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Allenyl(vinyl)methane Photochemistry. Photochemistry of 4,4,7-Trimethyl-5-phenyl-2,5,6-octatrienate Derivatives

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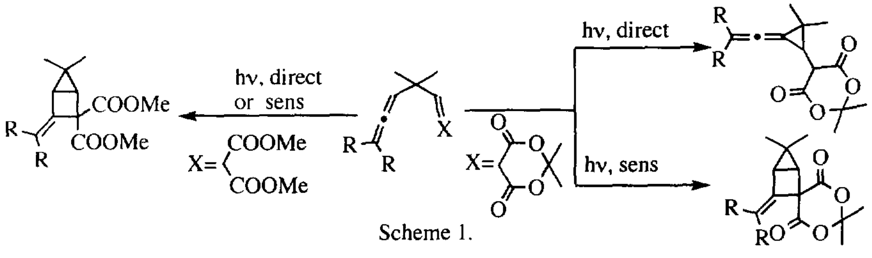
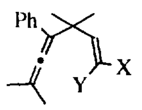
Abstract: The direct photolysis of the diester in the title compounds gave a cross conjugated triene, [2+2] cycloadduct, pyran, and cyclopropene. The direct photolysis of the monoester afforded a cross conjugated triene, [2+2] cycloadduct, cyclopropene, and its *Z*-form. The sensitized photolysis of these esters afforded the trienes and [2+2] cycloadducts, which were derived from the triplet excited state of the different chromophores. © 1997 Elsevier Science Ltd. All rights reserved.

Previously, we reported the photochemistry of alkylidenemalonates and alkylidene Meldrum's acids possessing an allenyl group at the γ-position which is either the 1,2-propadienyl, 1,2-butadieneyl, or 3-methyl-1,2-butadienyl group, and these esters underwent the photoreaction as described in Scheme 1.[1,2] The photoreactions of these esters occur from the excited state of the vinyl chromophore or from the CT excited state between both chromophores and presented the possibility of new multiplicity control on the photochemistry of divinymethanes.[3] We then noted the photochemistry of allenyl(vinyl)methane **1a** and **1b** in which the allenyl group is attached to a phenyl group. It is expected that these compounds **1a** and **1b** will undergo the reaction not only via the above photoexcitation but also the allene excitation. We now wish to report the photochemistry of **1a** and **1b**.

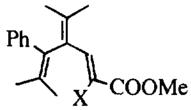


Scheme 1.

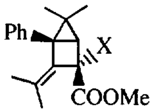
The diester **1a**[4] was obtained by the condensation of 2,2,5-trimethyl-3-phenyl-3,4-hexadienal[5] with dimethyl malonate using Lehnert's method.[6] The monoester **1b** was also prepared by the reaction of the above aldehyde with methyl diethylphosphonoacetate in the presence of sodium hydride. Analogous to our previous reported allenyl(vinyl)methanes,[1,2] the esters **1a** and **1b** in several solvents showed a CT band in the range of 250 to 310 nm. The direct photolysis of **1a** (0.005 mol dm^{-3}) in hexane (400 cm^{3}) using a 6-W low-pressure mercury lamp with a quartz jacket (254 nm irradiation) under argon gave a cross conjugated triene **2a**, intramolecular [2+2] cycloadduct **3a**, pyran **4**, and cyclopropene **5a** in 4%, 15%, 18%, and 4% isolated yields, respectively.[7] In a similar manner, the direct photolysis of **1b** gave **2b**, **3b**, **5b**, and **6** in 1%, 25%, 15%, and 2% isolated yields, respectively. In the case of the CT excitation (> 280 nm irradiation) of **1a** and **1b**, these photoproducts were not obtained. The acetone-sensitized photolysis of **1a** gave **2a** and **3a** in 12% and 3% yields, respectively, as intramolecular photoproducts. Moreover, the acetone-sensitized photolysis of **1b** afforded **2b** (7%) and **3b** (14%), respectively. During both acetone sensitizations, polymeric materials were significantly produced. The structures of the photoproducts were established from spectroscopic data and HRMS. Further, **3a** was established by X-ray crystallographic analysis (Fig. 1).[8]



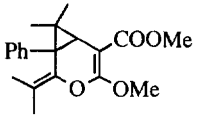
1a: X=Y=COOMe
b: X=COOMe, Y=H
6: X=H, Y=COOMe



2a: X=COOMe
b: X=H



3a: X=COOMe
b: X=H



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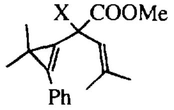


5a: X=COOMe
b: X=H

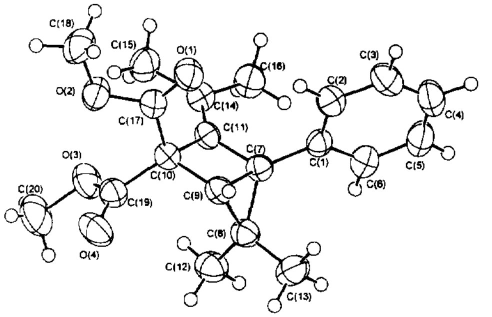


Fig. 1. ORTEP drawing of the [2+2] cycloadduct **3a**.

Table 1 shows quantum yields for the isomerization of **1a** and **1b** under the direct or sensitized irradiation. In the direct photolyses, the isomerization to **5a** or **5b** has a very low quantum efficiency and their formations showed an induction period by GLC during the direct photolyses of **1a** and **1b**. Moreover, the isolated [2+2] cycloadducts **3a** and **3b** were irradiated to afford **5a** and **5b**. Therefore, **5a** and **5b** are apparently photoproducts of **3a** and **3b**. Photochemical *E-Z* isomerization of **1b** was expected, but scarcely occurred during the direct photolysis alone; the maximum yield of **6** was 3% by GLC. In the case of the direct photolyses in the presence of 2-methyl-1,3-butadiene as a quencher, the quantum yields for the formation of the [2+2] cycloadducts, pyran, and *Z*-form are within experimental errors in comparison with the non-additive conditions, although those of **2a** and **2b** decrease in *ca.* 35% (**1a**→**2a**) and 38% (**1b**→**2b**), respectively. Acetone and acetophenone are good sensitizers for the isomerization to the trienes and [2+2] cycloadducts. Benzophenone has sensitizing effects on their isomerization, although the quantum

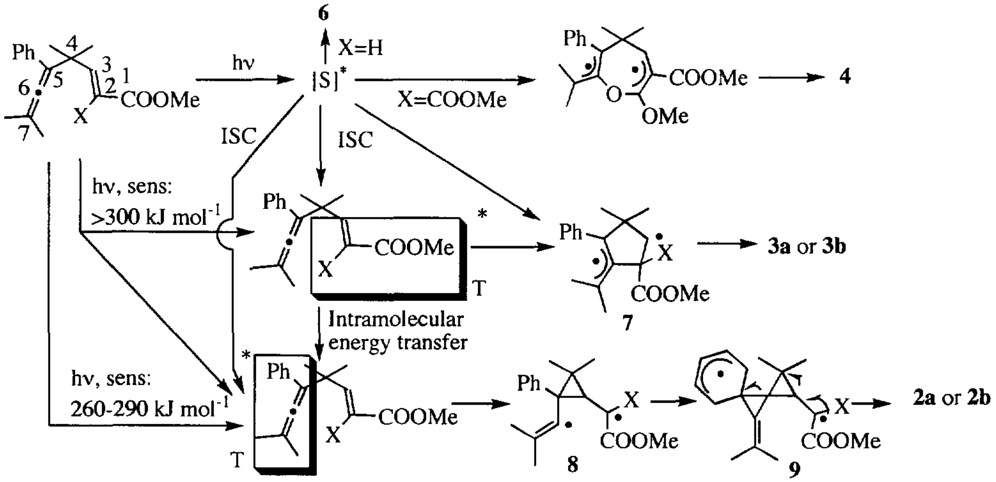
Table 1. Quantum Yields[a] for the Isomerization of **1a** and **1b**

Substrate	λ	Additive (E_T/kJ mol^{-1})[b]	Quantum Yields				
1	nm		$\Phi_{1\to2}$	$\Phi_{1\to3}$	$\Phi_{1\to4}$	$\Phi_{1\to5}$	$\Phi_{1\to6}$
1a	254	none[c]	0.013	0.043	0.030	<0.0001	
		2-Methyl-1,3-butadiene (251)[c,d]	0.0085	0.041	0.028	<0.0001	
	313	Acetone (377-334)[c]	0.25	0.027			
	365	Acetophenone (310)[c]	0.37	0.016			
		Benzophenone (287)[c]	0.29	0.0018			
		2-Benzoylpyridine (279)[c]	0.16	<0.0001			
		Anthraquinone (259)[e]	0.082	<0.0001			
		4-Phenylacetophenone (254)[c]	0.012	<0.0001			
		1-Acetonaphthone (236)[c]	0.0031	<0.0001			
1b	254	none[c]	0.0065	0.14		0.0096	0.014
		2-Methyl-1,3-butadiene (251)[c,f]	0.0040	0.15		0.0095	0.012
	313	Acetone (377-334)[c]	0.026	0.054			
	365	Acetophenone (310)[c]	0.045	0.016			
		Benzophenone (287)[c]	0.040	0.0022			
		2-Benzoylpyridine (279)[c]	0.021	<0.0001			
		Anthraquinone (259)[e]	0.0066	<0.0001			
		4-Phenylacetophenone (254)[c]	0.0055	<0.0001			
		1-Acetonaphthone (236)[c]	0.0028	<0.0001			

a) Total quantum yields for the formation of the photoproducts corresponded with the quantum yield for the disappearance of **1a** or **1b** below the conversion of 20%. b) Sensitizers absorb > 95% of incident light. c) In hexane. d) Quencher concn.: 0.03 mol dm^{-3}. e) In benzene. f) Quencher concn.: 0.07 mol dm^{-3}.

yields of the formation of the [2+2] cycloadducts **3a** and **3b** are smaller values than those obtained with use of acetone or acetophenone. Furthermore, 2-benzoylpyridine, anthraquinone, 4-phenylacetophenone, and 1-acetonaphthone having triplet energy less than benzophenone show sensitizing effects for the formation of the triene only and the later two sensitizers have slight quantum efficiency.

Because these isomerizations did not occur by the CT excitation of **1a** and **1b**, it is considered that the photoproducts, except **5a** and **5b**, were derived from the excited state of either the allenyl or α,β-unsaturated ester chromophore. Sensitizing effects suggest that the trienes and [2+2] cycloadducts are derived from the triplet excited state of a different chromophore in the substrates. Based on our previous report,[1] the triplet energy required for the formation of the [2+2] cycloadducts is estimated to be ca. 300 kJ mol^{-1}; hence, the triplet excited state of the vinyl chromophore in the substrates affords the [2+2] cycloadducts. On the other hand, the triplet energy required for the formation of the trienes **2a** or **2b** is estimated to be ca. 260 kJ mol^{-1}. This triplet energy is nearly value to the triplet energy of the phenyl-substituted allene.[9] Hence, acetone or acetophenone having a higher triplet energy competitively affects both chromophores in **1a** or **1b**, although the allenyl chromophore is excited effectively by sensitizers in the range of 260 to 290 kJ mol^{-1}. By "the rule of five",[10,11] it is considered that the vinyl chromophore excited state in **1a** and **1b** initially bonds between the 2- and 6-positions to yield a cyclopenta-1,3-diyl radical **7** from which ring closure give the [2+2] cycloadduct (Scheme 2).[12] The formation of **3b** during the direct irradiation predominant rather than during the sensitized irradiation, and, further, by the quenching effect, it seems that the [2+2] cycloaddition during the direct irradiation involves the singlet pathway. For the formation of the trienes, it is considered that the allenyl chromophore excited state bonds between the 3- and 5-positions to afford **8**, which affords a spirobiradical **9** and subsequent cyclopropane ring cleavage give the trienes **2a** and **2b** (Scheme 2). This mechanism was supported by PM3 MO calculation;[13] the optimal structure of biradical **9** (X=H) corresponded to the structure of **2b**. Furthermore, it is considered that **4** was derived via the photochemical *oxa*-Diels-Alder reaction by the singlet excited state of the carbonyl at the *cis*-position of **1a**.[2a,14]



Scheme 2.

Generally, the photoreaction via the triplet excited state of bichromophoric compounds takes place from the lower triplet of either chromophore by an intramolecular energy transfer.[15] However, it is interesting that, despite the short length between the allenyl and vinyl chromophores in **1a** and **1b**, the triene and [2+2] cycloadducts are derived from the triplet excited state of different chromophores.

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3. For reports for the multiplicity control of acyclic divinylmethanes, see Ref. 2a.
4. **1a**: IR (neat) 1965, 1734, 1638 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (6H, s), 1.81 (6H, s), 3.68 (3H, s), 3.77 (3H, s), 7.20 (1H, s), 7.25-7.28 (5H, m); ^{13}C NMR ($CDCl_3$) δ 20.4, 27.5, 40.5, 52.5, 54.6, 98.9, 110.8, 125.0, 126.4, 127.9, 128.3, 136.9, 154.7, 166.9, 201.5; MS *m/z* (rel intensity) 328 (M$^+$, 6), 143 (100). HRMS Found: *m/z* 328.1650. Calcd for $C_{20}H_{24}O_4$: 328.1675.
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6. Lehnert. W. *Tetrahedron* **1973**, *29*, 635.
7. **2a**: IR (neat) 1737, 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.66 (3H, s), 1.69 (6H, s), 1.85 (3H, s), 2.02 (3H, s), 3.51 (3H, s), 3.75 (3H, s), 7.24 (5H, s), 7.85 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.2, 22.0, 23.1, 23.3, 51.9, 52.5, 122.6, 126.0, 127.3, 129.3, 129.8, 131.9, 133.2, 135.0, 140.5, 147.6, 165.9, 166.5. HRMS Found: *m/z* 328.1725. Calcd for $C_{20}H_{24}O_4$: 328.1675. **3a**: mp 102-105 °C (hexane); IR (neat) 1733, 1602 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (3H, s), 1.27 (3H, s), 1.57 (3H, s), 1.73 (3H, s), 2.29 (1H, s), 3.77 (3H, s), 3.84 (3H, s), 7.22-7.50 (5H, m); ^{13}C NMR ($CDCl_3$) δ 18.0, 19.1, 20.1, 23.7, 29.2, 36.4, 48.1, 52.1, 52.6, 57.4, 126.7, 127.9, 129.0, 130.2, 131.2, 137.7, 170.9, 171.3. HRMS Found: 328.1731. Calcd for $C_{20}H_{24}O_4$: 328.1675. **4**: IR (neat) 1720, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (3H, s), 1.27 (3H, s), 1.68 (3H, s), 1,73 (3H, s, CH_3), 1.78 (1H, s), 3.70 (3H, s), 3.98 (3H, s), 7.21-7.36 (5H, m); ^{13}C NMR ($CDCl_3$) δ 17.5, 19.9, 24.4, 29.4, 29.7, 32.1, 50.9, 55.6, 79.4, 118.2, 126.1, 128.3, 130.2, 14[illegible].4, 144.6, 163.5, 167.8. HRMS Found: *m/z* 328.1693. Calcd for $C_{20}H_{24}O_4$: 328.1675. **5a**: IR (neat) 1824, 1741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.32 (6H, s), 1.54 (3H, d, *J*=0.8 Hz), 1.82 (3H, d, *J*=1.1 Hz), 3.78 (6H, s), 6.08 (1H, septet, *J*=1.1 Hz), 7.26-7.49 (5H, m); ^{13}C NMR ($CDCl_3$) δ 19.0, 23.1, 24.7, 26.5, 53.0, 58.3, 120.3, 123.4, 125.1, 128.3, 128.5, 129.1, 129.6, 138.6, 169.3. HRMS Found *m/z* 328.1670. Calcd for $C_{20}H_{24}O_4$: 328.1675.
8. Crystal data for **3a**: $C_{20}H_{24}O_4$, Mw = 328.41, Monoclinic, space group *P*21/c (#14); a = 7.639(5), b = 20.832(9), c = 22.658(9) Å, β = 104.57(4)°, V = 1795.6 (16) Å^3, Z = 4, Dc = 1.20 g cm^{-3}, Cu-$K\alpha$ (λ = 0.71073 Å^{-1}), R = 0.0482, Rw = 0.0804 for 5033 unique reflections.
9. The triplet of 3-phenyl-1,2-butadiene is quenched by 1,3-pentadiene (E_T =247 kJ mol^{-1}),[9a)] while the triplet of xanthene-9-thione (274 kJ mol^{-1}) is quenched by phenylallene. Hence, it is considered that the triplet energy of the monophenyl-substituted allene lies in a range of 250 to 270 kJ mol^{-1}.[9b)] a) Fujita, K.; Matsui, K.; Shono, T. *J. Am. Chem. Soc.* **1975**, *97*, 6256; b) Kamphuis, J.; Bos, H. J. T.; Visser, R. J.; Huizer, B. H.; Varma, C. A. G. O. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1867.
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12. We confirmed that the biradical intermediate for the intramolecular [2+2] cycloaddition of allenyl(vinyl)methane is a cyclopenta-1,3-diyl radical by the photochemistry of methyl 4,4,7-trimetyl-2,5,6-octatrienate in the presence of hydrogen selenide. Tsuno, T.; Sugiyama, K. unpublished result.
13. MO calculation was performed using UHF PM3 method of Mac Spartan Plus of Wavefunction, Inc.
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