The Photochemical Synthesis of Oxetanes from Diethyl Oxalate[*1]

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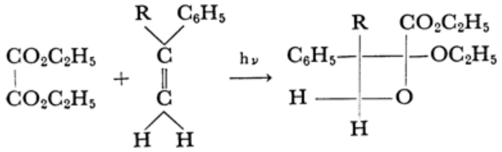
Although the synthesis of various oxetanes[1] by the photocycloaddition of ketones or aldehydes to olefins has been carried out extensively, no report upon the photochemical formation of oxetanes from carboxylate ester with olefin has been made as yet.

In a previous paper,[2] the present authors reported on the photochemical synthesis of oxetanes from ethyl cyanoformate. The present paper will deal with the photochemical synthesis of some new oxetanes from diethyl oxalate.



Ia ($R=C_6H_5$) Ib ($R=C_6H_5$)
IIa ($R=CH_3$) IIb ($R=CH_3$)

In the present study, 1, 1-diphenylethylene and α-methylstyrene were selected as the olefins, and the light irradiation of a solution of diethyl oxalate and an olefin with a light of approximately 3660 Å, provided by a 1kW high-pressure mercury lamp, was carried out under nitrogen stream at room temperature for 45—75 hr.

The structures of each obtainable oxetanes (Ib and IIb) were characterized by the infrared and nuclear magnetic resonance spectra, molecular weight measurements and elemental analyses.

The photocycloaddition probably proceeds through the carbonyl n-π^* triplet state and the direction of addition may be rationalized through the initial addition of an electron defficient oxygen to form the more stable diradical intermediate as suggested by Büchi.[3]

Further studies on the photochemical formation of oxetanes from other carboxylate esters will be reported in the near future.

Experimental

Materials. Diethyl oxalate and α-methylstyrene were commercial grade chemicals, and were purified according to the usual method before use. 1, 1-Diphenylethylene was prepared by the method of Allen and Converse.[4]

Oxetane (Ib) from Diethyl Oxalate with 1, 1-Diphenylethylene. A solution of diethyl oxalate (37 g; 0.26 mol) and 1, 1-diphenylethylene (15 g; 0.085 mol) was irradiated with a 1 kW high-pressure mercury lamp under nitrogen atmosphere at room temperature for 75 hr. During the irradiation, a small amount of gas (110 m*l*) was evolved and was shown by gas chromatography to be carbon monoxide, carbon dioxide and ethylene.

After the irradiation, the reaction mixture was fractionally distilled under reduced pressure to give the oxetane (Ib), bp 151—153°C/3 mmHg, which was crystallized on standing. Yield, 2.5 g (15.7% based on consumed diethyl oxalate). The crystals were recrystallized from *n*-heptane, mp 72—73°C.

The pertinent infrared spectrum (KBr) showed peaks at 960 (ether, –COC–) and 1740 cm^{-1} (ester, C=O). NMR (CCl_4) showed the following bands: τ 9.14 (triplet, 3H), 8.86 (triplet, 3H), 6.30 (quartet, 2H), 6.15 (quartet, 2H), 4.49 (quartet, 2H), and 2.73 (multiplet, 10H).

Found: C, 73.63; H, 6.85%; mol wt, 323 (cryoscopically, C_6H_6). Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%; mol wt, 326.

Oxetane (IIb) from Diethyl Oxalate with α-Methylstyrene. Irradiation of a solution of diethyl oxalate (57 g; 0.5 mol) and α-methylstyrene (21 g; 0.17 mol) was carried out for 45 hr in a same way as described above. The reaction mixture was fractionally distilled under reduced pressure to give the oxetane (IIb), bp 156—160°C/8 mmHg, Yield, 10.2 g (36% based on consumed diethyl oxalate). The infrared spectrum showed peaks at 970 (ether, –COC–) and 1760 cm^{-1} (ester, C=O). NMR (CCl_4) showed the following band; τ 8.98 (triplet, 3H), 8.63 (triplet, 3H), 8.51 (doublet, 2H), 6.60 (quartet, 2H), 5.77 (quartet, 2H), 5.12 (quartet, 2H) and 2.83 (multiplet, 5H).

Found: C, 67.86; H, 7.86%; mol wt, 257 (cryoscopically, C_6H_6). Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63; mol wt, 264.

[*1] "New Oxetanes from Carboxylate Esters" Part II.

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