134. Photochemical Reactions

145th Communication[1])

Carbonyl *vs.* Epoxyketone Photochemistry: Photolysis of 1,2;3,4-Diepoxy-2,6,6-trimethyl-1-cyclohexyl Methyl Ketone

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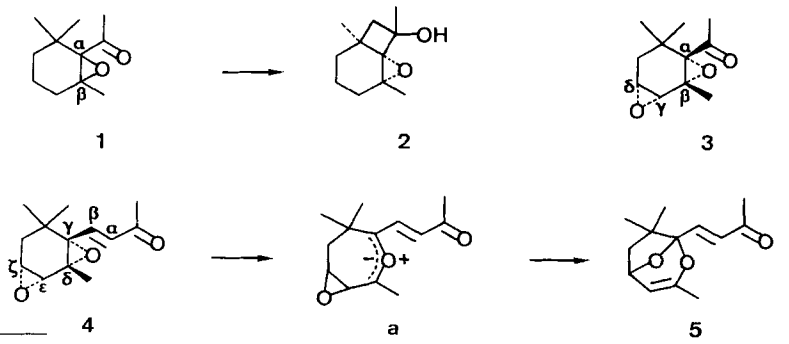
The synthesis and photolysis of the title compound **3** is described. Irradiation ($\lambda > 280$ nm, MeCN) of the di-epoxyketone **3** leads predominantly to γ–H abstraction. Cyclization furnishes the cyclobutanols **22–24**, while cleavage gives compound **25**, presumably *via* the allene-oxide intermediate **36**. Further, products **27** and **28** are formed by *Norrish* fragmentation and by initial cleavage of the C(α)–O bond of the oxirane, respectively. The structures of the products **22–25**, **27**, and **28** were assigned on the basis of the spectral data of the photolysis products of the ^{13}C-labelled diepoxyketone [*6,6-dimethyl*-$^{13}C_2$]-**3** and by X-ray analysis of the compounds **24** and **35**, the latter being the *p*-nitrobenzoate of **22**.

1. Introduction. – Numerous publications on the photochemistry of α,β-epoxyketones disclosed that the predominant processes are the cleavages of the C(α)–O and C(α)–C(β) bonds of the oxirane ring [2]. However, with compounds in which the carbonyl group has intramolecularly abstractable γ–H-atoms, these reactions may be suppressed. Thus, *e.g.* it was reported in [3] that the epoxyketone **1** exclusively undergoes γ–H abstraction and bicyclooctanol formation (**1**→**2**, *Scheme 1*).

Scheme 1



1 **2** **3** **4** **a** **5**

[1]) 144th Communication: [1].

[2]) Part of the planned Ph. D. thesis of *R.P.*

[3]) These authors carried out the X-ray analyses.

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Continuing our studies of the photochemistry of α,β-epoxyketones [3] [4], the diepoxyketone **3** was investigated to delineate the influence of a second, neighboring, γ,δ-epoxy function. The behavior of **3** is of particular interest in comparison with that of the diepoxyenone **4**, which undergoes transformation *via* the ylide intermediate **a** leading to the bicyclic acetal **5** [5] *(Scheme 1)*.

2. Preparation of the Diepoxyketone 3. – Compound **3** was synthesized *via* two different ways starting from the dienol **6**, which was obtained by treatment of safranal (**7**) [6] with MeLi *(Scheme 2)*. Reaction of **6** with $^1O_2$ in MeOH gave the diastereoisomeric endoperoxides **8A** + **B**[5]) (*ca.* 1:1 mixture; 74%), which on treatment with Co(II)-*meso*-tetraphenylporphyrin (CoTPP) [7] in Et_2O afforded the diepoxyalcohols **9A** (32%) and **9B** (35%), as well as the hydroxycyclohexenone **10** (7%) [8] (see *Table*). Oxidation of **9A** + **B** with pyridinium chlorochromate (PCC) [9] gave the diepoxyketone **3** (89%; overall yield from **7**: 40%).

Preparation of **3** *via* the dienone **11** [3] was less efficient (10% overall yield) due to the sluggish oxidation of **6** with MnO_2 at r.t. which afforded **11** in only 28% yield at 60%

Scheme 2

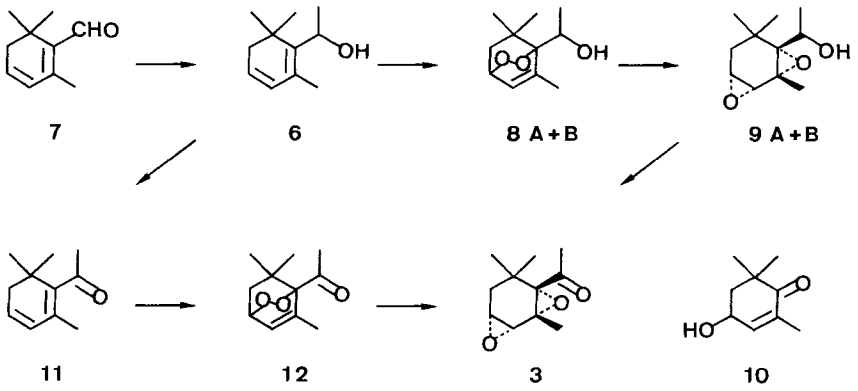


Table. *Results of the Catalytic Rearrangements of* **8A, 8B,** *and* **12** *(Et_2O, 40°)*

Substrate	Reaction conditions		Conversion	Product distribution [%][6])			
	Catalyst	Time	[%]	**3**	**9A**	**9B**	**10** [8]
8A + **8B** (1:1)	CoTPP	18 h	100	–	32	35	7
8A + **8B** (1:1)	Cu_2Cl_2	40 h	87[a])	–	24	35	5
8A + **8B** (1:1)	$FeSO_4$	72 h	91[a])	–	19	32	14
8A	$FeSO_4$	72 h	84	–	43	–	21
8B	$FeSO_4$	16 h	100	–	–	38	21
12	CoTPP	15 h	100	56	–	–	26
12	Cu_2Cl_2	15 h	100	60	–	–	33
12	$FeSO_4$	15 h	93	–	–	–	67

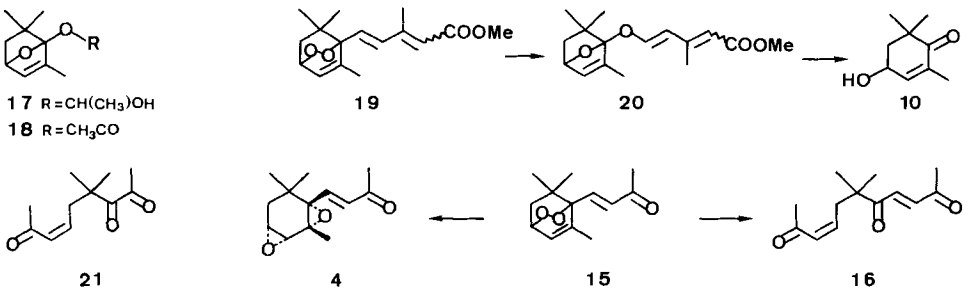
[a]) Only the diastereoisomer **8A** was recovered.

[5]) The terms **A** and **B** are used for the description of diastereoisomers whose configuration was not assigned conclusively.

conversion of 6[6])[7])[8]). Reaction of **11** with $^1O_2$ in MeOH gave the endoperoxide **12** (67%) which, on subsequent treatment with CoTPP, afforded **3** (56%) and the by-product **10** [8] (26%, see *Table*).

In the synthesis of the diepoxyenone **4** *(Scheme 1)*, it was found that the course of the transformation of the endoperoxide **15** to **4** *(Scheme 3)* strongly depends on the catalyst. Thus, the reaction of **15** in the presence of CoTPP [12], Cu_2Cl_2 or $FeSO_4$ [13] led to **4** and the triketone **16**, respectively, in various ratios [5]. Therefore, compounds **8A**, **8B**, and **12** were treated under the same conditions with these three reagents; the results are given in the *Table*.

Scheme 3



The hydroxycyclohexanone **10** is presumably formed by hydrolysis of the postulated acetals **17** or **18** *(Scheme 3)*. A process analogous to **8A** + **B**→**17**→**10** and **12**→**18**→**10** was described originally by *Mousseron-Canet et al.* [8] (**19**→**20**→**10**; *Scheme 3*). It is worth noting that on treatment of **12** with $FeSO_4$, the triketone **21** was not detected, whereas the analogous treatment of **15** led to the triketone **16** in 60% yield [4]. On the other hand, on reaction of **15** compound **10** was not detected[9]).

3. Photolysis of 3. – Irradiation of a *ca.* 0.05M MeCN solution of **3** ($\lambda > 280$ nm, 92% conversion) gave the following products[6])[10]): **22** (29%), **23** (4%), **24** (9%), **25** (7%)[11]), **27** (13%), and **28** (5%).

4. Structure of the Photoproducts. – The structures of compounds **26–28** are derived unequivocally from their spectral data. Most of the evidence stems from the 300-MHz ^{1}H-NMR and the ^{13}C-NMR spectra; for full data and NMR assignments see *Exper. Part.*

The structures of the cyclobutanols **22–24**, however, *(Schemes 4* and *5)* could not be established on the basis of the spectral data available. As alternative structures, formulas **I–III** *(Scheme 5)* had to be considered. For the structure elucidation, the ^{13}C-labelled diepoxide [*6,6-dimethyl-*$^{13}C_2$]-**3** *(Scheme 6)* was, therefore, prepared.

[6]) Yields are based on converted starting material.

[7]) At 40°, the reaction went to complete conversion of **6**; however, the yield of **11** was only 25%, and the by-products **13** (10%) and **14** [10] (16%) were obtained.

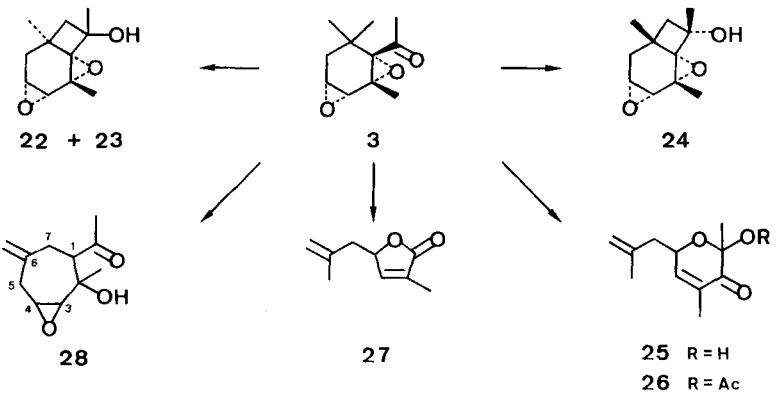
[8]) Similar problems were reported for the oxidation of (2,6,6-trimethyl-1,3-cyclohexadienyl)methanol (safranol), from which safranal (**7**) could be obtained in decent yield only by oxidation with MnO_2 [11].

[9]) Additional experiments to clarify the differing behavior of **12** and **15** are necessary.

[10]) The product distribution was determined by ^{1}H-NMR and GC analysis of the fractions obtained on SiO_2 chromatography of the mixture.

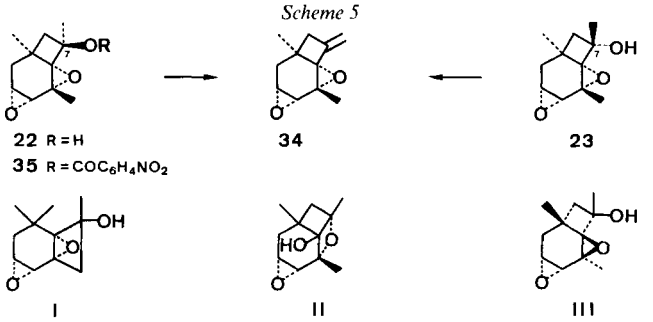
[11]) Compound **25** was unstable and could not be isolated in pure form; therefore, it was transformed to the acetate **26**, which could be purified on SiO_2.

Scheme 4



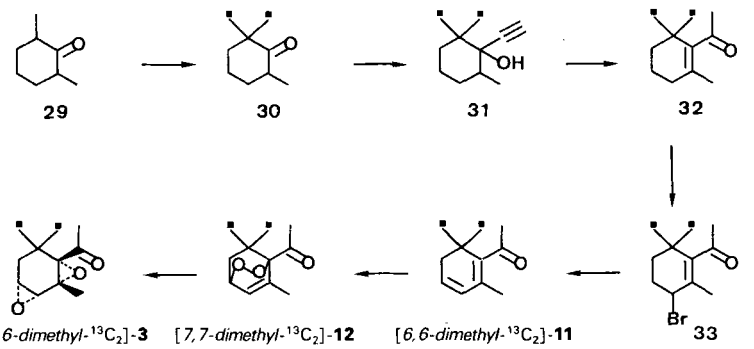
The Synthesis of [*6,6-dimethyl*-$^{13}C_2$]-**3** was achieved as shown in *Scheme 6*. Reaction of the potassium enolate of 2,6-dimethylcyclohexanone (**29**) with [^{13}C]H_3I according to [14] gave [*2,2-dimethyl*-^{13}C]-2,2,6-trimethylcyclohexanone (**30**) which was converted to the propargylic alcohol **31** by reaction with the lithium-acetylide-ethylenediamine complex [15]. Acid-catalyzed rearrangement of **31** with *Dowex 50* (H^+-form) [16] afforded the methyl ketone **32** (overall yield 40% based on [^{13}C]H_3I), which was converted to the dienone [*6,6-dimethyl*-$^{13}C_2$]-**11** (84%)

Scheme 5



by allylic bromination with *N*-bromosuccinimide (**32**→**33**) and subsequent dehydrobromination with LiCl/Li_2CO_3/DMF [17] [3]. Compound [*6,6-dimethyl*-$^{13}C_2$]-**11** was mixed with unlabelled **11** to obtain material with 32% ^{13}C-enrichment. Reaction of [*6,6-dimethyl*-$^{13}C_2$]-**11** with $^1O_2$ and treatment of the endoperoxide [*7,7-dimethyl*-$^{13}C_2$]-**12** with Cu_2Cl_2 furnished [*6,6-dimethyl*-$^{13}C_2$]-**3** (38%; 32% ^{13}C).

Scheme 6



Photolysis of [*6,6-dimethyl*-$^{13}C_2$]-**3** afforded besides the labelled compounds **25**, **27**, and **28**, the bicyclooctanols **22–24**, each incorporating both a ^{13}C-labelled CH_3 and CH_2 group. This finding eliminated structure **I** as a possibility for **22–24**. Furthermore, dehydration of **22** and **23** with $SOCl_2$ led to compound **34**, whereas under the same conditions, **24** gave rise to rearranged products only. On the basis of these results, it was evident that **22** and **23** are C(7) epimers and that they can not be represented by structures of type **II**, they still could, however, incorporate the two epoxides in *trans*-relation (see **III**, *Scheme 5*)[12]), or a *trans*-bicyclooctane moiety (see **24**, *Scheme 4*). To get final evidence for the structures of **22–24**, the crystalline compound **24** and the *p*-nitrobenzoate **35** derived from **22** were subjected to X-ray analysis (see below).

Acetate **26** *(Scheme 4)*. The IR bands at 1740, 1690 and 1645 cm^{-1} are characteristic of the acetate and the cyclohexenone moiety, respectively. The latter is also evidenced by the UV maximum at 238 nm (ε = 5100). In the ^{13}C-NMR spectrum, the *s* at 99.9 ppm is assigned to the acetal C-atom. Furthermore, the spectrum of the corresponding ^{13}C-labelled compound obtained on photolysis of [*6,6-dimethyl*-$^{13}C_2$]-**3** shows enhanced signals at 22.8 ppm (*q*) and 114.0 ppm (*t*). Characteristic ^1H-NMR signals are a *dq* (6.65 ppm) of the enone H-atom, a *dddq* (4.74 ppm) of the allylic H-atom in geminal position to the acetal O-atom, and an *AB* system (2.35 ppm) of the allylic CH_2 group showing further coupling with the neighboring allylic CH and the CH_2=C group (for coupling constants, see *Exper. Part*).

Unsaturated Lactone **27**. The MS shows a molecular peak at *m/z* 152 indicating the molecular formula $C_9H_{12}O_2$. The spectral evidence for the butenolide moiety includes an IR band at 1765 cm^{-1} and, in the ^{13}C-NMR, a *s* at 174.0 ppm of the C=O group. The spectrum of the corresponding ^{13}C-labelled compound shows enhanced signals at 22.9 ppm (*q*) and at 114.0 ppm (*t*). Furthermore, the coupling patterns (*Exper. Part*) of the ^1H-NMR signals of the allylic CH_2 group (2.37 ppm), the allylic CH group (5.01 ppm), and the olefinic CH group (7.06 ppm) establish the structure of **27**.

Cycloheptyl Methyl Ketone **28**. The IR bands at 3540–3400 and 1705 cm^{-1} are characteristic of the OH and the Ac groups, respectively. They are also evidenced by the ^{13}C-NMR signals at 70.9 ppm (*s*) and 210.8 ppm (*s*). The spectrum of the corresponding ^{13}C-labelled compound shows enhanced signals at 35.4 ppm (*t*, C(7)) and 115.8 ppm (*t*, CH_2=C(6)). Conclusive evidence for the assigned structure was obtained from the ^1H-NMR signals and coupling patterns of H–C(3), H–C(4) and 2H–C(5) as well as of H–C(1) and 2H–C(7) (*Exper. Part*).

X-Ray Analyses. – *Bicyclooctanol* **24** *(Fig. 1)*. Monoclinic space group $P2_1/c$, a = 7.85, b = 11.63, c = 11.66 Å, β = 98.99°, Z = 4. Intensity measurements were made at r.t. with a *SYNTEX* $P2_1$ diffractometer (graphite monochromator, Mo$K\alpha$ radiation, λ = 0.7107 Å, 1961 independent reflexions with $\theta > 25°$). The structure was solved by direct methods with MULTAN 80 [19] and refined by full-matrix least-squares analysis using 1197 reflexions ($I > 3\sigma(I)$) with the weighting schemes $\sigma^{-2}(F)$ and $\sigma^{-1}(F_o)\cdot\exp(5\sin^2\theta/\lambda^2)$ [20] (SHELX 76 [21], XRAY-72 [22]). H-Atoms were located at an intermediate stage and included in the refinement with isotropic vibrational parameters (other atoms anisotropic), final R was 0.073; R_w = 0.079[13]).

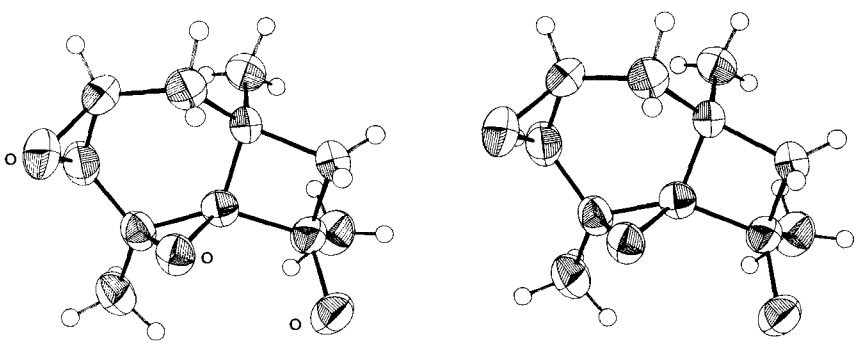


Fig. 1. *Stereoview of the molecule* **24** *drawn by ORTEP* [23] *with thermal vibration ellipsoids at the 50% probability level*

[12]) For the photolytic conversion of diastereomeric epoxides *via* C–C bond cleavage of the oxirane, see [2c] and ref. cited therein.

[13]) Atomic parameters have been deposited with the *Cambridge Crystallographic Data Centre*, Lensfield Road, Cambridge C2B 1EW, England.

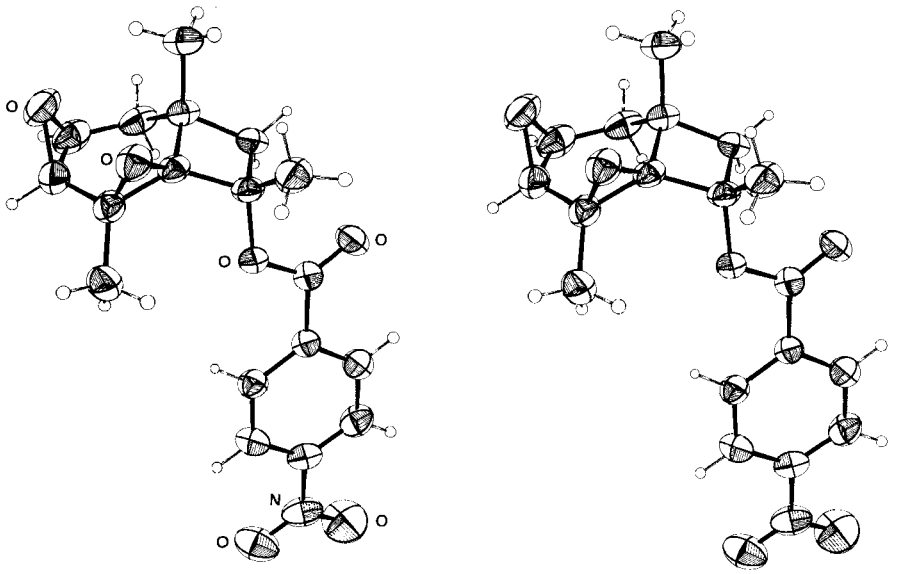
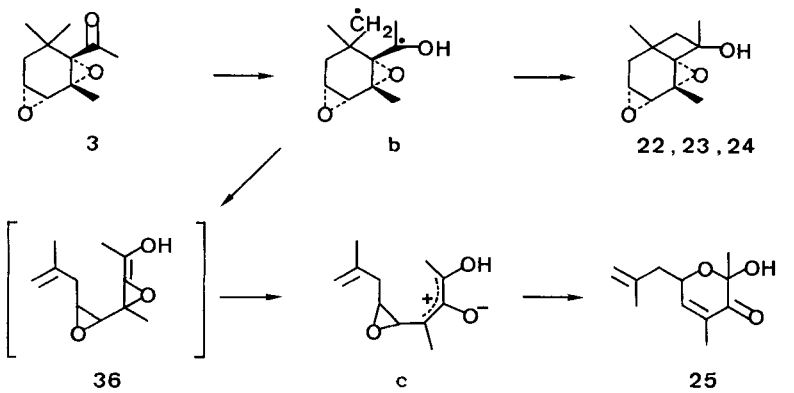


Fig. 2. *Stereoview of the molecule* **35** *drawn by ORTEP* [23] *with thermal vibration ellipsoids at the 50% probability level*

p-Nitrobenzoate **35** *(Fig. 2).* Monoclinic space group $P2_1/n$, $a = 7.86$, $b = 15.59$, $c = 13.78$ Å, $\beta = 97.12°$, $Z = 4$. Intensity measurements were also made at r.t. with a *SYNTEX* $P2_1$ diffractometer (3084 independent reflexions with $\theta < 22.5°$), and the structure was solved and refined (1166 reflections) as described above for **24**, final R was 0.056; $R_w = 0.052$[13]).

5. Discussion. – As the main photoprocess, the α,β;γ,δ-diepoxyketone **3** undergoes γ–H abstraction to the diradical **b** followed by ring closure to the diastereoisomeric bicyclooctanols **22–24** *(Scheme 7)*. Thus, **3** behaves analogously to the α,β-epoxyketone **1** which shows exclusively *Norrish* type-II reaction furnishing two bicyclooctanols of structure **2** *(Scheme 1)* [3]. The main products of the photolyses of **1** and **3** – compounds **2** and **22**, respectively – have the same relative configuration incorporating a *cis*-fused bicy-

Scheme 7

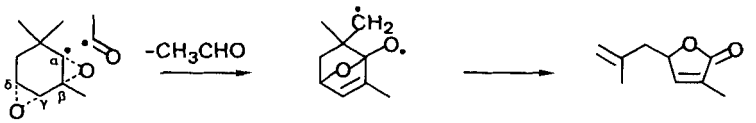


clooctanol moiety and a *trans*-relation of the OH and epoxy functions. In contrast to the photolysis of **1**, from which only two *cis*-bicyclooctanols of structure **2** were isolated in 28% combined yield, on irradiation of **3**, the *trans*-bicyclooctanol **24** (9%) was obtained in addition to the *cis*-compounds **22** (29%) and **23** (4%).

The formation of **25** may also be initiated by a *Norrish* type-II process. Thus, it is proposed that, alternatively to the cyclization, the 1,4-diradical **b** could be cleaved to the allene-oxide intermediate **36**. The latter is unstable and, instead of an enol→ketone tautomerization, **36** rapidly reacts to the dihydropyranone **25** *via* the oxallyl intermediate **c** *(Scheme 7)*[14]). In the postulated intermediate **c**, a 1,4 O-migration of the neighboring epoxy function, analogously to **a**→**5** *(Scheme 1)*, could finally lead to **25**[15]).

For the formation of the fragmentation product **27**, another photoreaction, which is typical of carbonyl compounds, is considered. It is assumed that the loss of CH_3CHO is initiated by *Norrish* type-I cleavage to the radical pair **d** *(Scheme 8)*. H abstraction from a geminal CH_3 group by the Ac radical, followed by a multi-step process involving cleavage of the C(β)–O and the C(γ)–O oxirane bonds, as well as bond formation between C(α) and the O-atom at C(δ) may lead to the 1,4-diradical intermediate **e**. Fragmentation of the latter finally furnishes **27**[16]).

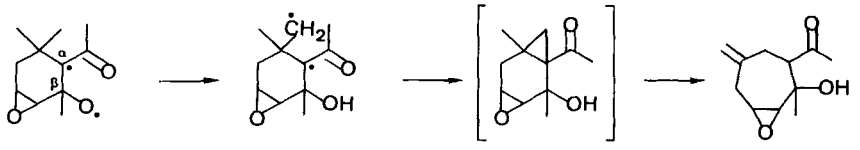
Scheme 8



d **e** **27**

Finally, the cycloheptanol **28** may give evidence for an initial cleavage of the C(α)–O bond of the oxirane, a photoprocess typical of α,β-epoxyketones [2] [28]. In this way, scission of the C(α)–O bond of **3** may give the diradical intermediate **f**, which, presumably due to steric factors, undergoes an H abstraction from one of the geminal CH_3 groups (**f**→**g**) instead of ring contraction or migration of the CH_3 group from C(β) to C(α). In a next step, radical recombination in **g** may produce the cyclopropyl compound

Scheme 9



f **g** **37** **28**

[14]) For the reactivity of allene oxides, see [24].

[15]) *Osuka* [25] recently reported that epoxynaphthoquinones also undergo preferentially cyclization *via Norrish* type-II reaction, while type-II fragmentation yields an allene oxide which gives rise to further isomerizations.

[16]) For two recent papers describing photochemical transformations of α,β-epoxyketones involving also *Norrish* type-I cleavage and subsequent isomerization *via* scission of the C(β)–O bond of the oxirane, see [26] [27].

37[17]) which, however, could not be isolated, since it presumably underwent a photochemical [29] or thermal [30] [1,5] homosigmatropic H-shift to the final product **28** *(Scheme 9)*.

Conclusion. – While on photolysis of the α,β-epoxyketone **1** only two bicyclooctanols of structure **2**, products of cyclization *via Norrish* type-II reaction, were isolated, the α,β;γ,δ-diepoxyketone **3** undergoes besides this process (**3**→**22**–**24**), *Norrish* type-II cleavage (**3**→**25**), as well as *Norrish* type-I fragmentation (**3**→**28**). The latter two reactions involve multi-step processes with participation of the neighboring, γ,δ-epoxy function. With **3** as with **1**, the typical carbonyl photoreactions are dominant over the process involving C(α)–O bond scission. On the other hand, products arising from the cleavage of the C(α)–C(β) bond of the oxirane ring adjacent to the carbonyl group could not be detected.

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Experimental Part

General. See [32]. Anal. gas chromatography (GC) was performed using a 25 m × 0.33 mm *Ucon HB-5100* glass capillary. Column chromatographies (CC) were carried out on silica gel (SiO_2) 60 *Merck*, 0.040–0.63 mm, 230–400 mesh ASTM. Analytically pure samples were obtained, in general, after repeated CC, in some cases further purification was necessary on HPLC (*Du Pont Instruments Model 830*, UV detector), using a 25 cm × 23.6 mm SiO_2 column, or by prep. GC. ^{1}H-NMR spectra were taken in CCl_4 solns. on a *Varian HA-100* instrument (100 MHz) or exceptionally (as indicated below) on a *Bruker-WP-80/CW* (80 MHz) or *a WM-300* (300 MHz) instrument in $CDCl_3$ solns.

1. Preparation of 3. – 1.1. *1-(2,6,6-Trimethyl-1,3-cyclohexadienyl)ethanol* (**6**). To a soln. of *2,6,6-Trimethyl-1,3-cyclohexenecarbaldehyde* (**7**; 10 g, 66 mmol) in dry Et_2O (50 ml) was added dropwise MeLi (1.6M in Et_2O; 45 ml, 72 mmol) at −10° under Ar. The mixture was stirred for 1 h at r.t., treated with a sat. aq. NH_4Cl soln. and worked up with Et_2O affording **6** (10.6 g, 96%).

1.2. *Endoperoxides* **8A** + **B**. A soln. of **6** (1.7 g, 10 mmol) and *Rose Bengale* (0.17 g, 0.17 mmol) in MeOH (200 ml) was irradiated (lamp *B*, $Na_2Cr_2O_7$ filter) for 22 h while bubbling with O_2. CC (Et_2O/hexane 3:7) gave a *ca.* 1:1 mixture of **8A** + **B** (1.49 g, 74%). Anal. samples of **8A** and **8B** were obtained by repeated CC.

1-(6',7',7'-Trimethyl-2',3'-dioxabicyclo[2.2.2]oct-5'-enyl)ethanol, Isomer A (**8A**). M.p. 103–104° (Et_2O/hexane). IR: 3630*m*, 3540*m* (br.), 3040*w*, 2960*s*, 2920*s*, 2870*m*, 2860*m* (sh), 1640*w*, 1465*m* (sh), 1450*m* (sh), 1440*m*, 1380*s*, 1360*m*, 1340*m*, 1300*w*, 1270*m*, 1255*w* (sh), 1210*w*, 1155*w* (sh), 1135*m*, 1110*s*, 1080*m* (sh), 1065*m*, 1050*m*, 1035*w* (sh), 1020*m*, 1000*m*, 960*s*, 930*m*, 900*m*, 860*w*. ^{1}H-NMR: 0.98, 1.24 (2*s*, 2 CH_3–C(7')); 1.18 (*dd*, J_1 = 12, J_2 = 2, H–C(8'), overlapping with *s* at 1.24 and *d* at 1.32); 1.32 (*d*, *J* = 6, 3H–C(2)); 1.60 (*d*, *J* = 5, OH); 1.86 (*dd*, J_1 = 12, J_2 = 3, H–C(8')); 2.07 (*d*, *J* = 2, CH_3–C(6')); 4.10 (*dq*, J_1 = 5, J_2 = 6, H–C(1), appears as *q*, (*J* = 6) after

[17]) A transformation analogous to **f**→**g**→**37** was previously observed on photolysis of the epoxydiene **38** furnishing **39** [31].

Scheme 10

38 **39**

D_2O exchange); 4.20–4.40 (*m*, H–C(4)); 6.06–6.24 (*m*, H–C(5')). MS: 198 (< 1, M^+, $C_{11}H_{18}O_3$). 154 (29), 139 (30), 125 (19), 111 (32), 98 (45), 96 (19), 95 (13), 83 (16), 81 (10), 71 (12), 70 (26), 69 (24), 68 (22), 56 (21), 55 (20), 53 (10), 45 (22), 44 (20), *43* (100), 42 (20), 41 (48). Anal. calc. for $C_{11}H_{18}O_3$ (198.25): C 66.64, H 9.15; found: C 66.52, H 9.00.

Isomer B (**8B**). B.p. 120°/0.04 Torr. IR: 3590*s*, 3040*w*, 3010*m* (sh), 2980*s*, 2950*s*, 2920*s*, 2880*m*, 2850*m*, 1640*w*, 1460*w*, 1455*m* (sh), 1440*m*, 1400*m*, 1385*m*, 1375*m*, 1365*m*, 1340*w*, 1300*m*, 1275*s* (sh), 1270*s*, 1220*w*, 1205*w*, 1165*w*, 1145*w*, 1105*s*, 1080*m*, 1020*m*, 995*m*, 980*s*, 920*s*, 900*m*, 890*m*, 865*w*. ^{1}H-NMR: 0.92, 1.17 (2*s*, 2 CH_3–C(7')); 1.20 (*dd*, J_1 = 13.0, J_2 = 2.5, overlapping with *s* at 1.17, H–C(8')); 1.38 (*d*, *J* = 7, 3H–C(2)); 1.86 (*dd*, J_1 = 13, J_2 = 3, H–C(8')); 2.16 (*d*, *J* = 2, CH_3–C(6') overlapping with *s* of OH); 3.90 (*q*, *J* = 7, H–C(1)); 4.20–4.38 (*ddd*, $J_1 = J_2 = 3$, J_3 = 6, H–C(4')); 6.08–6.26 (*dm*, *J* = 6, $w_{½}$ = 4, H–C(5')). MS: 166 (3, $M^+ - 32$), 125 (19), 111 (26), 107 (9), 98 (47), 83 (25), 81 (14), 71 (15), 70 (33), 69 (26), 56 (16), 55 (20), 45 (28), 44 (12), *43* (100), 41 (34). Anal. calc. for $C_{11}H_{18}O_3$ (198.25): C 66.64, H 9.15; found: C 66.57, H 8.99.

1.3. *Catalytic Rearrangements of* **8A** *and* **8B** *to the Diepoxides* **9A** + **B**. 1.3.1. *With CoTPP*. A soln. of **8A** + **B** (1:1; 477 mg, 2.4 mmol) in Et_2O (20 ml) and CoTPP (20 mg) were heated under reflux for 18 h. CC (Et_2O/hexane 3:1) gave a 4:1 mixture (195 mg) of **9B** (35%) and **10** (7%; ^{1}H-NMR, GC), and **9A** (154 mg, 32%).

1.3.2. *With* Cu_2Cl_2. A soln. of **8A** + **B** (1:1; 192 mg, 0.97 mmol) in Et_2O (10 ml) an Cu_2Cl_2 (20 mg) were heated under reflux for 40 h. CC (Et_2O/hexane 3:1) gave **8A** (25 mg), a 6:1 mixture (67 mg) of **9B** (35%) and **10** (5%; ^{1}H-NMR; GC), and **9A** (41 mg, 24%).

1.3.3. *With* $FeSO_4$. *a*) A soln. of **8A** + **B** (1:1; 207 mg, 1.07 mmol) in Et_2O (10 ml) and $FeSO_4$ (powder; 20 mg) were heated under reflux for 72 h. CC (Et_2O/hexane 3:1) gave **8A** (18 mg), a 7:3 mixture (83 mg) of **9B** (32%) and **14** (14%; ^{1}H-NMR, GC), and **9A** (36 mg, 19%). *b*) A soln. of **8A** (210 mg, 1.06 mmol) in Et_2O (10 ml) and $FeSO_4$ (powder; 20 mg) were heated under reflux for 72 h. CC (Et_2O/hexane 3:1) gave **8A** (33 mg), **9A** (65 mg, 43%), and **10** (30 mg, 21%), *c*) A soln. of **8B** (114 mg, 0.57 mmol) in Et_2O (10 ml) and $FeSO_4$ (powder; 20 mg) were heated under reflux for 72 h. CC (Et_2O/hexane 3:1) gave a 5:3 mixture (62 mg) of **9B** (38%), and **10** (21%).

(1'RS,2'RS,3'RS,4'RS)-1-(1',2',3',4'-Diepoxy-2',6',6'-trimethylcyclohexyl)ethanol, Isomer A (**9A**). M.p. 127° (Et_2O/hexane). IR: 3620*w*, 3530*m* (br.), 3000*s*, 2960*s*, 2920*s*, 2870*m*, 1465*m*, 1440*m*, 1405*m*, 1380*m*, 1370*m*, 1320*w*, 1280*w*, 1260*w*, 1230*w* (sh), 1195*w*, 1155*w*, 1135*w*, 1125*w* (sh), 1085*m*, 1060*m*, 1020*w*, 1015*w* (sh), 1000*m*, 985*w* (sh), 960*w*, 940*m*, 930*m*, 910*s*, 880*m*, 830*m*. ^{1}H-NMR ($CDCl_3$): 0.98, 1.12 (2*s*, 2 CH_3–C(6')); 1.23 (*d*, *J* = 7, 3H–C(2)); 1.40–1.80 (*m*, overlapping with *s* at 1.68 and *s* at 1.86, 2H–C(5')); 1.68 (*s*, CH_3–C(2')); 1.86 (*s*, OH); 2.84–3.16 (*m*, H–C(3'), H–C(4')); 4.40 (*q*, *J* = 7, H–C(1)). MS: 154 (42, $M^+ - 44$), 139 (56), 125 (26), 112 (11), 111 (32), 107 (12), 84 (10), 83 (17), 71 (10), 69 (13), 56 (12), 55 (18), 45 (32), *43* (100), 41 (30). Anal. calc. for $C_{11}H_{18}O_3$ (198.25): C 66.64, H 9.15; found: C 66.75, H 8.99.

Isomer B (**9B**). M.p. 114° (Et_2O/hexane). IR: 3540*m* (br.), 3000*s*, 2970*s*, 2960*s*, 2925*s*, 2875*w*, 2840*w*, 1465*s*, 1440*m*, 1430*m*, 1400*m*, 1380*s*, 1370*s*, 1345*w* (sh), 1340*w*, 1275*s*, 1260*m*, 1225*w*, 1200*m*, 1160*m*, 1150*w*, 1140*w*, 1070*s*, 1060*s*, 1005*s*, 990*m*, 935*m* (sh), 900*s*, 890*s*, 835*m*. ^{1}H-NMR ($CDCl_3$): 1.02, 1.05, (2*s*, 2 CH_3–C(6')); 1.36 (*d*, *J* = 7, 3H–C(2)); 1.30–1.84 (*m*, overlapping with *d* at 1.36 and *s* at 1.75, 2H–C(5')); 1.75 (*s*, CH_3–C(2')); 2.30 (*s*, OH); 2.86–3.14 (*m*, H–C(3'), H–C(4')); 4.35 (*q*, *J* = 7, H–C(1)). MS: 198 (< 1, M^+, $C_{11}H_{18}O_3$), 125 (32), 111 (25), 84 (13), 83 (20), 81 (10), 71 (13), 69 (10), 55 (16), 45 (28), *43* (100), 41 (23). Anal. calc. for $C_{11}H_{18}O_3$ (198.25): C 66.64, H 9.15; found: C 66.26, H 9.07.

1.4. *Oxidation of* **9A** + **B**. To a soln. of a *ca.* 1:1 mixture of **9A** + **B** (5.9 g, 30 mmol) in dry CH_2Cl_2 (700 ml) was added pyridinium chlorochromate (50 g, 0.23 mol). The mixture was stirred for 2 h at r.t., diluted with Et_2O and filtered through SiO_2 to give **3** (5.0 g, 85%).

(1RS,2SR,3SR,4SR)-1,2;3,4-Diepoxy-2,6,6-trimethyl-1-cyclohexyl Methyl Ketone (**3**). M.p. 37–38° (Et_2O/hexane). B.p. 110°/0.005 Torr. UV (2.845 mg in 5 ml): 296 (40). IR: 2990*m*, 2960*s*, 2925*m*, 2870*m*, 1705*s*, 1460*m*, 1445*m*, 1430*m*, 1420*m* (sh), 1400*m*, 1380*s*, 1370*s*, 1350*s*, 1280*m*, 1255*m* (sh), 1250*m*, 1210*m*, 1155*w*, 1120*w*, 1080*w*, 1050*m*, 1020*m*, 990*w*, 960*w* 930*s*, 905*m*, 890*m*, 830*m*. ^{1}H-NMR: 0.94, 1.15 (2*s*, 2 CH_3–C(6)); 1.40 (*s*, CH_3–C(2)); 0.90–1.70 (*m*, 2H–C(5)); 2.08 (*s*, CH_3CO)); 2.70–2.96 (*m*, H–C(3), H–C(4)). ^{13}C-NMR: 19.4, 29.6 (2*q*, *C*H_3–C(2), *C*H_3CO); 24.0, 25.3 (2*q*, 2 *C*H_3–C(6)); 35.6 (*t*, C(5)); 46.8, 51.2 (2*d*, C(3), C(4)); 35.4 (*s*, C(6)); 59.1, 73.0 (2*s*, C(1), C(2)); 207.6 (*s*, CO). MS: 196 (< 1, M^+, $C_{11}H_{16}O_3$), 125 (31), 98 (10), 83 (18), 81 (12), 69 (10), 55 (15), *43* (100), 41 (24), 39 (14). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.19, H 8.35.

1.5. *Oxidation of* **6** *with* MnO_2. *a*) A soln. of **6** (10.4 g, 62 mmol) in CH_2Cl_2 (400 ml) was stirred vigorously with MnO_2 (110 g, 1.27 mol) for 4 d at r.t. The mixture was filtered through *Celite* and the residue washed with 100-ml portions of CH_2Cl_2 (8×) and Et_2O (2×). CC (Et_2O/hexane 3:7) gave starting material **6** (4.1 g) and **11** (1.76 g, 28%[6])). *b*) Analogously, a soln. of **6** (19.2 g, 116 mmol) in CH_2Cl_2 (200 ml) was oxidized with warm MnO_2 (200 g, 2.3 mol) furnishing after CC **13** (1.92 g, 10%), and a 3:2 mixture (7.79 g) of **11** (25%) and **14** (16%).

3-Acetyl-2,4,4-trimethyl-2,5-cyclohexadien-1-one (**13**). UV (0.27 mg in 25 ml): 232 (11 500). UV 0.70 mg in 2 ml): 302 (350), end absorption to 400. IR: 3070*w* (sh), 3040*w*, 2970*m*, 2930*m*, 2910*w*, 2870*w*, 1700*s*, 1660*s*, 1635*s*, 1610*w*, 1465*m* (sh), 1460*m*, 1420*m*, 1400*m*, 1375*m*, 1360*m*, 1350*s*, 1290*s*, 1220*s*, 1190*m*, 1150*m*, 1120*m*, 1055*w*, 1015*w*, 985*w*, 940*m*, 925*w*, 880*w*, 830*m*. ^{1}H-NMR ($CDCl_3$): 1.29 (*s*, 2 CH_3–C(4)); 1.80 (*s*, CH_3–C(2)); 2.37 (*s*, CH_3CO); 6.44 (*AB* system, J = 10, δ_A = 6.17, δ_B = 6.71, H–C(5), H–C(6)). ^{13}C-NMR: 12.4, 32.1 (2*q*, CH_3CO, CH_3–C(2)); 26.0 (*q*, 2 CH_3–C(4)); 125.6, 156.4 (2*d*, C(5), C(6)); 38.2 (*s*, C(4)); 128.1, 160.0 (2*s*, C(2), C(3)); 185.3, 204.5 (2*s*, CH_3CO, C(1)). MS: 178 (20, M^+, $C_{11}H_{14}O_2$), 163 (32), 137 (10), 136 (96), 135 (57), 121 (38), 108 (15), 107 (28), 93 (13), 91 (49), 79 (14), 77 (13), 65 (17), 51 (10), *43* (100), 41 (16).

1.6. *Endoperoxide* **12**. A soln. of **11** (8.37 g, 51 mmol) and *Rose Bengal* (1 g, 1 mmol) in MeOH (800 ml) was irradiated (lamp *B*, $Na_2Cr_2O_7$ filter) for 20 h while bubbling with O_2. CC (Et_2O/hexane 1:9) gave starting material **11** (1.5 g), and **12** (5.5 g, 67%)[6]).

Methyl 6,7,7-Trimethyl-2,3-dioxabiclo[2.2.2]oct-5-enyl Ketone (**12**). B.p. 80°/0.2 Torr. UV (3.72 mg in 5 ml): 289 (116). IR: 3045*w*, 2960*s*, 2920*s*, 2870*m*, 2850*m*, 2820*w*, 1735*s*, 1720*s*, 1675*w*, 1665*w* (sh), 1645*w*, 1460*m*, 1440*m*, 1410*m*, 1380*m*, 1360*m*, 1350*s*, 1340*w*, 1310*w*, 1270*w*, 1245*m*, 1205*w*, 1195*w* (sh), 1130*w*, 1070*m*, 1050*w*, 1020*m*, 990*m*, 965*m*, 930*m*, 920*m*, 895*w*, 855*w*, (sh), 850*w*. ^{1}H-NMR: 0.95, 1.14 (2*s*, 2 CH_3–C(7)); 1.26 (*dd*, overlapping with *s* at 1.14, J_1 = 12, J_2 = 2, H–C(8)); 1.77 (*d*, J = 2, CH_3–C(6)); 1.92 (*dd*, J_1 = 12, J_2 = 4, H–C(8)); 2.09 (*s*, CH_3CO); 4.30–4.50 (*m*, H–C(4)); 6.12–6.28 (*m*, H–C(5)). ^{13}C-NMR: 19.0, 29.6 (2*q*, CH_3–C(6), CH_3CO), 24.9, 28.0 (2*q*, 2 CH_3–C(7)); 40.7 (*t*, C(8)); 71.9 (*d*, C(4)); 125.5 (*d*, C(5)); 36.6 (*s*, C(7)); 90.1 (*s*, C(1)); 140.4 (*s*, C(6)); 205.1 (*s*, CO). MS: 196 (< 1, M^+, $C_{11}H_{16}O_3$), 154 (30), 153 (37), 152 (32), 139 (30), 125 (27), 111 (29), 110 (10), 109 (17), 107 (20), 98 (41), 96 (42), 95 (10), 91 (12), 83 (17), 81 (15), 70 (17), 69 (23), 68 (49), 67 (16), 57 (10), 56 (13), 55 (21), *43* (100), 42 (10), 41 (46). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.14, H. 8.32.

1.7. *Catalytic Rearrangements of* **12** *to the Diepoxide* **3**. 1.7.1. *With CoTPP*. A soln. of **12** (1.39 g, 7.0 mmol) in Et_2O (100 ml) was heated under reflux with a catalytic amount of CoTPP for 15 h. CC (Et_2O/hexane 1:9) afforded **3** (773 mg, 56%) and **10** (284 mg, 26%).

1.7.2. *With* Cu_2Cl_2. A soln. of **12** (475 mg, 2.3 mmol) in Et_2O (30 ml) was heated under reflux with a catalytic amount of Cu_2Cl_2 for 15 h. CC (Et_2O/hexane 3:7) gave **3** (286 mg, 60%) and **10** (122 mg, 33%).

1.7.3. *With* $FeSO_4$. A soln. of **12** (245 mg, 1.25 mmol) in Et_2O (20 ml) was heated under reflux with $FeSO_4$ (20 mg) for 15 h. CC (Et_2O/hexane 3:7) gave starting material **12** (18 mg) and **10** (102 mg, 67%).

2. Preparation of [6,6-dimethyl-$^{13}C_2$]-3. – 2.1. *Methyl [*6,6-dimethyl-$^{13}C_2$*]-2,6,6-Trimethyl-1-cyclohexenyl Ketone* (**32**). A soln. of the potassium enolate of 2,6-dimethylcyclohexanone (**29**) was prepared by dropwise addition of **29** (3.51 g, 25.1 mmol) to a suspension of KH (20% in oil suspension, 3.90 g, 19.5 mmol, washed 3× with dry pentane) in dry THF (10 ml). After stirring for 1 h at r.t., the mixture was diluted with dry THF to a total volume of 22 ml, 2 ml of which were removed, quenched with an excess of MeI, and analyzed. The mixture (20 ml) was cooled in liquid N_2 and [^{13}C]H_3I (1.2 ml, 19.2 mmol, 90% ^{13}C) was added. The cooling bath was removed, the mixture warmed up to r.t. over 40 min, and quenched by the addition of aq. THF (2 ml, 70%). After removing the solvent, the residue was worked up in Et_2O. Cap. GC indicated starting material **29** (30%), *[*2,2-dimethyl-$^{13}C_2$*]-2,2,6-trimethylcyclohexanone* (**30**, 64%), and 2,2,6,6-tetramethylcyclohexanone (6%). This mixture was dissolved in dry benzene/THF (1:1, 10 ml) and added dropwise to a suspension of lithium-acetylide-ethylenediamine complex (4.0 g, 43 mmol) in dry benzene/THF (1:1, 20 ml) at 40° under Ar. The mixture was then stirred for 20 h at r.t., treated carefully with H_2O (5 ml), and heated under reflux for 1 h. The cold mixture was then poured into sat. aq. NH_4Cl and worked up with Et_2O. The residue obtained after removal of the solvent was dissolved in AcOH (40 ml) and H_2O (4 ml), and heated under reflux with *Dowex 50 W X 8* (200–400 mesh, H^+-form, 7 g) for 3 h. The suspension was filtered and the residue washed with Et_2O. The filtrate was neutralized with dilute KOH, worked up with Et_2O, and chromatographed to give **32** (1.3 g, 80% pure, 40% yield based on [^{13}C]H_3I).

*Methyl [*6,6-dimethyl-$^{13}C_2$*]-2,6,6-Trimethylcyclohexenyl Ketone* (**32**). Characteristic ^{1}H-NMR signals (80 MHz, $CDCl_3$, 80% pure): 1.05 (*d*, J = 126, [^{13}C]H_3–C(6)); 1.05 (*d*, J = 5, CH_3–C(6)); 1.59 (*s*, CH_3–C(2)); 2.27 (*s*, CH_3CO). MS[18]): 167 (27, M^+, $^{13}CC_{10}H_{18}O$), 152 (51), 151 (22), 124 (100), 110 (22), 109 (17), 108 (14), 107 (11), 93 (10).

2.2. *Methyl [*6,6-dimethyl-$^{13}C_2$*]-2,6,6-Trimethyl-1,3-cyclohexadienyl Ketone* ([*6,6-dimethyl-*$^{13}C_2$]-**11**). A soln. of **32** (80% pure; 1.24 g, 5.9 mmol) in CCl_4 (15 ml) was treated with *N*-bromosuccinimide (1.32 g, 7.43 mmol) at 60°. After the reaction was complete, pentane was added, the mixture filtered, and the solvent evaporated. A soln. of the crude *methyl 3-bromo-[*6,6-dimethyl-$^{13}C_2$*]-2,6,6-trimethyl-1-cyclohexenyl ketone* (**33**) in DMF (14 ml) was

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[18]) Recorded on a GC/MS (*Carlo Erba fractovap 2150*, 12.5 m SE-52 cap. column. *MS/MAT 112 INCOS Data Syst. FINN*). Only peaks of m/z > 69 were recorded. We are grateful to Mr. *F. Behm* for this measurement.

heated at 130–140° with LiCl (1.4 g, 33 mmol) and Li_2CO_3 (1.4 g, 19 mmol). After no further CO_2 evolution was observed, the mixture was allowed to cool to r.t. and was then poured into sat. aq. NaCl soln. and extracted with pentane. CC (Et_2O/hexane 3:7) afforded a 1:3 mixture (865 mg) of starting material **32** and [*6,6-dimethyl-*$^{13}C_2$]-**11** (84%[6]).

To the 1:3 mixture of **32** and [*6,6-dimethyl-*$^{13}C_2$]-**11** (1.73 g, 90% ^{13}C) was added a 1:3 mixture of unlabelled **32** and **11** (3.22 g). The enrichments of the two compounds were determined by MS to be 32%.

2.3. *[*6,6-dimethyl-*$^{13}C_2$*]*-**3**. A soln. of [*6,6-dimethyl-*$^{13}C_2$]-**11** (75% pure; 32% ^{13}C; 4.91 g, 22 mmol) in CH_2Cl_2 (1000 ml) was irradiated (lamp *B*, $Na_2Cr_2O_7$ filter) in the presence of ca. 100 mg *Sensitox* [33] while bubbling with O_2. After 18 h, the mixture was filtered and chromatographed (Et_2O/hexane 3:7) affording [*7,7-dimethyl-*$^{13}C_2$]-**12** (2.66 g, 60%; 32% ^{13}C). A soln. of [*7,7-dimethyl-*$^{13}C_2$]-**12** (2.60 g, 13.3 mmol) in Et_2O (100 ml) was stirred in the presence of a catalytic amount of Cu_2Cl_2 for 90 h at r.t. CC (Et_2O/hexane 3:7) afforded [*6,6-dimethyl-*$^{13}C_2$]-**3** (1.65 g, 63%; 32% ^{13}C) and *4-hydroxy-[*6,6-dimethyl-*$^{13}C_2$*]-2,6,6-trimethyl-2-cyclohexenone* ([*6,6-dimethyl-*$^{13}C_2$]-**10**; 0.44 g, 19%).

3. Photolyses. – 3.1. *Photolysis of* **3**. A soln. of **3** (2.72 g, 13.9 mmol) in MeCN (270 ml) was irradiated (*Pyrex*, lamp B, 125 W, 92% conversion). The products and yields[6]) determined by ^{1}H-NMR and cap. GC of the fractions obtained from CC (AcOEt/hexane/CH_2Cl_2 2:1:1) were: **22** (29%), **23** (4%), **24** (9%), **25** (7%), **27** (13%), and **28** (5%).

*(1*RS,*3*SR,*4*SR,*5*SR,*6*SR,*7*SR*)-3,4;5,6-Diepoxy-1,5,7-trimethylbicyclo[4.2.0]octan-7-ol* (**22**). M.p. 123° (Et_2O/hexane). IR: 3620*m*, 3470*m* (br.), 2980*s*, 2960*s*, 2925*s*, 2860*m*, 2840*m* (sh), 1480*w*, 1440*m*, 1430*m*, 1410*m*, 1390*m* (sh), 1375*s*, 1360*m*, 1330*w*, 1320*w* (sh), 1245*m*, 1215*s*, 1155*m* (br.), 1090*m*, 1045*m*, 1005*m*, 980*m*, 945*s*, 910*m*, 890*m* (sh), 880*m*, 865*m*, 855*m* (sh). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.14 (*s*), 1.44 (*d*, $J = 0.6$), and 1.64 (*s*) (CH_3–C(1), CH_3–C(5), CH_3–C(7)); 1.70–1.76 (*m*, OH); 1.93 (*AB* system, $J = 13.2$, $\delta_A = 1.83$, broad, $\delta_B = 2.03$, 2H–C(8)); 1.98 (*AB* system, $J = 15.1$, $\delta_A = 1.87$, broad, $\delta_B = 2.09$, split into *d*, $J = 2.8$, 2H–C(2)); 3.16 (*AB* system, $J = 3.8$, $\delta_A = 3.15$, H–C(4), $\delta_B = 3.17$ split into *dd*, $J_1 = 2.8$, $J_2 = 0.6$, H–C(3)). ^{13}C-NMR: 18.3, 25.4 (2*q*, CH_3–C(5), CH_3–C(7)); 24.4 (*q*, CH_3–C(1)); 35.6 (*t*, C(2)); 49.1 (*t*, C(8)), 51.7, 52.2 (2*d*, C(3), C(4)); 30.6 (*s*, C(1)); 58.5, 68.0, 75.2 (3*s*, C(5), C(6), C(7)). MS: 196 (2, M^+, $C_{11}H_{16}O_3$), 139 (11), 138 (20), 111 (18), 110 (17), 109 (24), 98 (59), 95 (18), 85 (10), 83 (13), 70 (10), 69 (20), 67 (12), 55 (12), *43* (100), 41 (26). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.26, H 8.08.

*(1*RS,*3*SR,*4*SR,*5*SR,*6*SR,*7*RS*)-3,4;5,6-Diepoxy-1,5,7-trimethylbicyclo[4.2.0]octan-7-ol* (**23**). B.p. 140°/0.04 Torr. IR: 3620*m*, 3500*w* (br.), 3000*s*, 2960*s*, 2930*s*, 2880*m*, 1465*w* (sh), 1450*m* (sh), 1440*m*, 1430*m*, 1420*m*, 1400*w*, 1375*w* (sh), 1355*w* (sh), 1300*w*, 1285*w* (sh), 1255*w*, 1245*w*, 1210*m*, 1180*m*, 1155*m*, 1070*m*, 1040*m*, 1020*w*, 985*w*, 970*w*, 945*m*, 920*s*, 910*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.32 (*s*, CH_3–C(1)); 1.51 (*m*, $w_{1/2} = 1.5$) and 1.62 (*s*, CH_3–C(5), CH_3–C(7)); 1.60–1.75 (*m*, OH, H–C(2)); 1.79–1.99 (*m*, H–C(2)); 1.90 (*AB* system, $J = 11$, $\delta_A = 1.82$, $\delta_B = 1.98$, broad, $w_{1/2} = 2$, 2H–C(8)); 2.91–2.98 (*m*, H–C(3), H–C(4)). ^{13}C-NMR: 17.8, 25.7 (2*q*, CH_3–C(5), CH_3–C(7)); 23.2 (*q*, CH_3–C(1)); 32.0 (*t*, C(2)); 45.6 (*t*, C(8)); 49.1, 52.8 (2*d*, C(3), C(4)); 37.6 (*s*, C(1)); 60.7, 65.7, 81.7 (3*s*, C(5), C(6), C(7)). MS: 196 (< 1, M^+, $C_{11}H_{16}O_3$), 111 (10), 109 (13), 98 (20), 95 (12), 83 (14), 69 (12), 55 (10), *43* (100), 41 (21). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.01, H 8.43.

*(1*RS,*3*RS,*4*RS,*5*RS,*6*RS,*7*SR*)-3,4;5,6-Diepoxy-1,5,7-trimethylbicyclo[4.2.0]octan-7-ol* (**24**). M.p. 113–115° (Et_2O/hexane). IR: 3540*m*, 2980*s*, 2930*s*, 2870*w*, 2850*w* (sh), 1460*m* (sh), 1450*m*, 1430*m* (sh), 1425*m*, 1400*m*, 1385*s*, 1380*s*, 1360*s*, 1340*m*, 1300*w*, 1250*w*, 1230*s*, 1200*w*, 1170*s*, 1150*s*, 1130*m*, 1110*w*, 1070*m*, 1045*m*, 985*m*, 960*s*, 950*m*, 935*m*, 920*m*, 910*m*, 880*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.31 (*d*, $J = 1$, CH_3–C(1)); 1.61 (*s*, CH_3–C(5), CH_3–C(7)); 1.83 (*AB* system, $J = 13$, $\delta_A = 1.75$, $\delta_B = 1.91$, *A* and *B* split to *m*, 2H–C(2)); 1.98 (*AB* system, $J = 11.5$, $\delta_A = 1.95$, $\delta_B = 2.01$, 2H–C(8)); 2.93–2.99 (*m*, H–C(3), H–C(4)); 3.10 (*m*, $w_{1/2} = 3$, OH). ^{13}C-NMR: 17.4, 23.5 (2*q*, CH_3–C(5), CH_3–C(7)); 23.0 (*q*, CH_3–C(1)); 33.3 (*t*, C(2)); 48.6 (*t*, C(8)); 49.0, 52.3 (2*d*, C(3), C(4)); 33.3 (*s*, overlapping with *t*, C(1)); 63.2, 75.4, 79.1 (3*s*, C(5), C(6), C(7)). MS: 196 (< 1, M^+, $C_{11}H_{16}O_3$), 111 (14), 109 (16), 98 (17), 95 (14), 83 (13), 69 (15), *43* (100), 41 (19). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.20, H 8.15.

2,4-Dimethyl-6-(2'-methyl-2'-propenyl)-3-oxo-1-oxa-4-cyclohexen-2-yl Acetate (**26**). UV (0.420 mg in 10 ml of EtOH): 238 (5100). UV (1.765 mg in 2 ml of EtOH): 325 (73), end absorption to 400: IR: 3075*w*, 2965*m*, 2940*m*, 2920*m*, 2880*w* (sh), 2850*w* (sh), 1740*s*, 1690*s*, 1650*m* (sh), 1645*m*, 1443*m*, 1432*m* (sh), 1365*w*, 1335*w*, 1290*w*, 1250*s*, 1220*s*, 1180*s*, 1120*m*, 1080*s*, 1038*m*, 1005*m*, 990*m* (sh), 960*m*, 925*s*, 895*m*, 855*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.66 (*s*, CH_3–C(2)); 1.75–1.80 (*m*, $w_{1/2} = 2.5$, CH_3–C(2')); 1.87 (*dd*, $J_1 = 2.0$, $J_2 = 1.7$, CH_3–C(4)); 2.01 (*s*, CH_3COO); 2.35 (*AB* system, $J = 14.5$, $\delta_A = 2.29$, $\delta_B = 2.41$, *A* split to *dd*, $J_1 = 6.0$, $J_2 = 1.0$, *B* split to *dd*, $J_1 = 7.0$, $J_2 = 1.0$, 2H–C(1')); 4.74 (*dddq*, $J_1 = 7.0$, $J_2 = 6.0$, $J_3 = J_4 = 2.0$, H–C(6)); 4.80, 4.90 (2*m*, $w_{1/2} = 4.5$, 2H–C(3')); 6.65 (*dq*, $J_1 = 2.0$, $J_2 = 1.7$, H–C(5)). ^{13}C-NMR: 15.3, 21.2, 23.3 (3*q*, CH_3–C(4), CH_3–C(2), CH_3COO); 22.8 (*q*, CH_3–C(2')); 42.9 (*t*, C(1')); 114.0 (*t*, C(3')); 69.6 (*d*, C(6)); 144.2 (*d*, C(5)); 99.9 (*s*, C(2)); 131.8, 140.9 (2*s*, C(2'),

C(4)); 169.8 (*s*, COO); 189.5 (*s*, C(3)). MS: 179 (28, $M^+ - 57$), 178 (28), 163 (12), 135 (10), 123 (15), 109 (11), 107 (17), 95 (16), 93 (20), 91 (21), 83 (22), 79 (12), 69 (13), 67 (12), 60 (22), 55 (23), 45 (29), ***43*** (100), 41 (24).

*3-Methyl-5-(2'-methyl-2'-propenyl)dihydrofuran-2(5*H*)-one* (**27**). Decomposes on distillation. UV (1.34 mg in 2 ml): end absorption to 370. IR: 3080*w*, 2980*w* (sh), 2930*m*, 2880*w* (sh), 1765*s*, 1720*w* (sh), 1660*w* (sh), 1650*w*, 1445*w*, 1380*w*, 1335*w*, 1320*w* (sh), 1285*w*, 1250*w*, 1210*w*, 1095*m*, 1060*m*, 1030*w* (sh), 1020*w* (sh), 990*w*, 960*w*, 900*m*, 855*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.79 (*m*, $w_{1/2}$ = 3, CH_3–C(2')); 1.92 (*dd*, $J_1 = J_2$ = *ca.* 1.5, CH_3–C(3)); 2.37 (*AB* system, J = 14.3, δ_A = 2.31 split into *d*, J = 6.5; δ_B = 2.43, split into *d*, J = 7.0, 2H–C(1')); 4.81–4.83 and 4.90–4.93 (2*m*, 2H–C(3')); 5.01 (*dddq*, J_1 = 7.5, J_2 = 6.5, $J_3 = J_4$ = 1.5, H–C(5)); 7.06 (*dq*, $J_1 = J_2 \approx$ 1.5, H–C(4)). ^{13}C-NMR: 10.5 (*q*, CH_3–C(3)); 22.9 (*q*, CH_3–C(2')); 41.7 (*t*, C(1')); 114.0 (*t*, C(3')); 79.7 (*d*, C(5)); 148.9 (*d*, C(4)); 129.9, 140.2 (2*s*, C(2'), C(3)); 174.0 (*s*, CO). MS: 152 (12, M^+, $C_9H_{12}O_2$), *97* (100), 69 (17), 55 (22), 41 (46).

3,4-Epoxy-2-hydroxy-2-methyl-6-methylidenecycloheptyl Methyl Ketone (**28**). M.p. 72–74° (from pentane). UV (0.93 mg in 2 ml): end absorption to 380. IR: 3540*m*, 3430*m* (br.), 3080*w*, 2980*s*, 2940*s*, 2870*w*, 1740*m* (sh), 1705*s*, 1640*m*, 1450*m*, 1440*m* (sh), 1430*m*, 1380*s*, 1360*s*, 1290*m*, 1265*m*, 1230*s*, 1215*s*, 1190*m*, 1170*m*, 1145*m*, 1135*m* (sh), 1120*m*, 1110*m*, 1070*m*, 1055*m* (sh), 1020*m*, 970*m*, 940*m*, 910*s*, 900*s*, 860*m*, 840*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.36 (*s*, CH_3–C(2)); 2.25 (*s*, CH_3CO); 2.27 (*dd*, J_1 = 13.5, J_2 = 3.5 (br.), H–C(7)); 2.57 (*dd*, J_1 = 10.0, J_2 = 3.5, H–C(1)); 2.63 (*ddd*, J_1 = 13.5, J_2 = 6.5, J_3 = 1.0, H–C(5)); 2.74 (*dd*, J_1 = 13.5, J_2 = 5.0, broadened, H–C(5)); 2.77 (*ddd*, J_1 = 13.5, J_2 = 10.0, J_3 = 1.5, H–C(7)); 2.96 (*d*, J = 4.5, H–C(3)); 3.06 (*ddd*, J_1 = 6.5, J_2 = 5.0, J_3 = 4.5, H–C(4)); 3.66 (*s*, OH); 4.85 and 4.87 (2*m*, $w_{1/2}$ = 4.0, CH_2=C(6)). ^{13}C-NMR: 27.4, 28.9 (2*q*, CH_3CO, CH_3–C(2)); 35.4 (*t*, C(7)); 36.3 (*t*, C(5)); 115.8 (*t*, CH_2=C(6)); 53.9, 60.9, 61.5 (3*d*, C(1), C(3), C(4)); 70.9 (*s*, C(2)); 142.0 (*s*, C(6)); 210.8 (*s*, CO). MS: 196 (1, M^+, $C_{11}H_{16}O_3$), 135 (13), 107 (10), 97 (10), 93 (14), ***43*** (100), 51 (11). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.33, H 8.22.

3.2. *Photolysis of Enriched [*6,6-dimethyl-$^{13}C_2$*]*-**3**. A soln. of [*6,6-dimethyl*-$^{13}C_2$]-**3** (2.30 g, 11.7 mmol 20% ^{13}C) in MeCN (400 ml) was irradiated (*Pyrex*, lamp *B*, 450 W; 90% conversion). The yields[6]) of the ^{13}C-enriched products determined by capillary GC of the fractions obtained from CC (AcOEt/hexane/CH_2Cl_2 2:1:1) were: **22** (32%), **23** (5%), **24** (11%), **25** (6%), **27** (7%), and **28** (13%).

4. Additional Experiments. – 4.1. *Acetylation of 2-Hydroxy-2,4-dimethyl-6-(2'-methyl-2'-propenyl)-1-oxa-4-cyclohexen-3-one* (**25**). A mixture (116 mg) of **3** (*ca.* 45%), **25** (*ca.* 20% 0.12 mmol), and **27** (*ca.* 35%) was stirred with Ac_2O, pyridine (1 ml) and *N,N*-dimethylaminopyridine (300 mg, 2.5 mmol) at r.t. for 4 h. The mixture was worked up in Et_2O with aq. $CuSO_4$ soln. and chromatographed (Et_2O/hexane 3:2) to give **26** (13 mg, *ca.* 60%).

4.2. *Dehydration of* **22** *and* **23**. *a*) A soln. of **22** (332 mg, 1.69 mmol) and dry pyridine (1.5 ml) in dry CH_2Cl_2 (40 ml) was treated at –10° with $SOCl_2$ (0.4 ml, 5.5 mmol). After 24 h, the mixture was worked up in Et_2O and chromatographed (Et_2O/hexane 3:7) affording **34** (98 mg, 33%). *b*) Treatment of a soln. of **23** (33 mg, 0.17 mmol) and dry pyridine (0.14 ml) in dry CH_2Cl_2 (6 ml) with $SOCl_2$ (0.04 ml, 0.55 mmol) gave after workup and CC **34** (2 mg, 6%).

*(1*RS*,2*SR*,3*SR*,4*SR*,6*SR*)-1,2;3,4-Diepoxy-2,6-dimethyl-8-methylidenebicyclo[4.2.0]octane* (**34**). M.p. 41–46° (Et_2O/hexane). IR: 3080*w*, 3000*m*, 2960*m*, 2920*s*, 2860*w*, 2840*w*, 1680*w*, 1470*w* (sh), 1460*w*, 1450*w*, 1430*m* (sh), 1425*m*, 1400*w*, 1380*m*, 1370*m*, 1320*w*, 1250*w*, 1220*w*, 1200*w*, 1180*w*, 1160*w*, 1130*w*, 1100*m*, 1060*w*, 1050*m*, 1010*w* (sh), 1005*s*, 950*w*, 940*m*, 910*m*, 900*m* (sh), 890*s*. ^{1}H-NMR: 1.14, 1.38 (2*s*, CH_3–C(2), CH_3–C(6)); 1.89 (*AB* system, J = 14, δ_A = 1.73 broad, δ_B = 2.05 with fine structure, 2H–C(5)); 2.16–3.50 (*m*, 2H–C(7)); 3.02 (*m*, $w_{1/2}$ = 3, H–C(3), H–C(4)); 4.80–5.00 (*m*, CH_2=C(8)). ^{13}C-NMR: 16.5, 23.3 (2*q*, CH_3–C(2), CH_3–C(6)); 34.0, 42.7 (2*t*, C(5), C(7)); 109.8 (*t*, CH_2=C(8)); 51.9, 52.2 (2*d*, C(3), C(4)); 36.4 (*s*, C(6)); 58.8, 65.4 (2*s*, C(1), C(2)); 145.7 (*s*, C(8)). MS: 178 (1, M^+, $C_{11}H_{14}O_2$) 163 (19), 161 (13), 149 (17), 136 (22), 135 (58), 134 (15), 133 (12), 123 (37), 121 (39), 117 (20), 109 (66), 108 (16), 107 (37), 106 (12), 105 (24), 98 (16), 95 (44), 94 (20), 93 (42), 92 (19), 91 (75), 85 (28), 81 (35), 79 (92), 77 (64), 69 (27), 68 (22), 67 (40), 65 (28), 55 (24), 53 (46), 51 (25), ***43*** (100), 41 (79).

4.3. *p-Nitrobenzoate* **35**. A mixture of **22** (192 mg, 1.0 mmol), *p*-nitrobenzoyl chloride (500 mg, 2.5 mmol), *N,N*-dimethylaminopyridine (200 mg, 2.0 mmol), and pyridine (10 ml) was stirred at 40° for 70 h. Workup and CC (Et_2O/CH_2Cl_2) yielded **35** (232 mg, 80%).

*(1*RS*,3*SR*,4*SR*,5*SR*,6*SR*,7*SR*)-3,4;5,6-Diepoxy-1,5,7-trimethylbicyclo[4.2.0]oct-7-yl* p-*Nitrobenzoate* (**35**). M.p. 203–204° (Et_2O/hexane). UV (0.092 mg in 10 ml EtOH): 260 (13100). UV (1.13 mg in 2 ml EtOH): end absorption to 400. IR ($CHCl_3$): 3110*w*, 3020*w* (sh), 2990*m*, 2960*m*, 2950*w* (sh), 2920*w*, 2860*w*, 2840*w* (sh), 1720*s*, 1685*w* (sh), 1605*m*, 1525*s*, 1505*m* (sh), 1485*w* (sh), 1440*m*, 1430*m* (sh), 1410*w*, 1375*m*, 1350*s*, 1320*m*, 1300*s*, 1285*s*, 1260*s*, 1190*m*, 1170*w*, 1150*m*, 1110*m*, 1095*s*, 1045*w*, 1010*m*, 1005*m*, 970*w*, 960*w*, 950*w*, 930*m*, 905*m*, 890*w*, 885*w* (sh), 870*m*, 865*w* (sh), 840*m*, 830*m*, 820*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.23 (*s*, CH_3–C(1)), 1.64 (*s*, CH_3–C(5)); 1.71 (*d*, J = 0.5, CH_3–C(7)); 2.10 (*d*, J = 1.8, 2H–C(2)); 2.34 (*AB* system, J = 12.9, δ_A = 2.22, δ_B = 2.46, broad $w_{1/2}$ = 2.5, 2H–C(8)); 3.21 (*AB* system, J = 3.8, δ_A = 3.18, H–C(4), δ_B = 3.24, split into *t*, J = 1.8, H–C(3));

8.08–8.16, 8.26–8.34 (2*m*, arom. H). ^{13}C-NMR: 18.7, 22.7, 24.5 (3*q*, CH_3–C(1), CH_3–C(5), CH_3–C(7)); 35.3 (*t*, C(2)); 45.9 (*t*, C(8)); 51.6, 52.0 (2*d*, C(3), C(4)); 123.7, 130.5 (2*d*, 4 arom. C); 32.5 (*s*, C(1)); 59.0, 66.4, 83.5 (3*s*, C(5), C(6), C(7)); 136.1, 150.7 (2*s*, 2 arom. C); 163.4 (*s*, CO). MS: 247 (2), 178 (2), 177 (2), 163 (2), 151 (12), *150* (100), 104 (22), 76 (12), 43 (44), 41 (11).

REFERENCES

[1] U. Goldener, B. Frei, O. Jeger, *Helv. Chim. Acta* **1985,** *68,* 919.

[2] a) O. Jeger, K. Schaffner, H. Wehrli, *Pure Appl. Chem.* **1964,** *9,* 555, b) A. Padwa, *Org. Photochem.* **1967,** *1,* 91; c) N. R. Bertoniere, G. W. Griffin, *ibid.* **1973,** *3,* 115.

[3] E. P. Müller, O. Jeger, *Helv. Chim. Acta* **1975,** *58,* 2173.

[4] B. Frei, H. R. Wolf, *Helv. Chim. Acta* **1976,** *59,* 82.

[5] a) N. Bischofberger, B. Frei, O. Jeger, *Helv. Chim. Acta* **1983,** *66,* 1061; b) N. Bischofberger, G. de Weck, B. Frei, H. R. Wolf, O. Jeger, *ibid.* **1981,** *64,* 1766.

[6] R. Kuhn, A. Winterstein, *Naturwissenschaften* **1933,** *21,* 527.

[7] P. Rothenmund, A. R. Menotti, *J. Am. Chem. Soc.* **1948,** *70,* 1808.

[8] M. Mousseron-Canet, J.-P. Dalle, J. C. Mani, *Bull. Soc. Chim. Fr.* **1968,** 1561.

[9] E. J. Corey, W. Suggs, *Tetrahedron Lett.* **1975,** 2647.

[10] M. Winter, M. Rautenstrauch **1975,** *Ger. Offen.* 2, 45, 649.

[11] E. Bächli, P. Karrer, *Helv. Chim. Acta* **1955,** *38,* 1863.

[12] J. D. Boyd, C. S. Foote, D. K. Imagawa, *J. Am. Chem. Soc.* **1980,** *102,* 3641.

[13] W. Herz, R. C. Ligon, J. A. Turner, J. F. Blount, *J. Org. Chem.* **1977,** *42,* 1885.

[14] W. T. Colwell, C. Soottoo, J. I. De Graw, *J. Lab. Compds.* **1979,** *16,* 551.

[15] S. J. Branca, R. L. Lock, A. B. Smith III, *J. Org. Chem.* **1977,** *42,* 3165.

[16] M. S. Newman, *J. Am. Chem. Soc.* **1953,** *75,* 4740.

[17] K. S. Ayyar, R. C. Cookson, D. A. Kagi, *J. Chem. Soc., Chem. Commun.* **1973,** 161.

[18] Program PLUTO, Crystallographic Data Centre, University Chemical Laboratory, Cambridge England.

[19] P. Main, MULTAN 80. A system of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England 1980.

[20] J. D. Dunitz, P. Seiler, *Acta Crystallogr., Sect. B* **1973,** *29,* 598.

[21] G. M. Sheldrick, SHELX 76. A Program for Crystal Structure Determination, University of Cambridge, England 1976.

[22] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, S. R. Hall. The X-Ray System, Version of June 1972. Technical Report 192, Computer Science Centre, University of Maryland, MD.

[23] C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee 1965.

[24] T. H. Chan, B. S. Ong, *Tetrahedron* **1980,** *36,* 2269.

[25] A. Osuka, *J. Org. Chem.* **1982,** *47,* 3131.

[26] K. Maruyama, A. Osuka, *J. Org. Chem.* **1980,** *45,* 1898.

[27] K. S. Feldmann, *Tetrahedron Lett.* **1983,** 5585.

[28] a) C. Lehmann, K. Schaffner, O. Jeger, *Helv. Chim. Acta* **1962,** *45,* 1031; b) H. Wehrli, C. Lehmann, T. Iizuka, K. Schaffner, O. Jeger, *ibid.* **1967,** *50,* 2403.

[29] W. G. Dauben, L. Schutte, R. E. Wolf, *J. Org. Chem.* **1969,** *34,* 1849.

[30] J. M. Conia, P. Le Perchec, *Synthesis* **1975,** 1.

[31] B. Frei, O. Jeger, N. Nakamura, H. R. Wolf, *Tetrahedron* **1981,** *37,* 3339.

[32] A. P. Alder, H. R. Wolf, O. Jeger, *Helv. Chim. Acta* **1980,** *63,* 1833.

[33] A. P. Schaap, A. L. Thayer, E. C. Blossey, D. C. Neckers, *J. Am. Chem. Soc.* **1975,** *97,* 3741.