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THE ACID-CATALYSED OLIGOMERISATION OF *p*-BENZOQUINONE

HOLGER ERDTMAN and HANS-ERIK HÖGBERG
Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden

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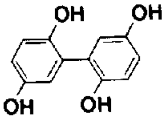
Abstract—*p*-Benzoquinone is transformed by mineral acids into a series of complex dibenzofuran derivatives. The phenolic trimer **5a** is the dominant crystalline species. Small amounts of a helical tetrameric phenol (**11**) and a non-phenolic, cyclic tetramer the furo-[8]-circulene (**6a**) are also formed together with compounds of higher molecular weight. The furan rings are not generated by dehydration of 2,2'-dihydroxybiphenyl elements. A mechanism involving quinone hemiketals is suggested.

It was early observed that many quinones are unstable in the presence of strong acids. Examples are β-naphthoquinone,[1] toluquinone[2,3] and methoxyquinone,[3] which readily dimerise giving crystalline dihydroxybiphenylquinones. In contrast, *p*-benzoquinone gives large amounts of highly coloured, amorphous products.[4]

In the early literature there are also reports[4,5] of the formation of colourless, crystalline, high-melting products, apparently derived from more than two quinone molecules, but these were not further investigated because of poor yields or of difficulties in isolation and characterisation.

During studies on oxidative phenol coupling one of us (H.E.) long ago subjected some of these products to a brief examination.[6]



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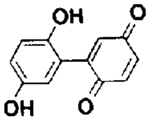

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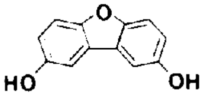

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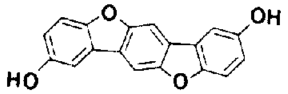

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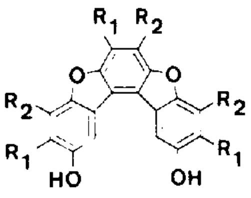
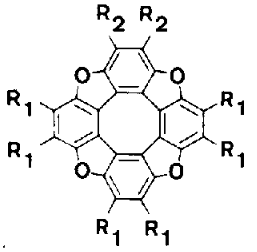
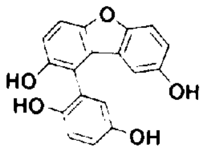


5a: $R_1 = R_2 = H$
5b: $R_1 + R_2 = (CH)_4$
5c: $R_1 = CH_3; R_2 = H$



6a: $R_1 = R_2 = H$
6b: $R_1 + R_1 = R_2 + R_2 = (CH)_4$
6c: $R_1 + R_1 = (CH)_4; R_2 = H$



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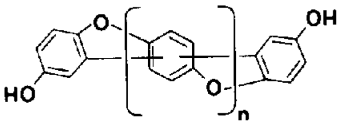

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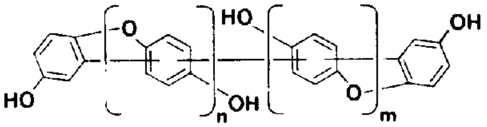

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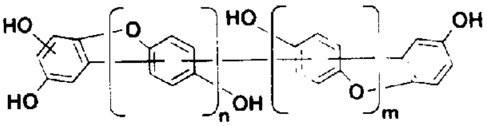

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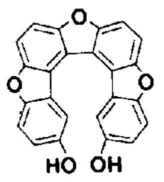

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Unexpectedly it was found that the diacetate of a colourless trimer, $C_{18}H_8O_2(OH)_2$ can be isolated from the intractable benzoquinone product by reductive acetylation. The yield was low.

Toluquinone furnished a better yield of an analogous phenol $C_{21}H_{14}O_2(OH)_2$. α-Naphthoquinone gave large yields of a mixture of a phenol $C_{30}H_{14}O_2(OH)_2$ and a non-phenolic compound $(C_{10}H_4O)_n$ which was characterised by its extremely low solubility and high thermal stability.

It was suggested that the benzoquinone product might possess the linear structure **4**. The phenol from α-naphthoquinone was assigned the structure **5b** and a similar angular structure was assumed for the toluquinone product.

At that time the molecular weight of the neutral compound from α-naphthoquinone could not be determined. Shortly afterwards Marschalk[7] discovered that it is obtained in about 90% yield simply by treating the quinone with aluminium chloride in nitrobenzene.

These quinone studies were later resumed, particularly with Stjernström[8] and the present co-author on whose thesis[9] this paper is partly based. The phenol from p-benzoquinone was shown to possess the isomeric angular structure **5a**.[10] The main product from toluquinone has the structure **5c**.[11] The molecular weight of the neutral α-naphthoquinone product was determined by mass spectrometry. It turned out to be a cyclic tetramer, a circulene, possessing the novel structure **6b**.[12,13] It is by far the most readily available of all known circulenes.

Like α-naphthoquinone, several 2,3-dialkylated benzoquinones give large amounts of angular trimers and circulenes.[14,15] In most of these oligomerisation reactions the corresponding hydroquinones are also formed as well as dimeric compounds, for instance benzoquinone gives hydroquinone, bihydroquinone **1**, and the dibenzofuran **3**. The yields of these compounds vary greatly with the nature of the quinone used and the experimental conditions.

For our continued studies on the chemistry of the termolecular compounds we needed large amounts of the benzoquinone trimer **5a** and we therefore tried to increase the yield. We had reason to suspect that p-benzoquinone also yields minor amounts of other products whose structures might provide clues as to the nature of the polymers.

p-Benzoquinone gives a much larger yield of polymeric material than other quinones, obviously due to its multiple reactivity.

In this paper we describe some of our experiments and discuss the mechanism of the reactions leading from simple quinones to complex condensation products.

RESULTS

In the early experiments with p-benzoquinone, mixtures of water, acetic acid and sulfuric acid were used.[6] Higher yields of trimer were obtained if acetic acid was omitted or if fluoboric or perchloric acid was employed instead of sulfuric acid.

a. *Experiments with sulfuric acid.* p-Benzoquinone was treated with sulfuric acid of different concentrations for varying lengths of time to give solids (A) and filtrates (B). The solids were reduced with sodium bisulfite to give solids (C) and filtrates (D). The amounts of hydroquinone (HQ), bihydroquinone (BHQ) **1** and trimer **5a** isolated in some of the experiments from B, C and D (as acetates) are given in Table 1. (In the case of 7.5 M H_2SO_4 the filtrates B and D were mixed). All yields refer to 100 g of benzoquinone. For details see Experimental.

Although no "analytical accuracy" is claimed the figures indicate considerable formation of polymer even at low acid concentration. The amount of hydroquinone produced during the early stages of the reaction decreases with time—faster than the amount of bihydroquinone. (These phenols isolated from filtrate D occur as quinhydrones in solid A.) The formation of the trimer **5a** was slow at low acid concentration and for preparative purposes 7.5 M H_2SO_4 and a reaction time of about two weeks was found suitable. (The trimer yield in experiment 9 is probably too low due to difficulties encountered during work-up.)

Not included in the table are figures for the dibenzofuran **3**. It is always present in small amounts (tlc) but the yields were difficult to determine with the simple method used. In experiment No. 6, for example, about 0.5 g was isolated from the filtrates B + D.

Higher acid concentrations lead to diminished yields of

Table 1.

Exp. No.	Acid conc. M	Time days	Solid A (g)	Solid C (g)	Filtrate B HQ (g)	Filtrate B BHQ (g)	Filtrate D HQ (g)	Filtrate D BHQ (g)	Trimer from solid C (g)
1	2	32	83	a	22	2.5	26	7	2
2	4	3	81	a	17	5	20	5	4
3	4	15	78	a	6	2	15	5	5
4	7.5	4	a	70			12[b]	6[b]	12
5	7.5	6	a	64			10[b]	4[b]	14
6	7.5	14	a	74			3[b]	6[b]	20
7	7.5	19	a	a			c	c	23
8	7.5	59	a	a			c	c	20.5
9	7.5	120	a	a			trace[b]	trace[b]	13

[a] Not determined.

[b] Combined filtrates B and D.

[c] Not investigated.

trimer **5a** and to the formation of products similar to those obtained with strong perchloric acid (see below).

b. *Experiments with fluoboric acid.* The best yields of the trimer **5a** (22–25 g/100 g of quinone, or 25–28% of theory) were obtained using 40% HBF_4 and a slightly modified method of work-up. This expensive method is useful for small scale preparations and has the advantage that shorter reaction times are required. For details see Experimental.

c. *Experiments with perchloric acid.* High yields, about 25–26% of the theoretical, were also obtained with 35% $HClO_4$. Several experiments were carried out with still stronger acid, and even with 70% (cooled to − 10° to avoid explosive reactions). High yields, 85–90%, of black, after reduction brownish yellow, products were obtained. Mass spectra of a product obtained from 70% $HClO_4$ recorded at gradually increasing probe temperatures up to 300° showed that the minute amounts of sublimable constituents in this product were mainly of type **8** ($n = 4$ and 5). This material also contained traces of compounds of type **8** ($n = 2$ and 3) and of type **9** ($n + m = 2$, 3, 4 and 5). These oligomers could also be obtained preparatively by sublimation of the crude product in high vacuum at temperatures around 500–600°, giving a light yellow sublimate which had a strong yellow fluorescence under UV radiation. The residue from this drastic treatment was not "charred" but apparently remained unchanged, indicating that the main structural element in the polymer is probably of types **8** and/or **9** with large n-values.

(d) *Isolation of minor products.* It was observed that the trimer **5a** obtained (as acetate) with 7.5 M H_2SO_4 contained small amounts of high-melting impurities. The solid C from Exp. No. 6 was therefore examined more carefully. After methylation and chromatography the dimethyl ethers of the dimer **3** (1.5%), the linear trimer **4** (1%) and the angular trimer **5a** (24%) were isolated and identified.

The methyl ether of the "open" trimer **7** was also isolated in a pure state. Owing to separation difficulties the yield was low. Several mixtures of methylated higher oligomers were obtained and studied by mass spectrometry. One of the fractions (1%) corresponded to phenols of type **8** ($n = 2$) and another (6%) to phenols of type **9** ($n + m = 1, 2, 3, 4$). The dominant component was apparently the methyl ether of phenol **7** mentioned above. A further fraction (4%) corresponded to phenols of type **10** ($n + m = 3$) which contain a newly introduced OH group (see later).

An experiment (Exp. No. 10 below) was also made using the conditions employed in the early work[6] (benzoquinone, HOAc, H_2SO_4, H_2O). The black product obtained, corresponding to "Solid A" in Table 1, was subjected to sublimation under reduced pressure. The major part of the volatile material was the trimer **5a**. The mass spectrum of one of the minor components also isolated indicated that this product was a pentameric phenol of type **8** ($n = 3$).

As already reported in the preliminary communication, the sublimate also contained a non-phenolic, high-melting (~ 470°) yellow compound. A comparison of its spectral properties with those of cyclo-tetramers from other quinones made it clear that it was the [8]-circulene **6a**, the parent compound of the furo - [8] - circulene series. This conclusion has been confirmed by an X-ray crystallographic investigation.[16] The molecule is planar.

Some thia-[7]-circulenes and the [8]-circulene **6a** (CH_2 instead of O) have recently been described.[17,18] Their properties are closely similar to those of the [8]-circulene **6a**.

The methylated black product from Exp. No. 10 furnished the methyl ethers of the trimer **5a** (11%) and of mixtures of the phenols **9** ($n + m = 3 - 5$) (9%) and of **10** ($n + m = 3 - 5$) (4%). Small amounts of the dimethyl ether of the "open" tetramer **11** (0.5%) were isolated and the presence of isomers of type **8** ($n = 2$) (1.5%) was demonstrated. The methyl ethers of the phenols **3**, **4** and **7** were not detected in this case.

The tetramer **11** itself was obtained by chromatography of the unmethylated black product from Exp. No. 10. The structure follows from its chemical and spectral properties. It gave the circulene **6a** in a 40% yield on heating with sodium chloroaluminate. The mass spectrum showed an abundant fragment ion $m/e = 360$ corresponding to the molecular ion of circulene **6a**. The NMR spectrum of the methyl ether showed resonances of the protons of the methoxyl groups as well as of the "inner" hydrogen atoms of the terminal rings which were shifted upfield from the positions expected for a planar compound. The open tetramer **11** is therefore a helicene. The non-phenolic analogue **11** (H instead of OH) has recently been synthesized.[19] It exhibits similar spectral properties and its helical nature has been confirmed by X-ray crystallographic studies.[16]

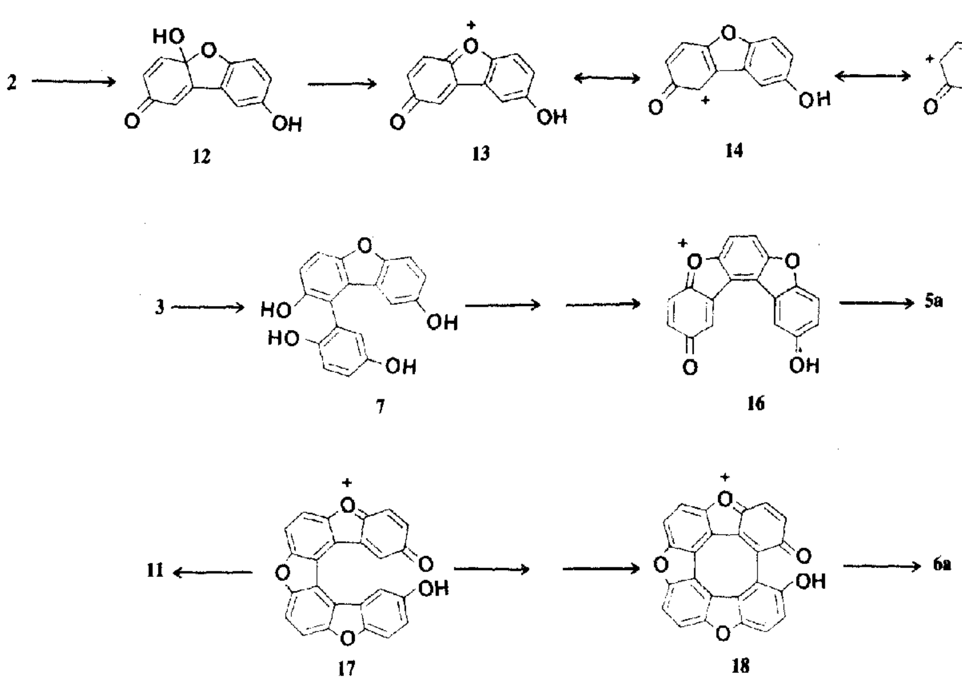
DISCUSSION

The mechanistic aspects of quinone oligomerisations have not been discussed in our previous work.

It seems clear that the corresponding hydroquinones must be either present or formed at the start of the reactions since the oligomerisation of, e.g. α-naphthoquinone is inhibited by the addition of a strong oxidant[4] such as chloranil to the reaction mixture.[13] In experiments with methyl- or 2,3-dimethylquinone the addition of limited amounts of the corresponding hydroquinones[11,15] increases the rate of reaction and leads to cleaner products. Obviously quinone-phenol couplings play a fundamental role in these reactions.

The first step in the oligomerisation of *p*-benzoquinone is coupling with hydroquinone to the tetrahydroxybiphenyl **1** which is then oxidised by quinone to the "intramolecular quinhydrone" **2**, whilst the quinone is reduced to hydroquinone. Formally, the hydroxyquinone **2** could similarly be transformed into a polyhydroquinone $(C_6H_4O_2)_n$ but this does not happen. The most characteristic feature of the actual course of quinone oligomerisation is the ease with which dibenzofuran structures are established. Furanoid products are formed even under weakly acidic conditions (see Table 1). The dehydration of *o,o'*-dihydroxybiphenyls, e.g. compounds of type **1**, does not occur under these conditions.[13,20] Instead it requires prolonged boiling with, e.g. concentrated hydrobromic acid (cf. Stjernström[8,21,22]).

We suggest that the oligomerisation of *p*-benzoquinone and similar reactions leading to the facile formation of dibenzofurans proceed *via* hemiketals such as **12** (Scheme 1). On protonation an ion is formed (represented by the mesomeric forms **13**, **14** and **15**) which can be regarded as the reactive species. This ion (**13**–**15**) can be reduced by hydroquinone to the dibenzofuran **3** which can be isolated, or the ion can couple with hydroquinone (*via* ionic form **14**) to give the open trimer **7** (isolated). (Ionic form **15** would give the *para* coupled isomer). Alternatively (relevant physical data are

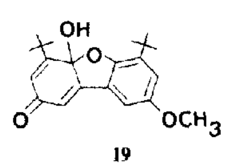


Scheme 1.

lacking) the dibenzofuran **3** may react with quinone giving **7**. Oxidation followed by protonation leads to the ion **16** which is reduced to the trimer **5a**, the major sparingly soluble product isolated. In exactly the same way compound **11** (isolated) is formed from **16** or **5a** *via* reduction of the ion **17**. Ring closure of **17** followed by oxidation and protonation leads to **18** which is reductively ring-closed to the circulene **6a**. (Possible "short-cuts" such as $\mathbf{3} + \mathbf{12} \rightarrow \mathbf{6a}$ are self-evident).

Scheme 1 gives a simplified picture of the route from quinone to the target circulene **6a**; in the case of *p*-benzoquinone this has been isolated only in trace amounts under special experimental conditions. All compounds isolated including quinhydrone and the hydroxyquinone **2** are sparingly soluble or almost insoluble in water. The relevant oxidation-reduction potentials and reaction velocities are unknown. There will be many alternatives to the route pictured. As mentioned, ion **15** would initiate reactions in a different direction and indeed the linear trimer **4** has been isolated and identified as its known[10] methyl ether. All components of the unresolved mixtures of higher oligomers (see **8** and **9**) whose presence was indicated by mass spectrometry can easily be accounted for. Only compounds of type **10** require additional, oxidative (?) hydroxylations (see Ref. 23). These appear to be common features of the alkaline polymerisation of quinone.[24] It is not surprising that it is difficult to imitate the various steps by model experiments.

However, we have found that the stable ketal **19**[25] reacts with resorcinol with extrusion of water and formation of a resorcyldibenzofuran.[26]



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Stjernström showed that treatment of a mixture of the dibenzofuran **3** and benzoquinone with sulfuric acid gives higher yields of the trimer **5a** than expected from the quinone alone.[27] Using the Marschalk conditions (AlCl$_3$, ϕ-NO$_2$) the naphthoquinone trimer **5b** reacts with naphthoquinone to give the cyclic tetramer **6b** (yield 50%).[13] With an excess of benzoquinone the corresponding "mixed" circulene **6c** is formed in similar yield.[13]

Polymers are invariably the main products from benzoquinone. With very strong sulfuric or perchloric acids they are formed almost exclusively. They will obviously be built up irregularly in very much the same fashion as the simpler dibenzofuranoids.

EXPERIMENTAL

Action of sulfuric acid on p-*benzoquinone*. *p*-Benzoquinone (usually 20 g in each experiment) was treated with sulfuric acid with mechanical stirring during the first day of reaction, then occasional shaking; the concentration and the reaction time were varied (Table 1). Filtration gave a solid, A, and a filtrate, B. The dried solid A was introduced into boiling water (500 ml). AcOH (5–10 ml) was added, followed by Na$_2$S$_2$O$_5$ (5–10 g) in portions. The colour of the solid changed from black to greyish-brown. Filtration gave solid C and filtrate D. The former was dried and acetylated with a tenfold amount of acetic anhydride. After 24–48 hr the crystalline precipitate was collected and washed with small amounts of AcOH and acetone. The product was distilled in a vacuum to give pure diacetate of the trimer 5a. Some Na$_2$S$_2$O$_5$ was added to the solns B and D which were then exhaustively extracted with ether and the ether-soluble materials were acetylated. Finally the crude acetate mixtures were distilled under reduced pressure and the distillate was subjected to gradient sublimations. The various zones were collected and weighed.

Preparation of the acetate of trimer **5a**

1. *With sulfuric acid*. *p*-Benzoquinone (100 g) was introduced in portions into an aqueous soln (1000 ml) containing 400 ml

conc H_2SO_4. The mixture was stirred for 24 hr then occasionally shaken. After 2 weeks the mixture was filtered and the black, still moist solid was transferred into boiling water (1 l). Solid $Na_2S_2O_5$ was added until the colour did not change appreciably. After 24 hr at ambient temp. the mixture was filtered (filtrate B) and the dark, greyish solid was carefully washed with water. The air-dried solid (70–74 g) was dissolved in boiling Ac_2O (250–300 ml) and pyridine (5 ml). After 1–2 days the ppt was filtered off and washed with AcOH and a little acetone. The crude acetate was recrystallised from Ac_2O or DMF containing some HOAc (charcoal), yield 25–27 g, slightly buff coloured product, m.p. usually about 230°. It was obtained quite pure (m.p. 240–242°) by sublimation (1 mm, 250–260°) and recrystallisation; solubility (100 ml, 20°), acetone, CH_2Cl_2, $EtOA_c$: 0.2, 0.7, 0.035 g, respectively. Small amounts of the acetate of **5a** (1–2 g) may be isolated, laboriously, by careful addition of water to the above filtrates and mother liquors.

Crude products can be considerably purified by dissolving in a 10–20-fold amount of hot (220–230°) paraffin oil and decanting from the black, sticky layer formed on the bottom of the vessel.

2. *With* 40% HBF_4. *p*-Benzoquinone (100 g) was introduced in portions into HBF_4 (40%, 1000 ml) with stirring. After 4 days the collected, moist solid was reduced as above and the dried product was acetylated (100 ml Ac_2O + 1 ml pyridine). When crystals began to appear acetone (100 ml) was added. After 1–2 days at room temp. the ppt was collected by filtration and washed carefully with acetone (100 ml), yield: 30 g of almost pure acetate (m.p. 230–238°) corresponding to 23.5 g trimer **5a** from 100 g quinone or 26% of the theoretical yield. From the filtrates, etc. altogether 18 g of hydroquinone, bihydroquinone and dihydroxydibenzofuran was isolated (as acetates). The formation of polymers was thus less pronounced than with strong sulfuric acid.

Shorter reaction times (e.g. 1 day) gave lower yields of trimer acetate (23 g).

3. *With* $HClO_4$. *p*-Benzoquinone (100 g), $HClO_4$ (35%, 500 ml); initial cooling to 0°; time 6 days. The dried reduced solid (71 g) was dissolved in acetone (500 ml). After filtration, Ac_2O (300 ml) and pyridine (5 ml) were added. The crystals deposited after 2 days were carefully washed with acetone (100–200 ml). The mother liquors were concentrated to give a small second crop. The first crop was almost pure trimer acetate, m.p. 230–238°, total yield about 30 g.

Divalerate of trimer **5a**. Trimer acetate was hydrolysed by boiling with a 2% soln of H_2SO_4 in HOAc in an inert atmosphere, and water was added to precipitate the phenol.[3] This (3 g) was esterified by boiling with valeric anhydride (7 ml) and a little pyridine. After cooling the voluminous ppt was collected by filtration and washed with MeOH. Recrystallisation from AcOH (charcoal) gave a colourless product melting at 150–152°. (Found: C 73.3, H 5.7. Calc. for $C_{28}H_{26}O_6$: C 73.3, H 5.7%). This compound is fairly easily soluble in CH_2Cl_2.

Chromatographic separation of solid C from Exp. No. 6

Solid C from Exp. No. 6 (10.0 g) was stirred under N_2 with MeOH in the presence of a trace of sodium dithionite and methylated [Me_2SO_4, NaOH]. After reflux, cooling and dilution with water the resulting solid (10.4 g) was collected. This material (3.0 g) was chromatographed on silica gel (300 g, eluent CH_2Cl_2, 25 ml fractions after a forerun of 400 ml).

From fractions 10–18 on concentration to 20 ml a solid, A (45 mg), separated. The mother liquor was evaporated to dryness and subjected to gradient sublimation (1 mm/200°) giving a volatile component, B (56 mg), and a less volatile component, C (50 mg).

Fractions 19–32 were pure by tlc and gave a solid, D (511 mg).

Fractions 33–87 were evaporated and sublimed (1 mm/200°) and gave more solid, D (436 mg). The sublimation residue was resublimed (1 mm/300°). The new sublimate was dissolved in a few ml of methylene chloride. Product E (43 mg) separated. The mother liquor was combined with the sublimation residue and evaporated to give a glass, F (286 mg).

Fractions 88–155 were evaporated to give a gum, G (215 mg).

From A–G the following products were isolated:

1. 2,8-*Dimethoxybenzo*[1,2-b:4,5-b′]*bisbenzofuran* (**4**, OMe instead of OH). Solid A was recrystallised from dimethylformamide, needles m.p. 258–260° (lit.[10] 257–259°C). Mixed m.p., IR.

2. 2,8-*Dimethoxydibenzofuran* (**3**, OMe instead of OH). Solid B was recrystallised from EtOH, m.p. 88–89° (lit.[28] 88–89°). NMR (60 MHz, $CDCl_3$): δ 3.84 (6H, s, 2 OCH_3), 7.03 (2H, dd, J = 2.6 and 9.2 Hz, 2 ArH), 7.32 (2H, d, J = 2.6 Hz, 2 ArH), 7.40 (2H, d, J = 9.2 Hz, 2 ArH) ppm.

3. 2,11-*Dimethoxybenzo*[1,2-b:3,4-b′]*bisbenzofuran* (**5a**, OMe instead of OH). Product D was recrystallised from dimethylformamide, needles (23.8%) m.p. 213–215° (lit.[10] 216–218°). NMR (60 MHz, $CDCl_3$): δ 3.96 (6H, s, 2 OCH_3), 7.08 (2H, dd, J = 2.7 and 9.2 Hz, 2 ArH), 7.55 (2H, d, J = 9 Hz, ArH), 7.61 (2H, s, 2 ArH), 7.85 (2H, d, J = 2.7 Hz, 2 ArH) ppm.

4. *Dimethoxybenzofurobisbenzofurans* (**8**, $n = 2$, OMe instead of OH). MS [70 eV, m/e (rel. int.)] of the amorphous solid E showed that it must possess the general structure **8** ($n = 2$, OMe instead of OH): 408(100), M^+ (Calc. for $C_{26}H_{18}O_5$: 408). This is probably a mixture of isomers.

5. *Tetramethoxyoligomers* **9** (OMe instead of OH). According to its MS (70 eV) exhibiting molecular ion peaks at m/e 364, 454, 544 and 634 fraction F mainly consisted of Me ethers of type **9** with $n + m = 1$, 2, 3 and 4, respectively. Minor amounts of the above dimethyl ethers of tetramers of type **8** ($n = 2$) were also present.

6. 1 - (2,5 - *Dimethoxyphenyl*) - 2,8 - *dimethoxydibenzofuran* (**7**, OMe instead of OH). Sublimation of fraction F *in vacuo* gave a volatile product. It was purified by preparative tlc on silica gel (CH_2Cl_2) giving a band of $R_f = 0.4$. After several recrystallisations from EtOH the product furnished a few mg of colourless crystals, m.p. 133–134°. [Found: m/e 364.1306 (M^+, 100%). Calc. for $C_{22}H_{20}O_5$: 364.1310]. NMR (270 MHz, $CDCl_3$): δ 3.59, 3.64, 3.77, 3.81 (12H, 4s, 4 OCH_3), 6.45 (1H, d, J = 2.8 Hz, ArH), 6.91 (1H, dd, J = 0.8 and 2.8 Hz, ArH), 6.93 (1H, dd, J = 2.8 and 9.0 Hz, ArH), 6.99 (1H, dd, J = 2.8 and 8.5 Hz, ArH), 7.03 (1H, dd, J = 0.8 and 8.5 Hz, ArH), 7.13, 7.37, 7.46 (3H, 3d, all J = 9.0 Hz, 3 ArH) ppm. The amount available did not permit an elementary analysis.

7. *Pentamethoxyoligomers* **10** (OMe instead of OH). MS indicated that the product G was a mixture of the methyl ether of compound **1** (m/e 274) and of the methyl ethers of compounds of type **10** with $n + m = 2$ and 3 (m/e 484 and 574, respectively).

Treatment of p-*benzoquinone with sulfuric acid in dilute acetic acid, Exp. No.* 10

p-Benzoquinone (100 g) was stirred with H_2SO_4 in AcOH and water (250, 500 and 500 ml, respectively) for 21 days. Water (300 ml) was added and after 24 hr the mixture was filtered. The solid was washed with water until free of H_2SO_4. The dried black polymer weighed 65 g.

This product (40 g) was carefully sublimed (10 mm) in 2 g portions in test tubes (20 × 2 cm) over a free flame. A plug of asbestos wool prevented the residue from contaminating the sublimate. The sublimate was collected and partly dissolved in acetone (200 ml). This mixture was stored in a refrigerator for 1 week and then filtered to give a solid, A (0.5 g). The filtrate was evaporated to dryness to give slightly impure **5a** (4.7 g, 9%). The solid A was subjected to gradient sublimation (0.05 mm, 400°C). A brownish-yellow zone, B (0.2 g), was obtained, followed by a less volatile product, C (0.3 g).

1. *Tetraphenyleno*[1,16-bcd:4,5-b′c′d′:8,9-b″c″d″:12,13-b‴c‴d‴]-*tetrafuran* (**6a**). The product B was moistened with dil NaOHaq, dried and then resublimed. A yellow sublimate was obtained (180 mg, 0.3%), yellow needles from pyridine or quinoline, m.p. approx. 470°. (Found: C 79.9, H 2.3. Calc. for $C_{24}H_8O_4$: C 80.0, H 2.2). MS see ref. 14. UV see Ref. 19. IR (KBr, cm^{-1}): 1470(w), 1440(w), 1420(s), 1355(w), 1350(m), 1220(m), 1170(m), 1090(m), 1010(s), 870(m), 790(m), 770(m), 730(w). This circulene gives a yellow fluorescence on UV radiation. It was also obtained when the black product from Exp. No. 10 was treated with strong alkali and excess hydrogen peroxide (30%), which destroyed the phenolic oligomers but left the circulene **6a** unaffected. This was collected by filtration and purified as above.

2. *Pentamer of type* **8** ($n = 3$). The above product C was resublimed to give light yellow crystals (0.24 g, 0.4%). No m.p. below 400°. MS [70 eV, *m/e* (rel. int.)]: 498(100), M^+. IR (KBr, cm^{-1}): 3300–3000 (broad, phenolic OH). On acetylation this compound gave a diacetate as judged by IR (KBr, cm^{-1}): 1740 and MS [70 eV, *m/e* (rel. int.)]: 582(25), M^+, 540(40) and 498(100).

Chromatographic separation of the black product from Exp. No. 10

Chromatography of the methylated black product from Exp. No. 10 (3.0 g) as described above gave a solid, A (0.03 g), the methylated trimer **5a** (11%), dimethyl ethers of tetramers of type **8** ($n = 2$) (1.5%), tetramethyl ethers of oligomers of type **9** ($n + m = 2$, 3 or 4) (9%) and pentamethyl ethers of oligomers of type **10** ($n + m = 2$, 3 or 4) (4%).

1. 2,14 - *Dimethoxy*[b,b′]*furo*[3,2 - :4,5 - e′]*bisbenzofuran* (**11**, OMe instead of OH). The above solid A was sublimed and recrystallised from AcOH, yield 0.5%, m.p. 222–223°. [Found: C 76.3, H 4.0. Calc. for $C_{26}H_{16}O_5$: C 76.5, H 4.0]. NMR (60 MHz, $CDCl_3$): δ 3.40 (6H, s, 2 OCH_3), 7.05 (2H, dd, J = 2.5 and 9.0 Hz, ArH), 7.54 (2H, d, ArH, J = 9.0 Hz, ArH), 7.55 (2H, d, J = 2.5 Hz, ArH), 7.69 (4H, s, ArH) ppm. This compound was also obtained by methylation of the phenol **11**.

2. *Phenol* **11**. The black material from Exp. No. 10 (10 g) was mixed with acetone and silica gel (50 g) and the solvent evaporated. The product was placed on top of a column of silica gel (500 g) in ether. Ether eluted first the phenol **11** (50 mg). It was recrystallised from ether and sublimed in a vacuum, m.p. over 340°. [Found: C 75.4, H 3.1. Calc. for $C_{24}H_{12}O_5$: C 75.8, H 3.2]. MS [70 eV, *m/e* (rel. int.)]: 380(100), M^+, 360(35), 351(9), 336(9), doubly charged ions: 190.0(3), 181.0(10), 180.5(8), 180.0(11), 153.0(10), metastable ions: 344.6 (calc. for 380–362 = 344.8) and 324.5 (calc. for 380–351 = 324.2) and 172.5 (calc. for 190.0–181.0 = 172.4).

3. *Diacetate of phenol* **11**. The preceding phenol was acetylated (Ac_2O, pyridine), m.p. 231–232° (Ac_2O). [Found: C 72.1, H 3.4. Calc. for $C_{28}H_{16}O_7$: C 72.4, H 3.5]. UV [EtOH, nm (log ϵ)]: 218(4.42), 232(4.42), 241(4.34 sh), 250(4.13 sh), 277(3.82), 295(4.13), 304(4.35), 327(4.10 sh), 339(4.35), 356(4.45) nm.

Tetraphenylenotetrafuran (**6a**). The diphenol **11** (10 mg) was treated under N_2 with molten $NaAl_2Cl_7$ at 180° for 2 min. Conc HCl was carefully added and the solid was collected and washed with pyridine and acetone. The residue was moistened with dilute alkali, dried and sublimed *in vacuo* to give a yellow product which was identical (MS, IR) with **6a** previously described.

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