Tetrahedron Vol 37, No. 19, pp. 3339 to 3344, 1981
Printed in Great Britain

PHOTOCHEMISTRY OF 5,6-EPOXY-1,3-DIENES

INFLUENCE OF A 7-HYDROXY SUBSTITUENT[a]

BRUNO FREI, OSKAR JEGER[a], NORIO NAKAMURA[b] and HANS RICHARD WOLF[c]
Organishe-chemisches Laboratorium der Eidgenösuschen Technischen Hochschule, Universitälstrasse 16, CH-8092 Zürich, Switzerland

(*Received in USA April* 1981)

Abstract—Triplet sensitization of the 7-hydroxy-5,6-epoxy-1,3-diene **10** causes cleavage of the C(5),O epoxide bond followed by the formation of the three isomers **11–13** or induces scission of the C(6), C(7) bond followed by the formation of the aldehyde **14** and the bicyclo[3.2.0]heptanols **15** and **16**. However, irradiation of the corresponding acetate **18** gives only C(5),O epoxide bond scission (**18** → f) followed by the cyclization process f → **19**, the 1,2-Me shifts f → **20**, **21** and the γ-H abstraction f → g leading to the cyclopropane formation g → **22**.

In previous reports,[2] the photochemistry of α,β-unsaturated γ,δ-epoxy enones was shown to be determined by C(γ), C(δ) and/or C,O bond cleavage of the oxirane. On further investigation[1,3] we observed that introduction of an ε-OH substituent has a substantial influence on the reaction path. Thus in the case of the ε-hydroxy-γ, δ-epoxy enone **1** the fission of the C(γ),*O* bond (**1** → a) is followed by the cleavage of the C(δ), C(ε) bond (via a → b).[3,4] This sequence of reactions is evidenced by the novel type of products **2–6**[4] (Scheme 1). The hydroxy diketone **7**[4] can arise directly from the diradical a by a 1,2-shift of C(ε), whereas the formation of compounds **2–6** can be explained via the 1,4-diradical b which is derived from a. In contrast to $^1n,\pi^*$-excitation ($\lambda > 347$ nm) of **1**, selective $^1\pi,\pi^*$-excitation ($\lambda = 254$ nm) also induces competitive C(γ), C(δ) bond cleavage to a ketonium ylide intermediate which photochemically forms the carbenoid c affording the allene **8** and the cyclopropene **9**. On the assumption that compounds **2–7** arise from a ^{1}T-excited state, we sought further evidence for the multiplicity of the proposed novel processes. Therefore in the present study the photochemical behaviour of the 7-hydroxy-5,6-epoxy-1,3-diene **10**[4] has been examined (Scheme 2), since its diene chromophore allows clean ^{1}T-sensitization unlike the enone **1**.

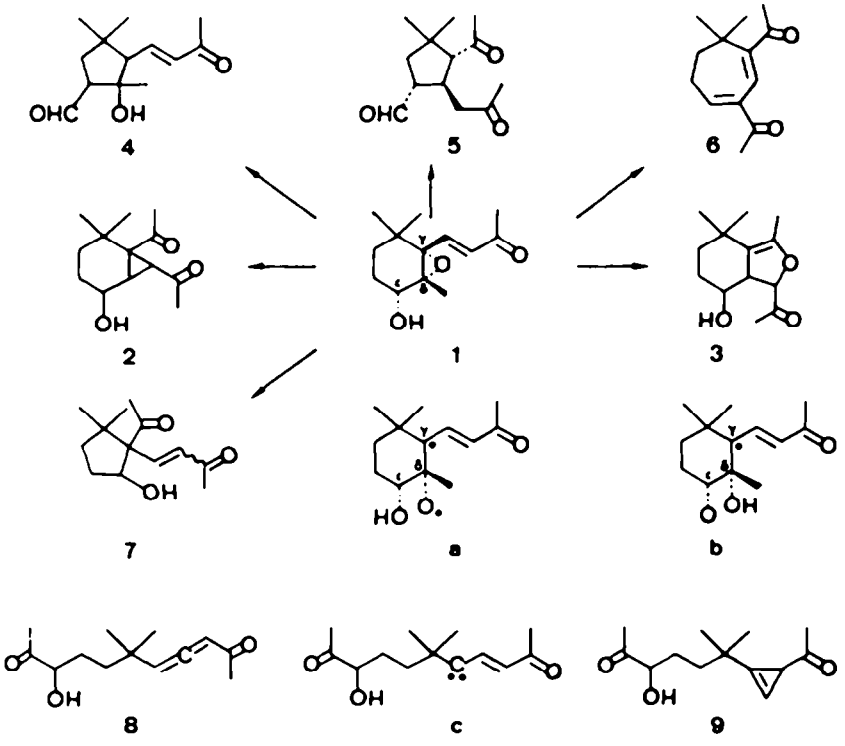
[a]Photochemical Reactions, 120th communication[1].

[b]Present address: Central Research Laboratories, Sankyo Co. Ltd., Hiromachi 1-2-58, Shinagawa-ku, Tokyo 140, Japan.

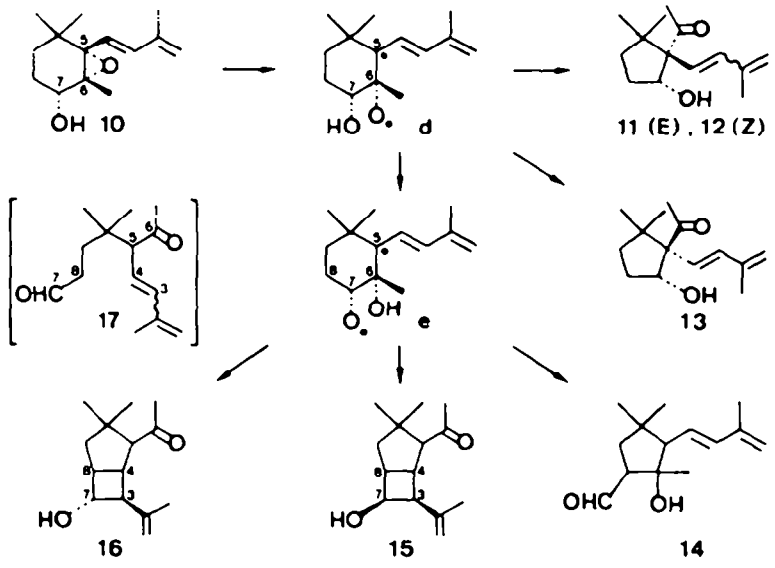
[c]Present address: F. Hoffmann-La Roche & Co. Ltd., CH-4002 Basle, Switzerland.

[d]Two diastereomers of structure **2**, four diastereomers of structure **3** and three diastereomers of structure **7** have been isolated.

[e]This numbering of the chromophore differs from that in the experimental.



Scheme 1.



Scheme 2.

RESULTS AND DISCUSSION

Irradiation of the 7-hydroxy-5,6-epoxy-diene **10**.[a] Triplet sensitization of **10** (acetone, $\lambda > 280$ nm; 70% conversion) gave the photoisomers **11** (17%), **12** (8%), **13** (5%), **14** (9%), **15** (16%) and **16** (16%)[f,g,h] (Scheme 2).

The cyclopentanols **11–13** are formed via the diradical **d** in an analogous manner to the rearrangement **a**→**7**, whereas the formation of the aldehyde **14** corresponds to the transformation **1**→**4**, and can result from the 1,4-diradical **e** via the undetected aliphatic aldehyde **17** (see discussion in Ref. 3*d*).

The detection of **15** and **16** as the main photoproducts supports the hypothesis for the intermediacy of **17** because they could be cyclization products of **17** arising from bond formation between C(3) and C(7), and between C(4) and C(8)[i] (Scheme 2).

Irradiation of the 7-acetoxy-5,6-epoxy-diene **18**.[a] Triplet sensitization of **18** (acetone, $\lambda > 280$ nm; 74% conversion) gave the photoproducts **19** (15%), **20** (16%), **21**(32%), **22** (6%), **23** (7%) (Scheme 3) and 6% of an isomer ($C_{16}H_{24}O_3$) of undetermined structure. In a manner similar to the hydroxy compound **10**, ^{1}T-sensitization of the acetate **18** shows C(5),O bond cleavage to the intermediate diradical **f**. By a known process,[3] **f** undergoes addition of the alkoxy radical to C(3) of the diene to give the dihydrofurane **19**, or a 1,2-Me shift to yield the cyclohexanones **20** and **21**.

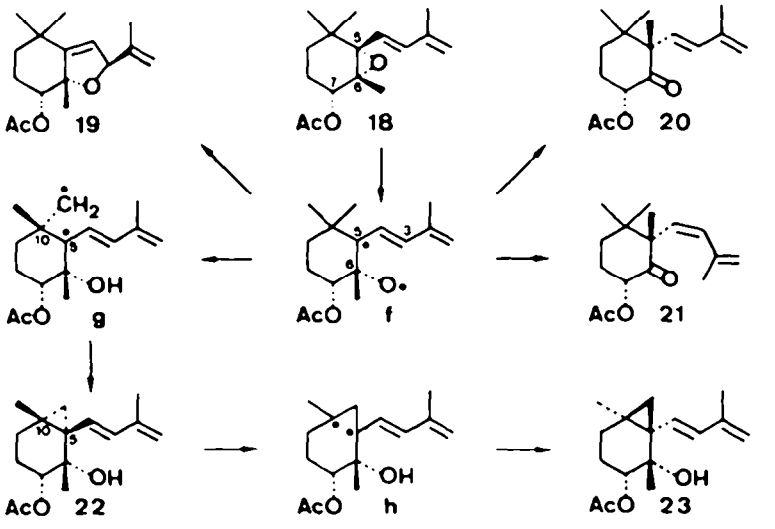
However, in contrast to the photolysis of **10**, irradia-

[f] The product distribution was determined by ^{1}H NMR-analysis and the weight of the fractions obtained from column chromatography ("flash" chromatography[4]).

[g] Yields are calculated on the basis of converted starting material.

[h] The aldehyde **27** (Scheme 4) (~ 2%) was also detected; it was shown that **27** is a product of a thermal rearrangement of **15**.

[i] The fact that the novel photoproduct **15** thermally rearranges to **27** (Scheme 4) suggests that the mechanism for the formation of the aldehyde **5** from **1** (Scheme 1) may be analogous to the sequence **10**→**15**→**27**.



Scheme 3.

tion of the acetate **18** does not afford products arising from C(6), C(7) bond cleavage. An alternative and hitherto unobserved sequence of reactions leads to the cyclopropane compound **22**. This novel product can arise from γ-H-abstraction by the alkoxy radical at the C(10)-Me group (f→g). Recombination of the 1,3-diradical **g** yields the isomer **22**. On further irradiation, **22** is isomerized to **23** via the diradical **h**.[4,k]

Structure of the products

Cyclopentanols **11–13** (Scheme 2). The structures of these products were elucidated by comparison of their spectra with those of the corresponding enones **7** (Scheme 1). Catalytic hydrogenation (Pd/C) of **11** and **12** gave **25**, hydrogenation (Pd/C) of **13** afforded **24**. The assignment of the stereochemistry of **24** and **25** is based on the presence of an associated OH absorption in the IR spectra of **25**, even in very dilute solution. This can be attributed to an intramolecular H-bond with the acetyl CO oxygen, which is unlikely for **24**. Furthermore, the NMR spectrum of **25** shows a multiplet at 4.00–4.22 ppm for the proton geminal to the OH group, whereas in **24** this signal is shifted to 4.50–4.74 ppm by an anisotropic effect of the acetyl group. Finally, **24** and **25** were oxidized by the method of Brown[7] to the cyclopentanone **26** (Scheme 4).

Aldehyde **14** (Scheme 2). This structure was assigned by comparison of the spectra of **14** with those of **4** (Scheme 1). The unstable aldehyde **14** could not be isolated in pure form and was therefore characterized after oxidation and esterification in form of the corresponding methyl ester (see the interpretation of the data in the experimental).

Bicyclic alcohols **15** and **16** (Scheme 2). The structures of **15** and **16** were deduced from their NMR data (see assignments in the experimental). At 110°, **15** undergoes a 1,5-sigmatropic H-shift giving the aldehyde **27** (Scheme 4), whereas the alcohol **16** is stable. This evidence supports the assigned configuration of **15** and **16** (Scheme 2). Both alcohols were converted to the cyclobutanone derivative **28** (Scheme 4) by catalytic hydrogenation (Pd/C) followed by oxidation with pyridinium dichromate. This result indicates that compounds **15** and **16** differ only in the relative configuration of their hydroxy functions.

Dihydrofurane **19** *and cyclohexanones* **20** *and* **21** (Scheme 3). The structures of compounds **19–21** were elucidated by comparison of their spectra with those of the corresponding photoproducts obtained in the enone series.[3d]

Cyclopropanes **22** *and* **23** (Scheme 3). The structures of these products were deduced from their NMR spectra (see interpretation of the data in the experimental). The assigned stereochemistry at C(5) and C(10) is based on the observation that in the ^{1}H NMR, isomer **22** shows one cyclopropyl H-atom at 0.54 ppm and due to an anisotropic effect of the acetoxy and of the OH group in the *cis*-position, the second cyclopropyl hydrogen is shifted downfield. In contrast, the cyclopropyl H-atoms of **23** give an AB-system at 0.54 ppm ($\delta_A = 0.40$, $\delta_B = 0.69$).

CONCLUSION

On irradiation of 5,6-epoxy-1,3-dienes, the presence of a 7-OH group has the same profound effect on the character of the photoproducts as did the ε-OH function in the corresponding γ,δ-epoxy enones. The structure of the photoproducts **14–16** reflects the influence of the OH function on the process associated with fragmentation between C(6) and C(7). Acetylation of the OH function affords the substrate **18** which behaves similarly to C(7) unsubstituted 5,6-epoxy-1,3-dienes.[5] Finally, the detection of the photoproducts **11–16** (and **27**) on acetone sensitization of **10** provides convincing evidence that compounds **4**, **7** (and **5**) arise from a ^{1}T-excited state of the enone **1**.[l]

EXPERIMENTAL

General. See Ref. 8. ^{1}H NMR: 300 MHz spectra were taken on a Bruker spectrometer model WM 300.

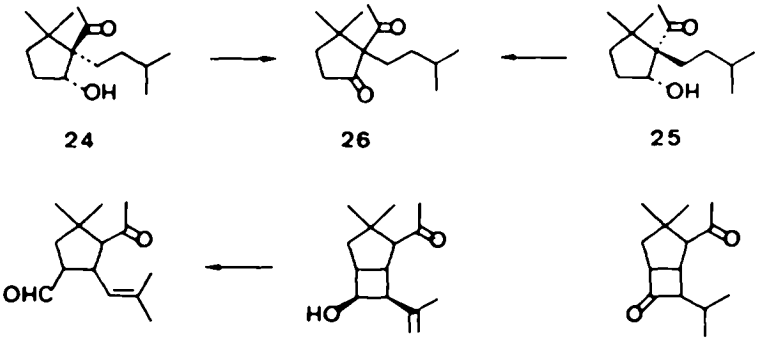
Preparation of **10** *and* **18**

Epoxydiene **10**. To a soln of 16.3 g (72.7 mmol) of **1**[3e] in 400 ml dry ether were added 250 ml of a 0.45 M soln of methylene triphenyl phosphorane in dry ether (prepared from 40.4 g (113.1 mmol) methyl triphenyl phosphonium bromide and $NaNH_2$ in liq. NH_3) at 0° under argon. After stirring for 1 hr, the mixture was filtered through SiO_2 and the solvent was evaporated at reduced pressure. To remove the remaining triphenyl phosphine oxide the residue was suspended in pentane and filtered. Distillation at 120°/0.01 mm afforded 15.8 g (97%) of **10**.

[l]Analogous interconversion of vinyl-cyclopropanes is commonly observed.[6]

[k]On reexamination of the $^1n,\pi^*$-photolysis of the epoxyenone corresponding to **18**[3d] the cyclopropyl-enones analogous to **22** and **23** were isolated in only 2% yield.

[l]Investigation of the selective ^{1}S-excitation of **10** and **18** is in progress.



24 26 25

27 15 28

Scheme 4.

(1R*, 2R*, 3S*) - 3 - [(E) - 3' - *Methyl* - 1',3' - *butadienyl*] - 2,3-*epoxy* - 2,4,4 - *trimethyl* - *cyclohexanol* (10). M.P. 52–53.5°. UV: 232 (26500). IR: 3570 m, 3485 br.w, 3085 w, 3040 w, 2970 s, 1610 m, 892 s. ^{1}H NMR: 0.92, 1.03 (2 s, 2 H_3C-C(4); 1.21 (s, H_3C-C(2)); 1.0–1.8 (m, 2H-C(5), 2H-C(6)); 1.81 (s, H_3C-C(3')); 2.01 (d, J = 11, H-O); 3.63 (m, H-C(1)); 4.93 (br.s, $w_{1/2}$ = 4, 2H-C(4')); 5.96 (AB-system, J = 16, ν_A = 5.68, ν_B = 6.24, H-C(1'), H-C(2')). ^{13}C NMR: 17.7, 18.6, 25.5, 26.1 (4qa, 2 H_3C-C(4), H_3C-C(2), H_3C-C(3')); 27.1, 32.6 (2t, C(5), C(6)); 116.9 (t, C(4')); 69.4 (d, C(1)); 124.1, 136.0 (2d, C(1'), C(2')); 33.5 (s, C(4)); 67.8, 73.4 (2s, C(2), C(3)); 140.8 (s, C(3')). MS: 222 (28, M^+), 207 (72), 123 (39), 43 (100). (Found: C 75.65, H 9.93. Calc. for $C_{14}H_{22}O_2$: C 75.63, H 9.97%).

Acetylation of 10. A soln of 2.01 g (9.04 mmol) of 10 in 10 ml dry pyridine and 5 ml Ac_2O was stirred at rt for 16 hr. After adding ice-water, the mixture was stirred for 1 hr, extracted with EtOAc and the organic phase was worked up. Crystallization from petroleum ether gave 2.01 g (88%) of 18.

(1R*, 2R*, 3S*) - 2,3 - *Epoxy* - 3 - [(*E*) - 3' - *methyl* - 1',3' - *butadienyl*] - 2,4,4 - *trimethyl* - 1 - *cyclohexyl* - *acetate* (18). M.P. 51–52°. UV: 232 (27850). IR: 3080 w, 2960 m, 1735 s, 1235 s, 890 m. ^{1}H NMR: 0.80–1.70 (m, 2H-C(5), 2H-C(6)); 0.94, 1.04, 1.08 (3s, H_3C-C(2), 2 H_3C-C(4)); 1.81 (m, $w_{1/2}$ = 3, H_3C-C(3')); 2.03 (s, H_3C-CO); 4.85–5.05 (m, 2H-C(4'), H-C(1)); 5.96 (AB-system, J = 17, ν_A = 5.69, ν_B = 6.24, H-C(1'), H-C(2')). MS: 264 (3, M^+), 249 (16), 123 (91), 43 (100). (Found: C 72.74, H 9.08. Calc. for $C_{16}H_{24}O_3$: C 72.69, H 9.15%).

Photolysis experiments

Irradiation of 10 *in acetone at* $\lambda > 280$ nm. A soln of 2.0 g (9.0 mmol) of 10 in 250 ml acetone was irradiated (pyrex, lamp B, under argon; 70% conversion). Chromatography (SiO_2; pentane/DME 10:1) gave mixed fractions which were analyzed by NMR spectroscopy. Analytical samples of the photoproducts were obtained by repeated chromatography on SiO_2. Product distribution[7]: 17% 11, 8% 12, 5% 13, 9% 14, 16% 15, 16% 16 and ~2% 17.

(1R*, 5S*) - (1 - [(Z) - 3' - *Methyl* - 1',3' - *butadienyl*] - 5 - *hydroxy* - 2,2 - *dimethylcyclopentyl*) *methyl ketone* (12). B.p. 90°/0.05 mm. UV: 225 (5800), 290 (97). IR: 3480 m, 3080 w, 2965 s, 1687 s, 1635 m, 910 s. ^{1}H NMR: 1.13, 1.16 (2s, 2 H_3C-C(2)); 1.78 (m, $w_{1/2}$ = 4, H_3C-C(3')), 1.98 (s, H_3C-CO); 1.0–2.2 (m, 2H-C(3), 2H-C(4)); 4.34–4.48 (m, H-C(5)); 4.66 (m, $w_{1/2}$ = 4, H-O); 4.82, 4.98 (2m, $w_{1/2}$ = 4, 2H-C(4')); 5.69 (AB-system, J = 13, ν_A = 5.52, ν_B = 5.86, H-C(1'), H-C(2')). ^{13}C NMR. (contaminated by ~15% of 17): 23.3, 26.4, 27.6, 30.5 (4qa, 4 CH_3); 31.6, 38.9 (2t, C(3), C(4)); 116.9 (t, C(4')); 82.3 (d, C(5)); 130.2, 133.3 (2d, C(1'), C(2')); 45.1 (s, C(2)); 67.7 (s, C(1)); 140.0 (s, C(3')); 214.6 (s, H_3C-CO). MS: 222 (7, M^+), 207 (41), 147 (62), 43 (100), (Found: C 75.79, H 10.00. Calc. for $C_{14}H_{22}O_2$: C 75.63, H 9.97%).

(1R*, 5S*) - (1 - [(E) - 3' - *Methyl* - 1',3' - *butadienyl*] - 5 - *hydroxy* - 2,2 - *dimethylcyclopentyl*) *methyl ketone* (11). B.p. 90°/0.05 mm. UV: 236 (19700), 302 (245). IR: 3570 m, 3090 w, 2970 s, 1688 s, 1608 w, 893 s. ^{1}H NMR: 0.90, 1.05 (2s, 2 H_3C-C(2)); 1.85 (m, $w_{1/2}$ = 3, H_3C-C(3')); 2.02 (s, H_3C-CO); 1.2–2.3 (m, 2H-C(3), 2H-C(4)); 2.48 (d, J = 10, H-O); 4.20–4.48 (m, H-C(5)); 4.96 (m, $w_{1/2}$ = 5, 2H-C(4')); 6.15 (AB-system, J = 16, ν_A = 5.84, ν_B = 6.45, H-C(1'), H-C(2')). ^{13}C NMR. (~90% pure): 18.6, 25.7, 26.4, 32.0 (4qa, 4 CH_3); 31.8, 37.4 (2t, C(3), C(4)); 116.7 (t, C(4')); 79.3 (d, C(5)); 128.8, 134.2 (2d, C(1'), C(2')); 44.8 (s, C(2)); 69.0 (s, C(1)); 141.5 (s, C(3')); 212.3 (s, H_3C-CO). MS: 222 (2, M^+), 147 (72), 123 (38), 43 (100). (Found: C 75.51, H 10.09. Calc. for $C_{14}H_{22}O_2$: C 75.63, H 9.97%).

(1R*, 5R*) - (1 - [(E) - 3' - *Methyl* - 1',3' - *butadienyl*] - 5 - *hydroxy* -2,2 - dimethylcyclopentyl) methyl ketone (13). B.p. 95°/0.05 mm. UV: 236 (22800), 290 (168). IR: 3590 m, 3080 m, 3030 w, 2960 s, 1690 s, 890 m. ^{1}H NMR: 0.92, 1.17 (2s, 2 H_3C-C(2)); 1.86 (m, $w_{1/2}$ = 3, H_3C-C(3')); 2.10 (s, H_3C-CO); 0.8–2.3 (m, 2H-C(3), 2H-C(4), H-O); 4.50–4.76 (m, H-C(5)); 4.90 (m, $w_{1/2}$ = 4, 2H-C(4')); 5.70 (AB-system, J = 16, ν_A = 5.54, ν_B = 5.85, H-C(1'), H-C(2')). MS: 222 (2, M^+), 147 (30), 123 (51), 43 (100).

3 - [(E) - 3' - *Methyl* - 1',3' - *butadienyl*] - 2 - *hydroxy* - 2,4,4 - *trimethyl* - 1 - *cyclopentanecarboxaldehyde* (14) (~80% pure). IR: 3620 m, 3550 br.m, 3085 w, 2960 s, 2730 m, 1715 s, 1608 m, 890 s. ^{1}H NMR. 0.99, 1.04 (2s, 2 H_3C-C(4)); 1.25 (s, H_3C-C(2)); 1.85 (m, $w_{1/2}$ = 4, H_3C-C(3')); 1.5–2.3 (m, 2H-C(5), H-C(3), H-O); 2.4–2.7 (m, H-C(1)); 4.84 (m, $w_{1/2}$ = 4, 2H-C(4')); 5.85 (AB-system, J = 16, ν_A = 5.66, split into d, J = 9, H-C(1'), ν_B = 6.04, H-C(2')); 9.72 (d, J = 2, H-CO). MS: 222 (< 1, M^+), 161 (86), 43 (100).

(6 - *Hydroxy* - 3,3 - *dimethyl* - 7 - [2' - *propenyl*] - *bicyclo*[3.2.0]2 - *heptyl*)*methyl ketone, isomer I* (15) (contaminated with ~15% of 27). IR: 3600–3400 br.w, 1708 s, 1645 m. ^{1}H NMR (300 MHz, $CDCl_3$): 0.78, 1.31 (2s, 2 H_3C-C(3)); 1.66 (dxd, J_1 = 13, J_2 = 1.5, H-C(4)); 1.75 (m, $w_{1/2}$ = 3, 3H-C(3')); 1.88 (dxd, J_1 = 13, J_2 = 8.5, H-C(4)); 1.96 (d, J = 8.5, H-O); 2.14 (s, H_3C-CO); 2.41–2.56 (m, H-C(5)); 2.62 (d, J = 7, H-C(2)); 2.84–2.91 (m, H-C(7)); 3.21–3.31 (m, H-C(1)); 4.04–4.14 (m, H-C(6)); 4.92, 5.12 (2m, $w_{1/2}$ = 5, 2H-C(1')). ^{13}C NMR: 23.3, 28.3, 31.6 (4qa, 2qa at 23.3, 4 CH_3); 48.3 (t, C(4)); 112.0 (t, C(1')); 40.3, 45.8, 52.2, 69.7, 73.2 (5d, 5 CH); 48.6 (s, C(3)); 143.2 (s, C(2')); 209.0 (s, H_3C-CO). MS: 222 (18, M^+), 151 (100), 43 (98).

(6 - *Hydroxy* - 3,3 - *dimethyl* - 7 - [2' - *propenyl*] - *bicyclo*[3.2.0]2 - *heptyl*)*methyl ketone, isomer II* (16). B.p. 100°/0.05 mm. IR: 3620 m, 3550–3400 br.w, 1708 s, 1645 m. ^{1}H NMR (300 MHz, $CDCl_3$): 0.78, 1.40 (2s, 2 H_3C-C(3)); 1.58 (dxd, J_1 = 12.5, J_2 = 8, H-C(4)); 1.71 (m, $w_{1/2}$ = 3, 3H-C(3')); 1.79 (d, J = 5.5, H-O); 2.04 (dxd, J_1 = 12.5, J_2 = 10.5, H-C(4)); 2.15 (s, H_3C-CO); 2.45–2.54 (m, H-C(7)); 2.67 (d, J = 4.5, H-C(2)); 2.69–2.78 (m, H-C(1)); 2.82–2.96 (m, H-C(5)); 4.04–4.14 (m, H-C(6)); 4.72, 4.75 (2m, $w_{1/2}$ = 5, 2H-C(1')). ^{13}C NMR: 20.7, 23.6, 28.8, 31.4 (4qa, 4 CH_3); 42.3 (t, C(4)); 108.6 (t, C(1')); 37.4, 41.6, 59.9, 67.4, 71.1 (5d, 5 CH); 47.8 (s, C(3)); 145.4 (s, C(2')); 209.7 (s, H_3C-CO). MS: 222 (11, M^+), 151 (100), 43 (72). (Found: C 75.55, H 9.89. Calc. for $C_{14}H_{22}O_2$: C 75.63, H 9.97%).

Irradiation of 18 *in acetone at* $\lambda > 280$ nm. A soln of 2.00 g (7.58 mmol) of 18 in 250 ml acetone was irradiated (pyrex, lamp B, under argon; 74% conversion). Chromatography (SiO_2; hexane/EtOAc 50:1 to 2:1) afforded 219 mg (15%) of 19, 242 mg (16%) of 20, 480 mg (32%) of 21, 84 mg (6%) of 22, 101 mg (7%) of 23 and 89 mg (6%) of an isomer ($C_{16}H_{24}O_3$) of undetermined structure.

(5R*, 6S*, 8S*) - 5 - *Acetoxy* - 8 - (2' - *propenyl*) - 7 - *oxa* - 2,2,6 - *trimethylbicyclo*[4.3.0]9 - *nonene* (19). IR: 1740 s, 1650 m, 1370 s. ^{1}H NMR: 1.12, 1.20 (2s, 2 H_3C-C(2)); 1.25–2.10 (m, 2H-C(3), 2H-C(4)); 1.43 (s, H_3C-C(6)); 1.65 (m, $w_{1/2}$ = 3, 3H-C(3')); 1.94 (s, H_3C-CO_2); 4.68 (m, $w_{1/2}$ = 5, H-C(5)); 4.87 (m, $w_{1/2}$ = 5, H_2C=C, H-C(8)); 5.30 (d, J = 2, H-C(9)). MS: 264 (2, M^+), 204 (100), 189 (78), 43 (89).

(2R*, 6S*) - 6 - *Acetoxy* - 2 - [(Z) - 3' - *methyl* - 1',3' - *butadienyl*] - 2,3,3 - *trimethylcyclohexanone* (21). M.p. 68–69° (from pentane). UV: endabsorption to 240 nm; 293 (38). IR: 1750 s, 1725 s, 1620 w, 1230 s. ^{1}H NMR: 0.93, 0.97 (2s, 2 H_3C-C(3)); 1.30–2.20 (m, 2H-C(4) and 2H-C(5)); 1.46 (s, H_3C-C(2)); 1.75 (m, $w_{1/2}$ = 3, H_3C-C(3')); 2.04 (s, H_3C-CO_2), 4.66, 4.78 (2m, $w_{1/2}$ = 4, 2H-C(4')); 5.20–5.40 (m, H-C(6)); 5.67 (AB-system, J = 13, ν_A = 5.39, ν_B = 5.93 (with fine structure), H-C(1'), H-C(2')). ^{13}C NMR: 17.7, 20.7, 23.9, 24.8 (5qa, 2qa at 23.9, 5 CH_3); 28.0, 33.7 (2t, C(4), C(5)); 114.2 (t, C(4')); 72.9 (d, C(6)); 128.4, 134.2 (2d, C(1'), C(2')); 41.5 (s, C(3)); 58.4 (s, C(2)); 142.8 (s, C(3')); 169.8 (s, H_3C-CO_2); 206.8 (s, C(1)). MS: 264 (9, M^+), 222 (16), 43 (100). (Found: C 72.76, H 9.29. Calc. for $C_{16}H_{24}O_3$: C 72.69, H 9.15%).

(2R*, 6S*) - 6 - *Acetoxy* - 2 - [(E) - 3' - *methyl* - 1',3' - *butadienyl*] - 2,3,3 - *trimethyl* - *cyclohexanone* (20). M.p. 75–76° (from pentane). UV: 229 (25600); 288 (51). IR: 1750 s, 1725 s, 1605 m, 1230 s. ^{1}H NMR: 0.86, 0.88 (2s, 2 H_3C-C(3)); 1.20–2.30 (m, 2H-C(4), 2H-C(5)); 1.35 (s, H_3C-C(2)); 1.87 (m, $w_{1/2}$ = 3, H_3C-C(3')); 2.04 (s, H_3C-CO_2); 4.84 (m, $w_{1/2}$ = 4, 2H-C(4')); 5.26–5.48 (m, H-C(6)); 5.99 (s, H-C(1'), H-C(2')). In C_6D_6: AB-system at 6.16 ppm (J = 17, ν_A = 6.04, ν_B = 6.28, H-C(1'), H-C(2')). ^{13}C NMR: 17.4, 18.7, 20.7, 24.3, 24.4 (5qa, 5 CH_3); 28.1, 34.4 (2t, C(4), C(5)); 115.8 (t, C(4')); 73.2 (d, C(6)); 129.6, 133.1 (2d, C(1'), C(2')); 41.4 (s, C(3)); 56.8 (s, C(2)); 142.2 (s, C(3')); 170.0 (s, H_3C-CO_2), 207.3 (s, C(1)). MS: 264 (33, M^+), 222 (11), 122 (100), 43 (95). (Found: C 72.45, H 9.28. Calc. for $C_{16}H_{24}O_3$: C 72.69, H 9.15%).

(1R*, 2R*, 3S*, 6R*) - 3 - *Acetoxy* - 2,6 - *dimethyl* - 1 - [(E) - 3' - *methyl* - 1',3' - *butadienyl*] - *bicyclo*[4.1.0]2 - *heptanol* (23). M.p. 83.5–84.5° (from pentane). UV: 237 (20800). IR: 3600 m, 3500–3300 br.w, 1740 s, 1640 w, 1605 m, 1235 s. ^{1}H NMR: 0.54 (AB-

system, J = 6, ν_A = 0.40, ν_B = 0.69, 2H-C(7)); 0.98, 1.10 (2s, H_3C-C(2), H_3C-C(6)); 1.30–2.00 (m, 2H-C(4), 2H-C(5)); 1.53 (s, H-O); 1.85 (m, $w_{1/2}$ = 2, H_3C-C(3')); 1.99 (s, H_3C-CO_2); 4.32–4.56 (m, H-C(3)); 4.80 (m, $w_{1/2}$ = 3, 2H-C(4')); 6.01 (AB-system, J = 16, ν_A = 5.92, ν_B = 6.10, (H-C(1'), H-C(2')). ^{13}C NMR: 18.9, 21.2, 23.2, 24.4 (4qa, 4 CH_3); 20.9, 22.8, 30.0 (3t, C(4), C(5), C(7)); 115.1 (t, C(4')); 75.7 (d, C(3)); 129.0, 135.6 (2d, C(1'), C(2')); 22.8 (s, overlapped with t, C(6)); 38.3 (s, C(1)); 72.1 (s, C(2)); 142.0 (s, C(3')); 170.3 (s, H_3C-CO_2). MS: 264 (3, M$^+$), 204 (23), 43 (100). (Found: C 72.79, H 9.22. Calc. for $C_{16}H_{24}O_3$: C 72.69, H 9.15%).

(1R*, 2S*, 3R*, 6R*) - 3 - *Acetoxy* - 2,6 - *dimethyl* - 1 - [(E) - 3' - *methyl* - 1',3' - *butadienyl*] - *bicyclo*[4.1.0]2 - *heptanol* (22). M.p. 62–63° (from pentane). UV: 234 (20100). IR: 3600 m, 3580–3360 br.w, 1740 s, 1640 w, 1605 m, 1235 s, 1230 s. ^{1}H NMR: 0.54 (d, J = 5, H-C(7)); 0.98, 1.19 (2s, H_3C-C(2), H_3C-C(6)); 1.20–2.00 (m, 2H-C(4), 2H-C(5), H-C(7)); 1.47 (s, H-O); 1.80 (m, $w_{1/2}$ = 3, H_3C-C(3')); 1.99 (s, H_3C-CO_2); 4.34–4.54 (m, H-C(3)); 5.84 (m, $w_{1/2}$ = 3, 2H-C(4')); 5.91 (AB-system, J = 16, ν_A = 5.72, ν_B = 6.10, H-C(1'), H-C(2')). ^{13}C NMR: 18.8, 21.3, 22.5, 26.9 (4qa, 4 CH_3); 18.3 (t, C(7)); 22.5 (overlapped with qa), 29.6 (2t, C(4), C(5)); 115.4 (t, C(4')); 77.6 (d, C(3)); 130.1, 136.1 (2d, C(1'), C(2')); 23.8 (s, C(6)); 36.6 (s, C(1)); 71.4 (s, C(2)); 141.7 (s, C(3')); 170.3 (s, H_3C-CO_2). MS: 264 (< 1, M$^+$), 204 (19), 43 (100). (Found: C 72.50, H, 9.12. Calc. for $C_{16}H_{24}O_3$: C 72.69, H 9.15%).

Isomer ($C_{16}H_{24}O_3$) *of undetermined structure.* B.p. 115–120°/0.05 mm. IR: 3600 m, 3560–3300 br.w, 1745 s, 1640 w, 1235 s. ^{1}H NMR: 1.14, 1.31 (2s, 6H); 1.30–2.10 (m, 6H); 1.67 (m, $w_{1/2}$ = 3, 3H); 1.98 (s, 3H); 2.06 (s, 1H, exchangeable); 3.30 (t, with fine structure, J = 8, 1H); 4.55–4.76 (m, 3H); 5.56 (d, J = 2, 1H). ^{13}C NMR: 20.5, 21.1, 24.9, 26.0 (4qa); 24.9 (overlapped with qa), 34.3, 50.2, 109.1 (4t); 49.2, 77.8, 126.2 (3d); 46.5, 71.8, 148.4, 153.9, 170.5 (5s). MS: 264 (3, M$^+$), 204 (27), 161 (100), 43 (100). (Found: C 72.69, H 9.26. Calc. for $C_{16}H_{24}O_3$: C 72.69, H 9.15%).

Irradiation of 22 *in acetone at* $\lambda > 280$ nm. A soln of 36 mg (0.13 mmol) of 22 was irradiated (pyrex, lamp B, under argon). After 2 hr the mixture was filtered through SiO_2 (ether/hexane 1:1) and evaporation of the solvent gave 31 mg of a 1:1 mixture of 22 and 23 (^{1}H NMR analysis).

Additional experiments

Catalytic hydrogenation of 11, 12 *and* 13. (a) A mixture of 39 mg (0.18 mmol) of 12, 5 ml EtOH and 46 mg 10% Pd/C catalyst was stirred for 7 hr under H_2. Suction filtration and evaporation of the solvent gave 40 mg (100%) of 25.

(b) Catalytic hydrogenation of 32 mg (0.14 mmol) of 11 in 5 ml EtOH with 43 mg 10% Pd/C catalyst as described above gave 31 mg (95%) of 25 as a colorless oil. An analytical sample of 25 was obtained by chromatography (SiO_2; ether/hexane 1:3) followed by a KR-distillation (80°/0.05 mm).

(1R*, 5S*) - (1 - [3' - *Methylbutyl*] - 5 - *hydroxy* - 2,2 - *dimethylcyclopentyl*)*methyl ketone* (25). B.p. 80°/0.05 mm. UV: 292 (34). IR: 3510 m, 2950 s, 1685 sS, 1678 s. ^{1}H NMR: 0.90 (d, J = 6, H_3C-C(3'), 3H-C(4')); 1.06 (s, 2 H_3C-C(2)); 1.1–2.0 (m, 2H-C(3), 2H-C(4), 2H-C(1'), 2H-C(2'), H-C(3')); 2.05 (s, H_3C-CO)); 3.44 (d, J = 6, H-O); 4.00–4.22 (m, H-C(5)). MS: 226 (14, M$^+$), 169 (100), 113 (90), 43 (66). (Found: C 74.43, H 11.53%. Calc. for $C_{14}H_{26}O_2$: C 74.29, H 11.58%).

(c) To a soln of 77 mg (0.35 mmol) of 13 in 5 ml EtOH, 35 mg 10% Pd/C catalyst was added and the mixture was stirred for 7 hr under H_2. After suction filtration the solvent was evaporated and the residue was chromatographed (SiO_2; ether/hexane 1:1) to afford 41 mg (52%) of 24.

(1R*, 5R*) - (1 - [3' - *Methylbutyl*] - 5 - *hydroxy* - 2,2 - *dimethylcyclopentyl*)*methyl ketone* (24). B.p. 90°/0.05 mm. UV: 283 (34). IR: 3630 m, 3595 m, 3490 br.w, 2955 s, 1685 s. ^{1}H NMR: 0.86, 1.12 (2s, 2 H_3C-C(2)); 0.89 (d, J = 6, H_3C-C(3'), 3H-C(4')); 1.2–2.2 (m, 2H-C(3), 2H-C(4), 2H-C(1'), 2H-C(2'), H-C(3'), H-O); 4.50–4.74 (m, H-C(5)). MS: 226 (6, M$^+$), 169 (64), 113 (74), 43 (100).

Oxidation of 24 *and* 25. (a) To a stirred soln of 47 mg (0.21 mmol) of 25 in 5 ml ether was added dropwise ~1 ml of a $Na_2Cr_2O_7/H_2SO_4$ soln.[7] After stirring for 15 min at 0°, the mixture was diluted with ~50 ml ether and worked up. Chromatography (SiO_2; ether/hexane 1:1) of the residue gave 33 mg (70%) of 26.

(b) Treatment of 18 mg (0.08 mmol) of 24 in 2 ml ether with 0.5 ml of a $Na_2Cr_2O_7/H_2SO_4$ soln[7] as described above gave 12 mg (67%) of 26.

2 - *Acetyl* - 2 - (3' - *methylbutyl*) - 3,3 - *dimethylcyclopentanone* (26). B.p. 100°/0.08 mm. UV: 303 (84). IR: 1730 s, 1690 s. ^{1}H NMR: 0.84, 0.86 (2d, J = 6, 3H-C(4'), H_3C-C(3')); 0.96, 1.06 (2s, 2 H_3C-C(3)); 2.09 (s, H_3C-CO); 0.75–2.42 (m, 4 CH_2, H-C(3')). MS: 224 (2, M$^+$), 182 (11), 167 (100). (Found: C 74.74, H 10.82. Calc. for $C_{14}H_{24}O_2$: C 74.95, H 10.78%).

Thermolysis of 15 *and* 16. (a) A soln of 95 mg (0.43 mmol) of 15 in 4 ml toluene was heated under reflux for 1 hr. Chromatography (SiO_2; ether/hexane 1:3) gave 60 mg (63%) of 27. (b) Treatment of 16 mg (0.072 mmol) of 16 under the same conditions as under (a) gave a quantitative recovery of the unchanged starting material.

3 - *Acetyl* - 4,4 - *dimethyl* - 2 - (2' - *methyl* - 1' - *propenyl*) - *cyclopentanecarboxaldehyde* (27). B.p. 90°/0.05 mm. IR: 2965 s, 2820 m, 2730 m, 1728 s, 1710 s. ^{1}H NMR (300 MHz; $CDCl_3$): 0.90, 1.30 (2s, 2 H_3C-C(4)); 1.61 (dxd, J_1 = 13, J_2 = 7.5, H-C(5)); 1.66, 1.70 (2m, $w_{1/2}$ = 3, H_3C-C(2'), 3H-C(3')); 2.06 (dxd, J_1 = 13, J_2 = 9, H-C(5)); 2.62 (d, J = 10, H-C(3)); 3.08 (dxdxdxd, J_1 = 10, J_2 = 9, J_3 = 7, 5 J_4 = 2, H-C(1)); 3.82 (dxdxd, J_1 = J_2 = J_3 = 10, H-C(2)); 4.95 (dxm, J_1 = 10, $w_{1/2}$ = 5, H-C(1')); 9.64 (d, J = 2, H-CO). Irradiation at 4.95 ppm collapsed dxdxd at 3.82 ppm to dxd and the 2*m* at 1.66 and 1.70 to 2s. ^{13}C NMR: 18.3, 24.1, 25.7, 29.4, 32.4 (5qa, 2 H_3C-C(4), H_3C-CO, H_3C-C(2'), C(3')); 41.8 (t, C(5)); 42.0, 51.9, 68.5, (3d, C(1), C(2), C(3)); 123.4 (d, C(1')); 203.6 (d, HCO); 42.2 (s, C(4)); 208.1 (s, H_3C-CO). MS: 222 (12, M$^+$), 151 (100), 43 (68). (Found: C 75.25, H 10.10. Calc. for $C_{14}H_{22}O_2$: C 65.63, H 9.97%).

Transformation of 15 *and* 16 *into* 28. (a) To a soln of 94 mg (0.42 mmol) of 16 in 5 ml EtOH was added 56 mg 10% Pd/C catalyst and the mixture was stirred under H_2 for 1.5 hr. After suction filtration through *Celite*, the solvent was evaporated. Chromatography (SiO_2; pentane/DME 10:1) of the residue gave 52 mg (55%) of dihydro-16. To a soln of 32 mg (0.14 mmol) of dihydro-16 in 3 ml dry CH_2Cl_2 was added 370 mg pyridinium dichromate and the mixture was stirred for 4.5 hr. The mixture was diluted with ether, filtered through SiO_2 and chromatography (SiO_2; ether/hexane 1:1) afforded 23 mg (72%) of 28. (b) Catalytic hydrogenation of 198 mg (0.89 mmol) of 15 with 100 mg 10% Pd/C catalyst in 5 ml EtOH for 2 hr as described for 16 gave 66 mg (33%) of dihydro-15. Oxidation of 37 mg (0.17 mmol) of dihydro-15 with 420 mg of pyridinium dichromate as described under (a) afforded 27 mg (73%) of 28.

2 - *Acetyl* - 3,3 - *dimethyl* - 7 - [2' - *propyl*] - *bicyclo*[3.2.0]6 - *heptanone* (28). B.p. 100°/0.05 mm. IR: 1770 s, 1705 s. ^{1}H NMR. (300 MHz; $CDCl_3$): 0.86, 1.30 (2s, 2 H_3C-C(3)); 0.92, 0.98 (2d, J = 6, 3H-C(1'), 3H-C(3')); 1.79 (AB-system, J = 13, ν_A = 1.72 (split to d, J = 9.5), ν_B = 1.86 (split to d, J = 8.5), 2H-C(4)); 1.80–1.96 (m, overlapped by AB-system at 1.79, H-C(2')); 2.66 (dxdxd, J_1 = 9, J_2 = 4.5, J_3 = 3, H-C(7)); 2.72 (d, J = 6.5, H-C(2)); 3.08 (dxdxd, J_1 = 9, J_2 = 6.5, J_3 = 4.5, H-C(1)); 3.55 (dxdxdxd, J_1 = 9.5, J_2 = 9, J_3 = 8.5, J_4 = 3, H-C(5)). ^{13}C NMR: 20.3, 23.2, 28.2, 32.0 (5qa, 2 qa overlapped at 20.3, 5 CH_3); 44.3 (t, C(4)); 29.3, 37.2, 60.3, 70.0, 72.4 (5d, 5 CH); 49.7 (s, C(3)); 208.1, 213.7 (2s, C(6), H_3C-CO). MS: 222 (4, M$^+$), 139 (19), 138 (32), 95 (100).

Oxidation and esterification of the crude mixture obtained from the photolysis of 10 *at* $\lambda > 280$ nm *in acetone.* The crude material obtained from the irradiation of 1.0 g (4.5 mmol) of 10 in 200 ml acetone at $\lambda > 280$ nm as described above (conversion ~75%) was dissolved in 25 ml ether. The stirred soln was cooled to 0° and 8.5 ml of a $Na_2Cr_2O_7/H_2SO_4$ soln[7] was added dropwise. After stirring for 45 min at 0°, the mixture was diluted with 50 ml ether and the organic phase was washed with 20 ml water. The organic phase was then extracted with three 20 ml portions sat. Na_2CO_3 aq and the combined extracts were acidified to pH ≈ 1 and extracted with ether. The residue (227 mg) was dissolved in 5 ml ether and was treated with 5 ml of a ~1M soln of CH_2N_2 in ether. After stirring the mixture overnight, the solvent was evaporated and chromatography (SiO_2; ether/hexane 1:3) afforded 46 mg (5%) of methyl 3 - [(E) - 3' - methyl - 1',3' - butadienyl] - 2 - hydroxy - 2,4,4 - trimethylcyclopentanecarboxylate. B.p. 100°/0.05 mm. UV: 234 (23200). IR: 3605 m, 3540–3400 br.w, 1735 s, 1605w. ^{1}H NMR: 0.98, 1.02, 1.10 (3s, 2 H_3C-C(4),

H_3C-C(2)); 1.49 (s, H-O); 1.77 (d, J = 9, 2H-C(5)); 1.85 (m, $w_{1/2}$ = 3, H_3C-C(3')); 1.93 (d, J = 9.5, H-C(3)); 2.96 (dxd, $J_1 = J_2$ = 9, H-C(1)); 3.62 (s, H_3C-O); 4.85 (m, $w_{1/2}$ = 3, 2H-C(4')); 5.85 (AB-system, J = 17, ν_A = 5.62, split to d, J = 9.5, H-C(1'), ν_B = 6.08, H-C(2')). Irradiation at 5.62 collapsed d at 1.93 to s. ^{13}C NMR: 18.8, 23.5, 26.3, 28.9 (4qa, 4 CH_3); 51.5 (qa, H_3C-O); 42.7 (t, C(5)); 115.5 (t, C(4')); 56.0, 64.0 (2d, C(1), C(3)); 125.7, 137.1 (2d, C(1'), C(2')); 41.7 (s, CO(4)); 82.8 (s, C(2)); 142.1 (s, C(3')); 174.8 (s, H_3CO-CO). MS: 252 (7, M^+), 234 (65), 171 (65), 111 (100).

Acknowledgements—For financial support we wish to thank to the *Swiss National Science Foundation* and to Ciba-Geigy Ltd., Basle.

We are indebted to the following coworkers from our analytical service for their cooperation: Miss B. Brandenberg, Mr. K. Hiltbrunner and Mr. P. Müller (NMR., under the direction of Prof. Dr. J. F. M. Oth); Mrs. L. Golgowski and Prof. Dr. J. Seibl (MS.); Mr. D. Manser (elemental analysis) and Mr. H. U. Hediger (IR., under the direction of Prof. Dr. W. Simon). We are also grateful to Mr. K. Job for the preparation of starting materials, to Miss E. Meier for her help in the laboratory and to Dr. T. Lyle for his help in compilation of the English manuscript.

REFERENCES

[1]119th communication: G. de Weck and H. R. Wolf, *Helv. Chim. Acta* **64**, 224 (1981).

[2a]B. Prei, H. Eichenberger, B. von Wartburg, H. R. Wolf and O. Jeger, *Ibid.* **60**, 2968 (1977); [b]H. Eichenberger, H. R. Wolf and O. Jeger, *Ibid.* **59**, 1253 (1976); [c]K. Tautsumi and H. R. Wolf, *Ibid.* **63**, 2370 (1980).

[3a]B. Frei, G. de Weck, K. Müllen, H. R. Wolf and O. Jeger, *Helv. Chim. Acta* **62**, 553 (1979); [b]B. Frei, H. R. Wolf and O. Jeger, *Ibid.* **62**, 1645 (1979); [c]K. Murato, H. R. Wolf and O. Jeger, *Ibid.* **63**, 2212 (1980); [d]N. Nakamura, W. B. Schweizer, B. Frei, H. R. Wolf and O. Jeger, *Ibid.* **63**, 2230 (1980).

[4]W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.* **43**, 2923 (1978).

[5]A. P. Alder, H. R. Wolf and O. Jeger, *Helv. Chim. Acta* **61**, 2681 (1978).

[6]F. Pickenhagen, F. Näf, G. Ohloff, P. Müller and J.-C. Perlberger, *Ibid.* **56**, 1868 (1973).

[7]H. C. Brown, C. P. Garg and K. T. Liu, *J. Org. Chem.* **36**, 387 (1971).

[8]A. P. Alder, H. R. Wolf and O. Jeger, *Helv. Chim. Acta* **63**, 1833 (1980).