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PHOTOCHEMICAL SYNTHESIS OF 3-OXETANOLS

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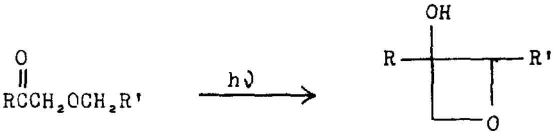
Yang[1] and Jeger[2] and their coworkers have observed the formation of cyclobutanols on irradiation of ketones which possess a γ-carbon atom bearing hydrogen. It has now been found that a cognate reaction can be effected with α-alkoxy ketones (I), providing a method for the preparation of 3-oxetanols (II).[3]



I II

Irradiation of a 1% solution of α-methoxyacetophenone (I, R = C_6H_5, R' = H) in benzene under nitrogen with a Hanovia 450 w. water-cooled high pressure Hg lamp for 12 hours gave a mixture of products from which 3-phenyl-3-oxetanol (II, R = C_6H_5, R' = H) was obtained in 29% yield by chromatography on silica. An analytical sample was obtained by molecular distillation and recrystallization from pentane as needles, m.p. 55-56°, $\lambda_{max}(CCl_4)$ 2.77, 2.93, 8.50, 10.17 μ.[4] (Anal. Calcd. for

$C_9H_{10}O_2$: C, 71.98; H, 6.71; M.W. 150, Found: C, 72.18; H, 6.73; M.W. (osm.) 163). The n.m.r. spectrum (Me_2SO)[5] is in accord with the assigned structure, showing a singlet due to the hydroxyl hydrogen atom at δ = 6.28 p.p.m., an AB system of relative intensity four assigned to the methylene hydrogen atoms with δ = 4.70 and 4.79 p.p.m. (J = 6.5 c./s.),[6] and a multiplet of relative intensity five, due to the aromatic hydrogen atoms, centered at 7.5 p.p.m.; the signal at 6.28 p.p.m. was absent after treatment of the solution with D_2O. The structural assignment was confirmed by the demonstration that the photochemical product is identical to the product, m.p. 54.5-55.5° (mixed m.p. 55-56°), obtained by treatment of 3-oxetanone[7] with phenylmagnesium bromide followed by aqueous ammonium chloride. The identification of acetophenone and formaldehyde among the other products of the photochemical reaction indicates that the formation of the oxetanol is accompanied by a "Norrish type II" cleavage[8] of the alkoxy ketone.[9]

Similar irradiation of α-ethoxyacetophenone (I, R = C_6H_5, R' = CH_3) gives 2-methyl-3-phenyl-3-oxetanol (II, R = C_6H_5, R' = CH_3) in 34% yield after chromatography of the reaction mixture on silica. The analytical sample was obtained by molecular distillation at 75-80° (0.5 mm.) as a colorless liquid, n_D^{25} 1.5392, $\lambda_{max}(CCl_4)$ 2.77, 2.93, 8.53, 10.31 μ, λ_{max}(MeOH) 258 mμ (ε 287)[10] (*Anal*. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.21; H, 7.30). Its n.m.r. spectrum (Me_2SO) shows in addition to signals due to phenyl hydrogen (δ = 7.4 p.p.m., complex multiplet(5H)) and hydroxyl hydrogen atoms (δ = 5.89 p.p.m., singlet(1H), absent after treatment with D_2O), an AX_3 system assigned to the CH_3CH

grouping with δ = 4.87(1H) and 1.37(3H) p.p.m. (J = 6.5 c./s.), and an AB system assigned to the CH_2 grouping with δ = 4.59 and 4.67 p.p.m. (J ~ 6.5 c./s.); this n.m.r. spectrum suggests that the product isolated consists largely or entirely of a single diastereoisomeric form of the oxetanol.

Irradiation of 1-methoxy-3,3-dimethyl-2-butanone (I, R = $(CH_3)_3C$, R' = H) gave 3-t-butyl-3-oxetanol (II, R = $(CH_3)_3C$, R' = H), indicating that the reaction is not restricted to aromatic ketones; the yield (5%) was, however, appreciably lower in this case. The oxetanol was isolated by chromatography on silica. Sublimation gave needles, m.p. 118-119.5°, $\lambda_{max}(CCl_4)$ 2.78, 2.93, 8.54, 10.24 µ, δ (CCl_4) 0.98 (singlet, $(CH_3)_3C$), 2.83 (broad, OH), 4.34 and 4.60 (AB(J = 7 c./s.), CH_2) p.p.m. (Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.69, 64.17; H, 10.44, 10.77).

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7. We thank Dr. G.H. Berezin, Explosives Department, Experimental Station, E.I. du Pont de Nemours and Co., for his kindness in providing us with a generous sample of this compound.
8. R.G.W. Norrish, *Trans. Faraday Soc*. **33**, 1521 (1937).
9. R. Srinivasan, *J.Am.Chem.Soc*. **84**, 2475 (1962), has shown that photolysis of methoxyacetone in the vapor phase gives acetone and formaldehyde and has proposed that these products are formed by a process of this type.
10. This is the most intense of a group of characteristic benzenoid fine-structure bands in the 240-270 mμ region.
11. Holder of N.R.C. Studentship, 1963-65.