 105°, 106°, 108°C (150). Knoevenagel (151) reports the initial formation of an unstable form melting at 96° that slowly changes to a 105° melting form after one and one-half to two days.

Benzil Dianil*--Five grams (0.0238 moles) of benzil, 9.1 ml. (0.010 moles) of aniline, and one drop of concentrated hydrochloric acid were heated at 165° ± 3° for three hours. The dark, red-brown, viscous liquid was then seeded with some of the impure material from the benzil monoanil preparations and the material placed in the refrigerator for several days. The solid which precipitated was filtered and washed with cold absolute ethanol. Yield 1.71 g. (20.0%), m.p. 132-137°. After seven recrystallizations from 95% ethanol and drying overnight over $CaCl_2$ at 15 mm. Hg the bright yellow plates melted at 140.8-141.6°C. Reported m.p. 140°, 141-142°, 142°C (150).

## 2. Preparation of Simple Aromatic Diazo Compounds

9-Fluorenone Hydrazone*--Hydrazine hydrate, 11.5 ml. (0.236 moles), was added to a warm solution of 16.00 g. (0.0889 moles) of fluorenone dissolved in 20 ml. of absolute ethanol. The mixture was heated on the steam bath for 25 minutes at which time the contents of the flask solidified to a dark yellow-light orange mass. Twenty one milliliters of absolute ethanol was added, the mixture warmed on the steam bath for five minutes, then cooled in ice, filtered, and the solid washed with cold absolute ethanol. Yield 14.81 g. (85.8%). After four recrystallizations from 95% ethanol and drying over $CaCl_2$ at 15 mm. Hg the very pale yellow fine needles melted at 150.8-151.3°C with decomposition. Reported m.p. 149° (152) and 149-150° (153). A second preparation using one-half of the above amounts gave an 81.3% yield.

9-Diazofluorene*--This compound was prepared according to the method of **Nenitzescu** and Solomonica (154). A mixture of 4.00 g. (0.0206 moles) of 9-fluorenone hydrazone, 7.0 g. (0.032 moles) of yellow mercuric oxide, and 2.1 g. of anhydrous sodium sulfate, after being finely ground together in a mortar, was placed in a 125 ml. glass-stoppered flask and covered with 50 ml. of dry ether. After the addition of 0.5 ml. of a saturated solution of potassium hydroxide in ethanol the suspension was shaken mechanically for 45 minutes. The dark olive-drab-colored solid was filtered off and thoroughly washed with dry ether until the washings were faint pink. The ether was removed from the filtrate with a jet of dry air leaving 3.90 g. (98.6%) of very dark red needles, m.p. 97.8-98.4°C. After five recrystallizations from reagent ether the deep red needles melted at 95.9-96.2°C with decomposition. Reported m.p. 95° (155), 94-95° (156). The product is very soluble in ether; in another run using one-half of the above quantities of materials the ether extracts were evaporated to 5 ml. instead of to dryness. Yield 1.31 g. (66.1%), m.p. 98.1-98.5°C.

Benzophenone Hydrazone*--Seven and one-half milliliters (0.155 moles) of hydrazine hydrate was added to a solution of 25.0 g. (0.137 moles) of benzophenone dissolved in 14 ml. of hot absolute ethanol. The clear solution was then refluxed gently for sixty-four and three-quarters hours. The white solid that separated upon cooling the solution was filtered off, washed with cold absolute ethanol, and dried. Yield 25.8 g. (95.9%), m.p. 94.8-99.8°C. After one recrystallization from 95% ethanol and drying over $CaCl_2$ at 15 mm. Hg the snow-white needles melted at 97.5-98.7°C. Reported m.p. 97-98°C (157,158).

Diazodiphenylmethane*--A mixture of 7.22 g. (0.0368 moles) of benzophenone hydrazone, 19.65 g. (0.0906 moles) of yellow mercuric oxide, and 10.97 g. of anhydrous sodium sulfate was placed in a glass-stoppered flask and covered with 50 ml. of dry petroleum ether (b.p. 30-40°). After the addition of several drops of a saturated solution of sodium hydroxide in absolute ethanol, the mixture was shaken mechanically for five hours. The dark olive-drab-colored solid was filtered off and washed with dry petroleum ether until the washings were faint pink. The solvent was removed from the combined filtrates with a jet of dry air and the solid then recrystallized once from methanol. Yield 5.85 g. (81.9%), m.p. 30.0-31.2°C. In another run using similar quantities of starting materials and shaking for 63 minutes the yield was 59.0%. After eight recrystallizations from petroleum ether (b.p. 30-40°) the large deep-red needles melted at 30.8-31.5°C. Reported m.p. 29-30° (158) and 30.5-31.0° (159).

## 3. Preparation of Diazo Alkanes

4-Methyl-4-(methylnitrosamino)-2-pentanone (N-Nitroso-β-methylaminoisobutyl methyl ketone).--This material was prepared several times by the method of Redemann, et al. (160). The procedure using methylamine hydrochloride rather than aqueous methylamine was employed. Yields 62.6, 58.9, 68.1, 65.3, 57.2, 54.2, 65.8, and 62.8%, all based upon approximately two moles of mesityl oxide.

Diazomethane.--This compound was prepared by the method of Redemann, et al. (160) by the action of sodium isopropoxide on N-nitroso-β-methylaminoisobutyl methyl ketone. Larger amounts of ether were employed than suggested by Redemann. The ether-isopropanol solution of the nitrosoketone was allowed to drop slowly into the sodium isopropoxide solution; the ethereal diazomethane then distilled over through a large Claisen head and was collected in a three-neck flask of appropriate size that could be used later in the preparation of the diazo ketone. This procedure avoided the transferring of the diazomethane solution to another flask later on. The diazomethane was never purified further except once in the attempted preparation of trifluorodiazoacetone. The entrance to the dropping funnel and the exit to the trap were protected by drying tubes filled with calcium chloride. The all-glass apparatus consisted entirely of pieces with standard-taper ground-glass joints that were very heavily and thoroughly lubricated with Lubriseal (Arthur H. Thomas Company) stopcock grease. The diazomethane solutions were not assayed; a yield of 45-60% is reported for this preparation (160). This procedure worked satisfactorily in all cases, the amounts of starting material (nitrosoketone) used varying from 0.110 to 0.768 moles.

Ethyl N-Ethylcarbamate.--This compound was prepared by a variation of the preparation of ethyl N-methylcarbamate by Hartman and Brethen (161). A mixture of 300 ml. of commercial grade ether and 271 g. (2.01 moles) of a 33% aqueous solution of ethylamine was placed in a two liter three-neck flask equipped with a stirrer, thermometer, and two dropping funnels arranged so as to enter the same flask opening. After the rapidly stirred solution was cooled below 5° in an ice-salt bath 217 g. (2.00 moles) of ethyl chloroformate was added dropwise, the temperature being kept below 4°. When one-half of the ethyl chloroformate solution had been added, a solution of 80 g. (2.0 moles) of sodium hydroxide in 120 ml. of water was slowly added from the other dropping funnel at the same rate and simultaneously with the remainder of the chloroformate in such a manner that the temperature remained below 4°. The entire addition required two and one-quarter hours; the solution was then rapidly stirred for another one and three-quarter hours. The ether layer was separated and the aqueous layer extracted once with 100 ml. of ether and again with 50 ml. of ether. The combined ether extracts were quickly dried with two 10 g. portions of anhydrous potassium carbonate and filtered. All solvent was removed at room temperature under reduced pressure with a water aspirator and the residue distilled: 3.6 g., forerun (1.5 mm.), $n_D^{25.2°}$ 1.4184; 224.2 g., b.p. 50.5-52.5° (1.2 mm.), $n_D^{25.2°}$ 1.4195. Total yield of clear liquid, 97.3%. Reported b.p. 59-60° (3 mm.) and 79-80° (14 mm.), (57).

Ethyl N-Ethyl-N-Nitrosocarbamate (N-Nitroso-N-Ethylurethane).--This compound was prepared by a variation of the preparation of nitrosomethylurethane by Hartman and Phillips (162). A mixture of 225.0 g. (1.920 moles) of ethyl N-ethylcarbamate, 580 ml. of commercial grade ether, 200 g. of ice, and a solution of 635 g. (9.21 moles) of sodium nitrite in 970 ml. of water was placed in a five liter three-neck flask equipped with a thermometer, dropping funnel (with an extension tube leading to the bottom of the flask), and a tube which led off evolved gases to the drain. The flask and its contents were placed in an ice bath, and a solution of dilute nitric acid (425 ml. of concentrated nitric acid poured onto 600 g. of ice) was added slowly over a period of two and three-quarters hours in such a manner that the temperature did not rise above 5°. The mixture was swirled occasionally and allowed to stand for three hours, the temperature being kept below 10°. The dark green ether layer was separated from the clear blue aqueous layer and the aqueous layer extracted twice with 200 ml. portions of ether. The combined ether extracts were washed twice with cold water and then four times with a concentrated potassium carbonate solution until free of acid, dried over anhydrous potassium carbonate, and filtered. After all low-boiling materials were removed at room temperature under reduced pressure with a water aspirator, the residue was distilled through a 30 cm. Vigreaux column; one fraction of pink liquid was collected: 267.4 g. (95.3%), b.p. 45.0-45.7° (3.2 mm.), $n_D^{24.7°}$ 1.4339. Reported b.p. 52.5-53.5° (5 mm.), (57); 86° (32 mm.), 90° (42 mm.), (163).

Diazoethane.--This compound was prepared according to the directions of Wilds and Meader (57) from 0.1712 moles of N-ethyl-N-nitrosourethane. The urethane solution was added to the potassium hydroxide solution within from four to six minutes; Wilds and Meader state that the yield is 75% of theoretical if the urethane is added within five minutes, the yield decreasing with increasing time of addition. The diazoethane solutions were not assayed. The ground-glass standard-taper joints of the all-glass apparatus were heavily and thoroughly lubricated with Lubriseal. The entrance to the dropping funnel and the exit to the ether trap were protected by drying tubes filled with calcium chloride. The ethereal diazoethane solution was collected in a three-neck flask of appropriate size that could be used later in the preparation of the diazo ketones, thus avoiding the necessity of transferring the solution.

## 4. Preparation of Aromatic Diazo Ketones and Derivatives

Azibenzil was prepared by the oxidation of benzil monohydrazone. 2-Diazopropiophenone was prepared by the reaction between diazoethane and benzoyl chloride. The rest of the aromatic diazo ketones were prepared according to the methods of Newman and Beal (62) and Berenbom and Fones (63) with some modifications. Both methods use triethylamine to absorb the liberated hydrogen chloride. Newman and Beal add a solution of the acid chloride in ether to a solution containing equimolar amounts of diazomethane and triethylamine placed in an ice-salt bath; Berenbom and Fones reverse the method of addition by adding a solution of equimolar amounts of diazomethane and triethylamine to an ethereal solution of an equimolar quantity of the acid chloride at 0°. The following aromatic diazo ketones were prepared by adding an ethereal solution of the acid chloride dropwise to a rapidly stirred ethereal diazomethane solution containing triethylamine. Equivalent amounts of acid chloride and triethylamine were used; a slight excess of diazomethane was present. The addition of the acid chloride usually required about one-half hour. All reactions were run in a dry ice bath and were protected from moisture by tubes filled with calcium chloride.

Following the addition the mixtures were stirred in the dry ice bath for several hours and then placed in the refrigerator overnight. The reaction mixtures frequently had changed color from yellow to orange or red. After a precipitate of triethylamine hydrochloride was filtered off and washed with ether, the solvent was removed from the combined filtrates at room temperature with a jet of dry air and under reduced pressure with a water aspirator.

Sometimes the amount of triethylamine hydrochloride formed sharply decreased upon standing in the reaction mixture overnight. This decrease could be due presumably to a reaction between the triethylamine hydrochloride and excess diazomethane to yield nitrogen, methyl chloride, and triethylamine. The crude diazo ketones frequently smelled of triethylamine. Newman and Beal state that triethylamine hydrochloride does not react with diazomethane under the conditions of their experiments (i.e. equimolar amounts of all reactants); however, the following preparations were carried out with a slight excess of diazomethane.

<u>2-Diazo-2-phenylacetophenone (Azibenzil)</u>*--This compound was prepared according to the method of Nenitzescu and Solomonica (154). A mixture of 10.0 g. (0.0446 moles) of benzil monohydrazone, 20.0 g. (0.0923 moles) of yellow mercuric oxide, and 5.0 g. of anhydrous sodium sulfate, after being thoroughly pulverized in a mortar, was placed in a glass-stoppered flask and covered with 67 ml. of reagent ether. After the addition of 1.8 ml. of a saturated solution of potassium hydroxide in ethanol the mixture was

vigorously shaken for 15 minutes at room temperature. The dark olive-drab solid was filtered from the red solution and washed with ether until the washings were pale yellow. After the ether was removed from the combined filtrates by a jet of dry air, an orange solid, 8.95 g. (90.4%), was obtained which melted at 77.9-79.6° with decomposition. After nine recrystallizations from reagent ether the long yellow-orange needles melted at 80.3°C with decomposition. Reported m.p. 79°, corrected (45,85). The method of Ritter and Wiedeman (85), which uses no basic catalyst, gave very poor yields of impure product. Similar amounts of starting materials (with no base present) stirred for 45 1/2 hours gave a 12.0% yield; stirring for 10 3/4 hours gave a negligible yield.

2-Diazoacetophenone (α-Diazoacetophenone)*--This compound was prepared by the general method previously described from 6.00 g. (0.0427 moles) of benzoyl chloride (redistilled, b.p. 85.7-86.1° at 16.5 mm.), 4.32 g. (0.0427 moles) of triethylamine, and the diazomethane prepared from 0.1229 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield of product, 3.47 g. (55.7%). m.p. 46.4-48.0° after one crystallization from petroleum ether. After five recrystallizations from dry petroleum ether (b.p. 30-40°) the long, thin, yellow, flat blades melted at 47.7-48.5°C. Reported m.p. 48-49° (80), 49-50° (33). Two other runs with similar amounts of starting materials gave yields of 42.0% and 47.4%.

<u>2'-Bromo-2-diazoacetophenone (o-Bromo-α-diazoacetophenone</u>*--This compound was prepared by the general method previously described from 11.50 g. (0.00524 moles) of o-bromobenzoyl chloride (redistilled, b.p. 125-130° at 15 mm.; reported b.p. 116° at 11 mm., reference 164), 5.70 g. (0.0563 moles) of triethylamine, and the diazomethane from 0.1487 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield of product, 10.50 g. (89.0%). m.p. 41.1-43.1° after one crystallization from petroleum ether. After five recrystallizations from dry petroleum ether (b.p. 30-40°) the fine pale yellow needles melted at 42.2-43.1°C. Reported m.p. 42-43° with gas evolution (165). Two other runs with similar amounts of starting materials resulted in yields of 65.7% and 78.3%.

<u>Anal</u>. Calcd. for $C_6H_5BrN_2O$: C, 42.69; H, 2.24; Br, 35.51; N, 12.45. Found: C, 42.72, 42.84; H, 2.17, 2.36; Br, 35.61, 35.45 [as AgBr by the methods of Pringsheim (166) and Willard and Furman (167)]; N,[a] 12.61, 12.82, 13.30, 13.33.

<u>o-Bromophenylacetic Acid*(Wolff rearrangement on 2'-Bromo-2-diazoacetophenone)</u>.--The procedure that was used is essentially that of Bachmann and Struve (48, pp. 50-51). A mixture of 1.25 g. of anhydrous sodium carbonate, 0.7 g. of sodium thiosulfate, 0.5 g. of silver oxide, and 50 ml. of water was heated to 70°. A solution of 4.00 g. (0.0178

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[a] The analyst reported that this compound was very readily and quickly decomposed by heat during the Dumas nitrogen determination yielding macro-sized bubbles of gas rather than the desirable micro-bubbles.

moles) of 2'-bromo-2-diazoacetophenone in 25 ml. of dioxane was added dropwise to the above mixture with vigorous stirring over a period of ten minutes. Additional small portions of silver oxide were added periodically to the very rapidly stirred mixture over a period of two hours, the temperature being maintained at 70°. The temperature was then raised to 92° (reflux temperature) for twenty minutes after which the mixture was filtered. The filtrate was acidified with 5 N nitric acid and then extracted four times with 25 ml. portions of ether. After the ether was removed with an air jet, the semisolid residue was crystallized once from an acetic acid-water mixture, yield 2.20 g. (57.5%), m.p. 101-103.4°. After three recrystallizations from water and drying overnight over $P_2O_5$ at 15 mm. Hg the long, flat, white needles melted at 105.0-106.0°C. Reported m.p. 103-104° (168), 102.5-103° (169).

<u>2-o-Bromophenylacetamide*(Wolff rearrangement on 2'-Bromo-2-diazoacetophenone)</u>.--The procedure used is essentially that of Bachmann and Struve (48, p. 52). A solution of 2.57 g. (0.0114 moles) of 2'-bromo-2-diazoacetophenone in 11.8 ml. of dioxane was treated with a solution of 5.2 ml. of M/2 aqueous silver nitrate, 5.0 ml. of dioxane, and 16.6 ml. of concentrated ammonium hydroxide at 72°. The temperature was immediately raised and maintained at reflux temperature (89-92°) for three hours during which time small portions of ammoniacal silver nitrate solution were periodically added to the rapidly stirred solution. After standing overnight at room temperature the mixture

was heated, filtered, and about 500 ml. of water added to the filtrate. The flocculent precipitate was filtered and dried, yield 0.62 g. (25.4%). After three recrystallizations from 95% ethanol the long, flat, white needles melted at 186.3-186.8°C. Reported m.p. 186-187° (170), 181° (171).

m-Bromobenzoyl Chloride.--The method used is essentially that of McElvain and Carney (172). A mixture of 41.00 g. (0.204 moles) of m-bromobenzoic acid and 30.0 ml. (0.414 moles) of thionyl chloride was refluxed for six and two-thirds hours and then fractionally distilled; yield 42.02 g. (93.5%) of product, b.p. 126-128° (19 mm.) after redistillation. Reported b.p. 122.5-123.5° (14-15 mm.), (173).

**3'-Bromo-2-diazoacetophenone (m-Bromo-α-diazoacetophenone)*.--This compound was prepared by the general method previously described from 33.4 g. (0.152 moles) of m-bromobenzoyl chloride, 15.7 g. (0.155 moles) of triethylamine, and the diazomethane prepared from 0.494 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Upon the addition of a small amount of low-boiling petroleum ether two crops of pale orange-yellow crystals were obtained, 23.11 g., m.p. 68.1-72.1°; 8.14 g., m.p. 63.3-68.8°. Total yield 91.2%. After six recrystallizations from dry petroleum ether (b.p. 30-40°) the fine pale yellow needles melted at 76.2-76.7°C.

Anal. Calcd. for $C_8H_5BrN_2O$: C, 42.69; H, 2.24; N, 12.45. Found: C, 42.81, 42.85; H, 2.29, 2.21; N, 12.09, 11.93.

3'-Bromo-2-chloroacetophenone*.--Excess dry hydrogen chloride gas was passed into a solution of 1.00 g. (0.00444 moles) of 3'-bromo-2-diazoacetophenone in 30 ml. of 95% ethanol, the temperature being kept below 30°. Excess ice water was added and the precipitate that formed quickly filtered off and dried over $P_2O_5$. Yield 0.84 g. (81.0%) of yellow powder. After three recrystallizations from dry petroleum ether (b.p. 60-75°) and drying over $P_2O_5$ at 25 mm. Hg the silvery-white plates melted at 48.2-48.6°C. Reported m.p. 47-48° (174). Another run gave a 78.2% yield.

Anal. Calcd. for $C_8H_6BrClO$: C, 41.15; H, 2.59. Found: C, 41.22; H, 2.60.

2,3'-Dibromoacetophenone*.--Excess anhydrous hydrogen bromide was passed into a solution of 1.00 g. (0.00444 moles) of 3'-bromo-2-diazoacetophenone in 30 ml. of 95% ethanol, the temperature being kept below 40°. Ice water was then added until the total volume was about 250 ml., and the precipitate filtered off and dried over $P_2O_5$. Yield 1.15 g. (93.1%). After three recrystallizations from dry petroleum ether (b.p. 60-75°) and drying over $P_2O_5$ at 25 mm. Hg the fine white needles melted at 50.2-50.6°C. Reported m.p. 51° (175).

Anal. Calcd. for $C_8H_6Br_2O$: C, 34.57; H, 2.18. Found: C, 34.85; H, 2.14.

p-Bromobenzoyl Chloride.--The method used is essentially that of McElvain and Carney (172). A mixture of 20.10 g. (0.100 moles) of p-bromobenzoic acid and 15.6 ml.

(0.215 moles) of thionyl chloride was refluxed for twelve hours and then fractionally distilled: yield 19.13 g. (87.3%), b.p. 129-130° (20 mm.). Reported b.p. 132-135° (17 mm.), (176).

4'-Bromo-2-diazoacetophenone (p-Bromo-α-diazoacetophenone)*--This compound was prepared by the general method described previously from 11.40 g. (0.0519 moles) of p-bromobenzoyl chloride, 6.10 g. (0.0602 moles) of triethylamine, and the diazomethane prepared from 0.1697 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 10.09 g. (86.4%) of orange crystals. The compound was quite impure; a considerable quantity of insoluble, orange-red, gummy material remained behind upon crystallization from petroleum ether. After five recrystallizations from dry petroleum ether (b.p. 30-40°) and drying over $CaCl_2$ at 15 mm. Hg the very fine pale yellow needles melted at 126.0-126.7°C with gas evolution. Reported m.p. 123.5-124.5° (80), 123.5-124° with gas evolution (177).

o-Nitrobenzoyl Chloride.--The method used is essentially that of McElvain and Carney (172). A mixture of 40.00 g. (0.2394 moles) of o-nitrobenzoic acid and 50.0 ml. (0.689 moles) of thionyl chloride was refluxed for two and one-half hours and then fractionally distilled: yield 39.50 g. (88.9%) of pale yellow product, b.p. 162.0-163.5° (20 mm.). Reported b.p. 148-151° (12 mm.), (178).

2-Diazo-2'-nitroacetophenone (α-Diazo-o-nitroacetophenone)*--This compound was prepared by the general method outlined previously from 11.50 g. (0.0620 moles) of o-nitrobenzoyl chloride, 6.70 g. (0.0662 moles) of triethylamine, and the diazomethane prepared from 0.188 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield of pale yellow solid, 11.96 g. (100.8%), m.p. 96.6-100.8°. After five recrystallizations from methanol and drying in a black desiccator over $CaCl_2$ at 25 mm. Hg the fine yellow prisms melted at 101.9-102.9°C with gas evolution. Reported m.p. 105-106° (51). The compound was very sensitive to light, changing in color very quickly from pale yellow to orange, and finally to a deep red-brown.

<u>m-Nitrobenzoyl Chloride</u>.--The method used is essentially that of McElvain and Carney (172). A mixture of 50.20 g. (0.301 moles) of m-nitrobenzoic acid and 45.0 ml. (0.620 moles) of thionyl chloride was refluxed for five hours and then fractionally distilled: yield 46.85 g. (84.1%) of pale yellow product, b.p. 159-160.3° (19 mm.). Redistillation gave a pale yellow liquid that solidified in the condenser into very long pale yellow needles, b.p. 159.5-161.5° (19 mm.). Reported b.p. 154-155° (18 mm.), (179).

**<u>2-Diazo-3'-nitroacetophenone (α-Diazo-m-nitroacetophenone)</u>*.--This compound was prepared by the general method described previously from 28.20 g. (0.152 moles) of m-nitrobenzoyl chloride, 16.30 g. (0.161 moles) of triethylamine, and the diazomethane from 0.492 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 28.55 g. (98.3%), m.p. 135.5-136.7°. After five recrystallizations from methanol and drying over $CaCl_2$ at 25 mm. Hg the pale yellow rods and needles melted at 143.6-144.9°C with gas evolution and decomposition. The melting point depends greatly upon the rate of heating and the amount of prior heating, for decomposition, when once started, is very rapid with gas evolution. Bachmann and Holmes (ref. 48, p. 60 and footnote, p. 42) have used this compound in syntheses but have not reported its physical properties. A sample of this compound was allowed to remain in the light in the laboratory at room temperature for ten hours (three of which were in direct sunlight); the only visible change was a slight deepening of the color, but the melting point did not change.

Anal. Calcd. for $C_8H_5N_3O_3$: C, 50.27; H, 2.64; N, 21.98. Found: C, 50.46, 50.41; H, 2.68, 2.64; N, 21.13, 21.22.

m-Nitrophenylacetic Acid*(Wolff rearrangement on 2-Diazo-3'-nitroacetophenone).--This derivative was prepared essentially by the previously outlined procedure of Bachmann and Struve for preparing acids from 4.00 g. (0.0209 moles) of 2-diazo-3'-nitroacetophenone. The orange semisolid material, 4.8 g., was recrystallized once from hot water after treatment with Norite; yield 2.19 g. (57.7%), m.p. 116.4-118.0°. After four more recrystallizations from hot water and drying over $P_2O_5$ at 25 mm. Hg the fine, very pale yellow needles melted at 118.4-119.1°C. Reported m.p. 117° (180), 120° (175).

2-Bromo-3'-nitroacetophenone*.--Excess anhydrous hydrogen bromide was slowly added to a solution of 1.00 g. (0.00523 moles) of 2-diazo-3'-nitroacetophenone in 75 ml.

of 95% ethanol, the temperature being kept below 40°. Water was then added until the total volume was about 125 ml., the solution cooled and filtered, and the precipitate dried. Yield 0.83 g. (65.0%), m.p. 90.7-93.2°. After two recrystallizations from a 9:8 mixture of 95% ethanol and water and drying over $P_2O_5$ at 22 mm. Hg the small white flakes melted at 94.5-95.0°C. Reported m.p. 96° (181-184).

Anal. Calcd. for $C_8H_6BrNO_3$: C, 39.37; H, 2.48. Found: C, 39.55; H, 2.42.

2-Diazo-4'-nitroacetophenone (α-Diazo-p-nitroacetophenone)*--This compound was prepared by the general method outlined previously from 11.60 g. (0.0625 moles) of p-nitrobenzoyl chloride, 6.60 g. (0.652 moles) of triethylamine, and the diazomethane prepared from 0.2144 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 11.49 g. (96.1%). After six recrystallizations from methanol and drying over $CaCl_2$ at 25 mm. Hg the fine yellow needles melted at 116.7-117.5°C with vigorous gas evolution and decomposition. The melting point is very sensitive to the rate of heating and the amount of prior heating. Reported m.p. 117-118° (185), 116-117° (68), 118° (187), 97-98° (61), 94-95° (186).

o-Toluoyl Chloride.--The procedure is essentially that of McElvain and Carney (172). A mixture of 26.40 g. (0.1938 moles) of o-toluic acid and 45.1 ml. (0.620 moles) of thionyl chloride was gently refluxed for five hours and then fractionally distilled; yield 28.80 g. (96.1%), b.p. 93.5-95.0° (15 mm.). Reported b.p. 99-100° (14 mm.), (188).

**2-Diazo-2'-methylacetophenone (α-Diazo-o-methylacetophenone)*.--This compound was prepared by the general procedure outlined previously from 22.40 g. (0.145 moles) of o-toluoyl chloride, 14.90 g. (0.147 moles) of triethylamine, and the diazomethane prepared from 0.550 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. The product was a dark red oil that smelled of triethylamine. The crystals that could be obtained by freezing the oil in dry ice readily melted at room temperature. The crystallizations were performed in a cold room (-7° to -8°). After one crystallization from petroleum ether 18.67 g. (80.3%) of orange-yellow crystals were obtained. After four more recrystallizations from dry petroleum ether (b.p. 30-40°) and drying at reduced pressure over $P_2O_5$ the yellow, long, flat blades melted at 20.7-21.2°C, uncorrected.

Anal. Calcd. for $C_9H_8N_2O$: C, 67.49; H, 5.03, N, 17.49. Found: C, 67.73, 67.43; H, 5.16, 4.93; N, 17.88, 17.81.

2-o-Tolylacetamide*(Wolff rearrangement on 2-Diazo-2'-methylacetophenone).--This derivative was prepared essentially by the previously outlined procedure of Bachmann and Struve for making amides from 6.46 g. (0.0403 moles) of crude 2-diazo-2'-methylacetophenone. The product was extracted from the aqueous solution with eighteen 50 ml. portions of ether. After removal of the ether with an air jet the residue was crystallized once from water after treatment with Norite; yield 2.39 g. (39.7%), m.p. 161.5-163.5°. After two more recrystallizations from water and drying over $P_2O_5$ at 15 mm. Hg the colorless prisms melted at 162.8-163.7°C. Reported m.p. 161° (189).

**<u>2-o-Tolylacetanilide</u>*--This derivative was prepared essentially by the previously outlined procedure of Bachmann and Struve for making amides from 3.39 g. (0.0212 moles) of crude 2-diazo-2'-methylacetophenone and 6.5 ml. of aniline. Yield, 5.03 g. of a brown powder that smelled of aniline. One crystallization from a methanol-water mixture after treatment with Norite yielded 3.82 g. (80.3%) of tan needles, m.p. 128.8-130.3°. After four more recrystallizations from a methanol-water mixture and drying over $P_2O_5$ at 20 mm. Hg the colorless needles melted at 130.0-130.7°C.

<u>Anal.</u> Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.87; H, 6.54; N, 6.33.

<u>Hydrolysis of 2-o-Tolylacetanilide</u>.--A solution of 1.85 g. (0.00821 moles) of 2-o-tolylacetanilide, 10.3 ml. of concentrated hydrochloric acid, 25.2 ml. of water, and 17.0 ml. of dioxane was gently refluxed for six hours. The solution was filtered and extracted with seven 50 ml. portions of ether. The residue, after removal of the ether with an air jet, was crystallized from petroleum ether; yield 1.01 g. (82.0%) of white needles, m.p. 86.2-87.7°. After three more recrystallizations from dry petroleum ether (b.p. 30-40°) and drying over $P_2O_5$ at 15 mm. Hg the long white needles melted at 88.6-89.3°C. Reported for o-tolylacetic acid* m.p. 85.6-86° (190). The original solution was made basic with 10% aqueous sodium hydroxide and extracted four times with 50 ml. portions of ether. The ex-

tracts were acidified with hydrochloric acid and evaporated to dryness with an air jet; yield 0.78 g. (73.3%) of crude aniline hydrochloride.

m-Toluoyl Chloride.--The procedure used is essentially that of McElvain and Carney (172). A mixture of 27.52 g. (0.202 moles) of m-toluic acid and 44.0 ml. (0.606 moles) of thionyl chloride was gently refluxed for seventeen and one-half hours and then fractionally distilled; yield 29.86 g. (95.6%) of product, b.p. 95.6-96.2° (12 mm.). Reported b.p. 109° (15 mm.), 105° (20 mm.), (193).

**2-Diazo-3'-methylacetophenone (α-Diazo-m-methylacetophenone)*--This compound was prepared by the general procedure outlined earlier from 20.50 g. (0.133 moles) of m-toluoyl chloride, 13.40 g. (0.132 moles) of triethylamine, and the diazomethane prepared from 0.4465 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 18.57 g. (87.4%), m.p. 62.6-64.4°. After seven recrystallizations from dry petroleum ether (b.p. 30-40°) and drying over $CaCl_2$ at 30 mm. Hg the pale yellow needles melted at 65.1-65.8°C.

Anal. Calcd. for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.43, 67.39; H, 4.95, 4.92; N, 17.44.

m-Tolylacetic Acid*(Wolff rearrangement on 2-Diazo-3'-methylacetophenone).--This derivative was prepared essentially by the previously outlined procedure of Bachmann and Struve for making acids from 3.35 g. (0.0209 moles) of 2-diazo-3'-methylacetophenone. Three recrystallizations of the orange-red oil from water gave a very impure product.

One recrystallization from petroleum ether (b.p. 30-40°) gave 1.20 g. (38.2%) of product, m.p. 55.7-57.7°. After two more recrystallizations from dry petroleum ether (b.p. 30-40°) and drying over $P_2O_5$ at 30 mm. Hg the very large, flat, colorless plates melted at 63.3-64.0°C. Reported m.p. 53-54° (194), 61° (195), 60.5-61.5° (196).

<u>2-m-Tolylacetamide*(Wolff rearrangement on 2-Diazo-3'-methylacetophenone)</u>.--This derivative was prepared essentially by the previously outlined procedure of Bachmann and Struve for making amides from 3.00 g. (0.0187 moles) of 2-diazo-3'-methylacetophenone. The aqueous solution was extracted with ten 50 ml. portions of ether. The ether extracts were evaporated to about 100 ml., cooled in dry ice, and the precipitated solid filtered off. Yield 1.77 g. (63.3%) of large plates. After three recrystallizations from water and drying over $P_2O_5$ at 15 mm. Hg the colorless, broad, flat blades and leaflets melted at 145.1-146.1°C. Reported m.p. 141° (189).

<u>Anal</u>. Calcd. for $C_9H_{11}NO$: C, 72.46; H, 7.43. Found: C, 72.48; H, 7.26.

<u>p-Toluic Acid</u>.--A mixture of 50.6 g. (0.432 moles) of p-tolunitrile, 140 ml. of water, and 75 ml. of concentrated sulfuric acid was refluxed for three and one-quarter hours. The product that separated upon cooling the reaction mixture was recrystallized once from 95% ethanol; yield 50.75 g. (86.4%), m.p. 179.8-180.7°C. Reported m.p. variable from 176° to 181° (197).

p-Toluoyl Chloride.--The procedure is essentially that of McElvain and Carney (172). A mixture of 27.27 g. (0.200 moles) of p-toluic acid and 25.0 ml. (0.344 moles) of thionyl chloride was gently refluxed for eighty-three minutes and then fractionally distilled; yield 28.2 g. (91.2%), b.p. 103-104° (12.5-13.0 mm.). Similar runs yielded 92.3%, b.p. 109-111.5° (20 mm.), two hours refluxing; 92.9%, b.p. 110.5-115.5° (20.5 mm.), two and one-half hours refluxing. Reported b.p. 108° (15 mm.), 95-95.5° (10 mm.), 101-102° (16 mm.), (198).

2-Diazo-4'-methylacetophenone (α-Diazo-p-methylacetophenone)*.--This compound was prepared by the general procedure outlined earlier from 16.10 g. (0.104 moles) of p-toluoyl chloride, 12.30 g. (0.122 moles) of triethylamine, and the diazomethane prepared from 0.378 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 15.33 g. (92.0%). After five recrystallizations from dry petroleum ether (b.p. 30-40°) the very pale yellow, fine needles melted at 52.5-53.1°C. Reported m.p. 49-51° (80), 48-51° (57).

1-Naphthoic Acid.--This compound was prepared according to the procedure of Gilman, St. John, and Schulze (199) by adding carbon dioxide to the Grignard reagent prepared from 1.00 mole of 1-bromonaphthalene. Yield 137.9 g. (80.0%). After one recrystallization from toluene the very pale tan powder melted at 161.4-162.4°C. Reported m.p. 160°, 162°, 160.5-161° (200).

1-Naphthoyl Chloride.--The procedure is essentially that of McElvain and Carney (172). A mixture of 52.65 g.

(0.306 moles) of 1-naphthoic acid and 35.0 ml. (0.483 moles) of thionyl chloride was gently refluxed for ten hours and then fractionally distilled; yield 54.39 g. (93.3%) of product, b.p. 179-179.5° (22 mm.). Redistillation yielded 51.60 g., b.p. 172-175° (20 mm.). Reported b.p. 172-173° (15 mm.), 187° (23 mm.), 164-167° (13 mm.), (201).

2-Diazo-1'-acetonaphthone (α-Diazo-1-acetonaphthone)*.--This compound was prepared according to the general procedure outlined earlier from 11.50 g. (0.0603 moles) of 1-naphthoyl chloride, 6.50 g. (0.0652 moles) of triethylamine, and the diazomethane prepared from 0.204 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 10.53 g. (89.1%) of orange-red needles. After five recrystallizations from dry petroleum ether (b.p. 30-40°) and drying over $CaCl_2$ at 25 mm. Hg the pale yellow needles melted at 53.3-53.6°C. Reported m.p. 48-50° (57), 54-55° (82), 56° (202).

2'-Acetonaphthone.--The procedure used was essentially that of Immediata and Day (203). Anhydrous aluminum chloride, 71 g. (0.53 moles), was added in small portions over a forty minute period to a rapidly stirred solution of 60.0 g. (0.468 moles) of naphthalene, 500 ml. of nitrobenzene, and 55.0 ml. (0.775 moles) of acetyl chloride; the temperature was kept below 6° during the addition. The mixture was then stirred for an additional five and one-half hours in an ice bath, poured onto an excess of ice, and strongly acidified with hydrochloric acid. After separation from the aqueous layer the nitrobenzene layer was washed with water, then with strong aqueous sodium hydroxide, and finally, twice with water. The solvent was removed by distillation under reduced pressure and the residue fractionated with the fraction boiling at 107-133° (1 mm.) being collected. Recrystallization from 95% ethanol yielded 35.77 g. (44.8%) after drying over $CaCl_2$ at 10 mm. Hg, m.p. 51.3-52.6°C. Reported m.p., variable from 51.6° to 56° (204). Similar runs yielded 33.2% and 43.3%.

2-Naphthoic Acid.--The procedure is essentially that outlined by Newman and Holmes (205). An aqueous solution of potassium hypochlorite was prepared by adding a solution of 119 g. of anhydrous potassium carbonate and 37 g. of potassium hydroxide in 336 ml. of hot water to a suspension of 176 g. of Perchloron (70% calcium hypochlorite, Penn. Salt Manuf. Co.) in 656 ml. of hot water. The suspension was shaken vigorously for several minutes, filtered twice by suction, and the residue washed with 136 ml. of hot water. 2'-Acetonaphthone, 39.0 g. (0.229 moles), was added to the vigorously stirred potassium hypochlorite solution at 55°. After the mixture was stirred for two hours at 65° ± 5° the excess hypochlorite was destroyed by the addition of 39 g. of sodium bisulfite in 133 ml. of water. After standing at room temperature overnight the mixture was acidified with 156 ml. of concentrated hydrochloric acid, cooled to 8°, and the solid which separated filtered off, washed with cold water, and dried. After one crystallization from 95% ethanol and drying over $CaCl_2$ at 10 mm. Hg the long colorless needles melted at 184.2-185.3°C. Yield 26.10 g. (66.2%). Reported m.p. 184° corrected, 182-182.5° (206). A similar run yielded

69.0% of product.

2-Naphthoyl Chloride.--The procedure is essentially that of McElvain and Carney (172). A mixture of 17.22 g. (0.100 moles) of 2-naphthoic acid and 18.9 ml. (0.261 moles) of thionyl chloride was gently refluxed for five hours and then fractionally distilled; yield 18.25 g. (95.8%) of product that immediately solidified to a white solid at room temperature, b.p. 179.5-181.0° (21 mm.). Reported b.p. 182-185° (25 mm.), (207).

**2-Diazo-2'-acetonaphthone (α-Diazo-2-acetonaphthone)*.--This compound was prepared by the general procedure outlined previously from 17.80 g. (0.0934 moles) of 2-naphthoyl chloride, 10.0 g. (0.0988 moles) of triethylamine, and the diazomethane prepared from 0.326 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. Yield 17.04 g. (92.9%) of yellow-orange crystals melting at 78.3-80.2°. After six recrystallizations from dry petroleum ether (b.p. 30-40°) and drying over $P_2O_5$ at 15 mm. Hg the fine pale yellow needles melted at 82.6-83.1°C.

Anal. Calcd. for $C_{12}H_8N_2O$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.48, 73.62; H, 3.94, 4.19; N, 14.34.

2-Bromo-2'-acetonaphthone*--Excess anhydrous hydrogen bromide was passed into a solution of 0.68 g. (0.0035 moles) of 2-diazo-2'-acetonaphthone in 40 ml. of dry ether, the temperature being kept below 30°. The ether was removed with a jet of dry air, and the crude solid remaining was crystallized from dry petroleum ether (b.p. 60-75°). Yield 0.42 g. (48.5%), m.p. 78.7-80.5°. After three more recrystallizations from petroleum ether and drying over $P_2O_5$ at 15 mm. Hg the silvery plates melted at 82.7-83.3°C. Reported m.p. 84-84.5° (208), 82.5-83.5° (209).

Anal. Calcd. for $C_{12}H_9BrO$: C, 57.86; H, 3.64. Found: C, 58.18; H, 3.49.

A similar run using 1.00 g. (0.0051 moles) of 2-diazo-2'-acetonaphthone in 30 ml. of absolute ethanol gave 1.11 g. (87.2%) of crude product.

2-Chloro-2'-acetonaphthone*--Excess hydrogen chloride was passed into a solution of 1.08 g. (0.00550 moles) of 2-diazo-2'-acetonaphthone in 25 ml. of absolute ethanol, the temperature being kept below 40°. Ice water was then added until the total volume was about 250 ml. and the mixture filtered. Yield 0.93 g. (82.6%) of pale yellow powder melting at 45-53°. After four recrystallizations from dry petroleum ether (b.p. 60-75°) and drying over $P_2O_5$ at 15 mm. Hg the fine colorless needles melted at 63.2-63.7°C. Reported m.p. 67-68° (210), 62-63° (209).

Anal. Calcd. for $C_{12}H_9ClO$: C, 70.43; H, 4.43. Found: C, 70.58; H, 4.27.

2-Diazopropiophenone (α-Diazopropiophenone)*--The procedure was essentially that given by Wilds and Meader (57). A solution of 8.14 g. (0.0579 moles) of reagent benzoyl chloride in 80 ml. of ether was added dropwise over a period of twenty-five minutes to a rapidly stirred ethereal solution of diazoethane (prepared from 0.1712 moles of N-ethyl-N-nitrosourethane) at -23° (carbon tetrachloride-dry ice bath). After stirring the solution for an additional one-half hour any excess diazoethane and most of the solvent was removed at -23° under reduced pressure with a water aspirator. Most of the remaining solvent was removed by leaving the material at room temperature and 0.1 mm. Hg for an hour. A yellow oil, 9.79 g. (105.5%), remained that smelled of n-propanol and contained a small amount of a flocculent white precipitate. Two other preparations also gave crude products in yields in excess of one hundred percent. The oil formed a very viscous glass-like material when cooled in a dry ice-acetone bath; this viscous material crystallized when placed in the refrigerator coil (-7°) overnight but readily melted below room temperature. The oil was purified by first dissolving it in a slight excess of dry petroleum ether (b.p. 30-40°) at room temperature, then cooling the solution until the oil separated out again and settled to the bottom, and finally sucking off the petroleum ether layer with a small capillary. After this procedure was repeated seven times, the deep yellow oil was dried at 10 mm. Hg and its infrared spectrum taken immediately. This spectrum was identical with one obtained from a sample that had been reprecipitated three times.

2-Phenylpropionanilide*--A mixture of 2.39 g. (0.0149 moles) of crude 2-diazopropiophenone and 13.0 ml. (0.143 moles) of aniline was heated at 190° ± 3° for fifty-seven minutes. After pouring the mixture onto 100 g. of ice and 10 ml. of concentrated hydrochloric acid the aqueous mixture was extracted with three 50 ml. portions of ether. After evaporation of the ether the remaining dark oil was crystallized once from a methanol-water mixture. Yield 1.62 g. (48.2%), m.p. 102-112°. A second preparation heated to 190° for twelve minutes gave a 20.7% yield. After four more recrystallizations from a 2:1 methanol-water mixture with treatment with Norite and drying over $P_2O_5$ at 10 mm. Hg the white needles melted at 135.9-136.6°C. Reported m.p. 131-132° (57), 133-134° (211).

Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.44.

2-Bromopropiophenone.--After excess anhydrous hydrogen bromide had been passed into a mixture of 3.61 g. (0.0226 moles) of crude 2-diazopropiophenone and 15 ml. of dry petroleum ether (b.p. 30-40°), the resulting deep red solution was fractionally distilled; yield of strongly lachrymatory product, 1.51 g., b.p. 85-90° (1.5 mm.), $n_D^{19.0°}$ 1.5550; 0.85 g., b.p. 90-92° (1.4 mm.), $n_D^{19.0°}$ 1.5639. Total yield 2.36 g. (49.1%). A similar run gave a yield of 35.3%. Reported b.p. 110-112° (4 mm.), (212); 136-137° (16 mm.), (213); 125-130° (10 mm.), (214). The crude light yellow liquid was used in the following preparation of 2-anilinopropiophenone without further purification.

2-Anilinopropiophenone*--A mixture of 0.84 g. (0.0039 moles) of crude 2-bromopropiophenone and 0.75 g. (0.0081 moles) of aniline was allowed to stand at room temperature for four and two-thirds hours and was then heated to 100° for several minutes. After the addition of 5 ml. of water the mixture was extracted with three 9 ml. portions of ether. Evaporation of the ether and washing of the residue with cold aqueous ethanol yielded 0.62 g. (69.9%) of orange-yellow crystals, m.p. 72-88°. After three recrystallizations from a 2:1 ethanol-water mixture and drying over $P_2O_5$ at 10 mm. Hg the long, narrow, yellow rods and prisms melted at 100.2-100.9°C. Reported m.p. 98° (215, 216). A similar preparation gave a 48.9% yield.

## 5. Preparation of Aliphatic Diazo Ketones

Pivaloyl Chloride (Trimethylacetyl Chloride).--The procedure is essentially that of Brown (217). A mixture of 19.66 g. (0.1923 moles) of pivalic acid and 54.2 g. (0.386 moles) of benzoyl chloride (redistilled, b.p. 85.7-86.1° at 16.5 mm.) was gently boiled for two hours. The pivaloyl chloride distilled over in the stream of evolved hydrogen chloride. All material collected as product boiled below 99° at 742.9 mm., $n_D^{23.6°}$ 1.4121, 20.99 g. (90.5%). Redistillation yielded 18.48 g. (79.6%), b.p. 101.5-103.5° (741.0 mm.), $n_D^{24.0°}$ 1.4109. Reported b.p. 103-104° (217), 102-104°, 105-106° (218), 70.5-71° (250 mm.), $n_D^{20°}$ 1.4118 (219).

1-Diazo-3,3-dimethylbutanone-2 (Diazomethyl-t-butyl ketone)*--This compound was prepared by the general method previously outlined for aromatic diazo ketones from 10.10 g. (0.0837 moles) of pivaloyl chloride, 8.59 g. (0.0848 moles) of triethylamine, and the diazomethane prepared from 0.354 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. After removal of the solvent the oily residue was fractionally distilled through a Claisen head with an 8 cm. Vigreaux column. Yield 9.18 g. (87.0%) of yellow liquid boiling at

76.0-77.3° (15 mm.), $n_D^{22.9°}$ 1.4632. After two refractionations the product boiled at 39.0-39.6° (1.6 mm.), $n_D^{21.6°}$ 1.4740. Reported b.p. 69° (15 mm.), $n_D^{25°}$ 1.4709 (91).

Trichloroacetyl Chloride.--The method used was essentially that of McElvain and Carney (172). A mixture of 65.47 g. (0.401 moles) of trichloroacetic acid and 91.0 ml. (1.253 moles) of thionyl chloride was refluxed for ninety-three hours and then fractionally distilled: fraction b.p. 90.0-112.0° (735.0 mm.), $n_D^{31°}$ 1.485; 33.37 g., b.p. 112.0-115.2° (735.0 mm.), $n_D^{27.5°}$ 1.4662. Refractionation of the first fraction yielded 8.22 g., b.p. 112.0° (735.3 mm.), $n_D^{24.8°}$ 1.4671. Total yield 41.59 g. (57.2%). A similar mixture refluxed for one hundred forty-five and one-half hours gave a 59.8% yield. The products of both runs were combined and refractionated with the material boiling at 114.0-115.3° (741.3 mm.), $n_D^{24.0°}$ 1.4683, being collected for use in the preparation of trichlorodiazoacetone. Reported b.p. 117.9° (754 mm.), $n_D^{20°}$ 1.46949 (220).

3-Diazo-1,1,1-trichloropropanone-2 (Trichlorodiazoacetone)*.--This compound was prepared according to the general procedure outlined previously from 10.05 g. (0.0553 moles) of trichloroacetyl chloride and the diazomethane prepared from 0.329 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. No triethylamine was used. After removal of the solvent the residue was fractionally distilled through a Claisen head with an 8 cm. Vigreaux column. Yield 1.92 g., b.p. 43-47.5° (0.7 mm.), $n_D^{20.1°}$ 1.5184; 3.53 g., b.p. 47.5-53.5° (0.7 mm.), $n_D^{20.0°}$ 1.5308. During an attempt to obtain a third fraction the material in the distilling flask decomposed quite suddenly. Total yield 5.45 g. (52.6%). Redistillation yielded a light yellow liquid, b.p. 46-48° (0.6 mm.), $n_D^{19.6°}$ 1.5292. Reported b.p. 60-61° (2 mm.), 93-95° (12 mm.), $n_D^{15°}$ 1.5309, (221); 60° (1 mm.), (222). Two attempts to prepare this compound using the method of Newman and Beal (62) with trichloroacetyl chloride and an equimolar amount of triethylamine gave impure products that were quite difficult to purify. Distillation gave either deep yellow or orange-red colored distillates with high refractive indices. Newman and Beal state that their method is best for the preparation of aromatic diazo ketones; their method gave unsatisfactory products with aliphatic acid chlorides such as caproyl chloride. Berenbom and Fones (63) report that their method gave satisfactory results with benzoyl chloride but failed with phenacetyl chloride.

<u>Diazopropanone-2 (Diazoacetone)</u>*--This compound was prepared according to the general procedure previously outlined from 9.14 g. (0.116 moles) of reagent acetyl chloride and the diazomethane prepared from 0.605 moles of N-nitroso-β-methylaminoisobutyl methyl ketone. No triethylamine was used. After removal of the solvent the residue was fractionally distilled through a Claisen head with an 8 cm. Vigreaux column. Yield, light yellow forerun smelling strongly of isopropanol, $n_D^{20.9°}$ 1.3893; 4.36 g., b.p. 39.5-40.0° (8 mm.), $n_D^{20.9°}$ 1.4889; 0.31 g., b.p. 40.0° (8 mm.), $n_D^{20.9°}$ 1.4878. Refractionation of the forerun yielded

a pure, bright yellow liquid, b.p. 37.5-38.5° (7.5 mm.), $n_D^{21.8°}$ 1.4919. Reported b.p. 46-47° (15 mm.), (223); 49° (13 mm.), (52); 46.0-46.8° (11.5 mm.), $n_D^{21°}$ 1.488, (81).

Trifluoroacetyl Chloride.--The method used was essentially that of Henne, Alm, and Smook (224). A 200 ml. three-neck flask was equipped with a dropping funnel, stirrer, and a 200 mm., Allihn, three-bulb condenser surmounted by a 300 mm., Graham, coiled-tube condenser. A piece of Tygon tubing led from the top of the Graham condenser to a trap placed in a dry ice-acetone bath. The entrances and exits to the system were protected from moisture with tubes filled with calcium chloride. Trifluoroacetic acid, 33.1 g. (0.290 moles), was added slowly over a period of several minutes to 55.9 g. (0.398 moles) of rapidly-stirred benzoyl chloride (redistilled, b.p. 85.7-86.1° at 16.5 mm.). The temperature was slowly raised to 149° over a period of seventy minutes and maintained at this temperature for thirty-one minutes. Distillation of the crude product by slowly warming to 0° gave 26.0 g. (67.6%) of trifluoroacetyl chloride and 2.46 g. (7.4% recovery) of trifluoroacetic acid. The materials was similarly distilled four more times before use in the following preparation. Reported b.p. -27° (224). Two other similar preparations gave yields of 63.0% and 63.9%.

Attempted Preparation of 3-Diazo-1,1,1-trifluoropropanone-2 (Trifluorodiazoacetone)*.--The preparation of this compound by the general method outlined previously was attempted by slowly distilling 15.3 g. (0.116 moles) of trifluoroacetyl chloride into a rapidly stirred ethereal solution of diazomethane (prepared from 0.768 moles of N-nitroso-β-methylaminoisobutyl methyl ketone and redistilled through a 28 cm. Vigreaux column); no triethylamine was used. After removal of the solvent attempted fractional distillation of the yellow liquid residue at 1 mm. Hg resulted in its very rapid decomposition with extremely vigorous gas evolution; a very viscous, orange, gummy material remained that started to distill at 76° (1.2 mm.). Two other attempted preparations with unredistilled diazomethane gave similar results. A clear pale yellow liquid that smelled like isopropanol was found in the dry ice-acetone (oil pump) trap; $n_D^{19.3°}$ 1.3681. Upon removal of solvent from this sample with a jet of dry air a deep yellow liquid remained, $n_D^{20°}$ 1.4010. The infrared spectrum of this liquid revealed strong bands at 2142 ± 2 $cm.^{-1}$ (NN), 1668 ± 2 $cm.^{-1}$ (CO), about 1400 $cm.^{-1}$ (CH def.), and about 1267 $cm.^{-1}$ and 1150 $cm.^{-1}$ ($CF_3$); the material appeared to be contaminated with a very small amount of isopropanol. Trifluorodiazoacetone has been prepared in 62.5% yield, b.p. 25° (1 mm.) by Brown and Musgrave (222) who state that the yield is particularly dependent upon careful distillation; the details concerning this careful distillation are missing.

Ethyl Diazoacetate*--The method used was essentially that of Smith and McKenzie (225). A solution of 50.0 g. (0.358 moles) of glycine ethyl ester hydrochloride and 0.25 g. of anhydrous sodium acetate in 100 ml. of water was placed in a one liter separatory funnel at room temperature. Sodium nitrite, 2 g. in a small amount of water, was added, the solution vigorously shaken, and then immediately extracted with 40 ml. of ether. Upon separation from the aqueous layer the ether extracts were run immediately into 75 ml. of saturated aqueous sodium carbonate solution and the mixture shaken. After adding 2 g. of sodium nitrite in a small amount of water followed by 3.5 ml. of 2 N sulfuric acid, the reaction mixture was extracted with 30 ml. of ether. After repeating this process twenty times the combined ether extracts were separated from the sodium carbonate solution, washed with a fresh saturated aqueous sodium carbonate solution, and dried over anhydrous sodium sulfate and magnesium sulfate. Upon removal of the ether with a jet of dry air the yellow residue, 35.4 g. (86.5%), was fractionally distilled; yield 30.16 g. (73.7%), b.p. 23° (2 mm.), $n_D^{21.0°}$ 1.4552. Upon refractionation the yellow liquid boiled at 30.0-30.4° (3.2 mm.), $n_D^{25.3°}$ 1.4595. Reported b.p. 32-33° (6 mm.), (226); 44° (10 mm.), 45° (12 mm.), 46° (11 mm.), (227); $n_D^{17.6°}$ 1.45876 (228).

# VII. SPECTRAL DATA

# TABLE III

## SPECTRAL BANDS IN THE "CARBONYL" AND "DOUBLE-BOND" REGIONS FOR BENZIL DERIVATIVES

| COMPOUND | $CM.^{-1}$[a] | INTENSITY[b] | STATE[c] | ASSIGNMENT[d] |
|---|---|---|---|---|
| Benzil | 1675 ± 2 | s | N | CO |
| | 1660 ± 2 | S | N | CO |
| | sh 1632-1644 | m | N | ? |
| | 1594.5 ± 2 | sm | N | aromatic |
| | sh 1613 | mw | N | ? |
| | 1580 ± 2 | sm | N | aromatic' |
| | sh 1563 | m | N | ? |
| | sh 1541-1546 | w | N | ? |
| | 1508 ± 2 | w | N | aromatic" |
| | 1491 ± 2 | w | N | aromatic" |
| Benzil Monoanil | 1665.5 ± 2 | s | N | CO |
| | sh 1686 | m | N | ? |

---

[a] The symbol "sh" signifies that the band appears as a shoulder on the band listed immediately before it.

[b] See Experimental Section, VI-A, for explanation of symbols.

[c] N = Nujol mull; F = thin liquid film; M = mixture of liquid compound and Nujol

[d] CO = carbonyl stretching vibration; C=N = C=N stretching vibration; NH,def. = NH deformation frequency; aromatic, aromatic', and aromatic" are vibrations reported to appear near 1600, 1600-1560, and 1525-1475 $cm.^{-1}$, respectively, in aromatic compounds (115, pp. 60-63); $NO_2$ = nitro valence vibrations.

TABLE III -Continued

| COMPOUND | CM.$^{-1}$[a] | INTENSITY[b] | STATE[c] | ASSIGNMENT[d] |
|---|---|---|---|---|
| Benzil Monoanil (continued) | 1622 ± 2 | s/sm | N | C=N |
| | sh 1616 | sm | N | ? |
| | 1592 ± 2 | s | N | aromatic |
| | 1577 ± 2 | s | N | aromatic' |
| | sh 1563 | m | N | ? |
| | 1544 ± 2.5 | m | N | ? |
| | 1482 ± 2 | sm | N | aromatic" |
| | sh 1490 | m | N | ? |
| Benzil Dianil | 1617 ± 3 | m | N | C=N |
| | sh 1647 | w | N | ? |
| | 1590 ± 2 | sm | N | aromatic |
| | 1578 ± 2 | m | N | aromatic' |
| | sh 1564 | mw | N | ? |
| | 1543 ± 2.5 | w | N | ? |
| | 1485 ± 2 | m | N | aromatic" |
| Benzil Mono-diphenyl-hydrazone, α form | 1640 ± 2 | s | N | CO |
| | 1597 ± 2 | m | N | aromatic |
| | 1590 ± 2 | m | N | aromatic' |
| | 1552 ± 2 | m | N | ? |
| | 1488 ± 2 | s | N | aromatic" |
| Benzil Mono-diphenyl-hydrazone, β form | 1676 ± 2 | s | N | CO |
| | 1656 ± 2 | mw | N | C=N |
| | 1638 ± 2 | mw | N | α-CO, impurity ? |
| | 1596 ± 2 | sm | N | aromatic |
| | 1588 ± 2 | sm | N | aromatic' |
| | 1561.5 ± 2 | mw | N | ? |

## TABLE III -Continued

| COMPOUND | CM.$^{-1a}$ | INTENSITY$^{b}$ | STATE$^{c}$ | ASSIGNMENT$^{d}$ |
|---|---|---|---|---|
| Benzil Mono-diphenylhydrazone, β form (continued) | 1550 ± 2 | mw | N | ? |
| | 1490.5 ± 2 | S | N | aromatic" |
| Benzil Monophenylhydrazone | 1649 ± 2 | sm | N | C=N ? |
| | 1638 ± 2 | s | N | CO ? |
| | 1605 ± 2 | sm | N | aromatic |
| | 1557 ± 2 | sm | N | aromatic' |
| | sh 1575 | m | N | ? |
| | 1544 ± 2 | s | N | NH,def. |
| | 1507 ± 2 | m | N | aromatic" |
| | 1487 ± 2 | m | N | aromatic" |
| Benzil β-Osazone | 1601 ± 2 | sm | N | aromatic |
| | 1579 ± 2 | m | N | aromatic' |
| | 1543 ± 2 | s | N | NH,def. |
| | 1505 ± 2 | sm | N | aromatic" |
| | 1493.5 ± 2 | m | N | aromatic" |
| Benzil Monohydrazone | 1628 ± 2 | S | N | CO |
| | 1599 ± 2 | m | N | aromatic |
| | 1576 ± 2 | m | N | aromatic' |
| | 1542 ± 2 | s | N | NH,def. |
| | 1492 ± 2 | m | N | aromatic" |
| Benzil Dihydrazone | 1622 ± 2.5 | m | N | C=N |
| | 1583 ± 2 | m | N | aromatic |
| | 1558 ± 2 | m | N | aromatic' |
| | sh 1544 | mw | N | NH,def. |
| | 1494 ± 2 | m | N | aromatic" |

## TABLE IV

## SPECTRAL BANDS BETWEEN 2200-2000 CM.$^{-1}$ FOR DIAZO KETONES AND SIMPLE DIAZO COMPOUNDS

| COMPOUND | CM.$^{-1}$ | INTENSITY[a] | STATE[b] | NO. MEAS.[c] | ASSIGNMENT[d] |
|---|---|---|---|---|---|
| 2'-Bromo-2-diazoacetophenone | 2173 $\pm$ 2 | w | N | 4 | ? |
| | 2114 $\pm$ 2 | s | N | 4 | NN |
| 3'-Bromo-2-diazoacetophenone | 2189 $\pm$ 2 | w | N | 4 | ? |
| | 2122 $\pm$ 2 | s | N | 4 | NN |
| 4'-Bromo-2-diazoacetophenone | 2177.5 $\pm$ 2 | w | N | 4 | ? |
| | 2117 $\pm$ 2 | s | N | 4 | NN |
| 2-Diazo-2'-nitroacetophenone | 2171 $\pm$ 2 | m | N | 8 | ? |
| | 2130.5 $\pm$ 2.5 | sm | N | 3 | NN |
| | 2115 $\pm$ 2 | sm | N | 8 | NN |
| | 2061 $\pm$ 4 | mw | N | 3 | ? |

[a] See Experimental Section, VI-A, for explanation of symbols.

[b] N = Nujol mull; F = thin liquid film; M = mixture of liquid compound and Nujol.

[c] Represents the number of spectra measured to obtain the average value reported in column two.

[d] NN = NN stretching vibration.

[e] Values obtained from spectra of the crude compound.

TABLE IV -Continued

| COMPOUND | CM.$^{-1}$ | INTENSITY[a] | STATE[b] | NO. MEAS.[c] | ASSIGNMENT[d] |
|---|---|---|---|---|---|
| 2-Diazo-3'-nitroacetophenone | 2189 ± 2 | m | N | 8 | ? |
|  | 2138 ± 2.5 | sm | N | 8 | NN |
|  | 2125 ± 2 | sm | N | 8 | NN |
|  | 2092 ± 2 | m | N | 5 | ? |
| 2-Diazo-4'-nitroacetophenone | 2173 ± 2 | m | N | 4 | ? |
|  | 2124 ± 2 | S | N | 4 | NN |
|  | 2067 ± 2.5 | mw | N | 7 | ? |
| 2-Diazo-2'-methylacetophenone | 2112 ± 2 | s | M | 7 | NN |
|  | 2112.5 ± 2 | s | F | 8 | NN |
| 2-Diazo-3'-methylacetophenone | 2198 ± 2 | m | N | 13 | ? |
|  | 2121 ± 3 | s | N | 13 | NN |
|  | 2110 ± 3 | s | N | 8 | NN |
| 2-Diazo-4'-methylacetophenone | 2182 ± 2 | w | N | 4 | ? |
|  | 2111.5 ± 2 | s | N | 4 | NN |
| 2-Diazoacetophenone | 2179 ± 2.5 | w | N | 6 | ? |
|  | 2119 ± 2 | m | N | 5 | NN |
| 2-Diazo-1'-acetonaphthone | 2112 ± 2 | s | N | 10 | NN |
| 2-Diazo-2'-acetonaphthone | 2171 ± 3 | w | N | 7 | ? |
|  | 2094 ± 2 | s | N | 7 | NN |
| 2-Diazo-2-phenylacetophenone | 2078 ± 2 | S | N | 5 | NN |

TABLE IV -<u>Continued</u>

| COMPOUND | CM.$^{-1}$ | INTENSITY[a] | STATE[b] | NO. MEAS.[c] | ASSIGNMENT[d] |
|---|---|---|---|---|---|
| 2-Diazopropiophenone | 2173.5 ± 2 | w | F | 10 | ? |
| | 2085 ± 2 | S | F | 10 | NN |
| Diazopropanone-2 | 2117 ± 2 | S | M | 9 | NN |
| | 2116.5 ± 2 | S | F | 13 | NN |
| 1-Diazo-3,3-dimethylbutanone-2 | 2116 ± 2 | S | M | 8 | NN |
| | 2116 ± 2 | S | F | 10 | NN |
| 3-Diazo-1,1,1-trichloro-propanone-2 | 2173 ± 3 | m | F | 11 | ? |
| | 2173 ± 3 | m | M | 12 | ? |
| | 2130 ± 2 | s | F | 11 | NN |
| | 2129 ± 2 | s | M | 12 | NN |
| 3-Diazo-1,1,1-trifluoro-propanone-2 | 2184 ± 2 | -[e] | F | 8 | ? |
| | 2142 ± 2 | -[e] | F | 9 | NN |
| Ethyl diazoacetate | 2121 ± 2 | S | M | 7 | NN |
| | 2122 ± 2 | S | F | 8 | NN |
| Diazodiphenylmethane | 2052 ± 2 | S | N | 15 | NN |
| 9-Diazofluorene | 2141 ± 3 | mw | N | 8 | ? |
| | 2093.5 ± 2 | s | N | 4 | ? |
| | 2068 ± 2 | S | N | 4 | NN |

## TABLE V

### SPECTRAL BANDS IN THE "CARBONYL" AND "DOUBLE-BOND" REGIONS FOR DIAZO KETONES AND SIMPLE DIAZO COMPOUNDS

| COMPOUND | CM.$^{-1}$[a] | INTENSITY[a] | STATE[a] | ASSIGNMENT[a] |
|---|---|---|---|---|
| 2'-Bromo-2-diazoacetophenone | 1614 ± 2 | S | N | CO |
| | sh 1623 | s | N | ? |
| | 1586 ± 2 | m | N | aromatic |
| | 1564 ± 2 | mw | N | aromatic' |
| | sh 1545 | w | N | ? |
| | 1512 ± 2 | w | N | aromatic" |
| 3'-Bromo-2-diazoacetophenone | 1602 ± 2 | S | N | CO |
| | 1564 ± 2 | s | N | aromatic' |
| | 1493 ± 2 | w | N | aromatic" |
| 4'-Bromo-2-diazoacetophenone | 1609 ± 2 | s | N | CO |
| | 1593 ± 2 | sm | N | aromatic |
| | 1564.5 ± 2 | m | N | aromatic' |
| | 1488 ± 2.5 | mw | N | aromatic" |
| 2-Diazo-2'-nitroacetophenone | 1614 ± 2 | s | N | CO ? |
| | sh 1608 | sm | N | aromatic ? |
| | 1576 ± 2 | m | N | aromatic' |
| | sh 1562 | mw | N | ? |
| | 1533 ± 2 | s | N | $NO_2$ |
| | 1525 ± 2 | s | N | $NO_2$ |
| | 1486 ± 2 | m | N | aromatic" |

[a] See Table III for explanation of symbols.

TABLE V -Continued

| COMPOUND | CM.$^{-1}$[a] | INTENSITY[a] | STATE[a] | ASSIGNMENT[a] |
|---|---|---|---|---|
| 2-Diazo-3'-nitroacetophenone | 1606.5 ± 2 | s | N | aromatic ? |
| | sh 1613 | s | N | CO ? |
| | 1576 ± 2 | sm/m | N | aromatic' |
| | 1534 ± 2.5 | s | N | $NO_2$ |
| | 1483 ± 2.5 | m | N | aromatic" |
| 2-Diazo-4'-nitroacetophenone | 1620 ± 2 | sm | N | CO ? |
| | 1594 ± 2 | S | N | aromatic ? |
| | sh 1572 | mw | N | aromatic' |
| | 1520 ± 2 | S | N | $NO_2$ |
| | sh 1491-1496 | mw | N | aromatic" |
| 2-Diazo-2'-methylacetophenone | 1622 ± 2 | s | M | CO |
| | 1621 ± 2 | s | F | CO |
| | 1602 ± 2 | sm | M | aromatic |
| | 1602 ± 2 | m | F | aromatic |
| | 1571 ± 2 | m | M | aromatic' |
| | 1570 ± 2 | mw | F | aromatic' |
| | 1488.5 ± 2 | m | M | aromatic" |
| | 1488 ± 2 | mw | F | aromatic" |
| 2-Diazo-3'-methylacetophenone | 1617 ± 2 | s | N | CO |
| | 1597 ± 2 | s | N | aromatic |
| | 1580.5 ± 2 | s | N | aromatic' |
| | 1504 ± 2 | mw | N | aromatic" |
| 2-Diazo-4'-methylacetophenone | 1603 ± 2 | S | N | aromatic ? |
| | sh 1614 | s | N | CO ? |

TABLE V -Continued

| COMPOUND | CM.$^{-1}$[a] | INTENSITY[a] | STATE[a] | ASSIGNMENT[a] |
|---|---|---|---|---|
| 2-Diazo-4'-methylacetophenone (continued) | 1565 ± 2 | m | N | aromatic' |
| | 1510 ± 2 | w | N | aromatic" |
| 2-Diazoacetophenone | 1618.5 ± 2 | s | N | CO |
| | 1599.5 ± 2 | s | N | aromatic |
| | 1575 ± 2 | s | N | aromatic' |
| | sh 1562 | m | N | ? |
| | 1498 ± 2 | m/mw | N | aromatic" |
| 2-Diazo-1'-acetonaphthone | 1626.5 ± 2 | m | N | aromatic |
| | 1613 ± 2 | S | N | CO |
| | 1592 ± 2 | sm/s | N | aromatic" |
| | 1579 ± 2 | m | N | ? |
| | sh 1563 | m | N | ? |
| | 1544 ± 3 | mw | N | ? |
| | 1510 ± 2 | m | N | aromatic" |
| 2-Diazo-2'-acetonaphthone | 1607 ± 2 | S | N | CO |
| | sh 1626 | m | N | aromatic |
| | sh 1597 | sm | N | aromatic' ? |
| | sh 1587 | m | N | aromatic' ? |
| | 1573 ± 2 | m | N | ? |
| | sh 1560 | mw | N | ? |
| | sh 1544 | w | N | ? |
| | sh 1526 | w | N | ? |
| | 1505 ± 2 | w | N | aromatic" |
| 2-Diazo-2-phenylacetophenone | 1620 ± 2.5 | s | N | CO |

TABLE V -Continued

| COMPOUND | CM.$^{-1a}$ | INTENSITY$^{a}$ | STATE$^{a}$ | ASSIGNMENT$^{a}$ |
|---|---|---|---|---|
| 2-Diazo-2-phenylacetophenone (continued) | 1597 ± 2 | m/sm | N | aromatic |
| | 1575.5 ± 2 | m | N | aromatic' |
| | sh 1563 | m | N | ? |
| | 1524 ± 3 | mw | N | ? |
| | 1500.5 ± 2 | sm | N | aromatic" |
| 2-Diazopropiophenone | 1621 ± 2.5 | s | F | CO |
| | 1609 ± 2 | s | F | aromatic |
| | 1575 ± 2 | m | F | aromatic' |
| | 1493 ± 2.5 | w | F | aromatic" |
| Diazopropanone-2 | 1647 ± 2 | s | F | CO |
| | 1646 ± 2 | s | M | CO |
| 1-Diazo-3,3-dimethylbutanone-2 | 1630 ± 2 | sm | F | CO |
| | 1630 ± 2 | m/sm | M | CO |
| 3-Diazo-1,1,1-trichloro-propanone-2 | 1665 ± 2 | s | F | CO |
| | sh 1604-1614 | w | F | ? |
| | 1667 ± 2 | sm | M | CO |
| | 1606 ± 2 | w | M | ? |
| | 1551 ± 4 | w | F | ? |
| | 1548 (poorly resolved) | w | M | ? |
| 3-Diazo-1,1,1-trifluoro-propanone-2 | 1668 ± 2 | -$^{e}$ | F | CO |

[e] Value obtained from spectrum of the crude compound.

TABLE V -Continued

| COMPOUND | CM.$^{-1a}$ | INTENSITY$^{a}$ | STATE$^{a}$ | ASSIGNMENT$^{a}$ |
|---|---|---|---|---|
| Ethyl diazoacetate | 1693 ± 2 | s | M | CO |
| | sh 1703 | s | M | ? |
| | 1693 ± 2 | s | F | CO |
| | sh 1703 | s | F | ? |
| Diazodiphenylmethane | 1598 ± 2 | m | N | aromatic |
| | 1580.5 ± 2 | mw | N | aromatic' |
| | 1499 ± 2 | m | N | aromatic" |
| 9-Diazofluorene | 1603 ± 2 | m | N | aromatic |
| | sh 1608 | m | N | ? |
| | 1571 ± 2 | m | N | aromatic' |

## TABLE VI

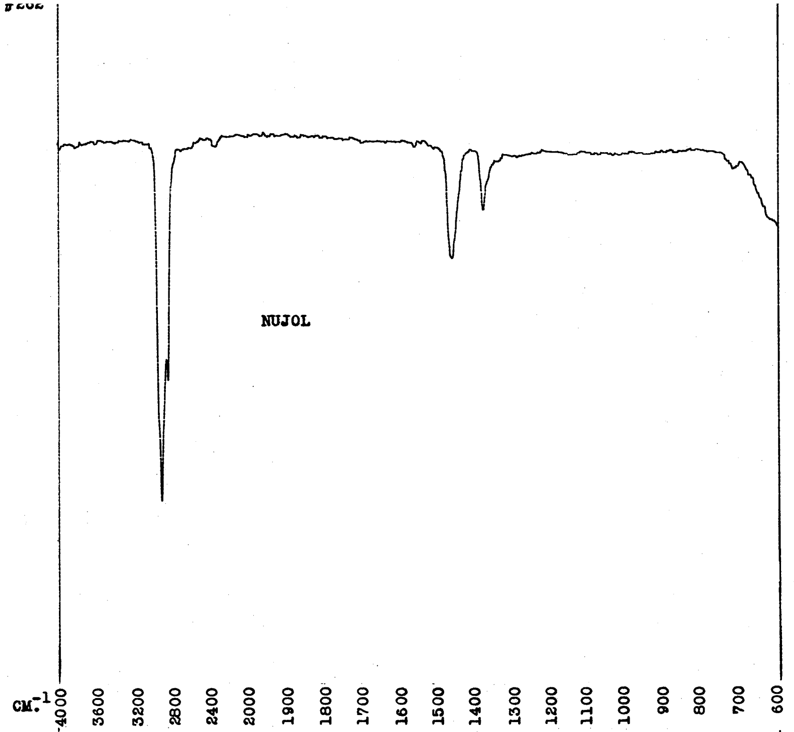
## SPECTRAL BANDS IN THE "CARBONYL" AND "DOUBLE-BOND" REGIONS FOR MISCELLANEOUS COMPOUNDS

| COMPOUND | $CM.^{-1}$ [a] | INTENSITY[a] | STATE[a] | ASSIGNMENT[a] |
|---|---|---|---|---|
| Benzophenone hydrazone | 1623 ± 2 | mw | N | C=N ? |
| | 1614.5 ± 2 | mw | N | C=N ? |
| | 1602 ± 2 | w | N | ? |
| | 1584 ± 2 | m | N | aromatic |
| | 1572 ± 2 | m | N | aromatic' ? |
| | 1561 ± 2 | m | N | NH,def. ? |
| | 1494.5 ± 2 | m | N | aromatic" |
| 9-Fluorenone hydrazone | 1638.5 ± 2 | mw | N | C=N |
| | 1611.5 ± 2 | m | N | aromatic |
| | 1577 ± 2 | m | N | aromatic' ? |
| | sh 1561-1564 | m/mw | N | NH,def. ? |

[a] See Table III for explanation of symbols.

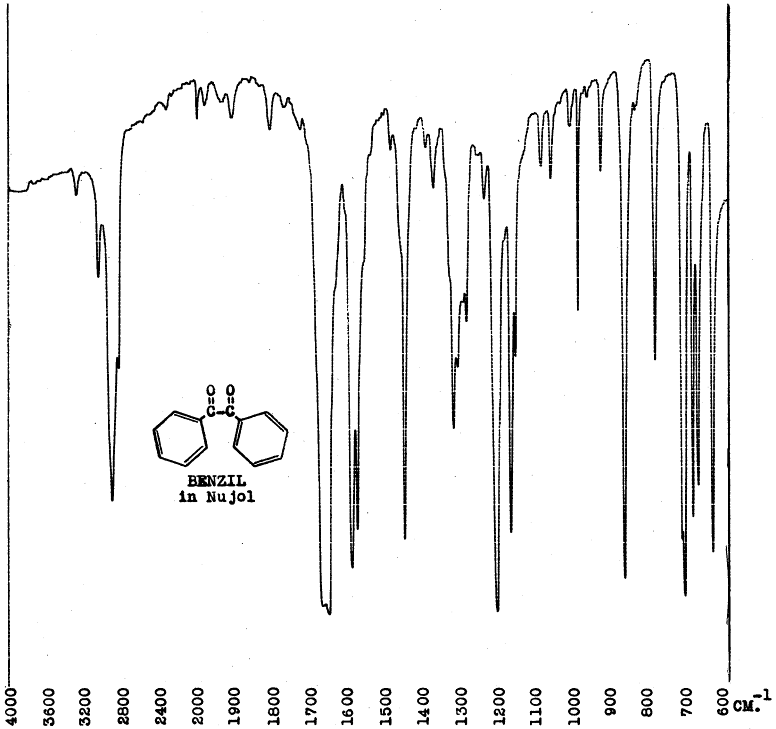
# VIII. INFRARED SPECTRAL CURVES

The small Arabic number found in the upper left hand corner of each spectrum is the identification number assigned the spectrum in the laboratory notebooks.



NUJOL

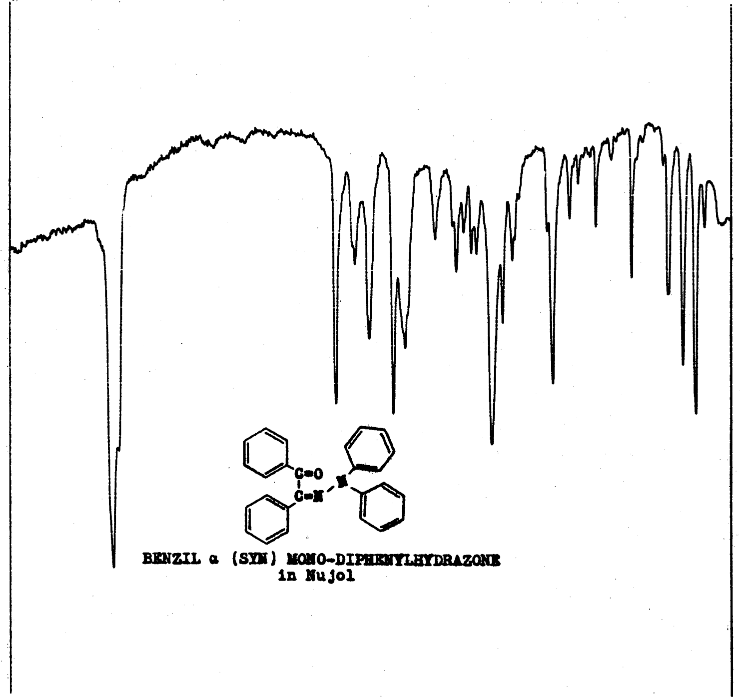
#260



BENZIL
in Nujol

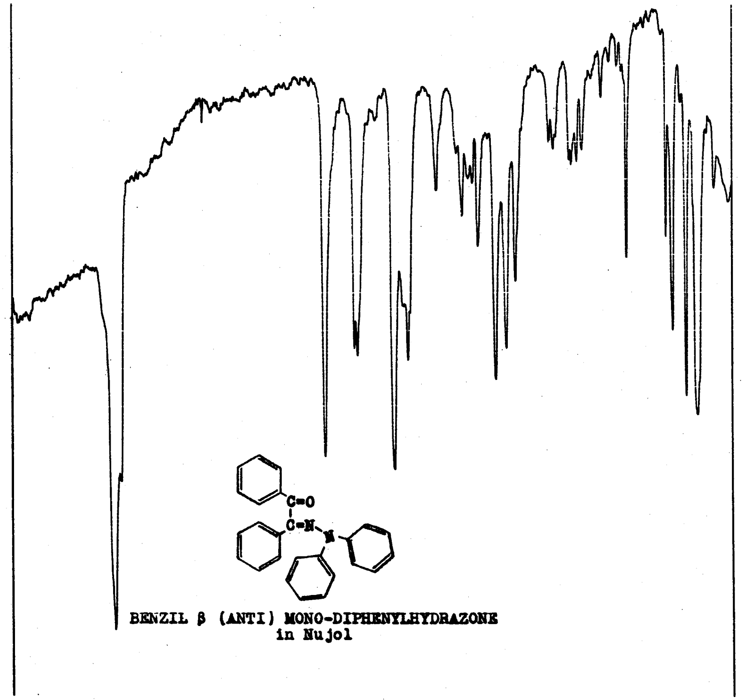
FREQUENCY

#453



BENZIL α (SYN) MONO-DIPHENYLHYDRAZONE
in Nujol

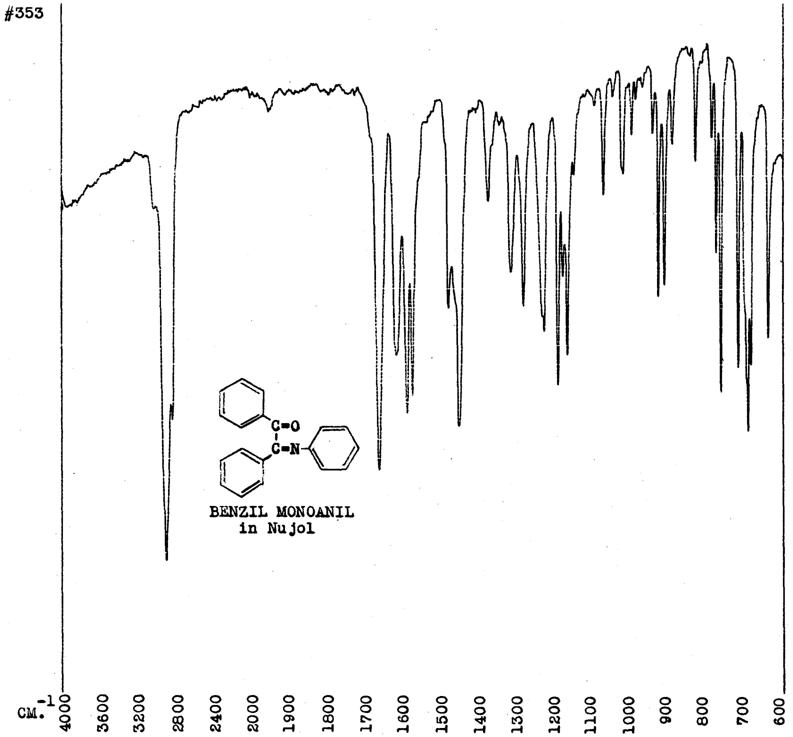
#456



BENZIL β (ANTI) MONO-DIPHENYLHYDRAZONE
in Nujol

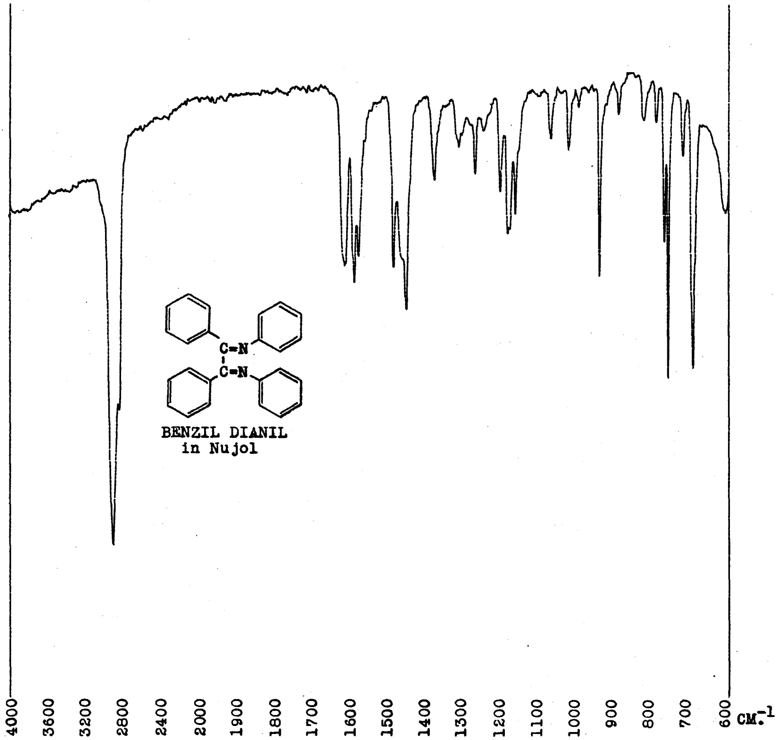
PLATE II

#353



BENZIL MONOANIL
in Nujol

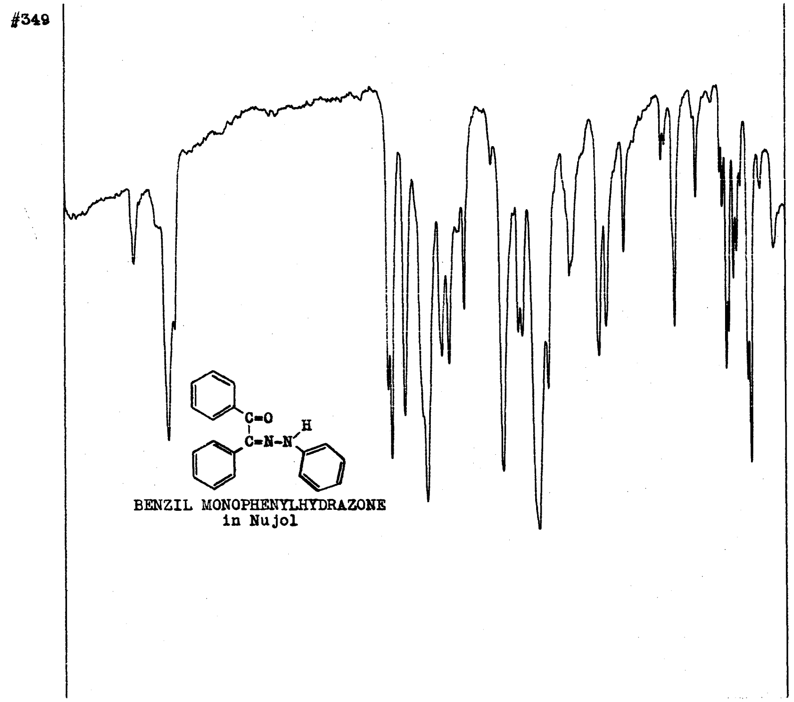
#352



BENZIL DIANIL
in Nujol

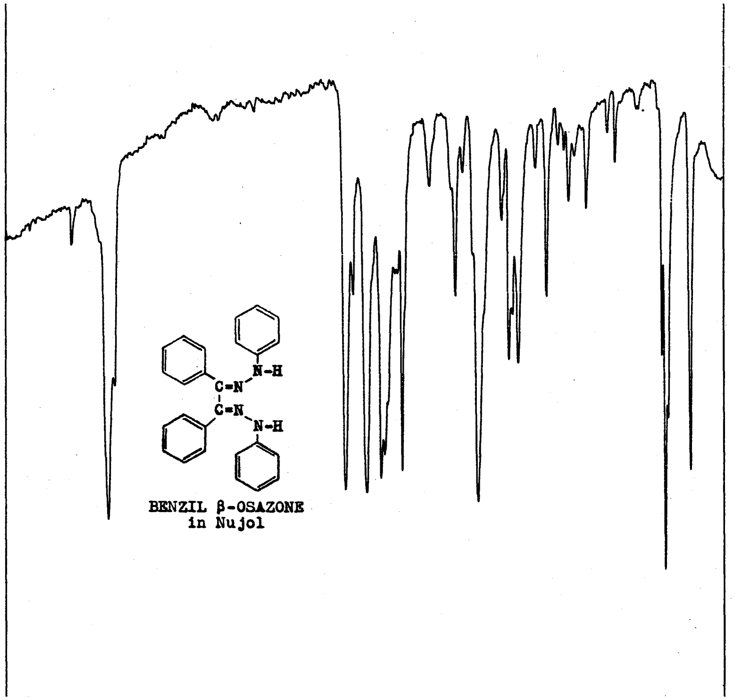
FREQUENCY

#349

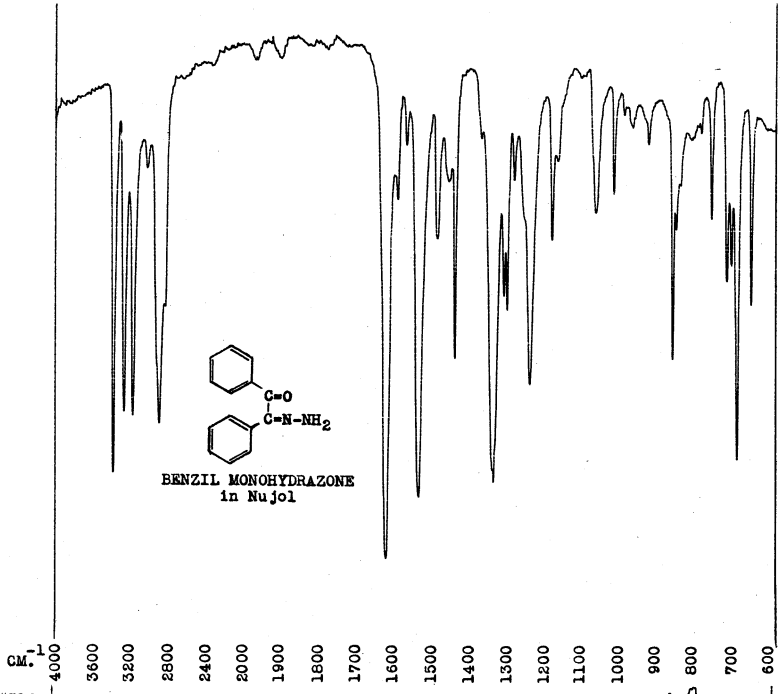


BENZIL MONOPHENYLHYDRAZONE
in Nujol

#348

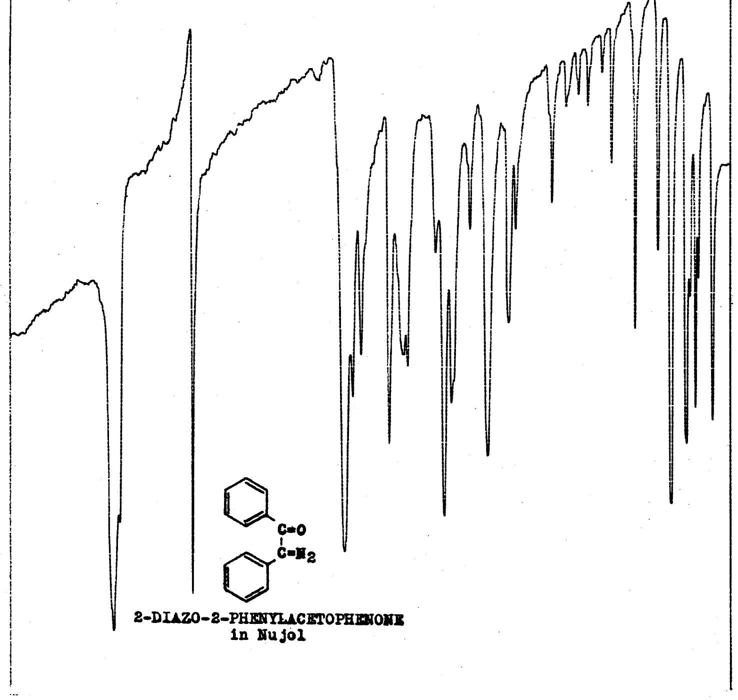


BENZIL β-OSAZONE
in Nujol



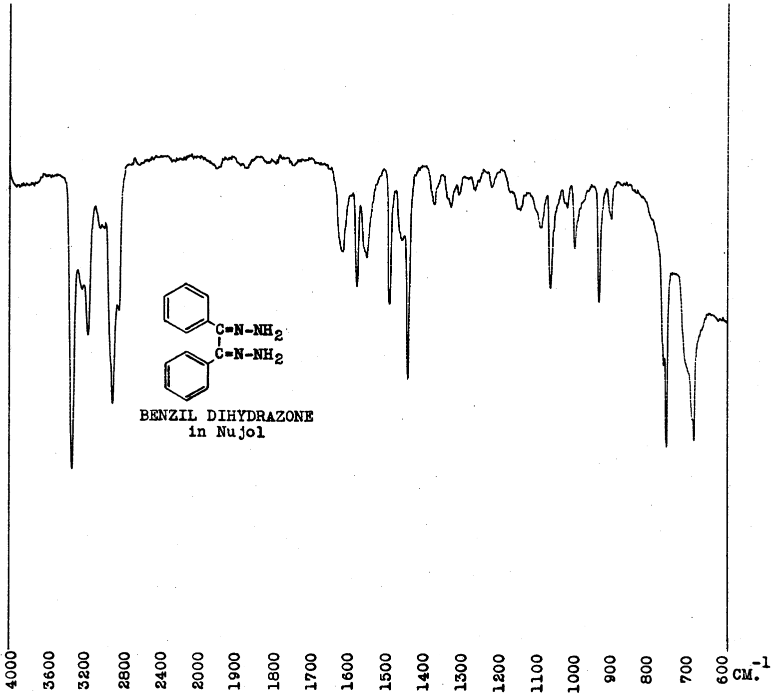
BENZIL MONOHYDRAZONE
in Nujol

#316



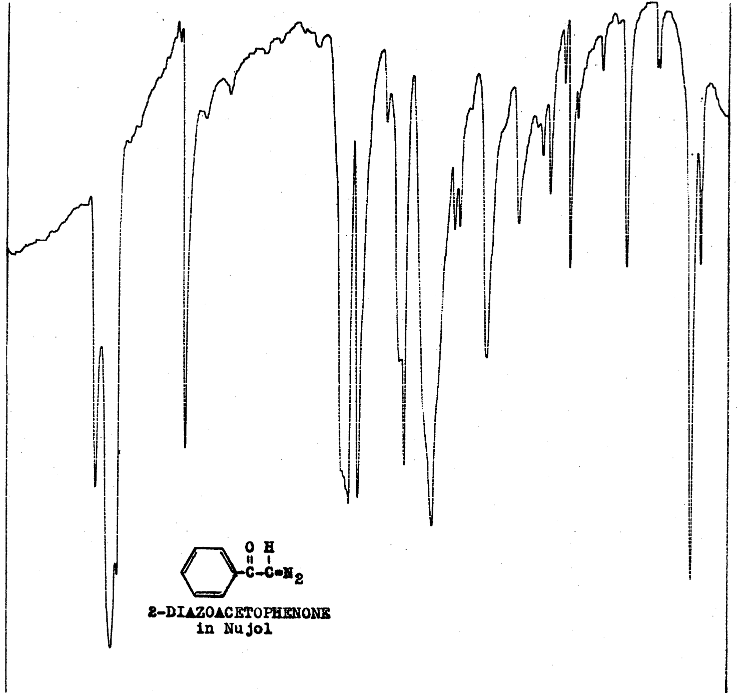
2-DIAZO-2-PHENYLACETOPHENONE
in Nujol

FREQUENCY



BENZIL DIHYDRAZONE
in Nujol

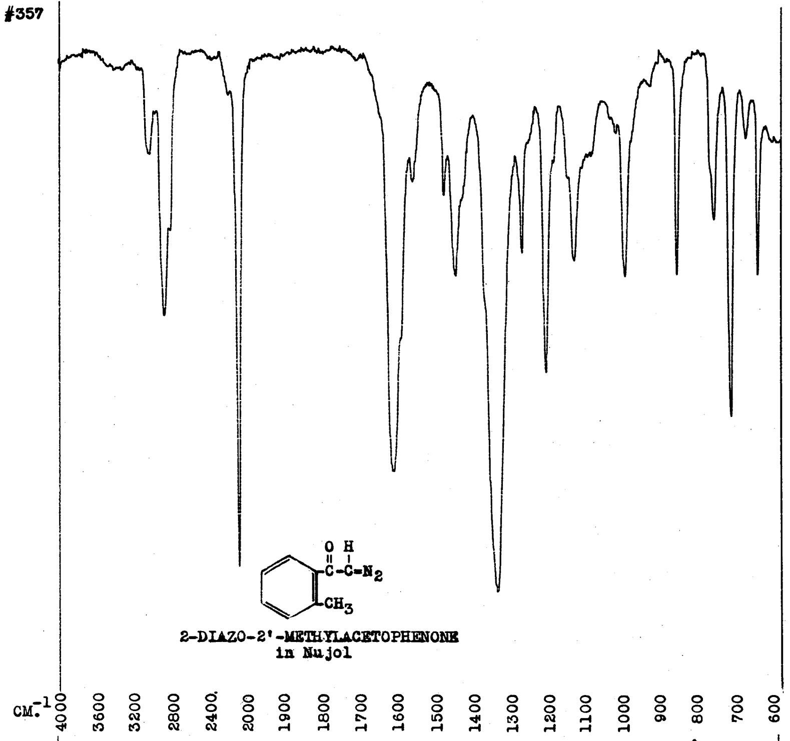
#163



2-DIAZOACETOPHENONE
in Nujol

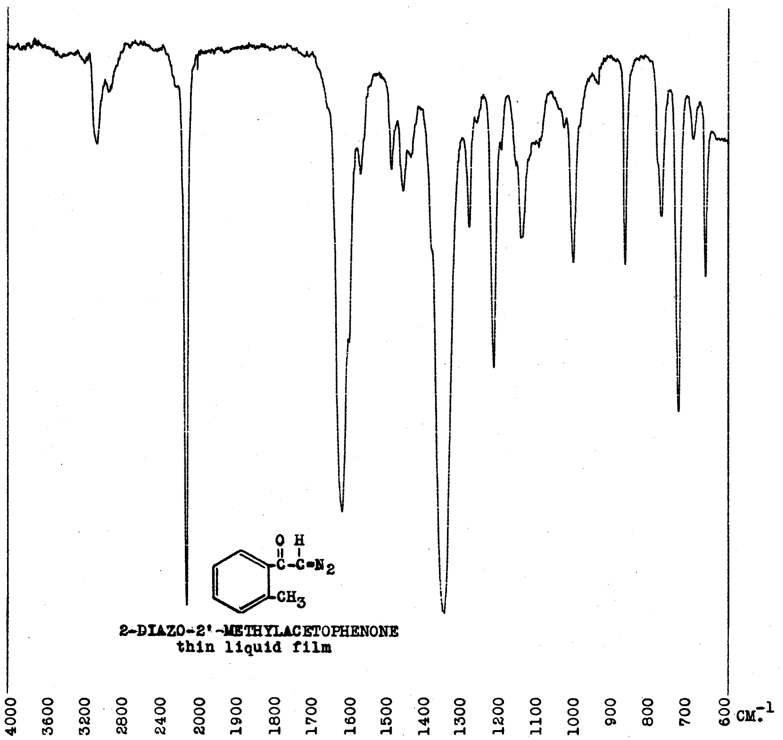
PLATE IV

#357



2-DIAZO-2'-METHYLACETOPHENONE
in Nujol

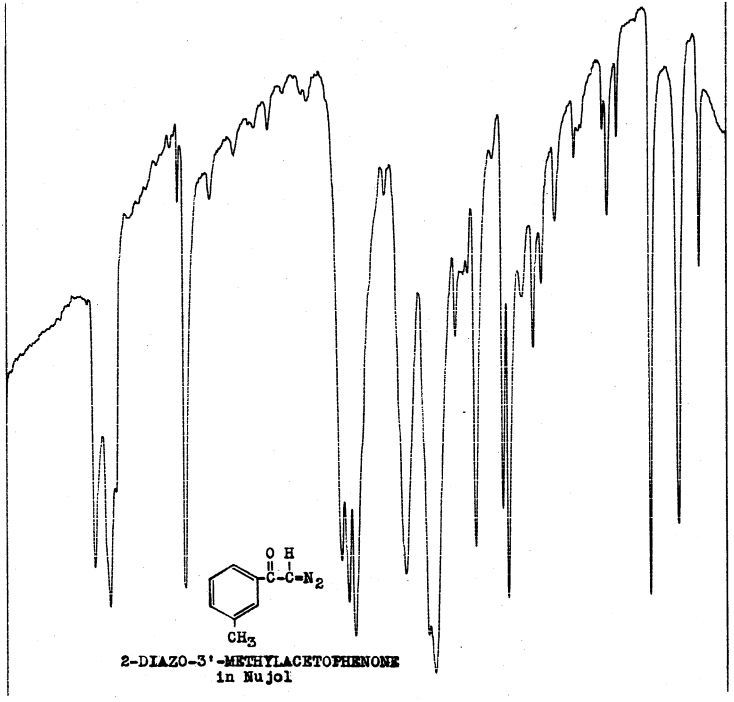
#358



2-DIAZO-2'-METHYLACETOPHENONE
thin liquid film

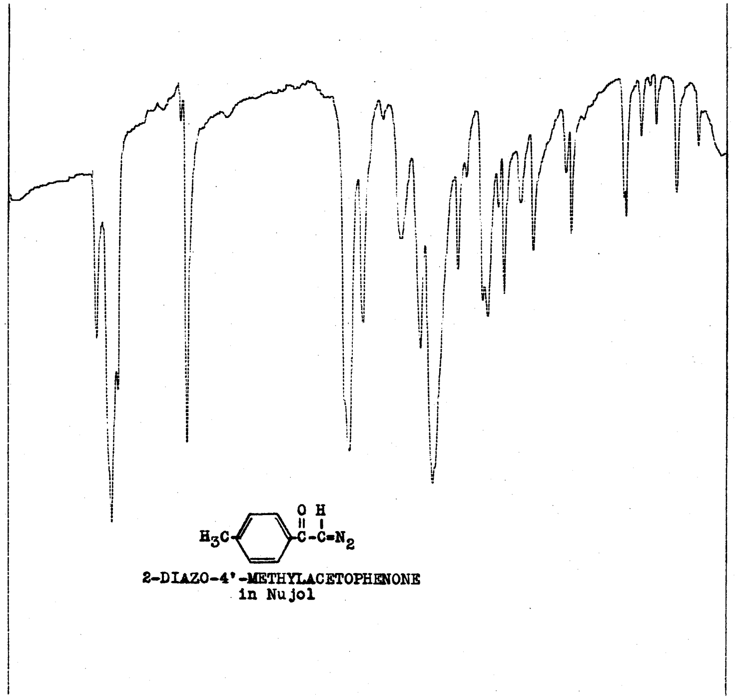
FREQUENCY

#324

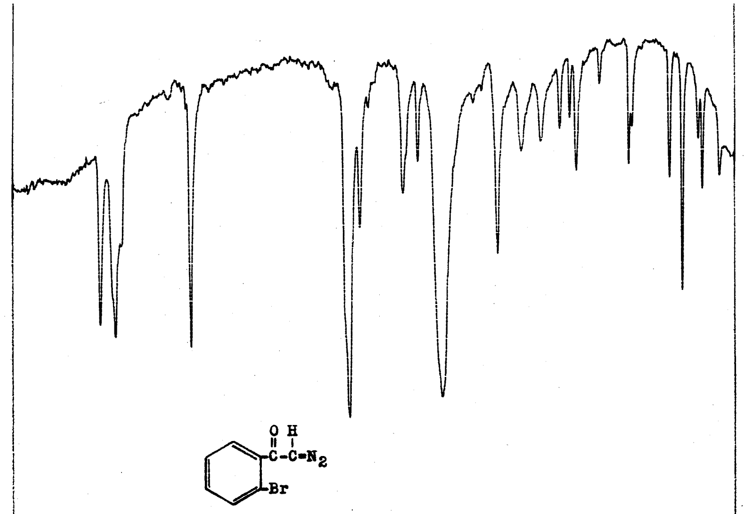


2-DIAZO-3'-METHYLACETOPHENONE
in Nujol

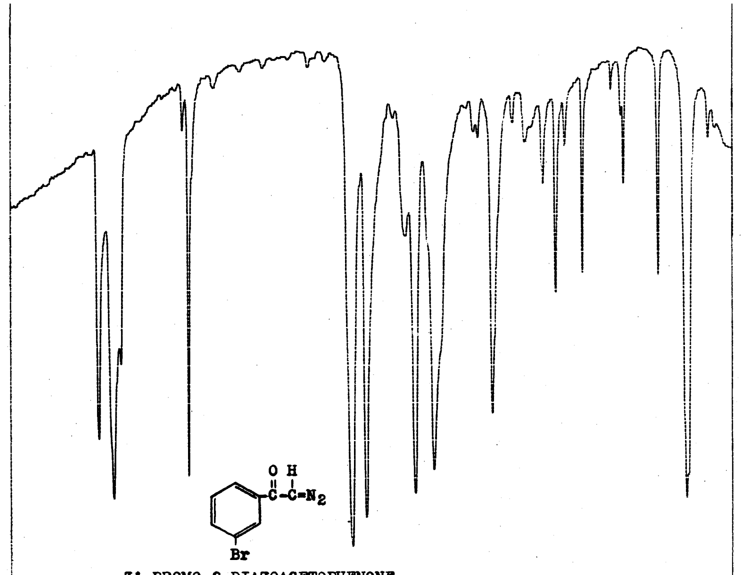
#197



2-DIAZO-4'-METHYLACETOPHENONE
in Nujol



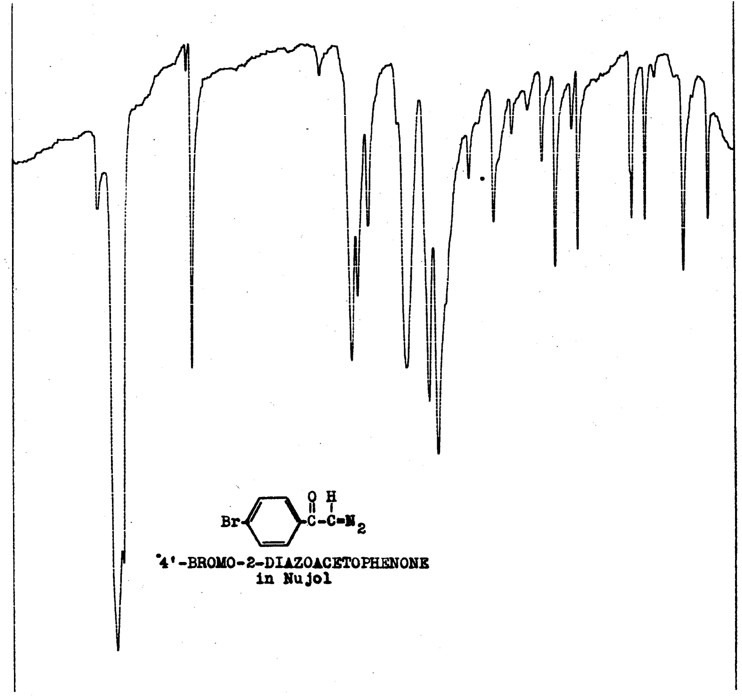
2'-BROMO-2-DIAZOACETOPHENONE
in Nujol



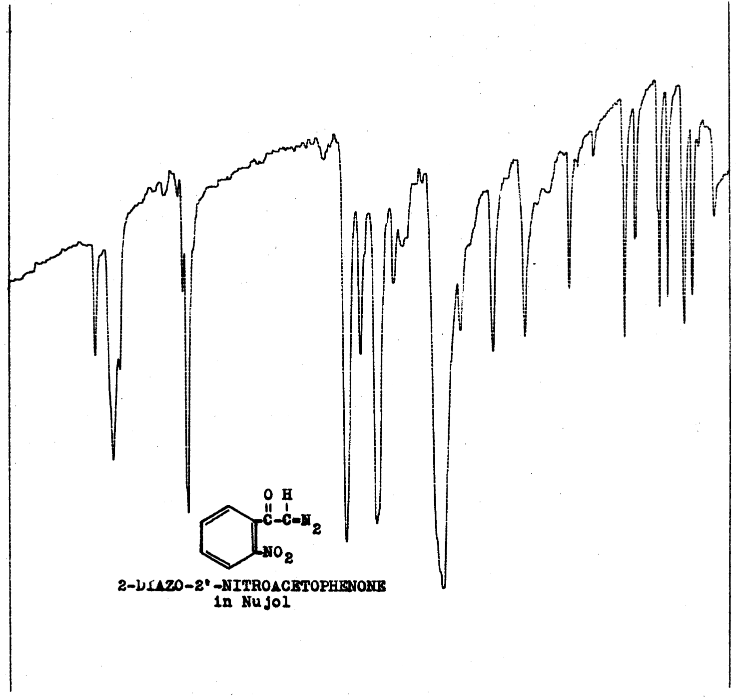
3'-BROMO-2-DIAZOACETOPHENONE
in Nujol

#189

#223



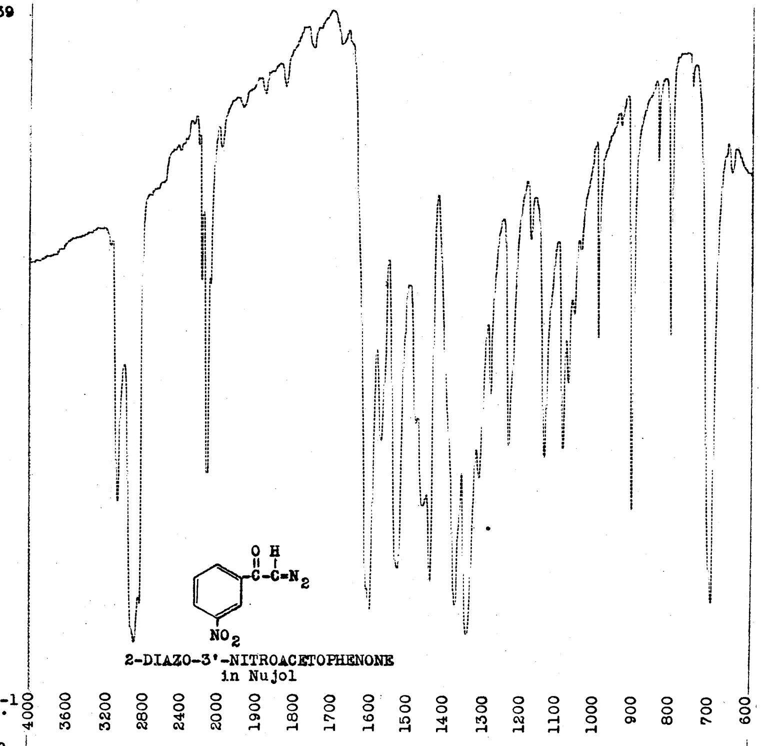
4'-BROMO-2-DIAZOACETOPHENONE
in Nujol



2-DIAZO-2'-NITROACETOPHENONE
in Nujol

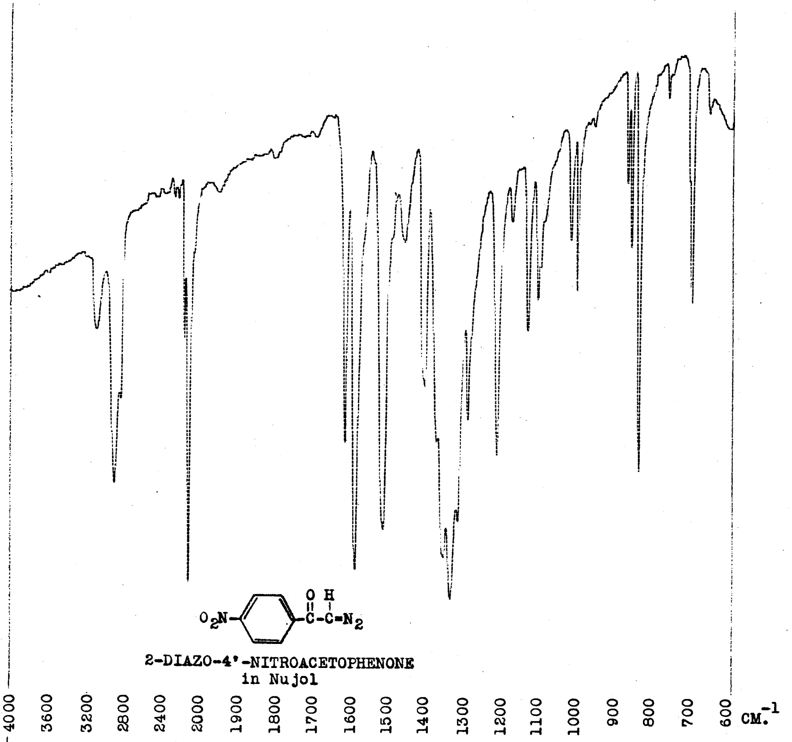
PLATE VI

#239



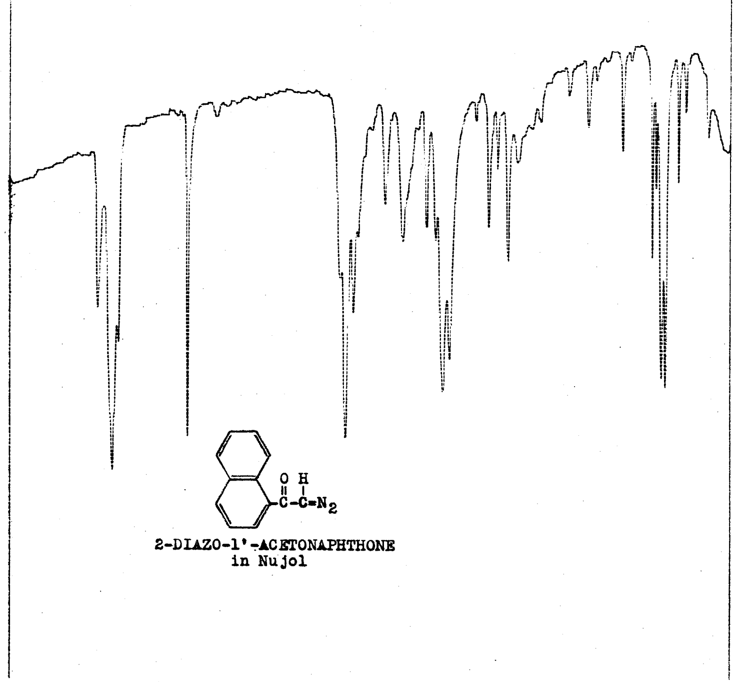
2-DIAZO-3'-NITROACETOPHENONE
in Nujol

#218



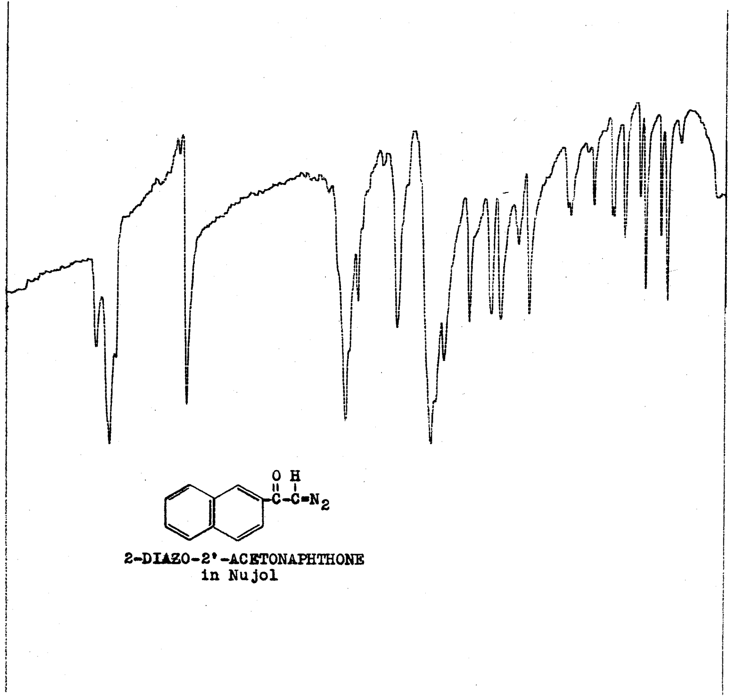
2-DIAZO-4'-NITROACETOPHENONE
in Nujol

#210

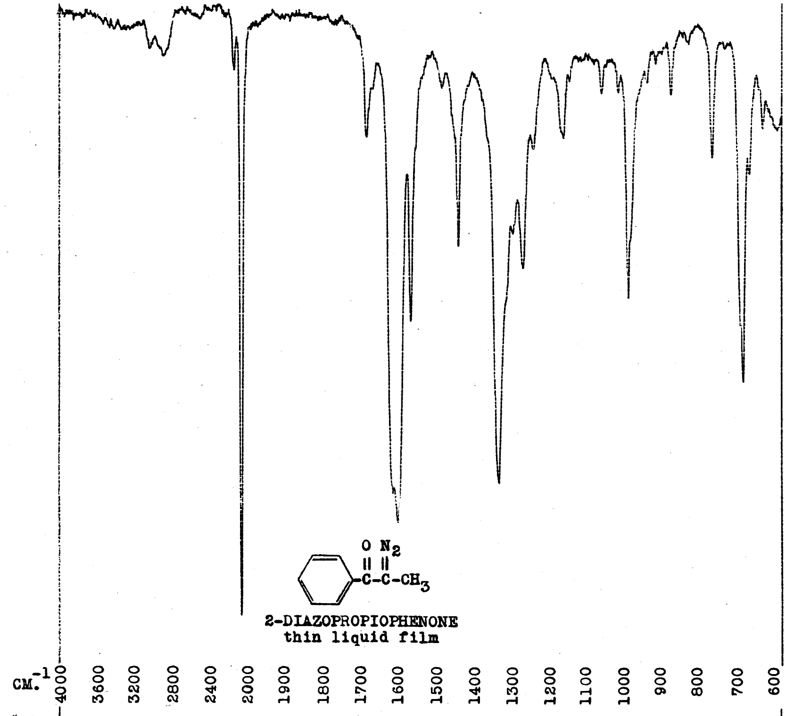


2-DIAZO-1'-ACETONAPHTHONE
in Nujol

#267



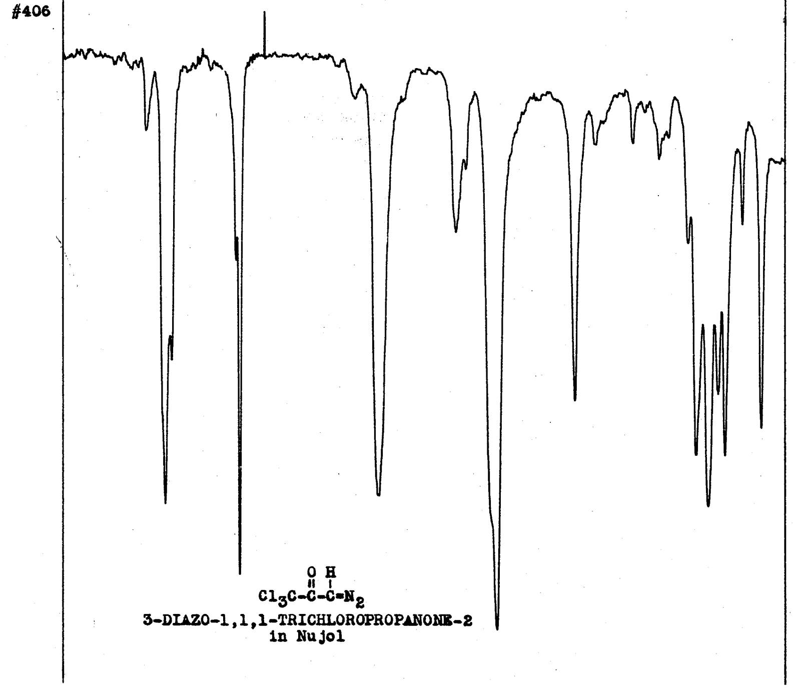
2-DIAZO-2'-ACETONAPHTHONE
in Nujol



$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{N_2}{\|}}{C}-CH_3$

2-DIAZOPROPIOPHENONE
thin liquid film

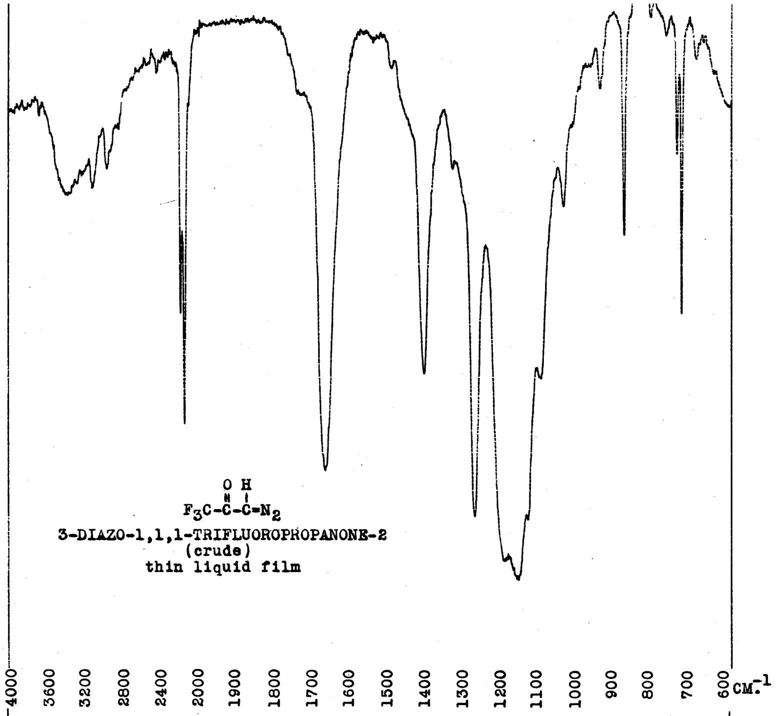
#406



$Cl_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

3-DIAZO-1,1,1-TRICHLOROPROPANONE-2
in Nujol

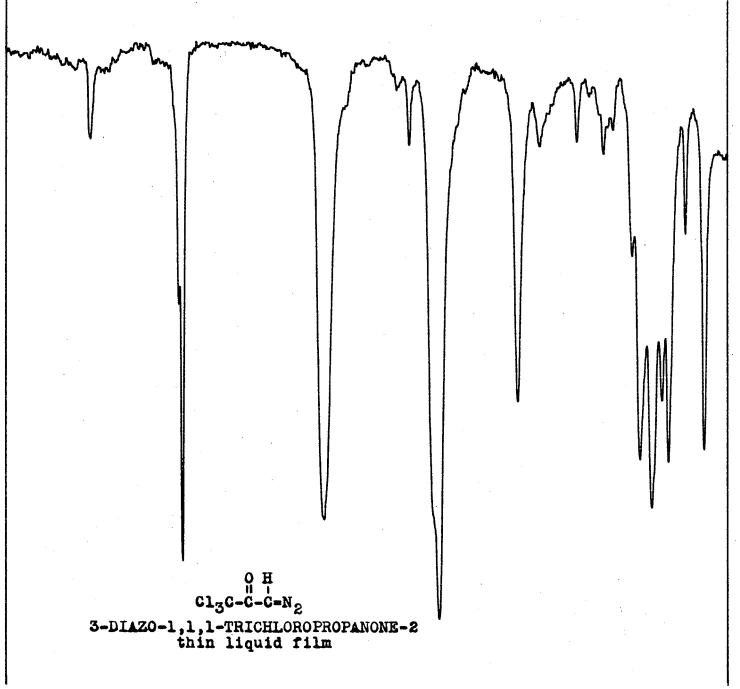
FREQUENCY



$F_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

3-DIAZO-1,1,1-TRIFLUOROPROPANONE-2
(crude)
thin liquid film

#405

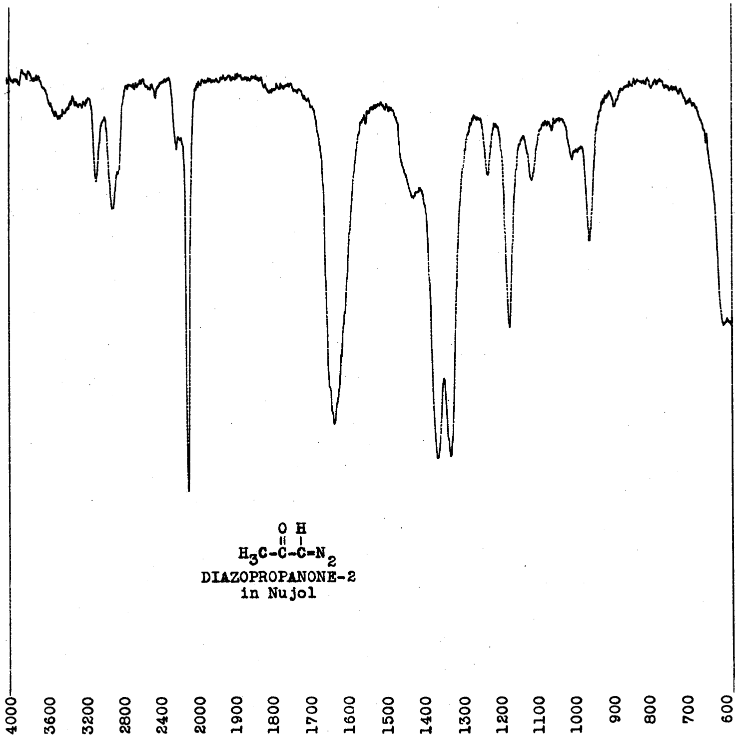


$Cl_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

3-DIAZO-1,1,1-TRICHLOROPROPANONE-2
thin liquid film

PLATE VIII

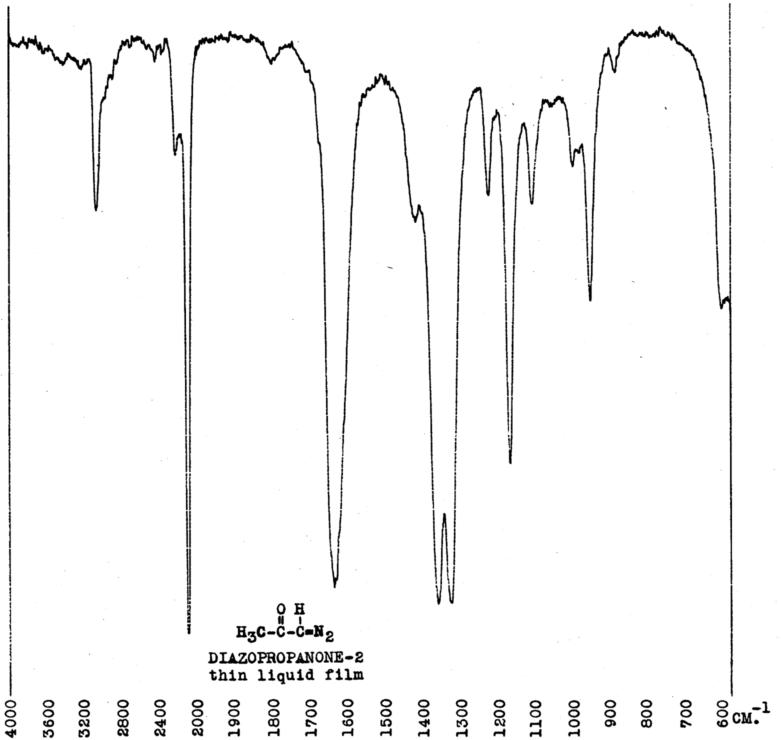
#418



$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

DIAZOPROPANONE-2
in Nujol

#415



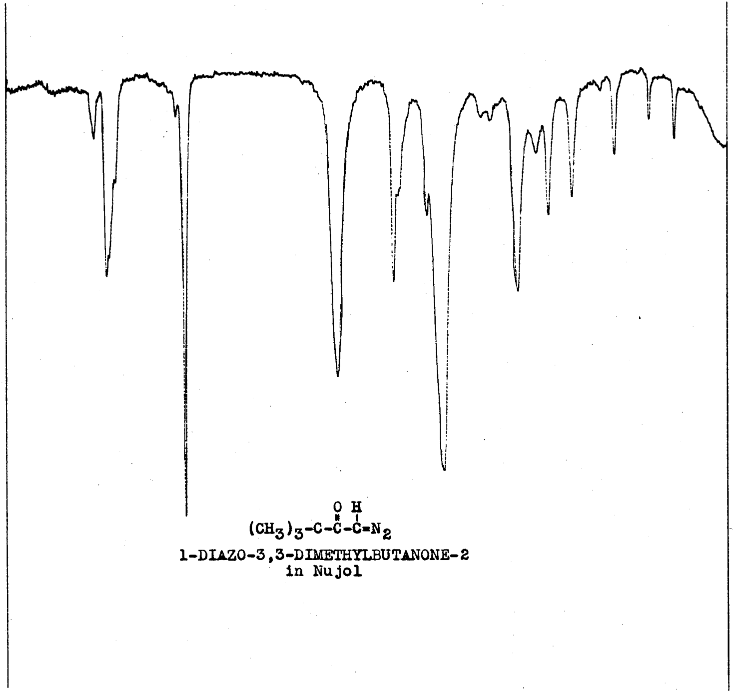
$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

DIAZOPROPANONE-2
thin liquid film

CM.$^{-1}$

FREQUENCY

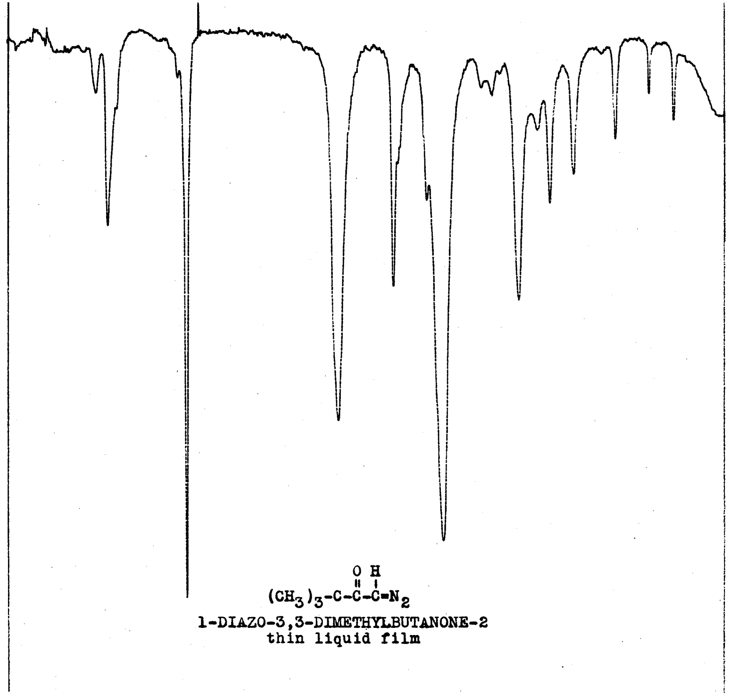
#377



$(CH_3)_3-C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

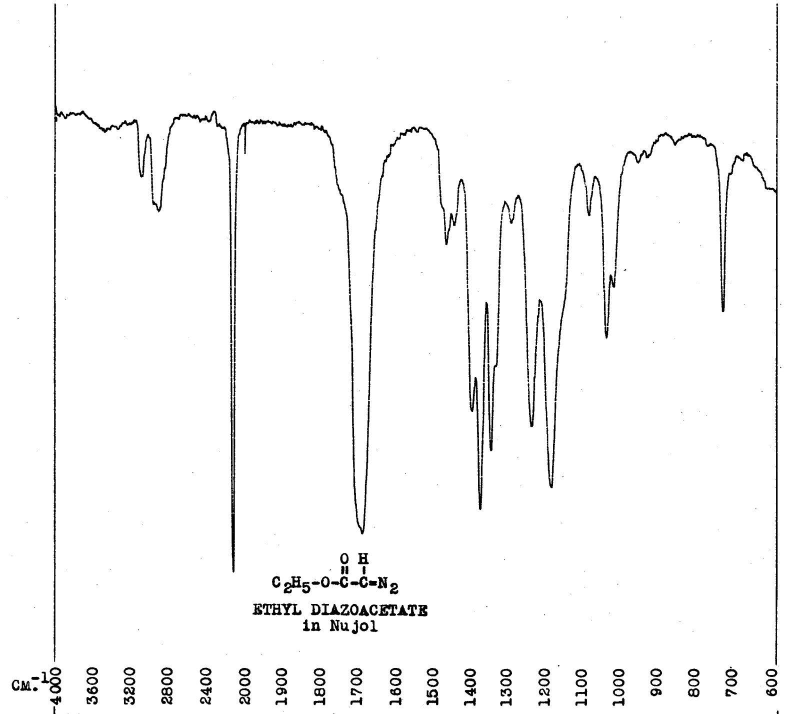
1-DIAZO-3,3-DIMETHYLBUTANONE-2
in Nujol

#375



$(CH_3)_3-C-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=N_2$

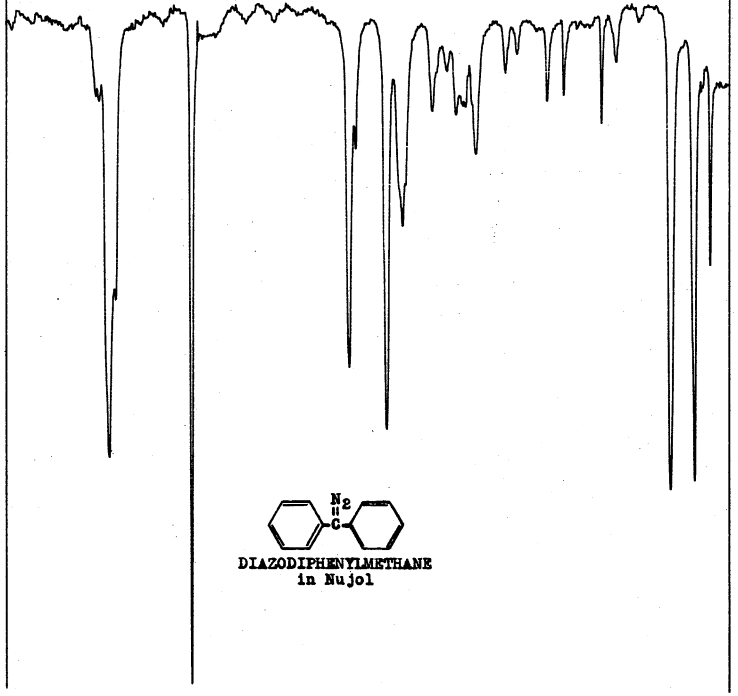
1-DIAZO-3,3-DIMETHYLBUTANONE-2
thin liquid film



$$C_2H_5{-}O{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{\overset{\large H}{|}}{C}{=}N_2$$

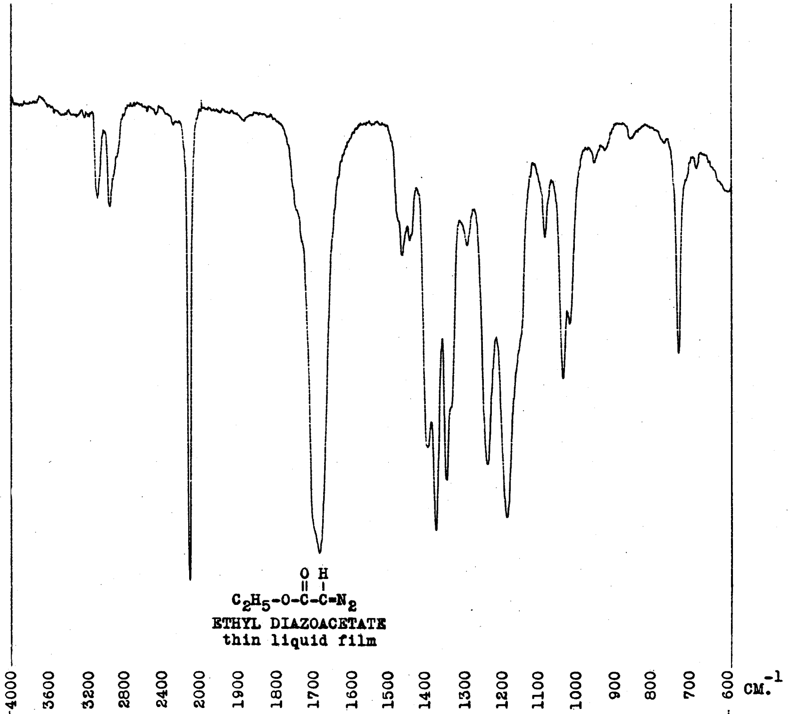
ETHYL DIAZOACETATE
in Nujol

#394



DIAZODIPHENYLMETHANE
in Nujol

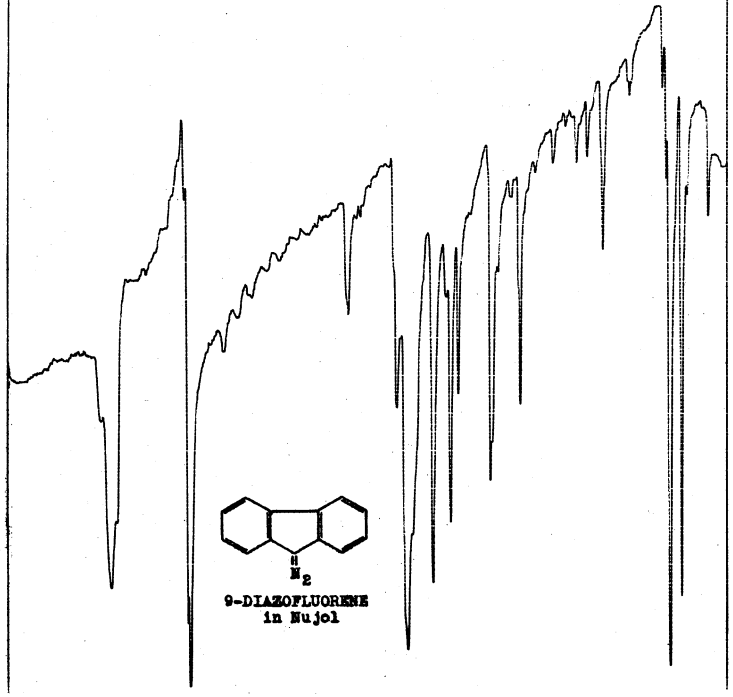
FREQUENCY



$$C_2H_5{-}O{-}\overset{\overset{\large O}{\|}}{C}{-}\overset{\overset{\large H}{|}}{C}{=}N_2$$

ETHYL DIAZOACETATE
thin liquid film

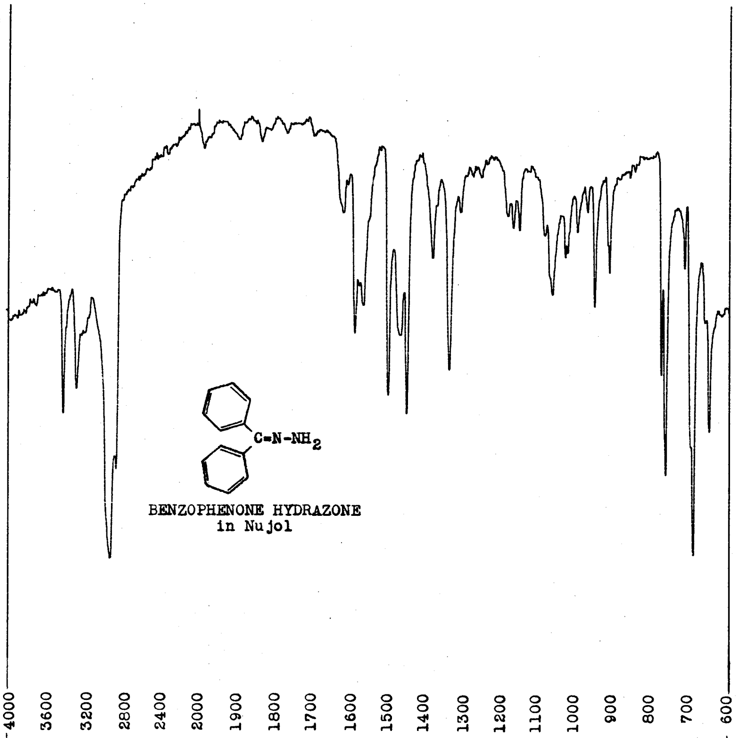
#315



9-DIAZOFLUORENE
in Nujol

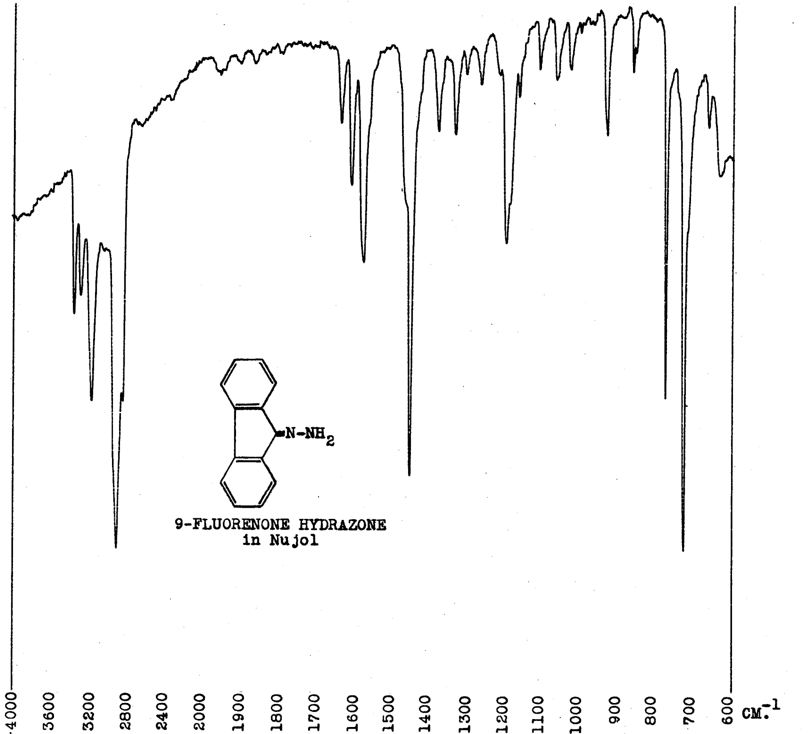
PLATE X

#384



BENZOPHENONE HYDRAZONE
in Nujol

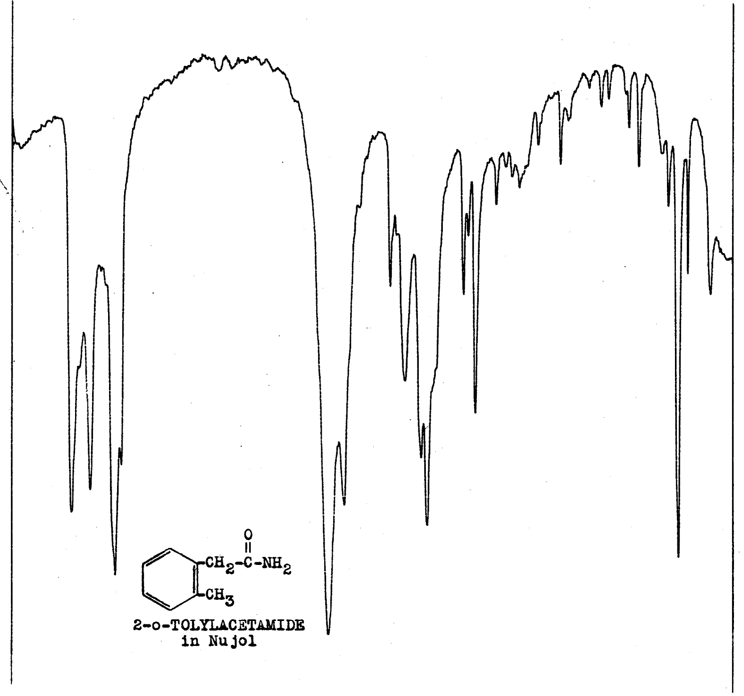
#354



9-FLUORENONE HYDRAZONE
in Nujol

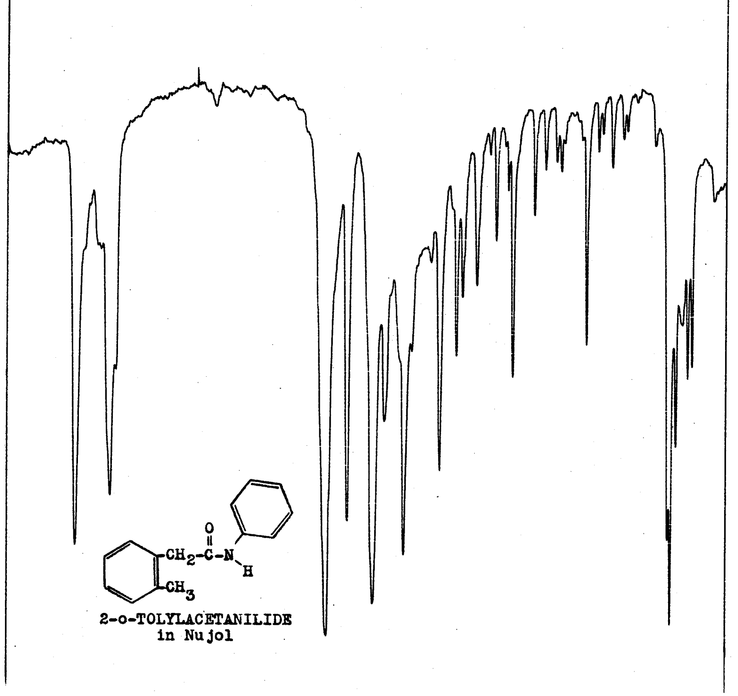
FREQUENCY

#344



2-o-TOLYLACETAMIDE
in Nujol

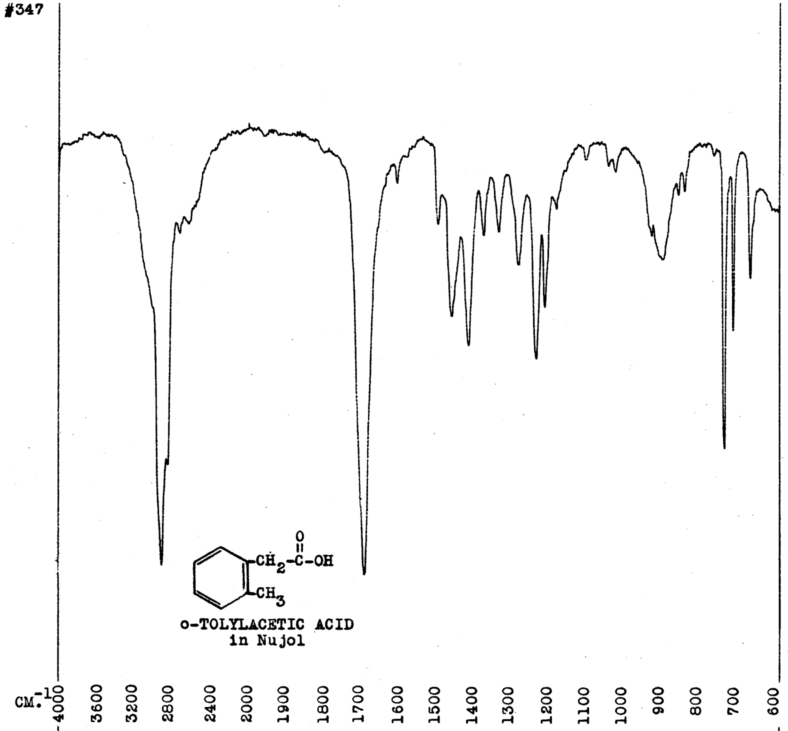
#346



2-o-TOLYLACETANILIDE
in Nujol

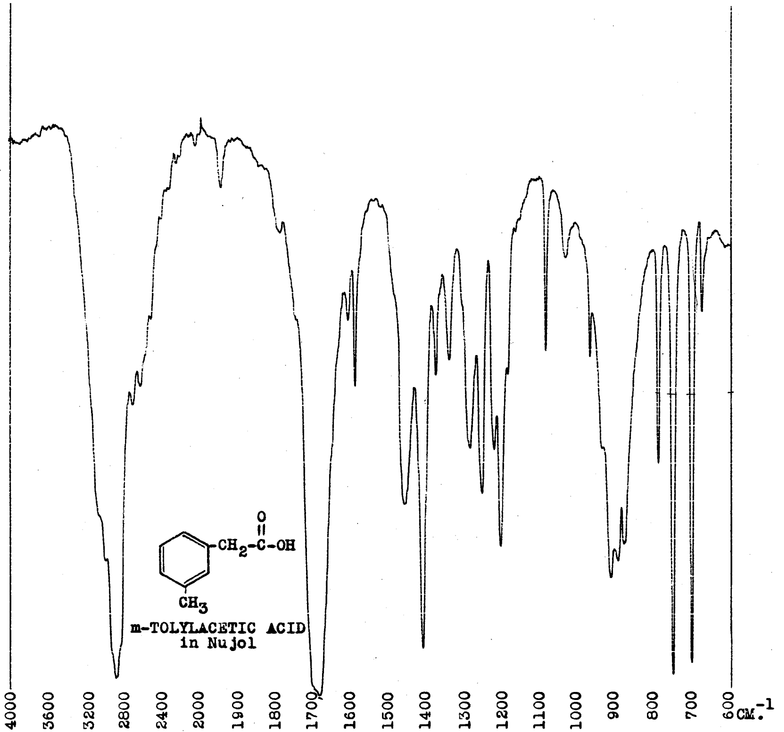
PLATE XI

#347



o-TOLYLACETIC ACID
in Nujol

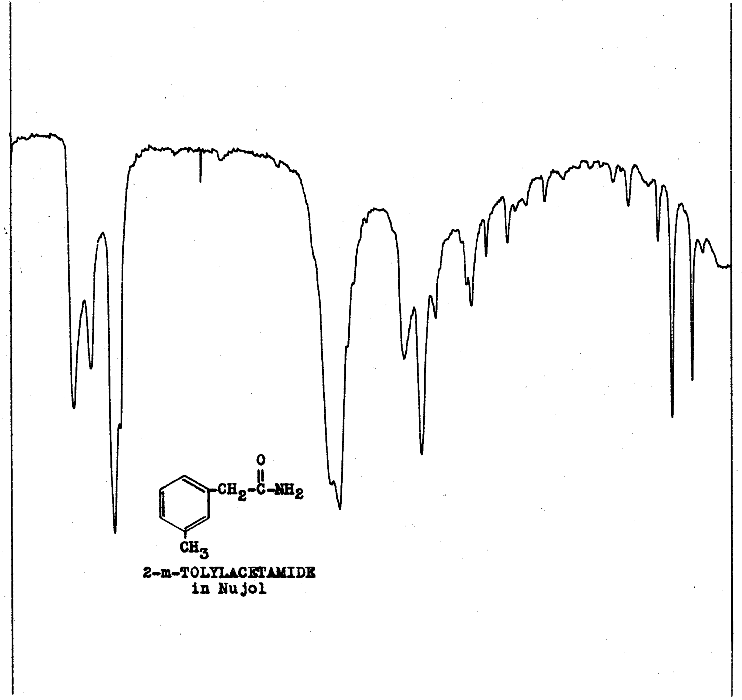
#340



m-TOLYLACETIC ACID
in Nujol

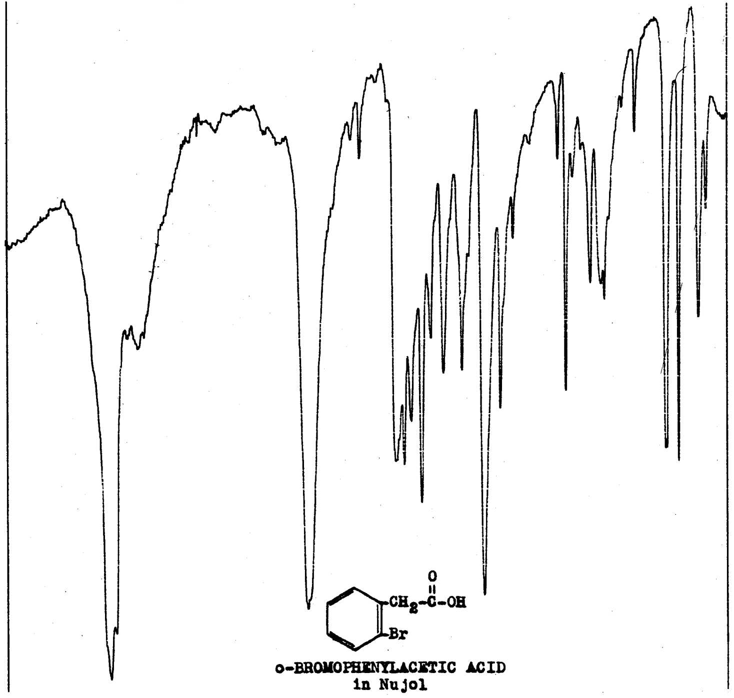
FREQUENCY

#342



2-m-TOLYLACETAMIDE
in Nujol

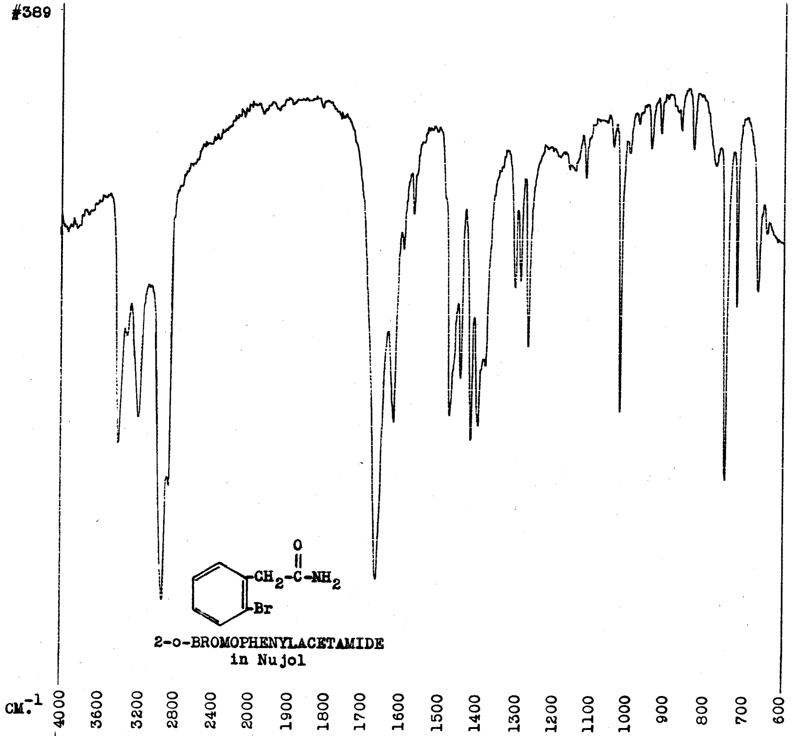
#388



o-BROMOPHENYLACETIC ACID
in Nujol

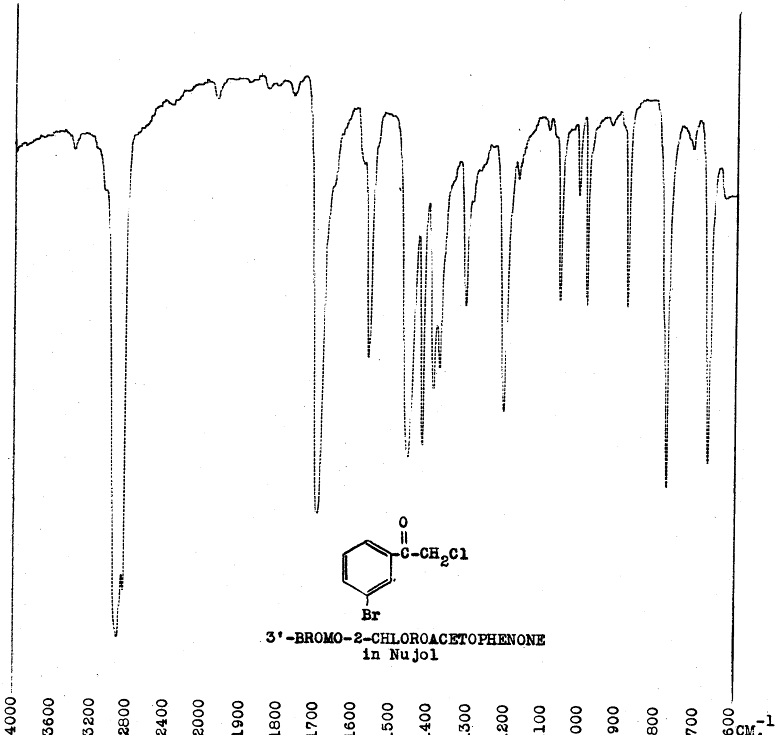
PLATE XII

#389



2-o-BROMOPHENYLACETAMIDE
in Nujol

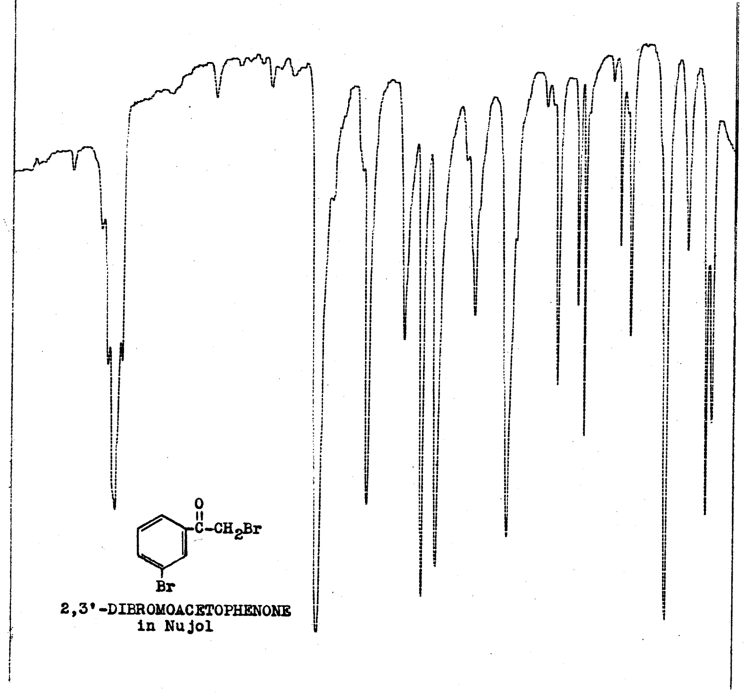
#236



3'-BROMO-2-CHLOROACETOPHENONE
in Nujol

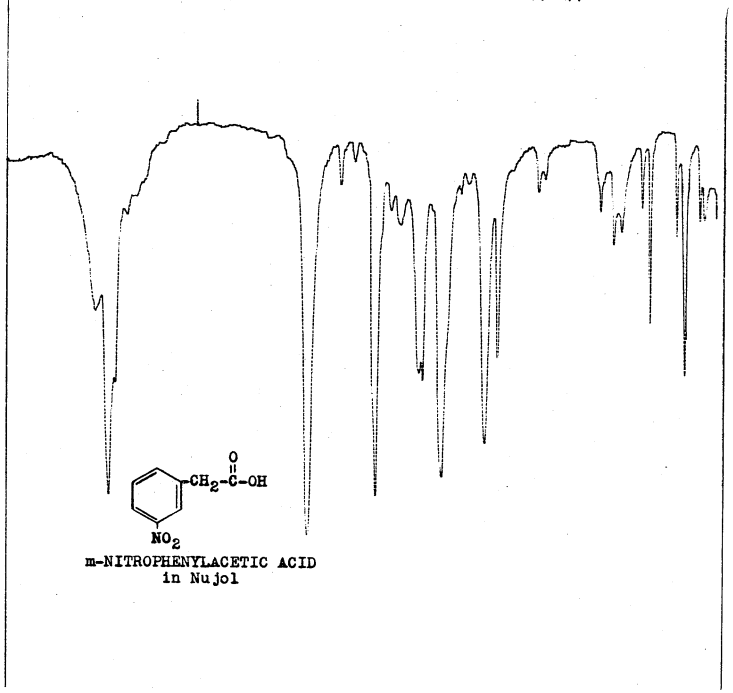
FREQUENCY

#242

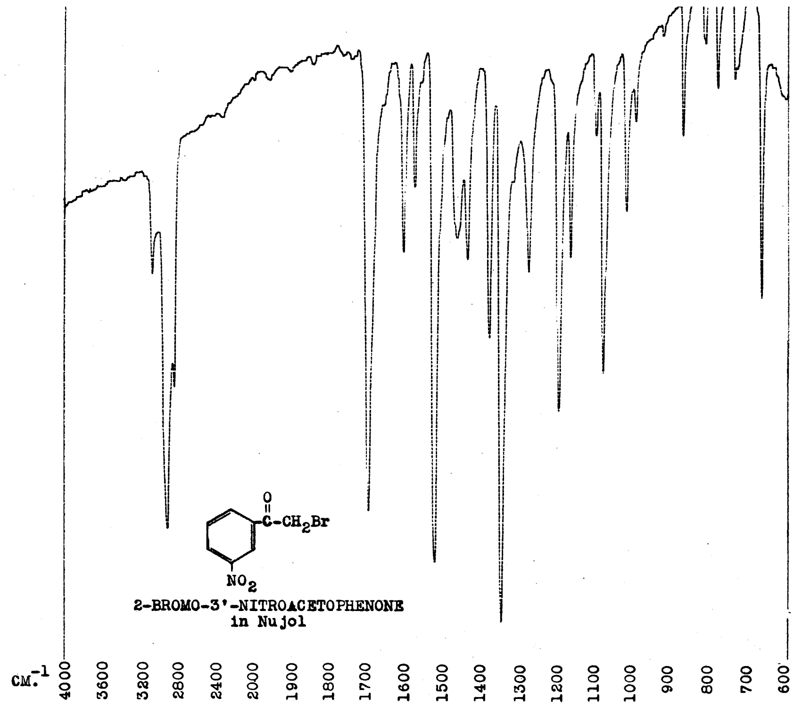


2,3'-DIBROMOACETOPHENONE
in Nujol

#232

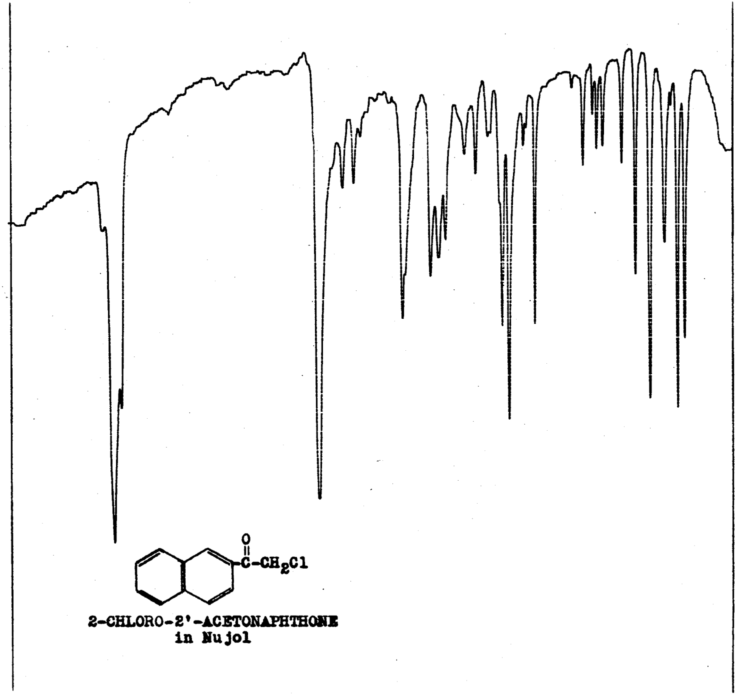


m-NITROPHENYLACETIC ACID
in Nujol

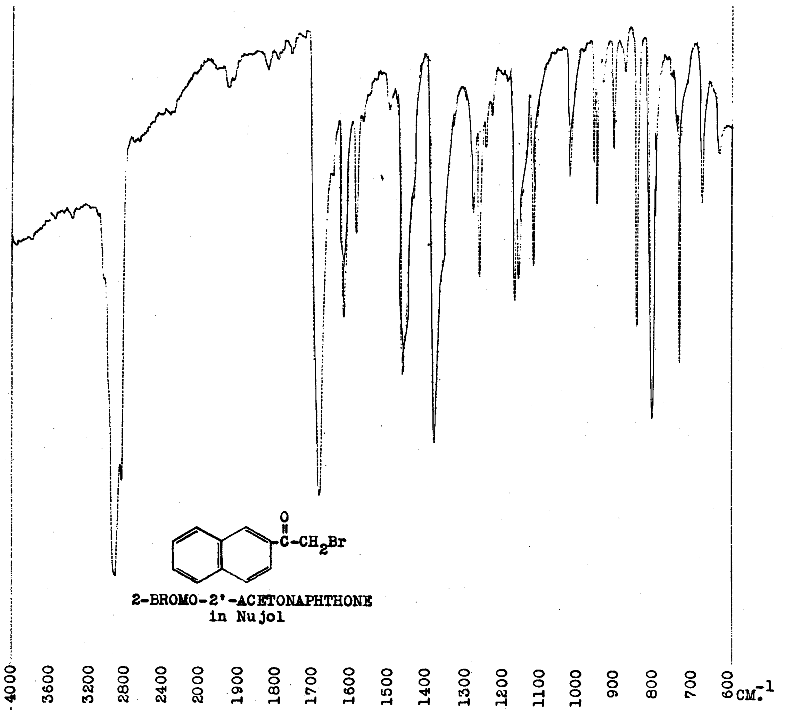


2-BROMO-3'-NITROACETOPHENONE in Nujol

#248

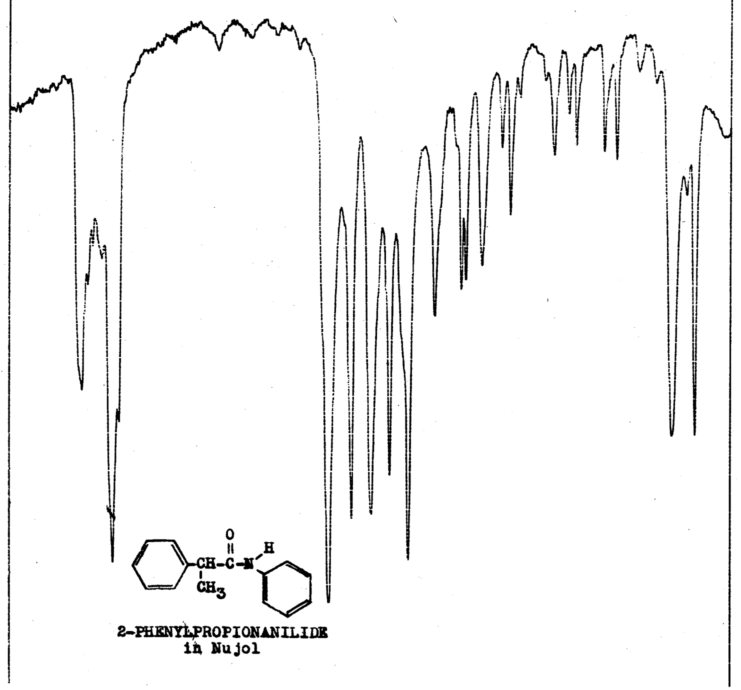


2-CHLORO-2'-ACETONAPHTHONE in Nujol



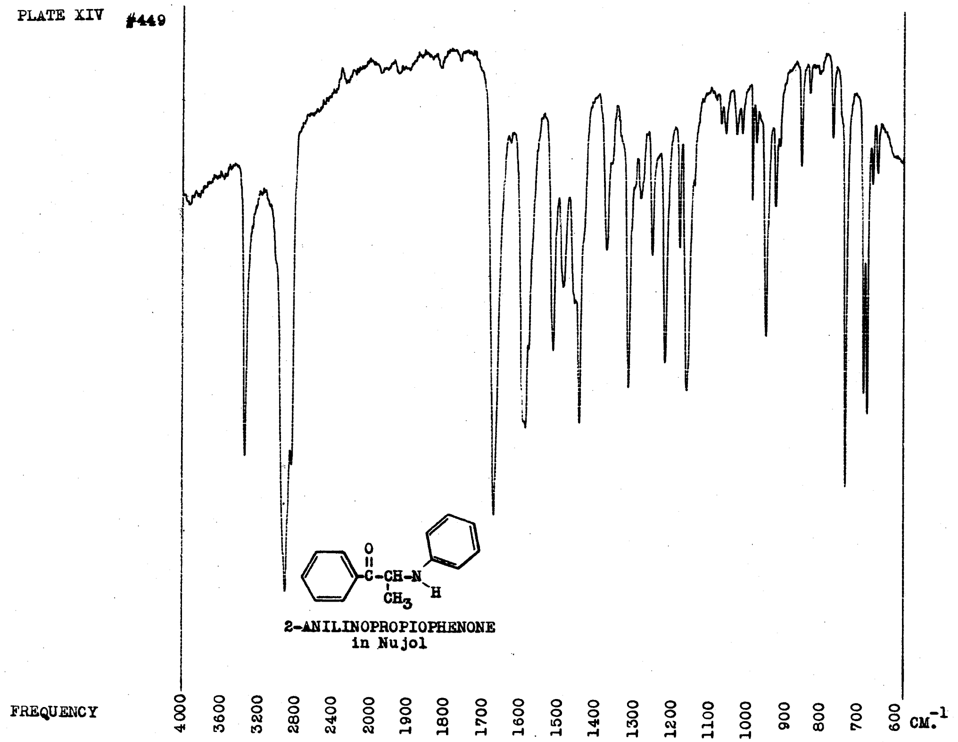
2-BROMO-2'-ACETONAPHTHONE in Nujol

#450



2-PHENYLPROPIONANILIDE in Nujol

PLATE XIV #449



# APPENDIX

## TABLE VII

## GROUP DIPOLE MOMENTS USED IN FIGURES 1, 3, AND 4

| GROUP | GROUP MOMENT IN DEBYES[a] | REFERENCES |
|---|---|---|
| $CH_3$ | +0.41 | 138,229,230 |
| $(CH_3)_3C$ | +0.47 | 230,231 |
| $C_2H_5O$ | +1.0 | 230,232 |
| Br | -1.53 | 138,229,230 |
| $CCl_3$ | -2.05 | 230,233 |
| $CF_3$ | -2.60 | 234 |
| $NO_2$ | -3.97 | 138,229,230 |

[a] "+" indicates that the group is electron-repelling, and "-" indicates that it is electron-attracting.

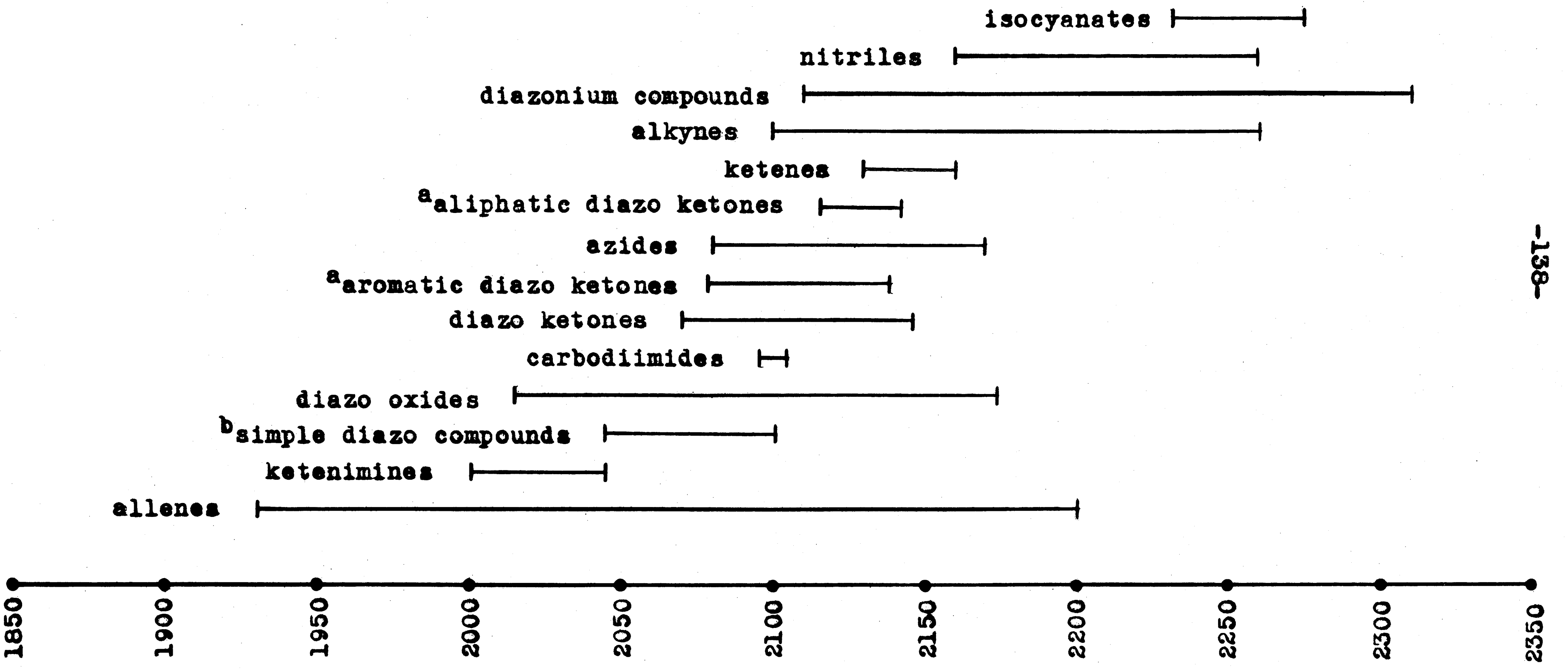
## TABLE VIII

## SIGMA CONSTANTS USED IN FIGURE 2

| GROUP | SIGMA VALUE | REFERENCES |
|---|---|---|
| m-$CH_3$ | -0.069 | 137,141 |
| p-$CH_3$ | -0.170 | 137,141 |
| H | 0.000 | 137,141 |
| p-Br | +0.232 | 137,141 |
| m-Br | +0.391 | 137,141 |
| m-$NO_2$ | +0.710 | 137,141 |
| p-$NO_2$ | +0.778 | 137,141 |
| o-$CH_3$ | -0.054 | 140 |
| o-$NO_2$ | +0.703 | 140 |

Figure 5

TYPICAL ABSORPTIONS IN THE "TRIPLE-BOND" REGION



[a] Values reported in this thesis.

[b] Includes values reported in this thesis.

# LIST OF REFERENCES

References to "Beilstein" refer to "Beilsteins Handbuch Der Organischen Chemie", Julius Springer, Berlin, 4th edition. The volume number is underscored once followed by the appropriate page numbers. Pages referred to in the main work immediately follow the volume number; page numbers in parentheses refer to the first supplement, and those in parentheses and underscored refer to the second supplement.

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