

233. Photoaddition Reactions of 5-Fluoro-4,4-dimethyl-2-cyclopentenone

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Summary. The photoaddition of 5-fluoro-4,4-dimethyl-2-cyclopentenone (**4**) to 2,3-dimethyl-2-butene leads specifically (in cyclohexane) and selectively (in acetonitrile) to the formation of the oxetanes **16**. The title compound is compared in its behaviour to the analogous 6-fluoro-4,4-dimethyl-2-cyclohexenone (**1**) and both α' -fluoro-4,4-dimethyl-2-cycloalkenones in turn are compared to the corresponding 2-cycloalkenones (**6** and **3**) and 4,4-dimethyl-2-cycloalkenones (**5** and **2**). The quantum yield for the addition of these enones to 2,3-dimethyl-2-butene and to cyclopentene are discussed.

We have recently discussed the factors which influence the oxetane *vs.* cyclobutane formation ratio in photoadditions of 2-cyclohexenones to olefins [1]. These are essentially: a) the nature of the substituents of the enone in the positions *vicinal* to the C=C (C-(4) or γ -position) and C=O bonds (C-(6) or α' -position) *i.e.* their steric and inductive effects, b) the nature of the olefinic reaction partner, *i.e.* the charge density on the olefinic carbon atoms and hence the ionisation potential, and c) the nature of the solvent. In this context we had shown that an α' -fluoro substituent increases the proportion of oxetane formation. In particular we had observed a strong preference for the formation of the oxetane **7** (90%) in the addition of 6-fluoro-4,4-dimethyl-2-cyclohexenone (**1**) to 2,3-dimethyl-2-butene in a hydrocarbon solvent²⁾.

We now report results on the photoaddition of 5-fluoro-4,4-dimethyl-2-cyclopentenone (**4**) to olefins and on a comparative study of the cycloaddition of the fluoroketones **1** and **4** as well as of the corresponding non-halogenated enones **2**, **3**, **5**, and **6**. These compounds and their photoadducts are shown in *Scheme 1*.

Compound **4** was synthesized from 4,4-dimethyl-2-cyclopentenone (**5**) (*Scheme 2*) in an analogous manner as **1** from the dimethylcyclohexenone **2** [1]. A preparation of **5** has previously been described [3], employing acid catalysed dehydration of 2-hydroxy-4,4-dimethylcyclopentanone with subsequent preparative separation by gas chromatography. In order to develop a more convenient approach to **5**, 2-methylpropanal was alkylated in a two phase medium [4] followed by acid-catalysed hydrolysis of the olefinic chloride [5] (the intermediate 1,4-dicarbonyl compound cyclizes under these conditions). The low yield (13%) of **5** in this simple sequence is advantageously compensated by the obtention of the desired product in pure form from inexpensive starting materials.

¹⁾ Graduate diploma thesis, University of Geneva, 1976.

²⁾ The enhancement of regioselectivity in the cyclobutane formation by a fluorine atom in the α -position of a somewhat enone-related system (uracil) has recently been reported [2].

Scheme 1

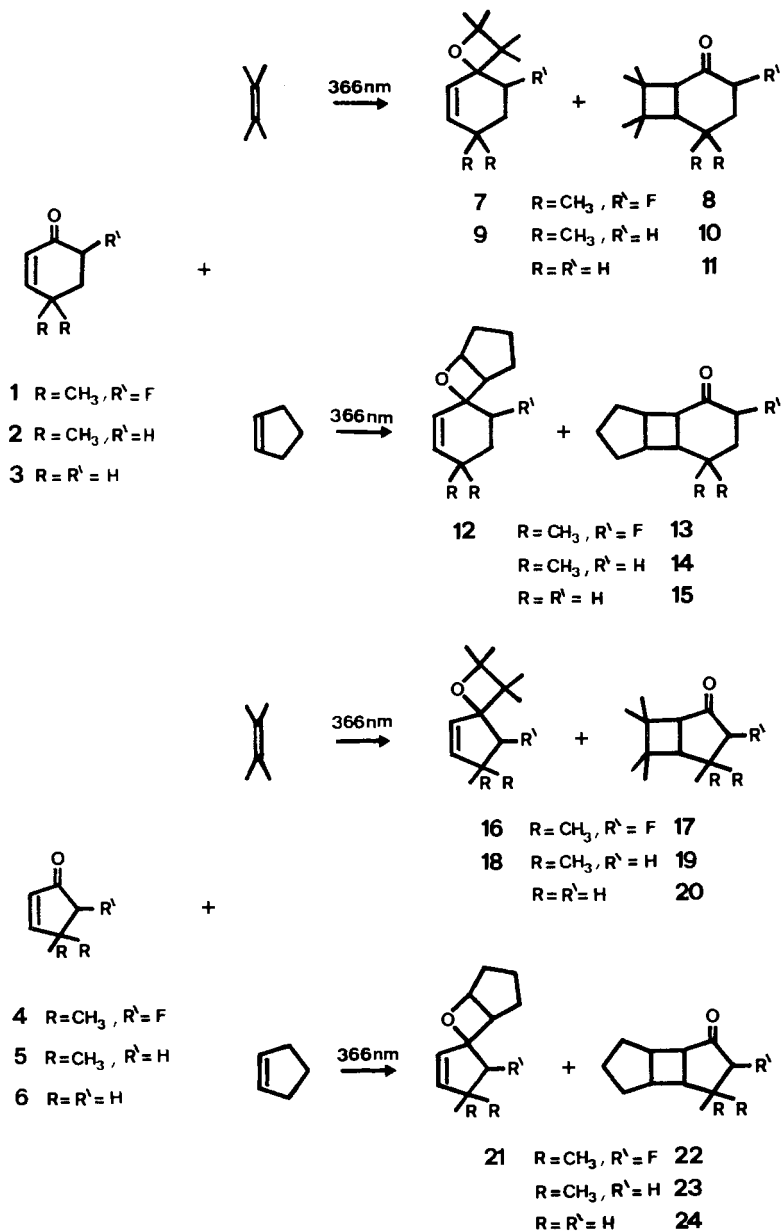
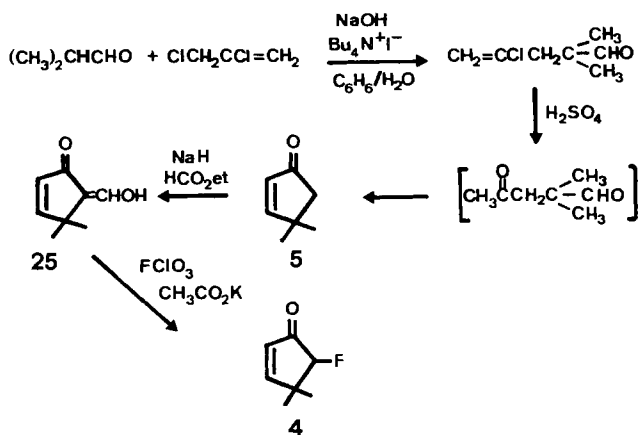


Table 1 shows that the preference for oxetane formation in the photoaddition of **4** to 2,3-dimethyl-2-butene is even more pronounced (\rightarrow **16**) than in that of **1**. It strongly predominates in acetonitrile and represents the exclusive reaction path in cyclohexane. NMR. analysis shows that in cyclohexane a 3:2 mixture of the diastereoisomeric oxetanes **16a** and **16b** is formed (the proton on C-(5) exhibits different

chemical shifts), whereas in the reaction of **1** only one diastereoisomeric oxetane **7** had been observed [1].

The structure of the photoadducts were assigned on the basis of their NMR., IR., and mass spectra (see Table 2).

Scheme 2



Scheme 3

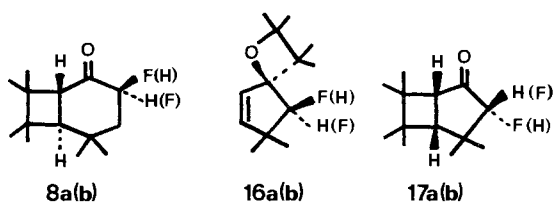


Table 1. Percentage of Adducts (Oxetanes and Cyclobutanones) in the Photoaddition of Enones to 2,3-Dimethyl-2-butene

Enone	Solvent	Adducts		Literature
		Oxetanes	Cyclobutanones	
1	<i>i</i> -C ₈ H ₁₈	90% 7	5% 8a , 5% 8b	[1]
1	CH ₃ CN	15% 7	45% 8a , 40% 8b	a)
2	<i>i</i> -C ₈ H ₁₈	52% 9	48% 10	[6]
2	CH ₃ CN	—	100% 10	[6]
3	<i>i</i> -C ₈ H ₁₈	—	100% 11	[1]
3	CH ₃ CN	—	100% 11	[1]
4	C ₆ H ₁₂	60% 16a , 40% 16b	—	a)
4	CH ₃ CN	45% 16a , 30% 16b	6% 17a , 19% 17b	a)
5	C ₆ H ₁₂	53% 18	47% 19	[7]
5	CH ₃ CN	29% 18	71% 19	[7]
6	C ₆ H ₁₂	—	100% 20	[8]
6	CH ₃ CN	—	100% 20	[8]

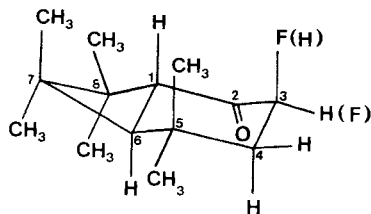
a) This work.

Table 2. *Spectroscopic Data of Photoadducts*

Compound	MS.	IR. (CCl ₄) $\nu(\text{C}=\text{O})^{\text{a}}$	NMR. (CDCl ₃) ^{b)}
8a	226 (<i>M</i> ⁺)	1733	e) 4.46 (H-C(3)), 3.24 (H-C(1)), 2.02 (H-C(6)), 1.40-2.04 (H-C(4)), 1.00-1.30 (CH ₃) $J_{\text{H1}, \text{F3}} = 5.5$, $J_{\text{H1}, \text{H6}} = 14.5$, $J_{\text{H1}, \text{H3}} = 0$, $J_{\text{H3}, \text{F3}} = 49.0$, $J_{\text{H3}, \text{H4}} = 3.2$ and 3.2
8b	226 (<i>M</i> ⁺)	1745	e) 4.82 (H-C(3)), 2.63 (H-C(1)), 2.06 (H-C(6)), 1.60-2.20 (H-C(4)), 0.97-1.27 (CH ₃) $J_{\text{H1}, \text{F3}} = 0$, $J_{\text{H1}, \text{H6}} = 14.5$, $J_{\text{H1}, \text{H3}} = 1.4$, $J_{\text{H3}, \text{F3}} = 48.0$, $J_{\text{H3}, \text{H4}} = 7.0$ and 12.0
16a, b ^{d)}	154 (<i>M</i> ⁺ - Acetone)	-	5.90 (H-C(2)), 5.70 (H-C(3)), 4.40 (H-C(5) of 16a) 4.16 (H-C(5) of 16b), 1.00-1.33 (CH ₃) $J_{\text{H2}, \text{H3}} = 5.0$, $J_{\text{H2}, \text{F5}} = 1.2$, $J_{\text{H3}, \text{F5}} = 1.2$, $J_{\text{H5}, \text{F5}} = 50.0$ (16a), $J_{\text{H5}, \text{F5}} = 50.0$ (16b)
17a	e)	1755	e)
17b	212 (<i>M</i> ⁺)	1755	5.08 (H-C(3)), 2.40 (H-C(1)), 2.18 (H-C(5)), 0.86-1.30 (CH ₃) $J_{\text{H1}, \text{H5}} = 8.5$, $J_{\text{H1}, \text{F3}} = 2.0$, $J_{\text{H5}, \text{F3}} = 6.0$, $J_{\text{H3}, \text{F3}} = 51.0$, $J_{\text{H1}, \text{H3}}$ and $J_{\text{H3}, \text{H5}} = 0$
22a	196 (<i>M</i> ⁺)	1750	3.95 (H-C(4)), $J_{\text{H4}, \text{F4}} = 52.0^{\text{f}}$
22b	196 (<i>M</i> ⁺)	1750	5.07 (H-C(4)), $J_{\text{H4}, \text{F4}} = 52.0^{\text{f}}$
23	178 (<i>M</i> ⁺)	1735	$J_{\text{H2}, \text{H6}} = 6.0$, $J_{\text{H4}, \text{H4}} = 17.0^{\text{g}}$

a) In cm⁻¹.b) Chemical shifts in ppm relative to TMS (= 0 ppm), coupling constants *J* in Hz.

c) For numbering see the following formula:



d) Structural assignment ambiguous.

e) Not recorded.

f) Other signals not resolved.

g) Shift reagent experiments.

We had reported previously that **1** gave with cyclopentene about 15% of unidentified (1 + 1)-addition products which lack carbonyl absorption in the IR. and could therefore be oxetanes **12** [1]. No oxetane formation at all was observed in the reaction of **2** [9] and of **5** [1] with the same olefin. Compound **4** now shows a similar behaviour since no more than 4% of an unidentified product (possibly **21**) is formed. These results were all obtained in hydrocarbon solvents.

In order to get additional information on the mechanistic aspect of these concurrent reactions (oxetane *vs.* cyclobutane formation) the quantum yield for the addition of the cyclopentenones **4**, **5** and **6**, as well as the cyclohexenones **1**, **2** and **3** to 2,3-dimethyl-2-butene and cyclopentene were determined (Table 3). Several

Table 3. *Quantum Yields for the Addition of Enones to Olefins in Argon Degassed Solutions* ($c_{\text{enone}} = 2.5 \cdot 10^{-2}$ mol./l, $c_{\text{olefin}} = 2.5 \cdot 10^{-1}$ mol./l, room temperature, irradiation wavelength: 366 nm, average error: $\pm 5\%$)

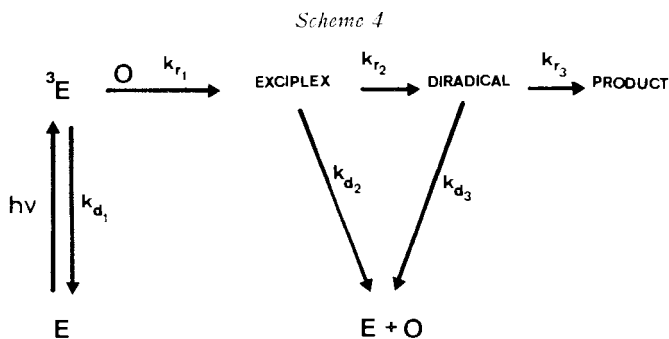
enone	solvent	olefin ^{a)}	Φ (-enone) ^{b)}	Φ (oxetane) ^{c)}	Φ (cyclobutane) ^{c)}
1	C ₆ H ₁₂	DMB	0.084	0.076	0.008
		CP	0.089	0.012	0.075
2	C ₆ H ₁₂	DMB	0.220	0.040	0.180
		CP	0.027	0.014	0.013
3	C ₆ H ₁₂	DMB	0.050	–	0.050
		CP	0.078	–	0.078
4	C ₆ H ₁₂	DMB	0.38	0.38	–
		CP	0.18	0.01	0.17
		CH ₃ CN	0.58	0.44	0.14
5	C ₆ H ₁₂	DMB	0.43	0.22	0.21
		CP	0.63	–	0.63
6	C ₆ H ₁₂	DMB	0.37	–	0.37
		CP	0.39	–	0.39

^{a)} DMB = 2,3-dimethyl-2-butene, CP = cyclopentene.

^{b)} Monitoring of enone disappearance by UV.

^{c)} Calculated from observed product distribution.

aspects of the results deserve a more detailed analysis. For the basic kinetic treatment we shall use the expression (1) developed by *de Mayo* [10] for cyclobutane formation in an (enone + olefin)-cycloaddition, wherein the triplet enone is assumed to react with the olefin *via* an exciplex which may decay to ground state enone and olefin or give a diradical intermediate (primary bond formation). This radical then gives the final product (ring closure) or dissociates to starting materials (*Scheme 4*).



$$\Phi_{\text{Prod}} = \Phi_{\text{ISC}} \cdot (k_{r_1}[\text{O}] / (k_{r_1}[\text{O}] + k_{d_1})) \cdot (k_{r_2} / (k_{r_2} + k_{d_2})) \cdot (k_{r_3} / (k_{r_3} + k_{d_3})) \quad (1)$$

A similar treatment can be derived for a system where oxetane and cyclobutane formation are concurrent, leading to the following set of equations (2):

$$\Phi_{\text{P}'} = \Phi_{\text{ISC}} \cdot (k'_{r_1}[\text{O}] / ((k'_{r_1} + k''_{r_1})[\text{O}] + k_{d_1})) \cdot (k'_{r_2} / (k'_{r_2} + k'_{d_2})) \cdot (k'_{r_3} / (k'_{r_3} + k'_{d_3})) \quad (2a)$$

$$\Phi_{\text{P}''} = \Phi_{\text{ISC}} \cdot (k''_{r_1}[\text{O}] / ((k'_{r_1} + k''_{r_1})[\text{O}] + k_{d_1})) \cdot (k''_{r_2} / (k''_{r_2} + k''_{d_2})) \cdot (k''_{r_3} / (k''_{r_3} + k''_{d_3})) \quad (2b)$$

The question whether the diradicals affording oxetane and cyclobutane products stem from one common or two different exciplex precursors is open (*cf.*[11]). We will therefore examine these cases separately.

For a *common exciplex* the product ratio $P':P''$ is determined by the ratio of the 'partition functions' K , a term for the fraction of intermediates leading to products [10]. As $k'_{r_1} \equiv k''_{r_1}$, we obtain:

$$\frac{P'}{P''} = \frac{K'}{K''} = \frac{(k'_{r_2}/(k'_{r_2} + k'_{d_2})) \cdot (k'_{r_3}/(k'_{r_3} + k'_{d_3}))}{(k''_{r_2}/(k''_{r_2} + k''_{d_2})) \cdot (k''_{r_3}/(k''_{r_3} + k''_{d_3}))} \quad (3)$$

In the presence of *two distinct exciplexes* the product ratio is additionally influenced by the different complexation rates of triplet enone to olefin; therefore:

$$P'/P'' = (k'_{r_1}/k''_{r_1}) \cdot (K'/K'') \quad (4)$$

The quantum yields for enone disappearance given in Table 3 are similar to those observed for the addition of 2-cyclopentenone (**6**) and 2-cyclohexenone (**3**) to 3-hexyne, *i.e.* 0.49 and 0.048, respectively [10]. The difference in order of magnitude depending on the ring size of the enone is probably due to differences in the k_{d_1} values, the more rapid decay rate of the cyclohexenone triplet reflecting a greater ease of twisting [12]. However, any attempt to scrutinize these data and their variations and to correlate them with the structural and solvent selectivities observed presently appears unprofitable in view of the complexity of the above kinetic expressions. In particular there are too many variable rate constants.

The problem is exemplified by the product distribution in the five- and six-membered ring series. Let us first consider the effects exerted by the substituents on the enone. The oxetane formation increases with the introduction of the *gem*-dimethyl group at C-(4) of the enone. This trend is still more pronounced by the introduction of a fluorine atom in the α' -position. At present it remains debatable which variations of rate constants are reflected by these changes. $\Phi(\text{enone})$ is almost identical for cyclopentenone (**6**) and its dimethyl derivative **5** while it drops to half in the cyclohexenone series in going from **3** to **2**. Also the introduction of a fluorine atom results in a decrease of $\Phi(\text{enone})$ in the fivemembered ring and in an increase in the six-membered ring series. Obviously, the enhancement of oxetane *vs.* cyclobutane formation may be caused by an increase of one or several of the k_r 's or by a decrease of one or more k_d values, or by a combination of both factors.

Regarding now the effect of the nature of the olefin on product distribution, we had previously suggested [1] that the oxetane formation should be favored by a high electron density on the olefinic carbon atoms in order to explain the different behaviour of **1** towards 2,3-dimethyl-2-butene and cyclopentene. This view is in accordance with PMO calculations on photocycloadditions [11] which underline the importance of the ionisation potential of the olefin in additions to a C=O bond. Alternatively, *de Mayo* [10] concluded that the ionisation potential of the substrate should not be a relevant feature in the formation of cyclobutanes, as the reaction rates and the quantum yields for the addition of enones to olefins and acetylenes are similar. In reconsidering our own case, one cannot exclude the possibility that the inefficiency of oxetane formation in the system (cyclopentene + **1** or + **4**) is due to a

large k_d value of the corresponding diradicals. An enhanced return to starting material could be favored by the difference in strain between a spiro compound consisting of only two alicyclic rings (*e.g.* **7** or **16**) and a product where one component of the spiro compound is incorporated in a bicyclo[3.2.0]system (*e.g.* **12** or **21**).

Finally, there remains the effect of the solvent. For **1**, **2**, **4** and **5** the increase in solvent polarity reduces to variable extent the amount of oxetane formed. We had explained this qualitatively [1] by complexation or dipolar interactions between the C=O group and solvent molecules, *i.e.*, reduction of the ability of the carbonyl groups towards reaction with the olefin. However, it can be seen from Table 3 that the reaction efficiency for **1** and **4** is much higher in acetonitrile than in hydrocarbon solvent. Here again, one might be oversimplifying by correlating this change with the variation of one specific rate constant in eqs. (2a) and (2b) only.

Experimental Part

General. Chemical shifts in the NMR. spectra are given in ppm relative to TMS (= 0 ppm) as internal standard, absorptions in the IR. spectra in cm^{-1} , and in UV. spectra in nm.

1. *Synthesis of 5-fluoro-4,4-dimethyl-2-cyclopentenone (4).* 1.1. *4-Chloro-2,2-dimethyl-4-pentenal.* Prepared in analogy to 2,2-dimethyl-4-pentenal [4] from 72.0 g (1.0 mol) of 2-methylpropanal and 83.2 g (0.75 mol) of 2,3-dichloropropene, yielding 49.3 g (45%) of **4**, b. p. 58–60°/15 Torr. – NMR. (CCl_4): 9.60 (s, 1H); 5.20 (m, 2H); 2.52 (s, 2H); 1.10 (s, 6H).

1.2. *4,4-Dimethyl-2-cyclopentenone (5).* 49.3 g (0.34 mol) of 4-chloro-2,2-dimethyl-4-pentenal were added with stirring to 600 ml of conc. H_2SO_4 at 0° during 10 min. After 2½ h the solution was poured on to 1 kg of ice. The mixture was extracted 3× with 100 ml of ether, the ether phases washed with saturated NaHCO_3 - and NaCl -solutions and dried. Distillation afforded 11.3 g of **5** (31%), b. p. 47–49°/15 Torr. The spectral data are identical with those given in [3].

1.3. *5-Hydroxymethylidene-4,4-dimethyl-2-cyclopentenone (25).* A mixture of 11.3 g (0.105 mol) of **5** and 10.0 g (0.13 mol) of ethyl formate was added to a suspension of 2.7 g (0.11 mol) of NaH in 300 ml of ether during 1 h. Stirring was continued for another 12 h. 200 ml of H_2O were added, the phases separated and the aqueous phase washed 1× with ether. Having added 200 ml of ether to the aqueous phase, diluted H_2SO_4 was added until pH = 2 was reached. The phases were separated and the aqueous phase extracted 2× with 100 ml of ether. After drying over MgSO_4 and evaporating the solvent 14.0 g of **25** (93%) were obtained as a yellow solid which was used without further purification in the next step. An analytical sample of **25** was obtained by sublimation (70°/0.1 Torr) giving white crystals, m. p. 74–75°. – NMR. (CCl_4): 11.30 (1H, OH); 7.10 (s, 1H); 7.06 (d, 1H); 6.10 (d, $J = 5.5$, 1H); 1.20 (s, 6H). – IR. (CCl_4): 1682, 1618. – MS.: 138 (M^+). – UV. (C_6H_{12}): 231 (8300), 290 (5200).

1.4. *Preparation of 4.* 14.0 g (0.101 mol) of **25** in 50 ml of CH_3OH containing 2.32 g of Na (0.101 g-atom) were treated with an excess of FCIO_3 . Water was added and the intermediate fluoro-formyl ketone extracted with 2×100 ml of CH_2Cl_2 . After drying and evaporating the solvent, the residue was dissolved in 50 ml of CH_3OH . Potassium acetate (2.0 g) was added and the solution was heated under reflux for 3 h. Again, water was added and after extraction with 2×100 ml of CH_2Cl_2 , drying over MgSO_4 and distillation 4.3 g of **4** (33%) were obtained, b. p. 35–37°/0.5 Torr. According to GLC. (5% SE 30 on chromosorb G, 130°) purity was greater than 97%. The overall yield starting from 2,3-dichloropropene was 4.3%. – $^1\text{H-NMR}$. (CCl_4): 7.50 ($d \times d$, $J = 4.2$ and 5.5, 1H); 6.00 ($d \times d$, $J = 1.4$ and 5.5, 1H); 4.54 (d , $J = 51.5$, 1H); 1.33 (s, 3H); 1.12 (d , $J = 4.25$, 3H). – $^{19}\text{F-NMR}$. ($(\text{CD}_3)_2\text{CO}$): 43.6 ppm upfield from C_6F_6 (m , $J = 51.5$, 4.2, 4.2, 4.2, 4.2 and 1.4, 1F). – IR. (CCl_4): 1735. – MS.: 128 (M^+). – UV. (C_6H_{12}): 213 (15000), 333 (39; vibrational spacing: 1424 cm^{-1}).

2. *Other compounds.* 2-cyclohexenone (**3**, *Fluka*) and 2-cyclopentenone (**6**, *Aldrich*) were distilled before use. 4,4-Dimethyl-2-cyclohexenone (**2**) [13] and 6-fluoro-4,4-dimethyl-2-cyclohexenone (**1**) [1] were synthesized according to literature procedures. Cyclopentene (*Fluka*) was of

analytical grade. 2,3-Dimethyl-2-butene (obtained from *Max-Planck-Institut für Kohlenforschung* in Mülheim/Ruhr) was vacuum distilled at 30° under N₂. The solvents used were of spectroscopic grade (*Fluka*).

3. *Photolyses*. They were carried out with a *Philips* HPK-125W mercury lamp through a filter solution with a cut-off at 340 nm [14] at room temp. Before irradiation the solutions were flushed with N₂. In a typical run 2·10⁻³ mol of enone and 2·10⁻² mol of olefin were irradiated in 15 ml of solvent for 16–18 h. The isolation of the photoadducts was achieved as described below. Their spectral data are summarized in Table 2.

3.1. *Photoaddition of 4 to 2,3-dimethyl-2-butene*. 3.1.1. *In cyclohexane*. The GLC. (5% SE 30 on chromosorb G, 130°) showed only one peak for the two 5-fluoro-3,3',4,4,4',4'-hexamethylcyclopent-2-en-1-spiro-2'-(oxetanes) (**16a** and **16b**). These were stable in solution but decomposed on standing – even at –30° – to give highly coloured unidentified materials.

3.1.2. *In CH₃CN*. The GLC. (same conditions as above) showed the additional formation of two minor products, the 3-fluoro-4,4,6,6,7,7-hexamethylbicyclo[3.2.0]heptan-2-ones (**17a** and **17b**) (retention times of **16** (75%), **17a** (6%), and **17b** (19%) were 1, 1.7 and 2.5, resp.). **17b** was obtained from the mixture in 85% purity by prep. TLC. (benzene) as the second fraction, the first one containing mainly **16**.

3.2. *Photoaddition of 4 to cyclopentene in benzene*. The GLC. (same column as above, 150°) showed the formation of two products, the 4-fluoro-5,5-dimethyltricyclo[5.3.0.0^{2,6}]decan-3-ones (**22a** and **22b**), in relative amounts of 3:2 (ret. times: 1 and 1.6). They were separated and isolated by prep. GLC. (15% QF1 on chromosorb G, 200°).

3.3. *Photoaddition of 5 to cyclopentene in cyclohexane*. GLC. (5% SE 30 on chromosorb G, 150°) revealed the exclusive formation of 5,5-dimethyltricyclo[5.3.0.0^{2,6}]decan-3-one (**23**).

3.4. *Photoaddition of 1 to 2,3-dimethyl-2-butene in acetonitrile*. GLC. (same conditions as above) showed the formation of two main products, the 3-fluoro-5,5,7,7,8,8-hexamethylbicyclo[4.2.0]octan-2-ones (**8**; 85%), in about equal amounts besides the 6-fluoro-3',3',4,4,4',4'-hexamethylcyclohex-2-en-1-spiro-2'-(oxetane) (**7**; 15%). The relative retention times of **7**, **8a**, and **8b** were 1, 1.3, and 2.6, resp. **8a** and **8b** were separated and isolated by prep. GLC. (15% QF1 on chromosorb G, 220°).

4. *Quantum Yields*. These were measured using an electronically integrating actinometer [15]. The decrease of starting material was monitored by UV. spectroscopy. Thus Ar-degassed solutions (*c*_{enone} = 2.5 · 10⁻² mol/l; *c*_{olefin} = 2.5 · 10⁻¹ mol/l) were irradiated in a UV. cell (3 ml) up to 10–15% conversion with light of λ = 366 nm and the spectra periodically recorded in the range of 340–420 nm. The loss of starting material was evaluated at 360–370 nm; when necessary extrapolation to 0% conversion was carried out.

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