

ENGINEERING RESEARCH INSTITUTE
UNIVERSITY OF MICHIGAN
ANN ARBOR

QUARTERLY REPORT NO. 2
(June 1, 1953 to August 31, 1953)

and

MONTHLY REPORT NO. 6

CHEMISTRY OF MATERIALS FOR CAPACITOR FILMS

By

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Project 2120

U. S. RUBBER COMPANY
SUBCONTRACT UNDER PRIME CONTRACT Nobs-55413

September, 1953

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INTRODUCTION

The work during the summer quarter has been directed along several lines. Our major effort has been devoted to finding suitable ways of preparing 9, 10-disubstituted anthracene derivatives without recourse to the allergenic 9, 10-dichloromethylantracene. We have explored the Friedel-Crafts reaction of anthracene with mesityl oxide, acrylic acid, and acrylonitrile, although without any great success.

The second major line of attack involves the use of 9, 10-dimetalloanthracene or 9, 10-dihydro-9, 10-dimetalloanthracene; again no great success has been achieved, although the results to date appear promising enough to warrant further effort.

A final line of approach involved the cyanoethylation of dihydroanthracene; in a great many attempts the only material which could be recovered was dihydroanthracene itself.

SUMMARY OF EXPERIMENTAL RESULTSThe Friedel-Crafts Reaction

Two workers this summer have been studying the Friedel-Crafts reaction. Several experiments were made using mesityl oxide as the alkylating reagent, in line with the work covered in some U.S. patents. It is well-known that benzene is readily alkylated by reagents containing conjugated double bonds, and there are examples of this type of reaction in the literature. Naphthalene, likewise, can be dialkylated using such reagents as acrylic acid and mesityl oxide. The logical extension to anthracene has not produced any evidence of a disubstitution product as yet, however. With acrylic acid it has been possible to isolate the anthracene 9-monopropionic acid in fair yield.

We have at present no evidence for the position of the alkyl group. We assume that it is in position 9 by analogy to the known acetylation of anthracene in the 9 position, but attempts to prove the structure of this monoacid by oxidation to anthraquinone or to anthraquinone carboxylic acid have been uniformly unsuccessful. This is surprising in view of the wide use of this oxidation reaction for structure proof of anthracene compounds. Either the starting material was recovered or the organic compound was completely destroyed by the oxidizing agents tried.

With mesityl oxide it was found possible to develop conditions which permitted isolation of a fair yield of a crystalline material. It obviously is a mixture of several different compounds, and partial success has been achieved in separating this mixture into constituents. It has not yet been possible to isolate anything other than unreacted anthracene in pure form, however.

In the experiments with acrylonitrile the only result to date is the recovery of most of the anthracene and the formation of a relatively large amount of polyacrylonitrile.

Cyanoethylation of Dihydroanthracene

A total of nine experiments were performed in an attempt to induce the addition of dihydroanthracene to acrylonitrile. The study was prompted by consideration of the known reaction of fluorene and indene with acrylonitrile using known conditions for cyanoethylation. With relatively long reaction times and high reaction temperatures, substantially all the dihydroanthracene charged was recovered. In some instances the acrylonitrile was polymerized; in other instances the bulk of it was recovered. After abandonment of attempts to cyanoethylate dihydroanthracene, it was learned from the American Cyanamid Company that they too had been unsuccessful, using sodium in boiling benzene as the condensing agent. This reaction appears to be unprofitable and will not be pursued further.

9, 10-Dimetalloanthracene by Halogen-Metal Interconversion

It had been reported in the Russian literature that 9, 10-dibromoanthracene could be converted to 9, 10-dilithioanthracene by the action of organolithio compounds. The earlier reports of the Russian workers were somewhat confusing and a good deal of time was lost in an attempt to repeat their results. When translations of their more recent work became available, it was found that they too had experienced considerable difficulty of the sort we had. In brief, it was found that 9, 10-dibromoanthracene is not readily converted into a dilithio compound by the action of phenyllithium. Butyllithium, on the other hand, reacts slowly enough with the second bromine so

that there is ample opportunity for side reactions to occur which reduce the yield of product. It does not appear, on the basis of the present knowledge, that it will be profitable to continue this study. It may well be that some other method can be used, but it is not apparent at present.

Addition of Alkali Metals to Anthracene

The most promising method for synthesis of anthracene derivatives appears to be the addition of metals such as lithium or sodium to the 9, 10-positions of anthracene. Considerable exploratory work has been done with this reaction in an effort to develop standard and reproducible conditions for the preparation of 9, 10-dimetallo-9, 10-dihydroanthracene. It was reported previously that tetrahydrofuran appeared to be an excellent solvent in the hands of the writer of this report. However, when other workers on the project attempted to duplicate his experiments, rather erratic results were obtained. Further work will be needed. It appears likely, though, that the addition of sodium or lithium metal to anthracene in either glycol dimethyl ether or tetrahydrofuran will be susceptible to standardization.

This reaction will be given considerable attention in the ensuing quarter.

Preparation of Polymers from Disubstituted Anthracenes

During the summer we have prepared super-polyesters from anthracene-9, 10-dipropionic acid, using ethylene glycol, diethylene glycol, trimethylene glycol, and hexamethylene glycol in varying ratios. The intention has been to use a slight excess of glycol to get a polymer which, although of low molecular weight, could be cross-linked to a more satisfactory material with diisocyanates. We have not explored the reactions with diisocyanates as yet. Ethylene glycol polymers appear to form quite a satisfactory film from a chloroform solution. The other polyesters formed films which are less continuous.

Since the preparation of a suitable polymer is the ultimate objective of this work, approximately half the effort of the project during the coming quarter will be devoted to attempted polymerizations. We plan, further, to use 9-allylanthracene with a dithiol in an effort to prepare addition polymers. Other condensation polymers will also be tried.

EXPERIMENTAL WORK

Friedel-Crafts Reaction of Anthracene with Mesityl Oxide

The conditions employed are essentially those described in U.S. Patent No. 2,497,673, with slight modifications. Several preliminary experiments indicated undesirable conditions. In the best run, to 53.5 g. (0.3 mole) of anthracene and 108 g. (0.81 mole) of aluminum chloride in 135 g. of purified petroleum ether was added 60.0 g. (0.61 mole) of mesityl oxide over a 40-minute period. The reaction was mildly exothermic. Then 125 ml of petroleum ether was added and the reaction mixture was stirred at room temperature for a total of 14 hours. The resulting dark-green fluid mixture was poured into ice and water. The upper dark-red oily layer was separated, and the aqueous layer was extracted with 500 ml of ether. The ether extract was combined with the dark-red layer, and the solution was washed with water, then with sodium carbonate solution, and then with water again. The solution was then steam-distilled, leaving a dark-brown crystalline solid which melted over a wide range. It was found that a portion of this material was soluble in acetone, giving a compound melting at 210°C. The acetone-insoluble fraction was found to contain aluminum. (The worker states that the customary extraction of the hydrolysate with hydrochloric acid had been omitted.) Further work will be necessary before it can be concluded that the reaction is an unsatisfactory method of introducing two alkyl groups into the 9 and 10 positions.

Friedel-Crafts Reaction of Anthracene and Acrylonitrile

To a solution of 53.5 g. (0.3 mole) of anthracene in 135 g. of purified petroleum ether was added 108 g. of aluminum chloride in the course of 30 minutes. After an additional half hour of stirring, 32.4 g. (0.61 mole) of acrylonitrile was added dropwise over 30 minutes. The reaction was rather exothermic, but it was not cooled. As the acrylonitrile was added, a fluffy mass formed at the point of addition. The mixture soon became too solid for stirring. When the products were worked up in the conventional manner, the bulk of the anthracene was recovered and there remained a substantial amount of material, insoluble in ethylene chloride, which was probably polyacrylonitrile. This result was not unexpected; it seems rather unlikely that conditions can be developed which will permit the cyanoethylation of anthracene by the Friedel-Crafts method without substantial polymerization by the aluminum chloride.

Friedel-Crafts Reaction of Anthracene with Acrylic Acid

A number of preliminary experiments were tried in an effort to force the reaction to yield a di-acid. In previously reported work the Friedel-Crafts reaction had given a mono-acid.

Tetrachloroethane, chlorobenzene, dichlorobenzene, and dioxane were tried as solvents. Chlorobenzene seemed to be the most suitable. A solution of 5 g. of anthracene and 33 g. of aluminum chloride in chlorobenzene was treated slowly with 8 g. of freshly distilled acrylic acid. The reaction mixture was maintained for 8 hours at 70-80°C, extracted with cold hydrochloric acid, and then with aqueous ammonium hydroxide. It had been found that the use of sodium bicarbonate or stronger bases resulted in difficult-to-handle emulsions. The ammonium hydroxide solution was acidified, giving 6 g. (85%) of acid, m.p. 160-170°C.

In a similar run at 30-35°C, 6.9 g. (m.p. 167-170°C, 99% yield) was obtained.

Attempts to purify the material by recrystallization from alcohol, benzene, petroleum ether, anisole, or acetic acid were unsuccessful in raising the melting point. The neutral equivalents of various samples of this acid ranged from 275 to 288 (calc'd for anthracenemonopropionic acid, 250). Since in a number of experiments it was not possible to accomplish dialkylation of anthracene with acrylic acid, this work will be abandoned. A few attempts will be made, using other catalysts like hydrogen fluoride.

Friedel-Crafts Reaction of Anthracene with Ethyl Chloroacetate

A solution of 0.056 mole of anthracene and 0.02 mole of ferric chloride in chlorobenzene was heated to 40°C, and an excess of ethyl chloroacetate was added in 1 hour. Very little evolution of HCl was observed, even though the temperature was raised to 90°C. After stirring for 10 hours at 40°C, the mixture was washed with dilute hydrochloric acid and water. After drying, a portion was vacuum-distilled and was found to be solvent and ethyl chloroacetate. The residue upon recrystallization was found to be anthracene.

It should not be concluded from this single experiment that the reaction is impossible, since the quantity of ferric chloride used was substantially less than that required for the Friedel-Crafts reaction. At least 1 mole of ferric chloride per mole of ethyl chloroacetate should have been used.

Attempted Cyanoethylation of 9, 10-Dihydroanthracene

A great many experiments were performed under varying conditions. In general, an excess of acrylonitrile was stirred with dihydroanthracene in an inert solvent in the presence of a basic catalyst. In dioxane with Triton B at the reflux temperature, 82-87% of the dihydroanthracene was recovered. In dioxane with a piperidine catalyst, the dihydroanthracene was recovered in 60% yield, and there was a substantial amount of a dark polymer, presumably polyacrylonitrile. With alcoholic potassium hydroxide in t-butyl alcohol, the recovery was substantially complete. With commercial sodium methoxide, the reaction also did not take place. With substantial quantities of hydroquinone present, there was still a small amount of polymer formed, and again the dihydroanthracene was recovered.

Attempts to Prepare Metal Derivatives of Anthracene by Halogen Metal Interchange

Before translations of all the pertinent Russian articles became available, a number of attempts were made to prepare 9, 10-dilithioanthracene by interchange reactions between 9, 10-bromoanthracene and phenyllithium. Interchange was never complete. The metal products obtained were allowed to react with such compounds as ethylene oxide, epichlorohydrin, and acrylonitrile. In no case were pure products isolated. When the complete Russian translations became available, it appeared that they had also found that interchange was not complete with dibromoanthracene, although it was satisfactory with monobromoanthracene.

We have made one attempt to prepare 9-allylanthracene for copolymerization with a dithiol. 9-Lithioanthracene was treated with allyl bromide. A pure product has not yet been obtained.

The preparation of disubstituted anthracenes by halogen-metal interchange apparently will not be successful, and accordingly this procedure will be abandoned in favor of the more promising addition reactions.

Addition of Metals to Anthracene

A variety of preliminary experiments has been conducted on the addition of lithium and sodium to anthracene. Several variables have received study. It has been found that the addition is extremely slow in the classical diethyl ether solvent. We have been able to accelerate addition markedly by the use of the newer ether solvents, ethylene glycol dimethyl ether and tetrahydrofuran. Very close control of the time and temperature is needed using the former solvent, however, since apparently attack of the organo-metallic

reagent on the solvent is fairly rapid. In one experiment, in which disodioanthracene was stirred in glycol dimethyl ether for 5 hours at 40°C, substantially all the anthracene was isolated as dihydroanthracene, and the small amount of acid obtained on carbonation was entirely anthracene monocarboxylic acid. The best procedure is described.

A solution of 3.56 g. of anthracene in 40 ml of tetrahydrofuran was stirred with 1 g. of sodium shot. A blue-green color developed almost immediately and the reaction was mildly exothermic. After stirring for 2 hours at room temperature, it was poured onto crushed carbon dioxide containing enough absolute ether to permit stirring. It was allowed to stand over the weekend, during which time the solvents evaporated. The yellowish residue was heated with 120 ml of water for 1/2 hour. The insoluble solid was washed with water and dried, yielding 0.28 g., m.p. 100-165°C. This is apparently a mixture of anthracene and dihydroanthracene and corresponds to 8% recovery. The aqueous solution was acidified and the yellow precipitate was collected, yielding 4.0 g., m.p. 200-300°C. This corresponds to 75% yield of di-acid, based on anthracene charged, or 81% based on unrecovered anthracene. This acid is a mixture of the cis and trans forms of 9, 10-dihydroanthracene-9, 10-dicarboxylic acid. It was found that a good separation of the cis and trans forms could be accomplished by boiling with acetonitrile, in which the cis form is soluble and the trans form insoluble.

The other workers on the project have since observed that this procedure is somewhat erratic. It is believed, however, that a little more work will render it reproducible. We plan then to study the reaction of the disodio compound with various reagents such as ethyl bromoacetate, epichlorohydrin, ethylene oxide, and related compounds. The resulting dihydroanthracene derivatives can then be dehydrogenated. We plan to study the use of N-bromo-succinimide, selenium dioxide, and chloranil as mild dehydrogenating agents. If this method can be developed, it will probably be the most convenient route to disubstituted anthracenes suitable for polymerization.

Preparation of Polymers

The dimethyl ester of anthracene-9, 10-bispropionic acid was prepared by methods outlined in the United States Rubber Company reports. Accurately weighed samples of the diester were mixed with varying ratios of glycols and heated at 180°C under reflux for 2 hours. The methanol was then distilled and the temperature maintained constant at 180°C for 10 hours. The system was then evacuated to 1 mm and held again at 180°C for 10 hours.

Ethylene glycol, diethylene glycol, trimethylene glycol, and hexamethylene glycol were used as the glycols in the ratio of 1 part diester to 1.1 part glycol. Since ethylene glycol appeared most promising in the preliminary experiments, other runs were made using 1:1, 1:1.1, and 1:1.2 molar ratios. The

polyesters were viscous dark materials when hot and solid brown materials when cool. They could be dissolved in chloroform and precipitated with acetone or alcohol. The ethylene glycol polymers formed good films when allowed to evaporate from chloroform.

We are continuing our examination of these polymers and samples will be submitted for testing in the near future.

PROJECT PERSONNEL

Most of the workers during the summer have returned to their academic work. As of this writing, one postdoctoral fellow is working full-time. A half-time man with a Master's degree will begin work on about September 21, and a second full-time postdoctoral fellow will begin about October 15. It is expected that this personnel arrangement will continue for the life of the contract. It is hoped that with experienced workers, the various possibilities for synthesis of these disubstituted anthracenes can be evaluated fairly, and that a thorough study of copolymers, both of the condensation and the addition type, can be carried out.

