261. Photochemical Reactions

125th Communication [1]

Photochemistry of Homoconjugated Cyclobutanones. I. Synthesis and Photolysis of a Spiro[3.6]deca-5,7-dien-1-one

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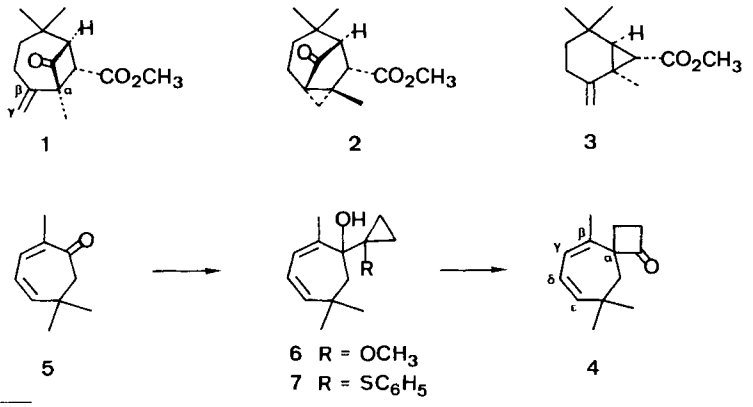
(1.X.81)

Summary

The title compound **4** was prepared in 54% overall yield from eucarvone (**5**). On triplet sensitization **4** gives two products resulting from a 1,2-acyl shift (**8** and **9**), whereas singlet excitation of **4** causes decarbonylation and ketene elimination (**4** → **10** and **11**).

1. Introduction. – In a previous report from this laboratory it was disclosed that on triplet excitation (acetone) the homoconjugated four-membered ring ketone **1** undergoes an oxa-di-π-methane rearrangement giving **2**; however, on singlet excitation ($\lambda > 280$ nm, CH_3CN) **1** decarbonylates forming **3** [2]. Although the conversion **1** → **3** is a well known photoprocess of cyclobutanones [3], the photoisomerization **1** → **2** represents a process having few reported precedents[1]). This

Scheme 1



[1]) For an example see [4].

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finding has encouraged the continuation of our studies of the photochemistry of homoconjugated cyclobutanones, in particular concerning the occurance of an oxa-di-π-methane rearrangement. The present communication describes the photochemistry of the spirocyclic compound **4** which incorporates a 1,3-diene system in homoconjugation with a cyclobutane carbonyl group.

The synthesis of **4** was achieved using the method of *Cohen & Matz* [5]: Reaction of eucarvone (**5**) with 1-lithio-1-methoxycyclopropane [6][2]) to give **6** followed by treatment with 50% aqueous HBF_4 solution/THF 1:4 afforded **4** in an overall yield of 54%[3]).

Scheme 2

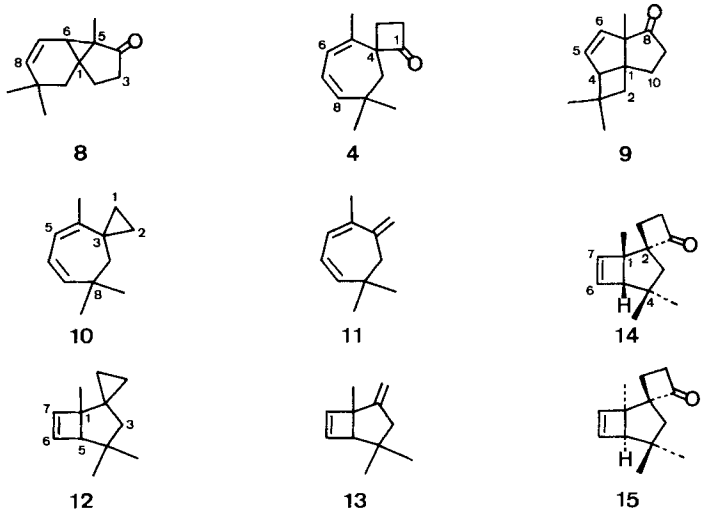

Table. *Results of the photolysis of* **4**

λ [nm]	Solvent	Conversion [%]	Product distribution [%][a])								
				8	**9**	**10**[c])	**11**[b])	[8] **12**[c])	**13**[c])	[8] **14**	**15**
>280	Acetone	~100	[d])	46	18	–	–	–	–	5	3
254	Pentane	~100	[e])	<1	–	~1	2	45	20	3	10
>327[f])	Pentane	37	[e])	–	–	65	30	–	2	–	–
>327[f])	Pentane	96	[e])	–	–	62	11	–	22	–	–

[a]) Yields are based on converted starting material.
[b]) Identified by coinjection with an authentic sample.
[c]) Isolated by preparative GLC.
[d]) Isolated yields after chromatography and distillation.
[e]) Yields were determined by capillary GLC. using nonadecane as an internal standard.
[f]) Acetone filter.

[2]) Prepared by reductive lithiation of 1-methoxy-1-(phenylthio)cyclopropane with lithium *N,N*-dimethylnaphthalenide [6].

[3]) Our attempts to synthesize **4** using the method of *Trost et al.* [7] *via* the thio derivative **7** were unsuccessful due to problems encountered in the rearrangement **7** → **4**. After extensive experimentation, the best conditions (85% aqueous formic acid) afforded **4** in only 25% yield (13% overall yield from **5**).

2. Photolysis experiments. – 2.1. *Irradiation of* **4**. The results are summarized in the *Table* and the photoproducts **8**–**15** are shown in *Scheme 2*.

2.2. *Irradiation of* **10**. Photolysis of **10** ($\lambda > 280$ nm, pentane) gave **12** as the only product.

3. Structure of the compounds. – *Spirocyclobutanone* **4**. The main structural features of this compound are evidenced by its spectral data. In particular, the band at 1780 cm^{-1} in the IR. spectrum signifies the cyclobutanone functionality. The UV. spectrum includes a structured π,π^*-band (258 nm, $\varepsilon = 11400$) typical for a homoconjugated diene chromophore. The ^{1}H-NMR. spectrum includes signals for three olefinic H-atoms, two H-atoms α to the carbonyl (2.80–3.24 ppm), and a vinylic methyl group at 1.80 ppm. Significant signals in the ^{13}C-NMR. spectrum are three *t* arising from C(2), C(3) and C(10).

Tricyclo[4.4.0.0^{1,5}]decenone **8**. The structure of **8** was elucidated from its spectral data. In particular, the IR. band at 1720 cm^{-1} is indicative of the α-cyclopropyl carbonyl moiety, and in the ^{1}H-NMR. spectrum one of the vinyl H-atoms indicates coupling ($J = 3$ Hz) with the cyclopropyl allylic H-atom at C(6).

Further evidence for structure **8** was obtained by reductive cleavage of the C(5), C(6) cyclopropyl bond with Li in NH_3, giving the expected mixture of interconvertable epimeric spiro ketones **16A**+**B** (see *Scheme 3*). The major epimer **16A**[4]) exhibits an IR. band at 1740 cm^{-1}, and in the ^{1}H-NMR. spectrum, the vinyl H-atom at 5.70 ppm shows the appropriate allylic coupling (*t*, $J = 4$ Hz) with 2 H–C(6), and H_3C–C(1) appears as a *d* at 0.88 ppm ($J = 7$ Hz).

Scheme 3

8 **16 A + B**

Tricyclo[5.3.0.0^{1,4}]decenone **9**. The spectral evidence for the homoconjugated cyclopentanone and the cyclobutane moieties includes: the fine structure and the large ε (207) of the n,π^*-band at 303 nm in the UV. spectrum, the IR. band at 1740 cm^{-1}, and a peak at *m/z* 134 in the MS. (loss of 2-methyl-1-propene). ^{1}H-NMR. (300 MHz) decoupling experiments included irradiation at 2.72 ppm which changed the three $d \times d$ at 1.61, 5.51, and 5.74 ppm to *d*, indicating the coupling of H–C(4) with H–C(2), H–C(6) and H–C(5); irradiation at 1.82 ppm simplified the *m* at 2.10–2.40 ppm and sharpened the $d \times d$ at 5.74 ppm, which led to the assignment of the *m* at 1.71–1.89 ppm to one of the C(10) H-atoms. The final assignment of all signals in the 300-MHz-^{1}H-NMR. spectrum was made by comparison of the spectrum of **9** with the spectrum of [$^2H_2$]-**9** (see *Figure*) which was obtained from **9** by base catalyzed deuterium exchange.

Bicycloheptene **12**. The structure of **12** was elucidated by comparison of its ^{1}H-NMR. spectrum with that of **13** [8], showing the same pattern for the protons at C(3), a very similar pattern for the olefinic protons at C(6) and C(7), and the allylic cyclobutane H-atom. The cyclopropyl function of **12** is evidenced by the high field signals in the ^{1}H-NMR. and the two upfield *t* in the ^{13}C-NMR. spectrum (see *Exper. Part*).

Bicyclospiroketones **14** *and* **15**. The structures of these diastereoisomers are supported by comparison of their spectra with each other and with the spectra of the corresponding bicycloheptenes **12** and **13**. Both compounds **14** and **15** exhibit almost identical IR. spectra. In the ^{1}H-NMR. spectrum the anisotropy due to the carbonyl group of **14** is evidenced by the separated pattern of the olefinic H-atoms, unlike the one of the olefinic H-atoms of **12**, **13**, and **15**. The influence of the carbonyl group also accounts for the deshielding of two methyl groups in **15**, whereas only one methyl group is deshielded in **14**.

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[4]) The minor epimer **16B** was not isolated in pure form.

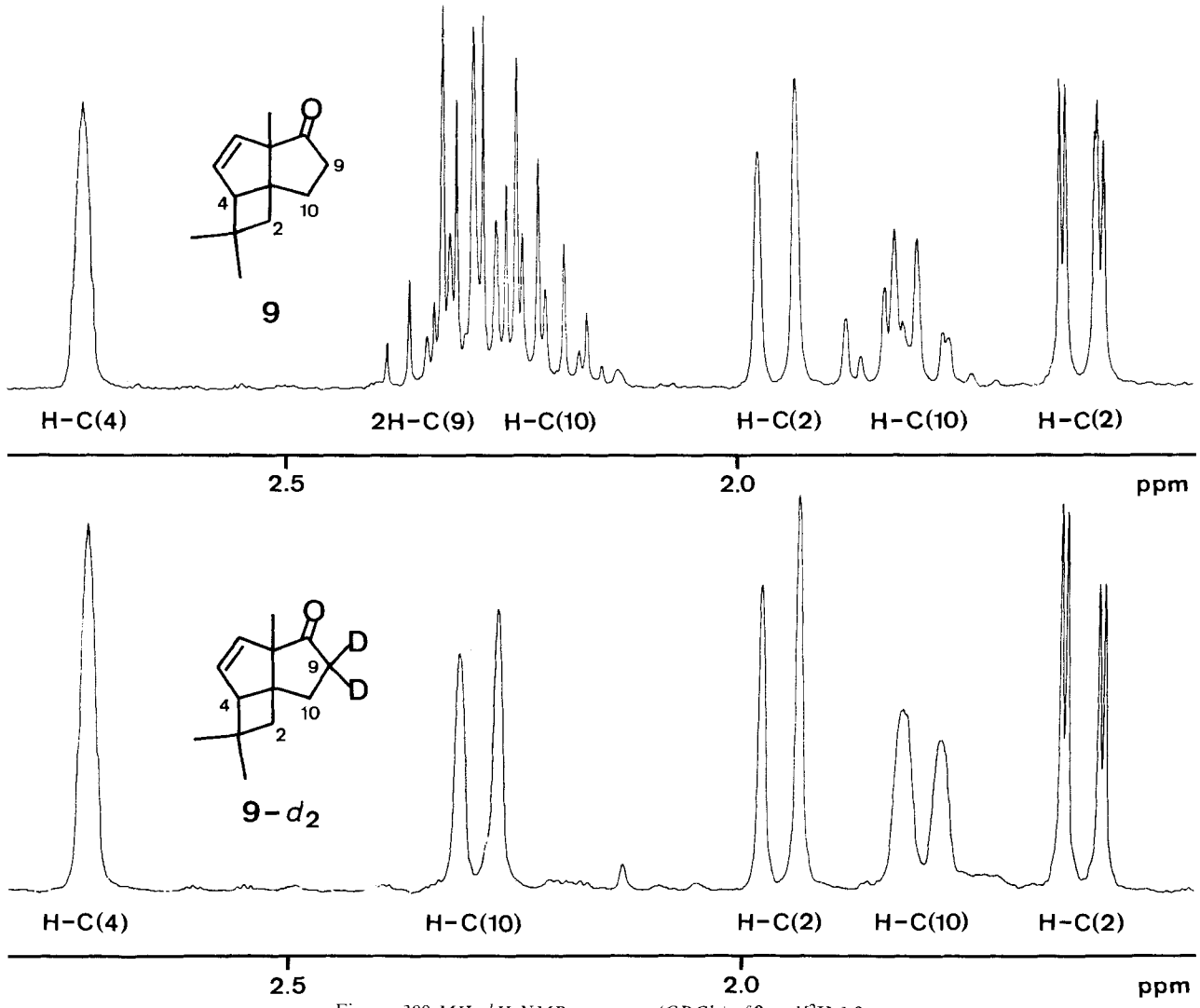
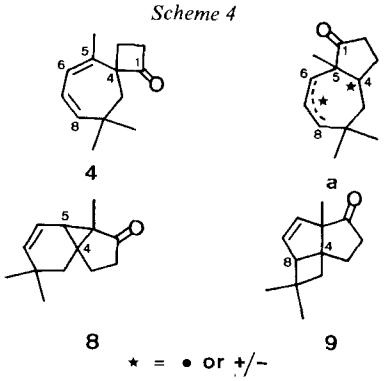


Figure. *300-MHz-^{1}H-NMR. spectrum ($CDCl_3$) of* **9** *and* [$^2H_2$]-**9**

4. Discussion. – In an analogous manner to the homoconjugated cyclobutanone **1** *(Scheme 1)*, compound **4** shows a strong dependence upon the mode of excitation. Thus, on triplet sensitization (acetone) **4** undergoes a 1,2-acyl shift (**4**→**a**) forming **8** by an oxa-di-π-methane rearrangement, and **9** by a vinylogous process[5]) (bond formation in **a** between C(4) andC(8) *(Scheme 4)*). On the other hand, singlet excitation of **4** in pentane ($\lambda = 254$ nm or $\lambda > 327$ nm) gives rise to decarbonylation (**4**→**10**) and ketene elimination (**4**→**11**) accompanied by electrocyclization (**10**→**12** and **11**→**13**) [8][6]). In addition to the aforementioned processes, on singlet ($\lambda = 254$ nm) and acetone sensitized excitation, **4** undergoes diene cyclization without cleavage of the cyclobutanone system giving **14** and **15**.

Scheme 4



This work was carried out with the financial support of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and *Ciba-Geigy Ltd.*, Basle.

Experimental Part

General. See [10] except as noted below. Melting points were determined in capillary tubes using a Büchi melting point apparatus and are uncorrected. Analytical gas chromatography (GC.) was performed using a 25 m × 0.36 mm *Ucon 50 HB 5100* capillary column. Prep. GC. was carried out using a 10′ × ⅜″ 5% *SE-30* column. All NMR. spectra were taken in $CDCl_3$ solution.

1. Preparation of 4. – 1.1. Via **6**. A stirred solution of 3.42 g (20 mmol) of 1-(*N*,*N*-dimethylamino)-naphthalene in 100 ml of THF was cooled to −45°, and 0.1 g (15 mmol) of Li wire was added in small pieces. The mixture was stirred for 4.5 h to insure complete reaction of Li. After cooling the mixture to −78°, a solution of 1.16 g (6.4 mmol) of 1-methoxy-1-(phenylthio)cyclopropane [6] in 10 ml of THF was added, and the mixture stirred for 45 min. Then 0.75 g (5.0 mmol) of eucarvone (**5**) in 10 ml of THF were added. The mixture was stirred for 15 min, quenched by the addition of water, and extracted with ether. After drying over K_2CO_3, the solvents were removed, and the residue chromatographed (ether/pentane 1:5) to give the crude α-methoxyalcohol **6** which was treated directly with 57 ml of 50% aq. HBF_4 solution/THF 1:4 for 20 min at 25°. After dilution with water, the mixture was extracted with hexane, and the organic layers were washed with water and dried over K_2CO_3. Removal of the solvent followed by distillation of the residue (120°/0.04 Torr) afforded 0.52 g (54%) of *5,9,9-Trimethylspiro[3.6]deca-5,7-dien-1-one* (**4**), b.p. 90°/0.01 Torr. – UV. (0.199 mg in 10 ml): 251 *S* (10500), 258 (11400), 268 (8300). – UV. (2.15 mg in 2 ml): end absorption to 350. – IR.: 3015*m*, 2960*s*, 2940*m*, 2920*m*, 2905*m*, 2890*m*, 2865*m*, 2835*w*, 1780*s*, 1620*m*, 1470*m*, 1460*m*, 1450*m*, 1430*w*, 1390*m*, 1375*m*, 1360*m*, 1235*w*, 1175*m*, 1150*m*, 1120*m*, 1080*s*, 1060*w*, 1040*m*, 910*w*, 885*w*, 860*w*. – ^{1}H-NMR.: 1.08 (*s*, 2 H_3C–C(9)); 1.80 (*s*, H_3C–C(5)); 1.76–2.38 (*m*, 2 H–C(10), 2 H–C(3)); 2.80–3.24 (*m*, 2 H–C(2)); 5.40–5.70 (*m*, H–C(6), H–C(7),

[5]) A similar rearrangement has been previously reported for homoconjugated dienyl imides [9].

[6]) In contrast to the triene **11**, the diene **10** is photostable at $\lambda > 327$ nm.

H–C(8)). – ^{13}C-NMR.: 23.3, 26.3, 31.7 (3 *qa*); 23.8 (*t*, C(3)); 44.4, 45.0 (2 *t*, C(2), C(10)); 121.4, 124.0, 142.9 (3 *d*, C(6), C(7), C(8)); 37.2 (*s*, C(9)); 74.4 (*s*, C(4)); 137.5 (*s*, C(5)); 211.7 (*s*, C(1)). – MS.: 190 (11, M^+, $C_{13}H_{18}O$), 148 (27), 133 (31), 119 (32), 106 (45), *105* (100), 91 (28), 77 (11), 41 (14).

$C_{13}H_{18}O$ (190.29) Calc. C 82.06 H 9.54% Found C 82.00 H 9.42%

1.2. Via **7**. – 1.2.1. *Preparation of* **7**. A solution of 1.2 g (8.0 mmol) of cyclopropyl phenyl sulfide [7] in 30 ml of dry THF was cooled to 0° and 3.5 ml (7 mmol) of 2M butyl lithium in hexane was added and stirred for 2 h. After cooling the solution to –78°, 1.0 g (6.7 mmol) of eucarvone (**5**) was added and rinsed in with 3 ml of dry THF. The solution was stirred for 1 h, 5 ml of H_2O were added, and the mixture was worked up with hexane. The residue was chromatographed (SiO_2, hexane/ether 4:1) to give an oil which was heated at 90°/0.01 Torr to remove **5**, affording 1.27 g (64%) of *2,6,6-Trimethyl-1-(1'-(phenylthio)cyclopropyl)-2,4-cycloheptadienol* (**7**) as a colorless oil. – UV. (0.156 mg in 10 ml): 253 (13900). – IR.: 3635*m*, 3550*w* br., 3080*w*, 3060*w*, 3015*s*, 2960*s*, 2915*m*, 2905*m*, 2865*m*, 1580*m*, 1480*s*, 1475*s S*, 1460*m*, 1450*m*, 1440*s*, 1420*w*, 1410*w*, 1375*m*, 1360*m*, 1350*w*, 1330*w*, 1290*w* br., 1250*w*, 1220*w* br., 1170*m* br., 1160*m S*, 1340*m S*, 1335*m*, 1085*w*, 1065*m*, 1060*m*, 1030*s*, 980*w*, 955*m*, 945*w*, 930*w*, 920*w*, 895*w*, 870*w*, 720*m*, 700*m*. – ^{1}H-NMR.: 0.75–1.50 (*m*, 2 H–C(2'), 2 H–C(3')); 1.10, 1.13 (2 *s*, 2 H_3C–C(6)); 1.78 (*d*, *A* part of *AB* system, J = 15, H–C(7)); 1.79 (*m*, $w_{1/2}$ = 2.5, H_3C–C(2)); 1.91 (*s*, HO); 2.62 (*d*, *B* part of *AB* system, J = 15, H–C(7)); 5.50–5.70 (*m*, H–C(3), H–C(4), H–C(5)); 7.12–7.31, 7.36–7.56 (2 *m*, C_6H_5S–C(1')). – ^{13}C-NMR.: 22.7, 26.0, 32.7 (3 *qa*, H_3C–C(2), 2 H_3C–C(6)); 12.5, 15.5 (2 *t*, C(2'), C(3')); 53.0 (*t*, C(7)); 121.7, 124.5, 126.9, 128.2, 132.6, 143.6 (8 *d*, 2 *d* at 128.2 and 132.6, 5 arom. *C*H, C(3), C(4), C(5)); 34.8, 35.6 (2 *s*, C(1'), C(6)); 78.3 (*s*, C(1)); 135.6, 141.9 (2 *s*, C(2), arom. S–*C*). – MS.: (4, M^+, $C_{19}H_{24}OS$), 173 (16), 158 (13), 157 (18), *151* (100), 150 (27), 149 (19), 143 (13), 142 (11), 131 (28), 129 (17), 128 (14), 117 (25), 116 (15), 115 (19), 109 (11), 105 (16), 91 (30), 77 (15), 65 (12), 43 (15), 41 (19).

$C_{19}H_{24}OS$ (300.46) Calc. C 75.95 H 8.05 S 10.76% Found C 75.99 H 8.10 S 10.55%

1.2.2. *Transformation of* **7** *into* **4**. A stirred solution of 200 ml of 85% aq. formic acid was cooled to –5°, and 2.0 g (6.6 mmol) of neat **7** was added. After stirring at –5° for ½ h, the cold bath was removed and stirring continued for 3 h. The mixture was poured into water and worked up with pentane, chromatographed (SiO_2, ether/hexane 1:9) and distilled (100°/0.01 Torr) to give 315 mg (25%) of **4** as a colorless oil.

2. Photolysis Experiments. – 2.1. *Irradiation of* **4**. 2.1.1. *Triplet sensitization of* **4** *in acetone at* $\lambda > 280$ *nm*. A solution of 748 mg (3.9 mmol) of **4** in 250 ml of acetone was irradiated (pyrex, lamp *B*, *ca.* 100% conversion). Chromatography (SiO_2, ethyl acetate/hexane 1:24) and distillation (80°/0.01 Torr) of the pure fractions gave 341 mg (46%) of **8**, 137 mg (18%) of **9** and 20 mg (3%) of **15**. HPLC. (SiO_2, ether/pentane 1:24) of a mixed fraction and distillation (80°/0.01 Torr) afforded 36 mg (5%) of **14**. *5,9,9-Trimethyltricyclo[4.4.0.0^{1,5}]dec-7-en-4-one* (**8**). M.p. 43° (pentane). – UV. (0.194 mg in 10 ml): 218 (9400). – UV. (1.70 mg in 2 ml): 281 (58). – IR.: 3020*m*, 2960*s*, 2930*s*, 2865*m*, 1720*s*, 1465*m*, 1460*m*, 1415*w*, 1390*w*, 1380*w*, 1375*w*, 1360*m*, 1325*m*, 1310*w*, 1280*w*, 1270*w S*, 1245*w*, 1180*w*, 1155*w*, 1120*w*, 1095*w*, 1075*m*, 1050*m*, 1020*w*, 985*w*, 950*w*, 910*w*, 865*s*, 840*w*. – ^{1}H-NMR.: 0.98 (6 H) and 1.10 (2 *s*, H_3C–C(5) and 2 H_3C–C(9)); 1.54–1.70 (*m*, H–C(6), 2 H–C(10)); 1.72–2.40 (*m*, 2 H–C(2), 2 H–C(3)); 5.48 (*d*×*d*, J_1 = 10, J_2 = 3, H–C(7)); 5.76 (*d*, J = 10, H–C(8)). – ^{13}C-NMR.: 6.0 (*qa*, H_3C–C(5)); 29.1, 29.6 (2 *qa*, 2 H_3C–C(9)); 30.6 and 32.6 (2 *t*, C(2) and C(10)); 39.7 (*t*, C(3)); 27.2 (*d*, C(6)); 121.0 and 142.9 (2 *d*, C(7) and C(8)); 31.7 and 32.8 (2 *s*, C(1) and C(9)); 43.3 (*s*, C(5)); 213.8 (*s*, C(4)). – MS.: 190 (73, M^+, $C_{13}H_{18}O$), 175 (28), 162 (24), 148 (46), 147 (61), 134 (18), 133 (61), 120 (19), *119* (100), 117 (12), 107 (10), 106 (28), 105 (75), 93 (12), 92 (18), 91 (45), 77 (22), 65 (13), 55 (13), 41 (28).

$C_{13}H_{18}O$ (190.29) Calc. C 82.06 H 9.54% Found C 81.92 H 9.49%

3,3,7-Trimethyltricyclo[5.3.0.0^{1,4}]dec-5-en-8-one (**9**). B.p. 80°/0.01 Torr. – UV. (1.76 mg in 2 ml): 295 *S* (159), 303 (207), 313 (205), 325 (114). – IR.: 3050*m*, 2950*s*, 2925*s*, 2900*m*, 2880*m*, 2860*m*, 1740*s*, 1600*w*, 1460*m*, 1450*m*, 1435*m*, 1410*m*, 1380*w*, 1370*m*, 1340*w*, 1280*w*, 1270*w*, 1260*w*, 1210*w*, 1180*w* br., 1070*m*, 1050*m*, 1020*w*, 965*w*, 935*w*, 900*w*, 875*w*. – ^{1}H-NMR. (300 MHz): 0.91, 1.08 and 1.28 (3 *s*, 2 H_3C–C(3) and H_3C–C(7)); 1.61 (*d*×*d*, *A* part of *AB* system, J_1 = 12.4, J_2 = 2.0, H–C(2)); 1.71–1.89 (*m*, H–C(10)); 1.95 (*d*, *B* part of *AB* system, J = 12.4, H–C(2)); 2.10–2.40 (*m*, 2 H–C(9) and H–C(10)); 2.72 (*m*, $w_{1/2}$ = 5.2, H–C(4)); 5.51 (*d*×*d*, J_1 = 5.3, J_2 = 1.3, H–C(6)); 5.74 (*d*×*d*, J_1 = 5.3, J_2 = 2.3, H–C(5)). – ^{13}C-NMR.: 15.0, 24.6 and 31.0 (3 *qa*, 2 H_3C–C(3) and H_3C–C(7)); 31.6, 35.9 and 39.2

(3 *t*, C(2), C(9) and C(10)); 61.0 (*d*, C(4)); 133.7 and 136.3 (2 *d*, C(5) and C(6)); 34.4 (*s*, C(3)); 48.0 (*s*, C(1)); 62.9 (*s*, C(7)); 218.9 (*s*, C(8)). – MS.: 190 (6, M^+, $C_{13}H_{18}O$), 134 (26), 119 (11), *92* (100), 91 (24).

$C_{13}H_{18}O$ (190.29) Calc. C 82.06 H 9.54% Found C 82.16 H 9.69%

(1R,2S*,5R*))-1,4,4-Trimethylbicyclo[3.2.0]hept-6-ene-2-spiro-1'-cyclobutan-2'-one* (**14**). B.p. 70°/0.01 Torr. – UV. (1.8 mg in 2 ml): 287 *S* (34), 300 (41), 312 *S* (39), 324 *S* (25). – IR.: 3140*w*, 3050*m S*, 3040*m*, 3000*m*, 2960*s*, 2925*s*, 2905*s*, 2870*m*, 1775*s*, 1465*m*, 1450*m*, 1395*w*, 1385*w*, 1375*w*, 1365*m*, 1300*w*, 1290*w*, 1260*w*, 1240*w*, 1225*w*, 1205*w*, 1175*w*, 1150*m*, 1110*m*, 1075*m*, 1020*m*, 1000*w*, 935*w*, 920*w*, 885*w*, 865*w*. – ^{1}H-NMR.: 0.91, 0.94 and 1.34 (3 *s*, 2 H_3C–C(4) and H_3C–C(1)); 1.52–2.04 (*m*, 2 H–C(3)); 2.22–2.70 (*m*, 2 H–C(4') and H–C(5)); 2.73–3.00 (*m*, 2 H–C(3')); 5.92–6.02, 6.12–6.22 (2 *m*, with *d* character, H–C(6) and H–C(7)). – ^{13}C-NMR.: 19.1, 25.2 and 28.6 (3 *qa*, H_3C–C(1) and 2 H_3C–C(4)); 23.7 (*t*, C(4')); 44.8 and 49.3 (2 *t*, C(3) and C(3')); 66.1 (*d*, C(5)); 133.9 and 142.8 (2 *d*, C(6) and C(7)); 36.1 (*s*, C(4)); 59.2 (*s*, C(1)); 71.9 (*s*, C(2)); 214.8 (*s*, C(2')). – MS.: 190 (3, M^+, $C_{13}H_{18}O$), 148 (23), 133 (32), 119 (43), 106 (56), *105* (100), 92 (15), 91 (44), 77 (14), 41 (16).

$C_{13}H_{18}O$ (190.29) Calc. C 82.06 H 9.54% Found C 81.97 H 9.46%

(1R,2R*,5R*)-1,4,4-Trimethylbicyclo[3.2.0]hept-6-ene-2-spiro-1'-cyclobutan-2'-one* (**15**). B.p. 70°/0.01 Torr. – UV. (2.0 mg in 2 ml): 289 *S* (48), 299 *S* (54), 303 (55), 312 *S* (53), 325 *S* (32)). – IR.: 3130*w*, 3045*m*, 3030*m S*, 2980*m S*, 2955*s*, 2925*s*, 2915*s*, 2865*s*, 2850*m*, 1770*s*, 1470*m*, 1455*m*, 1440*w*, 1400*w*, 1390*w*, 1375*w*, 1370*m*, 1305*m*, 1290*w*, 1270*w*, 1230*w* br., 1200*w*, 1185*w*, 1175*w*, 1160*w*, 1150*w*, 1105*m*, 1070*m S*, 1065*m*, 1050*m*, 1015*w*, 975*w*, 945*w*, 925*w* br., 885*w*, 855*w* br. – ^{1}H-NMR.: 0.92, 1.12 and 1.26 (3 *s*, H_3C–C(1) and 2 H_3C–C(4)); 1.52–2.14 (*m*, 2 H–C(3) and 2 H–C(4')); 2.37 (*s*, H–C(5)); 2.60–2.98 (*m*, 2 H–C(3')); 6.01–6.18 (*m*, H–C(6) and H–C(7)). – ^{13}C-NMR.: 18.2, 26.0 and 27.9 (3 *qa*, H_3C–C(1) and 2 H_3C–C(4)); 19.7 (*t*, C(4')); 42.2 and 48.9 (2 *t*, C(3) and C(3')); 65.6 (*d*, C(5)); 136.9 and 140.6 (2 *d*, C(6) and C(7)); 36.4 (*s*, C(4)); 59.6 (*s*, C(1)); 72.2 (*s*, C(2)); 213.5 (*s*, C(2')). – MS.: 190 (< 1, M^+, $C_{13}H_{18}O$), 147 (14), 134 (36), 133 (28), 120 (12), 119 (86), 107 (22), 106 (91), 105 (94), 93 (18), 92 (46), *91* (100), 79 (17), 77 (23), 65 (14), 55 (11), 53 (12), 41 (27).

$C_{13}H_{18}O$ (190.29) Calc. C 82.06 H 9.54% Found C 81.81 H 9.43%

2.1.2. *Irradiation of* **4** *in pentane at* $\lambda > 327$ *nm.* A solution of 90 mg (0.5 mmol) of **4** and 29 mg of nonadecane in 9 ml of pentane was irradiated (acetone, lamp *B*). The product yields as estimated by GLC. after 37% conversion were: 65% of **10**, 30% of **11** [8] and 2% of **13**; and after 96% conversion were: 62% of **10**, 11% of **11** [8] and 22% of **13**. *4,8,8-Trimethylspiro[2.6]nona-4,6-diene* (**10**). Isolation by GLC. – UV. (0.252 mg in 20 ml): 260 (11100). – IR.: 3090*m*, 3010*s*, 2970*s S*, 2955*s*, 2940*s S*, 2925*s*, 2905*s*, 2865*s*, 2835*m*, 1640*w*, 1605*s*, 1470*s*, 1460*s*, 1445*s*, 1425*m*, 1405*m*, 1375*s*, 1360*s*, 1340*w*, 1315*w*, 1250*w*, 1205*w*, 1170*m*, 1165*w*, 1150*m*, 1110*s*, 1065*w*, 1050*m*, 1030*w*, 1020*s*, 985*s*, 960*w*, 930*w*, 910*m*, 905*m*, 885*s*, 870*m*, 840*w*. – ^{1}H-NMR.: 0.54–0.99 (m, 2 H–C(1) and 2 H–C(2)); 1.04 (s, 2 H_3C–C(8)); 1.49 (m, $w_{1/2}$ = 3, H_3C–C(4)); 1.56 (s, 2 H–C(9)); 5.42–5.71 (m, H–C(5), H–C(6) and H–C(7)). – ^{13}C-NMR.: 22.4 (*qa*, H_3C–C(4)); 29.4 (2 *qa*, 2 H_3C–C(8)); 12.6 (2 *t*, C(1) and C(2)); 50.3 (*t*, C(9)); 121.5, 121.9 and 140.8 (3 *d*, C(5), C(6) and C(7)); 23.1 (*s*, C(3)); 38.1 (*s*, C(8)); 142.5 (*s*, C(4)). – MS.: 162 (32, M^+, $C_{12}H_{18}$), 147 (35), 133 (15), 120 (15), *119* (100), 117 (11), 106 (14), 105 (41), 93 (13), 91 (41), 79 (13), 77 (16), 55 (13), 41 (22).

$C_{12}H_{18}$ (162.28) Calc. C 88.82 H 11.18% Found C 88.80 H 11.18%

2.1.3. *Irradiation of* **4** *in pentane at* $\lambda = 254$ *nm.* A solution of 1.0 g (5.3 mmol) of **4** and 121 mg of nonadecane in 150 ml of pentane was irradiated (quartz, lamp *A*, *ca.* 100% conversion). The product yields as estimated by GLC. were: < 1% of **8**, *ca.* 1% of **10**, 2% of **11** [8], 45% of **12**, 20% of **13**, 3% of **14** and 10% of **15**. *1,4,4-Trimethylbicyclo[3.2.0]hept-6-ene-2-spiro-1'-cyclopropane* (**12**). Isolation by GLC. – IR.: 3125*w*, 3075*m*, 3040*m*, 3030*m S*, 2995*m*, 2955*s*, 2920*s*, 2900*s*, 2860*s*, 1460*m*, 1450*m*, 1420*w*, 1380*m*, 1370*m*, 1360*m*, 1300*m*, 1270*w*, 1230*w*, 1210*w*, 1200*w*, 1155*m*, 1125*w*, 1075*w*, 1045*w*, 1010*m*, 955*m*, 925*w*, 920*w S*, 910*w S*, 880*m*, 865*w*, 850*w*. – ^{1}H-NMR.: 0.06–0.77 (*m*, 2 H–C(2') and 2 H–C(3')); 0.86 (*d*, *A* part of *AB* system, *J* = 12, H–C(3)); 0.90 and 1.02 (2 *s*, H_3C–C(1) and 2 H_3C–C(4), *s* (6 H) at 0.90 overlapping with one peak of *d* at 0.86); 2.22 (*d*, *B* part of *AB* system, *J* = 12, H–C(3)); 2.36 (*s*, H–C(5)); 5.96–6.09 (*m*, H–C(6) and H–C(7)). – ^{13}C-NMR.: 18.2, 25.1 and 28.4 (3 *qa*, H_3C–C(1) and 2 H_3C–C(4)); 2.6 and 12.1 (2 *t*, C(2') and C(3')); 49.1 (*t*, C(3)); 65.6 (*d*, C(5)); 134.3 and 142.7 (2 *d*, C(6) and C(7)); 22.9 (*s*, C(2)); 37.2 (*s*, C(4)); 55.7 (*s*, C(1)). – MS.: 162 (1, M^+, $C_{12}H_{18}$), 147 (27), 134

(15), 133 (12), 120 (13), *119* (100), 117 (11), 107 (12), 106 (60), 105 (43), 93 (14), 92 (12), 91 (88), 79 (16), 77 (20), 65 (11), 55 (13), 41 (24).

$C_{12}H_{18}$ (162.28) Calc. C 88.82 H 11.18% Found C 88.65 H 11.04%

2.2. *Irradiation of* **10** *in pentane at* $\lambda > 280$ *nm.* A solution of 30 mg (0.18 mmol) of **10** in 10 ml of pentane was irradiated (pyrex, lamp *B*, 70% conversion) to give **12** as the only product.

3. Additional experiments. – 3.1. *Reductive cleavage of* **8**. A solution of 190 mg (1.0 mmol) of **8** in 10 ml of dry ether was added over 5 min to a stirred solution of 400 mg (58 mmol) of Li dissolved in 75 ml of liquid NH_3 at $-78°$. The cold bath was removed to allow the NH_3 to reflux for 1.75 h followed by the careful addition of sat. NH_4Cl-solution to quench the reaction. The mixture was diluted with 150 ml of ether and the NH_3 allowed to evaporate over several h. The resulting mixture was washed with 1M HCl and worked up with ether to give a yellow oil which was dissolved in 50 ml of ether and treated with dichromate solution for 2 min. Dilution of the mixture with water and work-up with ether gave a yellow oil which was chromatographed on SiO_2 (ethyl acetate/hexane 1:19) to give 48 mg (25%) of **16A** as a single isomer, and 64 mg (34%) of **16A** + **B** as a mixture of epimers.

3.2. *Base catalyzed equilibration of mixtures of* **16A** + **B**. Two 15-mg samples of **16A** + **B** consisting of 89 and 68% of **16A**, respectively (GLC.), were treated separately with 5 ml of 2M KOH in methanol for 17 h. GLC. of the two mixtures indicated a 3:1 ratio of **16A** and **16B**. *1,9,9-Trimethylspiro[4.5]-dec-7-en-2-one* (**16A**). B.p. 90°/0.01 Torr. – UV. (2.0 mg in 2 ml): 299 (25). – IR.: 3015*m*, 2975*s*, 2955*s*, 2930*s*, 2900*s*, 2870*s*, 2830*s*, 1740*s*, 1455*m*, 1430*w*, 1410*m*, 1395*w*, 1385*w*, 1375*w*, 1365*m*, 1350*w*, 1305*w*, 1295*w S*, 1280*w*, 1220*w*, 1170*m*, 1155*w*, 1140*w*, 1130*w S*, 1065*m*, 1030*w*, 1020*w*, 1010*w*, 990*w*, 980*w*, 960*w*, 880*w*. – ^{1}H-NMR.: 0.88 (*d*, J=7, H_3C–C(1)); 0.97 and 1.01 (2 *s*, 2 H_3C–C(9)); 1.22–2.46 (*m*, H–C(1), 2 H–C(3), 2 H–C(4), 2 H–C(6) and 2 H–C(10)); 5.25 (*d*×*m*, J=10, H–C(8)); 5.70 (*d*×*t*, J_1=10, J_2=4, H–C(7)). – ^{13}C-NMR. (~90% pure): 8.3 (*qa*, H_3C–C(1)); 27.5 and 32.3 (2 *qa*, 2 H_3C–C(9)); 35.3, 35.9 and 39.0 (3 *t*, C(4), C(6) and C(10)); 47.9 (*t*, C(3)); 54.7 (*d*, C(1)); 127.1 and 127.7 (2 *d*, C(7) and C(8)); 29.8 (*s*, C(9)); 44.6 (*s*, C(5)); 219.0 (*s*, C(2)). – MS.: 192 (39, M^+, $C_{13}H_{20}O$), 177 (13), 159 (12), 136 (14), 135 (12), 122 (12), 121 (39), 120 (49), 107 (31), 106 (10), *105* (100), 93 (32), 91 (16), 79 (22), 77 (16), 41 (17).

$C_{13}H_{20}O$ (192.30) Calc. C 81.20 H 10.48% Found C 81.38 H 10.61%

3.2. *Preparation of* [$^2H_2$]-**9**. To a stirred solution of 65 mg (0.34 mmol) of **9** in 5 ml of CH_3OD was added 5 ml of a solution of 30% NaOD in D_2O. After stirring at 22° for 15 h, the mixture was diluted with 20 ml of D_2O and acidified with HCOOH followed by the addition of *ca.* 2 g of $NaHCO_3$. Work-up with ether followed by distillation (80°/0.01 Torr) gave 56 mg (85%) of *9,9-Dideuterio-3,3,7-trimethyltricyclo[5.3.0.0^{1,4}]dec-5-en-8-one* (**9**-d_2). B.p. 80°/0.01 Torr. – ^{1}H-NMR. (300 MHz): same as **9**, except 1.71–1.89 (*m*) and 2.10–2.40 (*m*) replaced by 1.79 (*d*×*m*, *A* part of *AB* system, J=12.8, $w_{1/2}$=6.4, H–C(10)); 2.29 (*d*, *B* part of *AB* system, J=12.8, H–C(10)). – MS.: (estimated 92% d_2, 8% d_1), 192 (12, M^+, $C_{13}H_{16}D_2O$), 136 (47), 119 (22), 105 (13), 93 (29), *92* (100), 91 (43), 41 (11).

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