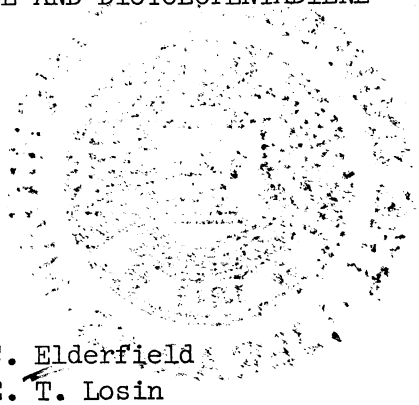
ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

Interim Report

INVESTIGATIONS OF POTENTIAL USES FOR CYCLOPENTADIENE AND DICYCLOPENTADIENE



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ABSTRACT

1. The Schmidt and Beckmann rearrangements of norcamphor and cyclopentanonorcamphor have been studied with the ultimate object of utilizing the products for the preparation of polyamides.

2. Isomeric pairs of lactams were obtained from each substance in the two reactions.

3. Preparation of polyamides was unsuccessful.

4. Dibasic acids have been prepared from norbornylene and dicyclopentadiene for evaluation as constituents of alkyd resins and for examination of representative esters as synthetic lubricants.

5. Preliminary studies have been made on the catalytic oxidation of derivatives of cyclopentadiene as a route to dibasic acids.

OBJECTIVE

The current investigation was undertaken to explore possible uses of dicyclopentadiene or cyclopentadiene as a source of chemicals.

INTRODUCTION

Appreciable tonnages of dicyclopentadiene are available from steam-cracking operations. Except for a few comparatively small outlets, there is at present no commercial use for this material. The current investigation was undertaken to explore possible uses of dicyclopentadiene or cyclopentadiene as a source of chemicals. Major emphasis has been placed on a study of the fundamental chemistry of various substances which can be prepared from cyclopentadiene or its dimer in the feeling that acquisition of such basic knowledge might point the way to realization of commercial exploitation of this unique substance.

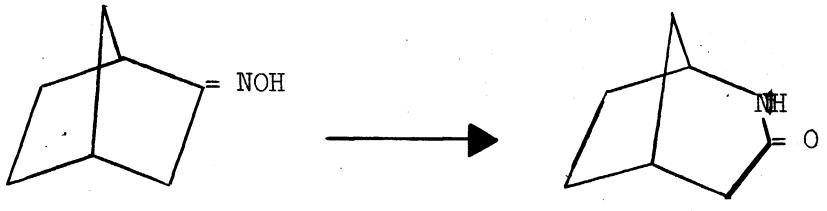
The work reported falls into several categories, as follows:

1. Investigation of the production of lactams which may be of importance in the formation of polyamides.
2. Investigation of dibasic acids which may be of importance in formulation of alkyd resins, synthetic lubricants, and polyesters.
3. Investigation of the catalytic oxidation of derivatives of cyclopentadiene as a source of dibasic acids.

I. LACTAMS FROM CYCLOPENTADIENE DERIVATIVES

INTRODUCTION

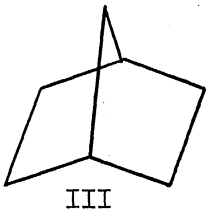
The formation of 2-azabicyclo[3.2.1]octan-3-one (I) by Beckmann rearrangement of the oxime of norcamphor (II) has been reported in a Swiss patent[1] and polyamides are reportedly formed from I when it is heated with hydrochloric acid.



II I

No structure proof for I was offered. It is assumed that the Swiss workers proposed the structure I on the assumption that the most heavily substituted carbon atom would migrate from carbon to nitrogen in the usual fashion.

The Schmidt reaction does not seem to have been applied to norcamphor (III - I).

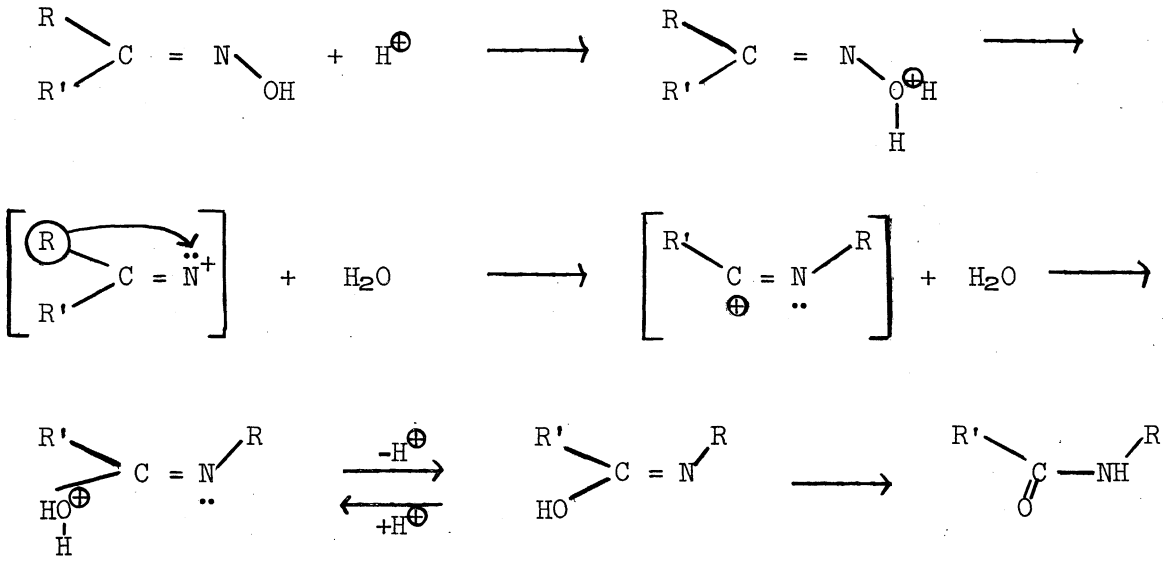


III

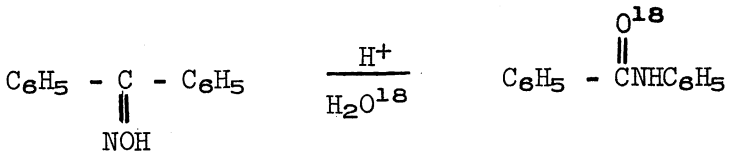
$$\xrightarrow[H_2SO_4]{NaN_3}$$ I

On the basis of currently held views on the mechanism of the Beckmann rearrangement and the Schmidt reaction, it would be expected that the same product (I) would result from either reaction. Further, material costs are quite appreciably lower when I is prepared by way of the Schmidt reaction than by the Beckmann route, and the operations involved are considerably simpler. Exploration of the application of the Schmidt reaction to norcamphor was therefore undertaken.

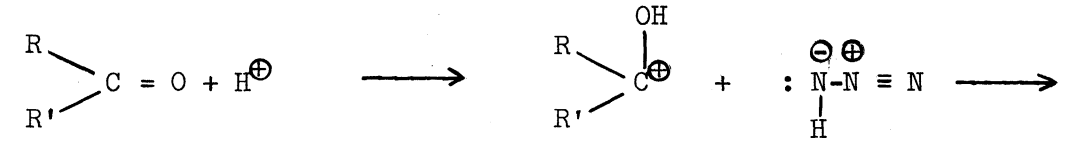
At this point it may be profitable to review briefly the present state of knowledge of the Beckmann rearrangement, particularly since the Schmidt reaction did not follow the anticipated course. As commonly written, the mechanism of the rearrangement may be expressed as follows:

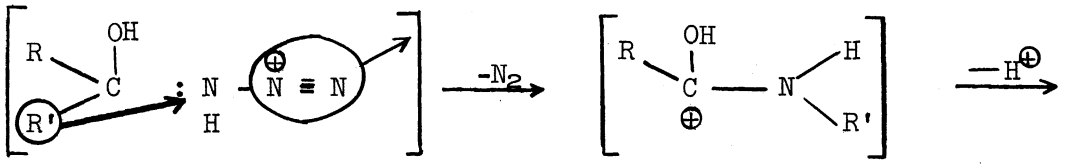


Such a scheme is consistent with retention of asymmetry by the migrating group R in cases in which R is asymmetric. Thus the R-N bond is forming before the R-C bond is completely broken, and the transformation may be considered as a typical intramolecular 1,2 shift. On the other hand, migration of the oxygen appears to involve an intermolecular transformation. Thus when benzophenone oxime is rearranged in H_2O^{18}, the isotopic oxygen appears in the resulting amide.[2]

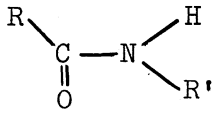


Newman and Gildenhorn[3] have suggested the following mechanism for the Schmidt reaction with ketones:

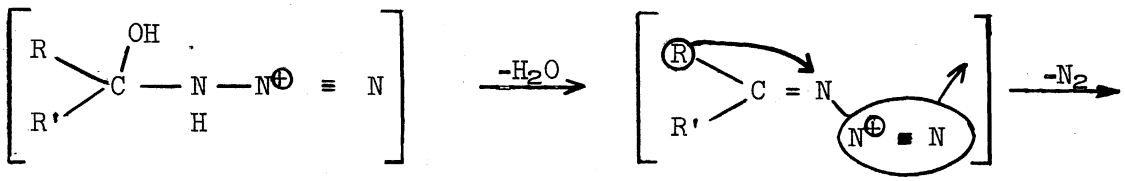




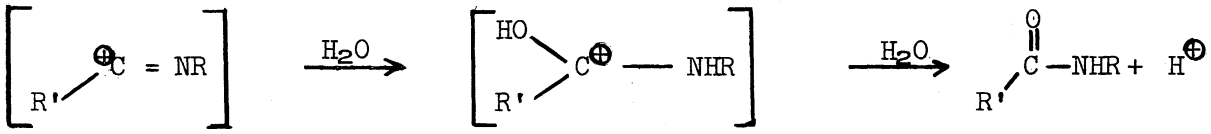
IV



Smith[4] has suggested a mechanism which departs from Newman's as far as the course of the reaction after formation of IV is concerned.



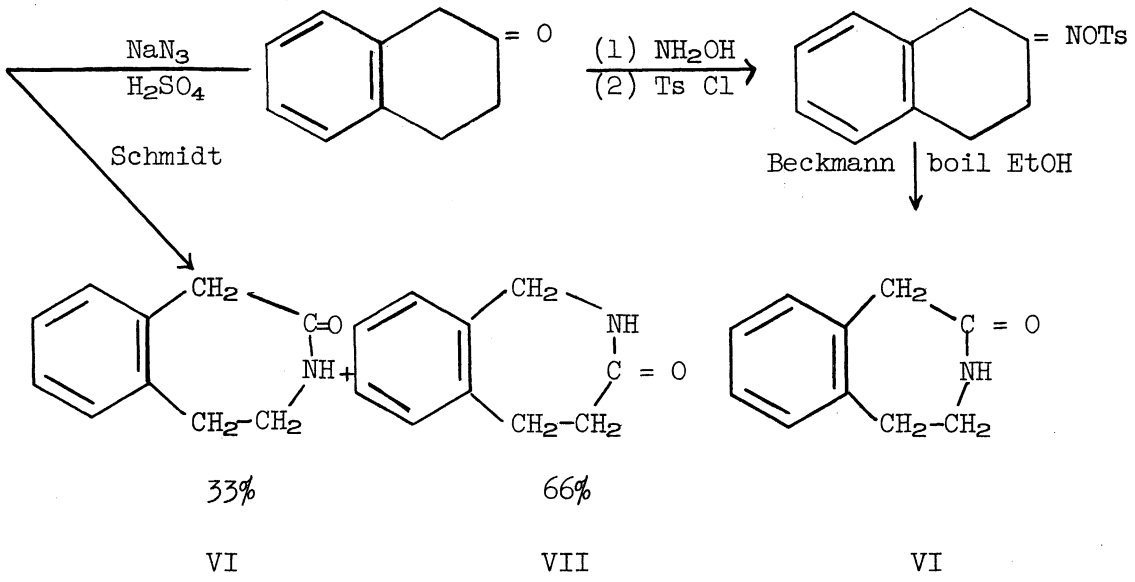
IV V



Thus the postulated intermediate, V, is expected to show the same <u>syn-anti</u> configurations as do the oximes in the Beckmann rearrangement and the Schmidt rearrangement is considered as involving a <u>trans</u> migration of R with simultaneous loss of nitrogen.

Although these considerations account fairly satisfactorily for the experimental observations with open-chain ketones, the situation becomes more complicated with cyclic and bicyclic ketones. β-Tetralone has recently been

investigated in both the Beckmann and Schmidt reactions[5] with the following results



33% 66%

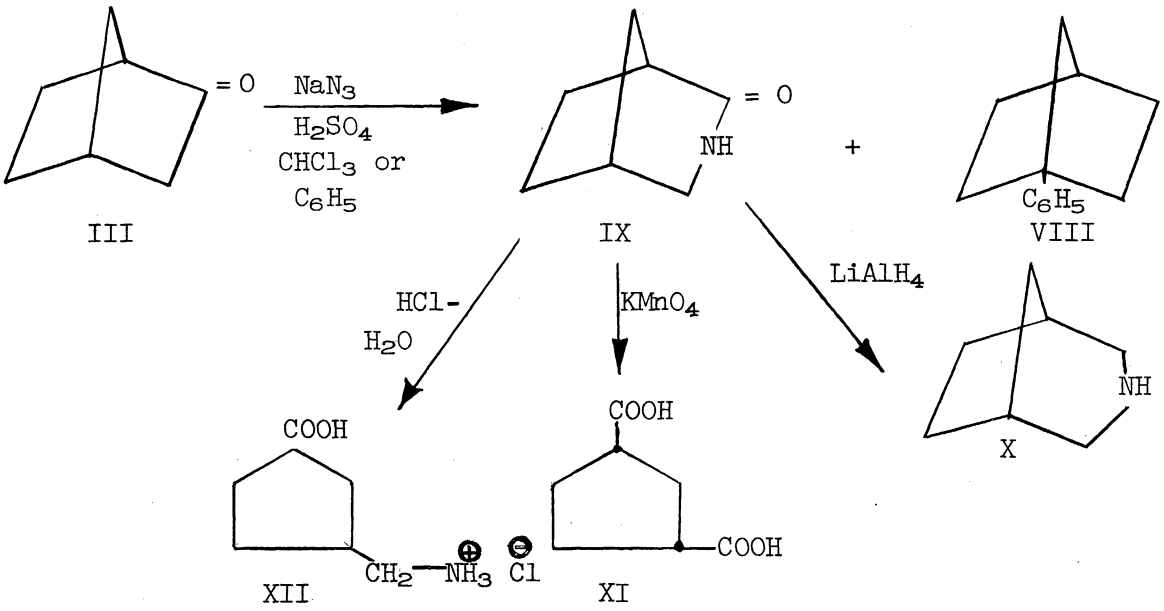
VI VII VI

A study of molecular models of the oxime indicates that, when the saturated ring is in the more favorable chain conformation, a cis arrangement of the OTs group relative to the C_6H_5-CH_2 - fragment is also favored. Thus the product of the Beckmann rearrangement (VI) is the product predicted on the basis of a trans migration.

On the basis of the Smith hypothesis considered above, the product of the Schmidt reaction with β-tetralone would be expected to be predominantly the same as the Beckmann product (VI). The experimental observations are not in harmony with this prediction since the major product of the Schmidt reaction is not VI, but rather VII. It thus appears that other factors, which are not important or are inoperative in acyclic systems, may be important in cyclic systems. As a corollary it follows that considerable caution must be exercised in arbitrarily assuming that both reactions will give the same products in such systems.

RESULTS

When norcamphor (III) is subjected to the conditions of the Schmidt reaction, the major product is not 2-azabicyclo[3.2.1]octan-3-one (I) as reported from the Beckmann rearrangement,[1] but rather 3-azabicyclo[3.2.1]octan-2-one (IX).



Evidence for the structure assigned to IX was provided by its oxidation by permanganate to cis-cyclopentane-1,3-dicarboxylic acid (XI).

Hydrolysis of IX with concentrated hydrochloric acid gave the amino acid hydrochloride (XII). All attempts at conversion of XII to polyamides have failed.

When the Schmidt reaction was carried out in benzene, appreciable amounts of a hydrocarbon were found among the reaction products. Infrared data indicated that it was a monosubstituted benzene. Oxidation with permanganate gave benzoic acid. On the basis of these observations, structure VIII or an isomer thereof is suggested for the hydrocarbon. Formation of alkylated benzenes is not uncommon under Schmidt reaction conditions in benzene solution. The hydrocarbon was not isolated when chloroform was the solvent.

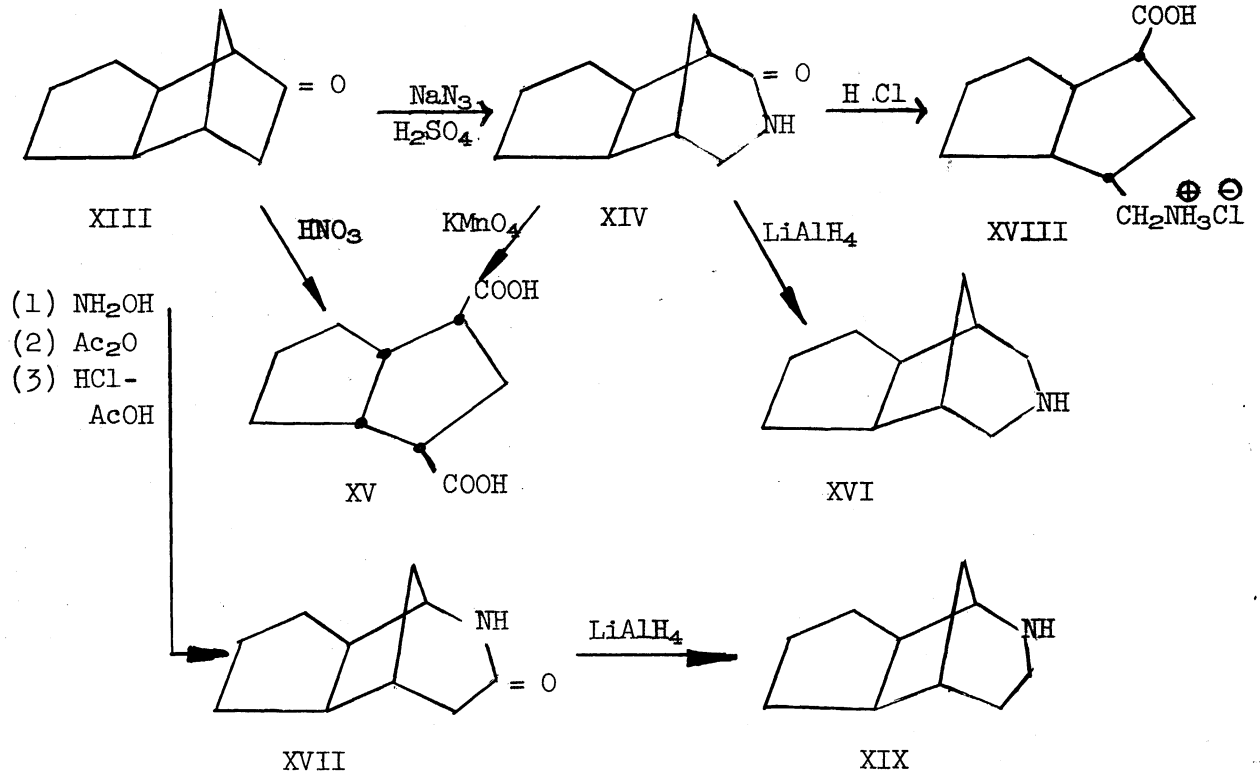
The behavior of norcamphor oxime on Beckmann rearrangement did not parallel that of norcamphor in the Schmidt reaction, nor did it agree with that reported in the patent literature.[1] After investigation of numerous procedures for accomplishing the rearrangement, the best one seemed to involve merely refluxing the p-toluenesulfonic acid ester of the oxime in ethanol. There was thus obtained a very small amount of the usual cleavage product, cyclopentene-3-acetonitrile, along with the major product, presumably the lactam, I. I and the Schmidt lactam, IX, were not identical as evidenced by divergent infrared spectra. Unfortunately all attempts to degrade oxidatively the Beckmann product to cyclopentanone-3-acetic acid have failed. Likewise attempts at conversion to polyamides have thus far been successful.

Hydrolysis of the Beckmann product to an amino acid has been unsuccessful. Analytical data suggest that one oxygen has been lost during treatment with concentrated hydrochloric acid.

Reduction of IX with lithium aluminum hydride gave 3-azabicyclo[3.2.1] octane (X). It was not possible to isolate a pure amine from the product of the similar reduction of the Beckmann rearrangement product (I).

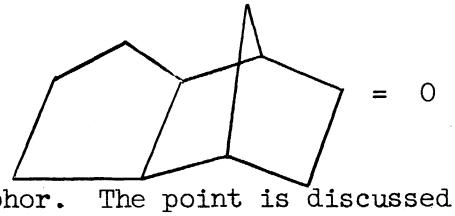
Inasmuch as cyclopentanonorcamphor (XIII)* was available from concurrent work with dicyclopentadiene, the Beckmann and Schmidt reactions were investigated with this substance.

From the products of the Schmidt reaction as applied to XIII a product, presumably the lactam (XIV) by analogy to the formation of IX from norcamphor, was obtained.**



*The shorter name "cyclopentanonorcamphor" rather than the awkward systematic name, 2,5-methanobicyclo[4.3.0]nonan-3-one, will be used to denote XIII in this report.

**The structure assigned to XIV is based on the structure



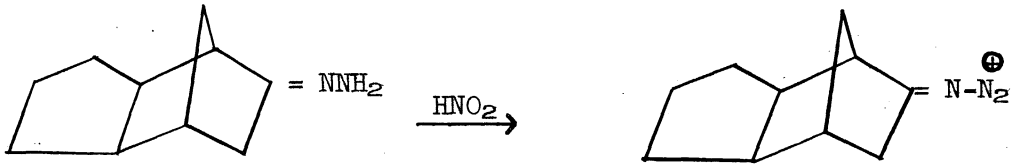
for cyclopentanonorcamphor. The point is discussed more fully in the section dealing with dibasic acids.

XIV on oxidation with alkaline permanganate gives the same dicarboxylic acid (XV) which is obtained by oxidation of XIII with nitric acid as judged by identical infrared spectra, melting points, and mixed melting points. Reduction of XIV with lithium aluminum hydride gave the amine (XVI).

When the acetate of cyclopentanonorcamphor oxime was refluxed in a mixture of hydrochloric and acetic acids, the expected Beckmann rearrangement occurred. Again, as in the case of norcamphor, the lactam isolated was different from the lactam (XIV) formed in the Schmidt reaction. It is formulated as XVII by analogy with the products obtained from norcamphor by the two routes.

The two lactams differed in their behavior on acid hydrolysis. XVI on treatment with boiling hydrochloric acid readily gave the hydrochloride of 1-aminomethylbicyclo[3.3.0]octan-3-carboxylic acid (XVIII). In contrast, acid hydrolysis of XVII gave a product the properties of which were not consistent with those of an amino acid. Reduction of XVII with lithium aluminum hydride gave an amine isomeric with XVI, which presumably is XIX.

If the course of the Schmidt reaction indeed involves an intermediate, V, then preparation of a substance of the type of V and a study of its decomposition could conceivably throw some light on the factors which are operative in the Schmidt and Beckmann reactions. Specifically, rearrangement of the diazonium compound, XXI, derived from cyclopentanonorcamphor would be expected



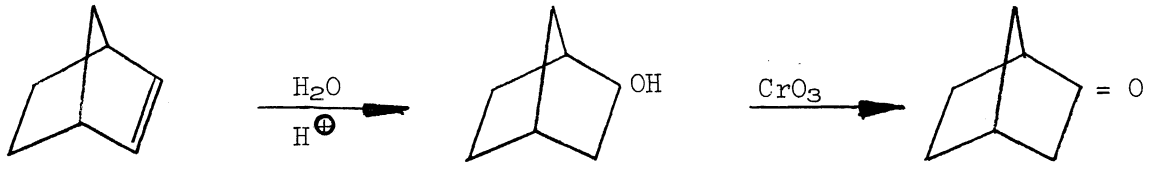
XX XXI

to follow a course similar to that of the Beckmann rearrangement of the oxime of cyclopentanonorcamphor since both the oxime and XXI presumably would have the same syn-anti steric relationship.

Attempts to prepare the hydrazone (XX) of cyclopentanonorcamphor have resulted in the formation of either the bishydrazone, the acetate of the monohydrazone, or a substance which appeared to be crude monohydrazone (XX). However, on attempted recrystallization of the crude XX it was converted to the bishydrazone. Reaction of either crude XX or its acetate with sodium nitrite in concentrated sulfuric acid gave an oil in very poor yield. Attempts to purify this oil were unsuccessful.

These observations parallel the difficulties encountered in the preparation and rearrangement of the hydrazones of open-chain aliphatic ketones.[6]

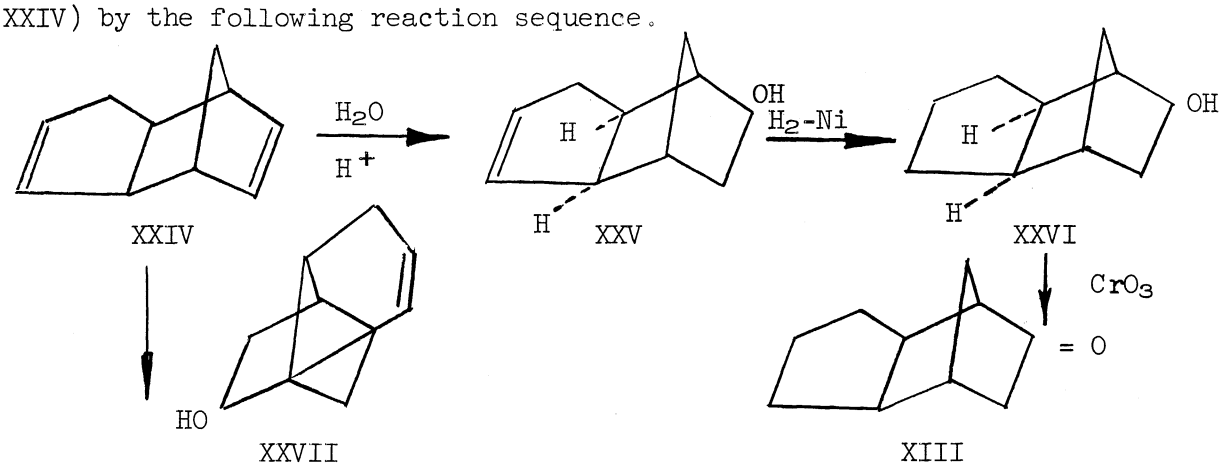
The norcamphor (III) required for these studies was prepared by oxidation of norborneol (XXIII) which was, in turn, prepared by hydration of norbornylene (XXII).



XXII XXIII III

Considerable improvements in the preparation of XXIII over those previously described have been accomplished. Details are given in the experimental section.

Cyclopentanonorcamphor (XIII) was prepared from dicyclopentadiene (XXIV) by the following reaction sequence.



XXIV XXV XXVI XXVII XIII

Hydration of dicyclopentadiene was accomplished essentially according to Bruson and Reiner.[7] However, for reasons which are discussed in detail later, we believe that the unsaturated alcohol resulting from this hydration is best represented by structure XXV rather than by XXVII as suggested by Bruson and Reiner. XXV may be accounted for on the basis of the usual Wagner-Meerwein shifts encountered in such systems, whereas the formation of XXVII requires extensive rearrangement of the carbon skeleton of XXIV.

Reduction of the double bond of XXV proceeded smoothly, as did oxidation of XXVI to cyclopentanonorcamphor.

EXPERIMENTAL

Norborneol by Hydration of Norbornylene

The procedure described by Bruson[8] for hydration of norbornylene using 40 weight percent sulfuric acid at 95-100° for 5 hours gives poor yields of norborneol and relatively large amounts of dinorbornyl ether. Accordingly a new procedure based on that of Walborsky and Loncsini[9] has been developed which gives satisfactory yields of norborneol.

A mixture of 50 g of norbornylene, 850 g of concentrated sulfuric acid, and 150 ml of water was stirred in an ice bath until homogeneous (about 1.5-2.5 hours). The mixture was diluted with 1.8 liters of water and extracted with ether. After washing the extract with water and drying over anhydrous sodium sulfate, removal of the solvent left a partially crystalline product. Recrystallization from 30-60° petroleum ether gave 30-35 g of norborneol, mp, 128-129° (reported mp, 125-126°,[9] 126-127°[10]). The phenylurethan melted at 149-150° (reported mp, 145-146°[10]).

Hydration of norbornylene was attempted using steam over Dowex 50-X8 cationic exchange resin (a polystyrene-type sulfonic acid). No significant yield of norborneol was obtained. A typical run is described.

Norbornylene (10 g) was introduced with excess steam preheated to approximately 200° into the bottom of a vertical 750- x 30-mm Vigreux-type column packed with Dowex resin heated to 110°. The top of the column was fitted with a downward condenser which was in turn connected to a flask carrying two efficient upright condensers. During the run the temperature of the top section was 115-133° and that of the center section was 105-115°. The condensate was extracted with ether and the extract was dried over anhydrous sodium carbonate. Removal of the solvent left a residue, mp, 44-46°, which was mainly norbornylene (reported mp, 44-46°,[11] 52-54°,[12] 50-52°[13]).

Norcamphor

A solution of 36 g of chromic oxide in 150 ml of glacial acetic acid and 50 ml of water was added dropwise with stirring to a solution of 33.6 g (0.3 mole) of norborneol in 150 ml of glacial acetic acid. After the addition was complete, the mixture was allowed to stand at room temperature for 30 minutes. It was partially neutralized with dilute sodium hydroxide solution and then extracted with ether. The ether extract was washed successively with water, dilute sodium hydroxide solution, and water, and dried over anhydrous sodium sulfate. Removal of the solvent left 24-26 g (80%) of norcamphor, mp, 96°.

Norcamphor Oxime

This was prepared according to Alder and Stein.[14] A solution of 5 g of norcamphor in 10 ml of methanol was added to a solution of 5 g of sodium acetate and 5 g of hydroxylamine hydrochloride in 5 ml of water. After standing for 16 hours at room temperature, the mixture was diluted with water and extracted with ether. After drying over anhydrous sodium sulfate, removal of the ether left the oxime as an oil which was distilled through a 6-cm Vigreux column to give 4.5 g of norcamphor oxime, bp, 72-74° (0.4 mm) [reported bp, 114-116° (12 mm)].[14]

Schmidt Reaction with Norcamphor

Procedure A.—A mixture of 55 g (0.5 mole) of norcamphor, 250 ml of

anhydrous benzene, and 250 ml of concentrated sulfuric acid was placed in a 1-liter 3-necked flask equipped with a stirrer and reflux condenser and chilled in an ice bath. To this were added 33 g of sodium azide in small portions with stirring at such a rate that the temperature was maintained at 15°. After addition of the sodium azide was complete, the reaction mixture was stirred for an additional 12 hours during which the ice bath was allowed to come to room temperature. The mixture was again cooled, diluted with water, and made alkaline with 25% sodium hydroxide solution. After extraction with several portions of chloroform, the combined chloroform extracts were washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled under reduced pressure to yield 9.5 g of liquid material, bp, 72-73° (20 mm), n_D^{29} 1.4671, and 6.5 g of crude lactam (IX). The crude lactam (3-azabicyclo[3.2.1]octan-2-one) was recrystallized from 30-60° petroleum ether and gave a crystalline product, mp, 93-94°.

Anal.: Calcd. for $C_7H_{11}NO$: C, 67.16; H, 8.86; N, 11.18.
Found: C, 67.23, 67.09; H, 8.91, 8.89; N, 11.07, 10.99.

The liquid fractions, bp, 72-75° (20 mm), from two such runs were combined and redistilled three times, yielding a water white liquid, bp, 70.5-71.5° (0.65 mm).

Anal.: Calcd. for $C_{13}H_{16}$: C, 90.63; H, 9.36.
Found: C, 90.39; H,9.60.

The infrared spectrum of this material shows it to be a mono-substituted benzene derivative. It resists oxidation by permanganate under mild conditions but is oxidized by hot alkaline permanganate to benzoic acid. A mixture of 1 g of the hydrocarbon, 4.0 g of potassium permanganate, 30 ml of water, and 6 drops of 25% sodium hydroxide solution was heated on the steam bath for 12 hours. After cooling and filtering, the solution was extracted with ether. After acidification with hydrochloric acid, the aqueous solution was again extracted with ether. Removal of the ether and recrystallization of the residue from water gave 0.25 g of benzoic acid identified by mixed melting points and infrared spectra.

Procedure B.—To a solution of 4.90 g (0.04 mole) of norcamphor in 10 ml of cold concentrated sulfuric acid and 20 ml of chloroform, 2.6 g (0.04 mole) of sodium azide was added in small portions with stirring, during which the temperature of the mixture was held at -10° by an ice bath. After addition of the azide, the mixture was allowed to come to room temperature and made alkaline with cooling with 25% sodium hydroxide solution. The basic solution was extracted three times with chloroform. After drying, removal of the solvent left an oil which was sublimed at 90° and 18 mm, giving 1.0 g of Δ^3-cyclopenteneacetonitrile and 1.5 g (30%) of crystalline material, mp, 72-79°. Resublimation of this at 100° and 18 mm followed by recrystallization from 30-60° petroleum ether gave the lactam, mp, 93-94°.

Procedure C.—To a stirred mixture of 15.5 g (0.14 mole) of norcamphor in 150 ml of concentrated sulfuric acid held at 7-12° with an ice bath, 9.8 g (0.15 mole) of sodium azide was added in small portions. After stirring overnight at room temperature, the mixture was poured onto crushed ice and made alkaline with 25% sodium hydroxide solution. Extraction with chloroform and removal of the solvent from the extract gave an oil from which 3.3 g (20%) of crude lactam, mp, 75-79°, was obtained after sublimation at 100° and 18 mm.

Oxidation of 3-Azabicyclo[3.2.1]octan-2-one

A mixture of 300 mg of the lactam and 20 ml of 0.1 N potassium permanganate solution was allowed to stand at room temperature for 20 hours. After removal of the manganese dioxide by filtration, extraction of the filtrate with ether gave 20 mg of unreacted lactam, mp, 88-89°. The aqueous layer was acidified with hydrochloric acid and concentrated to dryness under reduced pressure. The residue was extracted with chloroform. Removal of the chloroform from the extract left 150 mg of material, mp, 117-117.5°, after recrystallization from benzene. This was identified as cis-1,3-cyclopentanedicarboxylic acid on the basis of mixed melting points and comparison of the infrared spectrum with that of a known sample.

Hydrolysis of 3-Azabicyclo[3.2.1]octan-2-one

A mixture of 0.8 g of 3-azabicyclo[3.2.1]octan-2-one and 25 ml of concentrated hydrochloric acid was refluxed for 12 hours. After removal of the solvent in vacuo, the crystalline residue was dried in vacuo at 60° for 8 hours. The crude hydrochloride of 3-aminomethylcyclopentanecarboxylic acid (XII) melted at 119-121°. Recrystallization from ethanol-ether gave material, mp, 122.5-123.5°. The infrared spectrum of this amino acid hydrochloride shows disappearance of the bands at 3250, 1650, and 1625 cm^{-1} which are present in the spectrum of the original lactam. Weak absorption bands at 3200, 2600, 2000, and 1601 cm^{-1} are present. These are characteristic of most amino acid hydrochlorides.

Anal.: Calcd. for $C_7H_{14}ClNO_2$: C, 46.81; H, 7.86; N, 7.80.
Found: C, 46.55; H, 7.57; N, 7.67.

Beckmann Rearrangement of Norcamphor Oxime

To a solution of 16.0 g (0.128 mole) of norcamphor oxime in 400 ml of glacial acetic acid contained in a 1-liter round bottom flask equipped with a reflux condenser was added 26.2 g (0.256 mole) of acetic anhydride. After standing at room temperature and 12 hours, the mixture was saturated with anhydrous hydrogen chloride and heated slowly in an oil bath until gentle refluxing ensued. After refluxing for 6 hours, the mixture was resaturated with hy-

drogen chloride and refluxed for an additional 11 hours. After cooling, the mixture was poured into a dilute sodium hydroxide—ice mixture and partially neutralized with 25% sodium hydroxide solution. It was then extracted with four portions of chloroform. The combined chloroform extracts were washed successively with 5% sodium hydroxide solution and water and dried over anhydrous sodium sulfate. Removal of the solvent left a residue which was distilled through a 12-cm Vigreux column at 12-14 mm, yielding the following fractions:

Fraction	bp, °C	n_D^{23}	Weight, g
I	60-61	---	0.3
II	61-61.5	1.4619	3.0
III	62-66	---	1.0
IV	66-119.5	---	1.1
V	119.5-127	1.4794	1.75
VI	residue		

The infrared spectrum of Fraction II indicated that it was an unsaturated nitrile, presumably 3-cyclopenteneacetonitrile, with absorption bands at 3040 cm^{-1} (vinyl C-H stretching), 2240 cm^{-1} (C ≡ N stretching), 1610 cm^{-1}, presumably a carbonyl group.

Fractions I, II, and III were combined and redistilled through a 6-cm Vigreux column to yield Fraction VII, bp, 62.5-63.5° (12 mm), n_D^{24} 1.4610 (2.7 g). The infrared spectrum of Fraction VII showed the same type of absorption as Fraction II except that the carbonyl band was shifted to 1720 cm^{-1}.

Anal. (Fraction VII): Calcd. for C_7H_9N: C, 78.43; H, 8.46; N, 13.07.
Found: C, 79.92; H, 8.80; N, 11.25.

Reduction of Fraction VII with hydrogen over palladium on carbon in absolute ethanol at room temperature resulted in the uptake of 0.98 equivalents of hydrogen. The reduction product (cyclopentaneacetonitrile) was distilled, bp, 185-186°, n_D^{26} 1.4474. In the infrared it showed disappearance of the bands at 3040 cm^{-1} and 1610 cm^{-1}, but retained the typical nitrile absorption at 2240 cm^{-1} as well as the band at 1730-1740 cm^{-1}. Analysis indicated that the nitrile was contaminated by a small amount of norcamphor which had carried through.

Anal.: Calcd. for $C_7H_{11}N$: C, 77.00; H, 10.16; N, 12.83.
Found: C, 76.46, 76.44; H, 9.81, 9.82; N, 11.69, 11.61.

Fraction VI was distilled through a 6-cm Vigreau column at 0.45 mm, and gave the following fractions.

Fraction	bp, °C	$n_D^{23.5}$	Weight, g
VI-a	82.0-85.5	1.4787	0.51
VI-b	85.5-88.5	1.4740	0.97
VI-c	88.5-89.0	1.4677	2.62
VI-d	89.0-89.5	1.4673	0.3
VI-e	residue		

The infrared spectrum of Fraction VI-d indicated that it was a mixture showing N-H or O-H absorption between 3200 and 3400 cm^{-1}, nitrile absorption at 2240 cm^{-1}, and two bands in the double bond region at 1725 and 1660 cm^{-1}.

The residue (VI-e) was transferred to a semimicro molecular still and evaporatively distilled at 74° and 0.4 mm. The temperature was gradually raised and the following fractions were collected.

Fraction	Bath Temp., °C	n_D^{25}	Weight, g
VI-e-1	74	1.4937	--
VI-e-2	100-102	1.5020	0.40
VI-e-3	102-104	1.5025	0.35

The infrared spectrum of Fraction VI-e-3, taken as a thick film, showed no absorption in the triple bond stretching region, but showed two bands in the double bond stretching region at 1670 (strong) and 1730 (weak) cm^{-1} and an N-H stretching absorption at 3300-3200 cm^{-1}. This spectrum differs markedly from that of the lactam obtained by the Schmidt reaction on norcamphor.

Beckmann Rearrangement of Norcamphor Oxime Tosylate

The tosylate of norcamphor oxime was prepared by a modification of the procedures of Knunyants and Fabrichnyi[15] and Vargha and Gönczy.[16]

To a solution of 2.77 g (0.022 mole) of norcamphor oxime in 40 ml of dry pyridine at 0°, 4.23 g (0.0223 mole) of p-toluenesulfonyl chloride were added. The mixture was kept at 0° in an ice bath with frequent shaking for 4 hours. It was then allowed to warm up to room temperature overnight. After pouring the mixture into ice and water, concentration under reduced pressure at 30° left a partially crystalline hygroscopic material which was insoluble in 30-60° petroleum ether and soluble in ethanol. The dried residue was refluxed in 150 ml of absolute ethanol for 2.5 hours. Concentration under reduced pressure gave a tan crystalline residue which was taken up in 50 ml of 10% sodium hydroxide solution. Extraction of the alkaline solution with chloroform and removal of the solvent from the dried extract left a residue which was

evaporatively distilled in a molecular still at 0.5 mm and 85-90° bath temperature. After a few drops of forerun, material which solidified on the cold finger of the still was obtained. This was boiled with a mixture of 30-60° petroleum ether and ether. After decanting the supernatant liquid, refrigeration of the residue gave crystalline material which melted at room temperature. The yield was 1.0 g (35%) on the assumption that the substance was the expected lactam.

Anal.: Calcd. for $C_7H_{10}NO$: N, 11.18.
Found: N, 11.15.

The infrared spectrum of this material shows N-H absorption at 3220 cm^{-1} and carbonyl absorption at 1660 cm^{-1} consistent with a lactam structure. However, the spectrum is not identical with that of the lactam produced by the Schmidt reaction.

3-Azabicyclo[3.2.1]octane (X)

A solution of 0.5 g (0.004 mole) of 3-azabicyclo[3.2.1]octan-2-one (IX) in 70 ml of absolute ether was added dropwise to a stirred suspension of 0.2 g (0.002 mole) of lithium aluminum hydride in 50 ml of absolute ether. After addition of the lactam, the mixture was refluxed gently for 6 hours and then allowed to stand at room temperature for 12 hours. Water was carefully added to destroy the excess hydride until a clear ether layer resulted. Concentration of the ether layer gave the crystalline amine, mp, 137-138.5°. The infrared spectrum, taken as a Nujol mull, showed disappearance of the monosubstituted amide (lactam) absorption at 1625 and 1650 and 1490 cm^{-1}.

For characterization of the amine, the hydrochloride was prepared by saturating an ethereal solution of the amine with anhydrous hydrogen chloride. After recrystallization from absolute ethanol-ether, the amine hydrochloride darkened above 240° and decomposed above 300°.

Anal.: Calcd. for $C_7H_{14}NCl$: C, 56.93; H, 9.56; N, 9.49.
Found: C, 57.41; H, 9.91; N, 9.28.

2-Azabicyclo[3.2.1]octane

2-Azabicyclo[3.2.1]octan-3-one (XVII) was reduced with lithium aluminum hydride as in the above case. Evaporation of the ether layer left an oil which could not be crystallized. The amine hydrochloride was precipitated as above and purification was accomplished, not too satisfactorily, from absolute ethanol-ether, yielding a substance which softened at 220° and decomposed at 244°.

Anal.: Calcd. for $C_7H_{14}NCl$: C, 56.93; H, 9.56; N, 9.49.
Found: C, 58.48; H, 10.33; N, 9.93.

The infrared spectrum of this amine hydrochloride was not identical with that of the amine hydrochloride obtained by reduction of the lactam (3-azabicyclo[3.2.1]octan-2-one) obtained by the Schmidt reaction.

Schmidt Reaction with Cyclopentanonorcamphor. 2,6-Methano-4-Azabicyclo[5.3.0] decan-3-one (XIV)

This was done according to a general procedure described by Wolff.[17] To a stirred mixture of 30.0 g (0.2 mole) of cyclopentanonorcamphor, 200 ml of reagent grade chloroform, and 70 ml of concentrated sulfuric acid contained in a 1-liter flask equipped with a reflux condenser and stirrer, 13 g (0.2 mole) of sodium azide were added in small portions during which the temperature was held at 0-5° by means of an ice bath. After addition of the azide was complete, the mixture was stirred for an additional 4 hours and then allowed to come to room temperature as the ice bath melted. The cooled mixture was poured on to ice, made alkaline with 25% sodium hydroxide solution, and extracted with three portions of chloroform. The combined chloroform extracts were washed twice with water and dried over anhydrous sodium sulfate. Removal of the solvent left a residue which was evaporatively distilled at 16-18 mm, yielding the following fractions.

Fraction	Bath Temp., °C	Weight, g
I (liquid)	70-100	15.8
II (liquid)	100-125	2.5
III (solid)	100-125	0.2
IV (solid)	125 +	2.1

Two recrystallizations of Fraction IV gave white crystals, mp, 104.5-105.5°.

Anal.: Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48.
Found: C, 72.63, 72.49; H, 8.96, 9.09; N, 8.58, 8.54.

The infrared spectrum taken as a Nujol mull showed absorption bands at 3070-3200 cm^{-1} (N-H stretching) and 1665 cm^{-1} (amide carbonyl stretching).

The liquid fraction I was redistilled through a 6-cm Vigreux column and the following fractions were collected.

Fraction	bp, °C/12-14 mm	n_D^{22}	Weight, g
I-A	101.5-102.5	1.5018	8.7
I-B	102.5-103.5	1.5015	
I-C	103.5-106.5	1.5016	6.0
I-D	106.5 +	1.5013	0.4

Fraction I-C was recovered cyclopentanonorcamphor as shown by boiling point, refractive index, and infrared spectrum. Fractions I-A and I-B also were largely recovered ketone.

Oxidative Degradation of 2,6-Methano-4-azabicyclo[5.3.0]decan-3-one

A mixture of 0.5 g of the above lactam, 2.0 g of potassium permanganate, 0.5 ml of 25% sodium hydroxide solution, and 40 ml of water was refluxed for 2 hours. The cooled reaction mixture was filtered from manganese dioxide by gravity and the filtrate was extracted with ether. The aqueous solution was acidified with hydrochloric acid and extracted with ether. Concentration of the ether extract of acidic material gave 0.2 g of crystalline material, mp, 150-152°. Recrystallization from toluene raised the mp to 175-176°. Mixture mp's with an authentic sample of bicyclo[3.3.0]octan-2,4-dicarboxylic acid, mp, 178-179°, were 177-178°. The infrared spectra of the degradation product and the authentic sample of the di-acid were identical except for a weak absorption at 3425 cm^{-1} displayed by the degradation product which was absent in the authentic sample.

Hydrolysis of 2,6-Methano-4-azabicyclo[5.3.0]decan-3-one

A mixture of 200 mg of the lactam and 10 ml of concentrated hydrochloric acid was refluxed for 5 hours. Concentration to dryness gave the hydrochloride of 4-aminomethylbicyclo[3.3.0]octan-2-carboxylic acid, mp, 185-186°, after recrystallization from absolute ethanol-ether.

Anal.: Calcd. for $C_{10}H_{18}ClNO_2$: C, 54.67; H, 8.26; N, 6.38.
Found: C, 54.33, 54.31; H, 8.11, 8.06; N, 6.26.

Cyclopentanonorcamphor Oxime

A mixture of 90.0 g (0.6 mole) of cyclopentanonorcamphor, 60 g of hydroxylamine hydrochloride, 60 g of hydrated sodium acetate, 120 ml of methanol, and 60 ml of water was allowed to stand at room temperature for 48 hours and then heated on the steam bath for 0.5 hour. After cooling and diluting with water, the solution was extracted with ether. Removal of the solvent from the ether extract left a heavy oil which crystallized on cooling. Recrystallization from dilute ethanol gave the oxime as colorless plates, mp, 69-70°. The yield was 61 g (61%).

Anal.: Calcd. for $C_{10}H_{15}NO$: C, 72.70; H, 9.15; N, 8.48.
Found: C, 72.63; H, 9.16; N, 8.45.

Beckmann Rearrangement of Cyclopentanonorcamphor Oxime

A solution of 14.0 g (0.085 mole) of the oxime in 200 ml of glacial acetic acid and 17.3 g (0.17 mole) of acetic anhydride was allowed to stand at room temperature overnight. It was then saturated with anhydrous hydrogen chloride and refluxed for 3 hours. After resaturating with hydrogen chloride it was refluxed for an additional 7 hours. The cooled mixture was poured into a dilute sodium hydroxide—salt mixture, made alkaline with 25% sodium hydroxide solution, and extracted with chloroform. After washing with water and drying over anhydrous sodium sulfate, removal of the solvent left a heavy oil which was evaporatively distilled in a molecular still, yielding the following fractions.

Fraction	Bath Temp., °C	Pressure, mm Hg	Weight, g
I	96	16	1.03
	83	6.0	
II	96-100	14-16	2.60
III	104	0.4	1.85
IV	104+	0.4	2.20
V	residue		2.10

Recrystallization of Fraction III from 30-60° petroleum ether gave colorless plates, mp, 99-100°, which gave analytical figures agreeing with those of the expected lactam.

Anal.: Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48.
Found: C, 72.81; H, 9.12; N, 8.07, 8.10.

A mixture of equal parts of this lactam and that obtained by the Schmidt reaction on cyclopentanonorcamphor melted at 76-92°. Further, the infrared spectrum of this lactam shows bands at 3150 cm^{-1} (N-H stretching frequency) and at 1670 cm^{-1} (amide carbonyl stretching frequency). This spectrum is very different from that of the lactam obtained by the Schmidt reaction.

Fraction I appeared to be an unsaturated nitrile from its infrared spectrum. Catalytic hydrogenation of 0.77 g, n_D^{24} 1.4893, over palladium on carbon in absolute ethanol was very sluggish. After 20 hours, 145 ml of hydrogen was absorbed. Calculated absorption for one double bond: 130 ml. After filtering from the catalyst, removal of the solvent left a residue which was distilled at 72-73° (1.0 mm), n_D^{25} 1.4788. The calculated boiling point of the starting material is 56° at 1 mm. The infrared spectrum of the reduction produce showed disappearance of the bands at 3030 and 1615 cm^{-1} which are present in the starting material. Nitrile absorption at 2210 cm^{-1} and a band at 1740 cm^{-1} are shown in the spectra of both materials.

Acid Hydrolysis of 4,8-Methano-7-azabicyclo[0.3.5]decan-6-one

A solution of 0.2 g of the above lactam in 10 ml of concentrated hydrochloric acid was boiled under reflux for 9 hours. Concentration of the mixture in vacuo left a crystalline residue, mp, 177-179°. Recrystallization from absolute ethanol-ether followed by vacuum sublimation gave material, mp, 178-180°. The analytical data did not correspond to those demanded by the expected amino acid hydrochloride. No reasonable structure could be fitted to the data.

Anal.: Calcd. for $C_{10}H_{18}ClNO_2$: C, 54.67; H, 8.26; N, 6.38.
Found: C, 66.78, 66.85; H, 8.44, 8.41; N, 7.62.

The infrared spectrum shows a weak absorption band at 2650 cm^{-1} and strong bands at 2120, 1800, and 1660 cm^{-1}. This is radically different from the spectrum of the amino acid obtained via the Schmidt reaction.

2,6-Methano-4-azabicyclo[5.3.0]decane

A solution of 0.3 g (0.0018 mole) of 2,6-methano-4-azabicyclo[5.3.0]decan-3-one in 50 ml of absolute ether was reduced with 0.15 g (0.04 mole) of lithium aluminum hydride as in the preceding cases. After addition of the lactam, the mixture was refluxed for 8 hours and allowed to stand at room temperature for 12 hours. After careful addition of water, the ether layer was separated and concentrated leaving an oily residue. The oil was evaporatively distilled in a microstill at 60° and 18 mm, yielding a clear liquid. Anhydrous hydrogen chloride was passed into an absolute etheral solution of the liquid on which the hydrochloride of the amine separated. After drying in vacuo at 60° for 3 hours, it darkened at 260° and decomposed at 280°.

Anal.: Calcd. for $C_{10}H_{18}ClN$: C, 63.99; H, 9.66; N, 7.46.
Found: C, 64.00; H, 9.60; N, 7.41.

A portion of the amine hydrochloride was converted to the free amine by solution in dilute sodium hydroxide solution and extraction of the basic solution with ether. Addition of alcoholic picric acid solution to the ether extract and concentration gave a crystalline picrate of the amine, mp, 193.5-194.5°, after two recrystallizations from 95% ethanol.

Anal.: Calcd. for $C_{16}H_{20}N_4O_7$: N, 14.73.
Found: N, 14.79.

A mixture of this picrate with that of 2,6-methano-3-azabicyclo[5.3.0]decane (see below) melted at 150-168°.

2,6-Methano-3-azabicyclo[5.3.0]decane

2,6-Methano-3-azabicyclo[5.3.0]decan-4-one (0.2 g) was reduced with 0.2 g of lithium aluminum hydride in absolute ether as in the preceding case. The mixture was refluxed for 10 hours after addition of the lactam and then allowed to stand overnight at room temperature. The oil remaining after removal of the ether was evaporatively distilled in a microstill at 48° and 12 mm. A portion of the distillate was treated with anhydrous hydrogen chloride in absolute ether. The hydrochloride which precipitated immediately redissolved. Removal of the solvent left a crystalline material, mp, 161.5-163.5°, for the purification of which no suitable solvent could be found. It was dried in vacuo at 50° for 7.5 hours for analysis.

Anal.: Calcd. for $C_{10}H_{18}ClN$: C, 63.99; H, 9.66.
Found: C, 64.77; H, 10.38.

The infrared spectrum of this hydrochloride is not identical with that of the hydrochloride of the amine obtained by reduction of the lactam (2,6-methano-4-azabicyclo[5.3.0]decan-3-one) resulting from the Schmidt reaction.

A picrate of the amine was prepared in ethanol. After recrystallization from 95% ethanol the pale yellow crystals melted at 165.5-166°. However, analysis indicated some contamination.

Anal.: Calcd. for $C_{16}H_{20}N_4O_7$: C, 50.52; H, 5.30; N, 14.73.
Found: C, 51.23; H, 5.68; N, 14.74.

Reaction of Cyclopentanonorcamphor with Hydrazine

A. The Bis-hydrazone.—A solution of 10 ml of cyclopentanonorcamphor and 10 ml of 64% aqueous hydrazine solution in 100 ml of glacial acetic acid was heated on the steam bath for 2 hours. After cooling, the mixture was poured onto crushed ice, made alkaline with 10% sodium hydroxide solution, and extracted three times with ether. After drying the combined ether extracts over anhydrous sodium sulfate, removal of the solvent left a partially crystalline residue (2.5 g) which was recrystallized successively from 60-75° petroleum ether and absolute ethanol to give the bis-hydrazone, mp, 174-174.5°.

Anal.: Calcd. for $C_{20}H_{28}N_2$: C, 81.08; H, 9.52; N, 9.45.
Found: C, 80.89; H, 9.70; N, 9.37.

B. Acetyl Derivative of Cyclopentanonorcamphor Hydrazone.—A solution of 15 g of cyclopentanonorcamphor in 100 ml of glacial acetic acid was added to 10 g of 64% aqueous hydrazine solution and the mixture was heated on the steam bath for 6 hours. After pouring onto ice, the solution was made alkaline with 25% sodium hydroxide solution and extracted with ether. After drying the ether extract over anhydrous sodium sulfate, removal of the solvent left 5.0 g of

liquid. This was taken up in 30-60° petroleum ether. After refrigeration, the solution deposited 2.5 g of crystalline material, mp, 130-131.5°. Two recrystallizations from ether-petroleum ether raised the melting point to 133-133.5°.

Anal.: Calcd. for $C_{12}H_{18}N_2O$: C, 69.86; H, 8.79; N, 13.58.
Found: C, 69.82; H, 8.78; N, 13.74.

C. Cyclopentanonorcamphor Hydrazone.—The general procedure of Curtius and Pflug[18] was followed. A mixture of 15 g of cyclopentanonorcamphor, 7.0 g of 64% aqueous hydrazine solution, and 2.0 g of barium oxide was allowed to stand at room temperature for 65 hours. After addition of 250 ml of ether, the solution was filtered and concentrated, yielding 10 g of white crystalline material. On recrystallization of this from 30-60° petroleum ether, 0.5 g of crystalline material, mp, 56-57°, was obtained. Additional amounts of hydrazone, mp, 51.5-53°, were obtained from the mother liquors. On further recrystallization from ethanol, the hydrazone disproportionated to the bis-hydrazone.

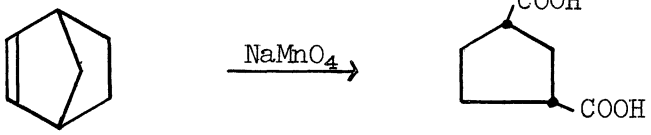
II. DIBASIC ACIDS FROM CYCLOPENTADIENE AND ITS DERIVATIVES

DISCUSSION

Two dibasic acids have been investigated, namely, cis-1,3-cyclopentanedicarboxylic acid and 2,4-bicyclo[3.3.0]octanedicarboxylic acid.

cis-1,3-Cyclopentanedicarboxylic Acid

For purposes of evaluation of the potential usefulness of this acid, methods for its preparation reported in the literature were used, although it was recognized from the outset thatthese are of no practical importance. Oxidation of norcamphor with sodium permanganate according to Birch[19] leads to the desired acid. The method is cumbersome and costly. A batch of about two

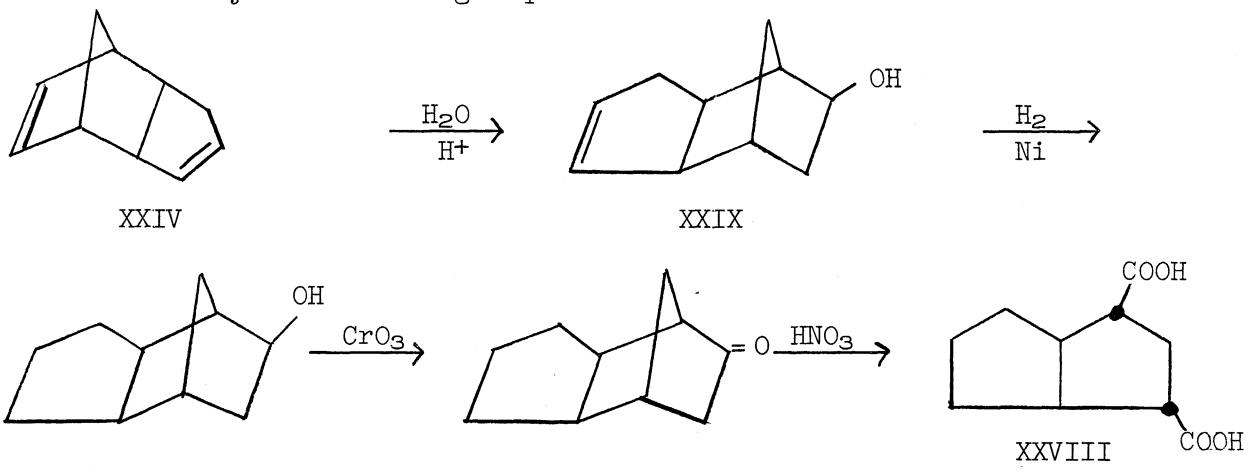


pounds of the acid was made in this manner and forwarded to ESSO Research and Engineering Company (Chemical Research Division) for evaluation as a component of alkyd resins and for evaluation of its esters as synthetic lubricants.

Subsequently, various catalytic oxidation procedures for the preparation of the acid were investigated. These are discussed in Section 3 of this report.

2,4-Bicyclo[3.3.0]octanedicarboxylic Acid

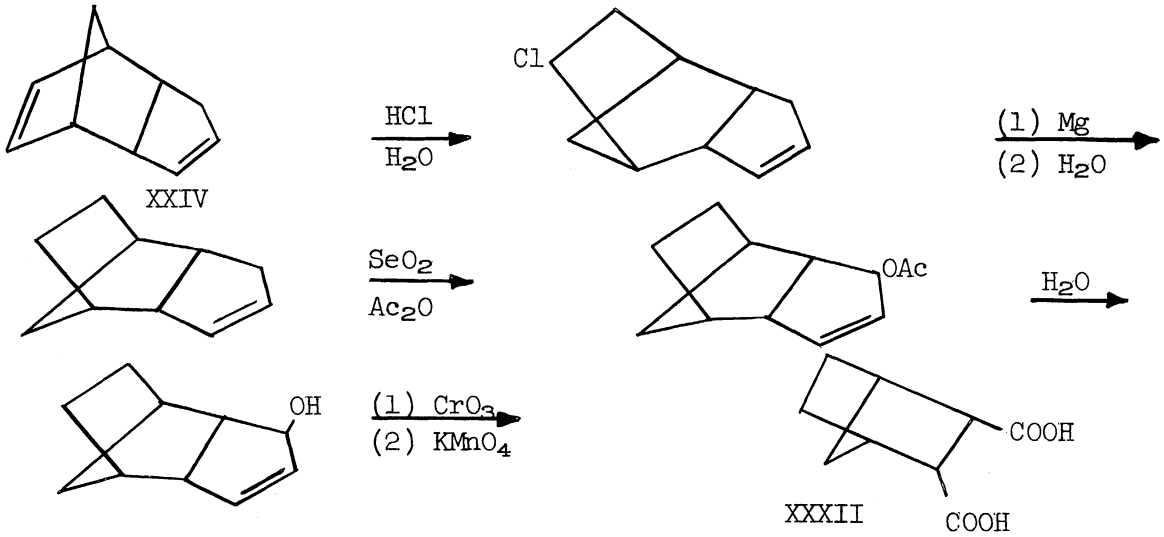
The preparation of this acid (XXVIII) from dicyclopentadiene (XXIV) is illustrated by the following sequence.



Hydration of endodicyclopentadiene was carried out by a procedure described by Bruson and Reiner.[7] However, these workers proposed tricyclo[4.2.2.$0^{1,5}$]decene-(2 or 3) ol-8 (XXX) as the structure for the hydration product. Obviously the formation of such a compound must involve extensive rearrangement of the carbon

skeleton of XXIV during the course of the reaction. The bicyclooctanedicarboxylic acid derived from XXX would then have the structure XXXI as claimed by Bruson and Reiner. For reasons set forth below it is now believed that the series of reactions leading to the bicyclooctanedicarboxylic acid is more correctly represented by the sequence XXIV-XXVIII and that the acid has the structure XXVIII.

Thus structure XXIX, representing the unsaturated carbinol formed on hydration of endodicyclopentadiene, may arise by the usual Wagner-Meerwein shifts commonly encountered in such bicyclic systems.[20,21] Furthermore, Bartlett and Schneider[22] have conclusively proved that addition of hydrogen chloride to endodicyclopentadiene occurs in such a fashion as to give the exochloro derivative.



The final dibasic acid has been shown to be β-(exo)-cis-3,6-methanohexahydrophthalic acid (XXXII). Since it is to be expected that the acid-catalyzed addition of water to XXIV parallels the addition of hydrogen chloride, assignment of structure XXIX to the unsaturated carbinol rather than structure XXX appears to be warranted.

Further confirmation for structure XXVIII for the bicyclooctanedicarboxylic acid is provided by the ready formation of diesters of the acid. An acid carrying a tertiary carboxyl group such as XXXI would hardly be expected to undergo such easy esterification.[23] Also the bicyclooctanedicarboxylic acid readily forms an anhydride on treatment with acetyl chloride in toluene. An acid of structure XXXI would be expected to give an anhydride only with difficulty since considerable strain would be involved.

The unsaturated carbinol XXXIX was readily reduced catalytically over Raney nickel to give the saturated carbinol which was in turn oxidized to the ketone with chromic oxide. Nitric acid oxidation of the ketone gave the acid XXVIII.

Representative esters of XXVIII with selected oxo alcohols have been prepared for evaluation as synthetic lubricants. Approximately 200 g of the acid have been prepared and supplied to ESSO Research and Engineering Company (Chemical Research Division) for further evaluation studies.

EXPERIMENTAL

cis-1,3-Cyclopentanedicarboxylic Acid

In a 12-liter 3-necked flask equipped with a reflux condenser, thermometer, dropping funnel, and gas inlet tube extending to the bottom of the flask, 140 g (1.5 moles) of norbornylene, 3 liters of water, and 400 ml of cyclohexane were placed. A stream of carbon dioxide was passed through the mix-

ture, and a solution of 780 g (4.0 moles) of sodium permanganate in 5 liters of water was added dropwise at such a rate that the temperature did not exceed 50°. After addition of the permanganate was complete, the mixture was stirred for an additional 12 hours at room temperature. Sulfur dioxide was passed into the mixture to reduce the precipitated manganese dioxide. The resulting clear solution was concentrated to 3 liters, acidified with 25% sulfuric acid, and extracted with four 500-ml portions of ether. The combined extracts were washed once with water, dried over anhydrous sodium sulfate, and concentrated almost to dryness. As a rule, the acid crystallized in a pure state at this point. However, if poor quality norbornylene is used, it may be necessary to recrystallize the acid from benzene. The yield of material, mp, 115-116°, averaged 142 g (60%). The reported mp is 116°.

Hydration of Dicyclopentadiene. 2,5-Methano[4.3.0]bicyclononen-7-ol-3 (XXIX)

A mixture of 600 g (4.55 moles) of dicyclopentadiene and 1600 g of 30% sulfuric acid was heated with stirring under gentle reflux for 3 hours and stirred an additional hour while cooling to room temperature. The cooled mixture was poured onto ice and extracted with ether. After washing the ether extract successively with water, twice with 10% sodium hydroxide solution, and twice with water, it was dried over anhydrous sodium sulfate. After removal of the ether, the residue was distilled under reduced pressure. Dicyclopentadiene (86.1g), bp, 74-75° (22 mm) was recovered followed by the carbinol (486.7 g), bp, 93-95° (2.5 mm), 89-91° (1.7 mm). The yield was 80% based on dicyclopentadiene reacted or 68.6% based on dicyclopentadiene used initially.

Reduction of 2,5-Methano[4.3.0]bicyclononen-7-ol-3. 2,5-Methano[4.3.0]bicyclononan-3-ol

The unsaturated carbinol was reduced either over platinum oxide in ethanol at room temperature and 40-psig hydrogen pressure, or over Raney nickel (W-5) catalyst[24] at 110° and 1500-psig hydrogen pressure. The saturated carbinol boiled at 77-79° (1 mm).

2,5-Methano[4.3.0]bicyclononan-3-one (Cyclopentanonorcamphor)

To a stirred solution of 1096 g (7.2 moles) of 2,5-Methano[4.3.0]bicyclononan-3-ol in 2 liters of glacial acetic acid, a solution of 5.80 g (5.8 moles) of chromic acid in 400 ml of water and 1.5 liters of acetic acid was added dropwise. After addition of the chromic acid was complete, the mixture was stirred and heated at 90-95° for 4 hours. After cooling, the mixture was poured onto ice and partially neutralized with 25% sodium hydroxide solution and extracted four times with ether. The combined ether extracts were washed successively with water, dilute sodium hydroxide solution until the washing remained alkaline to pH paper, and three times with water. After drying over an-

hydrous sodium sulfate, removal of the ether and distillation of the residue under reduced pressure gave 1000 g (90%) of cyclopentanonorcamphor, bp, 111-112° (14 mm). Bruson and Reiner report a yield of 63% of the ketone.[7]

2,4-Bicyclo[3.3.0]octanedicarboxylic Acid (XXVII)

To 200 g (1.33 moles) of cyclopentanonorcamphor in a 2-liter flask fitted with a reflux condenser and heated on a steam bath, 25-30 ml of nitric acid (sp gr 1.50) was added. After the formation of brown oxides of nitrogen had moderated, a second portion of nitric acid was added. This process was repeated until a total of 375 ml of nitric acid had been added, after which the mixture was heated on the steam bath for 7 days. After cooling and dilution with water the crude crystalline acid was collected and air dried. The yield of crude material was 107.4 g (50%). Recrystallization from water gave material, mp, 175-177°.

Anhydride of 2,4-Bicyclo[3.3.0]octanedicarboxylic Acid

A solution of 1 g of the dicarboxylic acid and 0.5 g of acetyl chloride in 10 ml of toluene was heated under reflux for 2 hours and taken to dryness. The residue was taken up in chloroform, filtered, and again concentrated to dryness. The crystalline residue was recrystallized from 90-100° petroleum ether to give fine, long, colorless needles of the anhydride, mp, 64.5-65°.

Anal.: Calcd. for $C_{10}H_{12}O_3$: C, 66.7; H, 6.7.
Found: C, 67.1; H, 7.1.

The infrared spectrum of the anhydride, taken as a Nujol mull, showed the typical double carbonyl absorption at 1810 and 1760 cm^{-1} with disappearance of the associated hydroxyl stretching absorption which is present in the spectrum of the dicarboxylic acid.

Esters of 2,4-Bicyclo[3.3.0]octanedicarboxylic Acid

A standard procedure was used for preparation of the esters. In a 50-ml round bottom flask, 2.0 g (0.01 mole) of the dicarboxylic acid, 4 ml of the selected alcohol, 8 ml of toluene, and 4 drops of concentrated sulfuric acid were placed. With the apparatus set for distillation through a 12-cm Vigreux column, the mixture was heated and the azeotropic distillate was collected until the temperature at the top of the column reached that of the boiling point of toluene (110°). The 12-cm column was replaced by a 6-cm one and excess toluene and alcohol were distilled off. The residue was transferred to a molecular still and evaporatively distilled at 0.9 mm. Data on the various esters prepared are given in Table I.

TABLE I

ESTERS OF 2,4-BICYCLO[3.3.0]OCTANEDICARBOXYLIC ACID

Alcohol Used	Evaporative Distillation Temp., °C	Pressure, mm Hg	n_D^{22}	Analysis			
				Calcd.		Found	
				C	H	C	H
n-octyl	175-185	0.8	1.4650	-	-	-	-
lauryl	200-220	3.0	1.4651	-	-	-	-
oxo C-8	165-170	1.5	1.4677	73.90	10.97	72.55	10.89
oxo C-10	175-185	0.9	1.4690	75.27	11.37	75.59	11.84
oxo C-13	180-190	0.9	1.4703	76.82	11.82	76.74	12.00

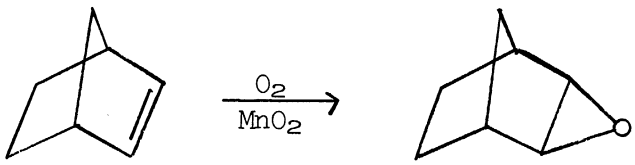
III. CATALYTIC OXIDATION OF DERIVATIVES OF CYCLOPENTADIENE

This portion of the report is preliminary and presents the results of various exploratory work undertaken with the objective of finding more efficient methods for the production of the dibasic acids discussed previously. The work has not progressed to the stage at which any definitive conclusions can be drawn. It is therefore presented purely as a progress report.

Oxidation of Norbornylene

Several experiments on catalytic oxidation of norbornylene under various conditions were carried out with the objective of providing a more economical route to cis-1,3-cyclopentanedicarboxylic acid.

A. With Manganese Dioxide as Catalyst in the Liquid Phase.—Oxidation of norbornylene in hexane solution at room temperature and atmospheric pressure with oxygen under ultraviolet irradiation in the presence of manganese dioxide gave a trace of a compound, the properties of which agreed with those of exo-2, 3-epoxybicyclo[2.2.1]heptane (XXXIII). Otherwise the norbornylene was not attacked.

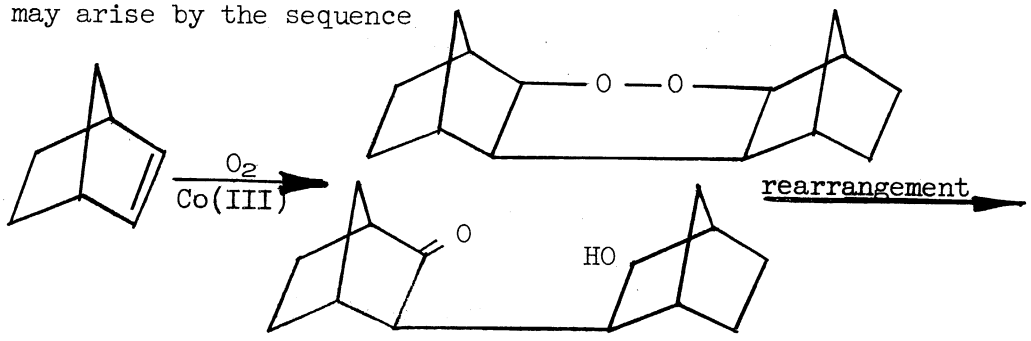


XXXIII

When the same oxidation was attempted at 100° under 500-psig oxygen pressure in the absence of a solvent, a violent explosion occurred which wrecked the autoclave in which the reaction was being carried out. Subsequently it was found that norbornylene apparently forms a highly explosive peroxide in the presence of oxygen. Experiments along these lines have been temporarily discontinued.

B. With Cobalt (III) Triacetylacetonate in the Liquid Phase.— Following essentially the procedure of Hearne et al.[25,26] for the liquid-phase catalytic oxidation of tertiary alkyl toluenes, the oxidation of norbornylene in refluxing benzene with oxygen in the presence of cobalt (III) acetylacetonate was investigated. At atmospheric pressure most of the norbornylene was recovered. A very small amount of what appeared to be XXXIII was isolated.

When the oxidation was carried out in benzene solution at 130-150° under 500-psig oxygen pressure, consumption of oxygen was good. From the products of the reaction a small amount of the epoxide (XXXIII) was isolated. In addition, a larger amount of what appeared to be a hydroxy carbonyl compound was isolated. It is speculated that this substance may be represented by structure XXXIV and may arise by the sequence



XXXIV

In support of structure XXXIV, the infrared spectrum showed both carbonyl and hydroxyl absorption. The compound gave a positive carbonyl test with dinitrophenylhydrazine. Finally, it did not react with periodic acid reagent, which indicates that the carbonyl and hydroxyl functions are not on adjacent carbon atoms.

C. With Vanadium Pentoxide in the Vapor Phase.—When norbornylene is passed over a supported vanadia catalyst with air, no oxidation occurs at temperatures below approximately 350-375°. At 400° a small yield of maleic acid was obtained. Since maleic acid was also obtained directly by similar oxidation of dicyclopentadiene, no further work was done along this line.

When oxygen was substituted for air in the vapor-phase oxidation of norbornylene, a violent explosion ensued in the cold vaporizer flask. The acual catalyst chamber was not damaged. It is concluded that norbornylene forms a highly explosive perioide on contact with pure oxygen. No difficulty has been encountered with air.

Oxidation of Norborneol

Vapor-phase oxidation of norborneol over vanadia gave maleic acid.

Oxidation of Norcamphor

Vapor-phase oxidation of norcamphor over vanadia gave maleic acid.

Oxidation of Cyclopentanonorcamphor

A. With Cobalt (III) Acetylacetonate in the Liquid Phase.—The compound was substantially unattacked by oxygen in benzene solution at 105° and atmosphere pressure.

B. With Vanadium Pentoxide in the Vapor Phase.—The product isolated in this case was phthalic anhydride.

Oxidation of Dicyclopentadiene

Dicyclopentadiene gave maleic acid when oxidized with oxygen over vanadia.

EXPERIMENTAL

Oxidation of Norbornylene with Oxygen in the Presence of Manganese Dioxide

A mixture of 47 g (0.5 mole) of norbornylene, 125 ml of benzene, and 38 g of manganese dioxide was placed in a 500-ml flask equipped with a reflux condenser and gas inlet tube. Oxygen was bubbled through the mixture for 3 days during which the flask was irradiated with a General Electric ultraviolet lamp. After filtering off the manganese dioxide, the solvent was removed and the residue was distilled through a 10-cm Vigreux column. Norbornylene (25 g), bp, 91-95°, was recovered along with 0.3 g of crystalline material, mp, 116-118°, which sublimed onto the walls of the receiver. This is presumably exo-2,3-epoxybicyclo[2.2.1]heptane for which an mp of 118-119°[27] and 125-127°[9] has been reported.

Cobalt (III) Triacetylacetonate[28]

Cobalt (III) hydroxide was prepared by oxidation of a solution of 29 g of cobalt (II) nitrate in 50 ml of 10% sodium bicarbonate solution with 75 ml of 3% hydrogen perioxide. To the resulting mixture 35 ml of acetylacetone and

20 ml of 10% sodium bicarbonate solution was added. After standing for 16 hours at room temperature, the mixture was extracted with benzene. Concentration of the dried benzene extract gave 3.5 g of cobalt (III) acetylacetonate. The crude green crystals were recrystallized from benzene, giving 2.5 g of product.

Oxidation of Norbornylene with Oxygen in the Presence of Cobalt (III) Acetylacetonate

A. At Atmospheric Pressure.[25,26]—In a 2-liter 3-necked flask equipped with a stirrer, reflux condenser, and gas inlet tube with a fritted glass disperser, a solution of 165 g (2.5 moles) of norbornylene in 1 liter of benzene and 1.8 g of cobalt (III) acetylacetonate was placed. A stream of oxygen was passed through the stirred solution which was gradually heated in an oil bath until the temperature reached 85-95°. Stirring was continued with passage of oxygen at this temperature for 24 hours, after which the mixture was cooled in an ice bath and transferred to a separatory funnel. After washing with 100 ml of 5% sodium hydroxide solution, the benzene layer was dried over anhydrous sodium sulfate. After removal of the solvent, 105 g of recovered norbornylene, bp, 90-95°, was obtained. Undoubtedly some norbornylene was carried over with the benzene. No attempt was made to secure a close fractionation at this stage. The residue weighed 8.4 g and was sublimed at 35-40° at 18 mm, yielding the following fractions.

Fraction	Weight, g	mp, °C
I	1.21	98-103
II	0.35	100-105
III	1.20	103-110

Fraction III was recrystallized from 30-60° petroleum ether, giving 0.5 g of exo-2,3-epoxybicyclo[2.2.1]heptane, mp, 123-123.5°.

The basic extract of the benzene solution gave on acidification 0.1 g of heavy yellow oil with a pungent odor which was not investigated further.

B. At 500 psig.—A mixture of 107 g (1.14 moles) of norbornylene, 2.5 g of cobalt (III) acetylacetonate, and 500 ml of benzene was placed in a 1-liter stirred autoclave under 500-psig oxygen pressure. The mixture was stirred and heated at 130-150° for 6 hours during which additional oxygen was added as required. The total oxygen absorption was 500 psig measured at the cylinder gauge. After washing the mixture four times with 5% sodium hydroxide solution and twice with water, the organic layer was dried over anhydrous sodium sulfate and the solvent was removed. After recovery of unreacted norbornylene, the residue was placed in a large molecular still and evaporatively distilled at 70-76° at atmospheric pressure, giving 15 g of distillate. This was redistilled through a 12-cm Vigreux column, giving 0.9 g of material, bp, 153-156°, which solidified in the condenser, and 8.1 g of partially crystalline residue. The

distillate was recrystallized from 30-60° petroleum ether, giving the same exo-epoxide of norbornylene, mp, 123-123.5°, obtained previously.

A portion of the residue in the still was centrifuged, giving crystalline material and a yellow oil. Recrystallization of the crystalline material from 30-60° petroleum ether gave a substance, mp, 114.5-115.5°. The infrared spectrum of this material showed it to be a hydroxy carbonyl compound rather than an epoxide. It gave a 2,4-dinitrophenylhydrazone, mp, 107-109°, from aqueous ethanol (not analyzed). It did not react with periodic acid reagent which indicated that the carbonyl and hydroxyl groups are not on adjacent carbon atoms. Sturcture XXXIV is very tentatively suggested for the compound.

Anal.: Calcd. for $C_{14}H_{20}O_2$ or $C_7H_{10}O$: C, 76.32; H, 9.15.
Found: C, 75.38; H, 9.24.

The yellow oil appeared to be a complex mixture of products and was not investigated further.

Vapor-Phase Oxidations over Vanadium Pentoxide

The apparatus consisted of a 24-mm Pyrex tube 16 in. long which was heated by a 2-section electric combustion furnace. The front 6 in. of the tube was packed with crushed fire brick to serve as a preheater. The rear 10 in. (the catalyst chamber) was packed with Harshaw, supported vanadia catalyst as 0.25-in. spheres (Lot No. V-X-L709-21-15). An air-cooled condenser was fitted to the exit end of the tube. An ice-cooled flask was fitted to the exit end of the condenser. A 2-liter suction flask equipped with a gas inlet tube was attached to the inlet end of the preheater by means of its side arm. The material to be oxidized was placed in the suction flask and swept into the hot tube by a stream of air or oxygen. Temperatures inside the preheater and catalyst chamber were measured with thermocouples and the gas-flow rate was measured by means of an Emil Greiner Predictability Flow Meter.

A. Norbornylene.—With the preheater at 250°, two runs were made with air with the catalyst chamber at 250° and 300°, respectively. Unreacted norbornylene was recovered from each.

One run using 20 g of norbornylene, a large excess of air, preheater temperature of 380°, and catalyst-chamber temperature of 400° gave 1.5 g of crystalline material in the receiver. This was identified as maleic acid by mixed mp's and infrared spectroscopy (see below).

Since no cyclopentane-1,3-dicarboxylic acid was formed, and in view of the apparently high explosive sensitivity of norbornylene peroxide (see below), no further runs were made.

B. Dicyclopentadiene.—In an orienting experiment, 5.2 g (0.04 mole)

of dicyclopentadiene was vaporized through the hot tube with excess air with both preheater and catalyst-chamber temperatures at 400°. The vaporizer flask was at room temperature and the dicyclopentadiene was allowed to vaporize at its own vapor pressure. From the receiver, 3.7 g (0.032 mole) of crude maleic acid, mp, 128-30°, was obtained. This was identified by mixed mp's, infrared spectroscopy, and by hydrogenation to succinic acid.

The high yield of maleic acid obtained in this experiment has not been duplicated. The particular catalyst used had served for several previous oxidations of a variety of compounds. It was slightly carbonized but otherwise appeared to be normal. The reason for the high yield remains obscure.

Since catalyst age appears to play a role in determining the yield of maleic acid, a series of runs was made with variations as shown in Table II. For this series fresh catalyst and fresh fire brick in the preheater were used. Prior to the first run both preheater and catalyst were heated at 400° for 18 hours. A series of 16 runs was then made. After each run the receiver was replaced by a new one and the subsequent run was begun immediately. The times for age of catalyst given in Table II are reckoned from the start of the first run with the intervals between runs representing the time required to change receivers. The vaporizer temperature was maintained by means of a bath of warm water.

TABLE II

SUMMARY OF VAPOR-PHASE OXIDATIONS OF DICYCLOPENTADIENE OVER VANADIA CATALYST

Run	Age of Cat., min	Air Flow Rate, ml/min	Yield Maleic Acid, %	Preheat. Temp., °C	Cat. Temp., °C	Vaporizer Temp., °C
1	0-5	1832	15	380-400	420-440	24
2	15-19	1832	31	380-400	420-440	24
3	27-31	1832	35.5	380-400	420-440	24
4	53-56	1832	37.3	380-400	420-440	24
5	59.5-64	1832	30.1	380-400	420-440	24
6	65-69	1832	35.2	380-400	420-440	40
7	70-73	1832	41.5	380-400	390	24
8	74-77	1832	40	380-400	369	24
9	78-82	2080	38.4	380-400	425	24
10	83-86	1955	40	380-400	440	42
11	87-91	1832	34	310	429	24
12	92-95	1832	34.6	299	382	33
13	96-99	1832	37.3	440	442	33
14	100-102	1832	34	390	448	33
15	103-105	1832	43	455	440	33
16	106-108	1832	40	474	420	33

C. Norcamphor.—With preheater temperature at 380° and catalyst at 400° with excess air, 5 g of norcamphor gave 0.4 g of maleic acid.

D. Norborneol.—Under similar conditions, 5 g of norborneol gave 0.5 g of maleic acid.

E. 2,5-Methanobicyclo[4.3.0]nonan-3-one. Cyclopentanonorcamphor.—Conditions were the same as in the previous runs except that the vaporizer flask was placed on a warm hot plate. After one week, 12 g of cyclopentanonorcamphor was vaporized. In the receiver, 0.5 g of crude crystalline material collected. Sublimation gave phthalic anhydride identified by mixed mp's, infrared spectroscopy, and conversion to phthalic acid.

REFERENCES

1. Swiss Patent 270,546, January 3, 1951; C.A., 46 (1952), 780.

2. G. P. Miklukhin and A. E. Brodskii, Compt. rend. acad. sci. (U.R.S.S.), 32 (1941), 558; C.A., 37 (1942), 1710.

3. M. L. Newman and H L. Gildenhorn, J. Am. Chem. Soc., 70 (1948), 317.

4. P. A. S. Smith, J. Am. Chem. Soc., 70 (1948), 320; P. A. S. Smith and J. P. Horwitz, ibid., 72 (1950), 3718.

5. I. L. Knunyants and B. P. Fabrichnyi, Doklady Akad. Nauk, S.S.S.R., 68 (1949), 523; C.A., 44 (1950), 1469.

6. D. E. Pearson et al., J. Am. Chem. Soc., 71 (1949), 1895; ibid., 75 (1953), 5905.

7. H. A. Bruson and T. W. Reiner, J. Am. Chem. Soc., 67 (1945), 723.

8. H. A. Bruson, U. S. Patent 2,345,573, April 4, 1944; C.A., 38 (1944), 4274.

9. H. M. Walborsky and D. F. Loncsini, J. Am. Chem. Soc., 76 (1954), 5396.

10. K. Alder, Ber., 71 (1938), 2451, 2458.

11. L. M. Joshel and L. W. Butz, J. Am. Chem. Soc., 63 (1941), 3350.

12. G. Komppa and S. Beckmann, Ann., 512 (1934), 184.

13. K. Alder and H. F. Rickert, Ann., 543 (1939), 1.

14. K. Alder and G. Stein, Ann., 525 (1936), 218.

15. I. L. Knunyants and B. P. Fabrichnyi, Doklady Akad. Nauk, S.S.S.R., 68 (1949), 701; C.A., 44 (1950), 1918.

16. L. Vargha and F. Gönczy, J. Am. Chem. Soc., 72 (1950), 2738.

17. H. Wolff in R. Adams, Organic Reactions (John Wiley and Sons, Inc., New York), Vol. 3 (1946), 307.

18. T. Curtius and L. Pflug, J. prakt. Chem., 2, 44 (1891), 535.

19. S. F. Birch, W. J. Oldham, and E. A. Johnson, J. Chem. Soc., (1947), 818.

20. H. Meerwein and K. van Emster, Ber., 53 (1920), 1815.

21. F. C. Whitmore, J. Am. Chem. Soc., 54 (1932), 3274.

22. P. D. Bartlett and A. Schneider, J. Am. Chem. Soc., 68 (1946), 6.

23. L. P. Hammett, Physical Organic Chemistry (McGraw-Hill Book Co., New York, (1940), 212.

24. H. Adkins and H. R. Billica, J. Am. Chem. Soc., 70 (1948), 695.

25. G. N. Hearne, T. W. Evans, V. W. Buls, and C. G. Schwarzer, Ind. Eng. Chem., 47 (1955), 2311; U. S. Patent 2,578,654, December 18, 1951.

26. D. S. Roebuck, British Patent 665,997, February 6, 1952; U. S. Patent 2,644,840, July 7, 1953.

27. H. Kwart and W. G. Vosburgh, J. Am. Chem. Soc., 76 (1954), 5400.

28. L. Gmelin, Handbuch der Anorganische Chemie (Verlag Chemie, Berlin), Vol. 58 (1932), 362.