## 91. Photorearrangement of 4,4-Dimethylcyclohex-2-enones with Alkyl or Fluoro Substituents at C(5) and C(6): in Search of the Mechanism

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The photorearrangement of cyclohex-2-enones **4a**-h to bicyclo[3.1.0]hexan-2-ones **5** and cyclopent-2-enones **6**  $(\lambda = 350 \text{ nm}, \text{ MeCN})$  was investigated. Both the quantum yield  $(\Phi_{-4} = 0.004 - 0.024)$  and the product ratio (5/6 = 65: 35-31: 69) vary only over a rather small range, indicating the rearrangement to be relatively insensitive to substituents on C(5) or C(6). Compounds **4b**, **4c**, and **4g** with just one alkyl group at either C(6) or C(5) rearrange selectively to the diastereoisomer **5** with alkyl group and three-membered ring in *trans*-configuration, while 6-fluorocyclohex-2-enones **4d** and **4f** afford mixtures of diastereoisomeric bicyclohexanones. Mechanistic conclusions regarding an intermediate trimethylene biradical are presented.

**Introduction.** – The light-induced photoisomerization of 4,4-dialkylcyclohex-2enones I with concomitant formation of bicyclo[3.1.0]hexan-2-ones II and cyclopent-2enones III has been investigated in the past by several groups [1–6] and more recently quite thoroughly by *Schuster et al.* [7–10]. Nevertheless, the question of the mechanism of this rearrangement remains unanswered, both concerted and stepwise mechanisms having been proposed but not proven. The lifetime of an eventual propane-1,3-diyl-biradical intermediate A has to be short, as a) the reaction proceeds with retention of configuration at the dialkyl-disubstituted C(4) [7], and b) no products derived from cyclopropyl-



carbinyl-radical-ring opening were detected in the rearrangement of 1 to 2 and 3 [5]. In a preliminary communication [11], we had discussed a hex-5-enyl-type radical **B** as possible precursor of **A** (*Scheme 1*), based on the observed product configuration. In this paper, we report detailed results on the photolysis of 4,4-dimethylcyclohex-2-enones 4a-h, the configuration of bicyclohexanones 5, and correlate our experimental results with the most recent theoretical descriptions of the reaction of trimethylene biradicals affording cyclopropanes and propylenes [12] [13].

**Results.** – The quantum yields for disappearance of starting material  $(\Phi_{-4})$  and product distribution (5 and 6) for irradiations ( $\lambda = 350$  nm) of 4 (10<sup>-1</sup> M in MeCN) measured at 10–15% conversion are given in *Scheme 2*. The <sup>1</sup>H-NMR and MS data of photoproducts 5 and 6 are summarized in the *Table*.



**Discussion.** – Several aspects regarding the results summarized in *Scheme 2* and in the *Table* are worth mentioning. The values of the quantum yield  $(\Phi_{-4})$  and the product ratio 5/6 do not show significant variations in dependence on the substituents on C(5) and C(6) of 4. In bicyclohexanones **5b**, **5c**, **5e**, **5f**<sub>y</sub>, and **5g** the five-membered ring has a puckered conformation (*cf.* NMR data in the *Table*). In **5b** and **5c**, the alkyl group is in *quasi*-equatorial position and in **5g** in *quasi*-axial, *i.e.* always *trans*-oriented to the three-membered ring. In **5f**<sub>y</sub>, the F-atom is most probably in *quasi*-axial position ( ${}^{3}J(F_{ax},H_{ax}) = 37$  Hz) and the Me group again *quasi*-equatorial. In 3-fluorobicyclohexanones **5d**, the cyclopentanone ring seems to be flexible, and, therefore, an unambiguous assignment of the configuration of **5d**<sub>x</sub> and **5d**<sub>y</sub> from the <sup>1</sup>H-NMR data is not possible. The fact that both fluoroenones **4d** and **4f** afford diastereoisomeric mixtures of bicyclohexanones **5** could be due to dipole-dipole interactions between the F-atom and the C=O bond somewhere on the reaction path.

The major goal of this investigation is to better understand the mechanism of the photorearrangement of 4 to 5 and 6. The concept of two essentially concerted pathways from triplet I to II and III, requiring intersystem crossing to the singlet state, cleavage of one bond, and formation of two new bonds (for 5), or the formation of one new bond and

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Com-	<sup>1</sup> H-NMR (CDC	[]3] [ppm] (J(H,F) [Hz])	i	Ĭ		WS
5.         1.65         2.25 (2 H)         2.18 (2 H)         1.82         1.24 (0, M <sup>+</sup> ), 87 (10)           5.6         1.22         2.32 (3 H)         2.18 (3 H)         2.18 (3 H)         2.18 (3 H)         2.18 (4 H)         2.10 (9)         2.23 (1 H_3)         2.18 (2 H_3)         2.18 (3 H_3)         2.23 (1 H_3)         2.18 (3 H_3)         2.23 (1 H_3)         2.24 (2 H_3)         2.23 (1 H_3)         2.24 (2 H_3)         2.24 (2 H_3)         2.26 (2 H_3)	punod	H-C(1)	H-C(3)	H-C(4)	H-C(5)	CH <sub>3</sub> -CF	[m/z] (%)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5a	1.65	2.25 (2 H)	2.18 (2 H)	1.82		$124(10,M^+),82(100)$
5         183         3.0 (9)         2.57 (H <sub>u</sub> ); 197 (H <sub>u</sub> )         1.88         122 (2, M <sup>+</sup> ), 99 (100           54         1.30 (30)         4.68 (51)         2.57 (H <sub>u</sub> ); 160 (H <sub>u</sub> )         1.38         122 (2, M <sup>+</sup> ), 99 (100           54         1.70 (2.0)         4.73 (50)         2.52 (10.8); 2.23 (60)         2.08         122 (20, M <sup>+</sup> ), 99 (100           54         1.70 (2.0)         4.73 (50)         2.52 (10.8); 2.23 (60)         2.08         122 (20, M <sup>+</sup> ), 99 (100           54         1.90 <sup>h</sup> -         2.24 (37.2); 2.03 <sup>b</sup> 1.95 <sup>b</sup> 1.36 (23)         132 (20, M <sup>+</sup> ), 113 (10           54         1.90 <sup>h</sup> -         2.46 (37.2); 2.03 <sup>b</sup> 1.95 <sup>b</sup> 1.36 (23)         135 (50, M <sup>+</sup> ), 113 (10           54         1.90 <sup>h</sup> -         2.46 (37.2); 2.03 <sup>b</sup> 1.97 <sup>b</sup> 1.36 (23)         135 (50, M <sup>+</sup> ), 110 (100           54         1.03 <sup>h</sup> 2.16 <sup>h</sup> 1.170         2.26 (37.4 <sup>h</sup> )         2.26 (35.4 <sup>h</sup> ), 113 (10         2.26 (35.4 <sup>h</sup> ), 113 (10           1/3.31         1.23 (1.2)         2.33 (1.2)         2.34 (37.2)         2.32 (10         2.32 (10, M <sup>+</sup> ), 2.20 (10           1/3.31         1.26 (23)         1.36 (23)         1.36 (23)         1.36 (21, M <sup>+</sup> ), 113 (10           1/3.31	5b	1.72	2.42	2.51 (H <sub>ax</sub> ); 1.77 (H <sub>eq</sub> )	1.80		$138 (20, M^{+}), 67 (100)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	50	1.82	3.20 (9.9)	$2.57 (H_{ax}); 1.97 (H_{eq})$	1.88		$192 (12, M^+), 82 (100)$
54, 1.70         1.70         2.72         9.00         1.76         1.76         1.72         1.70         1.76         1.70         1.76         1.70         1.76         1.70         1.22         0.4.73         57         100         54         1.70         1.23         0.4.73         57         100         54         1.70         1.24         0.20         1.76         100         1.22         0.4.7         113         100         56         5.4.7         113         100         100         113         101         100         100         101         100         101         100         101         101         100         101         100         101         100         101         100         101         100         101         100         101         100         101         101         100         101         101         100         101         101         100         101         101         100         101         101         100         101         101         100         101         101         101         101         101         101         101         101         101         101         101         101         101         101         101	5d <sub>x</sub>	1.80 (3.0)	4.68 (51)	2.52 (10.8); 2.28 (36.0)	2.08		$142 (20, M^+), 99 (100)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5dv	1.70 (2.0)	. 4.73 (50)	2.72 (9.6); 1.90 (21.7)	1.76		$142 (20, M^+), 99 (100)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5e	1.75	ł	$1.92 (H_{ax}); 1.60 (H_{eq})$	1.70		$152\ (20,\ M^+),\ 67\ (100)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5f <sub>x</sub>	a)					156 (15, M <sup>+</sup> ), 113 (100)
561.652.35 (H, u)2.261.70138 (I5, M <sup>*</sup> ), 96 (100519)7(3.3) = 19.2, 7(4.4) = 12 - 4.81(3.3) = 19.2, 7(4.4) = 12 - 4.813.3.10 (1007(3.5) = 5.2 - 5.5, 7(3ax, 4ac) = 18.1.8, 7(4cq), 3 = 0.8 - 1.87(3.5) = 5.2 - 5.5, 7(3ax, 4ac) = 5.4.9.413.3.10 (1007(3.6) = 7.2, 7(4.6) = 1.6 - 4.87(3.6) = 0.8 - 1.813.3.1 (1.5) = 5.2 - 5.5, 7(3ax, 4ac) = 5.4.9.413.3.1 (1.5) = 5.2 - 5.5, 7(3ax, 4ac) = 5.4.9.47(3eq, 4eq) = 3.0, 7(4ax, 5) = 6.8 - 7.2, 7(4eq, 5) = 0.8 - 1.87(3eq, 4eq) = 5.4.9.413.4 (40, M <sup>*</sup> ), 82 (100615.920.7 (1.14)2.4213.4 (60, M <sup>*</sup> ), 82 (100625.932.183.15 (10.2)13.15 (10.2)635.973.00 (6.8)5.00 (51)12.6 (50, M <sup>*</sup> ), 100 (10645.972.06 (21)-1.50 (22.6)132 (40, M <sup>*</sup> ), 130 (10655.842.92 (20.8)-1.50 (22.6)132 (30, M <sup>*</sup> ), 130 (10665.842.92 (20.8)1.50 (22.6)132 (30, M <sup>*</sup> ), 130 (10675.942.92 (20.8)1.50 (22.6)136 (30, M <sup>*</sup> ), 130 (1068582.982.963.03 (10.0)-1.50 (22.6)136 (30, M <sup>*</sup> ), 130 (1069582.962.031.00 (10.0)-1.50 (22.6)132 (40, M <sup>*</sup> ), 130 (1069582.982.051.00 (10.0)-1.50 (22.6)132 (40, M <sup>*</sup> ), 130 (107(4)18 (1.4) (1.5) = 18.41.40 (1.6) (1.5) = 2.0.341.50 (22.6)132 (30, M <sup>*</sup> ), 130	5f <sub>v</sub>	1.90 <sup>b</sup> )	I	2.46 (37.2); 2.03 <sup>b</sup> )	1.95 <sup>b</sup> )	1.36 (23)	156 (15, M <sup>+</sup> ), 113 (100)
5h         a)         132 (1, M <sup>-</sup> ), 110 (100 $J(3,3) = 192, J(4,4) = 12.6 - 148$ $J(3,3) = 52.55, J(3,3,4,4x) = 11.8 - 13.0, J(3,3,4eq) = 5.4.9, 41           J(1,5) = 5.2 - 55, J(3,3,4,4x) = 11.8 - 13.0, J(3,3,4eq) = 5.4.9, 41         J(3,2) = 5.2 - 55, J(3,3,4x) = 1.8 - 13.0, J(3,3,4eq) = 5.4.9, 41         J(3,3) = 5.2 - 55, J(3,4,4x) = 1.8 - 13.0, J(4,4x,5) = 0.8 - 1.8           66         5.92 o' f(14) H - C(5) CH_3 - CF 124, 40, M^+), 82 (100           66         5.97 2.12 3.15 (10.2) 3.15 (10.2) 123, 40, M^+), 82 (100           66         5.97 2.00 (51) 3.15 (10.2) 123, 60, M^+), 130 (10           67         5.97 2.00 (51) 2.76 123, (M - 5, 60, M^+), 130 (10           68         5.84 2.70 (2.08)  12.30, 0.22.6)         132 (30, M^+), 130 (10)           69         5.99 2.06 (3.1)  12.30, 0.22.6)         132 (30, M^+), 130 (10)           66         5.89 2.03 (30)  1.36 (22.6) 132 (30, M^+), 130 (10)           67         3.00 (51) -$	58	1.65	2.35 (H <sub>ax</sub> )	2.26	1.70		$138 (15, M^+), 96 (100)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5h	<sup>a</sup> )					$152(1, M^{+}), 110(100)$
6a         592 $c/(14)$ $H-C(5)$ $H-C(5)$ $CH_3-CF$ 124 (40, M <sup>+</sup> ), 82 (100         5.92 $c/(144)$ 124 (40, M <sup>+</sup> ), 82 (100           6b         5.92 $c/(144)$ 3.15 (10.2)         138 (45, M <sup>+</sup> ), 67 (100           6c         5.95         2.91         3.15 (10.2)         142 (30, M <sup>+</sup> ), 100 (10           6c         5.97         2.00 (51)         3.15 (10.2)         142 (30, M <sup>+</sup> ), 100 (10           6e         5.84         2.46 (2.H)         -         142 (30, M <sup>+</sup> ), 100 (10           6e         5.84         2.76 (0.0)         -         142 (30, M <sup>+</sup> ), 139 (10           6e         5.84         2.70 (10.0)         -         142 (30, M <sup>+</sup> ), 139 (10           6f         5.94         2.92 (208)         -         123 (40, M <sup>+</sup> ), 139 (10           6f         5.94         2.93 (100)         -         152 (40, M <sup>+</sup> ), 139 (10           6f         5.94         2.95 (100         -         142 (30, M <sup>+</sup> ), 141 (10           6f         5.89         2.98         -         -         152 (41, M <sup>+</sup> ), 139 (10           6g         5.89         2.98         2.05         138 (38, M <sup>+</sup> ), 95 (100         136 (36, M <sup>+</sup> ), 141 (10		J(3,3) = 19.2, J J(1,5) = 5.2-5.5 J(3eq.4eq) = 3.0	(4,4) = 12.6–14.8 5, J(3ax,4ax) = 11.8–13.0, 0, J(4ax,5) = 6.8–7.2, J(4,	J(3ax,4eq) = 5.4-9.4 eq.5) = 0.8-1.8			
H-C(2)H-C(4)H-C(5)H-C(4)H-C(5)6a $5.92$ $q' [14]$ $2.42$ $138 (45, M^+), 82 (100)$ 6b $5.89$ $2.85$ $2.42$ $1315 (10.2)$ $132 (40, M^+), 82 (100)$ 6c $5.95$ $2.91$ $3.15 (10.2)$ $3.15 (10.2)$ $124 (40, M^+), 82 (100)$ 6d $5.97$ $2.06 (83)$ $5.00 (51)$ $3.06 (63)$ $5.00 (51)$ $122 (40, M^+), 100 (10)$ 6e $5.84$ $2.70 (22.4)$ $ 142 (30, M^+), 100 (10)$ $142 (30, M^+), 100 (10)$ 6e $5.84$ $2.70 (22.6)$ $ 122 (40, M^+), 139 (10)$ 6f $5.94$ $2.292 (20.8)$ $ 1.50 (22.6)$ $156 (60, M^+), 141 (11)$ 6g $5.89$ $2.98$ $2.65$ $1.66 (M^+), 141 (11)$ $1.60 (22.6)$ $158 (60, M^+), 141 (11)$ 6g $5.89$ $2.98$ $2.65$ $1.50 (22.6)$ $158 (60, M^+), 141 (11)$ 6g $5.89$ $2.98$ $2.65$ $1.50 (22.6)$ $158 (M^+), 95 (10)$ 6g $5.89$ $2.98$ $2.65$ $1.50 (22.6)$ $158 (41, M^+), 139 (10)$ $7(4,4) = 18.0-190, J(5,5) = 18.4$ $J(4,5c) = 6.8-74, J(4,5f) = 2.0-3.44$ $J(4,5c) = 6.8-74, J(4,5f) = 2.0-3.44$ $J(2,4) = 0.8-1.5$							
6a5.92 $cf. [14]$ $124. (40, M^+), 82. (100)$ 6b5.892.852.913.15 (10.2)6c5.952.913.15 (10.2) $132. (63, M^+), 82. (100)$ 6d5.972.75 $3.15 (10.2)$ $142. (30, M^+), 100 (10)$ 6d5.97 $3.00 (6.8)$ $5.00 (51)$ $142. (30, M^+), 100 (10)$ 6e5.84 $2.46. 2H$ $ 142. (30, M^+), 139 (10)$ 6f5.94 $2.76 (20.8)$ $ 152. (40, M^+), 139 (10)$ 6g5.89 $2.98$ $2.65$ $1.50 (22.6)$ $158. (M^+), 95 (100)$ 6g5.89 $2.98$ $2.65$ $1.50 (22.6)$ $138. (38, M^+), 95 (100)$ 6g $5.89$ $2.98$ $2.65$ $1.66 (30, M^-), 141 (10)$ $7(4, 4) = 18.0 - 190, J(5,5) = 18.4$ $J(4, 5c) = 6.8 - 7.4, J(4, 5c) = 2.0 - 3.4$ $J(4, 5c) = 0.8 - 1.5$ $J(2, 4) = 0.8 - 1.5$		H-C(2)	H-C(4)	Н-С()		CH <sub>3</sub> -CF	
6h5.892.852.42138 (45, $M^+$ ), 67 (1006c5.952.913.15 (10.2)135 (10.2)192 (63, $M^+$ ), 82 (1006d5.973.00 (6.8)5.00 (51)5.00 (51)142 (30, $M^+$ ), 100 (106e5.842.46 (2.H)-142 (30, $M^+$ ), 139 (106f5.942.92 (20.8)-153 (40, $M^+$ ), 139 (106g5.842.942.92 (20.8)-153 (40, $M^+$ ), 139 (106f5.942.92 (20.8)153 (40, $M^+$ ), 139 (106g5.892.982.982.651.50 (22.6)138 (38, $M^+$ ), 95 (1006g5.892.982.03.141.50 (22.6)156 (60, $M^+$ ), 141 (106g5.892.982.062.03.341.50 (22.6)156 (60, $M^+$ ), 139 (106g5.892.982.063.00 (55) = 18.41.50 (22.6)138 (38, $M^+$ ), 95 (1006g5.892.082.03.342.651.41 (10 (10.0))1.52 (41, $M^+$ ), 139 (106g5.892.082.03.342.651.32 (20.8)1.33 (20 (10.0))7 (4,57) = 6.8-7.4, J(4,57) = 2.0-3.4J (2,4) = 0.8-1.5J (2,4) = 0.8-1.5J (2,4) = 0.8-1.5	6a	5.92	<i>cf.</i> [14]				$124 (40, M^{+}), 82 (100)$
6c5.952.913.15 (10.2)192 (63, $M^+$ ), 82 (1006d5.972.75142 (30, $M^+$ ), 100 (106e5.842.46 (2H)-1122.70 (22.4)112 (40, $M^+$ ), 139 (106f5.942.92 (20.8)-5.992.70 (10.0)-6g5.892.985.892.982.656h*)1.50 (22.6)138 (38, $M^+$ ) 95 (100673.9414(4) = 18.0-190, J(5.5) = 18.4J(4,5c) = 6.8-7.4, J(4,5c) = 2.0-3.4J(2,4) = 0.8-1.5	6b	5.89	2.85	2.42			$138(45, M^{+}), 67(100)$
$2.75$ $2.75$ $142 (30, M^+), 100 (10)$ 6d $5.97$ $3.00 (6.8)$ $5.00 (51)$ $142 (30, M^+), 139 (10)$ 6e $5.84$ $2.46 (2.H)$ $ 152 (40, M^+), 139 (10)$ 6f $5.94$ $2.92 (20.8)$ $ 152 (40, M^+), 139 (10)$ 6g $5.89$ $2.92 (20.8)$ $ 1.50 (22.6)$ $138 (38, M^+), 95 (100)$ 6g $5.89$ $2.98$ $2.65$ $2.65$ $1.50 (22.6)$ $138 (38, M^+), 95 (100)$ 6g $5.89$ $2.98$ $2.98$ $2.65$ $1.50 (22.6)$ $138 (38, M^+), 95 (100)$ $1(4,4) = 18.0 - 190, J(5.5) = 18.4$ $J(4,5t) = 2.0 - 3.4$ $J(4,5t) = 2.0 - 3.4$ $J(2,4) = 0.8 - 1.5$	6c	5.95	2.91	3.15 (10.2)			192 (63, M <sup>+</sup> ), 82 (100)
6d $5.97$ $3.00(6.8)$ $5.00(51)$ $142(30, M^+), 100(10)$ $6e$ $5.84$ $2.46(2.H)$ $ 132(40, M^+), 139(10)$ $6f$ $5.94$ $2.92(20.8)$ $ 1.50(22.6)$ $156(60, M^+), 141(10)$ $6g$ $5.89$ $2.98$ $2.65$ $1.50(22.6)$ $138(38, M^+), 95(100)$ $6g$ $5.89$ $2.98$ $2.65$ $138(38, M^+), 95(100)$ $1(4,4) = 18.0 - 190, J(5,5) = 18.4$ $J(4,5t) = 2.0 - 3.4$ $J(4,5t) = 2.0 - 3.4$ $J(2,4) = 0.8 - 1.5$ $J(2,4) = 0.8 - 1.5$ $J(2,4) = 0.8 - 1.5$			2.75				
6e5.84 $2.46(2.H)$ - $152(40, M^+), 139(10)$ 6f5.94 $2.92(20.8)$ - $1.50(22.6)$ $156(60, M^+), 141(10)$ 6g5.89 $2.98$ $2.65$ $1.50(22.6)$ $138(38, M^+), 95(100)$ 6h $^{3}$ $1(4.4) = 18.0 - 190, J(5.5) = 18.4$ $1(4.5t) = 2.0 - 3.4$ $132(41, M^-), 139(10)$ $J(4.5t) = 6.8 - 7.4, J(4.5t) = 2.0 - 3.4$ $J(2.4) = 0.8 - 1.5$ $1.50(22.6)$ $152(41, M^-), 139(10)$	6d	5.97	3.00 (6.8) 2.70 (22.4)	5.00 (51)			$142 (30, M^+), 100 (100)$
6f         5.94 $2.92(20.8)$ -         1.50(22.6)         156(60, $M^+$ ), 141(10           6g         5.89         2.98         2.65         138(38, $M^+$ ), 95(100           6h         a)         1(4,4) = 18.0-190, J(5,5) = 18.4         133(38, $M^+$ ), 139(10           144,5r) = 6.8-7.4, J(4,5r) = 2.0-3.4         2.65         132(41, $M^-$ ), 139(10           J(2,4) = 0.8-1.5         0.8-1.5	6e	5.84	2.46 (2 H)				$152 (40, M^{+}), 139 (100)$
$2.70 (10.0)$ $2.65$ $138 (38, M^+), 95 (100)$ 6g $5.89$ $2.98$ $2.65$ $138 (38, M^+), 95 (100)$ 6ha) $J(4,4) = 18.0-19.0, J(5,5) = 18.4$ $J(4,4) = 18.0-19.0, J(5,5) = 18.4$ $J(4,5c) = 6.8-7.4, J(4,5t) = 2.0-3.4$ $J(2,4) = 0.8-1.5$	6f	5.94	2.92 (20.8)	I		1.50 (22.6)	$156(60,M^+),141(100)$
<b>6g</b> 5.89 2.98 2.65 138 (38, $M^+$ ), 95 (100 <b>6h</b> <sup>a</sup> ) $J(4,4) = 18.0-19.0, J(5,5) = 18.4$ 152 (41, $M^-$ ), 139 (10 $J(4,5c) = 6.8-7, 4, J(4,5t) = 2.0-3.4$ 152 (41, $M^-$ ), 139 (10 J(2,4) = 0.8-1.5			2.70 (10.0)				
<b>6h</b> <sup>a</sup> ) 152 (41, $M^+$ ), 139 (10 J(4,4) = 18.0-19.0, J(5,5) = 18.4 J(4,5c) = 6.8-7.4, J(4,5t) = 2.0-3.4 J(2,4) = 0.8-1.5	6g	5.89	2.98	2.65			$138 (38, M^{+}), 95 (100)$
J(4,4) = 18.0-19.0, J(5,5) = 18.4 J(4,5c) = 6.8-7.4, J(4,5t) = 2.0-3.4 J(2,4) = 0.8-1.5	6h	a)					152 (41, M <sup>+</sup> ), 139 (100)
$J(4,5\ell) = 0.5 - 1.5$ J(2,4) = 0.8 - 1.5		J(4,4) = 18.0 - 1	9.0, J(5,5) = 18.4				
		$J(2,4) = 0.0^{-1.5}$	.+, J(+,Jl) = 2.0-J.+ 5				

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an 1,2-H shift (for 6) is very hard to accept. Taking into consideration that in a very similar system *both* the oxabicyclohexanones 7 and the unsaturated lactones 8 are formed in the triplet-sensitized photolysis of oxa-diaza precursors 9, undoubtedly *via* propane-1,3-diyl radical C [15] (*Scheme 3*), it is safe to assume that formation of 5 and 6 from triplet I proceeds *via* a propane-1,3-diyl (triplet) radical A.



The first question, thus, concerns the formation of triplet **A** from triplet **I**, *i.e.* the sequence of steps in this transformation. In [11], we had discussed a possible intermediate **B** as precursor of **A**, as **B** behaved as expected for a hex-5-enyl radical, a species known [16] [17] to undergo ring closure in the *exo*-mode to give five-membered rings selectively *and* to afford *trans*-disubstituted five-membered rings when bearing a substituent at C(2), *i.e.* C(6) of **4**. The fact that from **4g** again the *trans*-bicyclohexanone **5g** is formed selectively *clearly rules out such an intermediate*, as now a *cis*-disubstituted five-membered ring should be formed. The conversion of triplet **I** to triplet **A** is, therefore, best described as an intramolecular homolytic substitution ( $S_{\rm H}2$  reaction) with attack of the radical center C(3) on C(5), the leaving group, *i.e.* the dialkyl-substituted C(4), then being *trans* to the alkyl group at C(5) or C(6) (*Scheme 4*). Examples of intermolecular displacement



<sup>a</sup>) Formation of 5. <sup>b</sup>) Formation of 6.

reactions by alkyl radicals at saturated C-atoms are rarely encountered, but intramolecular examples involving strained alicyclic rings are known [18]. According to the newest IUPAC recommendations for the representation of reaction mechanisms [19], such a sequence would be termed *intra*  $A_R D_R$ .

The fate of the propane-1,3-diyl (triplet) radical  $\mathbf{A}$  is straightforward [12]. Once formed, it does *not* relax thermally on the triplet surface, *i.e.* it undergoes intersystem crossing very rapidly as shown by the observed retention of configuration at C(4) in these rearrangements. The barrier to H transfer on the singlet surface from singlet  $\mathbf{A}$  to  $\mathbf{6}$  is certainly lower than that of unsubstituted propane to propene, as the C=C bond formed is now conjugated to a C=O bond; this explains, why, in contrast to triplet-derived simple propane-1,3-diyl radicals, which give cyclopropane products and only very little propylenes, intermediates  $\mathbf{A}$  afford more or less equal amounts of both  $\mathbf{5}$  and  $\mathbf{6}$ .

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## **Experimental Part**

General. Anal. GC: 30-m SE 30 cap. column. Prep. GC: 2-m 10% QF1 on Chromosorb at 180°. <sup>1</sup>H, <sup>1</sup>H-COSY-NMR: at 400 MHz. MS: at 70 eV. Photolyses. Rayonet RPR 100 photoreactor equipped with 350-nm lamps. Starting Materials. Cyclohexenones 4a [20], 4b [21], 4c [11], 4d [22], 4e [23], 4f [22], 4g [20], and 4h [24] were synthesized according to literature.

Prep. Irradiations. Ar-degassed solns. of 4 (1 mmol) in MeCN (10 ml) were irradiated for 12-50 h up to 40-90% conversion (GC) of starting material.

## Irradiation of 4a. Cf. [1] [7] [14].

Irradiation of **4b**. Prep. GC afforded two fractions, the first one containing trans-3,6,6-trimethylbicyclo-[3.1.0]hexan-2-one (**5b**) of 65% purity and the second one 3-isopropyl-5-methylcyclopent-2-enone (**6b**) of 85% purity.

Irradiation of 4c. Prep. GC afforded trans-6,6-dimethyl-3-(trifluoromethyl)bicyclo[3.1.0]hexan-2-one (5c, 99% purity). Chromatography (SiO<sub>2</sub>, benzene/AcOEt 95:5) afforded 3-isopropyl-5-(trifluoromethyl)cyclopent-2-enone (6c) of 85% purity.

Irradiation of 4d. Monitoring the reaction by GC/MS indicates the formation of two diastereoisomeric 3-fluoro-6,6-dimethylbicyclo[3.1.0]hexan-2-ones  $5d_x$  and  $5d_y$  (initial ratio 1:1, final ratio 4:5) and 6d. The isomer with the lower  $t_R$  ( $5d_x$ ) also exhibits the higher  $R_f$  value. Chromatography (SiO<sub>2</sub>, benzene/AcOEt 1:1) afforded two fractions: A) 110 mg, a mixture of 65% 4d, 14%  $5d_x$ , and 21% 6d, and B) 28 mg, 1:4 mixture of  $5d_x$  and  $5d_y$ . Fraction A was rechromatographed (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to give 50 mg of a 1:2 mixture of 5-fluoro-3-isopropylcyclopent-2-enone (6d) and 4d, and 10 mg of  $5d_x$  of 65% purity.

Irradiation of 4e. Chromatography (SiO<sub>2</sub>, benzene/AcOEt 9:1) afforded 80 mg (53%) of 3,3,6,6-tetramethylbicyclo[3.1.0]hexan-2-one (2e, [14]). A 2:1 mixture of 3-isopropyl-5,5-dimethylcyclopent-2-enone (6e, [14]) and 4e was obtained by prep. GC.

*Irradiation of* **4f.** Monitoring the reaction by GC/MS indicates the formation of two diastereoisomeric 3-fluoro-3,6,6-trimethylbicyclo[3.1.0]hexan-2-ones ( $\mathbf{5f}_x/\mathbf{5f}_y$ ; initial ratio 2:1, final ratio 1:1) and **6f.** The isomer with lower  $t_R$  ( $\mathbf{5f}_x$ ) decomposes during workup. Chromatography (SiO<sub>2</sub>, benzene/AcOEt 9:1) affords two fractions: A) 30 mg of 5-fluoro-3-isopropyl-5-methylcyclopent-2-enone (**6f**) of 89% purity, and B) 110 mg of a 1:1 mixture **4f/5f**<sub>v</sub>. Fraction B was rechromatographed (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) to give 22 mg **5f**<sub>v</sub> of 85% purity.

Irradiation of 4g. Chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>) afforded 84 mg (60%) pure trans-4,6,6-trimethylbicyclo[3.1.0]hexan-2-one (5g) as colorless oil. Prep. GC gave a 5:1 mixture of 3-isopropyl-4-methylcyclopent-2-enone (6g) and 4g.

Irradiation of **4h**. Due to lack of material, this reaction was only pursued by GC/MS. The initial ratio of 4,4,6,6-tetramethylbicyclo[3.1.0]hexan-2-one (**5h**) and 3-isopropyl-4,4-dimethylcyclopent-2-enone (**6h**) was roughly 1:2. As in all irradiations described above, cyclopentenones **6** undergo slow photodecomposition on higher degree of conversion of **4**.

Actinometry. Solns. of 4 (0.1 mmol in 1 ml of MeCN) containing tetradecane as internal standard were irradiated using a 'merry-go-round' setup. The degree of conversion (10–15%) was monitored by GC. A MeCN soln. of 6-(prop-2-enyl)-4,4,6-trimethylcyclohex-2-enone [25] was used as chemical actinometer.

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