131. Formation of Dichloro Oxiranes from Ketones under Phase Transfer Conditions[1][2]

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Summary

Compounds **2**, **5** and **9** represent the first examples of isolable dichlorooxiranes formed by formal addition of dichloro carbene to a carbonyl group under phase transfer conditions. On heating, **2**, **5** and **9** rearrange into α-chloroacid chlorides **3**, **6** and **10**, respectively.

Transformations of aldehydes or ketones into α-hydroxy or α-chloro carboxylic acids by the use of dichlorocarbene generated under so called '*Mąkosza* conditions' have been reported recently [2] [3]. In these reports, as well as in a mechanistically similar case [4] formation of dichlorooxiranes as intermediates was proposed. These intermediates, however, owing to their high reactivity, had never been isolated. We now report the first synthesis of dichlorooxiranes generated from ketones under phase transfer conditions[4]) as well as their thermal rearrangement into α-chloroacid chlorides.

Reactions. – When the bicyclic ketone **1** reacted under the conditions shown in *Scheme 1* the starting material disappeared completely within 90 min at 20–25°. Work-up and distillation of the crude product gave a new compound **3** in 82% yield which contained the elements of 2 additional dichlorocarbene units according to elemental analysis. Proof of the structure of **3** was obtained spectroscopically as well as by its conversion into methyl ester **4**. Since an acid chloride such as **3** would not have survived under the strongly basic reaction conditions, it was reasonable to assume that the dichlorooxirane **2** was the genuine reaction product, and that **3** was formed on heating during distillation. When, however, the crude product was not distilled, but purified by chromatography, **2** was obtained in 85% yield.

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[1]) Presented at the Autumn Meeting of the Swiss Chemical Society, Berne, October 7–8, 1977.

[2]) Synthesis and Reactivity of Compounds with Cyclobutane Ring(-s), Part XII. Part XI: [1].

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[4]) The transformation of polyhalogenated ketones into dihalooxiranes has been effected under anhydrous conditions using phenyl trihalomethyl mercury compounds [5].

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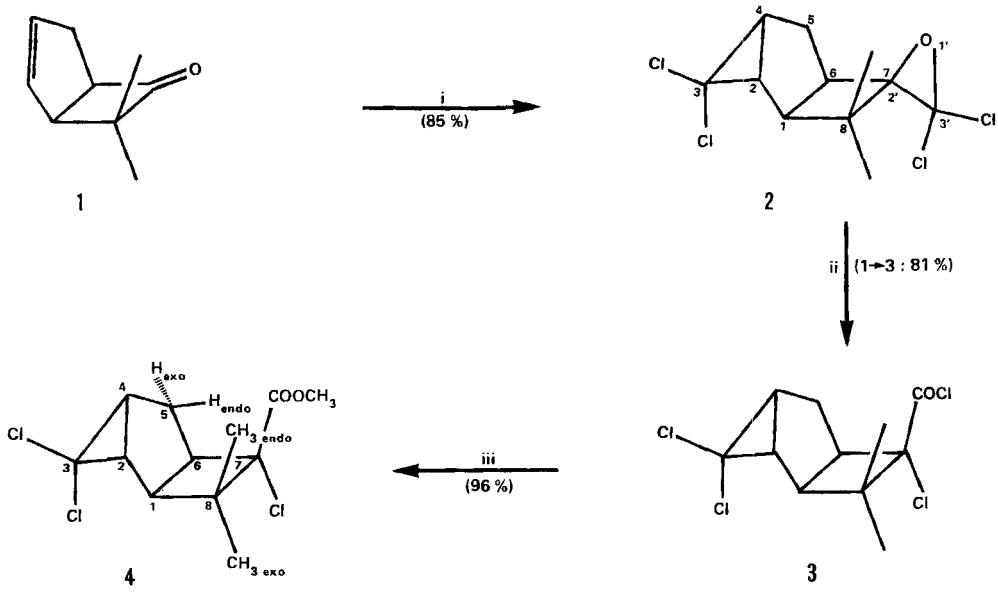
Scheme 1

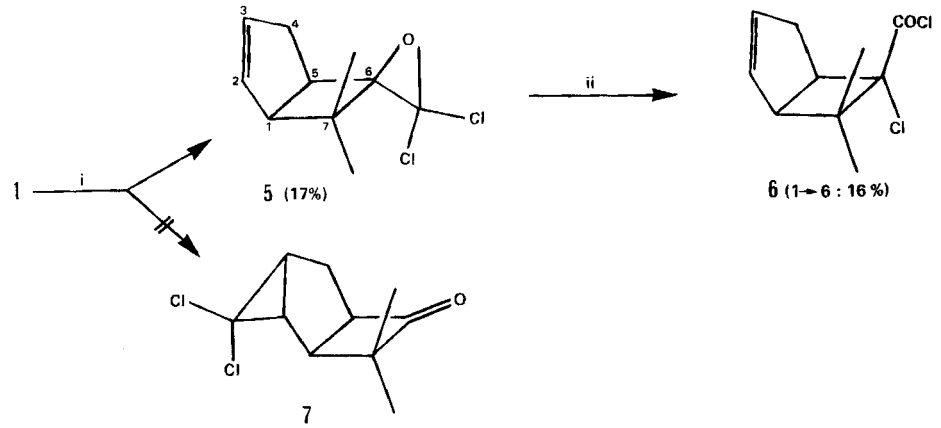
i) $CHCl_3$, 50% NaOH, $C_6H_5CH_2N^+(CH_3)_3Cl^-$ (0.05 eq.), 20–25°. ii) distillation.
iii) CH_3OH, C_5H_5N



By monitoring the reaction with GC., it became evident that **2** is formed *via* an intermediate. When the reaction was quenched after about 30–40% of **1** had been consumed and the crude mixture was separated by distillation, the acid chloride **6** was obtained in 16% yield. The other possible intermediate, **7**, could not be detected in the distillate (< 1%). Again, the unrearranged oxirane **5**, accompanied by some **2**, was isolated by chromatography.

Scheme 2

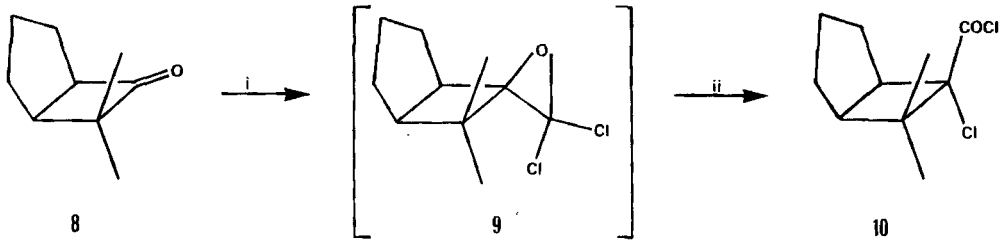
i) $CHCl_3$, 50% NaOH, $(C_4H_9)_4N^+OH^-$ (0.2 eq.), 10°, 33% conversion. ii) distillation



In an attempt to test the generality of this new synthesis of dichlorooxiranes from ketones, the cyclobutanones **8**, **11** and **12** reacted under the same conditions. Of these, only **8** reacted slowly in the presence of a large amount of catalyst to give **9**. On distillation **9** rearranged to **10**. Attempts to convert **11** and **12** to the corresponding dichlorooxiranes and/or α-chlorocarboxylic acid chlorides failed.

Scheme 3

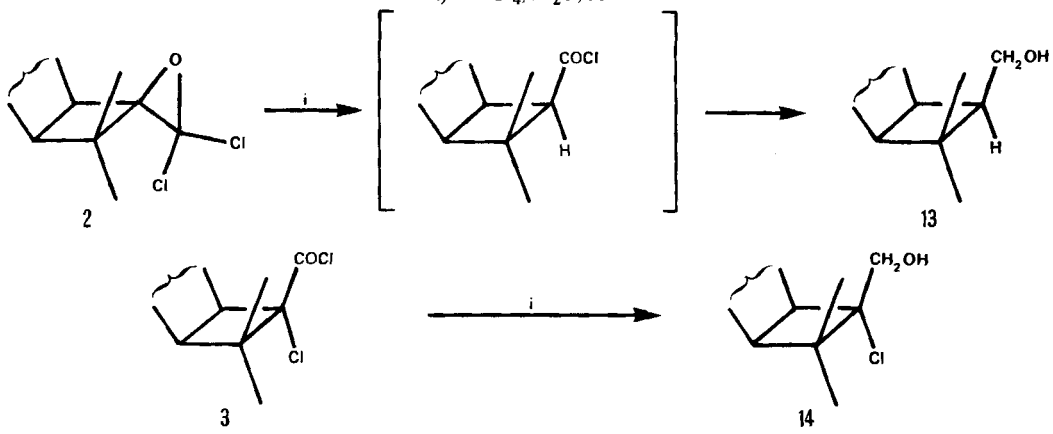
i) $CHCl_3$, 50% NaOH, $(C_4H_9)_4N^+OH^-$ (0.16 eq.), 10°, 50% conversion. ii) distillation



As already mentioned, **2** rearranges to **3** on distillation. At lower temperatures, **2** rearranges relatively slowly, possessing a half-life of 65 h in boiling dichloromethane. Surprisingly, the dichlorocyclopropane ring of **3** is thermally very stable and cannot be rearranged by heating at 150° for 24 h[5]).

Scheme 4

i) $LiAlH_4$, Et_2O, 35°



[5]) This behavior contrasts with the thermal lability of 6,6-dichloro-bicyclo[3.1.0]hexane (b.p. 69°/20 Torr) which on distillation rearranges partially to 2,3-dichlorocyclohexene [6].

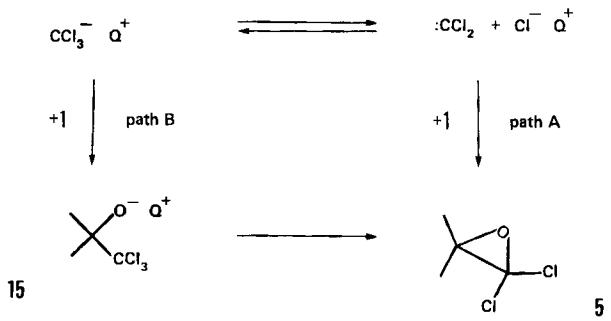
The relatively high thermal stability of **2** allows nucleophilic reactions to be carried out on its dichlorooxirane moiety. In order to prove the assumed configuration, **2** reacted with lithium aluminium hydride in ether and gave the alcohol **13** after 2 h at reflux in 84% yield. Under the same conditions, acid chloride **3** reacted rapidly to give chloro alcohol **14** in almost quantitative yield.

Structures. – The structures of all compounds were determined by spectroscopic methods, mainly by ^{13}C- and ^{1}H-NMR. spectroscopy. The oxirane **2** can easily be distinguished from the ketone **1** and the acid chloride **3** by the absence of ^{13}C-NMR. signals at lower field than 90 ppm. The carbon atoms C(7) and CCl_2–C(7), furthermore, absorb at rather high field, 79.1 and 88.7 ppm respectively, indicating the 3-membered heterocyclic ring. The *trans* arrangement of the 3- and the 4-membered carbocyclic rings in **2** (as well as in **3**, **4**, **13** and **14**) follows from the observation that the vicinal coupling constant ^{3}J between HC(1) and HC(2) is smaller than 1 Hz in all compounds, which indicates a dihedral angle of approximately 90° between the 2 protons. Such an angle is only compatible with a *trans* arrangement of the 2 rings. The configuration at C(7), however, could not be determined for compound **2**, as it did not complex sufficiently with the NMR. shift reagents Eu(fod)$_3$ or Eu(tfn)$_3$ [7] to induce noticeable shifts. The configuration of C(7), therefore, had to be deduced from chemical reactions (*i.e.* **2**→**3**→**4** as well as **2**→**13**). The configuration at C(7) of **4** has been established with the aid of its ^{1}H-NMR. spectrum in the presence of the shift reagent Eu(fod)$_3$. Complexation of the shift reagent with the ester group induces much larger downfield shifts for *endo*-H–C(5) and *endo*-CH_3–C(8) than for H–C(1) and *exo*-CH_3–C(8). The ester group, therefore, occupies the *endo* position *(cf. Scheme 1)*. The assignment of *endo* and *exo*-CH_3–C(8) in the ^{1}H-NMR. spectrum was possible by a selective $\{^{1}H\}$-^{13}C-decoupling experiment, connecting them with their ^{13}C-NMR. signals. These signals can easily be assigned on the basis of their chemical shifts (γ-effect induced by C(2)). The configuration at C(7) in **13** and **14** has been determined similarly. In the case of **13**, it can also be derived from the ^{13}C-chemical shifts of CH_3–C(8) of which the *exo* methyl group absorbs at lower field (32.6 ppm) than the corresponding methyl groups of **3**, **4** and **14** (26.9, 27.2 and 30.0 ppm respectively) owing to the absence of the γ-effect exerted by the *exo* substituent at C(7). The vicinal coupling between HC(6) and HC(7) (8 Hz, measured in the presence of Eu(fod)$_3$) is also in agreement with the *endo* configuration of the $-CH_2OH$ moiety.

Discussion. – The formation of dichlorooxiranes of type **2**, **5** and **9** may be explained by 2 mechanisms (*cf.* [3] and ref. therein). **A**: direct addition of dichlorocarbene to the carbonyl group, possibly *via* a carbonyl ylid, or **B**: addition of trichloromethyl anion to the carbonyl group followed by oxirane ring closure *(Scheme 5)*. Although we have no definite proof of mechanism **B** by isolating an intermediate of type **15**, the existing evidence strongly favors this mechanism. As shown by the primary formation of compound **5** *(Scheme 2)*, the electrophilic cyclobutanone carbonyl group of **1** is cyclopropanated first, while the comparably electron rich, nucleophilic C=C bond in the strained 5-membered ring of **1** reacts

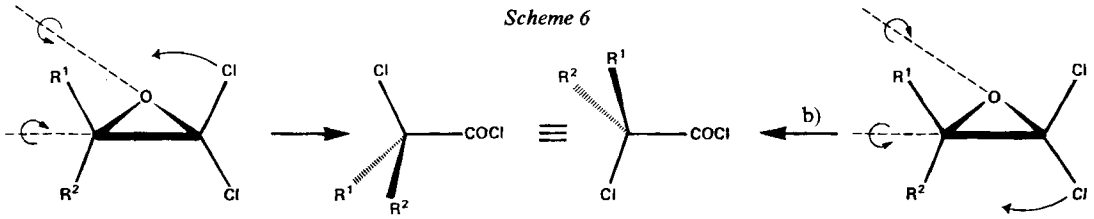
more slowly. This observation renders the occurrence of mechanism **A** unlikely, especially since this mechanism involves energetically unfavorable reactions such as direct combination of 2 electron-demanding species or interaction of the 'soft' dichlorocarbene with the 'hard' oxygen of the cyclobutane carbonyl group [8]. On the other hand, the nucleophilic trichloromethyl anion, being in equilibrium with dichlorocarbene and chloride ion [9] is perfectly suited to add to the carbonyl group to give **15** ($Q = C_6H_5CH_2N^+(CH_3)_3$). Ring closure to give **5** is in line with the observation that dihalooxiranes may be formed by treating polyhalogenated alcohols with a base [10].

Scheme 5



A noteworthy feature of dichlorooxiranes **2**, **5** and **9** is their relatively high stability as well as their stereospecific rearrangement into the corresponding α-chloroacid chlorides **3**, **6** and **10**. This rearrangement may follow the pattern of a cyclopropyl-allyl rearrangement [11] as illustrated in *Scheme 6*. In a concerted reaction, disrotatory opening of the R^1R^2C-O single bond may proceed in either direction *via* the energetically different modes a) or b). Since both modes lead to the same product, the configuration of the α-chloroacid chloride is determined by the configuration of the dichlorooxirane. Even in a concerted reaction the carbon atom bearing R^1 and R^2 becomes electron deficient. The stability of a dichlorooxirane, therefore, is determined by the capability of R^1 and R^2 to stabilize a positive charge. It is not surprising, in view of this, that the stable dihalooxiranes reported so far all possess electron-withdrawing substituents R^1 and R^2, destabilizing an adjacent positive charge. In analogy, the stability of **2**, **5** and **9** may be explained by the instability of the cyclobutyl cation as exemplified by the slow solvolysis of 1-chloro-1-methylcyclobutane compared with the much faster

Scheme 6



solvolysis of larger ring homologs [12]. In addition, oxirane ring opening requires movement of the substituents R^1 and R^2; this, however, is suppressed by R^1 and R^2 being part of a rigid polycyclic system. Finally, attack of external nucleophiles is largely shielded by the 2 methyl groups and the annelated cyclopentane ring.

Experimental Part

General remarks: [13].

1. rel-*(1R,2S,4R,6R,7R)-3,3,3',3'-Tetrachloro-8,8-dimethyl-(tricyclo[4.2.0.0^{2,4}]octane-7-spiro-2'-oxirane)* (**2**). A solution of 20.4 g (0.15 mol) **1** [14] and 1.5 g (8 mmol) benzyltrimethylammonium chloride in 150 ml $CHCl_3$ was stirred rapidly at 20° while 200 ml of 50% NaOH-solution were added in the course of 5 min. After the mixture had been stirred at 20–25° for 90 min, it was diluted with 250 ml water. The organic phase was separated and the aqueous phase extracted with ether (3 × 100 ml). The combined organic extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvent *in vacuo* at RT. gave 43.2 g of a dark oil giving a single spot (Rf 0.33, hexane) on TLC. The crude product was taken up in hexane and filtered through 200 g of silica gel. Evaporation of the pure fractions, finally at 0.01 Torr, left 38.5 g (85%) of a colorless oil which solidified on standing in the refrigerator to give a lowmelting wax. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.08 (*d* × *d* × *d*, $J_{6,5exo}$ = 8, $J_{6,1}$ = 7, $J_{6,5endo}$ = 2, HC(6)); 2.50 (*d*, $J_{1,6}$ = 7, HC(1)); 2.30–1.70 (*m*, 4 H); 1.37 and 0.96 (2*s*, 2 CH_3–C(8)). – ^{13}C-NMR. ($CDCl_3$): 88.7 (*s*, C(3')); 79.1 (*s*, C(7)); 67.1 (*s*, C(3)); 50.2 and 44.5 (2*d*, C(1) and C(6)); 41.6 (*s*, C(8)); 38.8 and 38.3 (2*d*, C(2) and C(4)); 27.7 (*t*, C(5)); 24.6 and 18.4 (2*qa*, 2 CH_3–C(8)).

2. rel-*(1R,2S,4R,6R,7S)-3,3,7-Trichloro-8,8-dimethyl-tricyclo[4.2.0.0^{2,4}]octane-7-carbonyl chloride* (**3**). Treatment of 102 g **1** as described under 1. yielded 184.8 g (82%) of a colorless oil, b.p. 93–97°/0.01 Torr which solidified on standing; m.p. 50–55°. – IR. ($CHCl_3$): 1799 (CO). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.15–2.05 (*m*, 6 H); 1.40 and 1.36 (2*s*, 2 CH_3–C(8)). – ^{13}C-NMR. ($CDCl_3$): 169.0 (*s*, COCl); 78.3 (*s*, C(7)); 65.8 (*s*, C(3)); 52.4 and 47.5 (2*d*, C(1) and C(6)); 45.3 (*s*, C(8)); 39.4 and 37.1 (2*d*, C(2) and C(4)); 31.6 (*t*, C(5)); 26.9 and 21.5 (2*s*, 2 CH_3–C(8)).

$C_{11}H_{12}Cl_4O$	Calc.	C 43.75	H 4.01	Cl 46.96	O 5.30%
(302.03)	Found	,, 43.61	,, 3.91	,, 46.76	,, 5.49%

3. rel-*(1R,2S,4R,6R,7S)-Methyl-3,3,7-trichloro-8,8-dimethyl-tricyclo[4.2.0.0^{2,4}]octane-7-carboxylate* (**4**). A mixture of 1.32 g (30 mmol) methanol and 2.0 g (25 mmol) pyridine was slowly added at +5° to a solution of 6.05 g **3** in 10 ml benzene. After stirring 2 h at 25°, ether (50 ml) and 1N H_2SO_4 (20 ml) were added. The organic phase separated was washed with water and $NaHCO_3$ solution and then dried (Na_2SO_4). Evaporation of the solvent left 5.7 g (96%) of colorless crystals, m.p. 118–119°. – IR. ($CHCl_3$): 1748 (CO). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.77 (*s*, OCH_3); 3.08–2.00 (*m*, 6 H); 1.33 (*s*, CH_{3exo}–C(8)); 1.18 (*s*, CH_{3endo}–C(8)). – On addition of Eu(fod)$_3$: 5.02 (*s*, OCH_3); 4.17 (*m*, $J_{5endo,5exo}$ = 16, $J_{5endo,6}$ = 5, $J_{5endo,4}$ = 4; H_{endo}C(5)), 3.80 (*m*, $J_{6,5exo}$ = 10, $J_{6,1}$ = 8, $J_{6,5endo}$ = 5, HC(6)); 3.36 (*d*, $J_{1,6}$ = 8, HC(1)), 2.67 (*d* × *d*, $J_{5exo,5endo}$ = 16, $J_{5exo,6}$ = 10, H_{exo}C(5)), 2.45–2.20 (*m*, HC(2) and HC(4)); 2.04 (*s*, CH_{3endo}–C(8)); 1.87 (*s*, CH_{3exo}–C(8)). – ^{13}C-NMR. ($CDCl_3$): 169.1 (*s*, CO); 72.0 (*s*, C(7)); 66.6 (*s*, C(3)); 52.1 (*qa*, OCH_3); 51.6 and 48.4 (2*d*, C(1) and C(6)); 43.4 (*s*, C(8)); 39.7 and 37.3 (2*d*, C(2) and C(4)); 31.1 (*t*, C(5)); 27.2 (*qa*, CH_{3exo}–C(8)); 21.8 (*qa*, selectively decoupled from the proton signal at 1.18 ppm, CH_{3endo}–C(8)).

$C_{12}H_{15}Cl_3O_2$ (297.61) Calc. C 48.43 H 5.08 Cl 35.74% Found C 48.48 H 5.14 Cl 35.74%

4. rel-*(1S,5R,6S)-6-Chloro-7,7-dimethyl-bicyclo[3.2.0]hept-2-ene-6-carbonyl chloride* (**6**). A solution of 27.2 g (0.2 mol) **1** in 100 ml $CHCl_3$ was rapidly stirred together with 150 ml of 50% NaOH solution. 26 g (0.04 mol) of a solution of tetrabutylammonium hydroxide (40% in water) was added in the course of 15 min while the temperature was held at 10±2°. The reaction was monitored by GC. (1 m 3% *SE 30* on *Varaport 30;* program 150–215°, 20°/min). After stirring for 2 h at 10±2° the GC.

showed the presence of **1**, **6** and **3** (retention time 0.8 min, 2.0 min, 4.8 min respectively) in the ratio 67:27:6. Work-up as described under 1. and distillation of the reaction mixture gave 16.3 g **1**, b.p. 69–75°/18 Torr, 4.4 g of a 1:1-mixture of **1** and 6, b.p. 30–58°/0.2 Torr and 7.2 g (16%) pure **6**, b.p. 59–61°/0.2 Torr. – IR. (film): 1798 (CO). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 5.93 and 5.65 (2*m*, HC(2) and HC(3)); 3.45–2.65 (*m*, 4 H); 1.44 and 1.17 (2*s*, 2 CH_3–C(7)). – ^{13}C-NMR. ($CDCl_3$): 169.0 (*s*, COCl); 135.4 (*d*, C(2)); 129.2 (*d*, C(3)); 79.9 (*s*, C(6)); 51.6 and 49.7 (2*d*, C(1) and C(5)); 47.9 (*s*, C(7)); 36.2 (*t*, C(4)); 27.3 and 22.0 (2*qa*, 2 CH_3–C(7)).

$C_{10}H_{12}Cl_2O$ (219.11) Calc. C 54.82 H 5.52 Cl 32.36% Found C 55.11 H 5.59 Cl 31.98%

5. rel-*(1S,5R,6R)-3',3'-Dichloro-7,7-dimethyl-(bicyclo[3.2.0]hept-2-ene-6-spiro-2'-oxirane)* (**5**). Treatment of 2.72 g **1** (20 mmol) under identical conditions as under 4 yielded a crude product, which was passed through 35 g of silica gel, with pentane. The pure fractions containing **5** (Rf 0.29, hexane) were combined and the solvent was evaporated, whereby 790 mg (17%) of a colorless oil were obtained. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 5.82 and 5.66 (*m*, HC(2) and HC(3)); 3.47 (*t*×*d*, $J_{5,4_{exo}}=J_{5,1}=7$, $J_{5,4_{endo}}=2$, HC(5)), 3.01 (*m*, HC(1)); 2.39–2.24 (*m*, $H_2C(4)$); 1.50 and 0.88 (2*s*, 2 CH_3–C(7)). – ^{13}C-NMR. ($CDCl_3$): 133.5 (*d*, C(2)); 130.0 (*d*, C(3)); 88.1 (*s*, CCl_2); 81.4 (*s*, C(6)); 54.0 (*d*, C(1)); 45.9 (*s*, C(7)); 38.7 (*d*, C(5)); 31.9 (*t*, C(4)); 24.4 (*qa*, $CH_{3_{exo}}$–C(7)); 17.6 (*qa*, $CH_{3_{endo}}$–C(7)).

6. rel-*(1S,5R,6R)-3',3'-Dichloro-7,7-dimethyl-(bicyclo[3.2.0]heptane-6-spiro-2'-oxirane)* (**9**) and rel-*(1S,5R,6S)-6-Chloro-7,7-dimethyl-bicyclo[3.2.0]heptane-6-carbonyl chloride* (**10**). A solution of 14.0 g (0.1 mol) **8** (b.p. 83°/31 Torr, obtained by hydrogenation of **1** in hexane in the presence of 5% Pd on C) in 50 ml $CHCl_3$ was stirred at 10° together with 80 ml of a 50% NaOH solution. In the course of 5 min, 5.0 g of a solution of tetrabutylammonium hydroxide (40% in water; *i.e.* 8 mmol) were added. After 1.5 h another 5 g of the catalyst solution were added. Work-up after 5.5 h proceeded as described under 1. The crude product consisted of an approximately 1:1-mixture of unreacted **8** and **9**. **9**: ^{13}C-NMR. ($CDCl_3$): 90.0 (*s*, C(3')); 80.4 (*s*, C(6)); 45.8 and 41.4 (*d*, C(1) and C(5)); 41.4 (*s*, C(7)); 27.4 and 26.3 (*t*, CH_2); 25.5 (*qa*, $CH_{3_{exo}}$–C(7)); 16.0 (*qa*, $CH_{3_{endo}}$–C(7)). On distillation, 5.4 g **8**, b.p. 73–75°/20 Torr, 4.1 g of a mixture of **8** and **10**, b.p. 48–83°/0.5 Torr and 8.2 g (37%) pure **10**, b.p. 83–84°/0.5 Torr were obtained. – IR. (film): 1789 (CO). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.10 and 2.60 (2*m*, HC(1) and HC(5)); 2.20–1.20 (*m*, 6 H); 1.35 and 1.24 (2 CH_3–C(7)). – ^{13}C-NMR. ($CDCl_3$): 169.1 (*s*, COCl); 79.2 (*s*, C(6)); 53.1 (*d*, C(1)); 45.5 (*s*, C(7)); 44.7 (*d*, C(5)); 30.1, 28.0, and 25.6 (3*t*, C(2), C(3), and C(4)); 28.7 and 21.7 (2*qa*, 2 CH_3–C(7)).

$C_{10}H_{14}Cl_2O$ (221.13) Calc. C 54.32 H 6.38 Cl 32.07% Found C 54.23 H 6.55 Cl 31.81%

7. *Attempted reactions with* **11** *and* **12**. a) A solution of 2.5 g (0.02 mol) **11** [15] in 20 ml $CHCl_3$ was stirred at 15° together with 15 ml of a 50% NaOH solution; 0.65 g (1 mmol) of a solution of tetrabutylammonium hydroxide (40% in water) were added and the mixture stirred 1 h at 15° and 6 h at 25°. GC. showed the formation of only very small amounts of products with retention time longer than that of **10**. Work-up and acidification of the aqueous phase produced only a faint cloudiness. b) 3.1 g **12** [16] reacted under identical conditions. GC. showed the formation of small amounts of at least 5 products with longer retention time than **12**. On work-up after 4 h at 25° **12** was recovered. Acidification of the aqueous phase gave only a faint cloudiness.

8. *Thermal rearrangements.* a) A solution of 3.8 g (13 mmol) **2** in 25 ml CH_2Cl_2 was heated under reflux. Samples were taken and the rearrangement **2**→**3** monitored by NMR. (integrals of the signals at 1.40–1.35 (2 CH_3 of **3** and 1 CH_3 of **2**) were compared with those of the *s* at 0.96 (CH_3 of **2**). The following conversions were observed: 0.4% (0.35 h), 3.1% (1 h), 4.4% (2 h), 5.7% (5.1 h), 6.8% (7.2 h), 8.7% (9.2 h), 13.1% (13.2 h), 16.8% (16.8 h), 20.0% (21 h), 23.3% (25.4 h); $k_1=(2.95\pm0.15)\times10^{-6}$ sec^{-1}; $\delta_{1/2}=(65\pm3)$ h. – b) A solution of 302 mg (1 mmol) **3** in 1 ml hexachlorobutadiene was heated in a NMR. tube. No change of the NMR. spectrum was observed after 24 h at 150°.

9. rel-*(1R,2S,4R,6R,7R)-3,3-Dichloro-8,8-dimethyl-tricyclo[4.2.0.0^{2,4}]oct-7-yl-methanol* (**13**). A solution of 2.0 g **2** (6.6 mmol) in 3 ml anhydrous ether was rapidly added to a suspension of 0.5 g $LiAlH_4$ (13.2 mmol) in 10 ml ether. The mixture was refluxed for 2 h and then poured onto ice. After acidification with 2N H_2SO_4, the organic phase was separated, washed with brine and dried (Na_2SO_4). The solvent was evaporated and the crude product which according to TLC. contained a small amount

of unreacted **2** (Rf 0.61; hexane/ether 1:1) as well as **13** (Rf 0.11) was chromatographed on 75 g of silica gel using hexane/ether (2:1). The pure fractions containing **13** were combined and the solvent evaporated giving 1.31 g (84%) of a colorless oil. – IR. (CCl_4): 3600, 3340 (OH). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.68 (*d*, J=8, CH_2–C(7)); 2.85–1.80 (*m*, 7 H); 1.41 (*s*, OH); 1.24 and 1.06 (2*s*, 2 CH_3–C(8)). – ^{13}C-NMR. ($CDCl_3$): 67.8 (*s*, C(3)); 60.8 (*t*, CH_2–C(7)); 51.3 (*d*, C(1)); 45.2 (*d*, C(6)); 39.7, 38.9, 37.6 (3*d*, C(2), C(4), C(7)); 35.3 (*s*, C(8)); 32.6 (*qa*, $CH_{3_{exo}}$–C(8)); 28.3 (*t*, C(5)); 19.4 (*qa*, $CH_{3_{endo}}$–C(8)). – MS.: 234 (M^+, 2 Cl, 0.1%), 216 (*M*-18, 2 Cl, 0.8%), 203 (*M*-31, 2 Cl, 1.5%), 199 (*M*-35, 1.6%), 148 (*M*-86, 2 Cl, 26%), 113 (*M*-121, 1 Cl, 100%), 77 (*M*-157, 43%).

10. rel-*(1R,2S,4R,6R,7S)-3,3,7-Trichloro-8,8-dimethyl-7-hydroxymethyl-tricyclo[4.2.0.0^{2,4}]oct-7-yl-methanol* (**14**). A solution of 2.0 g **3** (6.6 mmol) in 3 ml anhydrous ether was rapidly added to a suspension of 0.5 g (13.2 mmol) $LiAlH_4$ in 10 ml ether. A vigorous reaction ensued. After 30 min reflux the reaction mixture was worked up as described under 9. The extracts were dried (Na_2SO_4). Evaporation of the solvent left 1.72 g (97%) of a colorless oil which crystallized on standing, m.p. 55–61°. – IR. (CCl_4): 3580, 3470 (OH). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 3.93 and 3.80 (*AB* system, J_{AB}=12, H_2C–C(7)); 3.05 (*m*, $J_{6,5_{exo}}$=9, $J_{6,1}$=8, $J_{6,5_{endo}}$=2, HC(6)); 2.63 (*d*, $J_{6,1}$=8, HC(1)), 2.58 (*d*×*d*×*d*, $J_{5_{endo},5_{exo}}$=16, $J_{5_{endo},4}$=7, $J_{5_{endo},6}$=2, H_{endo}C(5)), 2.28 (*t*×*d*, $J_{4,2}$=$J_{5_{endo},4}$=7, $J_{5_{exo},4}$=1, HC(4)), 2.11 (*d*, $J_{4,2}$=7, HC(2)); 2.06 (br. *s*, OH); 1.97 (*d*×*d*×*d*, $J_{5_{endo},5_{exo}}$=16, $J_{6,5_{exo}}$=9, $J_{5_{exo},4}$=1, H_{exo}C(5)); 1.39 and 1.15 (2*s*, 2 CH_3–C(8)). – ^{13}C-NMR. ($CDCl_3$): 79.6 (*s*, C(7)); 68.1 (*s*, C(3)); 65.6 (*t*, CH_2–C(7)); 54.4 (*d*, selectively decoupled from the proton signal at 3.05 ppm, C(6)); 50.5 (*d*, C(1)); 42.3 (*s*, C(8)); 39.8 and 38.3 (2*d*, C(2) and C(4)); 30.0 (*qa*, $CH_{3_{exo}}$–C(8)); 28.4 (*t*, C(5)); 19.6 (*qa*, $CH_{3_{endo}}$–C(8)). – MS.: 250 (*M*-18, 0.2%), 232 (*M*-36, 1.2%), 163 (*M*-105, 2 Cl, 44%), 148 (*M*-120, 36%), 113 (*M*-155, 100%), 77 (*M*-191, 52%).

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