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Complex Dibenzofurans

II *. Synthesis of 2,2′,3′,2″-Dioxido-*p*-terphenyl

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In a search for a convenient synthetic route to dioxidoterphenyls, Ebel's dibenzofuran synthesis was investigated. 2,2′,3′,2″-Dioxido-*p*-terphenyl (II) was obtained in good yield starting from the sodium salt of 4-hydroxydibenzofuran which reacted with 2-bromo*cyclo*hexanone to give the expected keto-ether. This was cyclised with polyphosphoric acid and the product dehydrogenated with palladium.

The dihydroxy-dioxidoterphenyl obtained by the action of strong sulphuric acid on *p*-benzoquinone has recently been related to similar polymerisation products from monoalkyl-*p*-benzoquinones [1]. These products have for obvious reasons been considered to be derivatives of *o*-terphenyl (Ia) [2] and the structure Ib has consequently been suggested for the phenolic terphenyl derivative from *p*-benzoquinone.

On zinc dust distillation the above *p*-benzoquinone polymerisation product gave a dioxidoterphenyl which accordingly should possess structure Ic. Other structures are of course theoretically possible and an unambigous synthesis of compound Ic is therefore a matter of interest.

Of the five theoretically possible dioxidoterphenyls, only two have been prepared by reliable methods, namely 2,2′, 5′,2″-dioxido-*p*-terphenyl [1,3,4] and 2,6′,4′,2″-dioxido-*m*-terphenyl [5]. During attempts to find convenient methods for the preparation of dioxidoterphenyls 2,2′,3′,2″-dioxido-*p*-terphenyl (II) has now been obtained.

Most of the methods of preparing dibenzofurans appear to be suitable for the synthesis of dioxidoterphenyls. The Pschorr synthesis (for a recent review see Ref.[6]) and the procedure of Ebel [7] seemed to be especially suitable since the starting material would already contain a dibenzofuran nucleus.

The possibility of using the Pschorr synthesis was investigated first. It was found impossible to prepare the intermediate ether from the sodium salt

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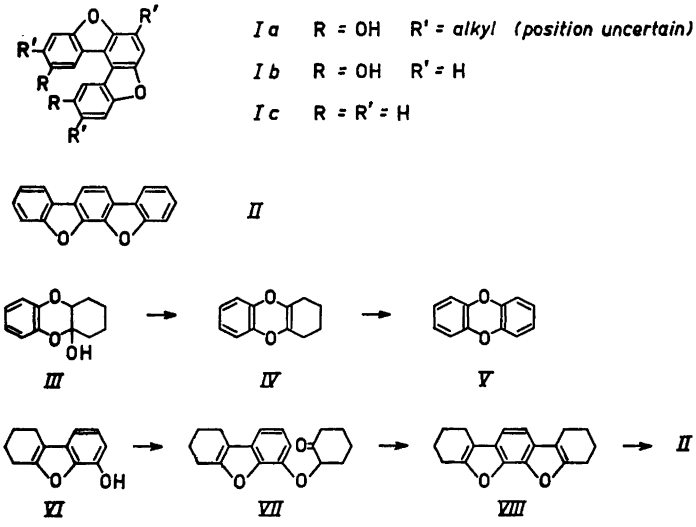
of 4-hydroxydibenzofuran and 2-bromonitrobenzene under sufficiently mild conditions (employing solvents as nitrobenzene, mono- and diglyme), since it was intended later to introduce a blocking bromine group in the dibenzofuran moiety. Blocking groups such as this have been used previously in the synthesis of phenanthrene derivatives in order to affect the direction of ring closure [2].

Ebel's dibenzofuran synthesis has recently been used in this laboratory for the preparation of 2,2′,5′,2″-dioxido-*p*-terphenyl from hydroquinone and 2-bromo*cyclo*hexanone [1].

The disodium salt of catechol reacted with 2-chloro*cyclo*hexanone to give a compound $C_{12}H_{14}O_3$. The infrared spectrum of this substance indicated the presence of a hydroxyl group, a benzene nucleus carrying four adjacent hydrogen atoms and methylene and aryl ether groups. The compound was therefore assumed to be 1,2,3,4-tetrahydro-4a-hydroxydibenzo-*p*-dioxin (III) and this was shown to be correct. Conversion of compound III by treatment with phosphorus oxychloride in pyridine yielded 1,2,3,4-tetrahydrodibenzo-*p*-dioxin (IV) (the position of the double bond in the hydroaromatic ring is slightly uncertain), which was dehydrogenated to dibenzo-*p*-dioxin (V). This was shown to be identical with an authentic specimen [8].

A successful synthesis of compound II was achieved as follows. 4-Hydroxy-6,7,8,9-tetrahydrodibenzofuran (VI) was easily prepared from the known methyl ether [7] by demethylation with hydrobromic acid. Its sodium salt reacted with 2-bromo*cyclo*hexanone to give 4-(2-keto*cyclo*hexyloxy)-6,7,8,9-tetrahydrodibenzofuran (VII). This substance was cyclised with polyphosphoric acid to give what must be 3,4,5,6,3″,4″,5″,6″-octahydro-2,2′,3′,2′-dioxido-*p*-terphenyl (VIII), which was then dehydrogenated to 2,2′,3′,2″-dioxido-*p*-terphenyl (II). This substance was not identical with the dioxidoterphenyl Ic.



A more convenient route to compound II started with the easily available 4-hydroxydibenzofuran [9], the sodium salt of which reacted with 2-bromo*cyclo*hexanone to give 4-(2-keto*cyclo*hexyloxy)-dibenzofuran (VII, left hand ring also aromatic) in a good yield. This keto-ether was cyclised to 3,4,5,6-tetrahydro-2,2',3',2''-dioxido-*p*-terphenyl (VIII, two rings aromatic). The position of the double bond in the hydroaromatic ring of these compounds (VIII, tetrahydro- and octahydro-) is almost certainly that indicated in formula VIII (*cf.* Ebel [7]). The tetrahydro-compound on dehydrogenation with palladium furnished 2,2',3',2''-dioxido-*p*-terphenyl (II).

This method seems to be of general applicability for the synthesis of dioxidoterphenyls and experiments aiming at the synthesis of compound Ic are now in progress.

EXPERIMENTAL

All melting points are uncorrected

1,2,3,4-Tetrahydro-4a-hydroxydibenzo-p-*dioxin (III).* Sodium (2.3 g) was dissolved in absolute ethanol (40 ml) and a solution of cathechol (5.5 g) in absolute ethanol (20 ml) was added with stirring under a stream of dry oxygen-free nitrogen. The alcohol was evaporated under reduced pressure, care being taken to avoid oxidation. The dry catechol sodium salt, 2-chloro*cyclo*hexanone [10] (14.0 g) and dry toluene (100 ml) were stirred and heated under reflux in an atmosphere of nitrogen for 3 h. The reaction mixture was allowed to cool to room temperature and was extracted with sodium hydroxide solution (10 %). The toluene layer was washed with water and saturated sodium chloride solution and then dried over magnesium sulphate. After evaporation of the toluene, the residue, a yellow oil, was thoroughly triturated with boiling light petroleum (400 ml). The petroleum extract was cooled to −40°, precipitating a greasy oil (crop A). The mother liquor was evaporated to a smaller volume (25 ml) and a crystalline material (crop B, 1.1 g) deposited. Crop B was purified by recrystallisation from *n*-pentane and sublimation *in vacuo* (90°, 20 mm), m.p. 104−105°. (Found: C 70.1; H 6.7; mol. wt. (Rast) 192. Calc. for $C_{12}H_{14}O_3$: C 69.9; H 6.8; mol. wt. 206.)

The infrared spectrum of compound III (KBr) was recorded on a Perkin-Elmer No 21 instrument using a sodium chloride prism. Relevant absorption maxima: 3 400 cm^{-1} (s), 3 000 cm^{-1} (w), 2 900 cm^{-1} (m,s), 1 600 cm^{-1} (m), 1 500 cm^{-1} (vs), 1 455 cm^{-1} (m) and 740 cm^{-1} (vs).

Crop A did not crystallise. Chromotography on neutral alumina yielded only a small amount of compound III, eluted with benzene. The desired product 1,2-di-(2-keto*cyclo*hexyloxy)-benzene could not be traced.

1,2,3,4-Tetrahydrodibenzo-p-*dioxin (IV).* 1,2,3,4-Tetrahydro-4a-hydroxydibenzo-*p*-dioxin (300 mg) was dissolved in dry pyridine (4 ml) and freshly distilled phosphorus oxychloride (1 ml) was cautiously added under stirring and cooling under the water tap. The mixture was stirred for three days at room temperature and was then poured into ice-water. The ether extract was washed with dilute hydrochloric acid and water. After drying over magnesium sulphate the solvent was evaporated and the somewhat oily reaction product (225 mg) was collected. The substance was purified by recrystallisation from absolute methanol and sublimation *in vacuo*, m.p. 61−62.5°. (Found: C 76.4; H 6.5. Calc. for $C_{12}H_{12}O_2$: C 76.6; H 6.4.)

Dibenzo-p-*dioxin (V).* Compound IV (40 mg) was thoroughly mixed with a palladium-charcoal catalyst (10 % Pd, 30 mg) and the mixture was heated to 230° for 5 h in an atmosphere of nitrogen. The reaction product was extracted with hot ethanol (15 ml). After evaporation of the alcohol, the residue (28 mg) was purified by sublimation *in vacuo* and recrystallisation from ethanol (0.5 ml). Yield of pure compound 4 mg, m.p. 117−120.5°. A mixed melting point with a sample of dibenzo-*p*-dioxin prepared according to Gilman [8] (m.p. 120.5−121.5°) showed no depression (m.p. 118−121°). The infrared spectra of the two samples were identical.

4-Hydroxy-6,7,8,9-tetrahydrodibenzofuran (VI). The starting material, 4-methoxy-6,7,8,9-tetrahydrodibenzofuran, was prepared according to Ebel [7] by cyclisation of 1-

methoxy-2-(2-keto*cyclo*hexyloxy)-benzene. The use of polyphosphoric acid as condensing agent instead of sulphuric acid as recommended by Ebel, did not increase the yield. The methyl ether (9 g) was stirred and heated under reflux with constant boiling hydrobromic acid (150 ml) for 12 h in an atmosphere of nitrogen. The reaction mixture was diluted with water (300 ml) and the crude product (8.2 g, violet due to superficial oxidation) was collected, thoroughly washed with water and dried. The substance was recrystallised from *cyclo*hexane and sublimed *in vacuo*. Yield 5.8 g, m.p. 117—118°. (Found: C 77.1; H 6.6. Calc. for $C_{18}H_{18}O_2$: C 76.6; H 6.4.)

*4-(2-Keto*cyclo*hexyloxy)-6,7,8,9-tetrahydrodibenzofuran (VII).* Sodium (0.7 g) was dissolved in absolute methanol (20 ml) and compound VI (5.6 g) in absolute methanol (20 ml) was added, care being taken to exclude moisture and air. The methanol was removed under reduced pressure and 2-bromo*cyclo*hexanone [11] (5.3 g) in dry benzene (125 ml) was added with mechanical stirring. The mixture was stirred at room temperature for 0.5 h and at reflux temperature for further 2 h; it was then extracted with dilute sodium hydroxide and water. The benzene solution was dried over magnesium sulphate and the solvent was evaporated under reduced pressure. The remaining brown oil (6.4 g) was chromatographed on neutral alumina. The fractions eluted with benzene-light petroleum mixtures were collected (3.0 g) and made to crystallise by scratching. The substance was purified by recrystallisation from ligroin and distillation *in vacuo*, m.p. 85—87°. (Found: C 75.9; H 7.0. Calc. for $C_{18}H_{20}O_2$: C 76.0; H 7.1.)

*3,4,5,6,3'',4'',5'',6''-Octahydro-2,2',3',2''-dioxido-*p*-terphenyl (VIII).* Compound VII (1.0 g) was stirred with a mixture of phosphorus pentoxide (15 g) and phosphoric acid (*d* 1.7, 30 ml) for 2 h at 100°. The hot reaction mixture was poured into water. The precipitate was collected, washed and dried. The yield almost quantitative. The product was recrystallised from *cyclo*hexane and sublimed *in vacuo*, m.p. 163—164°. (Found: C 81.6; H 6.8. Calc. for $C_{18}H_{18}O_2$: C 81.2; H 6.8.)

*2,2',3',2''-Dioxido-*p*-terphenyl (II) from compound VIII.* Compound VIII (50 mg) was mixed with a palladium-charcoal catalyst (10 % Pd, 50 mg) and the mixture was heated to 230° for 5 h in an atmosphere of nitrogen. The reaction product (30 mg) that sublimed on the cool parts of the reaction vessel was recrystallised from *cyclo*hexane. Two crystalline forms were observed (long needles which gradually changed to leaflets at ~ 179°), m.p. 180—183°. A mixed melting point with a sample of 2,2',3',2''-dioxido-*p*-terphenyl, synthesised as described below, showed no depression (m.p. 179—182°). The infrared spectra of the two samples were identical.

*4-(2-Keto*cyclo*hexyloxy)-dibenzofuran.* The sodium salt of 4-hydroxydibenzofuran [9] (prepared as described above from 1.2 g sodium and 9.2 g phenol), freshly distilled 2-bromo*cyclo*hexanone (9.0 g) and dry benzene (100 ml) were stirred at room temperature for 18 h and heated under reflux for additional 2 h. The reaction mixture was treated with dilute sodium hydroxide and the benzene extract was thoroughly washed with water and saturated sodium chloride solution and then dried over magnesium sulphate. After evaporation of the solvent the reaction product, colourless crystals (11.7 g), was recrystallised from ethanol and sublimed *in vacuo*, m.p. 142—142.5°. (Found: C 77.1; H 5.7. Calc. for $C_{18}H_{16}O_3$: C 77.1; H 5.8.)

*3,4,5,6-Tetrahydro-2,2',3',2''-dioxido-*p*-terphenyl.* The preceding substance (1.0 g) was stirred with a mixture of phosphorus pentoxide (10 g) and phosphoric acid (*d* 1.7, 20 ml) at 100° for 3 h. The reaction mixture was poured into water (250 ml) and the crystalline precipitate was collected, washed with water and dried. The substance (0.8 g) was recrystallised from *n*-butanol and sublimed *in vacuo*, m.p. 149—150°. (Found: C 82.7; H 5.4. Calc. for $C_{18}H_{14}O_2$: C 82.4; H 5.4.)

*2,2',3',2''-Dioxido-*p*-terphenyl (II).* The tetrahydrocompound (300 mg) was thoroughly mixed with a palladium-charcoal catalyst (10 % Pd, 200 mg) and heated to 230° for 5 h in an atmosphere of nitrogen. The reaction mixture was extracted with boiling *cyclo*hexane. The dioxido-*p*-terphenyl (200 mg) crystallised on cooling. Two crystal forms were observed, needles m.p. 178—179° which changed to leaflets m.p. 183—184°. The substance was purified for analysis by sublimation *in vacuo*. (Found: C 84.2; H 3.9. Calc. for $C_{18}H_{10}O_2$: C 83.7; H 3.9.)

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REFERENCES

1. Erdtman, H. and Stjernström, N. E. *Acta Chem. Scand.* **13** (1959) 653.
2. Erdtman, H. *Proc. Roy. Soc. London* **A 143** (1933) 228.
3. Schimmelschmidt, K. *Ann.* **566** (1950) 184.
4. Stjernström, N. E. *Acta Chem. Scand.* **14** (1960) 1274.
5. Stjernström, N. E. *Acta Chem. Scand. To be published.*
6. DeTar, D. F. *Org. Reactions* **9** (1957) 409.
7. Ebel, F. *Helv. Chim. Acta* **12** (1929) 3.
8. Gilman, H. and Stuckwisch, C. G. *J. Am. Chem. Soc.* **65** (1943) 1461.
9. Gilman, H., Cheney, L. C. and Willis, H. B. *J. Am. Chem. Soc.* **61** (1939) 951.
10. *Org. Syntheses Coll. Vol.* **3**, p. 188.
11. Allinger, J. and Allinger, N. L. *Tetrahedron* **2** (1958) 64.

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