

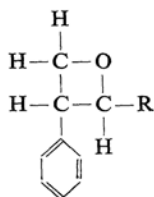
The Synthesis of Oxetanes by the Photochemical Reaction of Aliphatic Aldehydes and Styrene*

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We wish to report on the synthesis of oxetanes by the photoaddition of acetaldehyde and propionaldehyde to styrene.

An equimolar mixture of acetaldehyde and styrene was irradiated under nitrogen at 10–15°C for 8 hr. using a 350 W. high-pressure mercury lamp.¹⁾ After the irradiation, the unreacted materials were distilled off and a fraction with a b. p. of 69–70°C/2 mmHg (n_D^{20} 1.5202) was obtained. Found: C, 80.80; H, 8.23; mol. wt., 150.²⁾ Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16%; mol. wt., 148. λ_{max}^{EtOH} , 249, 253.5, 259, 262, 265.3 and 269 m μ (log ϵ , 2.94, 3.04, 3.12, 3.08, 2.97 and 2.93). The infrared spectrum of this product showed the presence of an oxetane³⁾ (980 cm⁻¹), but the absorption bands characteristic of hydroxy and carbonyl groups were not observed. The orientation of the addition was established by means of a study of the NMR spectrum. The NMR spectrum⁴⁾ showed a sextet (1 H) at τ 6.38 (hydrogen β to oxygen on the ring) and a complex multiplet (3 H) centered at τ 5.4 (hydrogens α to oxygen). It was assigned the structure Ia on the basis of these data.



Ia R = CH₃

Ib R = C₂H₅

From propionaldehyde and styrene, a fraction with a b. p. of 70–71°C/2 mmHg (n_D^{20} 1.5144) was obtained. Found: C, 81.40; H, 8.96; mol. wt., 162. Calcd. for $C_{11}H_{14}O$: C, 81.44; H, 8.70%; mol. wt., 162. λ_{max}^{EtOH} , 249, 254, 259.5, 262.5, 265.5 and 269.3 m μ (log ϵ , 2.92, 3.02, 3.09, 3.05, 2.95 and 2.91). It was proposed that the product was Ib.

The reaction conditions and the yield of products are summarized in Table I.

TABLE I. THE REACTION CONDITIONS AND THE YIELDS OF PRODUCTS

Aldehyde	Acetaldehyde	Propionaldehyde
Aldehyde used, g.	42	58
Styrene used, g.	104	104
Aldehyde consumed, g.	6	4
Styrene consumed, g.	16.3	13.3
Oxetane, g.	8	4.3
High boiling residue, g.	13	10.5
Wt.% of oxetane in the products	38	29
Ultimated yield of oxetane based on aldehyde consumed, mol. %	49.4	38.5
Ultimated yield of oxetane based on styrene consumed, mol.%	31.5	20.7

It is of interest to note that the photoaddition of aliphatic aldehydes to styrene gives only oxetanes, while the addition of the aldehydes to 1-olefins generally gives ketones, which are formed by the addition of the acyl radical to olefins.⁵⁾

These oxetanes will be stereochemically considered and the mechanistic implications will be discussed elsewhere.

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1) For reaction apparatus, cf. K. Shima, Y. Shigemitsu and S. Tsutsumi, This Bulletin, 35, 1728 (1962).

2) The molecular weight was determined by the cryoscopic method in benzene.

3) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London (1958), p. 119.

4) The NMR spectra of oxetanes show the α hydrogens to oxygen at 5.0–6.0 τ , while the β hydrogen to oxygen on the ring occurs at 6.4–7.4 τ . D. R. Arnold, R. L. Hinman and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

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