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CYCLOOLIGOMERIC PHENOL-ALDEHYDE CONDENSATION PRODUCTS I

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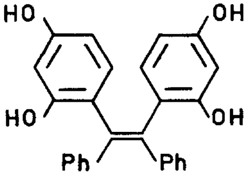
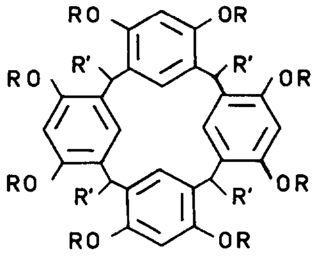
According to early observations (Baeyer (1), Michael (2), Liebermann and Lindenbaum (3) benzaldehyde condenses with resorcinol or pyrogallol in equimolar proportions under the influence of strong acids. The correct elementary composition of the very sparingly soluble, high melting, crystalline product $(C_{13}H_{10}O_2)_n$ from resorcinol and its acetate $\left(C_{13}H_8(OCOCH_3)_2\right)_n$ was established by Michael (2). Owing to the physical properties of the products no estimation of their molecular weights could be carried out at this time. Michael suggested the rather improbable structure I for the phenolic product, and this structure was later adopted by Fabre (4) and has been quoted in works on polymer chemistry (5).

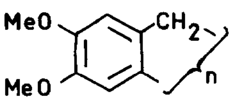


I



II: R = H
R′= Me, Et, Bu^i

III: R′= Ph
a: R = H; b: R = Me
c: R = Ac; d: R = COEt
e: R = COPr^n



IV: n = 3
V: n = 4

Niederl and Vogel have studied several condensation products obtained from aliphatic aldehydes and resorcinol and suggest that they possess the general structure II (6). The configurations were not discussed. It appears probable that the condensation products from aromatic aldehydes have a similar constitution III and in this connection it is of interest to note that the condensation of veratrol and formaldehyde gives IV (7,8) and V (8). (The latter in small yield.)

Theoretically compounds such as II and III can exist in four different configurations. If III is the correct structure for the resorcinol-benzaldehyde condensation product, then one would expect it to be a mixture of stereoisomers.

The elucidation of the configuration of the products formed would be a matter of interest since it may throw light on the course of the condensation reaction. Apparently steric factors and neighbouring groups play an important role in condensation reactions of this type. Orcinol, for example, gives only an amorphous, obviously high molecular weight condensation product with benzaldehyde.

We have now worked out optimum conditions for the condensation of benzaldehyde and other aromatic aldehydes with resorcinol as well as with pyrogallol. The yield of crude, crystalline product obtained from resorcinol and benzaldehyde was surprisingly high (90 - 95 %). On acetylation or methylation products were obtained each of which consisted of two main components (thin layer chromatography). Neither the methyl derivatives (IIIb) nor the acetates (IIIc) or the propionates (IIId) could be easily separated into pure compounds by fractional crystallisation.

Fractional crystallisation of the butyrates (IIIe), however yielded a compound A: $(C_{13}H_8(OCOC_3H_7)_2)_4$ m.p. 214 - 215°, λ_{max}^{EtOH} 270 mμ and 278 mμ (log $\epsilon = 3.72$ and 3.68), and an isomer B: m.p. 251 - 254°, λ_{max}^{EtOH} 271 mμ and 277 mμ (log $\epsilon = 3.53$ and 3.50). The molecular weights of both compounds were found to be 1354 (mass spectrometry) as expected for a macrocyclic tetramer $(C_{21}H_{22}O_4)_4$. The UV absorptions, which rule out the stilbene structures of type I, as well as the IR spectra were very similar but there were differences in the NMR spectra indicating steric differences.

The butyrates were hydrolysed to the corresponding phenols (IIIa) from which the acetates and methyl ethers were prepared. The butyrate A furnished an acetate $(C_{13}H_8(OCOCH_3)_2)_4$ m.p. 367° dec., and a methyl ether $(C_{13}H_8(OCH_3)_2)_4$ m.p. 401 - 405°. The butyrate B gave an acetate $(C_{13}H_8(OCOCH_3)_2)_4$ m.p. 351° dec., and a methyl ether $(C_{13}H_8(OCH_3)_2)_4$ m.p. 345 - 349°.*

A mixture of methyl ethers (IIIb) was obtained in 55 % yield by condensing benzaldehyde with resorcinol dimethyl ether, using hydrogen chloride as a catalyst, and a similar mixture was obtained by condensing benzaldehyde with 2,2',4,4'-tetramethoxy triphenylmethane or by treating 2,4-dimethoxy benzhydrol with strong acid. In the latter case the yield was small.

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* Melting points were recorded using a Perkin Elmer DSC-1 Differential Scanning Calorimeter calibrated from 327° (m.p. of lead) to 419° (m.p. of zinc).

2,2',4,4'-Tetramethoxy triphenylmethane was prepared according to Baeyer (9). It was also obtained in about 15 % yield by methylating a phenolic condensation product obtained from benzaldehyde and resorcinol (in large excess) in alkaline solution.

Fuming nitric acid cleaves the methyl ethers (IIIb) into 4,6-dinitroresorcinol dimethyl ether (60 % yield) and 3,5-dinitrobenzoic acid. This confirms the structure of the condensation product.

From the condensation product of resorcinol and p-bromobenzaldehyde a butyrate C $(C_{21}H_{21}BrO_4)_n$ melting at 240 - 244° was isolated (46 % yield). In order to determine the structure and configuration of this compound it was subjected to an X-ray analysis.

The unit cell dimensions are $\underline{a}$ = 13.99, $\underline{b}$ = 15.00, $\underline{c}$ = 20.23 Å, α = 81.66°, β = 75.26°, γ = 89.92°. The space group was determined to be $P\bar{1}$ and there is one molecule per asymmetric unit. There is no symmetry in the molecule despite the fact that it is a tetramer.

Data for 2936 independent reflections were collected using Weissenberg multiple film techniques. The positions of the four bromine atoms were obtained by addition and subtraction of Patterson vectors. Using the phases of the located heavy atoms the structure was then solved by successive structure factors calculation - Fourier synthesis - peak scanning cycles. Block diagonal least-squares refinement of positional and anisotropic vibrational parameters for all non-hydrogen atoms gave a final overall conventional $\underline{R}$ index of 0.105.

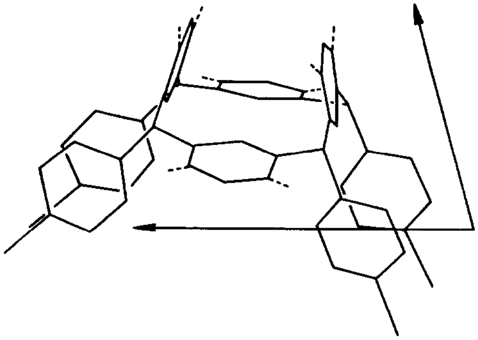

FIG. 1. Projection of the Molecule C. The Butyrate Chains are only indicated.

The configuration of the molecule is shown in FIG. 1. In order to present a clear picture the positions of the butyrate chains are only indicated. The four carbons at the condensation centres are planar, and the p-bromophenyl groups are all directed to the same side of that plane.

The three benzene rings that surround each condensation centre are roughly perpendicular to each other, the intersection angle ranging from 72° to 88°. A detailed account of the X-ray analysis will be given in a full paper (10).

We are continuing this work with the object of establishing the configurations of the above butyrates A and B as well as of several similar condensation products.

Acknowledgements

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