CARBONYL AND THIOCARBONYL COMPOUNDS

VIII.[1] SYNTHESIS OF FLUORENE ETHERS BY THE ACTION OF TETRAHALO-*o*-BENZOQUINONES

N. Latif and N. Mishriky
National Research Centre, Dokki, Cairo, U.A.R.

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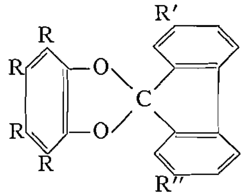
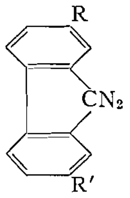
ABSTRACT

The halogenated fluorene ethers I*c*–I*f* are directly produced by the action of tetrachloro- and tetrabromo-*o*-benzoquinone on the corresponding halofluorene in boiling dry benzene. The preparation of the fluorene ethers by the action of tetrahalo-*o*-benzoquinones on 2-chloro- and 2,7-dichloro-fluorenone hydrazone is described. The ketohydrazones are readily oxidized by mercuric oxide to the corresponding 9-diazofluorenes which react readily with the halo-quinones yielding the methylene ethers.

Cyclic ethers have become important commercial materials for use both as synthetic intermediates and as solvents and this has directed the attention of various authors to study the chemistry of this group of compounds in more detail. The chemistry of halogenated cyclic ethers was the object of various investigators in this laboratory. It has been shown (1) that the fluorene ethers, I*a* and I*b*, can be directly synthesized by the action of tetrachloro- and tetrabromo-*o*-benzoquinone, respectively, on fluorene. In an attempt to generalize this reaction which provides a new and simple method for the direct synthesis of fluorenylidene cyclic ethers, the action of tetrahalo-*o*-benzoquinones on 2-chloro- and 2,7-dichloro-fluorene was investigated. It was found that the methylene ethers I*c* and I*e* are readily produced when tetrachloro-*o*-benzoquinone is allowed to react with the corresponding halofluorene in boiling dry benzene. The bromo analogues, I*d* and I*f*, are obtained similarly when using tetrabromo-*o*-benzoquinone. The constitution of the fluorene ethers is based on their lack of color, on analytical data, and on their formation from either the halofluorene itself or its corresponding 9-diazo derivative. Thus, I*c*–I*f* are produced in excellent yield by the action of 2-chloro- (II*a*) and 2,7-dichloro-9-diazofluorene (II*b*) on the corresponding tetrahalo-*o*-benzoquinone. The formation of methylene ethers by the action of diazoalkanes on tetrahalo-*o*-benzoquinones is well established (2). The 9-diazofluorenes are readily produced by oxidizing the corresponding



I*a*. R = Cl, R' = R'' = H.
I*b*. R = Br, R' = R'' = H.
I*c*. R = R' = Cl, R'' = H.
I*d*. R = Br, R' = Cl, R'' = H.
I*e*. R = R' = R'' = Cl.
I*f*. R = Br, R' = R'' = Cl.



II*a*. R = Cl, R' = H.
II*b*. R = R' = Cl.

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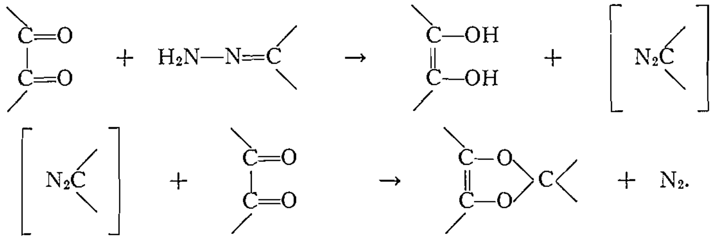
[1] *For Part VII of this series see N. Latif and I. Fathy, J. Org. Chem. 27, 1633 (1962).*

fluorenone hydrazone with yellow mercuric oxide. The hydrazones are prepared by the action of hydrazine hydrate on the corresponding fluorenone in *n*-butanol. The 2-chlorofluorenone hydrazone obtained is different from the product, described by Warren (3), which was obtained when the reaction was carried out in ethanol. However, both compounds give the same diazofluorene upon oxidation. It has been shown (3) that some 2-substituted fluorenones, such as 2-iodo- and 2-cyano-fluorenone, yield two different hydrazones when they are allowed to react with hydrazine hydrate in ethanol. In each case, both hydrazones yielded the same diazofluorene upon oxidation.

In a previous report (4) it has been shown that methylene ethers are directly produced by the action of tetrahalo-*o*-benzoquinones on ketohydrazones. In the present investigation it is found that 2-chloro- and 2,7-dichloro-fluorenone hydrazone react readily with tetrachloro- and tetrabromo-*o*-benzoquinone to give directly I*c*–I*f*, respectively, according to the scheme below. The production of the corresponding tetrahalocatechol in this reaction together with evolution of gas supports the suggested mechanism.



EXPERIMENTAL

Melting points were not corrected. Microanalyses were performed by A. Bernhardt, Germany, and by the microanalysis unit, National Research Centre, Cairo.

Preparation of 2-Chlorofluorenone Hydrazone

A solution of hydrazine hydrate (98–99%, 1.5 ml) and 2-chlorofluorenone (5) (2 g) in the least amount of *n*-butanol, was refluxed for 3 h, filtered while hot, concentrated, and left to cool. The product obtained was filtered off, washed with a few milliliters of methanol, and recrystallized from the same solvent to give 2-chlorofluorenone hydrazone (1.7 g) as yellow crystals, m.p. 145–146 °C.

Anal. Calcd. for $C_{13}H_9N_2Cl$: C, 68.42; H, 3.94; N, 12.28; Cl, 15.35. Found: C, 68.48; H, 4.11; N, 12.92; Cl, 14.53.

Preparation of 2,7-Dichlorofluorenone Hydrazone

This was obtained from 2,7-dichlorofluorenone (6) as yellow crystals, m.p. 175–176 °C.

Anal. Calcd. for $C_{13}H_8N_2Cl_2$: C, 59.31; H, 3.04; N, 10.64; Cl, 26.99. Found: C, 59.75; H, 3.26; N, 10.05; Cl, 26.06.

Preparation of 2-Chloro-9-diazofluorene (IIa)

2-Chlorofluorenone hydrazone (2 g) was oxidized with yellow mercuric oxide in the presence of ethanolic potassium hydroxide, according to the method described by Schönberg *et al.* (7). The diazo compound was obtained (1.6 g) as red crystals (from ether) which melted with vigorous decomposition at about 120 °C. The diazo compound is identical with that obtained by Warren (3).

Preparation of 2-Chloro-9-(tetrachloro-o-phenylenedioxy)fluorene (Ic)

Tetrachloro-*o*-benzoquinone (8) (1.2 g) was added in portions to a solution of 2-chloro-9-diazofluorene (1.1 g) in dry benzene (15 ml). A vigorous reaction with evolution of gas occurred after each addition. When all the quinone had been added, a solid crystalline product separated after a few minutes. This was filtered off, washed with acetone, and recrystallized from the same solvent to give I*c* (1.5 g) as colorless crystals, m.p. 281–282 °C.

Anal. Calcd. for $C_{19}H_7O_2Cl_5$: C, 51.35; H, 1.57; Cl, 39.98. Found: C, 51.83; H, 1.81; Cl, 38.87.

Preparation of 2-Chloro-9-(tetrabromo-o-phenylenedioxy)fluorene (Id)

Tetrabromo-*o*-benzoquinone (9) (2.1 g) was added to an ethereal solution of 2-chloro-9-diazofluorene (1.11 g) as above. The separated product was washed with acetone and crystallized from benzene to give I*d* as colorless crystals, m.p. 325-326 °C.

Anal. Calcd. for $C_{19}H_7O_2ClBr_4$: C, 36.65; H, 1.12; Cl, 5.62; Br, 51.44. Found: C, 37.38; H, 1.18; Cl, 5.66; Br, 51.29.

Reaction of Tetrachloro-o-benzoquinone with 2-Chlorofluorene

A solution of the quinone (2.4 g) and 2-chlorofluorene (10) (2.1 g) in dry benzene (30 ml) was refluxed (protected from moisture) for 6 h. The benzene was then evaporated to dryness under reduced pressure and a few ml of ether was added to the oily residue. The solid which separated was washed with acetone and crystallized from the same solvent to give I*c* (1.1 g). The infrared spectrum of the substance is identical with that obtained by the action of 2-chloro-9-diazofluorene on the quinone.

The bromo analogue I*d* was obtained in a similar manner by the action of tetrabromo-*o*-benzoquinone.

Reaction of Tetrachloro-o-benzoquinone with 2-Chlorofluorenone Hydrazone

The hydrazone (1.2 g) was added in small portions to a solution of the quinone (2.4 g) in dry ether (20 ml). When all the quinone had been added, the reaction mixture was refluxed for 10 min. The solid which separated (0.8 g) was crystallized from acetone and proved to be I*c*.

When tetrabromo-*o*-benzoquinone was used instead of the chloroquinone, I*d* was similarly obtained.

Preparation of 2,7-Dichloro-9-diazofluorene (IIb)

This was prepared as usual by oxidizing 2,7-dichlorofluorenone hydrazone with yellow mercuric oxide in benzene. It was obtained as light-red crystals (from ether) which melted with decomposition at about 160 °C.

Anal. Calcd. for $C_{13}H_6N_2Cl_2$: C, 59.77; H, 2.29; N, 10.72; Cl, 27.20. Found: C, 60.35; H, 2.62; N, 11.03; Cl, 26.02.

Preparation of 2,7-Dichloro-9-(tetrachloro-o-phenylenedioxy)fluorene (Ie)

Tetrachloro-*o*-benzoquinone (1.2 g) was added to a solution of II*b* (1.3 g) in dry benzene (15 ml), as in the case of the monochloro derivative. The reaction mixture was then warmed on a water bath for 15 min. The crystalline solid which separated on cooling was recrystallized from acetone to give I*e* (1.7 g) as colorless crystals which melted above 360 °C.

Anal. Calcd. for $C_{19}H_6O_2Cl_6$: C, 47.59; H, 1.25; Cl, 44.46. Found: C, 47.94; H, 1.53; Cl, 43.68.

Preparation of 2,7-Dichloro-9-(tetrabromo-o-phenylenedioxy)fluorene (If)

This was prepared from tetrabromo-*o*-benzoquinone (2.1 g) and II*b* (1.3 g), as in the case of I*e*. It was obtained as colorless crystals (2.4 g) from benzene, m.p. 355–357 °C.

Anal. Calcd. for $C_{19}H_6O_2Cl_2Br_4$: C, 34.7; H, 0.91; total halogen, 59.50. Found: C, 35.29; H, 1.09; total halogen, 58.42.

Reaction of Tetrachloro-o-benzoquinone with 2,7-Dichlorofluorene

A solution of the quinone (2.4 g) and the fluorene (11) (2.3 g) in dry benzene (30 ml) was refluxed for 6 h and worked up, as in the case of monochlorofluorene. The product which separated was crystallized from acetone to give I*e* (1.3 g). The infrared spectrum of the product is identical with that of the product obtained by the action of II*b* on the quinone.

When using tetrabromo-*o*-benzoquinone instead of the chloro derivative, the bromo analogue I*f* was obtained.

Reaction of Tetrachloro-o-benzoquinone with 2,7-Dichlorofluorenone Hydrazone

The quinone (2.4 g) and the hydrazone (1.3 g) were allowed to react together, as described in the case of the monochloro derivative. The product (0.85 g) was crystallized from acetone and proved to be I*e*.

When tetrabromo-*o*-benzoquinone was used in this experiment, the bromo analogue I*f* was similarly produced.

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