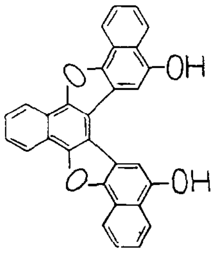
Tetrahedron Letters No.38, pp. 3389-3392, 1970. Pergamon Press. Printed in Great Britain.

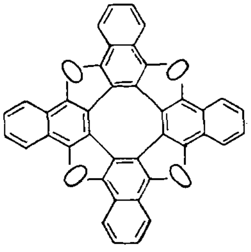
CYCLOOLIGOMERISATION OF QUINONES

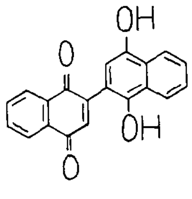
H. Erdtman and H.-E. Högberg
Department of Organic Chemistry, Royal Institute of Technology
S-100 44 Stockholm, Sweden

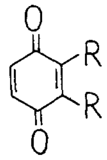
(Received in UK 9 July 1970; accepted for publication 19 July 1970)

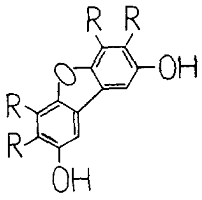
When treated with a mixture of sulphuric acid, acetic acid and water (method I) α-naphthoquinone gives trimeric and tetrameric condensation products (1 and 2, respectively). With aluminium chloride in nitrobenzene (method II) a 95 % yield of 2 is obtained[1].

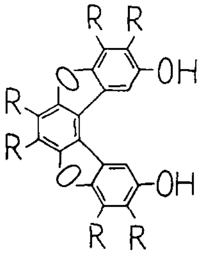

1

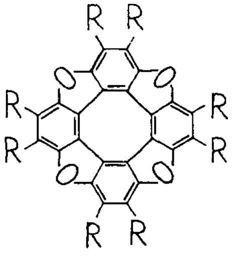

2

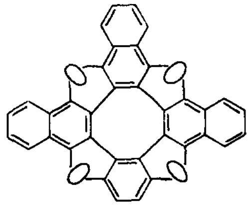

3


4


5


6


7


8

Similarly[2] (method I) *p*-benzoquinone (4, R=H) gives 6 (R=H)[2] and quinone 4 (R=CH_3) furnishes 5 (R=CH_3) and 6 (R=CH_3)[3]. Omitting the reductive acetylation step used in these experiments we have found that according to method I the quinone 4 (R=CH_3) also gives a 30 % yield and by method II a 60 % yield of the tetramer 7 (R=CH_3). The phenolic components of the reaction products were soluble in pyridine in which the tetramer was practically insoluble. Sublimation under reduced pressure of the latter fraction furnished pure 7 (R=CH_3). Similarly (method II) 2,3-dipropyl-*p*-benzoquinone (4, R=C_3H_7) gave octapropyltetraphenylenotetrafuran 7 (R=C_3H_7) in 60 % yield and 5,6,7,8-tetrahydronaphthoquinone furnished 7 (R pairwise = $(CH_2)_4$). Several other 2,3-disubstituted p-benzoquinones reacted in the same way, however, 2,3-dichloro- and 2,3-dimethoxy-p-benzoquinone and anthraquinone-1,4 furnished no cyclooligomerisation products.

p-Benzoquinone treated according to method I (time of reaction 48 h - 30 days) gave a sparingly soluble product which on distillation under reduced pressure gave a solid distillate consisting mainly of 6 (R=H) and a minute amount of less volatile products. The major portion of the reaction products was in the charred residue. The distillate was washed with acetone in which compound 6 (R=H) was soluble. The acetone insoluble material was subjected to gradient sublimation. A brown-yellow zone containing the slightly impure tetramer 7 (R=H) travelled fastest and was followed by another zone which according to ir and mass spectrum (M^+: m/e=470) contained a phenolic product with five benzene nuclei. The yield of compound 7 (R=H) based on p-benzoquinone was, as expected, very low, only 0.1 - 0.2 %. This substance was obtained pure, free from phenolic impurities, by moistening the product with a little alkali followed by sublimation. This furnished 7 (R=H) as pale yellow needles.

Apparently these yellow crystalline tetramers are formed along different converging routes, one involving successive di-, tri- and tetramerisation of the respective quinones, another dimerisation of primary dimers of the type 3 (the dimer 3 gives the tetramer 2 according to method II[1]).

Of particular interest is the fact that in the presence of the α-naphthoquinone trimer 1 p-benzoquinone gives compound 8 (method II). Its structure follows from the analysis, ir and ms (M^+: m/e=510). Under these conditions p-benzoquinone alone does not yield any crystalline condensation product.

In this connexion it is of interest that Hansson and Stjernström[4] observed that the yields of the trimers 6 (R=H) and 6 ($R=CH_3$) were considerably increased if the respective dihydroxydibenzofuran 5 was added to the reaction mixture. Obviously the formation of dibenzofuran elements directs the condensation reaction in such a way that extensive cyclooligomerisation occurs with 2,3-disubstituted quinones. p-Benzoquinone, possessing no blocking groups in the 2- and 3-positions, however, mainly undergoes irregular polymerisation. So far we have no evidence for the presence of open tetramerisation products in our reaction mixtures.

It would appear that the tetraphenylenotetrafurans are planar or very nearly so. An X-ray investigation is in hand.

All the tetraphenylenotetrafurans were yellow and exhibited a green-yellow fluorescence in uv-light (the trimers show a blue-white fluorescence). They were almost insoluble in the common solvents but somewhat soluble in high boiling solvents; for example one ml of boiling quinoline dissolved about one mg of the tetramer 7 ($R=CH_3$).

The compound 7 ($R=CH_3$) is sufficiently soluble in 1,2,4-trichlorobenzene to give the shape of the absorption curve in the 300 - 400 nm region but not the extinctions. Cyclohexane was the solvent used for studying the uv absorption of the tetramer 7 ($R=C_3H_7$). As seen from figure 1 there is a striking similarity between the uv absorption of the diacetate of 6 (R=H) and of 7 ($R=C_3H_7$). This seems to indicate that the final formation of the central eight-membered ring does not cause any specific conjugation effects.

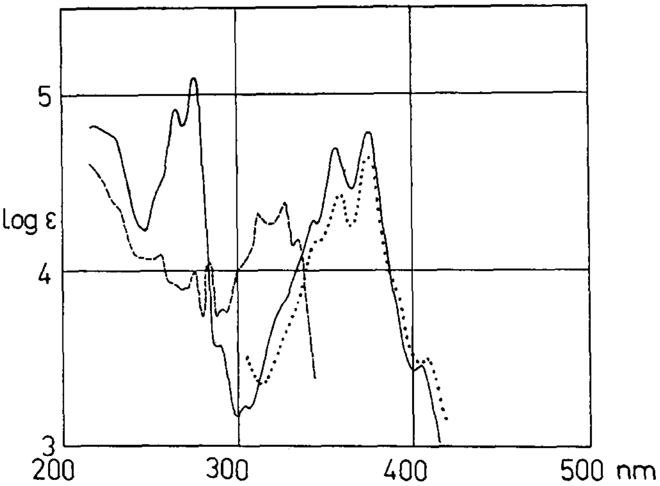


Fig. 1. Ultraviolet absorption curves of compound 7 ($R=C_3H_7$) in cyclohexane ———, of the acetate of compound 6 (R=H) in ethanol - - - -, of compound 7 ($R=CH_3$) in 1,2,4-trichlorobenzene ······· (arbitrary log ε values).

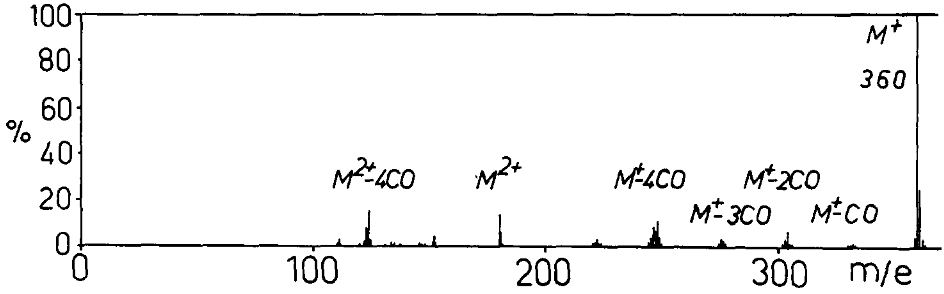
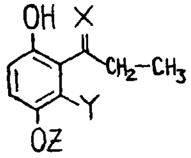


Fig. 2. Mass spectrum of compound 7 (R=H) at 70 eV.

The mass spectra bear witness of the great stability of these tetraphenylenotetrafurans. Of compound 2 the only peaks of any importance are those corresponding to M^+ (100 %), M^{2+} (36 %) and M^{3+} (6 %). No other peaks of abundance higher than 1 % were present. Figure 2 shows the ms of compound 7 (R=H). A major feature is the successive loss of four CO (M=28) from the singly and doubly charged molecular ions. In addition to this the alkylated tetramers lose alkyl fragments.

The melting points of these novel compounds are very high and therefore not easy to determine by simple means. The following melting points may be mentioned: Compound 2: 625°, 8: 540°, 7 ($R=CH_3$): 530°, 7 (R pairwise = $(CH_2)_4$): 480°, 7 (R=H): 470° and 7 ($R=C_3H_7$): 335°.

Quinone 4 ($R=C_3H_7$) m.p. 36-37° was prepared (cf ref. 5.) by allylation of 2,5-dihy-



9

droxypropiophenone to 9 (X=O, Y=H, Z=allyl) m.p. 50-51°, rearrangement to 9 (X=O, Y=allyl, Z=H) m.p. 90-91°, catalytic hydrogenation to 9 (X=O, $Y=C_3H_7$, Z=H) m.p. 114°, reduction with copper chromite to 9 ($X=H_2$, $Y=C_3H_7$, Z=H) m.p. 152-153° and finally oxidation with chromic acid to 4 ($R=C_3H_7$).

All new compounds gave satisfactory analytical results.

We thank the Swedish Board of Technical Development for economical support.

References:

1. Erdtman H., Högberg H.-E., Chem. Comm. 1968 773
2. Erdtman H., Proc. Roy. Soc. A 143 223 (1933)
3. Stjernström N.E., Arkiv Kemi 21 73 (1963)
4. Hansson S., Stjernström N.E., Arkiv Kemi 21 81 (1963)
5. Armstrong E.C. et al., J. Amer. Chem. Soc. 82 1928 (1960)