86. *Experiments with Halogenated* o*-Benzoquinone Derivatives.*

By Alexander Schönberg and Nazih Latif.

(i) Tetrabromo-*o*-benzoquinone reacts with acenaphthylene in hot benzene to give the compound (IV).

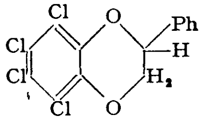
(ii) Tetrabromo- and tetrachloro-*o*-benzoquinone and 4-triphenylmethyl-1 : 2-benzoquinone are rapidly reduced by Grignard reagents to the corresponding catechols.

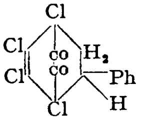
(iii) The reactions of 9-diazofluorene and of ethyl diazoacetate with various *o*-benzoquinone derivatives to give substituted benzodioxoles are described.

(i) Horner and Merz (*Annalen*, 1950, **570**, 89) found that styrene and tetrachloro-*o*-benzoquinone undergo a Diels–Alder condensation in the dark in boiling benzene to give (II) (yellow, m. p. 133°), whereas in sunlight (I) (colourless, m. p. 79°) is formed (Schönberg *et al.*, *J.*, 1951, 1364). Unlike (II), (I) does not form a quinoxaline derivative.

The reaction leading to (I) [cf. (*A*)] is characteristic of many photo-reactions (Schönberg and Mustafa, *J.*, 1944, 387; 1945, 551; 1947, 997) and in rare cases may also take place in the dark (Schönberg and Latif, *J. Amer. Chem. Soc.*, 1950, **72**, 4828).

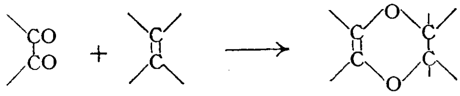
(I)



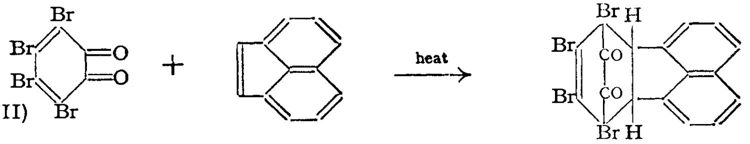


(II)

When tetrabromo-*o*-benzoquinone (III) is treated with acenaphthylene in boiling benzene, a deep yellow addition product, 7 : 8 : 9 : 10-tetrabromo-6*b* : 7 : 10 : 10*a*-tetrahydro-7 : 10-*endo*oxalylfluoranthene ("Ring Index" numbering) (IV), which forms a quinoxaline derivative, is obtained in good yield; (IV) seems to be an analogue of a substance obtained by Horner and Merz (*loc. cit.*) from tetrachloro-*o*-benzoquinone and acenaphthylene, but they did not assign a name or a structure to it. (IV) may be useful as a starting material for the syntheses of compounds related to fluoranthene.

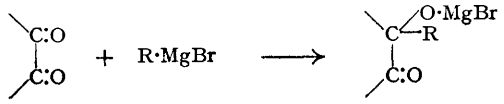


(*A*)

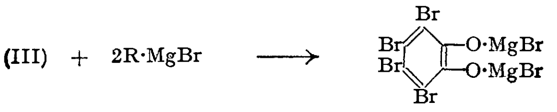


(III) (IV)

(ii) *Reduction of* o-*Benzoquinone Derivatives by Grignard Reagents.*—1 : 2-Diketones and *o*-quinones react with Grignard reagents, at least in the first stage of the reaction, according to (*B*). Such reactions have been observed with diacetyl, benzil, *cyclo*pentane-1 : 2-dione, camphorquinone, phenanthraquinone, and acenaphthenequinone (see Courtot in Grignard's "Traité de Chimie Organique," 1937, Vol. 5, pp. 386—390). We find that tetrabromo- and tetrachloro-*o*-benzoquinone and 4-triphenylmethyl-1 : 2-benzoquinone (V*a*) react with Grignard solution as shown in (*C*). When these intensely coloured quinones in ether or benzene are added in portions to an excess of Grignard solution, each portion reacts vigorously and decolorisation takes place immediately. When the product is decomposed, the corresponding catechol derivative is obtained (*e.g.*, VI*a* from V*a*). For further identification the catechol derivatives were converted into their diacetyl derivatives, *e.g.*, (VI*b*).

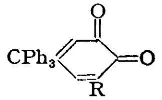


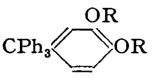
(*B*)



(*C*)

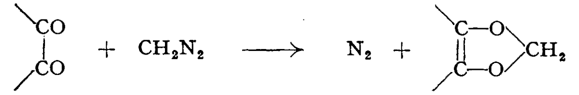
(V*a*, R = H; V*b*, R = Br)



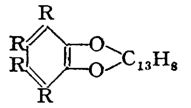


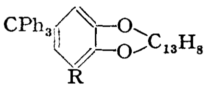
(VI*a*, R = H; VI*b*, R = Ac)

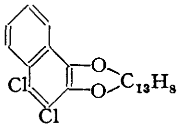
(ii) *Action of 9-Diazofluorene and of Ethyl Diazoacetate on* o-*Benzoquinone and* 1 : 2-*Naphthaquinone Derivatives.*—In a number of cases reactions between *o*-quinones and diazomethane and diphenyldiazomethane have been carried out [see (*D*)], but the reactions mentioned in the side-heading have not been reported. We find that phenanthraquinone is remarkably stable to diazofluorene under the conditions in which it reacts with diphenyldiazomethane according to (*D*) (Schönberg and Mustafa, *J.*, 1946, 746). However, tetrachloro-


(*D*)

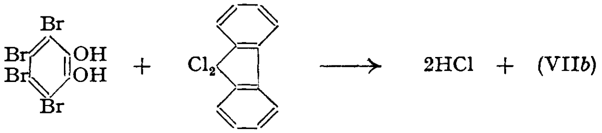
and tetrabromo-*o*-benzoquinone, 4-triphenylmethyl-1 : 2-benzoquinone (V*a*), 3-bromo-5-triphenylmethyl-1 : 2-benzoquinone (V*b*), and 3 : 4-dichloro-1 : 2-naphthaquinone react vigorously with 9-diazofluorene, giving, in good yield, the compounds (VII*a*), (VII*b*), (VIII*a*), (VIII*b*), and (IX) respectively. These products are colourless or nearly so; their constitution is based on analogy (cf. Schönberg, Awad, and Latif, *J.*, 1951, 1368) and on the fact that (VII*b*) can also be obtained by reaction between tetrabromocatechol and 9 : 9-dichlorofluorene.


(VII*a*, R = Cl; VII*b*, R = Br) *

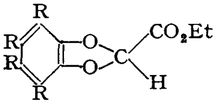

(VIII*a*, R = H; VIII*b*, R = Br) *


(IX) *

* In these structural formulæ, $C_{13}H_8$ represents a 9-fluorenylidene residue.



When tetrachloro- or tetrabromo-*o*-quinone is treated with ethyl diazoacetate, a reaction according to (*D*) takes place, leading to the colourless 2-carbethoxy-4 : 5 : 6 : 7-tetrahalogenobenzodioxole (X*a* or *b*).


(X*a*, R = Cl; X*b*, R = Br)

EXPERIMENTAL

(i) *Reaction between Tetrabromo-*o*-benzoquinone and Acenaphthylene.*—The quinone (0·9 g. and acenaphthylene (0·4 g.) in dry benzene (30 c.c.) were refluxed for one hour. After concentration, 7 : 8 : 9 : 10-*tetrabromo*-6b : 7 : 10 : 10a-*tetrahydro*-7 : 10-endo*oxalylfluoranthene* (IV) was obtained, and recrystallised from xylene in yellow crystals, m. p. 250°; it was dried at 100° before analysis (90% yield) (Found: C, 37·5; H, 1·7; Br, 55·7. $C_{18}H_8O_2Br_4$ requires C, 37·4; H, 1·4; Br, 55·6%). When (IV) in xylene was refluxed with water and left to cool, colourless crystals were obtained which became yellow when heated in a bath at 190° and gave the same m. p. and mixed m. p. as the yellow substance mentioned above: the colourless product is probably a hydrate.

The yellow or the colourless substance (1 mol.) was dissolved in a hot mixture of equal parts of methyl alcohol and glacial acetic acid, and a hot concentrated solution of *o*-phenylenediamine (3 mols.) in methyl alcohol added. After a few seconds, precipitation of a yellow crystalline *quinoxaline* derivative occurred; after being washed with boiling xylene, it had m. p. 260° (decomp.) (Found: C, 44·6; H, 1·7; N, 3·7; Br, 49·7. $C_{24}H_{12}N_2Br_4$ requires C, 44·4; H, 1·9; N, 4·3; Br, 49·4%).

When 5 : 6 : 7 : 8-tetrachloro-2-phenylbenzodioxen (I) was similarly treated with *o*-phenylenediamine, no quinoxaline derivative was obtained.

(ii) *Action of Grignard Reagents on* o-*Benzoquinone Derivatives.*—(a) *Tetrabromo-*o*-benzoquinone and phenylmagnesium bromide.* To an ethereal solution of phenylmagnesium bromide (from bromobenzene, 3 mols.) was added in portions an ethereal solution of tetrabromo-*o*-benzoquinone (Zincke, *Ber.*, 1887, **20**, 1777) (1 mol.); a vigorous reaction took place and the colour of the quinone faded after each addition. The mixture was then refluxed for one hour, decomposed with ice and dilute hydrochloric acid, and extracted with ether. The extract was washed with water and dried, and the ether evaporated. To the residue a few c.c. of benzene were added; crystals of tetrabromocatechol separated on cooling, and recrystallised from benzene in almost colourless crystals, m. p. 182—185° (yield about 75%) (Found: C, 17·4; H, 0·7. Calc. for $C_6H_2O_2Br_4$: C, 16·9; H, 0·5%). When boiled with acetic anhydride, this gave colourless crystals of the diacetyl derivative of tetrabromocatechol (m. p. and mixed m. p. 213°).

(b) *Tetrabromo*-o-*benzoquinone and ethylmagnesium iodide.* This reaction was carried out similarly to the preceding one and the bromocatechol (80% yield) was identified as before (Found: C, 17·2; H, 0·8%).

(c) *Tetrachloro*-o-*benzoquinone and phenylmagnesium bromide.* The experiment was carried out as for the tetrabromo-analogue. The dried ethereal solution was evaporated, the residue dissolved in hot benzene, and the solution left to concentrate slowly at room temperature; the semi-solid crystalline substance formed was washed with cold benzene, then with light petroleum (b. p. 40—60°), and recrystallised from benzene, forming colourless crystals of tetrachlorocatechol (Found: C, 28·7; H, 1·2. Calc. for $C_6H_2O_2Cl_4$: C, 29·0; H, 0·8%), identified by m. p. and mixed m. p., 190°, of its diacetyl derivative.

(d) 4-*Triphenylmethyl*-1 : 2-*benzoquinone and ethylmagnesium iodide.* To an ethereal solution of ethylmagnesium iodide (from ethyl iodide, 3·5 mols.) was added the quinone (Zincke and Wugk, *Annalen*, 1908, **363**, 284) (0·7 g.) in dry benzene; an immediate reaction took place, and after 30 minutes the reaction mixture was decomposed with ice and dilute hydrochloric acid and extracted with benzene. The dried benzene extract was concentrated and left to cool; the crystals which separated, m. p. 250—255°, were boiled with acetic anhydride for one hour and then set aside; crystals of 4-triphenylmethylcatechol diacetate (VI*b*) (Zincke and Wugk, *loc. cit.*) separated (m. p. and mixed m. p. 195°).

(iii) *Reaction of* o-*Quinone Derivatives with* 9-*Diazofluorene and with Ethyl Diazoacetate.*—(a) *Reactions of* 9-*diazofluorene.* (1) With tetrabromo-*o*-benzoquinone. To a solution of the quinone (0·6 g.) in benzene (10 c.c.) was added diazofluorene (Schönberg, Awad, and Latif, *loc. cit.*) (0·6 g.); immediately a vigorous evolution of gas took place. After a few minutes 9 : 9-(*tetrabromo*-o-*phenylenedioxy*)*fluorene* (VII*b*) separated; it recrystallised from xylene in colourless crystals, m. p. above 310° (yield almost quantitative). It was difficultly soluble in cold benzene, alcohol, or acetone (Found: C, 39·1; H, 1·6; Br; 54·2. $C_{19}H_8O_2Br_4$ requires C, 38·7; H, 1·3; Br, 54·4%).

(2) With tetrachloro-*o*-benzoquinone. The quinone (0·4 g.) (Jackson and MacLaurin, *Amer. Chem. J.*, 1907, **37**, 7) was dissolved in benzene (8 c.c.), and diazofluorene (0·6 g.) added; a vigorous reaction took place and after a few minutes (VII*a*), the *chloro*-analogue of the above, separated and was recrystallised from benzene, forming colourless crystals, m. p. 281°, difficultly soluble in cold acetone or alcohol (yield almost quantitative) (Found: C, 55·9; H, 2·1; Cl, 34·6. $C_{19}H_8O_2Cl_4$ requires C, 55·6; H, 1·9; Cl, 34·6%).

(3) With 3-bromo-5-triphenylmethyl-1 : 2-benzoquinone. To the quinone (0·3 g.) (Zincke and Wugk, *loc. cit.*) suspended in benzene (5 c.c.) was added a slight excess of diazofluorene; the mixture was gently warmed on the water-bath for a few seconds and set aside for 3 days. The crystalline deposit was filtered off, washed with acetone, and recrystallised from benzene. 9 : 9-(3-*Bromo*-5-*triphenylmethyl*-o-*phenylenedioxy*)*fluorene* (VIII*b*) was obtained in colourless crystals, m. p. 262°, difficultly soluble in cold acetone or benzene (70% yield) (Found: C, 77·2; H, 4·5. $C_{38}H_{25}O_2Br$ requires C, 76·8; H, 4·3%).

(4) With 4-triphenylmethyl-1 : 2-benzoquinone. The quinone (0·2 g.) was treated with diazofluorene (0·2 g.) in benzene (10 c.c.) as previously described. After 3 days the benzene was driven off under reduced pressure, a few c.c. of cooled acetone were added, and the mixture was cooled in ice. 9 : 9-(4-*Triphenylmethyl*-o-*phenylenedioxy*)*fluorene* (VIII*a*) separated and recrystallised from ice-cooled acetone in colourless crystals, m. p. 250° (50% yield) (Found: C, 88·4; H, 5·0. $C_{38}H_{26}O_2$ requires C, 88·6; H, 5·1%).

(5) With 3 : 4-dichloro-1 : 2-naphthaquinone. Diazofluorene (0·8 g.) in benzene (15 c.c.) and the quinone derivative (0·5 g.) (Zincke and Engelhardt, *Annalen*, 1894, **283**, 347) were left at room temperature for 4 days, during which the solvent evaporated. The residue was washed with ice-cold acetone several times and recrystallised from acetone; 9 : 9-(3 : 4-*dichloro*-1 : 2-*naphthylenedioxy*)*fluorene* (IX) separated in almost colourless crystals, m. p. about 255° (70% yield) (Found: C, 70·5; H, 3·1; Cl, 18·1. $C_{23}H_{12}O_2Cl_2$ requires C, 70·5; H, 3·1; Cl, 18·1%).

(6) With phenanthraquinone. To the quinone (0·5 g.) in benzene or chloroform (10 c.c.) diazofluorene (0·8 g.) was added, but after a week's standing the quinone was recovered unchanged.

(b) *Reactions of diazoacetic ester.* (1) With tetrachloro-*o*-benzoquinone. Diazoacetic ester (2·5 c.c.) in ether was added to a solution of the quinone (1 g.) in benzene (10 c.c.) and left overnight. The ether was driven off, and the benzene solution refluxed for 30 minutes; a few drops of methyl alcohol were added and the mixture was left overnight. The solution was evaporated under reduced pressure, and the residue dissolved in methyl alcohol and left to cool. *Ethyl* 4 : 5 : 6 : 7-*tetrachlorobenzodioxole*-2-*carboxylate* (X*a*) separated, and recrystallised from light petroleum (b. p. 40—60°) in colourless crystals, m. p. 82° (Found : C, 36·5; H, 2·0; Cl, 42·0. $C_{10}H_6O_4Cl_4$ requires C, 36·0; H, 1·8; Cl, 42·6%).

(2) With tetrabromo-*o*-benzoquinone. By similar means the *tetrabromo*-analogue (X*b*) was obtained; it was washed with methyl alcohol and recrystallised from light petroleum (b. p. 40—60°), forming almost colourless crystals, m. p. 121—122° (Found : C, 24·0; H, 1·3; Br, 63·3. $C_{10}H_6O_4Br_4$ requires C, 23·5; H, 1·2; Br, 62·7%).

Reaction of 9 : 9-*Dichlorofluorene with Tetrabromocatechol.*—Dichlorofluorene (1·25 mol.) and tetrabromocatechol (1 mol.) were heated (protected from moisture) in a boiling-water bath for 15 minutes. The product was dissolved in boiling xylene, and the solution filtered, concentrated, and left to cool; 9 : 9-(*tetrabromo*-o-*phenylenedioxy*)*fluorene* (VII*b*) separated in crystals, m. p. above 310° (yield 80%) (Found : C, 38·2; H, 1·4. $C_{19}H_8O_2Br_4$ requires C, 38·7; H, 1·3%).

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