The Light-induced Addition of Acetals to Olefins

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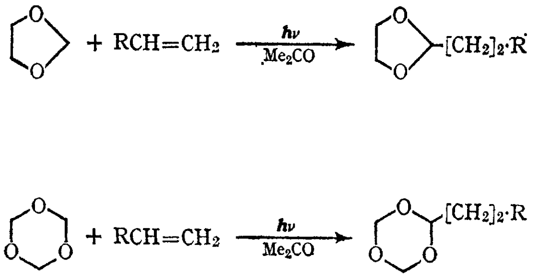
THE photochemical conversion of cyclic acetals into the corresponding carboxylic esters has been reported recently.[1] A similar ring cleavage of acetals occurs at elevated temperatures using peroxides as initiators.[2] We have now found that under ultraviolet irradiation at room temperature cyclic acetals can be added to terminal olefins without suffering such a ring cleavage.[3] The major products (1 : 1 adducts) of this reaction were the cyclic acetals of the corresponding aldehydes in the case of 1,3-dioxolan, and mono-alkylated 1,3,5-trioxans in the case of 1,3,5-trioxan. The monolkylated 1,3,5-trioxans have been unknown so far.

TABLE

Addition products of cyclic acetals and olefins (initiated photochemically by acetone)

Acetal	Olefin	Product	Yield[a] (%)
1,3-Dioxolan	Hept-1-ene	2-Heptyl-1,3-dioxolan, b.p. 115—116°/45 mm., n_D^{25} 1·4318	22[c], 34[d]
1,3-Dioxolan	Oct-1-ene	2-Octyl-1,3-dioxolan, b.p. 141—142°/40 mm., n_D^{25} 1·4348	22[c]
1,3-Dioxolan	Dec-1-ene	2-Decyl-1,3-dioxolan, b.p. 172—174°/35 mm., n_D^{25} 1·4389	20[c]
1,3,5-Trioxan	Hept-1-ene	Heptyl-1,3-5-trioxan, m.p. 22—24°	15[c]
1,3,5-Trioxan	Oct-1-ene	Octyl-1,3,5-trioxan, m.p. 28·5—29·5°	20[c], 19[d]
1,3,5-Trioxan	Dec-1-ene	Decyl-1,3,5-trioxan, m.p. 43—44°	21[c], 18[d]

[a] Yields are based on olefins employed. [b] All new compounds gave satisfactory analytical data. [c] Using Hanau Q 81 and Hanovia 450 w mercury-vapour lamps. [d] Using sunlight.



(R=C_5H_{11}, C_6H_{13}, C_8H_{17})

The reaction was effected by irradiation of a mixture of the olefin and the cyclic acetal in the presence of acetone. (In the case of trioxan, t-butyl alcohol was used as solvent). The presence of acetone seems to be vital for the addition reaction of 1,3,5-trioxan and the olefins, since in its absence none of the desired 1 : 1 adducts could be detected under the reaction conditions. Experimental data and the major products obtained are summarized in the Table.

The 2-alkylated 1,3-dioxolans, *i.e.*, the ethylene glycol acetals of the corresponding aldehydes, were identified by comparison with authentic samples. The parent aldehydes could be obtained by treatment of the addition product with dilute mineral acids. They were compared with authentic samples, and further the corresponding 2,4-dinitrophenylhydrazones were compared. The alkylated 1,3,5-trioxans were characterized through elemental analyses, infrared absorption, and n.m.r. spectra. The latter all showed a multiplet centred at τ 4·9 (5H; O–CH_2–O), a singlet at τ 8·7 (CH_2), and a triplet at τ 9·1 (3H; CH_2·CH_3). Hydrolysis with dilute mineral acids gave formaldehyde and the corresponding higher aldehydes which were characterized through their 2,4-dinitrophenylhydrazones.

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[1] D. Elad and R. D. Youssefyeh, *Tetrahedron Letters*, 1963, 2189.

[2] E. S. Huyser, *J. Org. Chem.*, 1960, **25**, 1820 and references cited therein.

[3] *Cf.* R. C. Cookson, I. D. R. Stevens, and C. T. Watts, *Chem. Comm.*, 1965, 259; T. M. Patrick, Jr., U.S. Patent-2,684,373 [*Chem. Abs.*, 1955, **49**, 7602].