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REACTION OF BENZYNE GENERATED FROM 1-(2-CARBOXYPHENYL)-3,3-DIMETHYLTRIAZENE WITH BENZALDEHYDE AND SOME OTHER CARBONYL COMPOUNDS

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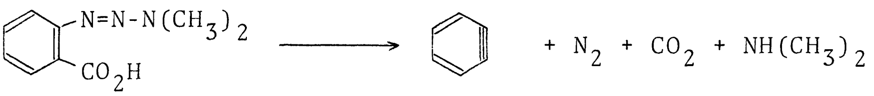
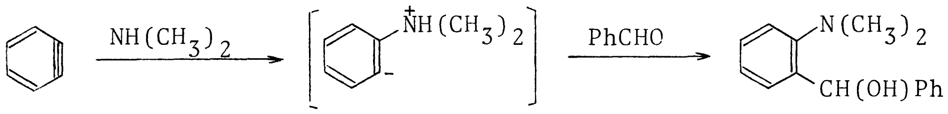
1-(2-Carboxyphenyl)-3,3-dimethyltriazene, on being heated in benzaldehyde, affords 2-dimethylaminobenzhydrol and cis- and trans-2,4-diphenyl-1,3-benzodioxins; similar products were obtained with some other carbonyl compounds.

Generation of benzyne from 3-substituted 1-(2-carboxyphenyl)triazenes has recently been described.1) Heating 1-(2-carboxyphenyl)-3,3-dimethyltriazene (I; 25 mmoles) at 160° in 100 ml of benzaldehyde for two hours under nitrogen gave a basic compound, $C_{15}H_{17}NO$ (II, 12%), and two isomeric products, $C_{20}H_{16}O_2$, one with m.p. 145-146° (III, 19%) and the other m.p. 84-86° (IV, 8%). Compound II, ν_{OH} (KBr) 3550 cm^{-1}, δ (DMSO-d_6) 2.6 (6H, s), 5.9 (1H, s), 6.3 (1H, s) and 7.0-7.5 (9H, multiplet), was identified with 2-dimethylaminobenzhydrol by mixed m.p. determination with a specimen prepared by reduction of 2-dimethylaminobenzophenone with lithium aluminium hydride. Compound III, ν_{max} (KBr) 1240 (aryl ether) and 1120, 1070, 1030 and 978 (acetal) cm^{-1}, δ ($CDCl_3$) 6.15 (1H, methine), 6.22 (1H, methine) and 6.5-7.8 (14H, aromatic), and compound IV, ν_{max} (KBr) 1240 (aryl ether) and 1055, 1030, 1000 and 975 (acetal) cm^{-1}, δ ($CDCl_3$) 5.92 (1H, methine), 6.04 (1H, methine) and 6.8-7.4 (14H, aromatic), were shown to be cis- and trans-2,4-diphenyl-1,3-benzodioxins, respectively, by separate preparation of these compounds by heating 2-hydroxybenzhydrol and benzaldehyde at 160° for 8 hours. The configurational assignment will be given below.

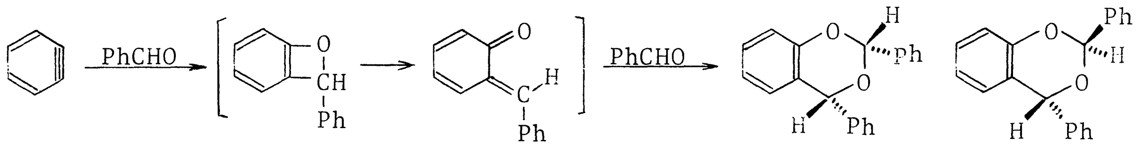
Thus, the reaction of 1-(2-carboxyphenyl)-3,3-dimethyltriazene with benzaldehyde may be formulated as follows:



(I)



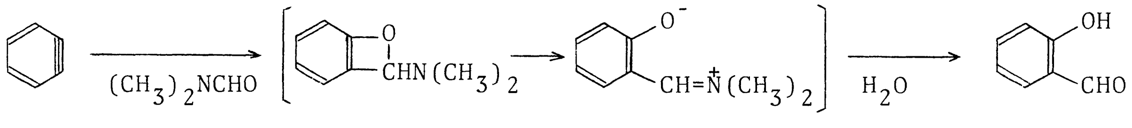
(V) (II)



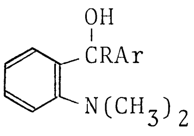
(VI) (VII) (III) (IV)

In the formation of 2-dimethylaminobenzhydrol (II), it seems probable that a betaine-like structure (V)[2] intervenes, its carbanionic centre attacking the carbonyl carbon of benzaldehyde to afford the final product (II). The cyclo-addition of benzyne to the carbonyl group of benzaldehyde gives a benzoxete intermediate (VI), which collapses to a quinone-methide (VII) by ring-opening, and this intermediate subsequently undergoes a 1,4-addition with benzaldehyde to yield the benzodioxins (III and IV). Heaney and Jablonsky has already postulated such cyclo-addition and ring-opening in the formation of 2H-chromenes from tetrachlorobenzyne and unsaturated aldehydes.[3]

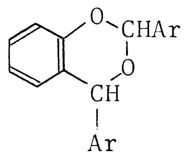
The decomposition of the triazene (I) in boiling dimethylformamide gave salicylaldehyde in 20% yield in agreement with the finding with benzenediazonium-2-carboxylate reported by Yaroslavsky.[4] The present result can best be explained in terms of cyclo-addition and ring-opening as shown below.



The following benzhydrols and 1,3-benzodioxins were obtained in similar ways, but the configurations of the 1,3-benzodioxins were not determined: VIII (23%), decompn. point of the hydrochloride, 159.5-160.5°; IX (16%), m.p. 72.5-73.0°; X (14%), m.p. 164-165° (lit.[5] 158-160°); XI (11%), m.p. 161-162°; XII (9%), m.p. 148-150°. Benzhydrols (IX) and (X) were obtained by heating the triazene (I) in acetophenone at 145-155° and by boiling the triazene and benzophenone in chlorobenzene, respectively. Satisfactory elementary analyses and supporting spectral data were obtained for all of these compounds.

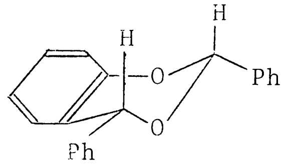


VIII: Ar = p-ClC_6H_4, R = H
IX: Ar = C_6H_5, R = CH_3
X: Ar = R = C_6H_5



XI: Ar = p-$CH_3OC_6H_4$
XII: Ar = p-ClC_6H_4

On the basis of the difference in chemical shift of methine proton signals between compounds III and IV, it is highly probable that the two phenyl groups are disposed cis in isomer III and trans in isomer IV.[6)] By reference to the figure below, it is obvious that IIIa is the more favoured conformation, both phenyl groups being in the equatorial position; the equilibrium position between IVa and IVb is not evident and does not seem to be much shifted in either direction, but the steric interaction between the phenyl group at position 4 and the hydrogen at position 5 in IVb may favour IVa slightly over IVb. Thus, the fact that the methine signals from compound IV are shifted to higher field regions relative to those of compound III is readily accounted for by the shielding of the axial hydrogens by the axial phenyl groups in IVa and IVb.



(IIIa)

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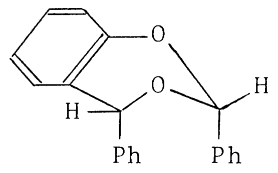
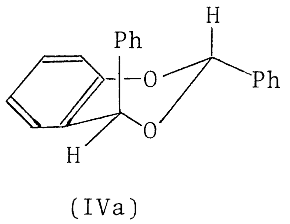


(IIIb)



(IVa)

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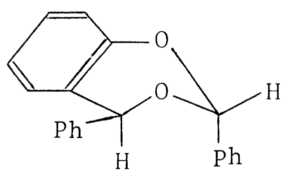

(IVb)

The above configurational assignment is supported by the fact that, in an equilibrium mixture, compound III is predominant over compound IV; obviously, the former is the more stable isomer, since in this compound both the phenyl groups can occupy equatorial positions. Thus, the condensation of benzaldehyde with 2-hydroxybenzhydrol at 160° for 2 hours gave an equilibrium mixture of the benzodioxins (III/IV = 57/43, as determined by n.m.r. measurements), whereas the triazene (I) on being heated with benzaldehyde at 135° and 160° for two hours gave mixtures of the benzodioxins in ratios of III/IV = 74/26 and 69/31, respectively. When the latter mixture was heated in benzaldehyde at 160° for 6 hours, the composition changed to the equilibrium ratio of 56/44, probably the isomerization being catalyzed by contaminating benzoic acid.

The reaction of benzyne generated from benzenediazonium-2-carboxylate7) with benzaldehyde in methylene dichloride at 40° was found to afford compound III exclusively. The selective formation of the cis isomer suggests that the 1,4-addition of intermediate VII with benzaldehyde takes place concertedly in the syn fashion with the endo orientation in keeping with the usual Diels-Alder type addition.8)

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