

Complex Dibenzofurans

XIV.* An Investigation of the Acid-catalysed Demethylation and Dehydration of Some Tetramethoxyterphenyls

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The reactions of 2,4',6',2''-tetramethoxy-*m*-terphenyl (I), 2,2',5',2''-tetramethoxy-*p*-terphenyl (II), and 2,2',3',2''-tetramethoxy-*p*-terphenyl (III) with refluxing hydrobromic acid have been investigated. All three compounds were rapidly demethylated to the corresponding tetrahydroxyterphenyls, but only the polyphenol from compound II underwent facile dehydration to give first a dibenzofuran then a benzobisbenzofuran as the final product. Dehydration of the tetrahydroxy-*m*-terphenyl was sluggish, only a little of the benzobisbenzofuran being formed after prolonged reaction. No ring-closure product was formed from compound III. These observations are discussed in the light of the resonance structures of the reaction intermediates.

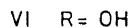
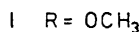
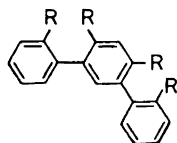
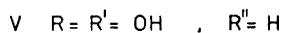
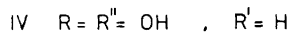
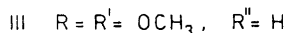
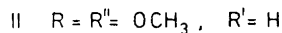
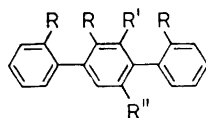
In previous papers in this series, the acid-catalysed demethylation and subsequent dehydration of substituted 2,2'-dimethoxybiphenyls has been investigated.¹⁻³ It was found that the dehydration step only proceeds readily in hydrobromic acid under reflux if resorcinol or hydroquinone groupings are present in at least one of the rings, whereas monophenolic and catechol groupings do not facilitate ring-closure.^{1,3} Furthermore, it was established that the hydroxyl group of the hydroquinone or resorcinol grouping, not that of the monohydroxy-substituted ring, is eliminated in the acid-catalysed dehydrations of 2,5,2'-trihydroxybiphenyl and 2,4,2'-trihydroxybiphenyl, respectively.²

In accordance with the observations on 2,2'-dimethoxybiphenyls, the reactions of suitably substituted polymethoxyterphenyls with refluxing hydrobromic acid afford benzobisbenzofurans or polyhydroxyterphenyls, depending on the substitution of the methoxyl groups in the rings.⁴⁻⁶ For example, hexamethoxy-*p*-terphenyls containing a hydroquinone grouping in the central ring and hydroquinone or suitable resorcinol groupings in the outer rings afford dihydroxybenzo[1,2-*b*:4,5-*b'*]bisbenzofurans with refluxing hydro-

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bromic acid, whereas 2,3,2',5',2'',3''-hexamethoxy-*p*-terphenyl and 2,3,4,2',5',2'',3'',4''-octamethoxy-*p*-terphenyl, containing catechol and pyrogallol groupings, respectively, in the outer rings, afford the corresponding polyhydroxy-*p*-terphenyls.^{4,5} As expected, 2,4,4',6',2'',4''-hexamethoxy-*m*-terphenyl, containing resorcinol groupings in all three rings, affords 3,9-dihydroxybenzo[1,2-*b*:5,4-*b'*]bisbenzofuran under the reaction conditions.⁶

It was considered it to be of interest to study the acid-catalysed demethylation and dehydration of some tetramethoxyterphenyls, in which the outer rings were monosubstituted and the central ring disubstituted. Three compounds were chosen, 2,4',6',2''-tetramethoxy-*m*-terphenyl (I), 2,2',5',2''-tetramethoxy-*p*-terphenyl (II), and 2,2',3',2''-tetramethoxy-*p*-terphenyl (III), in which the central ring contains resorcinol, hydroquinone, and catechol groupings, respectively.



The compounds were prepared by mixed Ullmann couplings between excess 2-iodoanisole and a suitable diiododimethoxybenzene. In order to prepare compound III, the previously unknown 3,6-diiodoveratrole was required. This compound could be obtained in 60 % yield from 3,6-diaminoveratrole, prepared in a several step synthesis essentially according to the method of Oxford,⁷ by bis-diazotizing and treating the diazonium solution with potassium iodide. However, a more direct method was to metallate veratrole with excess butyllithium in the presence of *N,N,N',N'*-tetramethylethylenediamine⁸ (TMEDA) and to iodinate the product. Although the required compound was formed in only 2 % yield, it was easily isolated by chromatography on silica.

The course of the reactions of the compounds I–III with refluxing 48 % hydrobromic acid was followed by means of thin layer chromatography. In the reaction of 2,4',6',2''-tetramethoxy-*m*-terphenyl (I), demethylation was complete within 1 h and only one phenol was detected after this time. On working up the reaction mixture after 1 h, 2,4',6',2''-tetrahydroxy-*m*-terphenyl (VI) was obtained. If the reaction was allowed to continue, another phenol was detectable within 2 h. This gradually increased in amount as the reaction proceeded, and a non-phenolic compound could be detected after 3 days. On working up the reaction mixture after 4 days, the main products were the

tetrahydroxy-*m*-terphenyl (VI) and 2-(2'-hydroxyphenyl)-3-hydroxydibenzofuran (VII). A small amount of benzo[1,2-*b*:5,4-*b'*]bisbenzofuran (VIII) was also obtained. Demethylation of 2,2',5',2''-tetramethoxy-*p*-terphenyl (II) was also complete within 1 h. After this time, TLC showed the presence of two phenols, one giving rise to an intense spot and the other to a faint spot. On working up the reaction mixture, 2,2',5',2''-tetrahydroxy-*p*-terphenyl (IV) having the same R_F value as the intense spot could be isolated and identified as the tetraacetate. On allowing the reaction to proceed, a non-phenolic compound was detected after 2 h. The amount of compound IV in the reaction mixture appeared to decrease, while that of the other two compounds increased for some time, but then the other phenol also decreased in amount and after 70 h, only the non-phenolic compound was detected. On working up the reaction mixture after this time, benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (X) was obtained. The phenol giving rise to the faint spot could be isolated by preparative TLC following work up of the reaction mixture after 48 h. It proved to be 3-(2'-hydroxyphenyl)-2-hydroxydibenzofuran (IX). The reaction with 2,2',3',2''-tetramethoxy-*p*-terphenyl (III) gave 2,2',3',2''-tetrahydroxy-*p*-terphenyl (V) as the final product, and was complete within 1 h.

In the reaction of compound II, double ring-closure to the benzobisbenzofuran occurs readily, the dibenzofuran being an intermediate. This reaction may be expected to take place *via* protonation of the ring containing the hydroquinone grouping in analogy with previous results.³ The proposed reaction mechanism is outlined in Fig. 1.

The ring-closure reaction of compound I is apparently sluggish, double ring-closure to the benzobisbenzofuran being particularly retarded. According to the expected reaction mechanism (Fig. 2), protonation at the 5'-position

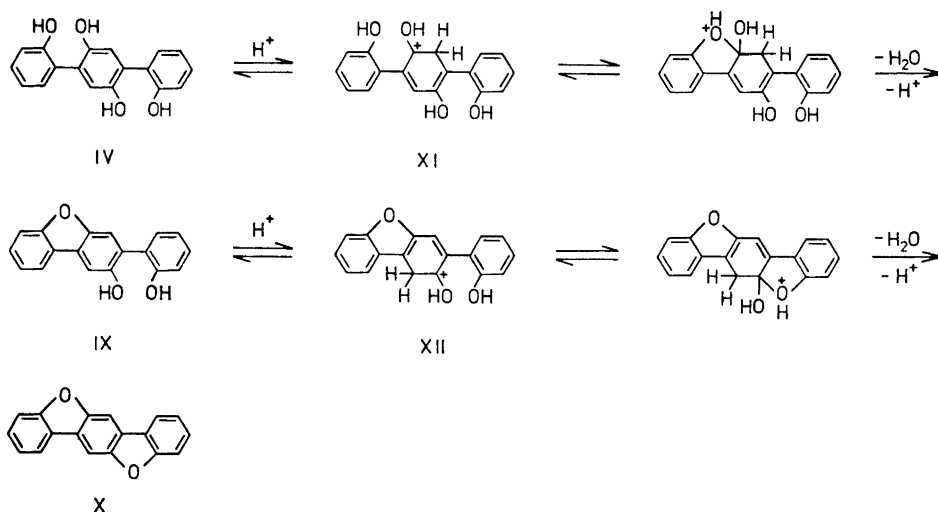


Fig. 1. Proposed mechanism for the acid-catalysed dehydration of 2,2',5',2''-tetrahydroxy-*p*-terphenyl₁ (IV) to 3-(2'-hydroxyphenyl)-2-hydroxydibenzofuran (IX) and benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (X).

of the central ring is necessary to lead to ring closure. Comparison of the protonated intermediates XI and XII (Fig. 1) on the one hand and XIII and XIV (Fig. 2) on the other reveals that only XI and XII can have additional resonance forms due to conjugation with a 2-hydroxyphenyl group. Thus intermediates XI and XII should be more stable than XIII and XIV, respectively, and their formation should be more favoured. Consequently, the activation energies of the two ring-closure steps in the reaction of 2,2',5',2''-tetrahydroxy-*p*-terphenyl (IV) with refluxing hydrobromic acid should be lower than those of the corresponding ring closure steps in the reaction of 2,4',6',2''-tetrahydroxy-*m*-terphenyl (VI). Thus the former tetrahydroxyterphenyl should react more rapidly, this being in agreement with the experimental findings.

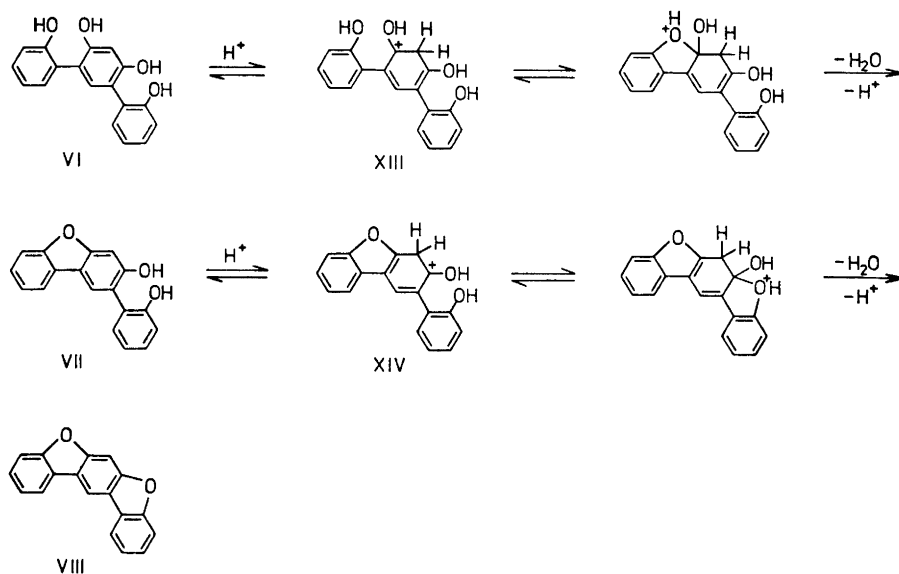


Fig. 2. Proposed mechanism for the acid-catalysed dehydration of 2,4',6',2''-tetrahydroxy-*m*-terphenyl (VI) to 2-(2'-hydroxyphenyl)-3-hydroxydibenzofuran (VII) and benzo-[1,2-b:5,4-b']bisbenzofuran (VIII).

That no ring-closure product is obtained with compound III may be expected in accordance with previous observations on polyhydroxybiphenyls and polyhydroxyterphenyls containing catechol groupings.^{1,3,5} However, it is interesting to note that there is a possibility of stabilization of the intermediate arising by protonation of compound V in the 5'-position, in the same way as intermediate XI is stabilized by the 2-hydroxyphenyl group in the 4'-position. In spite of this extra possibility of stabilization, no ring-closure occurs indicating the reason that catechol groupings do not facilitate the reaction is not due to instability of the requisite protonated intermediate. Recent evidence suggests that a stabilizing interaction between the *ortho*-hydroxyl groups best explains this lack of reactivity.

EXPERIMENTAL

All melting points are uncorrected. NMR spectra were measured on a Varian T-60 Spectrometer operating at 60 Mc/s with TMS as internal standard. Low resolution mass spectra were recorded on an LKB 9000 mass spectrometer operating at 70 eV and the high resolution mass spectrum on a Varian SM 1 instrument. IR spectra were recorded on a Perkin-Elmer Model 457 Infrared Spectrophotometer. Microanalyses were carried out at the Department of Analytical Chemistry, University of Lund or at the Microanalysis Laboratory, Lantbrukshögskolan, Uppsala.

2,4',6',2''-Tetramethoxy-m-terphenyl (I). A mixture of 2-iodoanisole (20.0 g) and 4,6-diiodoresorcinol dimethyl ether (3.9 g) with copper bronze (35 g) was heated to 220° whereupon an exothermic reaction occurred and the temperature rose to 270°. After cooling, the mixture was extracted in a soxhlet with chloroform. After removal of the solvent under reduced pressure, most of the 2,2'-dimethoxybiphenyl present was removed by distillation (b.p. 166–8°/10 mm) and the remaining material chromatographed on 160 g standardized aluminium oxide (Merck) deactivated by addition of 5 % water, the column being constructed in cyclohexane. Elution was carried out using a cyclohexane-benzene gradient. The fractions giving a spot R_F 0.39 on TLC (Merck Aluminiumoxid F₂₅₄) with benzene as moving phase were combined and the solvent removed. After two recrystallizations of the solid residue from cyclohexane-benzene, 1.01 g of crystalline product, m.p. 181.5–183° remained. Yield 29 %. NMR (CDCl₃): τ 2.5–3.2 (m, 9 H), 3.36 (s, 1 H), 6.19 (s, 6 H), 6.23 (s, 6 H). [Found: C 75.4; H 6.30; mol. wt. 350 (mass spectrometry). Calc. for C₂₂H₂₂O₄: C 75.4; H 6.33; mol. wt. 350.4.]

2,4',6',2''-Tetrahydroxy-m-terphenyl (VI). Compound I (100 mg) was heated under reflux for 1 h with a mixture of 10 ml 48 % hydrobromic acid and 10 ml glacial acetic acid under argon. After cooling, the reaction mixture was poured into water and extracted with ether. The ether phase was washed with saturated sodium bicarbonate solution and water, then dried over sodium sulphate. After removal of solvent, the residue was recrystallized twice from chlorobenzene giving 60 mg product, m.p. 185–186° (after sublimation *in vacuo*). [Found: C 73.2; H 4.76; mol. wt. 294 (mass spectrometry). Calc. for C₁₈H₁₄O₄: C 73.4; H 4.79; mol. wt. 294.3.]

2-(2'-Hydroxyphenyl)-3-hydroxydibenzofuran (VII). Compound I (250 mg) was heated under reflux for 96 h with a mixture of 15 ml 48 % hydrobromic acid and 15 ml glacial acetic acid under argon. The reaction mixture was poured into water (100 ml) and extracted with ether (3 × 30 ml). After washing the ether phase with saturated sodium bicarbonate solution and water and drying over sodium sulphate, the solvent was removed and the residue chromatographed on 25 g silica (Mallinckrodt SilicAR CC 4 100–200 mesh), the column being constructed in benzene and elution being performed with a benzene-ethyl acetate gradient. Three compounds were isolated, the first being benzo-[1,2-b:5,4-b']bisbenzofuran (VIII) (13 mg, 7 %), m.p. 229–231° after two recrystallizations from glacial acetic acid (lit.⁶ m.p. 229–231°). The second compound eluted (65 mg, 33 %) was recrystallized once from cyclohexane and twice from aqueous acetic acid giving the required product m.p. 150–151°. [Found: C 77.9; H 4.41; mol. wt. 276 (mass spectrometry). Calc. for C₁₈H₁₂O₃: C 78.2; H 4.38; mol. wt. 276.3.] The third compound eluted (92 mg, 44 %), m.p. 184–185° after recrystallization from chlorobenzene, was identical with compound VI (no depression of m.p. on admixture).

2,2',5',2''-Tetramethoxy-p-terphenyl (II). A mixture of 2-iodoanisole (20.0 g) and 2,5-diiodohydroquinone dimethyl ether (3.9 g) with copper bronze (35 g) was heated to 215°. An exothermic reaction occurred, the temperature rising to 280°. After cooling, the residue was extracted with chloroform in a soxhlet. After removal of the solvent, the residue was distilled *in vacuo*. A fraction, b.p. 200–210°/0.02 mm (1.3 g) was collected and recrystallized twice from acetic acid giving 1.1 g, 31 %, m.p. 184.5–186°. An analytical sample was prepared by chromatographing 220 mg of this material on 20 g standardized aluminium oxide (Merck) deactivated with 5 % water, benzene being used as eluent. Fractions giving a spot R_F 0.42 on TLC (Merck Aluminiumoxid F₂₅₄) with benzene as moving phase were combined and the solvent removed giving a residue which was recrystallized from benzene-cyclohexane, m.p. 184.5–186°. NMR (CDCl₃): τ 2.4–3.1 (m, 8 H), 3.08 (s, 2 H), 6.19 (s, 6 H), 6.28 (s, 6 H). [Found: C 75.8; H 6.31; mol. wt. 350 (mass spectrometry). Calc. for C₂₂H₂₂O₄: C 75.4; H 6.33; mol. wt. 350.4.]

2,2',5',2''-Tetrahydroxy-p-terphenyl (IV). Compound II (100 mg) was heated under reflux for 1 h with a mixture of 10 ml 48 % hydrobromic acid and 10 ml glacial acetic acid under argon. After cooling, the reaction mixture was poured into water and extracted with ether. The ether phase was washed with saturated sodium bicarbonate solution and water, then dried over sodium sulphate. After removal of the solvent, the residue was recrystallized from chlorobenzene giving 65 mg product, m.p. 231–233° (after sublimation *in vacuo*). [Found: mol. wt. 294 (mass spectrometry). Calc. mol. wt. 294.3.] The crystals became bluish-coloured on exposure to air due to superficial oxidation and the compound was therefore converted to *2,2',5',2''-tetraacetoxy-p-terphenyl* by acetylation with acetic anhydride in pyridine. The crude acetate was chromatographed on Merck Kieselgel 60 deactivated with 15 % water, the column being constructed in benzene and a benzene-isopropyl ether gradient being used as eluent. Fractions giving a spot R_F 0.29 on TLC (Merck Kieselgel F₂₅₄) with isopropyl ether as moving phase were combined and solvent removed giving the required compound, which was recrystallized twice from cyclohexane and once from ethanol giving a product m.p. 126.5–127.5°. NMR (CCl₄): τ 2.4–3.0 (m, 8 H), 2.99 (s, 2 H), 7.98 (s, 6 H), 8.03 (s, 6 H). IR (KBr): $\nu_{C=O}$ 1762 cm⁻¹. [Found: C 66.9; H 4.90; mol. wt. 462 (mass spectrometry). Calc. for C₂₆H₂₂O₈: C 67.5; H 4.80; mol. wt. 462.5.] The mass spectrum showed the presence of an impurity corresponding to the tetraacetate substituted with one bromine atom M⁺, m/e 540 (rel. int. to m/e 462, 1.3 %) and m/e 542 (rel. int. to m/e 462, 1.3 %). This impurity was not removed by recrystallization.

Benzo[1,2-b:4,5-b']bisbenzofuran (X). Compound II (200 mg) was heated under reflux for 72 h with 20 ml 48 % hydrobromic acid and 20 ml glacial acetic acid under argon. After cooling the reaction mixture, the solid product was removed by filtration, washed with water and triturated with ethyl acetate. After washing the ethyl acetate solution with 2 N sodium hydroxide solution and water, it was dried over sodium sulphate. Removal of the solvent afforded 33 mg product (m.p. 263–265° after sublimation *in vacuo*) (lit.⁴ m.p. 265.5–266.5°). Yield 22 %. The alkaline washings afforded no residue on acidification, extracting with ether and removal of the solvent. However, there was a considerable trituration residue of black, presumably polymeric, material.

3-(2'-Hydroxyphenyl)-2-hydroxydibenzofuran (IX). Compound II (100 mg) was heated under reflux for 48 h with a mixture of 10 ml 48 % hydrobromic acid and 10 ml glacial acetic acid under argon. After cooling, the reaction mixture was poured into water and extracted with ether. The ether solution was washed with saturated sodium bicarbonate solution and water, then dried over sodium sulphate. The solution gave 4 spots on a TLC plate (Merck Kieselgel F₂₅₄) with acetic acid-ethyl acetate-petroleum ether (1:2:7) as moving phase. These had R_F values 0.0, 0.30 (corresponding to compound IV), 0.55, and 0.80 (corresponding to compound X). The first three spots gave a positive phenolic reaction with bis-diazotized benzidine while the fourth was observable in short wave UV light. On removal of the solvent from the ether solution, 70 mg residue remained. This was chromatographed on two 20 × 20 cm preparative TLC plates (Merck PSC Fertigplatten, Kieselgel F₂₅₄) using the same moving phase as with analytical TLC. The material corresponding to the spot R_F 0.55 was extracted from the silica with chloroform. On removal of the solvent, ca. 4 mg crystalline residue remained which was sublimed *in vacuo*, m.p. 137–141°. (High resolution mass spectrometry: M⁺, m/e 276.0784. Calc. for C₁₈H₁₂O₃: m/e 276.0786.)

3,6-Diiodoveratrole. Method 1. 3,6-Diaminoveratrole dihydrochloride⁷ (0.60 g, 2.5 mmol) was bis-diazotized according to the method of Schoutissen¹⁰ by dissolving in 8.75 ml 85 % orthophosphoric acid and stirring at –5° while adding dropwise a solution of sodium nitrite (0.38 g, 5.5 mmol) in 3.8 ml 98 % sulphuric acid. After stirring at –5° for 30 min, 0.26 g urea was added to destroy excess nitrous acid. The solution was then added to a solution of potassium iodide (1.30 g, 6.0 mmol) in a minimum volume of ice-cold water. After 4 h, the mixture was diluted with water, extracted with chloroform and the organic phase washed with saturated sodium bisulphite solution and water, then dried over magnesium sulphate. After removal of the solvent, the residue (0.81 g) was chromatographed on a column of 25 g silica (Merck 0.05–0.20 mm) packed in cyclohexane. Elution was carried out using a cyclohexane-benzene gradient. The fractions giving a spot R_F 0.55 on TLC (Merck Kieselgel F₂₅₄) with isopropyl ether as moving phase were combined and the solvent removed giving a colourless oil, which was crystallized from ethanol giving 0.58 g product. Yield 59 %, m.p. 45.5–47° (after recrystalliza-

tion from aqueous ethanol). NMR (CDCl₃): τ 2.77 (s, 2 H), 6.13 (s, 6 H). (Found: C 25.0; H 1.94; I 64.4. Calc. for C₈H₆I₂O₂: C 24.6; H 2.07; I 65.1.)

Method 2. A solution of TMEDA (14.52 g, 0.125 mol) in 25 ml dry heptane was added to 66 ml of 1.9 M butyllithium (0.125 mol) in hexane under argon. A pale yellow precipitate formed and to the stirred suspension, a solution of veratrole (6.91 g, 0.050 mol) in 25 ml dry heptane was added. After stirring at room temperature for 20 h, the suspension was added during 1 h to a stirred mixture of iodine (38.1 g, 0.150 mol) and 100 ml dry heptane at -70° under argon. The mixture was stirred for 22 h during which time the temperature was allowed to rise to 10°. After addition of 50 ml water, the organic phase was separated and the aqueous phase extracted with ethyl acetate. The combined organic phases were washed with sodium bisulphite solution and water, then dried over magnesium sulphate. On removal of the solvent, 10.3 g residue remained which was chromatographed on a column of 200 g silica (Merck 0.05–0.20 mm) packed in cyclohexane. Elution was carried out as in method 1. Evaporation of the fractions containing the required product afforded a colourless oil which gave 0.35 g crystals on crystallization from aqueous ethanol, m.p. 45–46.5° after recrystallization. Yield 2.0%. There was no depression of m.p. on admixture with the product of method 1.

2,2',3',2''-Tetramethoxy-p-terphenyl (III). A mixture of 3,6-diiodoveratrole (0.39 g) and 2-iodoanisole (2.34 g) with copper bronze (3.5 g) was heated to 220° whereupon an exothermic reaction occurred and the temperature rose to 280°. After allowing to cool, the residue was extracted in a soxhlet with chloroform. After removal of the solvent, the residue was distilled *in vacuo* and the fraction b.p. 170–200°/0.015 mm (0.33 g) collected and chromatographed on a column of 20 g aluminium oxide (Merck, standardized) deactivated with 5% water. The column was constructed in cyclohexane and elution carried out with a cyclohexane-benzene gradient. Fractions giving a spot R_F 0.50 on TLC (Merck Aluminium oxide F₂₅₄) with benzene as moving phase were combined and the solvent removed giving an oil which was crystallized from ethanol giving 0.11 g, m.p. 98–100° (after recrystallization from ethanol). Yield 31%. NMR (CDCl₃): τ 2.6–3.3 (m, 10 H), 6.24 (s, 6 H), 6.40 (s, 6 H). [Found: C 75.1; H 6.41; mol. wt. 350 (mass spectrometry). Calc. for C₂₂H₂₂O₄: C 75.4; H 6.33; mol. wt. 350.4.]

2,2',3',2''-Tetrahydroxy-p-terphenyl (V). Compound III (10 mg) was heated under reflux for 2 h with 1 ml glacial acetic acid and 1 ml 48% hydrobromic acid under argon. After cooling, the mixture was diluted with 10 ml water, extracted with ether and the ether phase washed with saturated sodium bicarbonate solution and water, then dried over sodium sulphate. After removal of solvent, 8 mg residue remained, m.p. 166–168° (after recrystallization from toluene). On subliming *in vacuo*, crystals, m.p. 225–226°, were obtained. Both samples gave one spot, R_F 0.17 (red-brown colouration with bis-diazotized benzidine), on TLC (Merck Kieselgel F₂₅₄) with acetic acid–ethyl acetate–petroleum ether (1:2:7) as moving phase. On melting the material with the lower m.p., seeding with material with the higher m.p., allowing to solidify and remelting, the m.p. rose to 225–226° indicating the two samples to be dimorphic crystalline forms of the same compound. [Found: C 73.1; H 4.80; mol. wt. 294 (mass spectrometry). Calc. for C₁₈H₁₄O₄: C 73.4; H 4.79; mol. wt. 294.3.]

Demethylation and dehydration experiments followed by thin layer chromatography

General procedure. The tetramethoxyterphenyl (10 mg) was heated under reflux with a mixture of 1 ml 48% hydrobromic acid and 1 ml glacial acetic acid under argon, the bath temperature being 140°. Samples (0.1 ml) were withdrawn from the reaction mixture at certain intervals (0, 1, 2, 5, 10, 15, 30 min, 1, 1.5, 2, 3, 5, 8, 24, 48, 72, 96 h with some variations), diluted to 1 ml with water and extracted with 0.2 ml ether. An aliquot (20 μ l) of each ether solution was applied to a TLC plate (Merck Kieselgel F₂₅₄, 20 × 20 cm) and the plate developed with acetic acid–ethyl acetate–petroleum ether (1:2:7) as moving phase. The chromatograms were investigated in UV light before spraying with bis-diazotized benzidine.

Reaction of 2,4',6',2''-tetramethoxy-m-terphenyl (I). After only 2 min, five spots coloured by bis-diazotized benzidine could be detected. Only one of these remained after

1 h, and corresponded to 2,4',6',2''-tetrahydroxy-*m*-terphenyl (VI) (R_F 0.21). Another phenolic compound, R_F 0.50 (corresponding to compound VII), was detected after 1.5 h. After 72 h, a third spot (R_F 0.73) visible in UV, but not giving a positive phenolic reaction appeared. This corresponds to benzo[1,2-*b*:5,4-*b'*]bisbenzofuran (VIII). After 96 h, the main spots were those due to compounds VI and VII.

Reaction of 2,2',5',2''-tetramethoxy-p-terphenyl (II). After 1 min, four spots giving a positive phenolic reaction were observable. One of these remained after 1 h and corresponded to 2,2',5',2''-tetrahydroxy-*p*-terphenyl (IV) (R_F 0.30). A faint spot R_F 0.55, corresponding to compound IX, had appeared after 30 min. After 2 h, a spot not giving a positive phenolic reaction was detected (R_F 0.80). This corresponded to benzo[1,2-*b*:4,5-*b'*]bisbenzofuran (X). As the reaction proceeded, the spot R_F 0.30 decreased in intensity while that with R_F 0.80 increased in intensity. The spot R_F 0.55 increased in intensity at first, but appeared to remain constant after *ca* 5 h, then became weaker again after 48 h until only the spot at R_F 0.80, together with a spot R_F 0.0, remained after 72 h.

Reaction of 2,2',3',2''-tetramethoxy-p-terphenyl (III). After 5 min, five spots coloured by bis-diazotized benzidine were detected. After 1 h, only one spot remained, R_F 0.21, corresponding to 2,2',3',2''-tetrahydroxy-*p*-terphenyl (V). No other spots had been formed after 43 h.

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