Photocycloaddition of Propionaldehyde to Ethyl Vinyl Ether[1]

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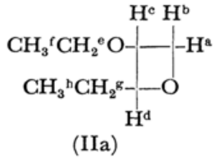
It has been reported that aliphatic aldehyde add to highly-alkylated olefins, such as tri- and tetramethylethylene, to give oxetanes photochemically.[2] However, in the cases of 1-olefins (*e. g.*, 1-hexene or 1-octene) ketones (I) are mainly formed by the radical chain mechanism.[3]

$$R_1CHO + R_2CH{=}CH_2 \xrightarrow{h\nu} R_2CH_2CH_2COR_1(I)$$

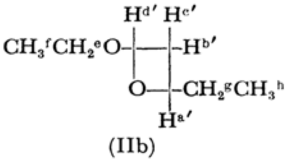
The photoreaction of aliphatic aldehydes with electron-deficient olefins also gives ketones.[4]

In this communication, we wish to report on the photochemical formation of oxetanes from propionaldehyde and ethyl vinyl ether.[5] A solution containing 70 g of ethyl vinyl ether and 32 g of propionaldehyde was irradiated, using a 350-W high-pressure mercury lamp and a Pyrex filter, at 20°C under nitrogen for 20 hr. After the subsequent evaporation of the unreacted materials, a fraction boiling at 60—70°C/27 mmHg was collected; yield, *ca.* 10 g.[6] It contained two main products (more than 85%) and several minor products.[7] A mixture of the two main products (in almost a 1 : 1 ratio) was isolated using a preparative VPC; bp 64°C/27 mmHg, n_D^{28} 1.4133. Found: C, 64.50; H, 11.08%; mol wt,[8] 133. Calcd for $C_7H_{12}O_2$: C, 64.58; H, 10.84%; mol wt, 130.

The structure IIa was assigned on the basis of spectral data. The IR spectrum showed a strong band at 970 cm^{-1} (oxetanes) and neither hydroxyl nor carbonyl absorptions. The NMR spectrum showed resonances at τ 5.3—6.2 (4H, complex multiplet), τ 6.68 (2H, quartet, H^e), τ 8.40 (2H, quintet, H^g), τ 8.88 (3H, triplet, H^f), and τ 9.12 (3H, triplet, H^h).[9] Four hydrogens on the oxetane ring appear at τ 5.3—6.2. If the oxetanes had the structure IIb, $H^{d'}$ would be present in the lower field due to the adjacent two oxygens and would have an appreciably different τ value from those of $H^{b'}$ and $H^{c'}$.[10] On the other hand, if they had the structure IIa, all of the four hydrogens on the ring would be in the α-position relative to the oxygens and would be expected to give complex multiplets because of their similar τ values and because of the complex coupling between them. On the basis of these data, two these oxetanes were confirmed to be *cis*- and *trans*-isomers of IIa.



(IIa)



(IIb)

Generally, one cannot obtain oxetanes in the photoaddition of aliphatic aldehydes to 1-olefins. This is mainly because of the slow rate of the formation of oxetanes compared with that of the formation of free radicals. It is well established that the formation of oxetanes proceeds *via* the attack by the electrophilic oxygen atoms of the $n\pi^*$ triplet states of carbonyl compounds on olefins with electron-donating groups. Therefore, oxetanes are easily obtained in the photoaddition of propionaldehyde to ethyl vinyl ether. In this case, very few ketones are formed. This may be due to the high probability of polymerization in ethyl vinyl ether. The orientation of the resulting oxetanes is that to be expected from a consideration of the more stable biradical intermediate. It is interesting that 1-olefins, with an electron-donating substituent, give mainly oxetanes upon the photoaddition of aliphatic aldehydes.

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[1] Organic Photochemical Reactions, Part IX. Part VIII: Y. Nagao, K. Shima and H. Sakurai, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **72**, 236 (1969).

[2] G. Buchi, C. G. Inman and E.S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954); H. Sakurai, K. Shima and S. Toki, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **89**, 537 (1968).

[3] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

[4] T. M. Patrick, Jr., *ibid.*, **17**, 1009, 1269 (1952). Recently, it was reported that aliphatic and alicyclic ketones add to electron-deficient olefins to give oxetanes by UV irradiation. The formation of oxetanes probably proceeds *via* $n\pi^*$ singlet ketones. N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold and A. Glick, *J. Am. Chem. Soc.*, **89**, 3950 (1967); J. A. Barltrop and H. A. J. Carless, *Tetrahedron Letters*, **1968**, 3901.

[5] We have already reported that the photoaddition of propionaldehyde to styrene gives oxetanes. H. Sakurai, K. Shima and I. Aono, This Bulletin, **38**, 1227 (1965).

[6] Residues, 15 g.

[7] By VPC, Dinonyl Phthalate, 120°C.

[8] VPO method in benzene.

[9] Solvent, CCl_4; internal standard, tetramethylsilane.

[10] The NMR spectra of oxetanes show the α-hydrogen to oxygen at 5.0—6.0τ; the presence of additional α-oxygen to $H^{d'}$ further lowers its value, while the β-hydrogen to oxygen on the ring occurs at 6.4—7.4τ. D. R. Arnold, R. L. Hinman and A. H. Glick, *Tetrahedron Letters*, **1964**, 1425.