205. Photochemical Reactions

140th Communication[1])

Acid-Catalyzed Rearrangement and Electron Transfer Photooxygenation of Cyclopropanols and their Silyl Ethers

by **Markus E. Scheller, Peter Mathies**[2]), **Walter Petter**[2])[3]) and **Bruno Frei***

Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Universitätstrasse 16, CH-8092 Zürich

(15.VIII.84)

Summary

On acid-catalyzed hydrolysis, the tricyclic compounds **2** and **10**, incorporating cyclopropyl-silyl-ether moieties undergo rearrangement to the *cis*-decalones **3** and **7**, respectively. Hydrolysis of **2** and **10** in the presence of oxygen leads additionally to the formation of the 1,2-dioxolan-3-ols **9** and **13**, respectively, which involves an electron-transfer oxygenation process as could be demonstrated by photooxygenation of the silyl ether **10** and the cyclopropanol **14** in the presence of 9,10-dicyanoanthracene. The configurations of **3** and **9** were assigned by X-ray analysis of the latter compound as well as of the *p*-nitrobenzoate **8** of **3**.

1. Results and Discussion. – On photolysis ($\lambda > 347$ nm) as well as on vapor phase thermolysis of the acylsilane **1**, the tricyclic compound **2** was formed [1] (see *Scheme 1*). To prove the structure and, in particular, to assign the configuration, the cyclopropyl (*t*-butyl)dimethylsilyl ether **2** was hydrolyzed (5% aq. HCl, MeOH, reflux). Under these conditions the decalone **3** was formed in 58% yield by a rearrangement of the cyclopropanol intermediate **4**[4]). Whereas the *cis*-decalone **3** has not yet been described as such, comparison of the spectral data reported for the *trans*-decalone **5** which has been synthesized previously by different routes [3–11] indicated some discrepancy between the literature data. The ^{1}H-NMR and MS data of our decalone **3** are in excellent agreement with that reported by *Munslow & Reusch* [10], however, they do not fit with those published by the other authors [5] [7] [9] [11]. The *trans*-decalone structure of **5** had been established by preparation of (−)-(9*S*,10*S*)-**5** from natural products of known configuration [5] [7]. Therefore, we assumed that the hydrolysis product of **2**

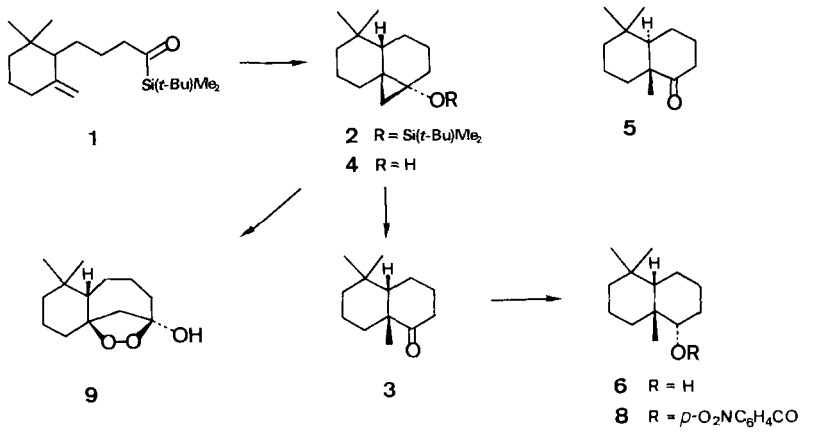
[1]) 139th Communication, see [1].

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

[3]) Institut für Kristallographie und Petrographie der Eidgenössischen Technischen Hochschule, CH-8092 Zürich.

[4]) For a review of the rearrangement of cyclopropanols, see [2].

Scheme 1



and the decalone prepared by *Munslow & Reusch* [10] must be the same *cis*-decalone **3**. To prove this hypothesis, compound **3** was reduced to the alcohol **6**[5]) with $NaBH_4$ followed by reaction of the latter with *p*-nitrobenzoyl chloride in pyridine leading to the crystalline *p*-nitrobenzoate **8** whose structure – and, most importantly, *cis*-anellation of the rings – was confirmed by X-ray analysis (see below).

If the transformation of **2**→**3** was carried out at r.t. without strictly excluding O_2, the 1,2-dioxolan-3-ol **9** was additionally formed in variable yield[6]). The structure of **9** was confirmed by X-ray analysis (see below).

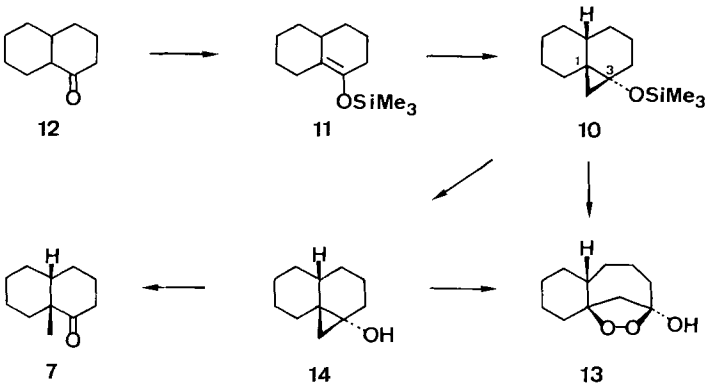
Recently, it has been demonstrated that aryl-substituted cyclopropanes can be converted to 1,2-dioxolanes by photooxygenation using 9,10-dicyanoanthracene (DCA) as an electron-transfer sensitizer [15–17]. It was of interest to check whether the transformation of the alicyclic cyclopropyl silyl ether **2** to the 1,2-dioxolan-3-ol **9** could also be promoted by electron-transfer photooxygenation. Due to the availability of only small amounts of **2**, we decided to study this process with the analogous cyclopropyl trimethylsilyl ether **10** (see *Scheme 2*). Compound **10** was prepared in 65% yield by *Simmons-Smith* reaction (CH_2I_2, Zn-Ag couple) [18] of the known trimethylsilyl enol ether **11** obtained from the decalone **12** [19]. The configuration of **10** was assigned by transformation to the known *cis*-9-methyldecalone (**7**) [20] in 78% yield. Analogously to the transformation of **2**→**9**, on hydrolysis of **10** in the presence of O_2, the 1,2-dioxolan-3-ol **13** (7%) was obtained in addition to **7** (73%). On the other hand, by treatment of the silyl ether **10** in a two-phase system (aq. HCl in Et_2O, r.t.) according to [21], the cyclopropanol **14** was obtained in 79% yield. Heating of the cyclopropanol **14** in MeOH at reflux temperature in the presence of O_2 for 3 h afforded compound **13** in 96% yield.

---

[5]) The alcohol **6** was obtained together with its C(1)-epimer (98% combined yield) in a ratio of 93:7. This finding is in good agreement with the results reported for the reduction of *cis*-9-methyldecalone (**7**) (see *Scheme 2*) with $LiAlH_4$ [12].

[6]) The formation of 1,2-dioxolan-3-ols by the reaction of cyclopropanols with O_2 was previously reported [13]. See [14] for the reaction of cyclopropyl *gem*-cyanohydrins with O_2.

Scheme 2



Photooxygenation (λ = 400–450 nm) of compound **14** in MeCN in the presence of 0.1 equiv. of 9,10-dicyanoanthracene (DCA) for 30 h gave the 1,2-dioxolan-3-ol **13** in 84% yield. *Schaap et al.* [15] have found that the rate of DCA-sensitized photooxygenation of tetraphenylcyclopropane to the corresponding dioxolane was dramatically enhanced by the addition of biphenyl (BP) as a co-sensitizer. Similarly, we observed that the oxidation of **14** was accelerated by BP. Thus, in the presence of 0.1 equiv. of DCA and 1.5 equiv. of BP, the reaction was complete in only 2 h affording **13** in 30% yield[7]). Photooxygenation of the silyl ether **10** under the same conditions showed also a quantitative conversion of **10** in 2 h giving **13** in 34% yield[7]). These findings demonstrate that, on photooxygenation, the cyclopropanol **14** and its silyl ether **10** behave analogously to aryl-substituted cyclopropanes[8]). Therefore it is assumed that the mechanism of the transformations of **10** and **14** into **13** corresponds to that proposed for the photooxygenation of aryl-substituted cyclopropanes [15]: electron-transfer quenching of singlet-excited DCA by **10** or **14**, respectively, generates the radical cations $\mathbf{10}^+$ and $\mathbf{14}^+$ which undergo cleavage of the C(1)–C(3) bond of the cyclopropane ring and subsequent reaction with superoxide ($O_2^{\cdot-}$) leading to **13**[9]).

By the transformations of **10** and **14** into **13**, the scope of the co-sensitized electron-transfer photooxygenation, which has been previously reported for phenyl-substituted cyclopropanes, has been extended to anellated cyclopropanols and cyclopropyl silyl ethers.

2. X-Ray Analyses. – 2.1. p-*Nitrobenzoate* **8** *(Fig. 1)*. Orthorhombic space group *Pbca*, a = 36.476, b = 8.326, c = 12.235 Å, Z = 8, d_{calc} = 1.23 g/cm^3. Intensity measurements were made at r.t. with an *Enraf-Nonius CAD4* diffractometer (graphite monochromator, Mo$K\alpha$ radiation, λ = 0.7107 Å, 3262 independent re-

[7]) The low yield of **13** is due to its decomposition during several chromatographic purifications which were necessary to remove BP (see *Exper. Part*).

[8]) Analogous to phenyl-substituted cyclopropanes, **10** exhibits an irreversible oxidation wave by cyclic voltammetry in MeCN with 0.1M tetraethylammonium perchlorate; scan rate = 300 mV/s; first oxidation peak potential, E_p^{ox} = +1.23 V *vs.* SCE. Consistent with this low potential is the large rate constant for quenching of DCA fluorescence in N_2 saturated MeCN, $k_q = 1.01 \times 10^{10}$M s^{-1}.

[9]) For a mechanistic interpretation of the co-sensitization of biphenyl, see [15].

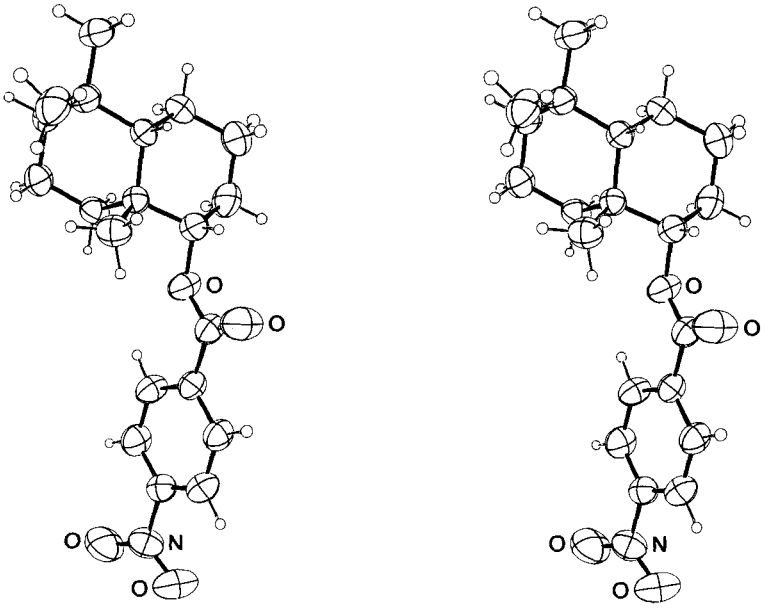


Fig. 1. *Stereoscopic view of molecule* **8** *drawn by ORTEP* [25] *with thermal vibration ellipsoids at the 50% probability level*

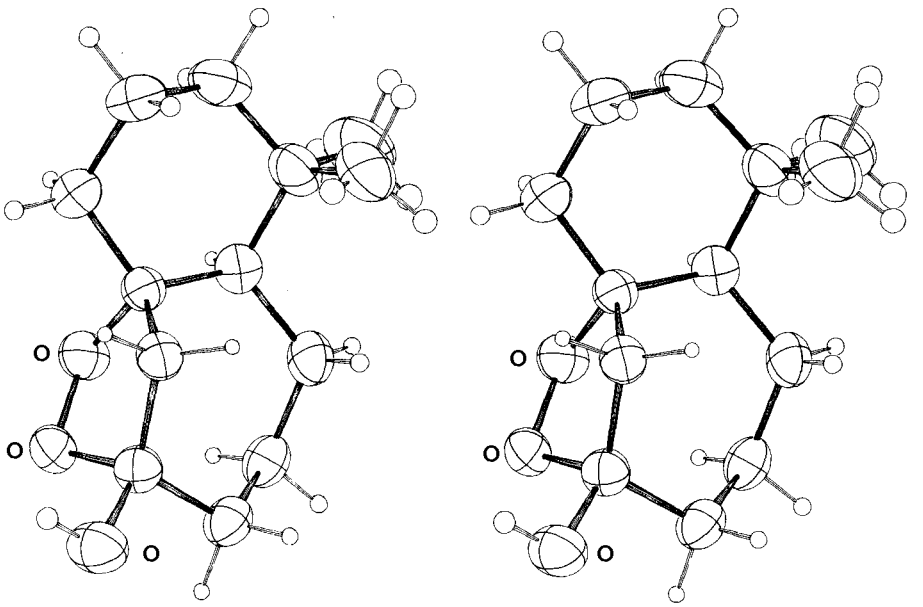


Fig. 2. *Stereoscopic view of molecule* **9** *drawn by ORTEP* [25] *with thermal vibration ellipsoids at the 50% probability level*

flections with $\theta < 25°$). The structure was solved by direct methods with MULTAN 80 [22] and refined by full-matrix least-squares analysis using 1519 reflections ($I > 3\sigma(I)$) with experimental weights (SHELX [23], XRAY-72 [24]). H-atoms were located at an intermediate stage and included in the refinement with isotropic vibrational parameters (other atoms anisotropic)[10]), final R was 0.040 ($R_w = 0.034$).

2.2. *1,2-Dioxolan-3-ol* **9** *(Fig. 2).* Monoclinic space group $P2_1/c$, $a = 16.070$, $b = 6.948$, $c = 12.455$ Å, $\beta = 114.97°$, $Z = 4$, $d_{calc} = 1.19$ g/cm^3. Intensity measurements were made at room temperature with a *SYNTEX* $P2_1$ diffractometer (graphite monochromator, Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å, 1825 independent reflections with $\theta < 22.5°$). The structure was solved and refined (1166 reflections) as described for **8**. The final R value was 0.040 ($R_w = 0.034$)[10]).

This work was supported by the *Swiss National Science Foundation* and *Ciba Geigy Ltd.*, Basle. We are indebted to the following persons for their help: Dr. *W. B. Schweizer* and Mr. *P. Seiler* (X-ray), Miss *B. Brandenberg*, Mr. *F. Fehr* and Mr. *M. Langenauer* (NMR), Mrs. *L. Golgowsky* and Prof. *J. Seibl* (MS), and Mr. *D. Manser* (elemental analysis). The authors also would like to thank Prof. *A. P. Schaap*, Wayne State University, Detroit, for helpful discussions, and his coworker, Mr. *E. Palomino*, for measuring the oxidation potential and the rate of DCA fluorescence quenching.

Experimental Part

General. See [1]. *$CuSO_4$-filter solution* [15]: $CuSO_4 \cdot 5H_2O$ (27 g), $NaNO_2$ (30 g), conc. aq. NH_4OH (50 ml) in H_2O (1000 ml). *$Na_2Cr_2O_7$-filter solution:* sat. aq. $Na_2Cr_2O_7/H_2O$ 1:10.

1. Transformations of 2. – 1.1. *Acid-Catalyzed Rearrangement of* **2**. *a*) A solution of **2** (14.9 mg, 0.048 mmol) in MeOH (3 ml) and a HCl-solution (2M, 1 ml) was heated under reflux, under Ar for 2 h. Workup and chromatography (hexane/Et_2O 2:1) yielded **3** (5.5 mg, 58%). *b*) To a solution of **2** (42 mg, 0.135 mmol) in THF (2 ml) and MeOH (5 ml) a HCl-solution (5%, 2 ml) was added dropwise, and the mixture was stirred for 20 h at r.t. Workup as described for *a* afforded the starting material **2** (3 mg), **3** (10 mg, 38%), and **9** (15 mg, 49%).

(9R,10S*)-5,5,9-Trimethyloctahydro-1(2H)-naphtalenone* (**3**). UV (2.32 mg in 2 ml): 274 (85), end absorption to 400 nm. IR: 2990*s*, 2940*s*, 2900*s*, 2870*s*, 2850*s*, 1702*s*, 1470*m*, 1455*s*, 1445*m*, 1425*m*, 1385*m*, 1375*m*, 1365*m*, 1315*w*, 1260*w*, 1245*w*, 1210*w*, 1170*w*, 1150*w*, 1120*m*, 1040*w*, 1020*w*, 990*m*, 975*m*, 875*w*, 860*w*, 840*w*. ^{1}H-NMR: 0.84, 0.94 (2*s*, 2 CH_3–C(5)); 1.23 (*s*, CH_3–C(9)); 1.00–2.80 (*m*, 2H–C(2), 2H–C(3), 2H–C(4), 2H–C(6), 2H–C(7), 2H–C(8), H–C(10)). ^{13}C-NMR: 24.9, 29.9, 32.2 (3*q*, 2 CH_3–C(5), CH_3–C(9)); 19.3, 20.3, 23.7, 35.0, 36.5 (5*t*, C(3), C(4), C(6), C(7), C(8)); 43.4 (*t*, C(2)); 54.3 (*d*, C(10)); 34.9 (*s*, C(5)); 48.3 (*s*, C(9)); 217.2 (*s*, C(1)). MS: 194 (6, M^+, $C_{13}H_{22}O$), 179 (13), 161 (7), 151 (6), 138 (7), 123 (18), *111* (100), 110 (13), 109 (18), 95 (27), 83 (10), 82 (21), 81 (22), 69 (22), 68 (14), 67 (21), 55 (23), 41 (29).

(1R,6S*,10R*)-5,5-Dimethyl-11,12-dioxatricyclo[8.2.1.0^{1,6}]tridecan-10-ol* (**9**). M.p. 153° (from Et_2O/hexane). IR: 3580*m*, 3400*w* br., 2930*s*, 2870*s*, 1460*m*, 1450*m*, 1440*m* (sh), 1390*m*, 1365*m*, 1355*m*, 1335*m*, 1290*m*, 1275*m*, 1150*m*, 1115*m*, 1090*m*, 1080*m*, 1010*w*, 980*w*, 965*w*, 960*w*, 940*w*, 905*m*, 885*m*. ^{1}H-NMR (300 MHz): 0.91, 0.95 (2*s*, 2 CH_3–C(5)); 1.20–2.10 (*m*, 2H–C(2), 2H–C(3), 2H–C(4), H–C(6), 2H–C(7), 2H–C(8), 2H–C(9)); 2.15 (*dd*, $J_1 = 12$, $J_2 = 2$, H–C(13)); 2.79 (*d*, $J = 12$, H–C(13)); 2.8–3.1 (br. *s*, OH). ^{13}C-NMR: 21.4, 31.8 (2*q*, 2 CH_3–C(5)); 20.0, 21.5, 24.8, 39.8, 40.3, 41.8, 49.7 (7*t*, C(2), C(3), C(4), C(7), C(8), C(9), C(13)); 50.1 (*d*, C(6)); 35.7 (*s*, C(5)); 89.6 (*s*, C(1)); 108.3 (*s*, C(10)). MS: 226 (11, M^+, $C_{13}H_{22}O_3$), 194 (15), *193* (100), 175 (39), 137 (12), 135 (34), 133 (14), 125 (18), 124 (12), 123 (49), 119 (15), 111 (63), 109 (37), 105 (13), 97 (40), 95 (54), 93 (25), 91 (13), 83 (32), 82 (20), 81 (52), 79 (18), 71 (13), 69 (96), 67 (39), 56 (12), 55 (83), 53 (18), 43 (47), 41 (92). Anal. calc. for $C_{13}H_{22}O_3$ (226.32): C 68.99, H 9.80; found: C 68.78, H 9.85.

1.2. *Reduction of* **3**. To a solution of **3** (5 mg, 0.026 mmol) in 2 ml abs. EtOH was added $NaBH_4$ (3 mg, 0.079 mmol). Workup in Et_2O afforded **6** (4.9 mg, 98%; mixture of diastereomers, ratio 93:7).

1.3. *Esterification of* **6**. A stirred solution of **6** (4.9 mg, 0.025 mmol) and *p*-nitrobenzoyl chloride (110 mg, 0.59 mmol) in dry pyridine (2 ml) was heated at 55° for 100 h, cooled to r.t., diluted with Et_2O, and washed twice with 2M HCl. Workup and chromatography (hexane/Et_2O 15:1) afforded **8** (4.9 mg, 57%).

---

[10]) Atomic parameters have been deposited with the *Cambridge Crystallographic Data Centre*, Lensfield Road, Cambridge CB2 1EW, England.

(1R,9S*,10S*)-5,5,9-Trimethyldecahydro-1-naphthyl p-Nitrobenzoate* (**8**). M.p. 129–131° (from EtOH). IR: 3105*w*, 3075*w*, 3050*w*, 3015*w*, 2940*s*, 2900*s* (sh), 2850*s*, 1715*s*, 1600*m*, 1520*s*, 1485*w*, 1460*m*, 1445*m*, 1405*m*, 1385*m*, 1375*m*, 1360*m*, 1340*s*, 1330*s*, 1315*s*, 1295*s*, 1270*s*, 1240*m*, 1230*m*, 1200*w*, 1165*w*, 1110*s*, 1095*s*, 1010*m*, 1000*m*, 980*m*, 960*w*, 940*s*, 915*w*, 895*w*, 870*m*, 850*m*, 830*m*. ^{1}H-NMR (300 MHz, 80% pure): 0.90, 1.16, 1.18 (3*s*, 2 CH_3–C(5), CH_3–C(9)); 1.00–1.90 (*m*, 2H–C(2), 2H–C(3), 2H–C(4), 2H–C(6), 2H–C(7), 2H–C(8), H–C(10)); 4.79 (*dd*, J_1 = 11, J_2 = 4, H–C(1)); 8.18 and 8.27 (2*m*, 4 arom. H). MS: 345 (10, M^+, $C_{20}H_{27}NO_4$), 330 (31), 178 (47), 177 (18), 163 (53), 151 (40), 150 (92), 135 (30), 124 (14), 123 (59), 122 (90), 121 (23), 120 (17), 110 (21), 109 (66), 108 (26), 107 (40), 104 (45), 97 (14), 96 (19), 95 (62), 94 (18), 93 (29), 92 (14), 83 (31), *82* (100), 81 (47), 79 (22), 76 (23), 75 (14), 69 (88), 67 (32), 57 (21), 55 (56), 43 (27), 41 (50).

2. Preparation and Transformations of 11. – 2.1. *Cyclopropanation of the Enol Ether* **11**. A hot solution of AgOAc (54.5 mg, 0.33 mmol) in AcOH (19 ml) was stirred under Ar, and granular Zn was added in one portion. The mixture was stirred for 5 min, the AcOH was decanted, the Ag-Zn couple was washed with AcOH (12 ml) and Et_2O (6 × 12 ml), covered with Et_2O (39 ml), and a spatula tip full of powdered Ag was added. CH_2I_2 (2.05 ml, 6.8 g, 23.4 mmol) was added dropwise over 15 min, and the mixture was stirred at r.t. for 1 h. Then, **11** [19] (3.29 g, 14.66 mmol; contaminated with *ca.* 25% of the 1,2-double bond isomer) was added dropwise over 10 min, and the mixture was heated at reflux for 18 h, cooled to 0°, and pyridine (5 ml) was added dropwise over 10 min. After stirring for 30 min at r.t., the Zn-salts were removed by filtration and washed well with Et_2O. The combined filtrates were concentrated affording after chromatography (hexane) **10** (1.75 g, 67%), and the cyclopropane derivative derived from the 1,2-double-bond isomer (576 mg).

(1R,3S*,7S*)-3-Trimethylsilyloxytricyclo[5.4.0.0^{1,3}]undecane* (**10**). IR: 3050*w*, 2990*w*, 2920*s*, 2840*s*, 1455*m*, 1440*m*, 1435*m*, 1365*w*, 1350*m*, 1340*m*, 1255*m*, 1245*s*, 1205*s*, 1190*m*, 1170*s*, 1135*m*, 1110*m*, 1085*m*, 1070*m*, 1040*m*, 1025*w*, 1005*w*, 970*s*, 960*s*, 930*m*, 890*m*, 870*s*, 860*s*, 835*s*. ^{1}H-NMR (300 MHz, C_6D_6): 0.27 (*s*, 3 CH_3–Si); 0.45 (*AB*-system J = 5, δ_A = 0.35 split into *d*, J = 1.5, δ_B = 0.54, 2H–C(2)); 1.00–2.15 (*m*, 15H). ^{13}C-NMR (75 MHz, C_6D_6): 1.7 (*q*, 3 *C*H_3–Si); 17.0 (*t*, C(2)); 24.1, 26.2, 26.4, 26.9, 31.7, 31.8, 32.8 (7*t*, C(4), C(5), C(6), C(8), C(9), C(10), C(11)); 35.8 (*d*, C(7)); 28.1 (*s*, C(1)); 61.0 (*s*, C(3)). MS: 238 (29, M^+, $C_{14}H_{26}OSi$), 209 (11), 196 (12), 195 (48), 167 (11), 148 (18), 143 (33), 130 (19), 115 (12), 91 (13), 79 (12), 75 (39), *73* (100), 67 (10), 55 (10), 45 (15), 41 (16).

2.2. *Hydrolysis of* **10**. – 2.2.1. *Under Ar. a*) A solution of **10** (78 mg, 0.32 mmol) in MeOH (2 ml) was heated to reflux under Ar, and an aq. HCl-solution (10%, 1 ml) was added at once. The mixture was heated under reflux for 1 h, worked up in Et_2O and chromatographed (hexane/Et_2O 5:1) affording **7** [20] (42 mg, 78%). *b*) A solution of **10** (137 mg, 0.577 mmol) in abs. Et_2O (3 ml) was purged with Ar until half of the solvent had evaporated, and then an aq. HCl-solution (10%, 1 ml) was added under Ar. The mixture was stirred for 30 min at r.t., diluted with Et_2O and worked up affording pure **14** (76 mg, 79%).

(1R,3S*,7S*)-Tricyclo[5.4.0.0^{1,3}]undecan-3-ol* (**14**). M.p. 55–57°. IR: 3600*m*, 3400*w* br., 3060*w*, 2990*m*, 2920*s*, 2850*s*, 2660*w*, 1455*m*, 1440*s*, 1370*w*, 1350*m*, 1280*m* br., 1230*m*, 1210*m*, 1180*m* (sh), 1170*s*, 1135*m*, 1115*m*, 1080*w*, 1070*m*, 1035*m*, 1005*m*, 930*m*, 915*m*, 860*w*, 845*w*. ^{1}H-NMR (300 MHz, C_6D_6): 0.41 (*AB*-system, J = 5, δ_A = 0.29 br., δ_B = 0.53, 2H–C(2)); 0.7–2.6 (*m*, 16H). ^{13}C-NMR(C_6D_6): 17.0 (*t*, C(2)); 23.9, 26.4, 26.6, 26.9, 31.3, 31.8[11]) (7*t*, C(4), C(5), C(6), C(8), C(9); C(10); C(11)); 35.9 (*d*, C(7)); 29.8 (*s*, C(1)); 59.2 (*s*, C(3)). MS: 166 (40, M^+, $C_{11}H_{18}O$), 151 (15), 148 (39), 137 (10), 133 (21), 124 (54), 123 (77), 122 (21), 119 (15), 111 (68), 110 (24), 109 (53), 108 (99), 107 (20), 106 (12), 105 (21), 98 (12), 97 (36), 96 (39), 95 (91), 94 (22), 93 (76), 91 (38), 84 (29), 83 (21), 82 (28), 81 (98), 80 (33), 79 (95), 78 (18), 77 (31), 71 (32), 70 (26), 69 (24), 68 (36), *67* (100), 65 (18), 55 (73), 54 (19), 53 (38), 43 (45), 41 (84).

(9R,10R*)-9-Methyloctahydro-1(2H)-naphthalenone* (**7**) [20]. ^{13}C-NMR: 25.9 (*q*, CH_3–C(9)); 22.9[11]), 25.3, 26.6, 28.9, 34.2 (6*t*, C(3), C(4), C(5), C(6), C(7), C(8)); 37.9 (*t*, C(2)); 44.8 (*d*, C(10)); 49.4 (*s*, C(9)); 215.8 (*s*, C(1)).

2.2.2. *Under* O_2. A solution of **10** (110 mg, 0.46 mmol) in Et_2O (1.5 ml) was stirred with an aq. HCl-solution (10%, 1 ml) while bubbling with O_2. After 1 h, quantitative conversion of **10** to **14** was detected (GC), and after 26 h the mixture was worked up and chromatographed (hexane/Et_2O 2:1) affording **7** (56 mg, 73%) and **13** (6 mg, 7%).

(1R,6R*,10R*)-11,12-Dioxatricyclo[8.2.1.0^{1,6}]tridecan-10-ol* (**13**). M.p. 83–84°. IR: 3590*w*, 3440*w* br., 2990*w*, 2920*s*, 2850*s*, 1465*m*, 1440*m*, 1430*m*, 1370*w*, 1345*m*, 1340*m*, 1310*w*, 1290*m*, 1280*w*, 1260*w*, 1230*m*, 1180*w*, 1160*w*, 1140*m*, 1080*s*, 1075*s*, 1035*m*, 975*w*, 960*m*, 940*w*, 925*m*, 910*m*, 895*m*, 860*w*, 840*w*. ^{1}H-NMR (300 MHz): 1.00–1.90 (*m*, 14H); 2.13 (*d*, J = 12.5, H–C(13)); 2.2–2.4 (*m*, H–C(6)); 2.7–2.9 (*m*, OH); 2.93 (*d*,

[11]) 2 signals overlapping.

J = 12.5, H–C(13)). ^{13}C-NMR: 18.1, 25.3, 25.8, 30.2, 30.9, 35.3, 35.6, (7*t*, C(2), C(3), C(4), C(5), C(7), C(8), C(9)); 48.5 (*t*, C(13)); 43.6 (*d*, C(6)); 89.8 (*s*, C(1)); 109.2 (*s*, C(10)). MS: 198 (7, M^+, $C_{11}H_{18}O_3$), 166 (13), *165* (100), 147 (20), 125 (15), 124 (21), 121 (14), 111 (21), 98 (21), 97 (30), 95 (21), 93 (13), 86 (48), 84 (70), 83 (17), 81 (89), 79 (19), 71 (13), 69 (17), 67 (27), 55 (37), 47 (14), 43 (33), 41 (40). Anal. calc. for $C_{11}H_{18}O_3$ (198.27): C 66.64, H 9.15; found: C 66.37, H 9.02.

2.3. *Hydrolysis of the cyclopropanol* **14** (28 mg, 0.168 mmol) as described for **10** (see *2.2.1.a*) yielded after chromatography (hexane/Et_2O 2:1) **7** (25 mg, 88%).

2.4. *Transformation of* **14** *into* **13**. – 2.4.1. *By Thermal Reaction with* O_2. A solution of **14** (60 mg, 0.36 mmol) in abs. MeOH (5 ml) was heated under reflux while bubbling with O_2 for 3 h. Workup in Et_2O gave **13** (69 mg, 96%) which was chromatographed (hexane/Et_2O 2:1) affording **13** (29 mg, 40%) as analytical pure sample.

2.4.2. *By an Electron-Transfer-Catalyzed Photooxygenation.* A solution of **14** (133 mg, 0.80 mmol) and 9,10-dicyanoanthracene (DCA, subl., 18 mg, 0.08 mmol) in abs. MeCN (200 ml) was irradiated (lamp *B*, $CuSO_4$-filter) while bubbling with O_2 for 30 h. The chromatography (hexane/Et_2O 1:1) afforded **13** (132 mg, 84%).

2.4.3. *By a Co-sensitized Electron-Transfer-Catalyzed Photooxygenation. a*) A solution of **14** (82 mg, 0.49 mmol), 9,10-dicyanoanthracene (DCA, 13 mg, 0.056 mmol), and biphenyl (BP, 115 mg, 0.74 mmol) in abs. MeCN (150 ml) was irradiated (lamp *B*, $CuSO_4$-filter) while bubbling with O_2 for 2 h. TLC indicated quantitative conversion of **14** into **13**, and chromatography (hexane/Et_2O 2:1) afforded pure **13** (29 mg, 30%). *b*) The analogous reaction of **10** (149 mg, 0.62 mmol), 9,10-dicyanoanthracene (DCA, 11 mg, 0.05 mmol) and biphenyl (BP, 96 mg, 0.62 mmol) in abs. MeCN (130 ml) afforded after chromatography **13** (42 mg, 34%).

REFERENCES

[1] *M.E. Scheller & B. Frei*, Helv. Chim. Acta *67*, 1734 (1984).
[2] *C.H. De Puy*, Acc. Chem. Res. *1*, 33 (1968).
[3] *J.D. Cocker & T.G. Halsall*, J. Chem. Soc. *1957*, 3441.
[4] *F. Sondheimer & D. Elad*, J. Am. Chem. Soc. *79*, 5542 (1957).
[5] *E. Wenkert & D.P. Strike*, J. Am. Chem. Soc. *86*, 2044 (1964).
[6] *N. Ototani, T. Kato & Y. Kitahara*, Bull. Chem. Soc. Jpn. *40*, 1730 (1967).
[7] *G. Ohloff, W. Giersch, K.H. Schulte-Elte & C. Vial*, Helv. Chim. Acta *59*, 1140 (1976).
[8] *S.C. Welch & A.S.C.P. Rao*, J. Org. Chem. *43*, 1957 (1978).
[9] *D.L. Snitman, M.-Y. Tsai, D.S. Watt, C.L. Edwards & P.L. Stotter*, J. Org. Chem. *44*, 2838 (1979).
[10] *W.D. Munslow & W. Reusch*, J. Org. Chem. *47*, 5096 (1982).
[11] *J.T.A. Reuvers & A. de Groot*, J. Org. Chem. *49*, 1110 (1984).
[12] *R. Zurflüh & Ch. Tamm*, Helv. Chim. Acta *55*, 2495 (1972).
[13] *D.H. Gibson & C.H. DePuy*, Tetrahedron Lett. *1969*, 2203.
[14] *A. Oku, T. Yokoyama & T. Harada*, Tetrahedron Lett. *1983*, 4699.
[15] a) *A.P. Schaap, L. Lopez, S.D. Anderson & S.D. Gagnon*, Tetrahedron Lett. *1982*, 5493; b) *A.P. Schaap, S. Siddiqui, G. Prasad, E. Palomino & L. Lopez*, J. Photochem., in press.
[16] *K. Mizuno, N. Kamiyama & Y. Otsuji*, Chem. Lett. *1983*, 477.
[17] *Y. Takahashi, T. Miyashi & T. Mukai*, J. Am. Chem. Soc. *105*, 6511 (1983).
[18] a) *J.M. Denis, C. Girard & J.M. Conia*, Synthesis *1972*, 549; b) *J.M. Conia & C. Girard*, Tetrahedron Lett. *1973*, 2767; c) *C. Girard & J.M. Conia*, J. Chem. Res. (S) *1978*, 182; d) *J.E. Baldwin & B.M. Broline*, J. Org. Chem. *47*, 1385 (1982).
[19] *H.O. House, L.J. Czuba, M. Gall & H.D. Olmstead*, J. Org. Chem. *34*, 2324 (1969).
[20] a) *W.S. Johnson*, J. Am. Chem. Soc. *65*, 1317 (1943); b) *F. Gautschi, O. Jeger, V. Prelog & R.B. Woodward*, Helv. Chim. Acta *37*, 2280 (1954); c) *R.O. Duthaler & P. Maienfisch*, ibid. *65*, 635 (1982).
[21] *G.M. Rubottom & M.I. Lopez*, J. Org. Chem. *38*, 2097 (1973).
[22] *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.
[23] *G.M. Sheldrick*, SHELX 76. A Programm for Crystal Structure Determination, University of Cambridge, England 1976.
[24] *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.
[25] *C.K. Johnson*, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee 1965.