1249. *Benzyl Radicals Derived from Cyclic Acetals of Hydrobenzoin*

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Some reactions of radicals derived from the *OO*-isopropylidene and *OO*-benzylidene derivatives of *meso*-hydrobenzoin are described. The dimers are the major products.

STUDY of the benzyl radicals $Ph{\cdot}\dot{C}H{\cdot}O{\cdot}R$, derived from benzyl ethers,[1] has recently been extended to cyclic systems such as phthalan, naphthalan, and diphenan [2] from which it is noted that attachment of the radical centre as part of a ring system can result in considerable modification to its properties. We now report an investigation of the radicals generated from two other cyclic benzyl ethers, namely, the *OO*-isopropylidene and *OO*-benzylidene derivatives of *meso*-hydrobenzoin.

Reaction of the former acetal with t-butoxy-radicals (from the peroxide at 125—130°) gave the dimer (II) in 60% yield, accompanied by traces of benzil. The dimer appeared to be a mixture of stereoisomers, but its extremely low solubility in organic solvents precluded separation of these isomers by the usual means. Its structure was established as follows. Treatment with hydrobromic acid in acetic acid for 2 hours afforded two products, a dihydroxy-derivative of tetraphenyltetrahydrofuran, probably (IV), and tetraphenylfuran, accompanied by some tar; prolonged treatment caused extensive resinification. These products clearly originate from the dimer (II) through hydrolysis to the tetraol (III), followed by cyclisation to (IV),[3] and thence by elimination of two molecules of water to the furan which itself is partially resinified by the halogen acid. Thus, in contrast with the radical $Ph{\cdot}\dot{C}H{\cdot}O{\cdot}CHMe_2$ generated from benzyl isopropyl ether, which has been shown [1] to exhibit about equal tendencies to dimerise and to disproportionate (to benzaldehyde and the isopropyl radical), the radical (I) appears to be relatively stable, preferring dimerisation. Disproportionation would give the radical (V), which would be expected to break down further, at least partly, to acetone and the desyl radical (VI) and this, as has been shown elsewhere,[2] should dimerise to bidesyl. No bidesyl, however, could be detected (spectroscopically). On the other hand the radical (V) could conceivably have abstracted a hydrogen atom (intra- or inter-molecularly), yielding benzil *via* the radical (VII).

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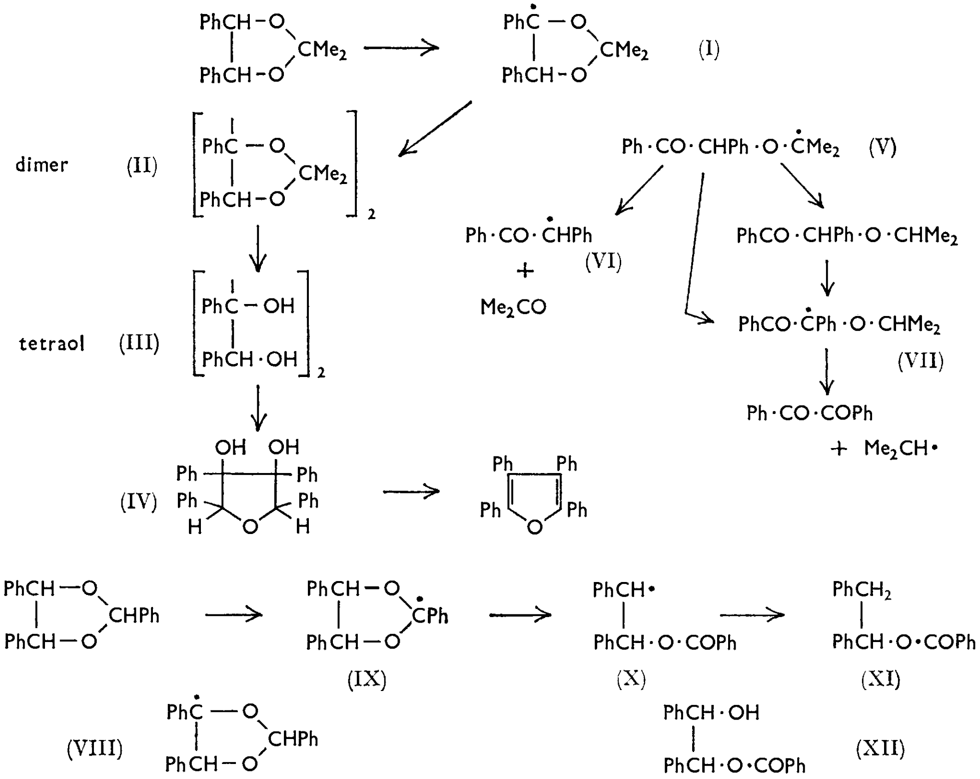
[1] R. L. Huang and S. Si-Hoe, *Proc. Chem. Soc.*, 1957, 354; " Vistas in Free-Radical Chemistry," ed. W. A. Waters, Pergamon, London, 1959, p. 242.
[2] R. L. Huang and H. H. Lee, *J.*, 1964, 2500.
[3] Cf. G. Bernhardt and F. Korte, *Angew. Chem. Internat. Ed.*, 1965, **4**, 149.

In benzylidene-*meso*-hydrobenzoin abstraction of hydrogen could occur to generate either the ether radical (VIII) or the acetal radical (IX). The latter would, in analogy



with those derived from acetals of benzaldehyde reported recently,[4] disproportionate to the ester radical (X). Action of t-butoxy-radicals on the acetal gave a complex mixture of products from which were isolated, in small quantities, the ester (XI) and the hydroxy-ester (XII). The origin of the former seems clearly to be the radical (X), while the latter could conceivably have been formed through partial hydrolysis of the unreacted acetal during the extensive chromatographic processes employed in the separation of the products. As the yields of identifiable substances were low, no conclusion could be drawn as to the course of the reaction.

EXPERIMENTAL

Microanalyses were carried out by Mrs. H. K. Tong, Singapore. M. p.s were taken on a Kofler hot-stage apparatus. Infrared absorption was determined on a Hilger H.800 spectrophotometer.

Isopropylidene meso-*Hydrobenzoin.*—A solution of *meso*-hydrobenzoin (2·14 g.) in acetone (50 c.c.) was shaken with anhydrous copper sulphate (5 g.) for 50 hr. at 28°. The copper sulphate was separated and the acetone evaporated, to give the required *acetal* (1·5 g., 60%), needles from light petroleum (b. p. 40—60°), m. p. 57—58° (Found: C, 79·8; H, 7·15. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·13%).

Reaction with Di-t-butyl Peroxide.—The above ketal (5·0 g.) and the peroxide (1·5 g.) were

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[4] E. S. Huyser and Z. Garcia, *J. Org. Chem.*, 1962, **27**, 2716; R. L. Huang and K. H. Lee, *J.*, 1964, 5957.

sealed under nitrogen in a glass tube and heated at 125—130° for 14 hr. On cooling, the *ketal dimer* separated, m. p. 259—263° (1·8 g., 60%), and was filtered. It was sparingly soluble in the usual organic solvents (ether, ethanol, benzene, chloroform, ethyl acetate, and dimethylformamide), and only slightly so in acetic acid. Repeated crystallisation from large volumes of chloroform did not improve the m. p. [Found: C, 81·0; H, 7·02%; *M*(Rast), 409. $C_{34}H_{34}O_4$ requires C, 80·6; H, 6·76%; *M*, 506]. The filtrate, on removal of volatile material, gave a residue (2·5 g.) which was adsorbed on neutral activated alumina and eluted with light petroleum, followed by light petroleum–benzene, benzene, and benzene–ether, to yield, respectively, (i) unchanged ketal (2·0 g.); (ii) benzil (traces), identified as the 2,4-dinitrophenylhydrazone (m. p. and mixed m. p.); (iii) a solid, m. p. 210—220° (*ca.* 0·005 g.) which could not be identified; and (iv) *meso*-hydrobenzoin (0·02 g.).

Degradation of Ketal Dimer.—The dimer (3·0 g.) was boiled with a mixture of 48% hydrobromic acid (10 c.c.) and glacial acetic acid (30 c.c.) for 2 hr. On cooling, the unchanged dimer (2·5 g.) was filtered off, and the filtrate poured into water (150 c.c.) basified with sodium carbonate (20%), extracted with ether, and dried ($MgSO_4$). Concentration yielded a gum which on trituration with light petroleum furnished a solid, probably 3,4-*dihydroxy*-2,3,4,5-*tetraphenyltetrahydrofuran*, m. p. 243—245° (0·1 g.) after recrystallisation from benzene, from which it separated as needles (Found: C, 82·7; H, 5·87; O, 11·9. $C_{28}H_{24}O_3$ requires: C, 82·3; H, 5·92; O, 11·75%).

The petroleum washings (see above) were partially concentrated and passed through a column of alumina, yielding tetraphenylfuran (0·005 g.), m. p. 173—175° (Found: C, 90·5; H, 5·66. $C_{28}H_{20}O$ requires: C, 90·3; H, 5·41%), identified by comparison of m. p. and infrared absorption with an authentic sample prepared as reported by Lutz *et al.*[5]

Reaction of Benzylidene meso-*Hydrobenzoin with Di-t-butyl Peroxide.*—The acetal was prepared by heating *meso*-hydrobenzoin (5 g.) in an excess of benzaldehyde (100 g.) at 100° for 2 hr. (nitrogen), and recrystallised from light petroleum, m. p. 109—110° (1·5 g.) (Found: C, 83·3; H, 6·12. Calc. for $C_{21}H_{18}O_2$: C, 83·4; H, 6·0%). Read *et al.*,[6] however, record m. p. 84°. The product from the acetal (6·0 g.), and the peroxide (1·5 g.) after removal of volatile material, gave a residue which could not be induced to crystallise. Chromatography in light petroleum solution gave 50 fractions, from which were obtained: (i) unchanged acetal (5 g.); (ii) α-benzoyloxybibenzyl, m. p. 71—73° $\nu_{max.}$ 1720, 1265 cm.$^{-1}$ (Found: C, 83·3; H, 6·03. Calc. for $C_{21}H_{18}O_2$: C, 83·4; H, 6·0%) identified by comparison of m. p. (lit.,[7] m. p. 69—71°) and infrared absorption with an authentic sample prepared from deoxybenzoin and benzoyl chloride; (iii) α-hydroxy-β-benzoyloxybibenzyl, m. p. 164—165° (lit.,[8] 160—161°) (0·10 g.), $\nu_{max.}$ ~3580, 1718, 1265 cm.$^{-1}$ (Found: C, 79·4; H, 5·89. Calc. for $C_{21}H_{18}O_3$: C, 79·2; H, 5·70%); (iv) a mixture of solids which did not give homogeneous material after further chromatography.

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[5] R. E. Lutz, C. R. Bauer, R. G. Lutz, and S. S. Gillespie, *J. Org. Chem.*, 1955, **20**, 218.

[6] J. Read, I. G. MacNaughton Campbell, and T. V. Baker, *J.*, 1929, 2305.

[7] R. Huisgen and C. Ruchardt, *Annalen*, 1956, **601**, 1.

[8] C. Forst and T. Zincke, *Annalen*, 1876, **182**, 241.