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PHOTOADDITION OF DIETHYL OXOMALONATE TO OLEFINS

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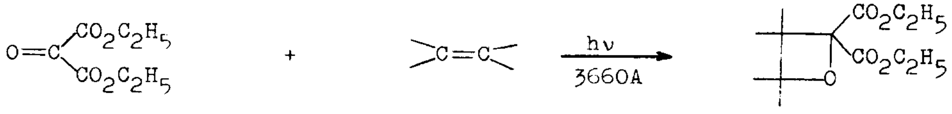
Although thermal reactions of diethyl oxomalonate with some olefins have been known[1,2], no report upon the photochemical reaction of diethyl oxomalonate with olefins has been made as yet. In this report, we wish to describe the photoaddition reactions of diethyl oxomalonate with monoenes such as 1,1-diphenylethylene, α-methylstyrene or norbornene and dienes such as isoprene or 2,3-dimethyl-1,3-butadiene.

A solution of diethyl oxomalonate (I) (0.1 mole) and an olefin (II) (0.2 mole) was irradiated at 3660A* under nitrogen at room temperature for 40-50 hours until the absorption band at 3720A of diethyl oxomalonate almost disappeared. After the irradiation, unreacted olefins were removed under reduced pressure and then the residues were chromatographed on silica gel or distilled under reduced pressure. The adducts (III) were characterized to be oxetane derivatives by infrared and nuclear magnetic resonance spectra, molecular weight measurement and elemental analysis.



I II III

The results are listed in Table 1.

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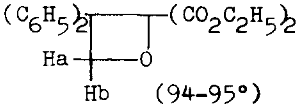
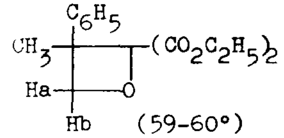
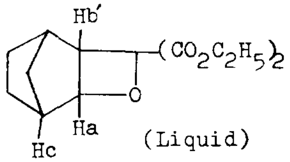
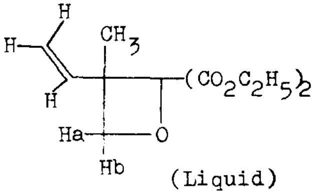
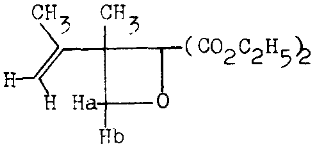
* Emitted light from 1 kw high-pressure mercury arc lamp was filtered through a solution (1 cm.) of naphthalene 12.6 g. in isooctane 1 l.

Table 1 Photoaddition of Diethyl Oxomalonate to Olefins

Olefin	Oxetane(m.p.)	Yield %[a]	NMR τ[b] Ha,Hb	IR cm.$^{-1}$[c]
1,1-Diphenylethylene	 (94-95°)	64	4.87s	967
α-Methylstyrene	 (59-60°)	76	4.75d 5.83d (J_{AB} =5 cps)	975
Norbornene	 (Liquid)	97[d]	exo-adduct 5.28d ($J_{AB'}$=5 cps) endo-adduct 5.82t ($J_{AB'}$=J_{AC} =4 cps)	986 990
Isoprene	 (Liquid)	90	5.30d 5.57d (J_{AB} =5 cps)	960
2,3-Dimethyl-1,3-butadiene	 (Liquid)	42[e]	4.96d 6.05d (J_{AB} =5 cps)	976

a) Based on consumed diethyl oxomalonate.

b) The NMR spectra of the oxetanes are generally found to show the hydrogens α to oxygen on the ring at 5.0-6.0τ while hydrogens β to oxygen occur at 6.4-7.4τ[3].

c) The infrared spectra of the oxetanes show the characteristic band at 970 cm.$^{-1}$ that has been assigned to the asymmetrical ring stretching vibration involving the carbon-oxygen bonds.

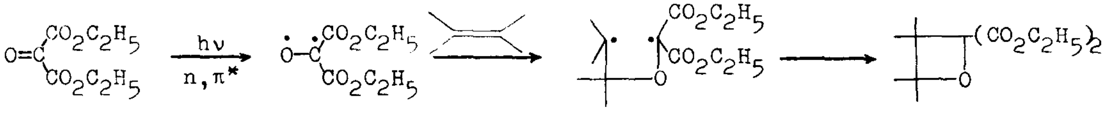
d) These two isomers were separated by chromatography on silica gel and characterized by the NMR spectra which were compared with those α- and α'-chlorocamphors[4]. Product ratio of exo-adduct to endo-adduct was 3 to 1.

e) A great proportion of 2,3-dimethyl-1,3-butadiene had polymerized.

We further studied the chemical and physical properties of diethyl oxomalonate (I). I had weak absorption bands at 372 mμ (ε 25) and 367 mμ (ε 24) in n-heptane and these bands showed a hypsochromic shift in more polar solvent. In addition, I was photo-reduced to give diethyl tartronate and its pinacol in cyclohexane. Moreover, I showed phosphorescent bands at 530 mμ (53.9 kcal./mole) and 527 mμ (54.2 kcal./mole) in 1,1-difluoro-1,1,2,2-tetrachloroethane. Consequently, 2,3-dimethyl-1,3-butadiene whose lowest triplet energy is 54 kcal./mole in s-cis form and 60 kcal./mole in s-trans one had largely polymerized by energy transfer from I to s-cis-2,3-dimethyl-1,3-butadiene. Furthermore, the quantum yield for formation of oxetane was 0.30 at 3660A. These chemical and physical data suggest that this reaction would proceed through a characteristic reaction of the carbonyl triplet n,π* excited state[5].

On the other hand, thermal reaction of I with α-methylstyrene gave diethyl (2-phenyl-propen-2-yl) tartronate (IV) in 58% yield but 1,1-diphenylethylene did not react with I. 2,3-Dimethyl-1,3-butadiene and I gave diethyl 3,4-dimethyl-5,6-dihydro-1,2-pyran-6,6-dicarboxylate in 82% yield.

From these results, we would like to propose the following schemes for these photochemical and thermal reactions.

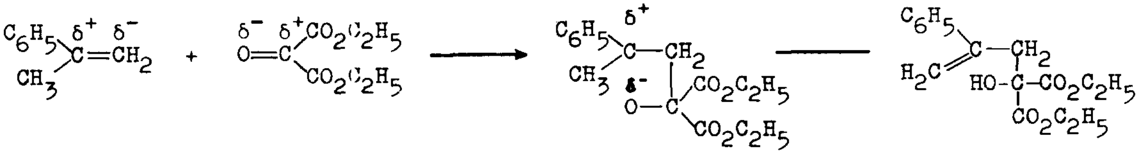


I triplet V III

The photochemical reaction of I with olefin would proceed by attack of the electron-defficient oxygen atom of the carbonyl n,π* excited state on the olefinic carbon atom with a high free valency to produce the more stable diradical intermediate (V) as proposed by Büchi et al.[6].

In contrast to photochemical reactions, thermal reactions may proceed through the polarized ground state of I and so lead to inverse addition products as reported by Achmatowicz for carbonyl cyanide[7].

α-Methylstyrene



I

IV

Interestingly, the oxetanes obtained here are relatively stable to acid, heat and alkali and accordingly it should be possible to convert them into useful derivatives retaining the trimethylene oxide ring.

References

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