[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DEPARTMENT, NATIONAL RESEARCH CENTER]

Carbonyl and Thiocarbonyl Compounds. IV.[1] Oxidations with Tetrahalo-*o*-benzoquinones: Synthesis of Cyclic Ethers

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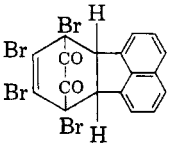
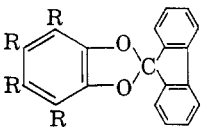
Dehydrogenation of acenaphthene with tetrachloro-*o*-benzoquinone has been investigated by Braude, Brook, and Linstead. The low recovery of total hydrocarbons reported might be attributed, among other possible factors, to the formation of an adduct by the action of the quinone on the acenaphthylene formed. This side reaction should be considered in the dehydrogenating power of tetrahalo-*o*-benzoquinones.

The action of tetrahalo-*o*-benzoquinones on fluorene provides a simple and new method for the synthesis of fluorylidene cyclic ethers. The cyclic ethers Va and Vb are obtained by the action of tetrachloro- and tetrabromo-*o*-benzoquinone on thioxanthione in a carbon dioxide atmosphere. In the presence of air, thioxanthione is oxidized to thioxanthone under the effect of tetrahalo-*o*-benzoquinones. Va and Vb could also be obtained by the action of the corresponding tetrahalo-*o*-benzoquinone on thioxanthone hydrazone.

Braude, Brook, and Linstead[2] studied the dehydrogenating power of various high potential quinones using tetralin, acenaphthene, and dibenzyl as donors and found that the most effective was 2,3-dichloro-5,6-dicyano-1,4-benzoquinone followed by tetrachloro-*o*-benzoquinone. The extent of dehydrogenation was determined by isolating the mixture of unchanged and dehydrogenated hydrocarbons chromatographically from the light petroleum extracts of the reaction mixture, then estimating the percentage composition spectrometrically. When using tetrachloro-*o*-benzoquinone as the dehydrogenating agent and acenaphthene as donor, the total hydrocarbon recovered was only 45% with 60% dehydrogenation, whereas with tetralin, the recovery was 80% with 100% dehydrogenation. This remarkable low recovery reported in the case of acenaphthene might be attributed, among other possible factors, to the possible reaction between acenaphthylene formed and the chloroquinone. Horner and Merz[3] showed that an adduct of the formula $C_{18}H_8O_2Cl_4$ is formed in good yield by refluxing a benzene solution of tetrachloro-*o*-benzoquinone and acenaphthylene for one to two hours. Schönberg and Latif[4] have shown that tetrabromo-*o*-benzoquinone reacts similarly giving the adduct I. These adducts are almost insoluble in light petroleum. Thus the adduct $C_{18}H_8O_2Cl_4$, presumably formed during the dehydrogenation of acenaphthene by tetrachloro-*o*-benzoquinone, should be precipitated during the light petroleum treatment as described by Braude, Brook, and Linstead. In the present investigation it has been possible to separate this adduct in the form of its quinoxaline derivative during the dehydrogenation of acenaphthene with tetrachloro-*o*-benzoquinone. Under these conditions this side reaction should be taken into consideration when evaluating the dehydrogenating power of tetrachloro-*o*-benzoquinone.

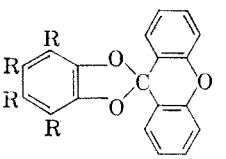


I

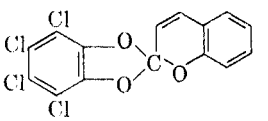


IIa. R = Cl
IIb. R = Br

Although quinones have been extensively used for the dehydrogenation of various hydrocarbons, the role of such quinones, as far as we are aware, involved only the removal of hydrogen without being incorporated into the molecules of the products formed. The authors have found, however, that tetrachloro- and tetrabromo-*o*-benzoquinone react with fluorene in boiling benzene giving the cyclic ethers IIa and IIb respectively. This reaction, which has not been described before, provides a simple and a new method for the synthesis of halogenated cyclic ethers derived from fluorene. IIa and IIb have been previously produced by the action of 9-diazofluorene on the corresponding quinones.[4]



IIIa. R = Cl
IIIb. R = Br

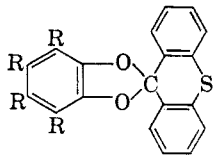


IV

The great reactivity of tetrahalo-*o*-benzoquinones has been previously utilized in the direct synthesis of halogenated cyclic ethers from certain thiones.[5] Thus, it has been found that tetrachloro- and tetrabromo-*o*-benzoquinone react readily with xanthione giving the cyclic ethers IIIa and IIIb respectively. The benzopyran derivative IV has been similarly obtained by the action of tetrachloro-*o*-benzoqui-

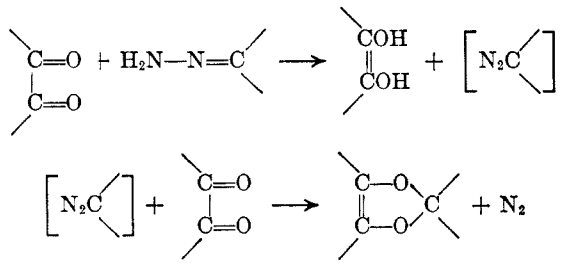
(1) Part III of this series, *J. Org. Chem.*, in press.
(2) E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).
(3) L. Horner and H. Merz, *Ann.*, **570**, 89, (1950).
(4) A. Schönberg and N. Latif, *J. Chem. Soc.*, 446, (1952).
(5) N. Latif and I. Fathy, *Can. J. Chem.*, **37**, 863, (1959).

none on coumarin-2-thione. In trying to apply this reaction to other heterocyclic thiones, the action of tetrahalo-*o*-benzoquinones on thioxanthione is investigated. In contrast to xanthione, thioxanthione reacts in two different ways depending on the atmosphere in which the reaction is carried out. In a carbon dioxide atmosphere, tetrachloro-, and tetrabromo-*o*-benzoquinone react with the thione in boiling dry benzene giving the cyclic ethers Va and Vb respectively in good yield. If the reaction is carried out while passing dry air instead of carbon dioxide, the thione is almost completely oxidized to thioxanthone and only slight amounts of the corresponding cyclic ethers are formed. The constitution of Va and Vb is based on analogy[5] as well as on the fact that they are colorless, easily hy-



Va. R = Cl
Vb. R = Br

drolyzed with dilute mineral acids giving thixanthone and the corresponding tetrahalocatechol. Va could also be obtained by the reaction between tetrachlorocatechol and 9,9-dichlorothioxanthene. The readiness with which Va and Vb are hydrolyzed with dilute hydrochloric acid can be explained on similar lines previously suggested for IIIa and IIIb.[5] Va and Vb are also obtained easily by the action of tetrachloro- and tetrabromo-*o*-benzoquinone on thioxanthone hydrazone. The formation of methylenedioxy derivatives by the action of tetrahalo-*o*-benzoquinones on ketohydrazones has been previously described.[6] The reaction proceeds through the intermediate formation of the corresponding diazo-derivative as follows:



The great ease with which thioxanthione is oxidized to thioxanthone by the action of tetrahalo-*o*-benzoquinones in air even in the absence of sunlight is rather remarkable. Thioxanthione is resistant to oxidation by oxygen except in presence of light.[7]

(6) N. Latif, I. Fathy, and (in part) Miss N. Mishriky, *J. Org. Chem.*, **24**, 1883, (1959).

(7) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 275 (1943).

EXPERIMENTAL

"Analar" benzene which had been dried over sodium was used in the reactions. The thioxanthione used was recrystallized to a sharp melting point 168°.

Reaction of tetrachloro-o-benzoquinone with acenaphthene. A solution of tetrachloro-*o*-benzoquinone (2.58 g.) and acenaphthene (1.54 g.) in benzene (15 ml.) was refluxed on the water bath for 10 hr. The reaction mixture was then filtered while hot, concentrated, and left to cool. On standing for about 24 hr. a solid separated from the viscid solution. This was filtered, washed first with a mixture of benzene and light petroleum (b.p. 40–60°), then with cold benzene and dissolved in the least amount of boiling glacial acetic acid. To the solution, a saturated solution of *o*-phenylenediamine in methyl alcohol was added, and the mixture boiled for about 5 min. The crystalline solid which separated was filtered and crystallized from benzene. It proved to be the quinoxaline of the adduct previously obtained by Horner and Merz[3] by the action of the quinone on acenaphthylene.

Action of tetrachloro-o-benzoquinone on fluorene. A solution of tetrachloro-*o*-benzoquinone (2.4 g.) and fluorene (1.8 g.) in benzene (30 ml.) was refluxed for 5 hr. on the water bath. The red color of the quinone disappeared and the reaction mixture became brown. This was filtered while hot and the benzene evaporated to dryness under reduced pressure. To the residue a few ml. of ether was added and the solid which separated was filtered and crystallized from acetone to give 9,9-(tetrachloro-*o*-phenylenedioxy)fluorene, IIa, as colorless crystals, m.p. 285° (undepressed when admixed with an authentic sample prepared by the action of 9-diazofluorene on the quinone. Both products have identical infrared spectra). Yield about 60%.

Action of tetrabromo-o-benzoquinone on fluorene. A solution of the quinone (4.2 g.) and fluorene (1.8 g.) in benzene (30 ml.) was refluxed as above. The product obtained was crystallized from xylene and shown to be 9,9-(tetrabromo-*o*-phenylenedioxy)fluorene, IIb, m.p. 338; yield about 50%.

Preparation of 9,9-(tetrachloro-o-phenylenedioxy)thiaxanthene, Va. A solution of tetrachloro-*o*-benzoquinone (2 g.) in benzene (10 ml.) was added dropwise to a boiling solution of thioxanthione (2 g.) in benzene (20 ml.) while passing dry carbon dioxide, and boiling was continued for 3 hr. The reaction mixture which became brown was filtered while hot and the solution was evaporated to dryness under reduced pressure. To the residue, acetone was added and the solid which separated was recrystallized from benzene to give Va as colorless crystals, m.p. 221°; yield about 70%.

Anal. Calcd. for $C_{19}H_8O_2Cl_4S$: C, 51.58; H, 1.81; Cl, 32.12; S, 7.24. Found: C, 51.74; H, 1.8; Cl, 31.8; S, 6.99.

Hydrolysis of Va. To a mixture of 1 ml. of concd. hydrochloric acid (sp. gr. 1.19) and dioxane (5 ml.) was added Va (0.2 g.) and the mixture boiled for 30 min., and left to cool. It was then poured onto ice and the yellowish precipitate formed was filtered, dried, and dissolved in the least amount of boiling methyl alcohol and left to cool. The solid which separated was recrystallized from alcohol and proved to be thioxanthone (by melting point and mixed melting point). The mother liquor was poured onto cold water which has been acidified with hydrochloric acid. The precipitate which formed was filtered, dried, dissolved in acetic anhydride, and the solution was refluxed for 30 min. It was then left to cool and poured onto ice. The solid which separated was crystallized from methyl alcohol and proved to be the diacetate of tetrachlorocatechol.

Reaction of tetrachlorocatechol with 9,9-dichlorothiaxanthene. To a solution of 9,9-dichlorothiaxanthene (0.1*M*, from thiaxanthone and thionyl chloride) in boiling benzene, a solution of tetrachlorocatechol in benzene (0.1*M*) was added dropwise while passing in a stream of dry carbon dioxide. A vigorous reaction took place with evolution of gas and the refluxing was continued for 5 hr. The reaction mixture was filtered while hot, and the benzene was evaporated to dryness under reduced pressure. To the residue obtained,

acetone was added and the solid which separated was crystallized from benzene and proved to be Va (undepressed when admixed with an authentic sample prepared by the action of tetrachloro-*o*-benzoquinone and thioxanthione. Both products have identical infrared spectra[8]).

Preparation of 9,9-(tetrabromo-o-phenylenedioxy)thiaxanthene, Vb. Thioxanthione (2.33 g.) and tetrabromo-*o*-benzoquinone (4.24 g.) were allowed to react as in the case of the chloro- analogue. Vb crystallized from ethyl acetate in colorless crystals m.p. 245° (yield about 70%).

Anal. Calcd. for $C_{19}H_8O_2Br_4S$: C, 36.77; H, 1.29; Br, 51.61; S, 5.16. Found: C, 36.87; H, 1.19; Br, 51.72; S, 4.00.

Hydrolysis of Vb. This was carried out as in the case of the chloroanalogue when thioxanthone and tetrabromocatechol (identified as the diacetate) were obtained.

Oxidation of thioxanthione in air. Tetrachloro-*o*-benzoquinone (0.5 g.) and thioxanthione (0.5 g.) in benzene (15 ml.) were refluxed on the water bath for 3 hr. while passing a stream of dry air. The reaction mixture was filtered while hot and the benzene was then driven off under reduced pressure. The residue was extracted with boiling methyl alcohol and the solid which remained was filtered and crystallized from benzene to give Va (about 0.5 g.). The alcoholic extract was concentrated and left to cool to give thioxanthone.

Reaction of tetrachloro-o-benzoquinone with thioxanthone hydrazone. A solution of tetrachloro-*o*-benzoquinone (0.5 g.) in dry ether (10 ml.) was added portionwise to a solution of the hydrazone (0.23 g.) in dry ether (15 ml.) at room temperature. A vigorous reaction with evolution of gas occurred after each addition and the color of the quinone disappeared. After all the quinone was added, a solid separated which was filtered, crystallized from benzene, and shown to be Va (melting point and mixed melting point); yield about 80%.

Reaction of tetrabromo-o-benzoquinone with thioxanthone hydrazone. The quinone (0.8 g.) and the hydrazone (0.23 g.) were allowed to react as in the case of the chloro- analogue. The solid which separated was crystallized from ethyl acetate and proved to be Vb (melting point and mixed melting point); yield about 75%.

Acknowledgment. The authors wish to express their appreciation to Professor F. G. Baddar, Faculty of Science, A' in Schams University, Cairo, for determination of infrared spectra.

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(8) Samples were dried under reduced pressure at 130° before infrared determination.

[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY, THE DOW CHEMICAL CO.]

Amidation and Hydrazidation of *O*-Aryl Phosphorodichloridothioates[1]

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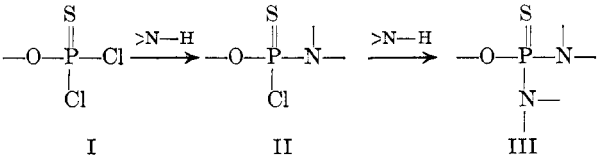
O-Aryl phosphorodichloridothioates on reaction with ammonia and aliphatic amines gave *O*-aryl phosphoramidochloridothioates and *O*-aryl phosphorodiamidothioates in high yields. *O*-Aryl phosphorodichloridothioates also react with substituted hydrazines to give *O*-aryl phosphorohydrazidochloridothioates and *O*-aryl phosphorodihydrazidothioates in high yields. The reactions were found to be dependent on temperature of reaction, mole ratio, and mode of addition of the reagents. Aromatic amines produced amido acid chlorides only, whereas hydrazine gave dihydrazides. *O*-Aryl phosphoramidohydrazidothioates were prepared by amidation of hydrazido acid chlorides and by hydrazidation of amido acid chlorides. A possible explanation of the difference observed in the reactions of the organophosphorus acid halides is presented.

The recent development of improved and convenient processes for the preparation of *O*-aryl phosphorodichloridothioates[2] prompted a study of the reactions of these phosphorus acid chlorides with compounds containing labile hydrogen atoms. The investigations described in this publication are concerned with the reactions of *O*-aryl phosphorodichloridothioates with ammonia, aliphatic and aromatic amines, hydrazine, and substituted hydrazines.

The first reported comprehensive study of the reactions of amines with phosphorus halides was by Michaelis.[3] *O*-Phenyl and *O*-tolyl phosphorodichloridothioates have been reported to form diamides and dihydrazides when treated with ammonia, benzylamine, hydrazine, and phenylhydrazine.[4-7] The patent literature cites examples of *O*-halophenyl phosphorodiamidothioates prepared from ammonia and amines.[8] However, no investigation has been reported on the stepwise substitution of the halogens in *O*-aryl phosphorodichloridothioates.

In the reaction I→III,



the logical pathway appeared to be through the partially amidated intermediate II. The remaining

(1) Presented before the Division of Organic Chemistry, 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958, page 102P of Abstracts.

(2) H. Tolkmith, *J. Org. Chem.* **23**, 1685 (1958).

(3) A. Michaelis, *Ann.* **326**, 129 (1903).

(4) W. Autenrieth and W. Meyer, *Ber.* **58**, 840, 848 (1925).

(5) W. Autenrieth and O. Hildebrand, *Ber.*, **31**, 1094, 1111 (1898).

(6) E. Ephraim, *Ber.*, **44**, 3414 (1911).

(7) W. Strecker and H. Heuser, *Ber.*, **57**, 1368 (1924).

(8) L. R. Drake and A. J. Erbel, U. S. Patent **2,552,537** (1951); L. R. Drake and C. Moyle, U. S. Patent **2,552,538** (1951).