CHEMISTRY LETTERS, pp. 503-506, 1991.

Photochemistry of Isopropylidene 3,3,6-Trimethyl-1,4,5-heptatriene-1,1-dicarboxylate and Its Homologues

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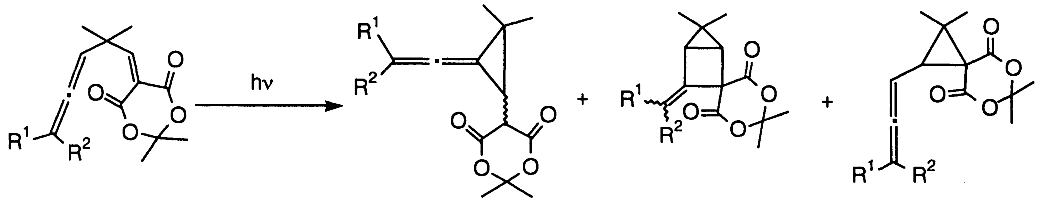
Direct photolysis of title compounds gave alkenylidenecyclopropanes as main products, while acetone-sensitized photolysis of those led to mainly intramolecular [2+2]cycloadducts.

The interaction between unconjugated two-π-functions in an excited state has been of interest and extensively investigated. In particular, the photochemistry of vinyl-vinyl methane compounds is well-known to give vinylcyclopropanes by a di-π-methane rearrangement.1) A number of papers have been published with the intention of relating this photochemistry to the substitution effect.1) On the other hand, the irradiation of some terminal allenes linked to cycloalkenones by hydrocarbon chains are known to afford intramolecular [2+2]cycloadducts.2) However, for the photochemistry of the allenyl-vinyl methane compounds there is only one report,3) as far as we are aware of, in which allenyl-styryl methane compounds have been reported to give mainly intramolecular [2+2]cycloadducts on the direct irradiation and to undergo a geometric isomerization on the acetone-sensitized irradiation.3) We investigated the photochemistry of novel allenyl-vinyl methane compounds, isopropylidene 3,3,6-trimethyl-1,4,5-heptatriene-1,1-dicarboxylate (1a) and its homologues (**1b** and **1c**), on the direct and sensitized irradiation, for these compounds CT interaction between the allenic group and the vinyl group is expected.

The starting materials **1a-c**4) were obtained by the reaction of Meldrum's acid with corresponding allenic aldehydes5) in pyridine. The direct irradiation of **1a** (0.01 mol dm^{-3}) in acetonitrile (400 cm^3) by a 6-W low-pressure mercury lamp with a quartz jacket under an argon atmosphere gave two photoproducts, which were separated by medium-pressure silica-gel chromatography (15% EtOAc/hexane) equipped with a RI detector (Table 1). These structures were elucidated by means of NMR and other spectral measurements.6) The IR spectrum of the main photoproduct, iso-



1 **2** **3** **4**

Table 1. Direct and Sensitized Photolyses of Isopropylidene 3,3,6-Trimethyl-1,4,5-heptatriene-1,1-dicarboxylate and Its Homologues

Substrate	R^1	R^2	Solvent	Irradiation time	Product(Yield/%)		
1				h	**2**	**3**	**4**
1a	CH_3	CH_3	CH_3CN	48[a]	**2a**(28)	**3a**(17)	
1b	CH_3	H	CH_3CN	48[a]	**2b**(23)[b]	**3b**(3)[c]	
1c	H	H	CH_3CN	46[a]	**2c**(23)	**3c**(3)	**4c**(3)
1a	CH_3	CH_3	Acetone	1.3[d]	**2a**(5)	**3a**(53)	
1b	CH_3	H	Acetone	3[d]		**3b**(37)[e]	
1c	H	H	Acetone	7.5[d]		**3c**(46)	

a) Using a 6-W low-pressure mercury lamp with a quartz jacket under an argon atmosphere at room temperature. b) Cis:trans=43:53. c) (E)-Form:(Z)-form=1:1. d) Using a 100-W high-pressure mercury lamp with a Pyrex jacket under an argon atmosphere at room temperature. e) (E)-Form:(Z)-form=57:43.

butenylidenecyclopropane **2a**, showed the characteristic allenic band 2030 cm^{-1} due to the alkenylidenecyclopropane,[7] which is higher than those of generally accepted values (1950-1970 cm^{-1}). In addition, the ^{13}C NMR spectrum for the three carbons [C=C=C, δ=89.1(s), 99.9(s), and 187.1(s)] of **2a** strongly supported the alkenylidenecyclopropane structure.[8] The minor photoproduct was an intramolecular [2+2]cycloadduct **3a** whose ^{1}H NMR spectrum showed six methyl and two methine protons on sp^3-carbons. Similar intramolecular photoproducts **2b** and **3b** were also identified in the reaction of **1b**. Both **2b** and **3b** were diasteromeric mixtures. The (E)- and (Z)-forms of **3b** could be separated by a chromatographic technique, but the cis and trans forms of **2b** were not isolated separately.[9] Moreover, the direct irradiation of **1c** gave three photoproducts. As in the cases of **1a** and **1b**, the main photoproduct and one of minor photoproducts were the ethenylidenecyclopropane **2c** and the adduct **3c**, respectively, while the third compound was an allenyl cyclopropane **4c**[10] expected from the typical di-π-methane rearrangement.

Next, the acetone-sensitized photolyses (>280 nm)[11] of **1a-c** afforded the corresponding adducts **3a-c**. However, from the sensitized photolysis of **1a**, **2a** was obtained in low yield (Table 1).

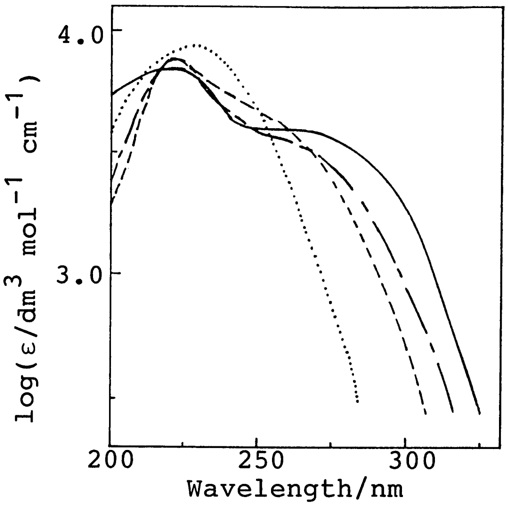


Fig. 1. UV-Absorption spectra of **1a**(———), **1b**(— — —), **1c**(- - - - - -), and **5**(··········) in acetonitrile.

Since alkyl-substituted allenes show the only very weak absorption above 200 nm,$^{12)}$ the UV-absorption spectra of **1a-c** are anticipated to be similar to that of 2,2-dimethylpropylidene Meldrum's acid (**5**).$^{13)}$ As shown in Fig. 1, the absorptions of **1a-c** exhibit the absorption maxima at 223-230 nm in acetonitrile, which are in agreement with that of **5**, but the second absorptions are observed at 250-280 nm and show bathochromic shifts in the order **1c**<**1b**<**1a**. The second absorptions suggest the formation of an intramolecular CT state between the allenic group and the α,β-unsaturated cyclic ester group of **1a-c**. The allenic groups of **1a-c** obviously act as electron-donating groups. The degree of bathochromic shifts observed corresponds to the number of electron-donating methyl groups linked to the allene.

Though a detailed mechanism for the present photolyses has not yet been clarified, it can be assumed that from the singlet excited state (probably intramolecular CT state) of **1a-c**, the alkenylidenecyclopropanes **2a-c** are generated via a proton or hydrogen atom transfer, while the adducts **3a-c** were formed by the triplet excited state (probably intramolecular CT state). As shown in Table 1, the irradiation time which was needed to complete the sensitized photolyses increased in the order **1a**<**1b**<**1c**.

Thus, these compounds **1a-c** are found to mainly afford the alkenylidenecyclopropanes by the direct photolysis (singlet excited state) and the intramolecular [2+2]cycloadducts by the sensitized photolysis (triplet excited state). This tendency of the photoreaction and the type of photoproducts **2a-c** are different from those of usual di-π-methane compounds.

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4) Typical procedure for the synthesis of isopropylidene 3,3,6-trimethyl-1,4,5-heptatriene-1,1-dicarboxylate (**1a**): A mixture of 2,2,5-trimethyl-3,4-hexadienal[5)] (0.12 mol) and Meldrum's acid (0.1 mol) in pyridine (20 cm^3) is stirred at room· temperature for 24 h. After removal of pyridine in vacuo below 40 °C, the crude product is purified by flash chromatography (silica gel, 5% acetone/hexane) to give **1a** (4.7 g, 18% yield): IR ($CHCl_3$) 1960, 1770, 1740, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.41(6H, s), 1.70(6H, d, J=3.1 Hz), 1.74(6H, s), 5.37(1H, septet, J=3.1 Hz), and 7.80(1H, s); ^{13}C NMR ($CDCl_3$) δ=20.2, 20.4, 26.6, 26.7, 27.1, 27.4(each q), 38.9(s), 96.2(d), 99.0, 104.4, 118.4, 158.7, 162.8(each s), 172.6(d), and 200.4(s).

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6) Typical spectral and analytical data of photoproducts are as follows: **2a**, mp 113-115 °C; IR ($CHCl_3$) 2030, 1780, and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.26(3H, s), 1.35(3H, s), 1.76(3H, s), 1.78(9H, s), 1.7-1.9(1H, m), and 3.25(1H, d, J=9.7 Hz); ^{13}C NMR ($CDCl_3$) δ =20.3, 21.2, 21.5(each q), 24.2(s), 25.8, 26.9(each q), 28.3(d), 28.8(q), 47.4(d), 89.1, 99.9, 105.1, 164.3, 164.9, and 187.1(each s): **3a**, mp 115-116 °C; IR ($CHCl_3$) 1780 and 1745 cm^{-1}; ^1H NMR ($CDCl_3$) δ =0.96(3H, s), 1.43(3H, s), 1.46(3H, s), 1.71(3H, s), 1.75(3H, s), 1.93(3H, s), 1.94 (1H, d, J=5.7 Hz), and 2.49(1H, br d, J=5.7 Hz); ^{13}C NMR ($CDCl_3$) δ=17.8, 18.5, 19.1, 25.0, 28.5, 28.7(each q), 29.3(s), 33.2, 36.6 (each d), 52.8, 104.5, 124.3, 128.1, 165.1, and 167.0(each s).

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9) The stereochemistry of these diastereomers was assigned from the effect of adding paramagnetic chelates [$Yb(FOD)_3$] on the ^1H NMR spectra.

10) **4c**: IR ($CHCl_3$) 1955, 1760, and 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40(3H, s), 1.44(3H, s), 1.70(3H, s), 1.74(3H, s), 3.18(1H, d, J=9.3 Hz), 4.7-4.9(2H, m), and 5.71(1H, ddd, J=6.6, 6.6, and 9.3 Hz).

11) The allenyl-vinyl methane compounds **1a-c** (0.01 mol dm^{-3}) in acetone (400 cm^3) were irradiated using a 100-W high-pressure mercury lamp with a Pyrex jacket under an argon atmosphere at room temperature.

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(Received November 20, 1990)