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Complex Dibenzofurans

IV *. Syntheses of 2,6′,3′,2″-dioxido-*o*-terphenyl, 2,2′,4′,2″-dioxido-*m*-terphenyl and 2,6′,4′,2″-dioxido-*m*-terphenyl **

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Dedicated to Professor *Holger Erdtman* on his 60th birthday

A phenolic trimeride is obtained when *p*-benzoquinone is treated with acid. Elimination of the phenolic hydroxyl groups by zinc dust distillation affords a neutral compound for which structure II has previously been advanced. This assumption has now been shown to be correct by an unambiguous synthesis of compound II. The syntheses of the *m*-terphenyl derivatives VI and VIIId are described. The five dioxidoterphenyls, II, III, V, VI and VIIId have now been prepared by reliable methods.

A certain interest has recently been shown in compounds of the dioxidoterphenyl type in connection with, *e.g.*, brazanquinone vat dyes [1] and the chemistry of thelephoric acid [2,3], the structure of which has finally been elucidated by Gripenberg [4].

Our interest in compounds of this type stems from previous work with the polymerisation of *p*-benzoquinones. Termolecular coupling products are readily formed when *p*-quinones are treated with strong sulphuric acid [5]. The dihydroxydioxidoterphenyl obtained from *p*-benzoquinone has recently been investigated in this laboratory and structure I was proposed for this compound [6]. Elimination of the phenolic hydroxyl groups by zinc dust distillation gave a neutral product for which structure II was consequently suggested [6].

Other structures were, however, theoretically possible and an unambiguous synthesis of compound II seemed desirable. In the search for a general synthetic route to dioxidoterphenyls Ebel's method [7] was successfully employed for

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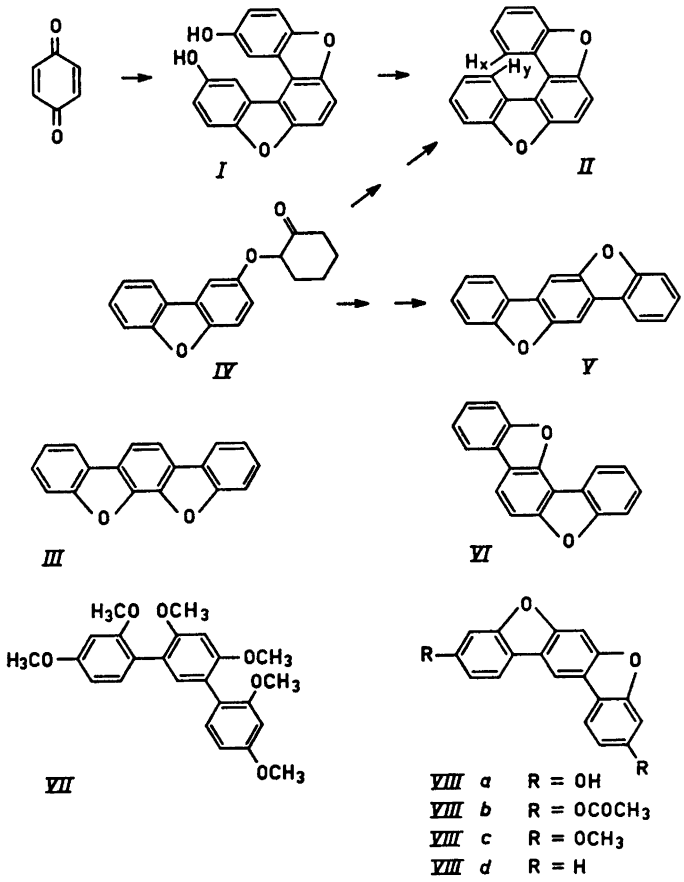

the preparation of 2,2′,3′,2″-dioxido-*p*-terphenyl (III)[8]. Compound II has now been prepared by this procedure.

The sodium salt of 2-hydroxydibenzofuran reacted with 2-bromo*cyclo*hexanone under anhydrous conditions to give 2-(2-keto*cyclo*hexyloxy)-dibenzofuran (IV). Cyclisation of this keto-ether was effected with polyphosphoric acid and a mixture of almost equal amounts of two compounds, A and B, was obtained. These were separated by chromatography on alumina. Compound A was dehydrogenated with palladium to 2,2′,5′,2″-dioxido-*p*-terphenyl (V), identical with an authentic specimen [6,9,10].

Compound A must therefore be 3,4,5,6-tetrahydro-2,2′,5′,2″-dioxido-*p*-terphenyl and B consequently 3,4,5,6-tetrahydro-2,6′,3′,2″-dioxido-*o*-terphenyl (condensation taking place at the 3- and 1-positions of the dibenzofuran moiety, respectively). When compound B was dehydrogenated with palladium it yielded 2,6′3′,2″-dioxido-*o*-terphenyl (II) identical with the above mentioned zinc dust distillation product from *p*-benzoquinone.

During the course of these synthetic experiments the PMR spectrum of the zinc dust distillation product in carbon tetrachloride was recorded at 40 Mc/s and was found to be in complete accordance with the proposed structure II. As only 60 mg of the substance was available at that time the signals were very weak and no fine structure could be observed. The spectrum contained two peaks with a relative intensity of 1:4. Both signals were found at lower fields than an internal *cyclo*hexane reference, the weaker at 268 c/s and the stronger at 240 c/s. As the total number of hydrogens in compound II is ten the PMR signals emanate from two and eight hydrogens, respectively. According to the ring current model [11] for the aromatic system one would expect the hydrogens x and y (II) to absorb at the lowest field. Taking steric interaction [12] into account it seems safe to assign the signal at 268 c/s to the hydrogens x and y (II) and the strong and fairly broad signal at 240 c/s to all the other hydrogens.

The positions of the hydroxyl groups in compound I have not been proved absolutely but considering the origin of the trimeride there can be little doubt about their situation.

Of the five theoretically possible dioxidoterphenyls only the two *m*-terphenyl derivatives VI and VIIId now remained unknown.

2,2′,4′,2″-Dioxido-*m*-terphenyl (VI) was prepared by Ebel's method. The starting material, 1-hydroxydibenzofuran, has previously been synthesised by a rather cumbersome procedure [13]. It was now prepared in the following way. 2-Iodoanisol and 2-iodoresorcinol dimethyl ether were subjected to a mixed Ullmann coupling in a ratio of 8:1 giving a mixture of 2,2′-dimethoxybiphenyl, 2,6,2′,6′-tetramethoxybiphenyl and 2,6,2′-trimethoxybiphenyl. This mixture on prolonged heating with conc. hydrobromic acid yielded 2,2′-dihydroxybiphenyl, 1,9-dihydroxydibenzofuran and 1-hydroxydibenzofuran. No attempt was made to isolate the two former compounds, they were removed from a solution of the reaction mixture in ether by extracting with sodium carbonate solution. The acidity of these two compounds is pronounced, probably due to intramolecular hydrogen bonding (*cf.* Refs.[14],[15]). 1-Hydroxydibenzofuran remained in the ether solution. The yield was about 40 % based on 2-iodoresorcinol dimethyl ether.

The sodium salt of 1-hydroxydibenzofuran reacted with 2-bromo*cyclo*hexanone to give 1-(2-keto*cyclo*hexyloxy)-dibenzofuran which was cyclised with polyphosphoric acid in the usual manner to 3,4,5,6-tetrahydro-2,2′,4′,2″-dioxido-*m*-terphenyl. This compound gave 2,2′,4′,2″-dioxido-*m*-terphenyl (VI) on dehydrogenation with palladium.

A method for preparing dioxido-*p*-terphenyl derivatives, based on dehydration of polyhydroxy-*p*-terphenyls with hydrobromic acid, has recently been developed in this laboratory [10]. This procedure was now successfully employed in the synthesis of 2,6′4′,2″-dioxido-*m*-terphenyl. The starting material, 2,4,4′,6′,2,″4″-hexamethoxy-*m*-terphenyl (VII) was obtained in good yield by a mixed Ullmann coupling of 4,6-diiodoresorcinol dimethyl ether and 4-iodoresorcinol dimethyl ether. It was easily converted to 4,4″-dihydroxy-2,6′,4′,2″-dioxido-*m*-terphenyl (VIIIa) by treatment with hydrobromic acid. The phenol VIIIa then furnished 2,6′,4′,2″-dioxido-*m*-terphenyl (VIIId) when subjected to distillation with zinc dust.

EXPERIMENTAL

All melting points are uncorrected.

2-(2-Ketocyclohexyloxy)-dibenzofuran (IV). Sodium (0.6 g) was dissolved in absolute methanol (20 ml) and 2-hydroxydibenzofuran (4.6 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-bromocyclohexanone [16] (4.5 g) in dry benzene (100 ml) was added with mechanical stirring. The mixture was stirred at room temperature for 0.5 h and at reflux temperature for a further 2 h; it was then extracted first with dilute sodium hydroxide and then with water. The benzene solution was dried over magnesium sulphate and the solvent evaporated under reduced pressure. The remaining slightly yellow oil (6.3 g) was dissolved in a small volume of methanol and crystallised on cooling to −30°. The precipitate (2.5 g) was collected and purified by recrystallisation from methanol and sublimation *in vacuo*, m.p. 107−108.5°. (Found: C 77.0; H 5.7. Calc. for $C_{18}H_{16}O_3$: C 77.1; H 5.8.)

Cyclisation of compound IV. 2-(2-Ketocyclohexyloxy)-dibenzofuran (IV, 1.0 g) was stirred with a mixture of phosphorus pentoxide (15 g) and phosphoric acid (*d* 1.7, 30 ml) for 3 h at 100°. The hot reaction mixture was poured into water. The precipitate (0.9 g, m.p. 95−117°) was collected, washed and dried. A sample (600 mg) was chromatographed on neutral alumina (150 g, column constructed in light petroleum). Two main fractions were obtained: the light petroleum eluate on evaporation gave compound B (265 mg) and the ether eluate gave compound A (271 mg).

Compound A. This substance was purified by recrystallisation from ethanol and sublimation *in vacuo*, m.p. 168−170°. (Found: C 81.9: H 5.6. Calc. for $C_{18}H_{14}O_2$: C 82.4; H 5.4.)

2,2',5',2''-Dioxido-p-terphenyl (V) from compound A. Compound A (50 mg) was thoroughly mixed with a palladium-charcoal catalyst (10 % Pd, 50 mg) and heated at 230° for 5 h in an atmosphere of nitrogen. The product (27 mg) sublimed on the cool walls of the reaction vessel and was purified by recrystallisation from acetic acid, m.p. 273−273.5°. A mixed melting point with a sample of 2.2',5',2''-dioxido-*p*-terphenyl [6,9,10] (m.p. 270.5−271.5°) showed no depression (m.p. 270.5−273°) and the infrared spectra of the two samples were identical. Compound A must therefore be 3,4,5,6-tetrahydro-2,2',5',2''-dioxido-*p*-terphenyl and compound B consequently 3,4,5,6-tetrahydro-2,6',3',2''-dioxido-*o*-terphenyl.

Compound B. 3,4,5,6-tetrahydro-2,6',3',2''-dioxido-o-terphenyl. This substance was purified by recrystallisation from ethanol and sublimation *in vacuo*, m.p. 125.5−126.5°. (Found: C 81.9; H 5.3. Calc. for $C_{18}H_{14}O_2$: C 82.4; H 5.4.)

2,6',3',2''-Dioxido-o-terphenyl (II). Compound B (25 mg) was thoroughly mixed with a palladium-charcoal catalyst (10 % Pd, 25 mg) and heated at 230° for 5 h in an atmosphere of nitrogen. The crude product (*ca.* 25 mg, m.p. 122−141°) sublimed on the cool walls of the reaction vessel and was purified by recrystallisation from acetic acid, m.p. 140−142.5°. A mixed melting point with a sample of the zinc dust distillation product, originating from *p*-benzoquinone [6], (m.p. 140−142.5°) showed no depression (m.p. 140−142.5°) and the infrared spectra of the two samples were identical.

1-Hydroxydibenzofuran. The 2-Iodoresorcinol dimethyl ether, used in this preparation, has been described by Adams *et al.*[17] It is, however, more easily synthesised *via* the lithium compound of resorcinol dimethyl ether (*cf.* the preparation of 3,5-dimethoxy-4-iodotoluene [18]). 2-Iodoresorcinol dimethyl ether (4.8 g), copper bronze (60 g) and 2-iodoanisol (35.5 g) were thoroughly mixed and heated to 220−240°, when a vigorous reaction started which raised the temperature to about 300°. After some minutes the reaction mixture was allowed to cool and the organic products were extracted with chloroform. After evaporation of the solvent a brown crystalline material remained. This was refluxed with hydrobromic acid (48 %, 250 ml) in an atmosphere of nitrogen for 40 h. The reaction mixture was allowed to cool and diluted with water. Ether was added and the ethereal extract washed with water, saturated sodium chloride solution, sodium carbonate solution (2 M) and finally dried over magnesium sulphate. After evaporation of the solvent the reaction product, a brown-red, somewhat oily crystalline material, was recrystallised from water (charcoal). The yield of 1-hydroxydibenzofuran was 1.4 g, m.p. 140−142° (lit.[13] m.p. 140−140.5°).

1-(2-Ketocyclohexyloxy)-dibenzofuran. The sodium salt of 1-hydroxydibenzofuran (prepared as described for 2-hydroxydibenzofuran from 100 mg sodium and 800 mg 1-hydroxydibenzofuran) and 2-bromocyclohexanone[16] (770 mg) in dry benzene (*ca.* 25 ml were stirred at room temperature for 0.5 h and at reflux temperature for an additional 2 h. The reaction mixture was worked up as described above for the preparation of 2-(2-ketocyclohexyloxy)-dibenzofuran (IV). The keto-ether (950 mg) was purified by recrystallisation from methanol, m.p. 138–139°. (Found: C 76.8; H 5.8. Calc. for $C_{18}H_{16}O_3$: C 77.1; H 5.8.)

3,4,5,6-Tetrahydro-2,2',4',2''-dioxido-m-*terphenyl.* 1-(2-Ketocyclohexyloxy)-dibenzofuran (200 mg) was treated with a mixture of phosphorus pentoxide (15 g) and phosphoric acid (*d* 1.7, 30 ml) in the same manner as described above for the cyclisation of compound IV. The conversion was almost quantitative and the product was purified by distillation *in vacuo* and recrystallisation from methanol, m.p. 107–108° (not sharp) (Found: C 82.3; H 5.4. Calc. for $C_{18}H_{14}O_2$: C 82.4: H 5.4.)

2,2',4',2''-Dioxido-m-*terphenyl (VI).* The above compound (90 mg) was thoroughly mixed with a palladium-charcoal catalyst (10 % Pd, 90 mg) and heated at 240° for 5 h in an atmosphere of nitrogen. Compound VI (*ca.* 50 mg) was isolated by extraction with ether. It was purified by recrystallisation from acetic acid and sublimation *in vacuo*, m.p. 169–170°. (Found: C 83.9; H 4.0. Calc. for $C_{18}H_{10}O_2$: C 83.7; H 3.9.)

2,4,4',6',2'',4''-Hexamethoxy-m-*terphenyl (VII).* 4,6-Diiodoresorcinol dimethyl ether (3.9 g, easily obtained from resorcinol dimethyl ether and an equivalent amount of iodine monochloride in acetic acid), copper bronze (35 g) and 4-iodoresorcinol dimethyl ether[10] were thoroughly mixed and heated to 240° when a vigorous reaction started. After some minutes the reaction mixture was allowed to cool to room temperature and extracted with chloroform in a Soxhlet apparatus. The solvent was evaporated and the residue distilled *in vacuo*. The combined products from three runs yielded resorcinol dimethyl ether (2 g), 2,4,2',4'-tetramethoxybiphenyl (22 g) and 2,4,4',6',2'',4''-hexamethoxy-*m*-terphenyl (VII) (7 g, b.p. *ca.* 300°, 1 mm). The terphenyl VII was purified by redistillation but could not be obtained crystalline. No attempt was therefore made to prepare an analytical sample and the product was demethylated directly.

4,4''-Dihydroxy-2,6',4',2''-dioxido-m-*terphenyl (VIIIa) and the corresponding diacetate (VIIIb) and dimethyl ether (VIIIc).* The terphenyl VII (3 g) was refluxed with hydrobromic acid (48 %, 60 ml) for 60 h in an atmosphere of nitrogen. The reaction mixture was allowed to cool to room temperature and the phenol (1.5 g, m.p. *ca.* 320°, decomp.), which was slightly bluish due to superficial oxidation, was collected and washed with water. This crude phenol was converted to the corresponding diacetate, 4,4''-diacetoxy-2,6',4',2''-dioxido-*m*-terphenyl, by acetylation with acetic anhydride and pyridine. The conversion was almost quantitative and the diacetate was purified by recrystallisation from chlorobenzene and sublimation *in vacuo*, m.p. 272–273°. (Found: C 70.2; H 3.9. Calc. for $C_{22}H_{14}O_6$: C 70.6; H 3.8.) The phenol was also methylated with dimethyl sulphate and sodium hydroxide to give a good yield of 4,4''-dimethoxy-2,6',4',2''-dioxido-*m*-terphenyl, which was purified by recrystallisation from chlorobenzene and sublimation *in vacuo*, m.p. 232.5–234°. (Found: C 75.3; H 4.3. Calc. for $C_{20}H_{14}O_4$: C 75.5; H 4.4.)

2,6',4',2''-Dioxido-m-*terphenyl (VIIId).* The preceding crude phenol (320 mg) was thoroughly mixed with zinc dust (10 g) in a test tube with an arrangement for the passage of gas. A brisk nitrogen stream was applied and the phenol-zinc dust mixture was heated to red heat. After only a few minutes the crude product (60 mg) could be collected from the cool walls of the test tube. This product was thoroughly washed first with dilute potassium hydroxide and then with water. The dry product was fractionally sublimed *in vacuo*. A fraction (20 mg), m.p. 219–227°, was collected and recrystallised from acetic acid. The analytical sample was purified by sublimation *in vacuo*, m.p. 229–231°. (Found: C 84.0; H 3.8. Calc. for $C_{18}H_{10}O_2$: C 83.7; H 3.9.)

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