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POLYFLUORO-AROMATIC COMPOUNDS—III*

TETRA- AND TRI-FLUORO-*p*-BENZOQUINONE

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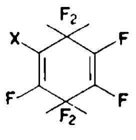
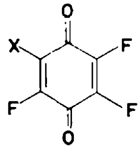
Abstract—Octafluorocyclohexa-1:4-diene gave, with oleum, tetrafluoro-*p*-benzoquinone which was reduced to the corresponding hydroquinone derivative, the dimethyl ether of which is identical with that formed from hexafluorobenzene and sodium methoxide. 1H-Heptafluorocyclohexa-1:4-diene gave 2:3:5-trifluorohydroquinone in a similar way.

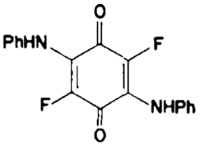
It is well-known in organic fluorine chemistry that an aromatic ring[1] or an olefinic bond[2] activates an adjacent trifluoromethyl group. In the former case, reaction with sulphuric acid followed by the addition of water converts $—CF_3$ into $—CO_2H$, benzotrifluoride itself giving benzoic acid. It appeared that the $>CF_2$ groups of fluorocyclohexadienes might be susceptible to similar types of attack. On treatment with fuming sulphuric acid at 100°, both $>CF_2$ groups of octafluorocyclohexa-1:4-diene[3] (I) were converted into $>C{=}O$. Though the primary product was probably a partly reduced quinone, after treatment with 50 per cent nitric acid, tetrafluoro-*p*-benzoquinone (II) was obtained in moderate yield. The quinone (II) was volatile, had a characteristic odour and oxidized iodide ion to iodine and N:N-dimethylaniline to methyl violet. It had ultra-violet and infra-red spectra consistent with its structure.



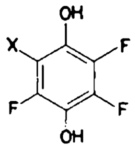
I, X = F
VI, X = H



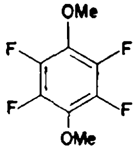
II, X = F,
VII, X = H,



III



IV, X = F
VIII, X = H



V

The fluorine atoms in tetrafluoro-*p*-benzoquinone (II) are rather labile towards alkaline reagents. Aqueous sodium hydroxide caused liberation of fluoride ion, and aniline in ether attacked the quinone to give a compound which, by analogy with the products of similar reactions[4] of tetrachloro-*p*-benzoquinone, is probably 2:5-difluoro-3:6-di (phenylamino)-benzo-1:4-quinone (III). It is not surprising that the presence of four fluorine atoms in this quinone (II) renders the unsaturated carbon atoms carrying them more electropositive than usual and hence particularly susceptible to nucleophilic attack with subsequent loss of fluoride ion.

Tetrafluoro-*p*-benzoquinone (II) in diethyl ether was reduced with hydrogen–Raney

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* Part II: *J. Chem. Soc.* 2019 (1959).

[1] G. M. Le Fave, *J. Amer. Chem. Soc.* 71, 4148 (1949).

[2] A. L. Henne, M. A. Smook and R. L. Pelley, *J. Amer. Chem. Soc.* 72, 4756 (1950).

[3] D. E. M. Evans and J. C. Tatlow, *J. Chem. Soc.* 3779 (1954); 1184 (1955).

[4] E. H. Huntress, *Organic Chlorine Compounds* p. 501. John Wiley, New York (1948).

nickel to give 2:3:5:6-tetrafluorohydroquinone (IV). Isolation without special precautions gave a hydrated form which, however, could be dried to give the anhydrous dihydric phenol. This was characterized also as its dibenzoate. With diazomethane the quinol gave tetrafluoro-*p*-dimethoxybenzene (V) which was identical with the dimethoxy-derivative obtained[5] by treatment of hexafluorobenzene with sodium methoxide in methanol. Thus, in this nucleophilic attack the second methoxy group enters the nucleus of 2:3:4:5:6-pentafluoroanisole in the position *para* to the first methoxy group.

1 H-Heptafluorocyclohexa-1:4-diene (VI) was prepared as before[6] and also by treatment of the octafluoro-1:4-diene (I) with lithium aluminium hydride in diethyl ether, a reaction used previously[6] to replace fluorine on a double bond by hydrogen. With fuming sulphuric acid this diene gave trifluoro-*p*-benzoquinone (VII), which, however, could not be obtained pure. Direct reduction of the reaction mixture gave 2:3:5-trifluorohydroquinone (VIII), characterized as its dibenzoate. Oxidation of the quinol (VIII) gave the quinone (VII) but this was too unstable for complete characterization.

Attempts to prepare tetrafluoro-*o*-benzoquinone from octafluorocyclohexa-1:3-diene[3] were unsuccessful. Though reaction of the diene with sulphuric acid occurred, isolation of either a quinone, or of a dihydric phenol by direct reduction of the crude reaction product, could not be accomplished.

After this work was done, Professor Wallenfels informed us of the preparation of tetrafluoro-*p*-benzoquinone by treatment of tetrachloro-*p*-benzoquinone with potassium fluoride, and of its conversion to the quinol and to the dimethyl ether of the last. Our two samples of the dimethoxide and Wallenfels' sample proved to be identical, affording useful confirmation of all the structures. Publication of Wallenfels' results[7] has revealed a minor discrepancy concerning the hydrate of the hydroquinone. Also, he reported[8] the formation of a tetra(phenylamino) quinone when tetrafluoro-*p*-benzoquinone was treated with aniline, presumably under more drastic conditions than ours.

EXPERIMENTAL

2:3:5:6-*Tetrafluoro*-p-*benzoquinone*. Octafluorocyclohexa-1:4-diene (16·0 g) was heated with vigorous shaking in a sealed tube at 100° with fuming sulphuric acid (20% SO_3; 50 cc) for 1½–2 hr. The reaction mixture was poured onto crushed ice (ca. 500 g) and the resulting solution was extracted continuously with ether for 72 hr. The ethereal extracts were dried ($MgSO_4$), filtered and evaporated. The residue was dissolved in dry ether, the solution filtered and the ether evaporated. The residue was then oxidized with nitric acid (50% v/v; 50 cc), the resulting yellow precipitate filtered off, and purified by sublimation *in vacuo* to give 2:3:5:6-tetrafluorobenzoquinone (3·9 g), m.p. (sealed tube) 179°, (Found: C, 40·1; F, 41·9. Calc. for $C_6O_2F_4$: C, 40·0; F, 42·2%). Wallenfels and Draber[7] cited m.p. 179°.

The quinone (*c*. 0·00176 g/l. in n-hexane) showed two absorption maxima in the ultra-violet at 2465 Å and 2535 Å with ε_{max} 20,250 and 20,460 respectively. In the infra-red the compound showed a strong band at 1674 cm^{-1} characteristic of the quinone structure. The quinone was a volatile yellow crystalline solid with characteristic odour. It was a strong oxidizing agent, liberating iodine from potassium iodide and giving a deep violet colour with NN′-dimethylaniline. The fluorine atoms were extremely labile and treatment with very dilute alkali or organic bases liberated some fluoride ion.

Reaction of 2:3:5:6-*tetrafluorobenzoquinone with aniline*. The quinone (0·7 g), aniline (3 g) and dry

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[5] J. A. Godsell, M. Stacey and J. C. Tatlow, *Nature, Lond.* **178**, 199 (1956).

[6] J. A. Godsell, M. Stacey and J. C. Tatlow, *Tetrahedron* **2**, 193 (1958).

[7] K. Wallenfels and W. Draber, *Chem. Ber.* **90**, 2819 (1957).

[8] K. Wallenfels and W. Draber, *Angew. Chem.* 313 (1958).

ether (30 cc) were shaken together at 20° for 1 hr. The deep brown precipitate was filtered off and recrystallized from dimethyl formamide to give shining black crystals of 2:5-*dianilino*-3:6-*difluorobenzoquinone* (1·0 g) m.p. 312° (decomp) (Found: C, 66·1; H, 3·9; F, 11·3. $C_{18}H_{12}O_2N_2F_2$ requires: C, 66·3; H, 3·7; F, 11·6%). Wallenfels and Draber[8] for—cited m.p. 310° but their reaction with aniline (no details quoted) gave 2:3:5:6-tetra-anilinobenzoquinone.

Reduction of 2:3:5:6-*tetrafluorobenzoquinone.* Tetrafluoro-*p*-benzoquinone (1·5 g) in dry diethyl ether (50 cc) was shaken at room temp. and atm. press. with Raney nickel and hydrogen for ca. 16 hr. The Raney nickel was filtered off and the filtrate evaporated to give a white solid (0·7 g). The crude solid was recrystallized from dry benzene to give white needles of 2:3:5:6-*tetrafluorohydroquinone* m.p. 168–169° (Found: C, 39·7; H, 1·2. $C_6H_2O_2F_4$ requires: C, 39·6; H, 1·1%).

Wallenfels and Draber[7] cited m.p. 166–167° for a compound which they claimed was hydrated. The infra-red spectrum of the above hydroquinone, however, showed it to be anhydrous. The hydroquinone, on standing in the atmosphere or on preparation using undried solvents, had m.p. 68–70° and showed a band at ca. 1640 cm^{-1} in the infra-red characteristic of the presence of water.

The anhydrous hydroquinone (*c.* 0·0044 g/l. in ethanol) showed two absorption maxima in the ultra-violet at 2130 Å and 2720 Å with ε_{max} 10,280 and 1406 respectively. In the infra-red the compound showed a strong absorption band at 1520 cm^{-1} characteristic of an aromatic ring.

The hydroquinone (0·1 g), benzoyl chloride (0·2 g) and pyridine (5 cc) were heated together for 5 min and cooled. The solution was poured into water, the precipitate filtered off, and washed with dil HCl, sodium carbonate solution and finally with water. The crude white solid was dried and recrystallized from ethyl alcohol to give 2:3:5:6-*tetrafluorohydroquinone dibenzoate* m.p. 157–158° (Found: C, 61·7; H, 2·7. $C_{20}H_{10}O_4F_4$ requires: C, 61·6; H, 2·6%).

1:4-*Dimethoxytetrafluorobenzene.* 2:3:5:6-Tetrafluoro-*p*-benzoquinone (1·0 g) in dry ether (50 cc) was shaken at room temp. and press. with Raney nickel and hydrogen for 16 hr. The Raney nickel was filtered off and the solution added to an ethereal solution of diazomethane at 0°. The reaction mixture was kept at 0–5° for 12 hr and then at 20° for a further 48 hr. The solution was filtered, evaporated and the residue recrystallized from aqueous methyl alcohol to give fine white needles of 1:4-dimethoxytetrafluorobenzene (0·5 g) m.p. 51–52° (Found: C, 45·9; H, 2·8. Calc. for $C_8H_6O_2F_4$: C, 45·7; H, 2·9%). Godsell *et al.*[5] cited m.p. 51·5–52·5°. The m.p. of the compound in admixture with that of Godsell *et al.* was 52° and the two compounds displayed identical infra-red spectra over the range 4000–700 cm^{-1}. The 1:4-dimethoxytetrafluorobenzene showed a band at 1500 cm^{-1} characteristic of an aromatic ring.

Reaction of lithium aluminium hydride with octafluorocyclohexa-1:4-*diene.* The diene (11·2 g) in dry ether (60 cc) was added rapidly to a stirred suspension of lithium aluminium hydride (1·8 g) in dry ether (200 cc) at −80°. Water (20 cc) was immediately added (cautiously) followed by sufficient aqueous sulphuric acid (50% v/v) to dissolve any remaining solid material. The ether layer was separated, dried ($MgSO_4$), filtered and evaporated through a 6 in. column packed with nickel gauzes. Separation of the product by preparative-scale gas chromatography (16′ × 3 cm column, dinonyl phthalate/kieselguhr 1:2, temp 80°, N_2 flow-rate 9·6 l/hr) gave:— (i) ether which was allowed to escape: (ii) 1H-heptafluorocyclohexa-1:4-diene (4·3 g), b.p. 67°, n_D^{18} 1·3288 (Found: C, 35·2; H, 0·6. Calc. for C_6HF_7; C, 35·0; H, 0·5%). Tatlow *et al.*[4] cited b.p. 66·5–67° and n_D^{18} 1·3275.

Reaction of 1H-*heptafluorocyclohexa*-1:4-*diene with sulphuric acid.* 1H-Heptafluorocyclohexa-1:4-diene (9·0 g) and fuming sulphuric acid (20% SO_3; 20 cc) were heated together in a sealed tube with vigorous shaking at 100° for 1½ hr. The reaction mixture was then poured onto crushed ice (ca. 300 g), zinc metal (15·0 g) was added and the mixture heated under reflux for 5 hr. The solution was cooled and extracted continuously with ether for 48 hr. The ether extract was dried ($MgSO_4$), filtered and evaporated in the presence of stannous chloride (2 g). The residue was sublimed at 90°/0·05 mm to give 2:3:5-*trifluorohydroquinone* (2·8 g), a white hygroscopic solid, m.p. 112–113° (in sealed tube) (Found: C, 44·0; H, 1·9. $C_6H_3O_2F_3$ requires: C, 43·9; H, 1·8%). The hydroquinone gave a violet colour with ferric chloride solution.

The hydroquinone (*c.* 0·0048 g/l. in ethanol) showed an absorption maximum in the ultra-violet at 2750 Å with ε_{max} 2187. In the infra-red the hydroquinone showed an absorption band at ca. 1500 cm^{-1} characteristic of an aromatic ring.

The hydroquinone (0·2 g), benzoyl chloride (0·5 cc) and dil aq NaOH were shaken mechanically together at 20° for 30 min. The reaction mixture was extracted several times with ether. The combined ethereal extracts were washed with sodium carbonate solution, dil HCl, water and dried ($MgSO_4$).

The extracts were evaporated and the residue recrystallized from ethanol to give 2:3:5-*trifluorohydroquinone dibenzoate* m.p. 80° (Found: C, 64·4; H, 2·9. $C_{20}H_{11}O_4F_3$ requires: C, 64·5; H, 2·9%).

Oxidation of 2:3:5-*trifluorohydroquinone*. Silver oxide, chromic oxide and conc HNO_3 all failed to convert the hydroquinone to the quinone.

The trifluorohydroquinone (1·0 g) was shaken mechanically at 20° for 1 hr with activated lead dioxide (3·0 g) and magnesium sulphate (1·5 g) in ether (50 cc). The solution was filtered and evaporated. The residue was sublimed *in vacuo* (ca. 70°/0·05 mm) to give the trifluoroquinone (0·1 g). The quinone was a bright yellow, hygroscopic solid but rapid decomposition in the atmosphere prevented characterization.

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