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FINAL REPORT

CHEMISTRY OF MATERIALS FOR CAPACITOR FILMS

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Project 2120

U. S. RUBBER COMPANY
SUBCONTRACT UNDER PRIME CONTRACT NOBS-55413
(NAVY BUREAU OF SHIPS)

June, 1954

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OBJECTIVES

The purpose of this contract was the development of new polymers capable of being formed into films of superior mechanical, thermal, and electrical properties. For theoretical reasons, polymers containing anthracene nuclei were thought to be desirable. Previous work by the prime contractor had resulted in methods for monomer synthesis, but unfortunately the key intermediate, 9,10-dichloromethylanthracene, is a potent allergen which has caused considerable personnel difficulty.

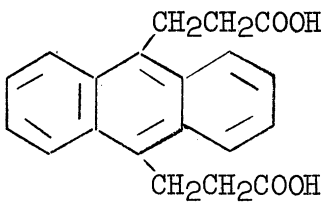
Therefore, a prime objective has been the development of new synthetic routes to polymerizable 9,10-disubstituted anthracenes. At the same time, monomers prepared by the old routes were polymerized and the polymers examined.

SUMMARY

I. POLYMERS

A. Scope of this Work

The polymers most extensively studied were derived from anthracene-9,10-dipropionic acid (I), which is readily available from 9,10-dichloromethylanthracene. One was prepared from anthracene-9,10-diacetic acid.



I

Since every polyamide prepared from I was practically infusible and highly insoluble and therefore unpromising for fabrication of films, most of the work was done with polyesters from I with various glycols. One all-hydrocarbon polymer was prepared by the action of sodium on 9,10-dichloromethylanthracene.

B. Properties of Polymers Prepared

1. Polyamides were black solids, insoluble in almost all common and uncommon solvents, and did not melt up to 300-350°.

2. Polyesters

a. As prepared by standard ester-interchange methods, the polymers from I and straight-chain glycols [$HO(CH_2)_nOH$, n = 2,3,6] were chloroform-soluble, methanol-insoluble, melted in the range 110-160°, and were obviously of low molecular weight. When molded into 25-mil wafers at 180-190°, the materials "cured" and then melted at a much higher temperature. Unfortunately, the cured material was extremely brittle. One such wafer had a dielectric constant of 2.66 at 1 megacycle.

b. Polyesters from I with polyethylene glycols [$HO(CH_2CH_2O)_nH$, MW 400-1500] were indeed less brittle, as expected from the internal plasticizing action of the polyglycol. However, the melting points were much lower. Those prepared from low MW polyglycols seemed hygroscopic and those from the higher MW polyglycols were actually water-soluble. Propylene glycol formed a polyester of mp 85-90°. No attempt was made to "cure" the polymers of this paragraph.

c. To avoid the brittleness observed in (a), a polymer was prepared incorporating sebacic acid which appeared to be very flexible. Electrical data are not available, however. A similar copolymerization to incorporate terephthalic acid did not seem to improve the flexibility.

d. One polyester was prepared from anthracene-9,10-diacetic acid and ethylene glycol. It was very brittle.

3. Polyester-polyamide. When ethanolamine ($NH_2CH_2CH_2OH$) was made into a polymer with I, the resulting material was extremely high-melting, like the polyamides prepared under paragraph 1.

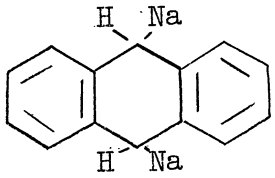
4. Poly-9,10-dimethyleneanthracene. When 9,10-dichloromethylanthracene was treated with sodium, a polymer was produced which was chlorine-free. It was so high-melting that it could not be molded in the available equipment. Being an all-hydrocarbon polymer, its electrical properties should be excellent if some method of making film could be devised.

II. SYNTHESIS OF MONOMERS

A review of possible methods for preparing 9,10-disubstituted anthracenes was given by the prime contractor in his final report for the calendar year 1952. We have concentrated on reactions of 9,10-dimetallo-9,10-dihydroanthracene and on Friedel-Crafts alkylations of anthracene.

A. Reactions of 9,10-Disodio-9,10-Dihydroanthracene (II)

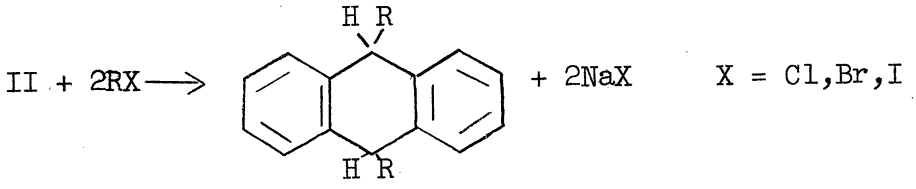
1. Preparation of



II

By the use of sodium dispersions in which the particle size was 1-15 μ, and by the use of tetrahydrofuran as a solvent, it possible to obtain a 70% yield of II (measured as 9,10-dihydroanthracene-9,10-dicarboxylic acid after carbonation) in two hours at room temperature. This compares to the literature figures of 9-100 hours for the additions in other ways. It may be noted that the diacid obtained was almost entirely the cis form. Small amounts of monoacid are formed, perhaps from traces of moisture.

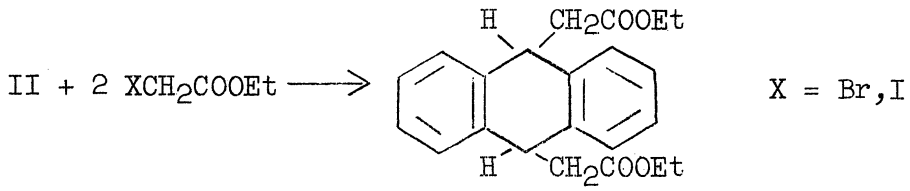
2. Metathetical reactions of II. The reactions reported in the literature are almost all of the type



III

The reported yields of type III compounds are high only where R = CH_3, CH_3CH_2.

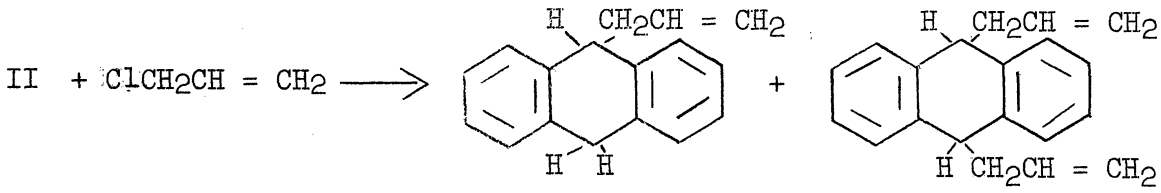
a. Reaction with ethyl haloacetate.



IV

If the reaction did proceed as expected, no product corresponding to IV could be isolated. Dihydroanthracene was recovered in small amounts, but the major product was a dark oil which could not be purified.

b. Reaction with allyl chloride.



Va Vb

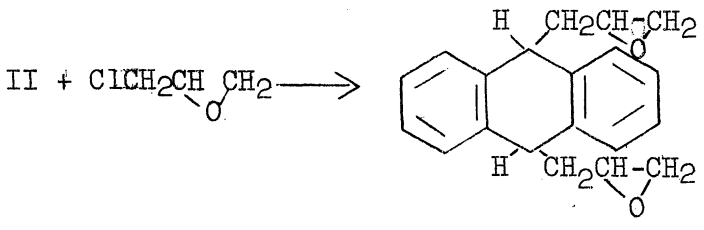
A careful workup of the reaction, including chromatography on alumina, led to a small amount of Va.

Anal. Calc. for $C_{17}H_{16}$: C, 92.68; H, 7.32

Found: C, 92.08; H, 6.47, n_D^{20} 1.5910;
bp 128-129°/0.30 mm

Though the analysis is not good, and the product does not react with trinitrobenzene nor with 2,4-dinitrobenzenesulfenyl chloride, it does react rapidly with permanaganate. The assignment of Va as the structure of the product is necessarily tentative.

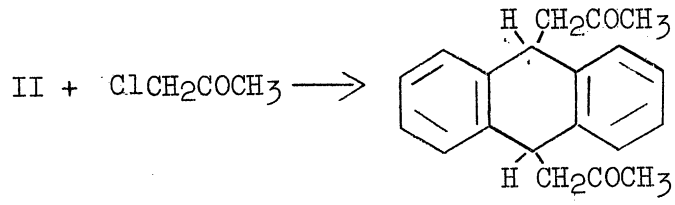
c. Epichlorohydrin



VI

Three attempts, in which the reaction temperature was varied from -35 to +55°C, led to recovered anthracene (50-60%) plus brown to black tars. A trace of material mp 335-345°C (dec.) was isolated in one run.

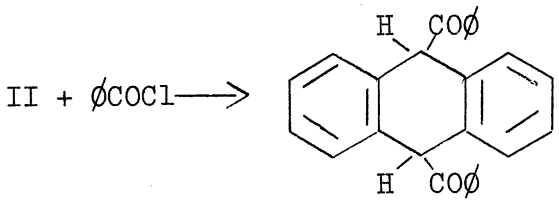
d. Chloroacetone



VII

About 40% of dihydroanthracene and 10% of anthracene was recovered, plus tar. Here, of course, as in (c), the polyfunctionality of the reactant may be responsible for the difficulty.

e. Benzoyl chloride

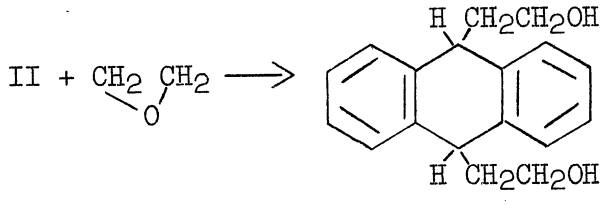


VIII

Over 50% of anthracene was recovered, plus the usual tars.

3. Addition reactions of II

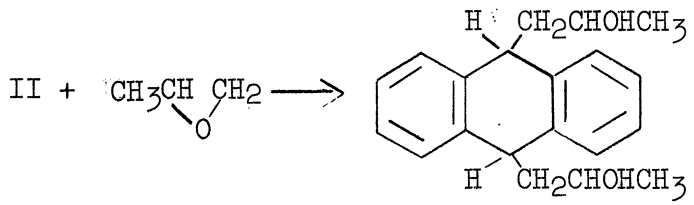
a. Ethylene oxide



IX

Mikhailov's reports are conflicting, but he did isolate trace amounts of what appears to be IX. We obtained mixtures of impure products which did not correspond to Mikhailov's compound.

b. Propylene oxide

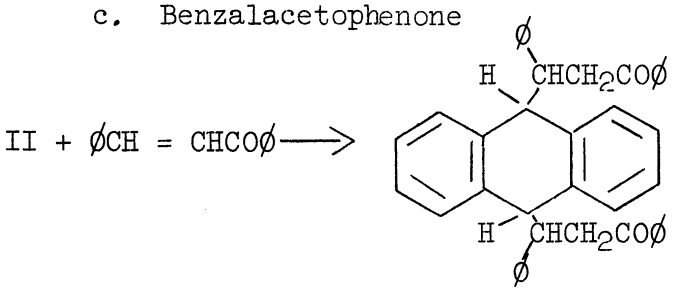


X

A mixture of products was obtained. After molecular distillation, small amounts of solid were obtained which melted over a wide range. A small amount could be recrystallized from ethylene chloride, mp 169-171.5°C.

If this product were X or the related mono compound, hypochlorite oxidation should produce the acid corresponding to IV or the related monoacid, or might result also in dehydrogenation to the anthracene compounds. No acid was obtained, but the neutral material was a black tar.

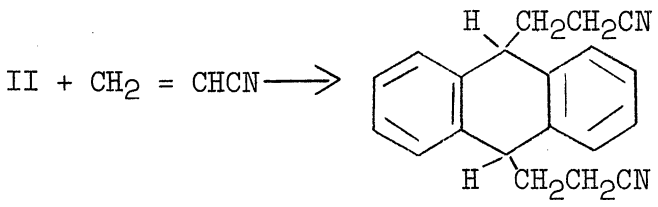
c. Benzalacetophenone



XI

Michael addition did not appear to occur as shown. Considerable anthracene was recovered, and two trace products were isolated which did not analyze correctly for XI or the mono adduct.

d. Acrylonitrile

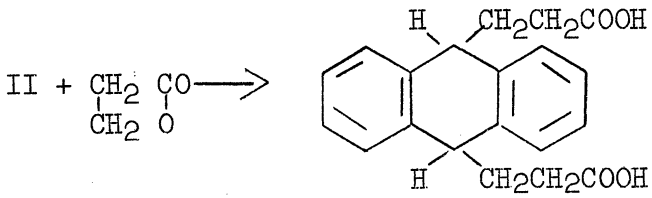


XII

Since XII could be hydrolyzed to I, considerable attention was devoted to this reaction. At 0°C, most of the acrylonitrile polymerized

(insoluble in most solvents). At -35°C, there appears to be no reaction. II was recovered as dihydroanthracene at either temperature.

e. β-Propiolactone



I

Only a trace of acidic material was formed, which proved to be a polyhydracrylic acid. Dihydroanthracene was recovered.

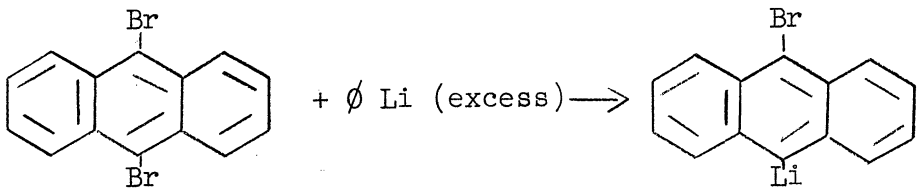
f. No study was made of addition of II to simple carbonyl compounds. The products of such reactions were felt to be of less interest as monomers and further, it was anticipated that aldol-type polymerizations would be major side reactions.

B. Metalation of 9,10-Dihydroanthracene

It was hoped that the cyanoethylation reaction which is successful with fluorene could be applied to dihydroanthracene to form XII. The reaction was unsuccessful on nine attempts with various conditions.

C. Metalation of 9,10-Dibromoanthracene

It was not possible to replace both halogens using phenyllithium.



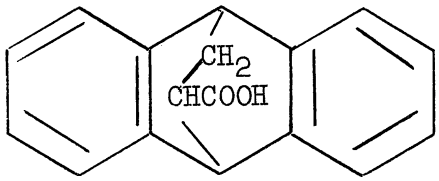
With butyllithium, the second halogen is replaced very slowly, and side reactions became dominant. Perhaps sodio compounds would be more reactive.

D. Friedel-Crafts Reactions

Anthracene is monoacetylated in the 9-position, but 9,10-diacetylation does not occur. (U.S. Rubber Report for 1952.) Compounds such as

benzene and naphthalene can be dialkylated by such reagents as acrylic acid and mesityl oxide. We attempted to dialkylate anthracene.

With acrylic acid only a mono adduct was obtained and this may be XIII resulting from Diels-Alder addition.



XIII

Mesityl oxide gave a mixture of products which could not be separated.

III. RECOMMENDATIONS FOR FURTHER WORK

A. Polymers

It is not now felt that the hypothesis that anthracene-based polymers should be superior plastics for electronic applications has been fairly tested. In particular, this phase of the program should be thoroughly evaluated by men skilled in the art of preparing and fabricating polymers. For example, the hydrocarbon polymer from dichloromethylanthracene and sodium could not be tested because of its high melting point. Doubtless a polymer expert could solve this problem and modify the product to get desirable physical properties. Our work was handicapped by unfamiliarity with polymerization procedures and film-forming techniques.

B. Monomer Synthesis

The Friedel-Crafts reaction is worthy of further study. It is not now felt that metal derivatives show enough promise to warrant further work unless a new approach is found.