

PHOTOCYCLOADDITION OF CARBAMATES TO I, I-DIPHENYLETHYLENE

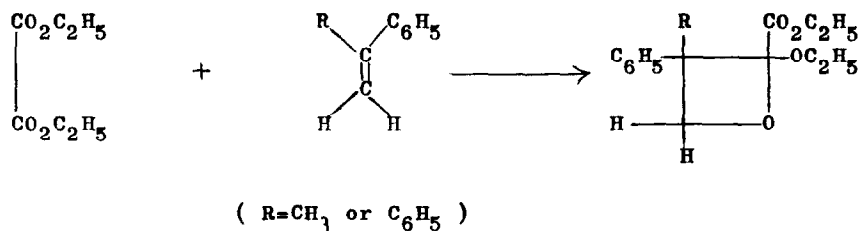
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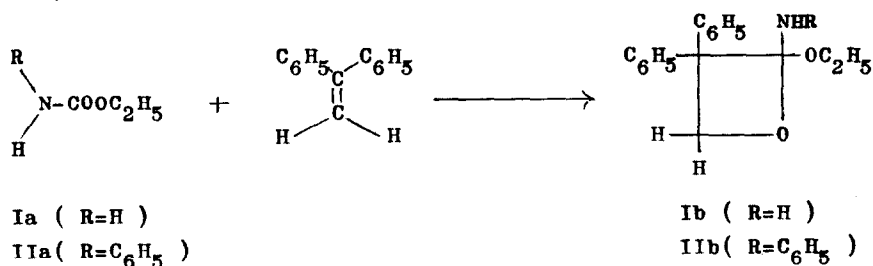
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Although the synthesis of various oxetanes<sup>1)</sup> by the photocycloaddition of ketones or aldehydes to olefins has been carried out as well known, there seems no report concerning the photochemical synthesis of oxetane having amino group.

In a previous paper,<sup>2)</sup> we have reported on the photochemical synthesis of oxetanes from diethyloxalate with olefins.



This paper deals with the photochemical synthesis of oxetanes from ethyl carbamates and I, I-diphenylethylene.

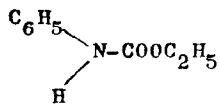
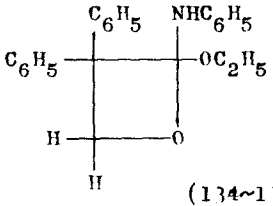
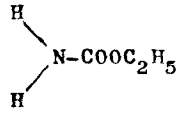
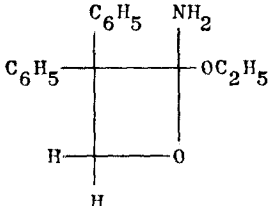


A solution of carbamates (Ia or IIa) (0.3 mole) and I, I-diphenylethylene (0.6 mole) was irradiated with a light of approximately 3660 Å, provided by a 1 Kw high pressure mercury lamp, under nitrogen at 70°C for 75 hours. After the irradiation had completed, unreacted materials were removed under reduced pressure and then the residual materials were chromatographed on silica gel or distilled under reduced pressure.

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

Table I

Photocycloaddition of Carbamates to I, I-Diphenylethylene

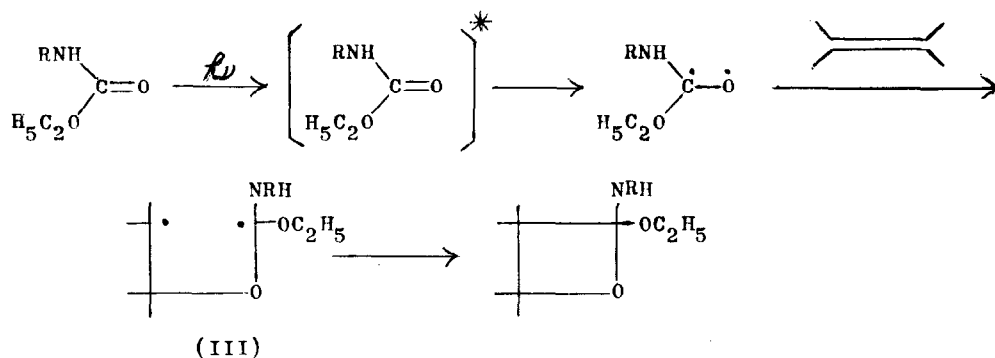
Carbamate	Oxetane (mp.°C)	Yield % <sup>a)</sup>	n.m.r. $\tau$	IR $\text{cm}^{-1}$
	 (134~135)	52	9.11 (t.) 6.32 (q.) 4.42 (q.) 2.92 (m.) 2.37 (m.)	3430 955
	 (120~121)	64	8.98 (t.) 6.21 (q.) 4.61 (q.) 2.86 (m.) 2.12 (m.)	3400 942

a) Based on consumed Carbamates

The oxetanes obtained are listed in Table I. It is interesting that new oxetanes having a amino group directly bonding to a carbon atom of a trimethyl-

eneoxide ring were synthesized in moderate yields by the photocycloaddition of ethyl carbamates to I,I-diphenylethylene.

The photocycloaddition probably proceeds through the carbonyl  $n-\pi^*$  triplet state and the direction of addition may be rationalized through the initial addition of an electron deficient oxygen to form the more stable diradical intermediate. Therefore, we would like to propose the following schemes for this photoaddition.



In this case, the biradical(III) may be stabilized by the resonance effect of the amino group. This stabilization of the biradical(III) may be responsible for the successful synthesis of the oxetanes from carboxylester derivatives.

References

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