

Cyclo-oligomerization of Quinones

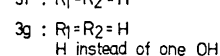
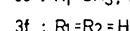
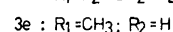
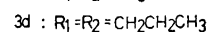
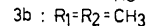
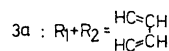
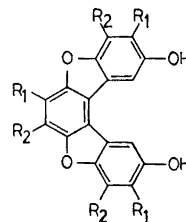
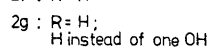
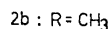
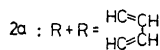
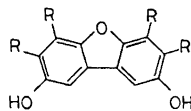
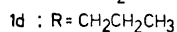
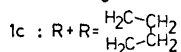
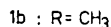
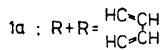
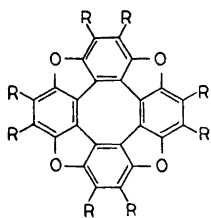
IV.* The Action of Strong Acids on 2,3-Dialkyl-*p*-benzoquinones

HANS-ERIK HÖGBERG

*Department of Organic Chemistry, Royal Institute of Technology,
S-100 44 Stockholm 70, Sweden*

In the presence of strong acids 2,3-disubstituted *p*-benzoquinones give tetramers, tetraphenyltetrafurans, and trimerization products. The tetramers from 2,3-dimethyl-*p*-benzoquinone, 5,6,7,8-tetrahydro- α -naphthoquinone and 2,3-dipropyl-*p*-benzoquinone are described.

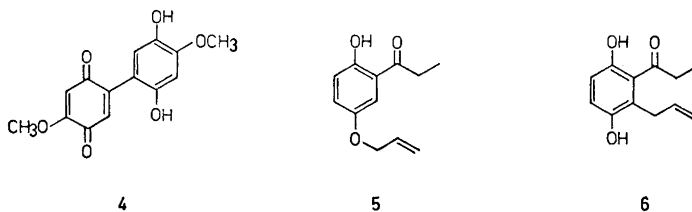
It has been shown¹ that α -naphthoquinone dissolved in acetic acid containing sulphuric acid gives a 45 % yield of a non-phenolic product recently identified as tetranaphthyltetrauran (*Ia*).^{2,3} In addition the di- and trimerization products *2a* and *3a* are formed.¹⁻³ A 90 % yield of compound *Ia* is obtained when α -naphthoquinone is treated with aluminium chloride in nitrobenzene.²⁻⁴ The phenolic oligomers may be intermediates in the formation of the tetramer



* For a preliminary communication, cf. Ref. 9. Part III: Ref. 3.

qa and this is supported by the condensation of the trimer 3a with α -naphthoquinone in nitrobenzene containing aluminium chloride to give a 60 % yield of the tetramer.³

Some simple *p*-benzoquinones are known to give di- and trimerization products with acids. Thus the highly reactive methoxy-*p*-quinone gives a quantitative yield of compound 4,⁵ toluquinone a 15 % yield of the trimer 3e¹ and 2,3-dimethyl-*p*-benzoquinone a 35 % yield of the trimer 3b.⁶ In the latter case a small amount of the dibenzofuran 2b is also formed. *p*-Benzoquinone itself, lacking activating and blocking substituents gives a very poor yield (5 %) of the trimer 3f together with large amounts of hydroquinone and amorphous products exhibiting quinonoid properties.^{1,7} Stjernström has shown that 2,5,2',5'-tetrahydroxybiphenyl and, particularly, 2,8-dihydroxydibenzofuran (2f) may be intermediates in the trimerization of *p*-benzoquinone.⁶ Addition of 2,8-dihydroxydibenzofuran to the reaction mixture increases both the rate of formation and the yield of the trimer 3f.^{6,8} Similarly 2-hydroxydibenzofuran (2g) reacts with *p*-benzoquinone to give a low yield of compound 3g.⁸



Prior to this investigation no tetramers similar to that from α -naphthoquinone had been obtained from alkyl-*p*-benzoquinones. While mono-substituted quinones such as methoxy- and methyl-*p*-benzoquinone, because of their pronounced reactivity in one position are not likely to give any tetramers, 2,3-dialkyl-*p*-benzoquinones could be expected to do this. In Stjernström's study⁶ of the action of acids on 2,3-dimethyl-*p*-benzoquinone, the reaction products were subjected to reductive acetylation with zinc and acetic anhydride. The phenolic products were isolated in the form of more or less soluble acetates. However, any tetramer of the structure 1b could easily have been removed with the excess zinc because of low solubility and have escaped observation.

Stjernström's experiment with 2,3-dimethyl-*p*-benzoquinone was therefore repeated omitting the reductive acetylation. When 2 mol of this quinone and 1 mol of the corresponding hydroquinone were dissolved in a mixture of sulphuric and acetic acid a precipitate rapidly formed. This was triturated with pyridine which dissolved the phenolic constituents. Sublimation of the residue under reduced pressure gave a high-melting light yellow compound very similar to the tetramer of α -naphthoquinone in 54 % yield. The mass spectrum ($m/e=472 (M^+)$) confirmed that the product was octamethyltetraphenyltetrahydrofuran (1b). The pyridine-soluble, phenolic fraction contained the trimer 3b⁶ which was isolated as the acetate. In the absence of the hydro-

quinone the yield of tetramer was about the same, the reaction was slower and the yield of amorphous products larger.

2,3-Dimethyl-*p*-benzoquinone alone on treatment with aluminium chloride in nitrobenzene gave a 70 % yield of the tetramer *Ib*.

In the same way 5,6,7,8-tetrahydro- α -naphthoquinone gave a 40 % yield of compound *Ic* which was characterized by its mass spectrum.

The quinone tetramers described above were extremely insoluble in the ordinary solvents and in order to obtain satisfactory UV data more soluble tetramers, such as tetraphenyltetrafurans containing long alkyl chains, were needed. Symmetrical long chain 2,3-dialkyl-*p*-benzoquinones would be suitable starting materials for such compounds. No such quinone was known, however. 2,3-Dipropyl-*p*-benzoquinone was therefore prepared as follows (*cf.* Ref. 10): Allylation of 2,5-dihydroxypropiophenone gave compound *5* which underwent thermal rearrangement to compound *6*. This was hydrogenated in two steps and the resulting hydroquinone oxidized to 2,3-dipropyl-*p*-benzoquinone. The thermal rearrangement of *5* to give *6* is analogous to that of 3-allyloxy-6-hydroxyacetophenone which is known to give 2-allyl-3,6-dihydroxyacetophenone.¹¹

With sulphuric acid a mixture of 2 mol of 2,3-dipropyl-*p*-benzoquinone and 1 mol of the corresponding hydroquinone gave the trimer *3d* in a 60 % yield (isolated as the acetate). However, a small amount of the tetramer *Id* was also formed. The structure of the trimeric acetate follows from its mass spectrum and the UV spectrum (Fig. 1), which is very similar to that of the acetate of the benzoquinone trimer *3f*.⁸

When 2,3-dipropyl-*p*-benzoquinone alone was treated with aluminium chloride in nitrobenzene a 60 % yield of the light yellow octapropyltetraphenyltetrauran (*Id*) was obtained. As expected, it was more soluble than the above mentioned tetramers. It could be recrystallized from pyridine and was sufficiently soluble in cyclohexane to permit the recording of a reliable UV spectrum.

The ultraviolet absorption curves of the tetramer *Id* and of the trimeric acetate *3d* are shown in Fig. 1. As expected, the long wavelength absorption

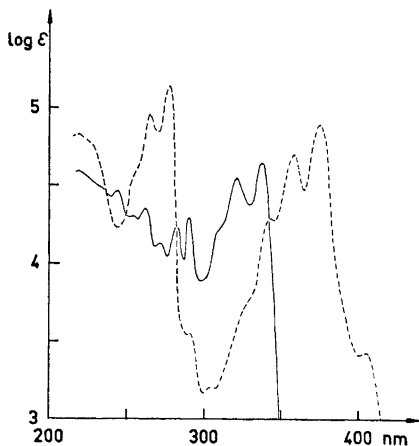


Fig. 1. UV spectrum of diacetoxyhexapropylbenzobisbenzofuran *3d* ———, and of octapropyltetraphenyltetrauran *Id* - - - -.

of the tetramer is shifted towards longer wavelength and shows an enhanced intensity relative to the trimer.

The characteristic feature of the mass spectra (70 eV, 250°) of the alkylated tetraphenyltetrafurans is the intensity of the peaks corresponding to the molecular ions M^{+} and M^{2+} . These ions together contribute 47 %, 40 %, and 42 % of the total ion current registered in the spectra of the tetramers *Ib*, *Ic*, and *Id*, respectively. Alkylated tetraphenyltetrafurans also show fragmentation of the substituents. Thus in the spectrum of octamethyltetraphenyltetrafuran (*Ib*) there are peaks corresponding to the successive loss of up to six methyl groups from the molecular ion, the intensities decrease with increasing number of methyl groups lost and, apart from the molecular ion peaks ($m/e=472$, M^{+} , 100 % and 236, M^{2+} , 17 %), the fragment $m/e=457$ ($M^{+}-CH_3$; 14 %) gives the strongest peak.

EXPERIMENTAL

Melting points are uncorrected. Melting points below 360° were determined on a micro hot stage, those above 360° using sealed evacuated capillary tubes heated in an air bath.

The mass spectra were registered at 70 eV. NMR standard: TMS.

1,2,4,5,7,8,10,11-Octamethyltetraphenyleno[1,16-bcd:4,5-b'c'd':8,9-b''c''d'':12,13-b'''c''d''']tetrafuran (Ib). A solution of aluminium chloride (3 g) in nitrobenzene (75 ml) was added rapidly to a stirred solution of 2,3-dimethyl-*p*-quinone¹² (3.0 g) in nitrobenzene (75 ml) at 90°. The solution immediately turned dark and a precipitate was formed. Stirring and heating was continued for 1 h. Ethanol (1 l) was then added and the resulting mixture was filtered and washed successively with ethanol, 2 M HCl, ethanol, and pyridine (to remove phenolic impurities). The yield of almost pure octamethyltetraphenyltetrafuran was 1.8 g (70 %). The compound was sublimed (350°/0.1 mm) forming large yellow prisms, m.p. approximately 530°. It was sparingly soluble in hot quinoline from which it crystallized as prisms. (Found: C 81.1, H 5.1. Calc. for $C_{32}H_{24}O_4$: C 81.4; H 5.1.) The IR spectrum (KBr) was simple. The most important peaks were at 780 w, 930 m, 1070 m, 1090 m, 1240 m, 1370 s, 1450 w, 1660 w, 2930 w, 2950 w cm^{-1} . UV (in trichlorobenzene): $\lambda_{max}(nm/\log \epsilon)$: 346/4.15; 360/4.40; 378/4.62; 412/3.45. (The log ϵ values are uncertain due to low solubility of the compound). MS: $m/e=472$ (M^{+} , 100 %); 457 ($M^{+}-CH_3$; 14 %); 236,0 (M^{2+} , 17 %); 228.5 ($M^{2+}-CH_3$; 13 %); 227.5 (14 %).

Treatment of 2,3-dimethyl-p-benzoquinone and 2,3-dimethylhydroquinone with sulphuric acid. 2,3-Dimethylhydroquinone (5 g) was dissolved in acetic acid (50 ml) and the solution mixed with a solution of sulphuric acid (15 ml) in acetic acid (35 ml). This solution was added to a stirred solution of 2,3-dimethyl-*p*-benzoquinone (10 g) in acetic acid (100 ml) at 50°. The colour soon deepened and a precipitate was formed after about 1 min. After 2 h the mixture was filtered while hot and the solid washed with hot acetic acid (filtrate A). The product was boiled with pyridine (50 ml), filtered while hot and washed with hot pyridine (filtrate B). The remaining solid was slightly impure octamethyltetraphenyltetrafuran (7 g, 54 %). The solution A was poured into water and the product reductively acetylated to give an amorphous material (3.0 g, 12 %) which was not further investigated. Filtrate B was mixed with acetic anhydride (25 ml), zinc dust was added and the mixture boiled and filtered while hot. On cooling 2,11-diacetoxy-3,4,6,7,9,10-hexamethylbenzo[1,2-b:4,3-b']bisbenzofuran (*3b*) (5.1 g, 30 %) separated as colourless needles m.p. 333–335° (lit.⁶ 320° dec.).

1,2,3,4,6,7,8,9,11,12,13,14,16,17,18,19-Hexadecahydrotetranaphthyleno-[5,6-bcd:11,12-b'c'd':17,18-b''c''d'':23,24-b'''c''d''']tetrafuran (Ic). A suspension of 5,6,7,8-tetrahydro- α -naphthoquinone¹³ (400 mg) in nitrobenzene (25 ml) was treated with aluminium chloride (0.4 g) with stirring for 1 h. The reaction mixture was poured into ethanol and worked up as described above. The solid obtained (138 mg, 39 %) was sublimed to give pure compound *Ic*. It formed light yellow prisms which melted at approximately 480°. (Found:

C 83.7; H 5.2. Calc. for $C_{40}H_{32}O_4$: C 83.3; H 5.6.) IR (KBr): 740 m, 760 s, 860 s, 915 s, 1025 s, 1055 s, 1100 s, 1350 s, 1455 m, 2960 $m\text{ cm}^{-1}$. MS: $m/e = 576$ (M^+ , 100 %); 572 ($M^+ - 4\text{ H}^+$, 24 %); 548 ($M^+ - \text{CO}$, 10 %); 288 (M^{2+} , 13 %); fragments due to loss of one, two, three, and four CO units from the doubly charged ion were also observed (intensities < 10 %). This compound was not soluble enough to permit the registration of its UV spectrum.

2,5-Dihydroxypropio-phenone. Boron trifluoride was passed into a stirred mixture of hydroquinone (220 g) and propionic acid (222 g) in tetrachloroethane (600 ml) at such a rate as to keep the temperature below 50°. After 4 h the mixture was saturated with boron trifluoride and the mixture stirred overnight. After heating and stirring on a steam-bath for an additional 6 h it was poured into a solution of sodium acetate (615 g) in water (2.5 l) and the product was extracted with ether. The ethereal layer was washed with water and the ether evaporated. The solvent was steam distilled and the residue was recrystallized (charcoal) from water. Yield 220 g (70 %) m.p. 99.0–99.5° (lit.¹⁰ 97–98°).

3-Allyloxy-6-hydroxypropio-phenone (5). A mixture of 2,5-dihydroxypropio-phenone (166 g), freshly distilled allyl bromide (122 g), dried and finely ground potassium carbonate (200 g), and acetone (1500 ml) was refluxed for 8 h. The solid was removed by filtration and washed with acetone. The residue obtained after evaporation of the acetone was dissolved in ether and the solution washed with water, dried over sodium sulphate and evaporated. The residue was distilled (163–165°/10 mm). Yield 135 g, 65 %. Recrystallization from pentane gave yellow prisms m.p. 50–51°. (Found: C 70.0; H 6.8. Calc. for $C_{12}H_{14}O_3$: C 69.9; H 6.8.) MS: $m/e = 206$ (M^+); 165 (base peak). NMR (CDCl_3): One enolic proton at low field ($\delta = 11.9$ ppm) was observed. The protons of the allyloxy group absorbed at $\delta = 4.5$ ppm (doublet, 2 allylic H); $\delta = 5 - 5.5$ ppm (unresolved peaks, 2 olefinic H); $\delta = 5.7 - 6.3$ ppm (complex multiplet, 1 olefinic H).

2-Allyl-3,6-dihydroxypropio-phenone (6). 3-Allyloxy-6-hydroxypropio-phenone (47.5 g) was heated under nitrogen on an oil bath. The temperature was raised from 180° to 225° during 1 h. After cooling the product was dissolved in boiling carbon tetrachloride. On cooling 2-allyl-3,6-dihydroxypropio-phenone (32 g, 65 %, m.p. 87–90°) separated. Repeated recrystallization from benzene gave needles, m.p. 90–90.5°. (Found: C 70.0; H 6.9. Calc. for $C_{12}H_{14}O_3$: C 69.9; H 6.9.) MS: $m/e = 206$ (M^+); 198 (base peak); 187; 159; 131; 121; 103; 91; 77. NMR (acetone d_6): Two phenolic H ($\delta = 7.83$ ppm) were observed. The protons of the allyl group absorbed at $\delta = 3.4$ ppm (doublet, 2 allylic H); $\delta = 4.7 - 5.2$ ppm (unresolved peaks, 2 olefinic H); $\delta = 5.6 - 6.3$ (complex multiplet, 1 olefinic H).

2-Propyl-3,6-dihydroxypropio-phenone. A mixture of 2-allyl-3,6-dihydroxypropio-phenone (25 g), palladium on charcoal (10 %, 0.6 g), and absolute ethanol (500 ml) was stirred under hydrogen at 1 atm. After 3.5 h the theoretical amount of hydrogen was consumed. The product (22.3 g, 89 %, m.p. 111–113°) was crystallized from benzene as colourless prisms, m.p. 114–114.5°. (Found: C 69.3; H 7.8. Calc. for $C_{12}H_{16}O_3$: C 69.3; H 7.7.) MS: $m/e = 208$ (M^+); 179 (base peak); 161. NMR (acetone d_6): Absorptions due to the hydrogens of one aromatic propyl group were observed.

2,3-Dipropylhydroquinone. 2-Propyl-3,6-dihydroxypropio-phenone (20.8 g) in absolute ethanol (100 ml) was mixed with copper chromite (4 g). In the reduction a Parr apparatus was used (140°, 160 atm, 1 h). The product obtained was recrystallized from benzene forming silky colourless needles, m.p. 152–153°. Yield: 16 g, 83 %. (Found: C 74.2; H 9.4. Calc. for $C_{12}H_{18}O_2$: C 74.2; H 9.3.) MS: $m/e = 194$ (M^+); 165; 137 (base peak). Absorptions due to the hydrogens of two aromatic propyl groups were observed in the NMR spectrum (acetone d_6).

2,3-Dipropylhydroquinone diacetate. 2,3-Dipropylhydroquinone was acetylated with acetic anhydride and pyridine in the usual way giving a viscous oil, b.p. 122–123/0.4 mm, $n_D^{20.5} = 1.4941$. (Found: C 68.9; H 8.0. Calc. for $C_{16}H_{22}O_4$: C 69.1; H 7.9.) MS: $m/e = 278$ (M^+); 236; 194 (base peak).

2,3-Dipropylhydroquinone dimethylether. 2,3-Dipropylhydroquinone was methylated with dimethyl sulphate and sodium hydroxide giving a colourless oil, b.p. 84–85/0.4 mm, $n_D^{21.0} = 1.5097$. (Found: C 75.3; H 10.0. Calc. for $C_{14}H_{22}O_2$: C 75.6; H 9.9.) MS: $m/e = 222$ (M^+ , base peak).

2,3-Dipropyl-p-quinone. 2,3-Dipropylhydroquinone in acetic acid was oxidized with chromic anhydride. The quinone (yield 94 %) formed yellow needles. Melting after sublimation at 36.5–37.5°. (Found: C 75.0; H 8.4. Calc. for $C_{12}H_{16}O_2$: C 75.0; H 8.3.) MS: $m/e = 192$ (M^+); 163 (base peak); 135; 107; 91; 79; 77; 65. NMR (CDCl_3): $\delta = 7.36$ ppm (singlet, 2 olefinic H); $\delta = 3.57$ ppm (triplet, 4 allylic H); $\delta = 2.55$ ppm (sextet, 4 methylenic

H); $\delta = 1.05$ ppm (triplet, 6 methyl H). IR (KBr): $\nu_{C=O}$: 1650 cm^{-1} , strong; $\nu_{C=C}$: 1600 cm^{-1} , medium. UV (cyclohexane) (λ_{max} (nm)/ ϵ): 448/33; 332/1350; 250/18000.

1,2,4,5,7,8,10,11-Octapropyltetraphenyleno[1,16-bcd:4,5-b'c'd':8,9-b''c''d'':12,13-b'''c''d''']tetrafulran (Id). 2,3-Dipropyl-*p*-quinone (1.0 g) was stirred in nitrobenzene (100 ml) at 90°C and aluminium chloride (1 g) in nitrobenzene (30 ml) was added. After 1 h the reaction mixture was poured into ethanol and worked up as described above. The solid obtained (0.61 g, 67 %) was recrystallized from quinoline furnishing long yellow needles m.p. 333–335°. (Found: C 82.8; H 8.0. Calc. for $\text{C}_{48}\text{H}_{56}\text{O}_4$: C 82.7; H 8.0.) MS: $m/e = 696$ (M^+ , 100 %); 667 (17 %); 639 (5 %); 623 (4 %); 595 (5 %); 551 (2 %); 348 (M^{2+} , 16 %); 333.5 (7 %); 319.5 (6.5 %); 305.0 (11 %); 291.0 (25 %); 269.0 (7 %). The successive loss of up to 19 alkyl carbons from the singly and doubly charged molecular ions could be observed although many of the peaks were of low intensity. The IR (KBr) was simple. The most important peaks were at: 740 w, 940 s, 1090 s, 1230 m, 1380 s, 1460 s, 1690 w, 2860 s, 2920 s, 2950 s cm^{-1} . The UV spectrum is shown in Fig. 1.

2,11-Diacetoxy-3,4,6,7,9,10-hexapropylbenzo[1,2-b:4,3-b']bisbenzofuran (diacetate of *3d*). 2,3-Dipropylhydroquinone (0.5 g) was dissolved in acetic acid (5 ml) and mixed with a solution of sulphuric acid (1.5 ml) in acetic acid (3.5 ml). This solution was added to a stirred solution of 2,3-dipropyl-*p*-quinone (1.0 g) in acetic acid (10 ml) at 50°. After about 30 sec a voluminous grey precipitate appeared. After 1 h the mixture was filtered and the solid washed with acetic acid. On dilution with water the filtrate gave a sticky precipitate (0.4 g) which was not further investigated. The solid was mixed with pyridine (20 ml). The resulting mixture was filtered and the solid washed with pyridine (combined filtrates A). The insoluble material (0.05 g) was identified as the tetramer (*Id*). Filtrate A was mixed with acetic anhydride (20 ml) and heated to the boiling point. Upon cooling the trimer *3d* (0.95 g, 58 %) separated. This gave long colourless needles from pyridine, m.p. 247–248°. (Found: C 76.6; H 8.1. Calc. for $\text{C}_{30}\text{H}_{30}\text{O}_6$: C 76.6; H 8.0.) MS: $m/e = 626$ (M^+ , base peak); 584 ($\text{M}^+ - \text{CH}_3\text{CO}$); 542 ($\text{M}^+ - 2\text{CH}_3\text{CO}$); 271 ($\text{M}^{2+} - 2\text{CH}_3\text{CO}$), peaks due to the successive loss of 16 of the 18 alkyl carbons from the ion corresponding to $m/e = 542$ could be observed. NMR (CDCl_3): $\delta = 7.8$ ppm (singlet, 2 aromatic ring H); $\delta = 2.9 - 3.3$ ppm (complex multiplet, 8 H of methylene groups attached to aromatic rings); $\delta = 2.7$ ppm (triplet, 4 H of methylene groups ortho to the acetoxy groups); $\delta = 2.41$ ppm (singlet, 6 acetate methyl H); $\delta = 1.5 - 2.1$ ppm (complex multiplet, 12 aliphatic methylene H); $\delta = 1.08$ ppm (triplet, 18 aliphatic methyl H). The UV spectrum is shown in Fig. 1.

Dihydroxyhexapropylbenzobisbenzofuran (3d). Diacetoxyhexapropylbenzobisbenzofuran (350 mg) was refluxed with sulphuric acid (1 ml) in ethanol (50 ml). After 4 h the mixture was filtered while hot and hot water added to the hot filtrate until crystallization began. After cooling compound *3d* (250 mg, 86 %) was collected. It formed silky needles melting at 255° after sublimation. (Found: C 79.4; H 8.6. Calc. for $\text{C}_{30}\text{H}_{30}\text{O}_4$: C 79.7; H 8.6.) MS: $m/e = 542$ (M^+ , base peak); 513; 271.0 (M^{2+}); 242.5; 228.0; 214.0.

Dimethoxyhexapropylbenzobisbenzofuran (dimethylether of *3d*). Dihydroxyhexapropylbenzobisbenzofuran was methylated with dimethyl sulphate and alkali in the usual way. The product was sublimed to give colourless needles, m.p. 240–243°. (Found: C 79.7; H 9.1. Calc. for $\text{C}_{38}\text{H}_{50}\text{O}_4$: C 80.0; H 9.1.) MS: $m/e = 570$ (M^+ , base peak); 556; 542; 541; 285.0 (M^{2+}); 256.5; 242.0; 228.0.

Acknowledgement. I thank Professor Holger Erdtman for his kind interest throughout this investigation, Miss Gurli Hammarberg for the NMR, IR, and UV-spectra, Miss Annette Grunewald for valuable technical assistance and the *Swedish Board of Technical Development* for financial support.

REFERENCES

1. Erdtman, H. *Proc. Roy. Soc. A* **143** (1933) 228.
2. Erdtman, H. and Högberg, H. E. *Chem. Commun.* **1968** 773.
3. Högberg, H. E. *Acta Chem. Scand.* **26** (1972) 309.
4. Marschalk, C. *Bull. Soc. Chim. France* (5) **5** (1938) 304.
5. Erdtman, H. *Proc. Roy. Soc. A* **143** (1933) 177.
6. Stjernström, N. E. *Arkiv Kemi* **21** (1963) 73.

7. Erdtman, H. and Stjernström, N. E. *Acta Chem. Scand.* **13** (1959) 653.
8. Stjernström, N. E. *Arkiv Kemi* **21** (1963) 81.
9. Erdtman, H. and Högborg, H. E. *Tetrahedron Letters* **1970** 3389.
10. Armstrong, E. C., Bent, R. L., Thirtle, J. R. and Weissberger, A. J. *Am. Chem. Soc.* **82** (1960) 1928.
11. Cruickshank, J. H. and Robinson, R. J. *Chem. Soc.* **1938** 2064.
12. Fieser, L. F. and Ardao, M. I. *J. Am. Chem. Soc.* **78** (1956) 778.
13. Skita, A. and Rohrmann, W. *Ber.* **63** (1930) 1473.

Received December 4, 1971.