32. Regiochemical Trends in Intramolecular [2 + 2] Photocycloadditions of 6-(Prop-2-enyl)cyclohex-2-enones and 5-(Prop-2-enyl)cyclopent-2-enones

by **Giuliano Cruciani** and **Paul Margaretha***

Institut für Organische Chemie, Universität, D-2000 Hamburg 13

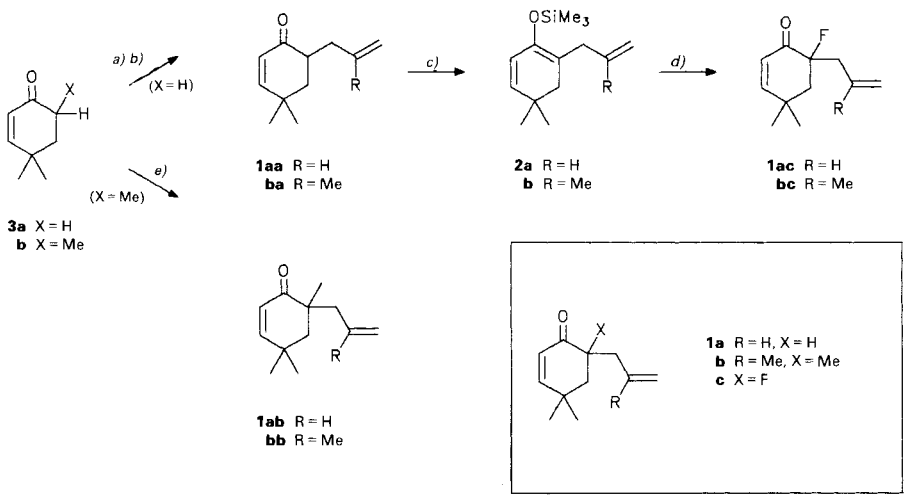
Dedicated to Prof. *H. F. Mark*, Brooklyn,
in admiration and reverence on the occasion of his 95th birthday

(12. XII. 89)

The effect of substituents (X = H, Me, or F at C(6), R = H or Me at C(2′) of the allyl side chain) on the photoisomerization (λ = 350 nm) of 6-allylcyclohex-2-enones **1** in MeCN is studied. Substituents X control the overall efficiency of intramolecular [2 + 2] photocycloadduct formation (Φ: Me > F > H) but do not exercise an influence on the orientation of addition of the exocyclic double bond to the enone C=C bond. In contrast, replacement of the prop-2-enyl (R = H) by a 2-methylprop-2-enyl (R = Me) side chain causes a change in the tricyclo[3.3.1.$0^{2,7}$]nonan-6-one **4** *vs.* tricyclo[4.2.1.$0^{3,8}$]nonan-7-one (**5**) product ratio from 100:0 (R = H) to roughly 2:1 (R = Me) but has almost no bearing on the relative rates of conversion of **1** to products. For C(6)-unsubstituted enones **1aa** and **1ba** (X = H), the efficiency of cyclization becomes low enough so that lumiketone rearrangement to bicyclohexanones **6** and 3-isopropylcyclopent-2-enones **9** becomes competitive. Enones **9** undergo consecutive intramolecular [2 + 2] photocycloaddition to tricyclo[3.2.1.$0^{3,6}$]octan-2-ones **7** and to tricyclo[3.2.1.$0^{3,6}$]octan-7-ones **8**, compounds **8** only being formed when R = Me.

Introduction. – Applications of intramolecular enone/olefin photocycloadditions in organic synthesis have been the subject of three recent reviews [1] [2]. As stated by one of the authors [1], there is still much that is not well understood about the mechanistic aspects of this important reaction. For cyclic enones bearing a side chain with an additional C=C bond at either C(2) or C(3), the regiochemistry seems to be controlled by the number of C-atoms in the chain connecting the two C=C bonds. Similarly, *Agosta* and coworkers showed in their studies devoted to the regiochemical control of intramolecular photochemical reactions of carbonyl-substituted hexa-1,5-dienes and hepta-1,6-dienes [3–6] that in such molecules two-atom bridges usually lead to crossed adducts while bridges with three atoms generally produce straight adducts. The empirical so-called 'rule of five' stating that the regioisomer formed *via* a five-membered cyclic biradical is always formed preferentially has been partially overemphasized in explaining these results [7], *inter alia* as it does not take into consideration the formation of an exciplex between the excited enone moiety and the additional double bond *prior* to biradical formation. Exciplexes have been shown to be the primary intermediates in both inter- [8] [9] and intramolecular [10] enone/olefin photocycloadditions. In a study on carbonyl-substituted hepta-1,6-dienes, *Agosta* and coworkers [5] discussed the possibility of initial 1,7-bonding and also mentioned that the regiochemical behaviour of substrates related to 5-allylcyclopent-2-enones and 6-allylcyclohex-2-enones had proven complicated.

Scheme 1

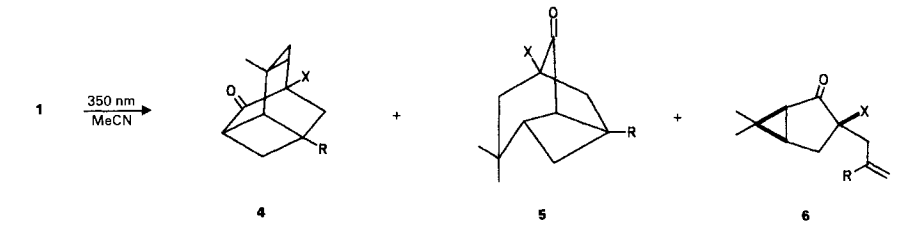


a) $C_6H_{11}NH_2$ ($-H_2O$). *b)* EtMgBr, CH_2=$CHCH_2Br$ or CH_2=$C(CH_3)CH_2Cl$, H^+. *c)* LDA, Me_3SiCl. *d)* *N*-Fluoropyridinium triflate [14]. *e)* LDA, CH_2=$CHCH_2Br$ or CH_2=$C(CH_3)CH_2Cl$.

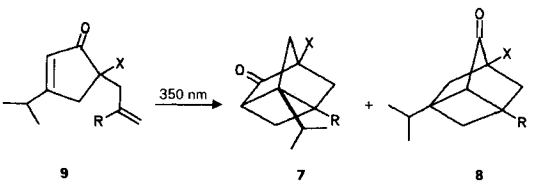
Indeed, some years ago, we had reported [11] preliminary results on the photoisomerization of a 6-allyl- and a 6-(2-methylprop-2-enyl)cyclohex-2-enone, and we had suggested that the product ratio was affected by steric interaction due to this additional Me group at C(2′) of this side chain. In other studies on substituent effects in enone photocycloadditions, we had observed [12] [13] that 2,3-dimethylbut-2-ene adds to excited 6-fluorocyclohex-2-enones or 5-fluorocyclopent-2-enones, affording oxetans instead of cyclobutanes. At that time, it was not possible for synthetic reasons to combine such studies in search of the effect of an F-substituent at C(α′) of the enone on *intramolecular* photocycloadditions. The very recent emergence of *N*-fluoropyridinium salts [14] [15] as very simple and selective reagents for the preparation of α-fluorocarbonyl compounds from the corresponding silyl-enol precursors allowed us to synthesize the 6-fluoro-6-(prop-2-enyl)cyclohex-2-enones **1ac** and **1bc** from dienones **1aa** and **1ba** *via* the (cyclohexadienyloxy)silanes **2a** and **2b**, respectively. We now report comparative results on the photochemical behaviour of six 6-allylcyclohex-2-enones **1**, easily available from either 4,4-di- or 4,4,6-trimethylcyclohex-2-enone (**3a** and **3b**, resp.) *(Scheme 1)*.

Results. – The (GC-analytical) product distribution for the preparative irradiations (λ = 350 nm) of **1** (10^{-1} M in MeCN) as well as the quantum yields (Φ) of conversion of **1** are given in *Scheme 2*. Both the 6-methyl- and the 6-fluoro-6-(prop-2-enyl)cyclohex-2-enones **1ab** and **1ac** provide tricyclo[3.3.1.$0^{2,7}$]nonan-6-ones **4** selectively, while the corresponding 6-(2-methylprop-2-enyl)enones **1bb** and **1bc** give mixtures of **4** and tricyclo[4.2.1.$0^{3,8}$]nonan-7-ones **5**. No oxetan formation is observed, neither from fluoroenone **1ac** nor **1bc**, not even in unpolar solvents as benzene or cyclohexane. The parent dienones **1aa** and **1ba** afford more complex product mixtures: besides tricyclononanones

Scheme 2



	1		Products					ϕ_{-1}
	R	X	4	5	6	7	8	
aa	H	H	57	–	29	14	–	0.037
ab	H	Me	100	–	–	–	–	0.260
ac	H	F	100	–	–	–	–	0.073
ba	Me	H	16	4	35	19	26	0.027
bb	Me	Me	80	20	–	–	–	0.247
bc	Me	F	57	43	–	–	–	0.046



4 and **5**, bicyclo[3.1.0]hexan-2-ones **6** and the isomeric tricyclo[3.2.1.$0^{3,6}$]octanones **7** and **8** are also formed. The most probable precursors of tricyclooctanones **7** and **8**, 3-isopropylcyclopent-2-enones **9**, could not be detected (GC) in relative amounts > 5% during irradiations. The spectroscopic data of compounds **1**–**8** is summarized in *Tables 1–3*.

Discussion. – The results described clearly demonstrate the complexity of the intramolecular [2 + 2] photocycloaddition of enones as **1** that are constrained structurally and can be considered to be either 3-oxohepta-1,6-dienes or 1-acylocta-1,7-dienes. The following facts are worth mentioning: *a*) The Me group at C(2′) of the allyl side chain influences the product ratio **4**/**5** but has almost no bearing on the overall efficiency of conversion of **1** to cycloadducts. *b*) The substituents X at C(6) of **1** seem to control the overall efficiency of photocycloadduct formation but not to exercise an influence on the orientation of the addition. *c*) In contrast to the efficient *intermolecular* oxetan formation between 6-fluorocyclohex-2-enones and 2,3-dimethylbut-2-ene, no such *intramolecular* reaction is observed for the 6-allyl-6-fluorocyclohex-2-enones **1ac** and **1bc**.

Regarding the first point, we had already reported [11] that in C_6H_{12}, **1ab** affords tricyclo[3.3.1.$0^{2,7}$]nonan-6-one **4ab** selectively, while **1bb** gives a mixture of **4bb** and **5bb**. In addition, *Martin* [16] has shown that O-linked substituents at C(1′) of the allyl side chain in molecules similar to **1** do not affect the regiochemistry of the intramolecular cycloaddition, *i.e.* tricyclo[3.3.1.$0^{2,7}$]nonan-6-ones are again formed selectively. We had tried to explain [11] the influence of R at C(2′) of the allyl side chain on the ratio **4**/**5** by arguing that there might be a steric interaction between R and the Me groups at C(4) of **1** favouring the formation of **5**. With more detailed data available on both inter- and intramolecular photocycloadditions [9] [10], it now seems more appropriate to correlate the product ratio **4**/**5** with the influence of R (H, Me) on the intermediates, *i.e.* the

Table 1. *Spectroscopic Data of Cyclohexenones* **1**

	1aa	**1ab**	**1ac**	**1ba**	**1bb**	**1bc**
IR [cm^{-1}]	1681	1678	1692	1684	1679	1691
UV [nm]	324 (20)	334 (58)	337 (75)	332 (25)	336 (55)	336 (47)
MS [*m/z*] (%)	164 (19), 96 (100)	178 (10), 96 (100)	182 (2), 96 (100)	178 (48), 96 (100)	192 (20), 96 (100)	196 (4), 96 (100)
^{19}F-NMR [ppm]			− 151.5			− 149.4
^{13}C-NMR [ppm] (*J*(C,F) [Hz])						
C(1)	200.3	203,5	192.8 (J = 18.8)	200.8	203.4	192.7 (J = 18.8)
C(2)	126.5	125.4	124.5	126.6	125.3	124.4
C(3)	158.7	157.4	160.1	158.7	157.2	160.1
C(4)	33.3	33.3	33.7 (J = 2.5)	33.5	32.9	33.6 (J = 2.0)
C(5)	41.5	45.6	43.9 (J = 18.8)	41.4	45.8	43.7 (J = 21.2)
C(6)	42.0	43.8	92.8 (J = 176.0)	40.2	43.8	93.3 (J = 176.0)
C(1′)	33.5	43.4	39.6 (J = 23.9)	37.2	47.2	42.6 (J = 22.6)
C(2′)	136.1	133.8	131.3 (J = 6.3)	143.1	142.5	140.3 (J = 2.5)
C(3′)	116.5	118.1	119.7	112.1	114.8	116.0
CH_3	30.5, 25.3	31.0, 30.1, 25.0	29.9 (J = 6.3), 29.7 (J = 3.6)	30.5, 25.1, 21.9	31.9, 29.5, 26.8, 24.3	30.3 (J = 0.9), 29.5 (J = 3.7), 23.9 (J = 3.2)
^{1}H-NMR [ppm] (*J*(H,F) [Hz])						
H−C(2)	5.80[a])	5.75[a])	5.80[a])	5.84[b])	5.75[b])	5.96 (J = 0.8)[b])
H−C(3)	6.00	6.04	6.08	6.60	6.49	6.72
H_a−C(5)	1.50	1.63	1.50 (J = 39.8)	1.50	1.85	1.83 (J = 36.2)
H_e−C(5)	1.30	1.35	1.90 (J = 12.6)	1.85	1.56	2.22 (J = 14.0)
H−C(6)	2.75	–	–	2.60	–	–
2 H−C(1′)	2.20, 2.10	2.31, 2.21	2.80 (J = 12.6), 2.46 (J = 26.4)	2.84, 1.90	2.48, 2.13	2.75 (J = 15.0), 2.41 (J = 30.8)
H−C(2′)	5.70	5.70	5.77	–	–	–
2 H−C(3′)	5.05	4.97	5.00	4.74	4.66	4.82
CH_3	0.75, 0.71	1.08, 0.90, 0.88	0.96, 0.68	1.70, 1.16, 1.12	1.60, 1.15, 1.11, 1.10	1.78, 1.26, 1.16

$J(5,5)$ = 12.0–15.2, $J(1',1')$ = 12.4–14.9
$J(2,3)$ = 8.8–10.2, $J(5a,6)$ = 12.0–13.5, $J(5e,6)$ = 4.0–4.5, $J(6,1')$ = 4.0–8.8
$J(3,5e)$ = 0.8–2.5

[a]) In C_6D_6.
[b]) In $CDCl_3$.

Table 2. *Spectroscopic Data of Tricyclononanones* **4** *and* **5**

	4aa	**4ab**	**4ac**	**4ba**	**4bb**	**4bc**
IR [cm^{-1}]	1724	1718	1741	1723	1719	1745
MS [*m/z*] (%)	164 (41), 107 (100)	178 (16), 121 (100)	182 (35), 125 (100)	178 (45), 123 (100)	192 (30), 137 (100)	196 (35), 96 (100)
^{19}F-NMR [ppm]			− 166.3			− 166.9
^{13}C-NMR [ppm] (*J*(C,F) [Hz])						
C(1)	33.1	33.4	34.3 (*J* = 7.8)		40.3	42.2 (*J* = 7.5)
C(2)	51.2	51.1	50.2 (*J* = 3.1)		57.0	56.1 (*J* = 3.1)
C(3)	29.5	30.1	33.5 (*J* = 8.4)		31.0	34.2 (*J* = 8.3)
C(4)	45.3	53.0	48.6 (*J* = 17.0)		53.2	48.7 (*J* = 17.0)
C(5)	44.7	45.2	95.0 (*J* = 205.0)		45.0	95.7 (*J* = 205.0)
C(6)	215.3	218.8	210.0 (*J* = 13.9)		219.0	210.1 (*J* = 15.0)
C(7)	49.7	49.3	49.8 (*J* = 1.5)		46.5	46.8 (*J* = 1.8)
C(8)	31.2	34.5	34.1		40.3	39.9
C(9)	34.2	38.5	36.6 (*J* = 17.6)		45.5	43.2 (*J* = 16.6)
CH_3	29.5, 29.5	29.4, 29.4, 20.7	29.3, 29.0		30.2, 30.0, 26.7, 20.5	30.0, 29.7, 26.3
^{1}H-NMR [ppm] (*J*(H,F) [Hz])						
H–C(1)	2.70[a])	2.70[a])	2.88 (*J* = 4.5)[a])	– [b])	– [a])	– [b])
H–C(2)	2.38	2.34	2.30	1.80	1.97	1.75
$H_{'endo'}$–C(4)	1.75	1.52	1.92 (*J* = 4.8)	1.66	1.48	2.08
$H_{'exo'}$–C(4)	1.82	1.58	1.96 (*J* = 5.2)	1.66	1.56	2.08
H–C(5)	2.50	–	–	2.44	–	–
H–C(7)	2.88	2.85	3.05 (*J* = 4.2)	2.78	2.85	2.94 (*J* = 6.8)
$H_{'endo'}$–C(8)	1.55	1.43	1.59	1.49	1.53	1.54
$H_{'exo'}$–C(8)	2.42	2.40	2.50 (*J* = 2.2)	1.89	2.03	1.95 (*J* = 2.0)
$H_{'endo'}$–C(9)	1.95	1.61	2.08 (*J* = 9.5)	1.78	1.65	1.88
$H_{'exo'}$–C(9)	2.05	2.01	2.45	1.55	1.75	1.88
CH_3	1.02, 0.85	1.04, 1.02, 0.85	1.09, 0.82	1.10, 0.90, 0.72	1.22, 1.04, 1.00, 0.84	1.14, 0.93, 0.74

J(4,4) = 10.4–14.0, *J*(8,8) = 8.2–9.6, *J*(9,9) = 10.4–14.0

J(1,2) = 4.4–5.6, *J*(1,8 *'exo'*) = 4.5–5.6, *J*(1,9 *'exo'*) = 4.5–5.6, *J*(2,7) = 4.2–5.6, *J*(4 *'endo'*, 5) = 2.2, *J*(4 *'exo'*, 5) = 2.2, *J*(5,9 *'endo'*) = 4.0, *J*(7,8 *'exo'*) = 5.2–7.0

J(1,7) = 4.2–5,6, *J*(8 *'exo'*, 9 *'exo'*) = 2.2–3.2, *J*(4 *'endo'*, 9 *'endo'*) = 2.2–2.4

Table 2 (cont.)

	5bb	**5bc**
IR [cm^{-1}]	1735	1758
MS [*m/z*] (%)	192 (53), 96 (100)	196 (14), 96 (100)
^{19}F-NMR [ppm]	–	–163.98
^{13}C-NMR		
[ppm] (*J*(C,F) [Hz])		
C(1)	34.9	34.1 (*J* = 10.0)
C(2)	35.1	34.7
C(3)	44.8	44.2
C(4)	31.6	32.3 (*J* = 8.2)
C(5)	53.4	48.4 (*J* = 19.0)
C(6)	46.5	96.5 (*J* = 207.0)
C(7)	223.0	216.0 (*J* = 15.0)
C(8)	50.6	48.2 (*J* = 1.8)
C(9)	55.0	51.5 (*J* = 20.8)
CH_3	28.7, 28.0, 27.0, 21.3	28.5, 27.9, 26.9

	5bb	**5bc**
^{1}H-NMR		
[ppm] (*J*(H,F)) [Hz]	[c])	[b])
$H_{'endo'}$–C(2)	1.68	1.86
$H_{'exo'}$–C(2)	1.93	2.25–2.10
H–C(3)	2.03	2.25–2.10
H_a–C(5)	1.49	2.25–2.10
H_e–C(5)	1.84	2.53
H–C(8)	2.34	2.55 (*J* = 4.0)
$H_{'endo'}$–C(9)	1.44	2.05
$H_{'exo'}$–C(9)	1.28	1.97 (*J* = 2.6)
CH_3	1.06, 0.87, 0.85, 0.66	0.98, 0.88, 0.80
J(2,2) = 11.4, *J*(5,5) = 13.6, *J*(9,9) = 12.0		
J(2 *'endo'*, 3) = 2.0, *J*(2 *'exo'*, 3) = 9.6, *J*(3,8) = 8.2		
J(2 *'exo'*, 9 *'exo'*) = 1.8, *J*(3, 5a) = 2.0, *J*(5a, 9 *'exo'*) = 1.8		

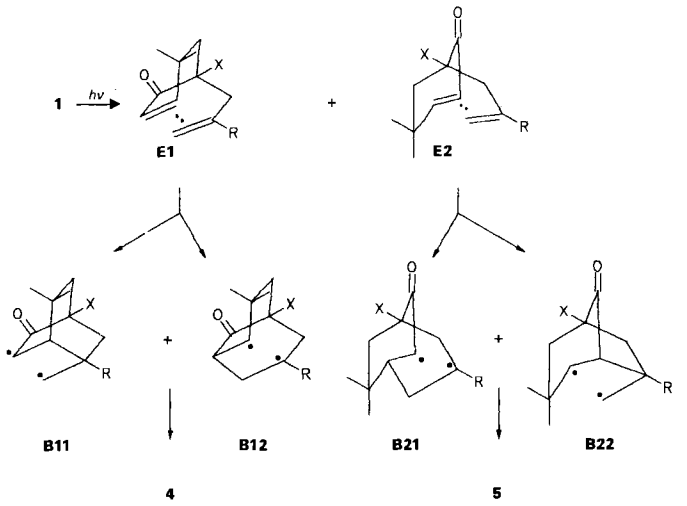
[a]) In $CDCl_3$.
[b]) In C_5D_5N.
[c]) In C_6D_6.

Table 3. *Spectroscopic Data of Photoproducts* **6–8**

	6aa	**6ba**		**7aa**	**7ba**	**8ba**
IR [cm^{-1}]	1722	1719		1746	1744	1758
MS [*m/z*] (%)	164 (6), 82 (100)	178 (18), 96 (100)		164 (100)	178 (100)	178 (8), 107 (100)
^{1}H-NMR [ppm]	[a])	[a])		[a])	[a])	[a])
H–C(1)	1.50	1.53	H–C(1)	2.60	2.47	2.14
H–C(3)	2.14	2.28	$H_{'endo'}$–C(2)	–	–	1.20
H_a–C(4)	1.95	2.02	$H_{'exo'}$–C(2)	–	–	1.60
H_e–C(4)	1.10	1.30	H–C(3)	2.12	2.07	–
H–C(5)	1.20	1.30	$H_{'endo'}$–C(4)	1.32	1.47	1.45
2 H–C(1′)	2.65, 1.81	2.60, 1.78	$H_{'exo'}$–C(4)	2.18	1.90	1.75
H–C(2′)	5.63	–	H–C(5)	1.88	–	–
H–C(3′)	4.90	4.65	H–C(6)	–	–	1.68
CH_3	0.78, 0.72	1.52, 0.79, 0.76	$H_{'endo'}$–C(7)	1.18	1.23	–
			$H_{'exo'}$–C(7)	1.00	1.16	–
			$H_{'endo'}$–C(8)	1.58	1.66	1.40
			$H_{'exo'}$–C(8)	1.47	1.35	1.48
			CH_3	0.70 (*d*), 0.66 (*d*)	0.81 (*s*), 0.72 (*d*), 0.68 (*d*)	0.82 (*s*), 0.60 (*d*, 6H)
J(4,4) = 13.0, *J*(1′,1′) = 14.4				*J*(4,4) = 10.0, *J*(7,7) = 10.8, *J*(8,8) = 11.2		*J*(2,2) = 11.6, *J*(4,4) = 9.0, *J*(8,8) = 11.6
J(1,5) = 6.0, *J*(3,4a) = 13.0, *J*(3,4e) = 6.9, *J*(3,1′) = 1.2 and 6.5, *J*(4a,5) = 7.0, *J*(4e,5) = 1.6				*J*(1,7 *'endo'*) = 1.2, *J*(1,8 *'endo'*) = 1.2, *J*(1,3 *'exo'*) = 3.1, *J*(3,4 *'exo'*) = 8.0, *J*(4 *'exo'*,5) = 6.4, *J*(5,3 *'exo'*) = 6.4		*J*(1,2 *'exo'*) = 3.0, *J*(1,3 *'exo'*) = 3.0
				J(1,3) = 0.8, *J*(3,5) = 5.6, *J*(7 *'endo'*,3 *'endo'*) = 1.2		*J*(2 *'exo'*,4 *'exo'*) = 2.0, *J*(2 *'exo'*,3 *'exo'*) = 2.0, *J*(4 *'exo'*,3 *'exo'*) = 2.0

[a]) In C_6D_6.

Scheme 3



exciplexes **E1** and **E2** and the four possible biradicals **B11**, **B12**, **B21**, and **B22**, which either lead to products or revert back to **1** *(Scheme 3)*.

Inspection of these intermediates reveals that substituting R = H by R = Me should favour **E1** over **E2** (**E1** corresponds to the preferred orientation in the intermolecular cycloaddition of enones to terminal alkenes, *e.g.* 2-methylpropene or 1,1-dimethoxyethylene [8] [9]). The result that products **5** are only formed when R = alkyl and not when R = H thus clearly indicates that the orientation in the exciplex is only of minor importance in such intramolecular reactions. On the other hand, substitution of R = H by R = Me will stabilize biradicals **B12** and **B21** and have no effect on the stability of **B11** or **B22**. Assuming [9] that the more stable biradicals will react to products more efficiently thus suggests that compounds **4** are preferentially formed *via* biradical **B11** and isomers **5** *via* biradical **B21**, which in turn result from primary 2,7- and 1,7-bonding in the excited 1,7-octadienes **1**, respectively. An analogous analysis can be applied to the selective formation of **7aa** from **9aa** (R = H) *vs.* the joint formation of **7ba** and **8ba** from **9ba** (R = Me). Such a trend, *i.e.* selective formation of tricyclo[3.2.1.$0^{3,6}$]octan-2-ones from 5-(prop-2-enyl)cyclopent-2-enones [17–19] *vs.* formation of mixtures of such compounds and the isomeric tricyclooctan-7-ones from cyclopent-2-enones bearing alkyl groups at C(2′) of the allyl side chain at C(5) [17] [20–22] has its precedents in the literature, but has usually not been discussed further.

Regarding the second point, *i.e.* the influence of substituent X at C(6) on the quantum yields *(Scheme 2)*, it is reasonable to assume that for X = Me (compounds **1ab** and **1bb**), cycloadduct formation proceeds with standard efficiency, while for X = F and X = H, the overall efficiency drops to *ca.* ¼ and $\frac{1}{10}$, respectively. This then leads to the search for possible deactivation paths for compounds **1** bearing either an H- or an F-atom at C(6). For **1aa** and **1ba** (X = H), we searched for tautomerization to a cyclohexadienol *via* intra- or intermolecular H-transfer to the carbonyl O-atom of excited **1** and sequential re-tautomerisation to ground state **1** as a possible deactivation path in monitoring the photoly-

sis of **1aa** in CD_3OD by MS and measuring the intensity ratio of the $[M + 1]^+/M^+$ peaks of **1aa** up to 50% conversion of starting material. The fact that the ratio remained unchanged ($= 0.117 \pm 0.002$) suggests that this sequence does *not* occur. Irrespective of the reason of the much lower efficiency of cycloadduct formation for compounds **1** with X = H, it allows lumiketone rearrangement, another rather inefficient ($\Phi \approx 0.015$) photoreaction of 4,4-dialkylcyclohex-2-enones [23], to become competitive. The efficiency of intramolecular photocycloaddition of cyclopent-2-enones **9** must be much higher than that for the corresponding cyclohex-2-enones **1**, as a buildup of compounds **9** during the irradiations was never observed.

Finally, the lower efficiency of compounds **1ac** and **1bc** (X = F) in undergoing cycloaddition as compared to enones **1** with X = Me could be related to the third point, *i.e.* to the fact that no oxetan formation is observed for these α′-fluorocyclohex-2-enones. As already proposed for a corresponding α′-chloro compound [24], energy dissipation could be caused by relative high rates of reversion of either the exciplex or the biradical on the oxetan-forming reaction path. Obviously, further evidence is needed to strengthen or to disprove this hypothesis and, especially, to explain the quantitative reversion of these latter intermediates in the intramolecular reactions studied.

We are grateful to Dr. *T. Umemoto, Sagami Research Center,* for a very generous gift of *N*-fluoropyridinium triflate, to Dr. *V. Sinnwell,* Hamburg, for measuring the $^1H,^1H$-COSY NMR spectra and to the *Fonds der Chemischen Industrie* and *Deutsche Forschungsgemeinschaft* for financial support of this work.

Experimental Part

General. Qual. GC: 30-m *SE 30* capillary column. UV spectra (MeCN): in nm (ε). IR spectra (film): in cm^{-1}. $^1H,^1H$-COSY NMR: at 400 MHz. ^{13}C-NMR spectra ($CDCl_3$): at 100.63 MHz. ^{19}F-NMR spectra ($CDCl_3$): at 75.4 MHz, chemical shifts in ppm rel. to CCl_3F. MS: at 70 eV.

Photolyses. Rayonet RPR 100 photoreactor equipped with 350-nm lamps using an additional liquid filter with cut-off at $\lambda < 340$ nm and a 'merry-go-round' setup.

Starting Materials. Cyclohexenones **3a** [25], **3b** [26], and **1aa** [24] were synthesized according to literature.

4,4-Dimethyl-6-(2-methylprop-2-enyl)cyclohex-2-enone (**1ba**) was synthesized in analogy to **1aa** [24] [27] from **3a** and 3-chloro-2-methylpropene in 48% yield. B.p. 57°/0.4 Torr.

6-(Prop-2-enyl)- and 6-(2-Methylprop-2-enyl)-4,4,6-trimethylcyclohex-2-enones (**1ab** and **1bb**, resp.). Deprotonation of **3b** with lithium diisopropylamide (LDA) in THF at −78° and subsequent alkylation with either 3-bromopropene or 3-chloro-2-methylpropene affords the C(6)-methylated enones in slightly better yields (85 and 79%, resp.) than using hexamethyldisilazane sodium salt in toluene [11].

{[4,4-Dimethyl-2-(prop-2-enyl)cyclohexa-1,5-dien-1-yl]oxy}trimethylsilane (**2a**). From **1aa**, LDA, and Me_3SiCl according to [28]; **2a** was used without further purification. ^1H-NMR (C_6D_6): 5.79 (*m*, 1H); 5.72, 5.37 (*AB*, $J = 10.0$); 5.05 (*m*, 2H); 2.95 (*d*, $J = 6.8$, 2H); 1.92 (*s*, 2H); 0.84 (*s*, 6H); 0.08 (*s*, 9H). MS: 236 (3, M^+), 73 (100).

{[4,4-Dimethyl-2-(2-methylprop-2-enyl)cyclohexa-1,5-dien-1-yl]oxy}trimethylsilane (**2b**). As described above from **1ba**. ^1H-NMR ($CDCl_3$): 5.53, 5.48 (*AB*, $J = 9.0$); 4.70 (*m*, 2H); 2.78 (*s*, 2H); 1.97 (*s*, 2H); 1.66 (*s*, 3H); 0.98 (*s*, 6H); 0.15 (*s*, 9H). MS: 250 (2, M^+), 73 (100).

4,4-Dimethyl-6-fluoro-6-(prop-2-enyl)cyclohex-2-enone (**1ac**). From **2a** and *N*-fluoropyridinium triflate in CH_2Cl_2 according to [14] in 87% yield. B.p. 48–50°/0.4 Torr.

6-Fluoro-4,4-dimethyl-6-(2-methylprop-2-enyl)cyclohex-2-enone (**1bc**). As described above from **2b** in 87% yield. B.p. 55–58°/0.4 Torr.

Preparative Irradiations. Ar-degassed solns. of **1** (2 mmol) in MeCN (20 ml) were irradiated for 72–96 h up to total conversion (GC) of starting material. The soln. was then evaporated and the residue chromatographed on SiO_2.

Irradiation of **1aa**. CH_2Cl_2 as eluent afforded *3,3-dimethyltricyclo[3.3.1.0^{2,7}]nonan-6-one* (**4aa**; 98 mg, 30%), *6-isopropyltricyclo[3.2.1.0^{3,6}]octan-2-one* (**7aa**; 24 mg, 7%), and *6,6-dimethyl-3-(prop-2-enyl)bicyclo[3.1.0]-hexan-2-one* (**6aa**; 50 mg, 15%), all colourless oils.

Irradiation of **1ab**. C_6H_6 as eluent afforded *3,3,5-trimethyltricyclo[3.3.1.0^{2,7}]nonan-6-one* (**4ab**; 303 mg, 85%) as colourless oil.

Irradiation of **1ac**. C_6H_6 as eluent afforded *5-fluoro-3,3-dimethyltricyclo[3.3.1.0^{2,7}]nonan-6-one* (**4ac**; 305 mg, 84%) as colourless oil.

Irradiation of **1ba**. C_6H_6/AcOEt 9:1 afforded *1,3,3-trimethyltricyclo[3.3.1.0^{2,7}]nonan-6-one* (**4ba**; 32 mg, 9%), a 2:1 mixture of *6,6-dimethyl-3-(2-methylprop-2-enyl)bicyclo[3.1.0]hexan-2-one* and *6-isopropyl-5-methyltricyclo-[3.2.1.0^{3,6}]octan-2-one* (**6ba** and **7ba**, resp.; 107 mg, 30%), and *3-isopropyl-5-methyltricyclo[3.2.1.0^{3,6}]octan-7-one* (**8ba**; 54 mg, 15%), all colourless oils.

Irradiation of **1bb**. C_6H_6 as eluent afforded *1,3,3,5-tetramethyltricyclo[3.3.1.0^{2,7}]nonan-6-one* (**4bb**; 230 mg, 60%) and *1,4,4,6-tetramethyltricyclo[4.2.1.0^{3,8}]nonan-7-one* (**5bb**; 46 mg, 12%) as colourless oils.

Irradiation of **1bc**. C_6H_6/AcOEt 9:1 afforded *5-fluoro-1,3,3-trimethyltricyclo[3.3.1.0^{2,7}]nonan-6-one* (**4bc**; 118 mg, 30%) and *6-fluoro-1,4,4-trimethyltricyclo[4.2.1.0^{3,8}]nonan-7-one* (**5bc**; 101 mg, 26%) as colourless oils.

Irradiation of **1aa** *in CD_3OD*. Starting material was monitored by GC/MS up to *ca.* 50% conversion to products. The intensity ratios of *m/z* 165/164 ($[M + 1]^+/M^+$) and *m/z* 150/149 ($[M + 1 - Me]^+/[M - Me]^+$) remained constant during this experiment indicating that there was no D-incorporation.

Actinometry. Solns. of **1** (0.1 mmol in 1 ml of MeCN) containing tetradecane as internal standard were irradiated using the 'merry-go-round' setup. The degree of conversion (5–10%) was monitored by GC. A C_6H_{12} soln. of **1ab** was used as chemical actinometer [11].

REFERENCES

[1] M. T. Crimmins, *Chem. Rev.* **1988,** *88,* 1453.
[2] D. Becker, N. Haddad, in 'Organic Photochemistry', Ed. A. Padwa, M. Dekker, New York, 1989, Vol. 10, p. 1; J. Cossy, P. A. Carrupt, P. Vogel, in 'The Chemistry of Double-Bonded Functional Groups', Ed. S. Patai, J. Wiley, New York, 1989, p. 1368.
[3] S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **1983,** *105,* 1292.
[4] S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **1983,** *105,* 1299.
[5] A. R. Matlin, C. F. George, S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **1986,** *108,* 3385.
[6] C. Schröder, S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **1987,** *109,* 5491.
[7] W. Oppolzer, *Acc. Chem. Res.* **1982,** *15,* 135.
[8] P. de Mayo, *Acc. Chem. Res.* **1971,** *4,* 41.
[9] J. Patjens, P. Margaretha, *Helv. Chim. Acta* **1989,** *72,* 1817.
[10] E. Fischer, R. Gleiter, *Angew. Chem.* **1989,** *101,* 925.
[11] W. Fröstl, P. Margaretha, *Helv. Chim. Acta* **1976,** *59,* 2244.
[12] G. VoThi, P. Margaretha, *Helv. Chim. Acta* **1976,** *59,* 2236.
[13] V. Desobry, P. Margaretha, *Helv. Chim. Acta* **1975,** *58,* 2161.
[14] T. Umemoto, K. Tomita, *Tetrahedron Lett.* **1986,** *27,* 3271.
[15] T. Umemoto, G. Tomizawa, *Bull. Chem. Soc. Jpn.* **1986,** *59,* 3625.
[16] S. F. Martin, *Tetrahedron Lett.* **1982,** *23,* 1982.
[17] A. J. Barker, M. J. Begley, M. Mellor, D. A. Otieno, G. Pattenden, *J. Chem. Soc., Perkin Trans. 1* **1983,** 1893.
[18] E. Gowda, T. B. H. McMurry, *J. Chem. Soc., Perkin Trans. 2* **1980,** 1516.
[19] E. Anklam, S. Lau, P. Margaretha, *Helv. Chim. Acta* **1985,** *68,* 1129.
[20] A. J. Parker, G. Pattenden, *J. Chem. Soc., Perkin Trans. 1* **1983,** 1901.
[21] W. Oppolzer, S. C. Burford, *Helv. Chim. Acta* **1980,** *63,* 788.
[22] P. Crabbé, G. A. Garcia, E. Velarde, *J. Chem. Soc., Chem. Commun.* **1973,** 481.
[23] D. I. Schuster, in 'The Chemistry of Enones', Ed. S. Patai, Wiley, New York, 1989, p. 623.
[24] I. Altmeyer, P. Margaretha, *Helv. Chim. Acta* **1977,** *60,* 874.
[25] M. E. Flaugh, T. A. Crowell, D. S. Farlow, *J. Org. Chem.* **1980,** *45,* 5399.
[26] C. Paris, S. Geribaldi, G. Torri, M. Azzaro, *Bull. Soc. Chim. Fr.* **1973,** 997.
[27] H. E. Zimmerman, F. X. Albrecht, M. J. Haire, *J. Am. Chem. Soc.* **1975,** *97,* 3726.
[28] P. Eilbracht, R. Jelitte, *Chem. Ber.* **1983,** *116,* 243.