3 H), 1.93–2.51 (m, 3 H), 3.776 (dq, *J* = 6.3 and 3.4 Hz, 1 H), 4.126 (q, *J* = 7.0 Hz, 2 H); HRMS calcd for $C_{14}H_{30}O_3Si$ 274.1964, found 259.1723 ($M^+ - CH_3$).

Ethyl *anti*-4-((*tert*-Butyldimethylsilyl)oxy)-2-(ethoxycarbonyl)-3-methylpentanoate: ^1H NMR ($CDCl_3$) δ 0.046 (s, 3 H), 0.052 (s, 3 H), 0.879 (2, 9 H), 0.968 (d, *J* = 7.0 Hz, 3 H), 1.095 (d, *J* = 6.0 Hz, 3 H), 1.265 (t, *J* = 7.0 Hz, 6 H), 2.262 (ddq, *J* = 6.0, 7.0, and 7.0 Hz, 1 H), 3.568 (d, *J* = 7.0 Hz, 1 H), 3.788 (dq, *J* = 6.0 and 6.0 Hz, 1 H), 4.12–4.23 (m, 4 H); HRMS calcd for $C_{17}H_{34}O_5Si$ 346.2176, found 346.2170.

Ethyl *syn*-4-((*tert*-Butyldimethylsilyl)oxy)-2-(ethoxycarbonyl)-3-methylpentanoate: ^1H NMR ($CDCl_3$) δ 0.00 (s, 3 H), 0.024 (s, 3 H), 0.884 (s, 9 H), 0.898 (d, *J* = 6.8 Hz, 3 H), 1.136 (d, *J* = 6.2 Hz, 3 H), 1.258 (t, *J* = 7.0 Hz, 3 H), 1.269 (t, *J* = 7.0 Hz, 3 H), 2.254 (ddq, *J* = 2.8, 6.8, and 10.1 Hz, 1 H), 3.432 (d, *J* = 10.1 Hz, 1 H), 3.904 (dq, *J* = 2.8 and 6.4 Hz, 1 H), 4.12–4.14 (m, 4 H); HRMS calcd for $C_{17}H_{34}O_5Si$ 346.2176, found 346.2174.

Ethyl *syn*-4-(Benzyloxy)-2-(ethoxycarbonyl)-5,5-dimethyl-3-methylhexanoate (23b): ^1H NMR ($CDCl_3$) δ 0.987 (s, 9 H), 1.032 (d, *J* = 6.8 Hz, 3 H), 1.268 (t, *J* = 7.2 Hz, 3 H), 1.282 (t, *J* = 7.2 Hz, 3 H), 2.668 (ddq, *J* = 1.0, 6.8, and 10.5 Hz, 1 H), 3.045 (d, *J* = 1.0 Hz, 1 H), 3.396 (d, *J* = 10.5 Hz, 1 H), 4.15–4.30 (m, 4 H), 4.562 (d, *J* = 11.0 Hz, 1 H), 4.646 (d, *J* = 11.0 Hz, 1 H), 7.33–7.40 (m, 5 H); HRMS calcd for $C_{21}H_{32}O_5$ 364.2250, found 364.2248.

Ethyl *syn*-3-(1-(Benzyloxy)-2,2-dimethylpropyl)-2-(ethoxycarbonyl)-heptanoate (23c): ^1H NMR ($CDCl_3$) δ 0.84 (t, *J* = 6.8 Hz, 3 H), 0.98 (s, 9 H), 1.257 (t, *J* = 7.0 Hz, 3 H), 1.283 (t, *J* = 7.0 Hz, 3 H), 0.9–1.6 (m, 5 H), 1.66–1.85 (m, 1 H), 2.38–2.48 (m, 1 H), 3.112 (d, *J* = 2.5 Hz, 1 H), 3.48 (d, *J* = 8.0 Hz, 1 H), 4.165 (q, *J* = 7.0 Hz, 2 H), 4.192 (q, *J* = 7.0 Hz, 2 H), 4.538 (d, *J* = 11.4 Hz, 1 H), 4.651 (d, *J* = 11.4 Hz, 1 H), 7.32–7.37 (m, 5 H); HRMS calcd for $C_{24}H_{38}O_5$ 406.2720, found 406.2716.

Supplementary Material Available: ^1H NMR spectra for **3–9** and **20–23** (21 pages). Ordering information is given an any current masthead page.

A Novel 1,8-Photoaddition of Dimethyl 1,4-Naphthalenedicarboxylate to Alkenes

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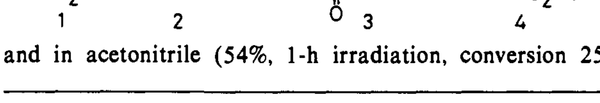
Abstract: Irradiation of dimethyl 1,4-naphthalenedicarboxylate (**1**) with various alkenes **2**, and **10a–d** is found to give novel 1,8-adducts **3**, **11a–d**, **12a,b,d**, and **13b,d**. The 1,8-photoaddition proceeds with retention of the stereochemistry of the alkenes in the reactions with *trans*- and *cis*-2-butene (**5** and **7**). Because there is no evidence for a preformed ground-state complex between **1** and the alkenes, the 1,8-addition proceeds from the singlet excited state of **1**. Fluorescence of **1** is inefficiently but significantly quenched by alkenes, and an exciplex emission is observed on quenching by **10c**. A possible mechanism for the 1,8-photoaddition, involving exciplex formation and an almost synchronous two-bond formation in the exciplex to give a zwitterionic intermediate **15** followed by suprafacial proton transfer, is proposed.

Introduction

Photoadditions of aromatic compounds to alkenes have been extensively investigated for the elucidation of the role of exciplexes and for the exploitation of the synthetic potentials, but considerable interest is still evident.[1] For benzene derivatives, 1,2- (ortho), 1,3- (meta), and 1,4-photoadditions (para) to alkenes have been reported.[1,2] The 1,2- and 1,3-additions are the most common, and the latter is currently receiving considerable attention.[3] On the other hand, for naphthalene derivatives, a number of instances of 1,2- and 1,4-photoaddition have been noted, but 1,3-additions have been seldom observed.[1] We here report a novel 1,8-photoaddition of dimethyl 1,4-naphthalenedicarboxylate (**1**) to alkenes, a formal [3 + 2] photoaddition, which proceeds stereospecifically possibly via a unique zwitterionic intermediate.

Results and Discussion

Irradiation of **1** (4 mM) in the presence of isobutene (**2**) (1 M) in ether leads to the efficient (77%) production of 1,8-adduct **3** (eq 1). The 1,8-photoaddition also proceeds in benzene (47%) and in acetonitrile (54%, 1-h irradiation, conversion 25%).



(1)

However, the secondary isomerization from **3** to the stereoisomer **4** to give an equilibrium mixture of **3** and **4** (**3**:**4** = 3:7) is observed only in acetonitrile with prolonged irradiation time (4 h). The facile isomerization from **3** to **4** is observed upon irradiation of **1** (4 mM), **3** (4 mM), and 1-hexene (**10a**) (800 mM) in acetonitrile with concomitant formation of adducts of **1** and **10a** (vide infra), while the product **3** is photostable in acetonitrile as well as in ether and in benzene.[4] Thus, the secondary isomerization from **3** to **4** observed in acetonitrile may occur through the conjugated base of **3** and **4** that is caused by a base formed during the course of the photoreaction.

The structures and stereochemistry of **3** and **4** are determined from the ^1H and ^{13}C NMR spectra. A smaller vicinal H^a–H^b coupling constant (2.0 or 2.9 Hz) in **3** compared with that (5.5 Hz) in **4** is consistent with a larger dihedral angle (H^a–C–C–H^b) of 95° in **3** compared with that of 30° in **4**, as predicted by the molecular models.

The photoreaction of **1** with **2** in 10% CH_3OD–benzene leads to **3** with a single deuterium incorporated α to the ester carbonyl (D content, 88%). The D contents in **3** and **4** for the reaction in 10% CH_3OD–acetonitrile are 75% and 100%, respectively. The D contents in **3** and **4** are maintained almost constant during the course of the photoreaction, even at low conversion, both in 10% CH_3OD–benzene and in 10% CH_3OD–acetonitrile.

Interestingly, the 1,8-photoaddition proceeds with retention of the stereochemistry of the alkenes. Thus, irradiation of **1** (4 mM) with *trans*-2-butene (**5**) (1 M) in ether gives **6** (85%), and that

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(1) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811 and references therein.

(2) (a) Mattay, J. J. *Photochem.* **1987**, *37*, 167 and references therein. (b) Hamrock, S. J.; Sheridan, R. S. *J. Am. Chem. Soc.* **1989**, *111*, 9247.

(3) Wender, P. A.; Von Geldern, T. W.; Levine, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 4858 and references therein.

(4) Isomerization from **3** to **4** is also observed upon irradiation of **1** (4 mM) and **3** (4 mM) at a slower rate (~1/10) than that observed in the presence of **10a**.

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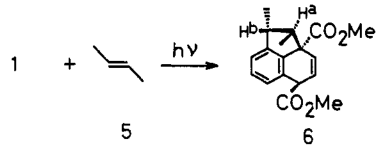
Table I. Product Distribution upon Photolysis of Dimethyl 1,4-Naphthalenedicarboxylate (**1**) and Unsaturated Compounds **10a–d**[a]

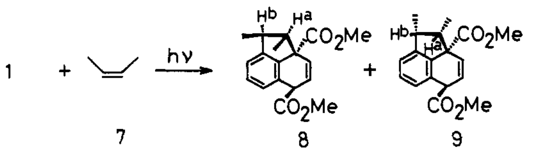
R^1	R^2	unsatd compd **10**	[**10**] (mM)	solvent	yield (%) **11**	**12**	**13**
Bu	H	**10a**	800	Et_2O	**11a** 68		
				C_6H_6	18		
				MeCN	22	**12a** 7	
CH=CH$_2$	H	**10b**	1100	Et_2O	**11b** 60		**13b** 13
				C_6H_6	51		18
				MeCN	56	**12b** 5	11
–$(CH_2)_3$–		**10c**	1100	Et_2O	**11c** 65		
				C_6H_6	70		
				MeCN	43		
Ph	H	**10d**	87	Et_2O	**11d** 60		**13d** 10
				C_6H_6	58		14
				MeCN	51	**12d** 7	9

[a] Irradiation conditions are as follows: *hν* (λ >320 nm), under N_2, [**1**] = 4 mM.

with *cis*-2-butene (**7**) (1 M) affords **8** (51%) and **9** (20%) (eqs 2, 3). The structures and stereochemistry of **6**, **8**, and **9** can be assigned by the vicinal H^a–H^b coupling constants and the chemical shifts of the methyl groups. A smaller vicinal H^a–H^b coupling (~0 Hz) in **6** compared with those (6.0 and 7.6 Hz) in **8** and **9**, respectively, is consistent with a larger dihedral angle of 90° in **6** compared with those of 30° and 30° in **8** and **9**, respectively, as predicted by the molecular models. Smaller chemical shift values (δ 0.86, 0.62) of the methyl groups (CH_3–C–H^a) in **6** and **8**, compared with those (δ 1.22, 1.20) of the other methyl groups (CH_3–C–H^b) in **6** and **8**, respectively, and also with those (δ 1.19, 1.29) of the two methyl groups in **9**, due to the anisotropic effect of the benzene ring as predicted by the molecular models, strongly support the structures and the stereochemistry of **6**, **8**, and **9**.

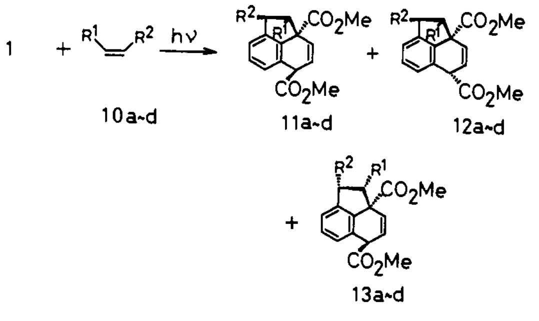


(2)



(3)

Other examples of the 1,8-photoadditions of **1** to unsaturated compounds, such as an aliphatic alkene **10a**, alicyclic alkene **10b**, diene **10c**, and styrene (**10d**), are shown in eq 4 and Table I suggesting that the 1,8-photoaddition is fairly general.



(4)

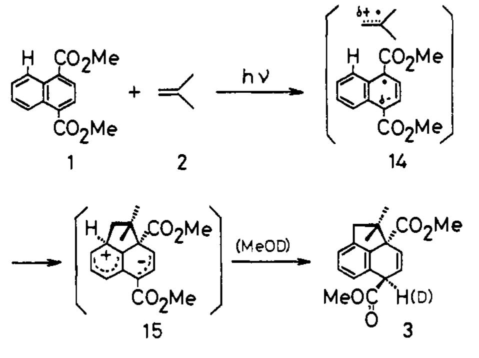
In the present case there is no evidence from the UV spectra for a preformed ground-state complex between **1** and the alkenes. Thus, the 1,8-addition proceeds from the singlet excited state of **1**, as suggested by the stereospecificity observed in the reactions with **5** and **7**. Fluorescence of **1** is inefficiently but significantly quenched by the alkenes as shown in Table II to support the singlet mechanism. Although certain photoadditions between aromatics and alkenes are thought to involve electron transfer,[5] application of the well-known Rehm–Weller equation[6] suggests that electron transfer between the singlet excited state of **1** (E_S = 80.0 kcal/mol, E^{red} = −1.35 V in 0.1 M Bu_4NClO_4/CH_3CN vs Ag/0.01 M $AgClO_4$) and **2** (E^{ox} = 2.39 V)[7] or **10a** (E^{ox} = 2.64 V)[7] would be endothermic by 6.0 or 11.8 kcal/mol and, hence, unlikely.[8] Thus, the 1,8-addition may be governed by the generation of reactive partners as an exciplex (or a contact ion pair) from the interaction between the singlet excited state of **1** and the alkenes. A weak emission at longer wavelengths, possibly from an exciplex, is observed in the case of the fluorescence quenching by **10c** in ether.

Table II. Quenching of the Fluorescence of Dimethyl 1,4-Naphthalenedicarboxylate (**1**) by Alkenes[a]

alkene	solvent	$k_q\tau^b$ (M^{-1})	τ (ns)	k_q (M^{-1} s^{-1})
1-hexene (**10a**)	C_6H_6	0.028	8.2	3.4×10^6
	Et_2O	0.030	6.5	4.6×10^6
	MeCN	0.032	8.5	3.8×10^6
2-ethyl-1-butene[c]	C_6H_6	0.18	8.2	2.2×10^7
	Et_2O	0.26	6.5	4.0×10^7
	MeCN	1.0	8.5	1.2×10^8
cyclopentene (**10c**)	C_6H_6	0.11	8.2	1.3×10^7
	Et_2O	0.18	6.5	2.8×10^7
	MeCN	3.9	8.5	4.6×10^8

[a] Experimental conditions are as follows: [**1**] = 1×10^{-4} M, at 25 °C, in an air-saturated solvent. [b] Stern–Volmer slope for the fluorescence quenching. [c] As a liquid model compound for isobutene (**2**).

As for the following steps, we propose the mechanism shown in eq 5. In the exciplex **14**, the alkene moiety may have some radial cationic nature and the diester moiety some radial anionic nature. Two-bond formation, namely, coupling between the radical center in the alkene moiety and that (1-position of the naphthalene ring) in the diester moiety and electrophilic attack of the cationic center of the alkene moiety at the 8-position of the naphthalene



(5)

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(5) Mattay, J. *Tetrahedron* **1985**, *41*, 2393, 2405.

(6) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(7) Mazzocchi, P. H.; Minamikawa, S.; Wilson, P. *Tetrahedron Lett.* **1978**, 4361.

(8) In less polar solvents such as ether and benzene, free energy changes (ΔG_{et}) associated with the electron transfer from the alkenes to the singlet excited state of **1** should be even higher. The decreasing yields of the photoproducts in acetonitrile might be caused by some ionic dissociation. The isomerization from **3** to **4** observed only in acetonitrile might be attributed to the ionic dissociation.

ring of the diester moiety, may thus proceed within **14** to give the zwitterionic intermediate **15**. The two-bond formation must be synchronous or nearly so, since the stereochemistry of **5** and **7** is maintained in the 1,8-photoaddition. Proton transfer within **15** affords the final product **3**. An interesting feature of the proton transfer process is the stereochemical course; the suprafacial proton transfer on the naphthalene ring proceeds even in the presence of CH_3OD (10%) in the solvent, because the formation of the single stereoisomer **3** is observed during the early stage of the reaction.

The present work exhibits a unique possibility for the chemical pathway from exciplexes. Furthermore, the present system provides not only a novel example of the 1,8-photoaddition of naphthalene derivatives to alkenes but also a unique instance of formal [3 + 2] photoaddition.[9] We are continuing to explore the scope and mechanistic details of this novel photoaddition.[10]

Experimental Section

General Information. Melting points were obtained on a Yanagimoto micro melting point apparatus and are uncorrected. NMR spectra were recorded on a JEOL JNM-GX-270 (270 MHz) instrument. Chemical shifts are reported in ppm (δ) relative to internal $SiMe_4$. IR spectra were determined by use of a Hitachi 260-50 spectrometer. Low resolution (EI, 70 eV) and high resolution (EI) mass spectra were recorded on a Hitachi M-80B mass spectrometer. Fluorescence spectra and fluorescence lifetimes were obtained on a Hitachi 850 spectrophotometer and on a Horiba NAES-1100 time-resolved spectrofluorometer, respectively. Combustion analyses were performed on a Yanagimoto CHN corder MT-5. Reduction potential was determined by use of a Yanaco cyclic polarography P-900. HPLC analyses were performed on a Hitachi 635S liquid chromatograph.

Materials. Dimethyl 1,4-naphthalenedicarboxylate (**1**), mp 66.0–67.0 °C (hexane–ether) (lit.[11] mp 67 °C), was prepared by methyl esterification[11] of 1,4-naphthalenedicarboxylic acid.[12] Unsaturated compounds **2**, **5**, **7**, and **10a–d** were commercially available and purified by distillation if liquid. Solvents were purified by distillation after dehydration. Fluorescence-spectrograde solvents obtained from Nacalai Tesque Inc. were used as received for the fluorescence spectrum measurement and the lifetime determination.

Photochemical Procedures and Product Isolation. UV irradiation of **1** (4 mM) and unsaturated compounds **2**, **5**, **7**, and **10a–d** (concentrations are given in the text or in Table I) in N_2-purged solvent was carried out with an Eikosha EHB-W-300 high-pressure Hg lamp through a uranium filter ($\lambda > 320$ nm). The reaction was monitored by TLC (Merck, kieselgel 60 F_{254}) analyses and ^{1}H NMR measurements and conducted to >95% conversion in the case of the reactions in ether or in benzene and to >65% conversion in the cases of the reactions in acetonitrile. After evaporation of the solvent, the residue was subjected to column chromatography (Wakogel C-200; eluent, benzene–ether) or HPLC (Wakopac-WS-5C8; eluent, methanol–water). Yields of the products are given in the text or in Table I.

Data for Photoproducts. Irradiation of 1 with Isobutene (2). Data for (±)-(2a*R*,5*S*)-dimethyl 2,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**3**): mp 105.0–107.0 °C (hexane–ether); ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 3 H), 1.26 (s, 3 H), 2.51 and 3.32 (AB, q, J = 15.1 Hz, 2 H), 3.58 (s, 3 H), 3.78 (s, 3 H), 4.26 (dd, J = 2.0, 2.9 Hz, H^a), 6.11 (dd, J = 2.0, 9.8 Hz, H^b or H^c), 6.29 (dd, J = 2.9, 9.8 Hz, H^b or H^c), 7.0–7.3 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 23.85 (q), 25.28 (q), 44.89 (t), 46.96 (d), 48.64 (s), 51.79 (q), 52.27 (q), 60.73 (s), 122.54 (d), 123.44 (d), 126.53 (d), 127.73 (d), 128.28 (d), 130.22 (s), 140.05 (s), 142.10 (s), 172.64 (s), 172.93 (s); IR (KBr) 1748, 1734, 1320, 1216, 1162, 772 cm^{-1}; MS *m/z* 300 (M^+, 2), 241 ($M^+ - CO_2Me$, 100), 209 (69), 167 (65), 149 (49); HRMS *m/z* 300.1376 (M^+, calcd for $C_{18}H_{20}O_4$ 300.1360). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.97; H, 6.80. Data for (±)-(2a*R*,5*R*)-dimethyl 2,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**4**): mp 108.0–109.0 °C (hexane–ether); ^{1}H NMR ($CDCl_3$) δ 0.76 (s, 3 H), 1.26 (s, 3 H), 2.48 and 3.36 (AB q, J = 15.0 Hz, 2 H), 3.58 (s, 3 H), 3.64 (s, 3 H), 4.32 (d, J = 5.5 Hz, H^a), 6.12 (dd, J = 5.5, 9.5 Hz, H^b), 6.37 (d, J = 9.5 Hz, H^c), 7.0–7.3 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 23.72 (q), 24.82 (q), 46.72 (t), 46.87 (d), 49.22 (s), 51.56 (q), 52.20 (q), 60.80 (s), 123.71 (d), 124.22 (d), 125.03 (d), 127.59 (d), 130.63 (d), 130.71 (s), 140.96 (s), 142.44 (s), 171.28 (s), 172.59 (s); IR (KBr) 1728, 1432, 1276, 1228, 1022 cm^{-1}; MS *m/z* 300 (M^+, 2), 241 ($M^+ - CO_2Me$, 100), 209 (68), 167 (67), 149 (59); HRMS *m/z* 300.1389 (M^+, calcd for $C_{18}H_{20}O_4$ 300.1360). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.04; H, 6.70.

Irradiation of 1 with *trans*-2-Butene (5). Data for (±)-(1*R*,2*R*,2a*S*,5*R*)-dimethyl 1,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**6**): mp 84.0–85.0 °C (hexane–ether); ^{1}H NMR ($CDCl_3$) δ 0.86 (d, J = 7.3 Hz, 3 H, CH_3–C–H^a), 1.22 (d, J = 7.3 Hz, 3 H, CH_3–C–H^b), 2.77 (q, $J_{H^a-H^b} = 0$, $J_{H-Me} = 7.3$ Hz, 1 H, H^b), 3.01 (q, $J_{H^a-H^b} = 0$, $J_{H-Me} = 7.3$ Hz, 1 H, H^a), 3.57 (s, 3 H), 3.82 (s, 3 H), 4.47 (br s, 1 H), 6.18 (br s, 2 H), 7.13 (d, 2 H), 7.25 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.08 (q), 20.90 (q), 45.38 (d), 47.51 (d), 48.38 (d), 52.24 (q), 52.47 (q), 58.40 (s), 122.93 (d), 123.03 (d), 128.18 (d), 128.55 (d), 129.02 (d), 131.56 (s), 137.66 (s), 145.04 (s), 172.69 (s), 174.71 (s); IR (KBr) 2955, 1738 (sh), 1728, 1433, 1315, 1218, 1158, 1008 cm^{-1}; MS *m/z* 300 (M^+, 2), 241 ($M^+ - CO_2Me$, 27), 209 (21), 167 (36), 165 (34), 59 (100); HRMS *m/z* 300.1363 (M^+, calcd for $C_{18}H_{20}O_4$ 300.1360). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.72; H, 6.75.

Irradiation of 1 with *cis*-2-Butene (7). Data for (±)-(1*R*,2*S*,2a*R*,5*S*)-dimethyl 1,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**8**): ^{1}H NMR ($CDCl_3$) δ 0.62 (d, J = 7.3 Hz, 3 H, CH_3–C–H^a), 1.20 (d, J = 7.3 Hz, 3 H, CH_3–C–H^b), 3.24 (dq, $J_{H^a-H^b} = 6.0$, $J_{H-Me} = 7.3$ Hz, 1 H, H^a), 3.50 (dq, $J_{H^a-H^b} = 6.0$, $J_{H-Me} = 7.3$ Hz, 1 H, H^b), 3.55 (s, 3 H), 3.81 (s, 3 H), 4.48 (br s, 1 H), 6.16 (br s, 2 H), 7.0–7.4 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 8.65 (q), 11.90 (q), 39.97 (d), 44.25 (d), 45.98 (d), 51.19 (q), 51.36 (q), 57.97 (s), 120.88 (d), 121.80 (d), 127.01 (d), 127.25 (d), 127.76 (d), 129.28 (s), 137.61 (s), 143.62 (s), 171.62 (s), 172.57 (s); IR (CCl_4) 2950, 1733, 1432, 1265, 1220 cm^{-1}; MS *m/z* 300 (M^+, 2), 241 ($M^+ - CO_2Me$, 71), 209 (43), 167 (47), 149 (58), 59 (88), 57 (100); HRMS *m/z* 300.1331 (M^+, calcd for $C_{18}H_{20}O_4$ 300.1360). Data for (±)-(1*R*,2*S*,2a*S*,5*R*)-dimethyl 1,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**9**): ^{1}H NMR ($CDCl_3$) δ 1.19 (d, J = 7.3 Hz, 3 H, CH_3–C–H^a), 1.29 (d, J = 7.3 Hz, 3 H, CH_3–C–H^b), 2.58 (dq, $J_{H^a-H^b} = 7.6$, $J_{H-Me} = 7.3$ Hz, 1 H, H^b), 3.14 (dq, $J_{H^a-H^b} = 7.6$, $J_{H-Me} = 7.3$ Hz, 1 H, H^a), 3.58 (s, 3 H), 3.83 (s, 3 H), 4.31 (dd, J = 1.7, 3.2 Hz, 1 H), 6.13 (dd, J = 1.7, 9.4 Hz, 1 H), 6.34 (dd, J = 3.2, 9.4 Hz, 1 H), 7.0–7.4 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 11.11 (q), 14.79 (q), 42.16 (d), 44.28 (d), 46.48 (d), 50.78 (q), 51.22 (q), 55.79 (s), 121.51 (d), 121.58 (d), 126.30 (d), 126.91 (d), 127.30 (d), 130.26 (s), 139.06 (s), 146.03 (s), 171.58 (s), 172.19 (s); IR (CCl_4) 2945, 1732, 1432, 1260, 1218 cm^{-1}; MS *m/z* 300 (M^+, 2), 241 ($M^+ - CO_2Me$, 71), 209 (43), 167 (42), 149 (47), 73 (57), 59 (100), 57 (93); HRMS *m/z* 300.1379 (M^+, calcd for $C_{18}H_{20}O_4$ 300.1360).

Irradiation of 1 with 1-Hexene (10a). Data for (±)-(2*R*,2a*R*,5*R*)-dimethyl 2-butyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**11a**): mp 60.0–61.5 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.7–1.0 (m, 4 H), 1.1–1.5 (m, 5 H), 2.65 (d, J = 15.6 Hz, 1 H), 3.0–3.1 (m, 1 H), 3.19 (dd, J = 5.9, 15.6 Hz, 1 H), 3.56 (s, 3 H), 3.83 (s, 3 H), 4.47 (dd, J = 1.2, 2.7 Hz, 1 H), 6.16 (dd, J = 1.2, 9.8 Hz, 1 H), 6.23 (dd, J = 2.7, 9.8 Hz, 1 H), 7.11 (d, J = 7.6 Hz, 1 H), 7.15 (d, J = 7.6 Hz, 1 H), 7.22 (t, J = 7.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.07 (q), 22.77 (t), 28.83 (t), 29.83 (t), 36.00 (t), 45.41 (d), 46.94 (d), 52.24 (q), 52.41 (q), 59.49 (s), 122.87 (d), 123.69 (d), 127.92 (d), 128.20 (d), 128.61 (d), 130.43 (s), 139.15 (s), 140.82 (s), 172.66 (s), 173.61 (s); IR (CCl_4) 2950, 1735 (br), 1454, 1432, 1308, 1268, 1225 cm^{-1}; MS *m/z* 328 (M^+, 2), 269 ($M^+ - CO_2Me$, 97), 237 (48), 199 (28), 155 (93), 153 (59), 59 (100), 57 (57); HRMS *m/z* 328.1684 (M^+, calcd for $C_{20}H_{24}O_4$ 328.1673). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.28; H, 7.45. Data for (±)-(2*R*,2a*R*,5*S*)-dimethyl 2-butyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**12a**): mp 80.0–82.0 °C (hexane); ^{1}H NMR ($CDCl_3$) δ 0.6–1.0 (m, 4 H), 1.1–1.6 (m, 5 H), 2.62 (d, J = 15.6 Hz, 1 H), 2.9–3.0 (m, 1 H), 3.24 (dd, J = 6.1, 15.6 Hz, 1 H), 3.54 (s, 3 H), 3.66 (s, 3 H), 4.38 (d, J = 5.3 Hz, 1 H), 6.22 (dd, J = 5.3, 9.7 Hz, 1 H), 6.33 (d, J = 9.7 Hz, 1 H), 7.2–7.3 (m, 3 H); IR (CCl_4) 2950, 1735 (br), 1456, 1434, 1275, 1227 cm^{-1}; MS *m/z* 328 (M^+, 2), 269 ($M^+ - CO_2Me$, 19), 237 (12), 199 (8), 153 (42), 152 (33), 59 (100), 57 (73); HRMS *m/z* 328.1663 (M^+, calcd for $C_{20}H_{24}O_4$ 328.1673). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 72.94; H, 7.36.

Irradiation of 1 with 1,3-Butadiene (10b). Data for (±)-(2*R*,2a*S*,5*S*)-dimethyl 2-vinyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**11b**): ^{1}H NMR ($CDCl_3$) δ 2.62 (d, J = 15.9 Hz, 1 H), 3.47 (dd, J = 6.1, 15.9 Hz, 1 H), 3.56 (s, 3 H), 3.75 (dd, J = 6.1, 9.5 Hz, 1 H), 3.81 (s, 3 H), 4.48 (br d, J = 2.7 Hz, 1 H), 5.00 (dd, J = 2.0, 9.9 Hz, 1 H), 5.15 (dd, J = 2.0, 16.9 Hz, 1 H), 5.34 (ddd, J = 9.5, 9.8, 16.9 Hz, 1 H), 6.09 (dd, J = 2.7, 9.8 Hz, 1 H), 6.16 (d, J = 9.8 Hz, 1

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(9) Some examples of formal [3 + 2] photoadditions by way of rearrangement of initially formed 1,4-biradicals have been reported: Rathjen, H.-J.; Margaretha, P.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 3904 and references therein.

(10) The 1,8-photoaddition is found to be general in the reactions of the corresponding cyano compounds and alkenes with high ionization potentials.

(11) Bradbrook, E. F.; Linstead, R. P. *J. Chem. Soc.* **1936**, 1739.

(12) Simon, Z.; Balaban, A. T.; Ciubotariu, D.; Balaban, T. S. *Rev. Roum. Chim.* **1985**, *30*, 985.

H), 7.11 (d, J = 7.7 Hz, 1 H), 7.14 (d, J = 7.7 Hz, 1 H), 7.22 (t, J = 7.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.55 (t), 45.38 (d), 51.89 (d), 52.27 (q), 52.55 (q), 58.85 (s), 116.42 (d), 123.00 (d), 123.54 (d), 128.22 (d), 128.35 (d), 128.75 (d), 131.00 (s), 138.02 (d), 139.11 (s), 141.03 (s), 172.63 (s), 173.02 (s); IR (CCl_4) 2940, 1742, 1728, 1432, 1315, 1218, 1022 cm^{-1}; MS *m/z* 298 (M^+, 2), 239 ($M^+ - CO_2Me$, 100), 207 (58), 180 (46), 179 (57), 165 (77), 59 (46); HRMS *m/z* 298.1205 (M^+, calcd for $C_{18}H_{18}O_4$ 298.1204). Data for (±)-(2*R*,2a*S*,5*R*)-dimethyl 2-vinyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**12b**): ^{1}H NMR ($CDCl_3$) δ 2.60 (d, J = 15.6 Hz, 1 H), 3.4–3.6 (m, 2 H), 3.55 (s, 3 H), 3.66 (s, 3 H), 4.33 (d, J = 5.6 Hz, 1 H), 4.96 (dd, J = 2.6, 9.7 Hz, 1 H), 5.14 (dd, J = 2.6, 17.1 Hz, 1 H), 5.1–5.3 (m, 1 H), 6.1–6.3 (m, 2 H), 7.1–7.3 (m, 3 H); IR ($CHCl_3$) 2940, 1722, 1430, 1308 cm^{-1}; MS *m/z* 298 (M^+, 2), 239 ($M^+ - CO_2Me$, 32), 207 (27), 179 (47), 178 (28), 165 (77), 152 (42), 59 (100); HRMS *m/z* 298.1207 (M^+, calcd for $C_{18}H_{18}O_4$ 298.1204). Data for (±)-(2*R*,2a*R*,5*R*)-dimethyl 2-vinyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**13b**): ^{1}H NMR ($CDCl_3$) δ 2.90 (dd, J = 7.1, 14.8 Hz, 1 H), 3.24 (ddd, J = 7.1, 7.8, 11.2 Hz, 1 H), 3.43 (dd, J = 11.2, 14.8 Hz, 1 H), 3.57 (s, 3 H), 3.82 (s, 3 H), 4.33 (dd, J = 1.7, 2.9 Hz, 1 H), 5.20 (br d, J = 9.4 Hz, 1 H), 5.25 (br d, J = 17.2 Hz, 1 H), 6.11 (ddd, J = 7.8, 9.4, 17.2 Hz, 1 H), 6.18 (dd, J = 1.7, 9.5 Hz, 1 H), 6.33 (dd, J = 2.9, 9.5 Hz, 1 H), 7.0–7.3 (m, 3 H); IR (CCl_4) 2940, 1734, 1432, 1262, 922 cm^{-1}; MS *m/z* 298 (M^+, 3), 239 ($M^+ - CO_2Me$, 100), 207 (58), 180 (44), 179 (60), 165 (77), 149 (40), 59 (45); HRMS *m/z* 298.1195 (M^+, calcd for $C_{18}H_{18}O_4$ 298.1204).

Irradiation of 1 with Cyclopentene (10c). Data for (±)-(1*R*,2*S*,2a*R*,5*S*)-dimethyl 3,6b,8,9,9a,9b-hexahydro-7*H*-cyclopenta[*a*]-acenaphthylene-3,9b-dicarboxylate (**11c**): mp 97.0–98.0 °C (hexane–ether); ^{1}H NMR ($CDCl_3$) δ 0.8–1.1 (m, 1 H), 1.2–1.6 (m, 2 H), 1.6–1.8 (m, 2 H), 1.9–2.1 (m, 1 H), 3.30 (ddd, J = 6.8, 7.3, 8.2 Hz, 1 H), 3.46 (s, 3 H), 3.73 (s, 3 H), 3.7–3.9 (m, 1 H), 4.40 (br s, 1 H), 6.11 and 6.15 (br AB q, J = 10.1 Hz, 2 H), 7.00 (d, J = 7.6 Hz, 2 H), 7.16 (t, J = 7.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.04 (t), 27.18 (t), 31.40 (t), 45.55 (d), 49.22 (d), 52.20 (d), 52.20 (q), 52.41 (q), 58.60 (s), 122.76 (d), 122.99 (d), 128.53 (d), 129.02 (d), 129.42 (d), 130.77 (s), 139.11 (s), 145.95 (s), 172.74 (s), 173.89 (s); IR (KBr) 2950, 1752, 1724, 1436, 1320, 1222, 1198, 1155, 778 cm^{-1}; MS *m/z* 312 (M^+, 1), 253 ($M^+ - CO_2Me$, 100), 221 (58), 194 (25), 165 (48), 155 (43), 67 (45), 59 (34); HRMS *m/z* 312.1374 (M^+, calcd for $C_{19}H_{20}O_4$ 312.1361). Anal. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.77; H, 6.52.

Irradiation of 1 with Styrene (10d). Data for (±)-(2*R*,2a*R*,5*S*)-dimethyl 2-phenyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**11d**): mp 122.0-124.0 °C (hexane–ether); ^{1}H NMR ($CDCl_3$) δ 2.96 (d, J = 16.1 Hz, 1 H), 3.61 (s, 3 H), 3.73 (dd, J = 7.1, 16.1 Hz, 1 H), 3.80 (s, 3 H), 4.40 (d, J = 7.1 Hz, 1 H), 4.47 (dd, J = 1.7, 3.2 Hz, 1 H), 5.75 (dd, J = 3.2, 9.8 Hz, 1 H), 5.95 (dd, J = 1.7, 9.8 Hz, 1 H), 6.7–6.8 (m, 2 H), 7.1–7.4 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 40.06 (t), 45.38 (d), 52.23 (q), 52.33 (d), 52.70 (q), 60.54 (s), 123.11 (d), 123.23 (d), 126.87 (d), 127.80 (d), 127.83 (d), 128.26 (d), 128.44 (d), 128.70 (d), 130.84 (s), 139.80 (s), 141.32 (s), 142.10 (s), 172.56 (s), 173.41 (s); IR (CCl_4) 2945, 2920, 1733, 1432, 1220, 698, 615 cm^{-1}; MS *m/z* 348 (M^+, 2), 289 ($M^+ - CO_2Me$, 37), 257 (27), 230 (33), 229 (67), 228 (32), 167 (57), 153 (53), 152 (53), 59 (100); HRMS *m/z* 348.1338 (M^+, calcd for $C_{22}H_{20}O_4$ 348.1360). Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.77; H, 5.92. Data for (±)-(2*R*,2a*R*,5*R*)-dimethyl 2,2-dimethyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**12d**): mp 108.0–109.0 °C (hexane–ether); ^{1}H NMR ($CDCl_3$) δ 2.95 (d, J = 16.1 Hz, 1 H), 3.60 (s, 3 H), 3.67 (s, 3 H), 3.76 (dd, J = 6.8, 16.1 Hz, 1 H), 4.25 (d, J = 6.8 Hz, 1 H), 4.33 (d, J = 5.4 Hz, 1 H), 5.87 (d, J = 9.5 Hz, 1 H), 5.98 (dd, J = 5.4, 9.5 Hz, 1 H), 6.6–6.8 (m, 2 H), 7.0–7.4 (m, 6 H); IR (CCl_4) 2940, 1728, 1428, 1220, 1198, 698 cm^{-1}; MS *m/z* 348 (M^+, 2), 289 ($M^+ - CO_2Me$, 24), 257 (18), 229 (42), 167 (34), 153 (28), 152 (33), 59 (100); HRMS *m/z* 348.1368 (M^+, calcd for $C_{22}H_{20}O_4$ 348.1360). Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79. Found: C, 75.72; H, 5.83. Data for (±)-(2*R*,2a*S*,5*R*)-dimethyl 2-phenyl-1,2,2a,5-tetrahydroacenaphthylene-2a,5-dicarboxylate (**13d**): ^{1}H NMR ($CDCl_3$) δ 3.10 (dd, J = 6.8, 14.7 Hz, 1 H), 3.31 (s, 3 H), 3.75 (dd, J = 6.8, 12.0 Hz, 1 H), 3.94 (dd, J = 12.0, 14.7 Hz, 1 H), 3.84 (s, 3 H), 4.29 (dd, J = 1.5, 2.9 Hz, 1 H), 6.18 (dd, J = 1.5, 9.5 Hz, 1 H), 6.47 (dd, J = 2.9, 9.5 Hz, 1 H), 7.0–7.4 (m, 8 H); IR (CCl_4) 2940, 1735, 1428, 1215, 1198, 695 cm^{-1}; MS *m/z* 348 (M^+, 2), 289 ($M^+ - CO_2Me$, 18), 257 (25), 229 (37), 228 (20), 167 (28), 153 (24), 152 (28), 59 (100); HRMS *m/z* 348.1368 (M^+, calcd for $C_{22}H_{20}O_4$ 348.1360).

Isomerization from 3 to 4 Induced by Irradiation of 1 in the Presence and in the Absence of 10a. An N_2-purged solution of **1** (4 mM), **3** (4 mM), and **10a** (800 mM) and an N_2-purged solution of **1** (4 mM) and **3** (4 mM) were irradiated at the same time for 2 h. The ^{1}H NMR measurements and HPLC analyses of the reaction mixtures indicated that 12% and about 1% of **3** isomerized to **4** in the presence and in the absence of **10a**, respectively. The conversion of **1** in the presence and in the absence of **10a** were 39% and nearly 0%, respectively. In the presence of **10a**, adducts **11a** (7.4%) and **12a** (2.7%) were also detected.

Fluorescence Quenching and Fluorescence Lifetime Measurement. For each quenching experiment five samples were prepared in 10-mL volumetric flasks, each containing 1.0×10^{-4} M **1** and appropriate concentrations of alkene in solvent. Fluorescence intensity at 406, 394, and 407 nm was measured for each sample at excitation wavelengths of 322, 338, and 317 nm in benzene, ether, and acetonitrile, respectively. A weak exciplex emission was observed only in a case of the fluorescence quenching by **10c** in ether. Stern–Volmer plots were linear, and the slopes are shown in Table II. Fluorescence lifetimes were measured on air-saturated solutions containing 1.0×10^{-4} M **1**.

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