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THE PHOTOCHEMISTRY OF o-BENZYLOXYBENZALDEHYDE.
A NOVEL PHOTOINDUCED CYCLIZATION

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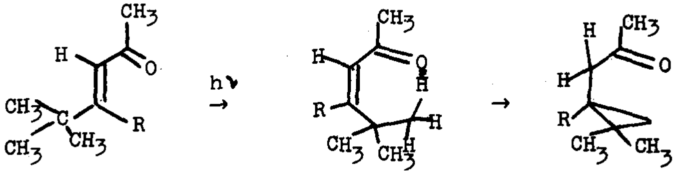
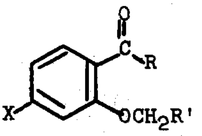
On excitation by light, saturated aldehydes and ketones are known to abstract hydrogen intramolecularly, via a six-membered ring transition state, to afford cyclobutanols.[2] The α,β-unsaturated ketones I undergo ring closure at the δ-position on irradiation, to provide the acetonylcyclopropanes II.[3] This reaction may involve intramolecular hydrogen abstraction via a seven-membered ring transition state.



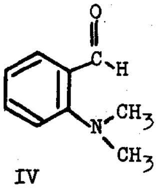
Ia, R=H
b, R=CH_3

IIa, R=H
b, R=CH_3

We have been investigating the photochemistry of the aromatic aldehydes and ketones III and IV in which the γ-position is occupied by a heteroatom, bearing no hydrogen, and would like to present a preliminary report of our results with o-benzyloxybenzaldehyde (IIIa).

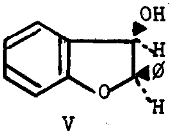


IIIa, R=H, R'=Ø, X=H
b, R=CH_3, R'=Ø, X=H
c, R=$COOCH_3$, R'=H, X=OCH_3

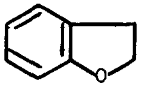


IV

Irradiation of o-benzyloxybenzaldehyde[4] (1.0 g. in 600 ml. of acetonitrile). for five hours by means of a Hanovia 450 watt immersion light source and Pyrex filter, led to the complete disappearance of the carbonyl band and the concommitent appearance of hydroxyl absorption, as determined by infrared analysis. Chromatography of the residual oil on basic alumina (Brockman activity 1 to which was added six per cent water) afforded two major fractions. The first fraction, eluted with benzene and recrystallized from benzene-hexane, afforded 150 mg. of a white solid, m.p. 126-7°, to which we assign the structure, cis-2-phenyl-3-hydroxyl-2,3-dihydrobenzofuran (V).



V

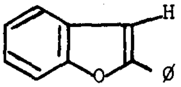


VI

The elemental analysis and molecular weight, as well as the infrared and ultraviolet spectra are consistent with the gross structural assignment -- Anal. Calc. for $C_{14}H_{12}O_2$: C, 79.3; H, 5.7. Found: C, 79.5; H, 5.8; Molecular weight, Calc.: 212. Found: 212 (Mass Spec.); $\nu^{OH}_{CHCl_3}$ 3.60 x 10^3 cm^{-1}; λ^{meth}_{max} 280 mμ (ϵ =3.1 x 10^3), 286 mμ (ϵ =2.7 x 10^3); Reported[5] for VI, $\lambda^{cyclohexane}_{max}$ 282 mμ (ϵ =3.3 x 10^3), 289 mμ (ϵ =3.0 x 10^3).

The n.m.r. spectrum[6] of V exhibits aromatic absorption (a singlet at 440 cps, superimposed on a multiplet centered at slightly higher field), an AB quartet for the methine hydrogens, δ = 327 and 306 cps (J = 6 cps) and a relatively sharp hydroxyl absorption at 92 cps (20% in $CDCl_3$), 85 cps (10% in $CDCl_3$), which disappears on addition of D_2O. The coupling constant of the AB quartet, indicative of a dihedral angle of about 30°,[7] as well as the relatively high field hydroxyl absorption, arising from anisotropic shielding, are consistent with the stereochemical assignment.

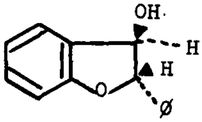
On passing anhydrous hydrogen chloride gas through a methanolic solution of the photoproduct V, the ultraviolet absorption spectrum changes rapidly -- the reaction is over in several minutes -- and becomes that of 2-phenylbenzofuran (VII), which, after one recrystallization from 95% ethanol, is isolated in 60% yield, m.p. 120-1° (reported[8] m.p. 120.8-121.2°). The ultraviolet spectrum is identical with that reported for VII.[8] The ready dehydration of V to 2-phenylbenzofuran provides chemical evidence for the gross structural assignment. Besides aromatic absorption, the n.m.r. spectrum of VII exhibits only a sharp singlet at 418 cps, attributable to the hydrogen in position three. The major peak in the mass spectrum is at m/e 194, corresponding to the molecular ion.



VII

As stated previously, two major fractions were obtained on chromatography of the photoproducts from o-benzyloxybenzaldehyde. The first fraction, eluted with benzene, afforded the crystalline photoproduct V. The second fraction,eluted with 50% solvent ether-50% benzene, accounted for about 50% of the total material balance. After many attempts to induce crystallization, a pale yellow oil was obtained which exhibited an n.m.r. spectrum, the predominent resonances of which were similar to that of the crystalline photoproduct V, except that the AB quartet had J = 3.6 cps, and the hydroxyl absorption, which disappeared on addition of D_2O, appeared as a broad peak at 170 cps (about 10% in $CDCl_3$). The ultraviolet and infrared spectra were also similar to that of V, except that the oil exhibited much stronger infrared absorption in the region of hydrogen-bonded hydroxyl stretching. Attempts to purify this material by either careful rechromotography on alumina or high vacuum sublimation (distillation) resulted in extensive decomposition.

While the physical properties of the oil suggest the isomeric structure VIII, we expect to obtain definitive evidence after pur-



VIII

fication by scanning partition chromatography,^{9} and will submit a detailed report of this study, including its mechanistic implications, in the near future.

ACKNOWLEDGEMENTS

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