dried over anhydrous potassium carbonate, filtered, and the product isolated by distilling the solvent *in vacuo.* This residue was dissolved in hot *n*-hexane and, on cooling to room temperature, white needle-like crystals were formed. The crystals melted at 96–97°. A sample was recrystallized several times from *n*-hexane, until a constant melting point at 101–102° was obtained. This material sublimed quite easily.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.92; H, 8.34.

Preparation of pseudocumohydroquinone dimethyl ether from the monomethyl ether. Two grams of pseudocumohydroquinone monomethyl ether was dissolved in a solution of 25 ml. of absolute methanol and 3 g. of freshly distilled dimethyl sulfate. This solution was heated to reflux, and the heat source was then removed. A saturated solution of methanolic potassium hydroxide was added dropwise, at a rate to maintain a moderate reflux, until the reaction mixture was alkaline to litmus paper. Steam distillation yielded a distillate containing an aqueous methanolic solution of the product. After diluting with water, the distillate was extracted with ether, ether fractions were combined, dried over anhydrous potassium carbonate, filtered, and the solvent distilled *in vacuo* to yield a light yellow liquid residue which was crystallized from methanol. Recrystallization of this solid from methanol yielded a material melting at 35–36°. A mixed melting point with 1,4-dimethoxy-2,3,5-trimethylbenzene showed no depression, and infrared spectra, in chloroform, of both samples were identical.

Preparation of 1,4-dimethoxy-2,5-dimethyl-3-chloromethylbenzene (2,5-dimethoxy-3,6-dimethylbenzylchloride). Twenty-five grams of 1,4-dimethoxy-2,5-dimethylbenzene was combined with 12.3 g. of 40% formalin and 150 ml. of concd. hydrochloric acid. The mixture was stirred at 70°C. for 6 hr. with hydrogen chloride bubbling through the reaction mixture at a moderate rate. On cooling, the aqueous solution was extracted with ether, the ether extracts were combined and washed three times with 200 ml. of water, washed twice with 200 ml. of saturated sodium bicarbonate solution, and finally washed with another 200 ml. of water. The ether solution was dried over anhydrous calcium chloride, filtered, and the solvent was removed from the filtrate *in vacuo* to give 27 g. of crude product. The crude product was recrystallized from *n*-hexane to yield a white solid melting at 166° which gave a positive Beilstein test. This material was 1,4-dimethoxy-2,5-dimethyl-3,6-dichloromethylbenzene, a side product of the desired reaction. Smith[18] describes this compound and reports its melting point at 165–166°. Solvent was distilled from the above crystallization filtrate leaving a white solid which was recrystallized from methanol. The product was recrystallized to give a white solid melting at 68–69°, which gave a positive Beilstein test.

Anal. Calcd. for $C_{11}H_{15}O_2Cl$: C, 61.07; H, 7.04; Cl, 16.51. Found: C, 61.27; H, 7.06; Cl, 16.31.

Preparation of 1,4-dimethoxy-2,5-dimethyl-3-deuteromethylbenzene. To a solution of 0.3 g. of 2,5-dimethoxy-3,6-dimethyl benzyl chloride in 10 ml. of ether a slight excess of lithium aluminum deuteride was added portionwise. The resulting mixture was heated at reflux for 5 hr. After refluxing for 0.5 hr., a white solid began to form. This indicated the formation of lithium and aluminum chlorides. Excess lithium aluminum deuteride was decomposed with ethyl acetate and 3 ml. of water was then added to decompose the organometallic complexes. The ether solution was decanted from the hydrated inorganic salts. Distilling the solvent from the dry organic solution yielded a light yellow liquid. This liquid was crystallized from methanol and recrystallized once to give a white solid melting at 36°.

Acknowledgment. The authors wish to thank Dr. Harold Conroy and Dr. Gary Griffin for their helpful discussions during this investigation. We also acknowledge with pleasure the support given this work by Research Corporation and through a research grant A3304 from the Division of Research Grants, the National Institutes of Health, Public Health Service.

NEW HAVEN, CONN.

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(18) L. I. Smith and J. Nichols, *J. Am. Chem. Soc.*, **65**, 1739 (1943).

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

Carbonyl and Thiocarbonyl Compounds. VI.[1] (a) Synthesis of Newer Fluorenylidene Cyclic Ethers from Tetrahalo-*o*-benzoquinones. (b) The Reductive Cleavage of Methylenedioxy Compounds by Lithium Aluminum Hydride

N. LATIF[1a] AND (MISS) N. MISHRIKY

Received January 6, 1961

The halogenated cyclic ethers IIc–IIf are obtained by the action of 2-bromo- and 2,7-dibromo-9-diazofluorene on tetrachloro- and tetrabromo-*o*-benzoquinone, respectively. The diazofluorenes are prepared in excellent yields by oxidizing the corresponding ketohydrazones with yellow mercuric oxide in the presence of alkali. IIc–IIf are also produced by the action of the appropriate tetrahalo-*o*-benzoquinone on the corresponding ketohydrazone or on the bromofluorenes themselves.

In contrast to other methylenedioxy compounds previously investigated xanthylene cyclic ethers of the general formula IV are quantitatively cleaved by lithium aluminum hydride. Similar compounds derived from fluorene are also attacked, but not so readily, by this reagent under similar conditions. A reaction mechanism, based on the formation of resonance stabilized carbonium ions, is suggested.

The preparation of cyclic ethers of the general formula I by the action of diazo compounds on *o*-quinones has been investigated by various authors.[2,3] Schönberg and Latif[4] synthesized various

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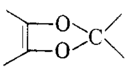
[1] Part V of this series, *J. Org. Chem.*, **26**, 3988 (1961).

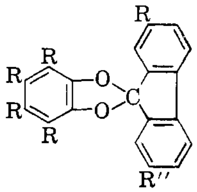
[1a] Present address, during this year, Carnegie Institute of Technology, Pittsburgh 13, Pa.

[2] C. David Gutsche, *Org. Reactions*, **VIII**, 364 (1954).

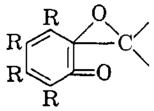
fluorenylidene derivatives from this group by the action of 9-diazofluorene on various *o*-quinones.



I



II



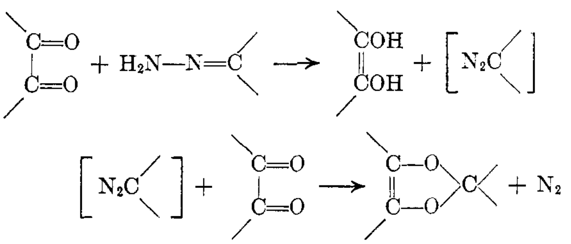
III

IIa. R = Cl; R′ = R″ = H.
IIb. R = Br; R′ = R″ = H.
IIc. R = Cl; R′ = Br; R″ = H
IId. R = Br; R′ = Br; R″ = H.
IIe. R = Cl; R′ = R″ = Br.
IIf. R = Br; R′ = R″ = Br.

In the present investigation the synthesis of 2-bromo- and 2,7-dibromo-9-diazofluorene is described. These are obtained, in excellent yield, by oxidizing 2-bromo- and 2,7-dibromofluorenone hydrazones with yellow mercuric oxide in presence of alcoholic potassium hydroxide following the procedure described by Schönberg *et al.*[5] for the preparation of 9-diazofluorene, with slight modifications. The diazo compounds are highly colored and are rather more stable than 9-diazofluorene itself. The fluorenone hydrazones are prepared by the action of hydrazine hydrate on the corresponding fluorenone in boiling *n*-butyl alcohol as described by Schönberg *et al.*[6] for the general preparation of diaryl ketohydrazones.

2-Bromo- and 2,7-dibromo-9-diazofluorene react with tetrachloro-*o*-benzoquinone at room temperature with vigorous evolution of gas giving the halogenated cyclic ethers IIc and IIe, respectively, in excellent yields. They react similarly with tetrabromo-*o*-benzoquinone giving IId and IIf. The constitution of the products obtained is based on analogy,[4] analytical data, and on the fact that they are colorless or almost so. The absence of a carbonyl stretching frequency band in their infrared spectra also supports the structure given and excludes an ethylene oxide ring formula III. The substances are recovered practically unchanged when boiled with a solution of hydrochloric acid in dioxane.

The preparation of halogenated cyclic ethers of the general formula I from tetrahalo-*o*-benzoquinones was the object of various investigations in this laboratory. It has been shown[7] that IIa and IIb can be obtained by the action of tetrachloro- and tetrabromo-*o*-benzoquinone on fluorenone hydrazone according to scheme A. It is found that 2-bromo- and 2,7-dibromofluorenone hydrazones react similarly with tetrachloro- and tetrabromo-*o*-benzoquinone giving the corresponding cyclic ethers IIc–IIf, respectively. The reaction is, however, slower than in the case of fluorenone hydrazone itself and is remarkably accelerated by heat giving the products in almost quantitative yields.



(A)

It has been shown recently[8] that IIa and IIb can be obtained directly by refluxing a dry benzene solution of fluorene with tetrachloro- and tetrabromo-*o*-benzoquinone. It is found that IIc–IIf can be similarly obtained by the action of the corresponding tetrahalo-*o*-benzoquinone on 2-bromo- and 2,7-dibromofluorene. The yields are, however, lower than in the case of IIa or IIb. This reaction provides a simple method for the direct synthesis of halogenated cyclic ethers derived from fluorenes.

Action of lithium aluminum hydride on cyclic ethers of the general formula I. The action of lithium aluminum hydride on cyclic ethers has been investigated by various authors.[9] It has been shown that they differ remarkably with respect to their attack by this reagent. Thus, while 1,2-epoxides are easily cleaved giving the corresponding carbinols, 1,4-epoxides such as tetrahydrofuran are resistant to attack under similar conditions. It has been reported also that cyclic ketals and methylenedioxy compounds do not react with this reagent.

In contrast to other methylenedioxy derivatives previously investigated, the authors have found that cyclic ethers of the general formula IV derived from xanthene are easily cleaved by lithium aluminum hydride. Thus it is found that when Va, Vb, or VI is allowed to react with this reagent in boiling ether, xanthene is produced in an excellent yield, whereas the analogous compound VII is practically recovered unchanged under similar conditions. It is assumed that cleavage takes place by the initial attack of a positive ion such as AlH_2^+, which

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(3) B. Eistert, *Newer Methods of Preparative Organic Chemistry*, Interscience Publishers Inc., New York, 1948, p. 513.

(4) A. Schönberg and N. Latif, *J. Chem. Soc.*, 1368 (1951).

(5) A. Schönberg, W. I. Awad, and N. Latif, *J. Chem. Soc.*, 1368 (1951).

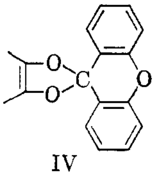
(6) A. Schönberg *et al.*, *J. Am. Chem. Soc.*, **79**, 6022 (1957).

(7) N. Latif and I. Fathy, *J. Org. Chem.*, **24**, 1883 (1959).

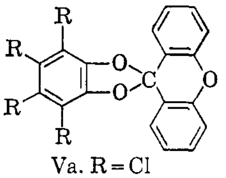
(8) N. Latif *et al.*, *J. Org. Chem.*, **25**, 1418 (1960).

(9) *Cf.* Norman G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, 1956, p. 643.

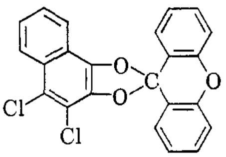
is furnished by the reducing agent[10] on the oxygen atom of the methylenedioxy group, followed by the heterolytic fission of the C—O bond to give a carbonium ion which is stabilized by resonance with the unshared electron pair of the xanthylene residue. The carbonium ion thus produced picks up a hydride ion giving finally xanthene and the corresponding hydroxy derivative (*cf.* VIII). In support of this mechanism is the fact that in the case of Va and Vb, tetrachloro- and tetrabromocatechol are isolated from the reaction mixtures.



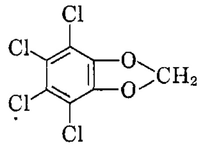
IV



Va. R = Cl
b. R = Br

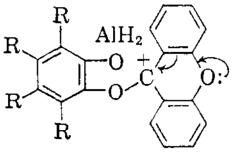


VI

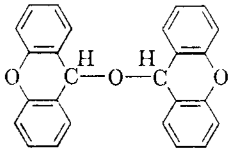


VII

According to this assumption which involves the participation of the unshared electron pair on the oxygen of the xanthylene residue in the cleavage of the methylenedioxy group, it is to be expected that xanthenyl ethers should be generally cleaved by lithium aluminum hydride. It is found that dixanthenyl ether IX reacts readily with this reagent under the same conditions giving xanthene in good yield. It is believed that cleavage proceeds in a similar manner and xanthydrol is produced as an intermediate product. The latter reacts further with the reagent to give xanthene. To confirm this mechanism, xanthydrol has been allowed to react with lithium aluminum hydride under similar conditions and xanthene has been produced. Hydrogenolysis of carbinols by the action of this reagent with the intermediate formation of resonance stabilized carbonium ions has been reported.[10]



VIII



IX

It is found also that methylenedioxy compounds derived from fluorene are cleaved, but not so readily, under similar conditions. For example, when IIa or IIb are allowed to react with lithium aluminum hydride in boiling ether, about 40% of the substance is recovered unchanged. Stabilization of the carbonium ion produced in this case is enhanced by resonance with the highly conjugated fluorenylidene residue.

EXPERIMENTAL

Preparation of 2-bromofluorenone hydrazone. To a solution of 2-bromofluorenone (2 g.) in the least amount of boiling *n*-butyl alcohol, hydrazine hydrate (98–99%, 2 ml.) was added. The solution was then refluxed for 3 hr., filtered while hot, concentrated, and left to cool. The crystals separated were washed with a few milliliters of cold methyl alcohol and recrystallized from cyclohexane to give 2-bromofluorenone hydrazone as yellow needles m.p. 130° (yield 1.8 g.).

Anal. Calcd. for $C_{13}H_9N_2Br$: C, 57.14; H, 3.29; N, 10.25; Br, 29.29. Found: C, 57.47; H, 3.41; N, 10.46; Br, 29.75.

Preparation of 2,7-dibromofluorenone hydrazone. The substance was prepared from 2,7-dibromofluorenone as above. It was crystallized from ethanol as yellow needles m.p. 210° (yield almost quantitative).

Anal. Calcd. for $C_{13}H_8N_2Br_2$: C, 44.31; H, 2.27; N, 7.95; Br, 45.45. Found: C, 44.21; H, 2.50; N, 7.00; Br, 46.16.

Preparation of 2-bromo-9-diazofluorene. A mixture of 2-bromofluorenone hydrazone (2 g.), yellow mercuric oxide (3.5 g.), and anhydrous sodium sulfate (1 g.) was ground well in a dry mortar and then transferred to a 100-ml. round-bottom flask guarded with a calcium chloride tube and containing 60 ml. of dry ether. Half a milliliter of a freshly prepared saturated solution of potassium hydroxide in absolute alcohol was then added and the reaction mixture stirred for 1 hr. at room temperature. The red ethereal solution was filtered, and the residue washed with dry ether. The combined ethereal solution was concentrated under reduced pressure in the cold. The solid separated was crystallized from ether to give 2-bromo-9-diazofluorene as red needles which melt with vigorous decomposition at about 110° (yield 1.5 g.).

Anal. Calcd. for $C_{13}H_7N_2Br$: C, 57.56; H, 2.54; N, 10.33; Br, 29.13. Found: C, 57.12; H, 2.23; N, 10.49; Br, 28.92.

Preparation of 2-bromo-9-(tetrachloro-o-phenylenedioxy)-fluorene (IIc). Tetrachloro-*o*-benzoquinone (1.2 g.) was added in small portions to a solution of 2-bromo-9-diazofluorene (1.3 g.) in dry ether (30 ml.). The reaction mixture was warmed gently after each addition and a vigorous reaction with evolution of gas took place. When all the quinone had been added, the reaction mixture was refluxed for a few minutes and left to cool. The crystalline solid was filtered off, washed with ether, then with acetone, and recrystallized from benzene to give IIc as colorless crystals, m.p. 305–306° (yield 1.8 g.).

Anal. Calcd. for $C_{19}H_7O_2Cl_4Br$: C, 46.62; H, 1.43; Cl, 29.03; Br, 16.35. Found: C, 46.72; H, 1.51; Cl, 28.00; Br, 16.36.

Preparation of 2-bromo-9-(tetrabromo-o-phenylenedioxy)-fluorene (IId). Tetrabromo-*o*-benzoquinone (2.1 g.) and 2-bromo-9-diazofluorene (1.3 g.) were allowed to react in dry ether as in the case of the chloro analog. The solid product was crystallized from benzene (using charcoal) to give IId as colorless crystals, m.p. 336–338°.

Anal. Calcd. for $C_{19}H_7O_2Br_5$: C, 34.18; H, 1.04; Br, 59.94. Found: C, 33.89; H, 1.40; Br, 60.20.

Reaction of tetrachloro-o-benzoquinone with 2-bromofluorenone hydrazone. To a solution of the quinone (1.2 g.) in dry ether (30 ml.), the hydrazone (1.3 g.) was added in small portions. The reaction mixture was then boiled under reflux for 30 min. when the red color of the quinone disappeared and a crystalline solid separated. This was filtered off, washed with acetone, and crystallized from benzene (using charcoal) to give IIc (yield 0.94 g.). The infrared spectrum of the product is identical with that of the substance obtained by the action of 2-bromo-9-diazofluorene.

When tetrabromo-*o*-benzoquinone was used instead of the

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[10] *Cf.* L. H. Conover and D. S. Tarbell, *J. Am. Chem. Soc.*, 72, 3586 (1950).

tetrachloro derivative in this reaction, IId was similarly obtained.

Reaction of tetrachloro-o-benzoquinone with 2-bromofluorene. A solution of the quinone (2.5 g.) and 2-bromofluorene (2.5 g.) in dry benzene (30 ml.) was refluxed (protected from moisture) for 6 hr., concentrated, and left to cool. The crystals separated were filtered off, washed with ether, then with acetone, and recrystallized from benzene to give IIc (yield 1.3 g.), identified as above.

When tetrabromo-*o*-benzoquinone was used in this reaction instead of the chloro derivative, IId was obtained.

Preparation of 2,7-dibromo-9-diazofluorene. The product was obtained from 2,7-dibromofluorenone hydrazone following the procedure described for the monobromo derivative. It was crystallized from ether as red crystals which melt with decomposition at about 170° (yield about 80%).

Anal. Calcd. for $C_{13}H_6N_2Br_2$: C, 44.57; H, 1.71; N, 11.20; Br, 45.70. Found: C, 44.76; H, 1.85; N, 10.29; Br, 44.5.

Preparation of 2,7-dibromo-9-(tetrachloro-o-phenylenedioxy)-fluorene (IIe). Tetrachloro-*o*-quinone (1.2 g.) was added in portions to a solution of 2,7-dibromo-9-diazofluorene (1.7 g.) in dry ether (30 ml.). A vigorous reaction with evolution of gas occurred after each addition. The product separated on standing was filtered off, washed with ether, then with acetone, and recrystallized from xylene (using charcoal) to give IIe as colorless crystals, m.p. above 360° (yield 2.4 g.).

Anal. Calcd. for $C_{19}H_6O_2Cl_4Br_2$: C, 40.14; H, 1.05; Cl, 25.00; Br, 28.16. Found: C, 40.45; H, 1.32; Cl, 24.06; Br, 28.41.

Preparation of 2,7-dibromo-9-(tetrabromo-o-phenylenedioxy)fluorene (IIf). Tetrabromo-*o*-benzoquinone (2.1 g.) and 2,7-dibromo-9-diazofluorene (1.7 g.) were allowed to react in dry ether as in the case of the chloro analog. The product was recrystallized from xylene (using charcoal) to give IIf as almost colorless crystals m.p. 350–352° (yield 2.5 g.).

Anal. Calcd. for $C_{19}H_6O_2Br_6$: C, 30.56; H, 0.80; Br, 64.34. Found: C, 30.12; H, 0.91; Br, 63.02.

Reaction of tetrachloro-o-benzoquinone with 2,7-dibromofluorenone hydrazone. The reaction was carried out as in the case of the monobromo derivative using 1.2 g. of the quinone and 1.8 g. of the hydrazone. The product was recrystallized from xylene and proved to be IIe (its infrared spectrum is identical with that obtained by the action of 2,7-dibromo-9-diazofluorene).

When tetrabromo-*o*-benzoquinone was used in this reaction, the tetrabromoanalog IIf was obtained.

Reaction of tetrachloro-o-benzoquinone with 2,7-dibromofluorene. The reaction was carried out as described in the case of the monobromo derivative using 1.2 g. of the quinone and 1.6 g. of 2,7-dibromofluorene. The product was recrystallized from xylene to give IIe (identified as above), yield 0.8 g.

When tetrabromo-*o*-benzoquinone was used in this experiment, IIf was similarly obtained.

Reaction of methylenedioxy compounds of the general formula IV *with lithium aluminum hydride.* To a suspension of lithium aluminum hydride (0.05 mole) in dry ether (70 ml.), the methylenedioxy derivative (0.005 mole) was added in small portions. When all the substance had been added, the reaction mixture was boiled under reflux (protected from moisture) for 6 hr., left to cool, and decomposed with alcohol then with dilute hydrochloric acid. It was extracted with ether several times, and the combined ethereal extracts were washed with small amounts of water and dried over anhydrous sodium sulfate. The dried ethereal extracts were evaporated to dryness under reduced pressure, and the oily residue was left to cool. The solid obtained was washed with a few milliliters of cold methyl alcohol and recrystallized from the same solvent to give xanthene, m.p. 100° (undepressed when admixed with an authentic sample).

In the case of Va and Vb, the alcoholic washings were poured onto ice, acidified with a few drops of dilute hydrochloric acid, and the solid was filtered off. It was dried, dissolved in acetic anhydride, and the solution refluxed for 30 min. and left to cool. This was poured onto water, and the solid was filtered off and crystallized from methyl alcohol as colorless crystals which were shown to be the diacetate of tetrachlorocatechol in the case of Va, and the diacetate of tetrabromocatechol in the case of Vb.

Reaction of dixanthenyl ether IX *with lithium aluminum hydride.* The reaction was carried out as in the case of IV. The dried ethereal extracts of the reaction mixture were concentrated under reduced pressure in the cold. The solid separated was shown to be unchanged IX (m.p. and mixed m.p.). The mother liquor was evaporated to dryness, and the oily residue was left to cool. The solid formed was washed with a few milliliters of cold methyl alcohol and crystallized from the same solvent to give xanthene (yield about 80%).

When xanthydrol was similarly treated with lithium aluminum hydride, xanthene and dixanthenyl ether were obtained.

Reaction of 9,9-(tetrachloro-o-phenylenedioxy) fluorene IIa *with lithium aluminum hydride.* The reaction was carried out as in the case of the xanthene analogs IV. The dried ethereal extract of the reaction mixture was concentrated to a small bulk and left to cool. The product was filtered off and crystallized from benzene to give IIa (m.p. undepressed when admixed with an authentic sample); yield, *ca.* 50%. The ethereal mother liquor was evaporated to dryness, and the residue was extracted several times with boiling petroleum ether (40–60°). The petroleum ether extracts were concentrated, cooled, and the crystals were dissolved in acetic anhydride and the solution refluxed for 30 min. and left to cool. It was then poured onto water and the solid was crystallized from methyl alcohol to give the diacetate of tetrachlorocatechol. The petroleum mother liquor was evaporated to dryness, and the solid formed on standing was crystallized from methyl alcohol to give fluorene.

DOKKI, CAIRO, EGYPT, U. A. R.