equalizing addition funnels, reflux condenser, and appropriate mechanical stirrers.
(31) The side arm of such flasks varied from 6 to 8-in. depending on the size of the flask. All parts were at 0.5–0.75 in. i.d.
(32) Heating of the pot in such distillations was best accomplished by means of a molten salt bath (equimolar NaNO$_2$, KNO$_3$) with the external liquid level up to the narrow neck of the Claisen flask. Near the end of the distillation the refluxing distillate in the side arm was easily forced over by use of a heat gun or a Bunsen burner played gently over the side arm.
(33) The conditions described led consistently to better yields than others in which lower temperatures and other solvents were used.
(34) K. Alexander and L. E. Schniepp, *J. Am. Chem. Soc.*, **70**, 1839 (1948).
(35) Analytical grade cation exchange resin, AG-50W-X$_4$, 200–400 mesh, obtained from Bio-Rad Laboratories.
(36) A boiling point of 148–162° (15 mm) is given in ref 20.
(37) A suitable apparatus is described in M. S. Newman, "An Advanced Organic Laboratory Course", Macmillan, New York, N.Y., 1972, p 110.
(38) Any unreacted sodium was not transferred to the high-dilution flask. In many runs an undetermined amount of sodium failed to react. However, since such a large excess of sodium *N*-methylanilide was used, the yield of product did not seem to be affected.
(39) To determine the setting of the plunger in the addition funnel[11] the drop rate (in this case, 1 drop in 3–3.5 sec) was determined by calibration.
(40) In larger runs (and when much solid was present on walls in some runs) it was preferable to use 50% alcohol during the first stages of quenching.
(41) If polymer had formed in a reaction, it separated at this stage and could be removed by filtration.
(42) A suspension of KH in mineral oil was used as obtained from AIFA Products, Beverly, Mass. No isoprene was used.
(43) The use of sodium bis(trimethylsilyl)amide for preparation of sodio derivatives of nitriles has been described by C. Kruger, *J. Organomet. Chem.*, **9**, 125 (1967), and references cited therein.
(44) An increase in volume is noted on saturation of CH$_3$OH with HCl, e.g., 900 ml of CH$_3$OH yields 1250 ml of methanolic HCl.
(45) For a description of the apparatus used see ref 36, p 102.
(46) Linde 4A, Ventron, Beverly, Mass.
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Mechanism and Stereochemistry of Oxetane Reactions. II. High Syn Stereoselectivity in the Oxetane Ring Opening of 6-Phenyl-7-oxabicyclo[4.2.0]octane under Acidic Conditions. Comparison with the Analogous Reactions of the Corresponding Oxirane

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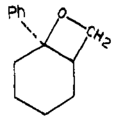
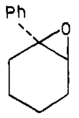
The direction and the stereochemistry of some oxetane ring opening reactions of 6-phenyl-7-oxabicyclo[4.2.0]octane (1) have been determined and compared with those of the corresponding oxirane (2). The reactions of 1 give mixtures of the syn and anti addition products, of the olefin 6 and of the unsaturated alcohol 9. Unexpectedly, some of the addition products are not stable under the reaction conditions and show facile epimerization at the tertiary carbon. The true kinetic product ratios were therefore obtained by extrapolation. The results reveal significant variation in the stereoselectivity and in the yields and ratios between the trichloroacetolysis and the solvolysis reactions of 1. A comparison of the reactions of 1 and 2 shows a much larger amount of nonaddition products in the case of oxetane 1 and marked differences in the syn stereoselectivity. The observed data can be explained by means of a mechanism involving transition states or intermediates with a high degree of carbocation character.

Whereas the stereochemistry of the ring opening of oxirane derivatives has received much attention and has been extensively investigated,[1,2] almost no data are available on that of their higher homologs, the oxetanes.[3] Although the structure and hybridization of orbitals in oxetanes and oxiranes are fundamentally different, the reactivity of the two systems is similar, especially under acidic conditions: the lesser degree of ring strain in oxetanes can be compensated by the greater electron donor capability of the ring oxygen atom.[3]

Previous work carried out in these laboratories on the stereochemistry of the ring opening of substituted oxiranes in acidic media has shown that these reactions are strongly influenced by several factors, such as structure, conformation, and configuration of the epoxide, solvent, type of reagent, etc. In order to get a better insight into the reactivity of the oxetane system and to establish how the stereochemical behavior of the ring opening of small-ring heterocycles can be modified depending on the size of the ring, we have undertaken a study of 6-phenyl-7-oxabicyclo[4.2.0]octane (1), a homolog of the oxirane 2 which has been thoroughly investigated and characterized.[2a,b,g,4,5] Furthermore, protonated oxetanes have been often suggested as intermediates in the Prins reaction,[6] so that a knowledge of the stereochemistry of oxetane ring opening under acidic conditions could offer a good tool for a better understanding of the debated mechanism of the Prins reaction.



1



2

Oxetane 1 has been prepared by conversion of the cis diol 3 into the tosylate 4, which on treatment with potassium *tert*-butoxide afforded 1 (Chart A). The structure of 1 was confirmed by its ir and NMR spectra: presence of an ir band at 10.3 μ[7] and a NMR signal at δ 4.45 due to the methylene protons of the oxetane ring.[8]

It was first necessary to define the regiochemistry of the ring opening of 1. In fact, whereas the attack of the nucleophile on the benzylic carbon of 1 can afford both cis and trans products, the attack on the oxetane methylenic carbon can give, evidently, only cis products. The acid-catalyzed solvolysis of 1 in anhydrous methanol gave mixtures of the two methyl ethers 7 and 8 and of small amounts of the olefin 6 and the unsaturated alcohol 9; the methyl ether 5 arising from a nonbenzylic attack of the nucleophile was not detected and less than 0.2% of it could have been present. The conversion of 1 was very rapid (it had com-

Chart A

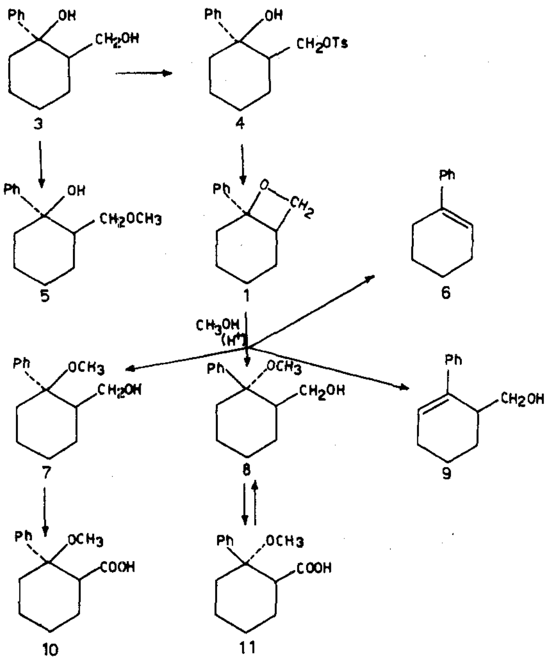
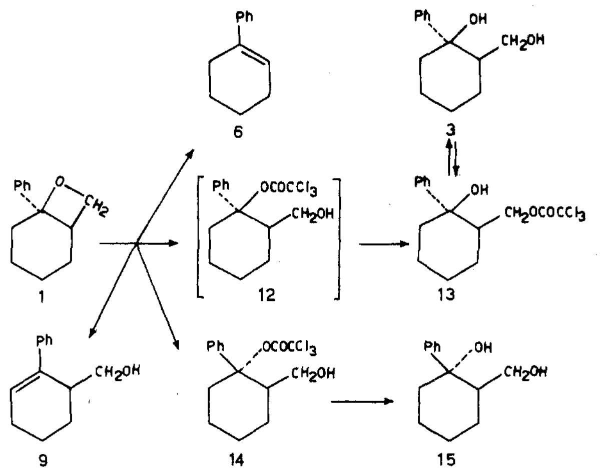


Chart B



pletely disappeared after 10 min). When the reaction mixture was stored for longer times, the amounts of **6** and **9** increased only slightly owing to a very slow conversion of **7** and **8**; the ratio between **7** and **8**, however, slowly changed to reach a constant value of ca. 72.5:27.5 because of a slow epimerization of the two ethers **7** and **8**. After short reaction times (10 min) the trans isomer **8** clearly prevailed (see Table I) and it could be purified by crystallization of the crude reaction mixture. The cis ether **7** was obtained by crystallization of a crude, obtained by longer contact times (3 days), in which it was the main product. Oxidation of **7** and **8** with Jones reagent[9] gave the corresponding acids **10** and **11**, respectively. Reduction of **11** with $LiAlH_4$ afforded the pure ether **8**. When the methanolysis of **1** was carried out in aqueous methanol the reaction was equally regiospecific but the ratio of the products **6**, **9**, **8**, and **7** was slightly different and small amounts of the diols **3** and **15** were also formed (see Table I). In the latter case the rearrangement and the epimerization of **7** and **8** was markedly slower then in the case of the reaction in anhydrous methanol. The relative configurations of the methyl ethers **7** and **8** were indicated by their ir spectra in the 3-μ range in dilute solution of CCl_4. The spectrum of the cis methyl ether **7** shows only a band at 3533 cm^{-1} indicative of a strong intramolecular OH···O bond;[10] such a band is possible in both chair conformers of **7**. On the other hand, compound **8** shows two strong absorptions at 3639 and 3601 cm^{-1} and a weak one at 3507 cm^{-1}, which can be attributed respectively to the free OH, to the OH bonded to the phenyl group and to an OH···O interaction.[10] This suggests that compound **8** should exist preferentially in a chair conformation in which the methoxy and the hydroxymethyl groups are axial with only a small contribution of the other chair conformer, the only one in which an intramolecular OH···O bond is possible. The configurations of **7** and **8** were confirmed by examining the NMR spectra of the corresponding acids **10** and **11**. Since the phenyl group should occupy an equatorial position in the preferred conformation of **10** and **11**, the half-band widths of the methinic proton (17.0 Hz for **10** and 9.0 Hz for **11**) are consistent with the assigned configurations.[2c,e,11]

Also the hydrolysis of **1** in 0.2 *N* aqueous H_2SO_4 was rapid (complete in less than 30 min) and gave mixtures of the cis (**3**) and of the trans diol **15**, the latter predominating, accompanied by minor amounts of **6** and **9**. However, whereas the total amounts of **6** and **9** did not change significantly with the reaction time, a fast pseudo-first-order epimerization of the trans diol **15** into the cis isomer **3** was observed (see Table II); the true kinetic product ratio between **3** and **15** was obtained by extrapolation.

The reaction of **1** with trichloroacetic acid in CH_2Cl_2 was very rapid (complete in less than 1 min) and led to a mixture of **6**, **9**, and the trichloroacetates **13** and **14** (Chart B) from which **6**, **9**, and **13** were separated by preparative TLC. On reduction with $LiAlH_4$ **13** afforded the cis diol **3**, which was reconverted to **13** by esterification with trichloroacetyl chloride; this confirmed the structure of the trichloroacetate **13**, since trichloroacetyl chloride should react preferentially with the primary, rather than with the tertiary, hydroxyl. It may be pointed out that the isolation of **13** from the reaction mixture of **1** with trichloroacetic acid

Table I
Initial Product Compositions for the Oxetane Ring Opening of 1 under Acidic Conditions

Solvent	Acid	6	9	Syn adduct	Anti adduct	Syn:anti ratio
Cyclohexane	CCl_3COOH	24.5	22.0	36.0[a,b]	17.5[b,c]	67.5:32.5
CCl_4	CCl_3COOH	23.0	24.0	35.0[a,b]	18.0[b,c]	66.0:34.0
Benzene	CCl_3COOH	24.5	20.0	40.0[a,b]	15.5[b,c]	72.0:28.0
$CHCl_3$	CCl_3COOH	22.0	25.5	42.0[a,b]	10.5[b,c]	80.0:20.0
CH_2Cl_2	CCl_3COOH	20.0	21.0	49.5[a,b]	9.5[b,c]	84.0:16.0
H_2O[d]	H_2SO_4	1.0	4.5	17.5[a,b]	77.0[b,c]	18.5:81.5
MeOH	H_2SO_4	5.5	9.0	15.0[e]	70.5[f]	17.5:82.5
MeOH–H_2O	H_2SO_4	1.0	4.5	12.0[e]	72.5[f]	14.0:86.0
(9:1 v/v)				1.0[a]	9.0[c]	10.0:90.0

[a] Cis diol **3**. [b] After $LiAlH_4$ reduction. [c] Trans diol **15**. [d] Extrapolated initial composition. [e] Cis methyl ether **7**. [f] Trans methyl ether **8**.

Table II
Production Compositions for the Acid-Catalyzed Reaction of Oxetane 1 in Water at Different Contact Times

Time	6	9	3	15
30 min	1.0	4.5	22.0	72.5
1 hr	1.0	5.0	27.0	67.0
3 hr	1.0	6.0	45.0	48.0
6 hr	1.0	6.5	61.5	31.0
1 day	1.0	8.0	86.5	4.5
2 days	1.0	8.5	87.5	3.0

does not imply that it is the primary reaction product; the tertiary ester **12** is very probably initially formed and rapidly transformed into **13** through an acyl shift involving a six-membered cyclic intermediate, favored by the decrease in steric crowding connected with the shift. Analogous behavior was observed in the reactions of 1,2-epoxides with trichloroacetic acid.[2a,c,12,13] Table I summarizes the product compositions of the crude mixtures resulting from the $LiAlH_4$ reduction of the reaction products of oxetane **1** with trichloroacetic acid in different solvents. The reaction products, **6**, **9**, **13**, and **14**, were stable under the appropriate reaction conditions for times (10 min) longer than the reaction times used (1 min). However, much longer contact times led to partial conversion of **13** and **14** into **6** and **9**.

The facile epimerization of the tertiary alcohols and ethers obtained from **1**, under mild reaction conditions in which the corresponding addition products of the oxirane **2**[1g] were completely stable, is somewhat surprising. The differences in reactivity between the two classes of compounds may be justified on the assumption that the ionization of the tertiary C–O bond should be easier in the adducts from **1** than in those from **2** because the nonbenzylic OH in the former is farther from the developing carbenium ion and should therefore exert to a much smaller degree its electron-withdrawing inductive effect.

The practically complete regiospecificity which is observed in the methanolysis of **1** and very probably is present also in the other reactions for which a direct proof is still lacking, is in accordance with previous results on the acid-catalyzed methanolysis[14] and on the reaction with HCl[15] of 2-aryloxetanes. After the protonation of the oxetane oxygen the rupture of the ring will occur between the oxygen and the tertiary benzylic carbon atom, in accordance with an intermediate stage with a high degree of carbocation character.

An interesting point in the reactions of **1** is the very significant difference in the stereoselectivity of the ring opening and in the yield and ratios of elimination products found between the trichloroacetolysis reactions on one hand and the solvolysis ones on the other. Some interesting differences also result from a comparison of the reactions of **1** with the analogous ones of epoxide **2**.

The stereochemistry of the reactions of **1** can be accounted for through a mechanism, analogous to the one admitted for aryloxiranes,[2,16] involving transition states in which bond breaking has proceeded more than bond formation[14] (Al or "borderline A2" type mechanism) (see Scheme I) in agreement with kinetic results.[14] In aprotic solvents the protonated oxetane **16** can evolve through an incipient carbocation **17** to an intimate ion pair **19**[2,16] in which the anion and the cation are probably held together by hydrogen bonding.[2,13] Attack of the nucleophile on **17** could only give the anti adduct **18**, since the C–O bond is not yet completely broken. On the other hand, the collapse of the ion pair **19** should afford preferentially the syn adduct **20**. Also the formation of the olefin **6** and of the unsaturated alcohol **9** can be justified by this mechanism: intermediate **17** and **19** could easily undergo a retro-Prins fragmentation[3] to **6** and formaldehyde or they can eliminate H^+ to give **9**. Any factor tending to favor one of the intermediates may change the course of the reaction.

Scheme I

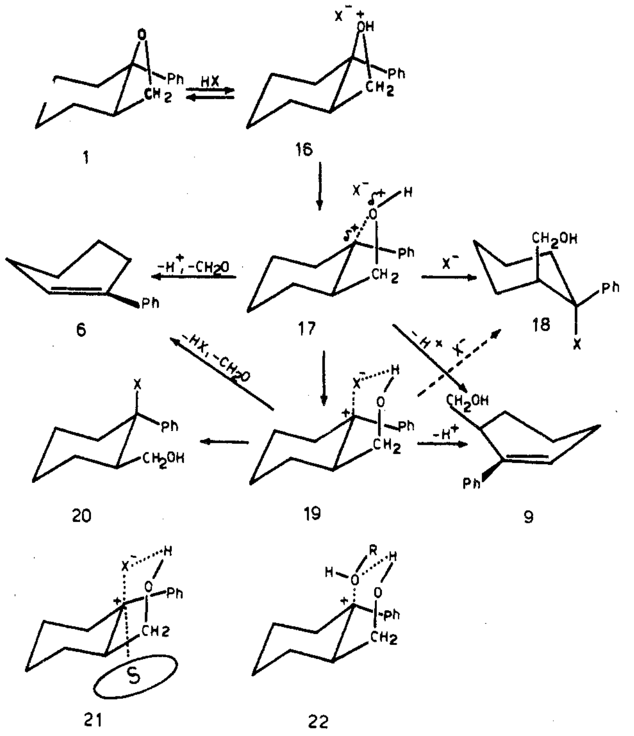


Table I reveals a very definite dependence of the product composition on the nature of the solvent in the trichloroacetolysis of **1** in nonprotic solvents. This effect can be accounted for, as previously pointed out for oxiranes,[2c,f,16] by a nucleophilic back-side solvation of the benzylic carbenium ion which can stabilize the ion pair **19** as shown in **21**. In such a way the intermediate **19** is more favored and consequently products arising from it should be preferentially formed. In fact, when the solvent is changed from cyclohexane (which has very low solvating power) to the chlorinated solvents (which can solvate the center of charge by means of the polarized chlorine atoms) the syn stereoselectivity increases and the increments parallel the order of polarization of the C–Cl bond in the solvents ($CCl_4 < CHCl_3 < CH_2Cl_2$), and therefore their solvating capability. Also benzene[2c,f,16] can solvate the intermediate carbenium ion by its π system in accordance with the results.

When the reactions of **1** are carried out in protic solvents, strong solvation effects and the large availability of attacking molecules can modify the picture of the opening process. The low amount of nonaddition products obtained in protic solvents must be likely due to the large excess of nucleophilic molecules (H_2O or MeOH)[2f] which can make the elimination paths leading to **6** and **9** less competitive. The benzylic carbenium ion formed can be selectively solvated to intermediates like **22**. The collapse of the solvent–carbenium ion complex **22** should also in this case afford the syn adducts. On the other hand, the nucleophilic solvation of the incipient carbenium ion **17** from the anti side should clearly favor the attack of the solvent on **17** before the complete rupture of the C–O bond and therefore should favor the formation of the anti adducts. An analogous higher anti stereoselectivity in the reactions carried out in pro-

Table III
Product Compositions for the Trichloroacetolysis and Hydrolysis of Oxetane 1 and Oxirane 2

Compd	Acid	Solvent	Syn adduct	Anti adduct	Other products
1	CCl_3COOH	Benzene	40.0	15.5	44.5
2[a]	CCl_3COOH	Benzene	95.0	<0.2	5.0
1	H_2SO_4	H_2O	17.5	77.0	5.5
2[a]	H_2SO_4	H_2O	60.0	40.0	<0.2

[a] Reference 18.

tic solvent has been also observed in the acid-catalyzed ring opening reactions of aryloxiranes.[2,16]

A further point of interest is in the differences in the reactions of **1** and of oxirane **2**. Table III gives the relative amounts of syn and anti adducts and nonaddition products obtained in the reactions of **1** and **2** in H_2O and benzene under acidic conditions. The reactions of epoxide **2**,[2a,f,g,4,17,18] when compared with those of oxetane **1** show a markedly higher syn stereoselectivity and much lower amounts of nonaddition products. If the mechanistic proposals discussed above are correct the differences in the amounts of nonaddition products should point to a higher degree of carbocationic character in the reactions of **1** in agreement with the statement (see above) that the carbenium ion derived from **1** is more stable than that from **2**. On the other hand, the same effect should also favor the syn stereoselectivity of the reactions of **1** with respect to that of **2**, in contrast with the obtained results. Evidently other factors, such as the lower stability of the intermediates **19** and **22**, compared with that of the corresponding intermediates derived from **2**, because of the higher steric repulsion, or different values of the differences between the entropic contents of the transition states leading to the syn and to the anti adducts,[17] could be responsible for the different stereoselectivity of the ring-opening reactions of oxetane **1** and oxirane **2** in acid media.

Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. Ir spectra for comparison between compounds were taken on paraffin oil mulls on a Perkin-Elmer Infracord Model 137 and those for the determination of OH stretching bands with a Perkin-Elmer Model 257 double beam grating spectrophotometer in dried (P_2O_5) CCl_4, using the indene band at 3110 cm^{-1} as a calibration standard; a quartz cell of 2-cm optical length was employed, and the concentration of the solutions was 5×10^{-3} *M* or lower to prevent intramolecular association. NMR spectra were determined on ca. 10% $CDCl_3$ solutions with a Jeol C-60 HL spectrometer using Me_4Si as an internal standard. GLC analyses were run on a Carlo Erba Fractovap apparatus with a flame ionization detector, using a dual columns system with glass columns. The relative percentages of compounds **3**, **6**, **7**, **8**, **9**, and **15** were obtained from two or more separate runs on each experiment and were determined using columns packed with 10% Carbowax 20M on 80–100 mesh silanized Chromosorb W (2 mm × 1.0 m); temperatures, low isotherm 135° (3 min), high isotherm 210° (increase 6°/min), evaporator 200°, detectors 200°, nitrogen flow 35–40 ml/min. The order of increasing retention times follow: **6**, **9**, **7**, **8**, **3**, and **15**. Preparative TLC was performed on 2 mm layer silica gel plates (Merck F_{254}) containing a fluorescent indicator; spots were detected under uv light (245 nm). All comparison between compounds were made on the basis of ir and NMR spectra and GLC. Magnesium sulfate was always used as drying agent. Evaporations were made in vacuo (rotating evaporator). Petroleum ether refers to the fraction boiling at 40–70°; cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 were refluxed over P_2O_5 and rectified; benzene was washed with concentrated sulfuric acid, refluxed over sodium, and rectified.

1-Phenyl-*c*-2-hydroxymethyl-*r*-1-cyclohexanol (3)[6f,19] **and 1-phenylcyclohexene (6)**[20] were prepared as previously described.

1-Phenyl-*c*-2-tosyloxymethyl-*r*-1-cyclohexanol (4). Tosyl chloride (36.8 g, 0.193 mol) was slowly added to a solution of **3** (9.2 g, 0.044 mol) in dry pyridine (100 ml), left 4 days at room temperature, treated with ice, and extracted with $CHCl_3$. The organic extracts were washed with dilute H_2SO_4 and water and evaporated to give a crude product (15.3 g) which crystallized from CCl_4 to yield pure **4** (12.2 g): mp 108–109°; ir λ_{OH} 2.82 μ; NMR δ 3.73 (d, 2, J = 5.5 Hz, CH_2O), 2.39 ppm (s, 3, CH_3). Anal. Calcd for $C_{20}H_{24}O_4S$: C, 66.66; H, 6.66; Found: C, 66.71; H, 6.75.

6-Phenyl-7-oxabicyclo[4.2.0]octane (1). A. A solution of **4** (4.8 g, 13.4 mmol) in anhydrous *tert*-butyl alcohol was treated with potassium *tert*-butoxide (2 g, 17.8 mmol), while keeping the temperature at about 5°. After 20 hr at room temperature the reaction mixture was diluted with petroleum ether, filtered, and evaporated to dryness to yield crude **1** (2.0 g). Distillation of crude **1** (2.0 g) from powdered KOH (0.050 g) gave pure **1** (1.6 g): bp 117° (1.5 mm); ir λ_{COC} 10.3 μ; NMR δ 4.45 ppm (m, 2, CH_2O). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.77; H, 8.37.

B. A solution of KOH (0.140 g) in 2-propanol (3 ml) was added to a solution of **4** (0.200 g) in *tert*-butyl alcohol (6 ml), left for 20 hr at room temperature, diluted with petroleum ether, and filtered. Evaporation of the organic solution gave crude **1** (0.090 g).

Reaction of 1 with Sulfuric Acid in Anhydrous Methanol. A solution of **1** (0.400 g) in 0.2 *N* H_2SO_4 in anhydrous methanol (40 ml) was stirred at 25° for 10 min, then treated with $NaHCO_3$, diluted with water, and extracted with ether. Evaporation of the washed (H_2O) and dried ether extracts yielded an oily residue (0.410 g), consisting of **6**, **9**, **7**, and **8** in the ratio of 5.5:9.0:15.0:70.5 (see Table I). The mixture was crystallized twice from petroleum ether (bp 30–50°) to yield pure (GLC). **1-phenyl-*t*-2-hydroxymethyl-*r*-1-methoxycyclohexane (8)** (0.080 g): mp 79–81°; ir ν_{OH} (CCl_4) 3639 (s, free OH), 3601 (s, $OH\cdots\pi$), and 3508 cm^{-1} (w, $OH\cdots O$); NMR δ 2.90 ppm (s, 3, CH_3). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 76.21; H, 9.19. Reactions of **1** carried out under the same conditions stopping after relatively longer reaction times (0.5 hr) yielded the same product compositions within the experimental error, but much longer contact times showed a partial rearrangement of **7** and **8** into **6** and **9** and a marked epimerization of **8** into **7**. Separate reactions quenched after 3 and 6 days yielded the following product compositions, respectively: **6**, 11.0; **9**, 23.5; **7**, 46.0; **8**, 19.5 and **6**, 11.5; **9**, 28.0; **7**, 44.0; **8**, 16.5. Analogous results were obtained when pure **7** or **8** were put under the same reaction conditions as **1**. Crystallization of a crude mixture (0.210 g) obtained from **1** (0.200 g) after a contact time of 3 days from petroleum ether (bp 30–50°) at 5° gave **1-phenyl-*c*-2-hydroxymethyl-*r*-1-methoxycyclohexane (7)** (0.040 g): mp 95–97°; ir ν_{OH} (CCl_4) 3553 cm^{-1} ($OH\cdots O$); NMR δ 3.25 ppm (s, 3, CH_3). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 76.49; H, 9.05.

Reaction of 1 with Sulfuric Acid in Methanol–Water. A solution of **1** (0.100 g) in methanol (9 ml) was treated with aqueous 2 *N* H_2SO_4 (1 ml) and stirred for 24 hr at 25°. Treatment with $NaHCO_3$, dilution with water, extraction with ether, and evaporation of the washed (saturated aqueous $NaHCO_3$ and H_2O) and dried extracts gave an oily mixture (0.118 g) of **6**, **9**, **7**, **8**, **3**, and **15** in the ratio of 1.0:4.5:12.0:72.5:1.0:9.0 (see Table I). Reactions carried out under the same conditions but stopping after 3 and 6 days yielded the same products in the following relative percentages, respectively: **6**, 2.0; **9**, 5.5; **7**, 23.5; **8**, 62.5; **3**, 3.5; **15**, 3.0 and **6**, 2.5; **9**, 8.0; **7**, 27.5; **8**, 56.0; **3**, 4.0; **15**, 2.0.

2-Phenyl-*c*-2-methoxy-*r*-1-cyclohexanecarboxylic Acid (10). A solution of **7** (0.030 g, 0.14 mmol) in acetone (1.5 ml) was treated with Jones reagent[9] (0.07 ml). After 10 min at room temperature the mixture was diluted with water and extracted with ether and the ether layer was extracted with 10% aqueous Na_2CO_3. Acidification of the alkaline solution with 10% aqueous HCl, extraction with ether, and evaporation of the washed (H_2O) and dried extract yielded **10** (0.028 g) which crystallized from petroleum ether: mp 146–148°; NMR δ 3.32 (s, 3, CH_3), 2.70 ppm (m, 1, $W_{1/2}$ = 17 Hz, CHCOO). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.52; H, 7.86.

2-Phenyl-*t*-2-methoxy-*r*-1-cyclohexanecarboxylic Acid (11). Oxidation of **8** (0.090 g), as described for the oxidation of **7**, gave **11** (0.085 g) which crystallized from petroleum ether at −5°, mp 131–132°, NMR δ 2.82 ppm (s, 3, CH_3). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.40; H, 7.92.

Reduction of 11 with Lithium Aluminum Hydride. A solution of **11** (0.110 g, 0.47 mmol) in ether (10 ml) was added dropwide to a stirred suspension of $LiAlH_4$ (0.300 g, 7.9 mmol) in ether (5 ml). After completion of the addition, the mixture was refluxed for 6 hr and then treated with H_2O and 2 *N* aqueous NaOH. Evaporation of the dried ether yielded pure (GLC) **8** (0.100 g).

2-Phenyl-3-hydroxymethylcyclohexene (9). A solution of **2-phenyl-3-acetoxymethylcyclohexene**[6f] (0.500 g, 2.77 mmol) in ether (20 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (0.500 g, 13.1 mmol) in ether (20 ml); the mixture was then refluxed for 7 hr and treated with H_2O and 2 *N* aqueous NaOH. Evaporation of the dried ether yielded crude **9** (0.400 g) which was purified by preparative TLC (eluent, a 7:3 mixture of petroleum ether and ether) giving pure **9**[6f] as an oil (0.360 g): ir λ_{OH} 2.98 μ; NMR δ 6.02 (m, 1, CH=), 3.50 ppm (d, 2, J = 5.25 Hz, CH_2O).

1-Phenyl-*c*-2-methoxymethyl-*r*-1-cyclohexanol (5). A solution of **3** (0.800 g) in DMFA (40 ml) and CH_3I (3.4 g) was stirred for 24 hr at room temperature with freshly prepared silver oxide (from 2.7 g of $AgNO_3$), then diluted with water and extracted with ether. Evaporation of the washed (H_2O) ether extracts gave an oily residue of crude **5** (0.800 g) which was purified by preparative TLC (85:15 mixture of petroleum ether and ether was used as the eluent) yielding pure **5** (0.530 g) as an oil: ir λ_{OH} 2.88 μ; NMR δ 3.12 ppm (s, 3, CH_3). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09. Found: C, 76.25; H, 9.18.

Compound **5** was recovered unchanged after treatment of its acetone solution with Jones reagent[9] for 10 min.

1-Phenyl-*c*-2-trichloroacetoxy-*r*-1-cyclohexanol (13). A. A solution of **3** (0.467 g, 2.25 mmol) in dry benzene (25 ml) and dry pyridine (0.355 g, 2.70 mmol) was treated with trichloroacetyl chloride (0.490 g, 2.70 mmol), left for 1 hr at room temperature, then diluted with water and extracted with ether. Evaporation of the washed (diluted aqueous HCl, 10% aqueous Na_2CO_3, H_2O) and dried ether layer yielded crude **13** (0.720 g) which crystallized from petroleum ether: mp 48–49°; ir λ_{OH} 2.77 μ; NMR δ 4.12 ppm (d, 2, J = 5.5 Hz, CH_2O). Anal. Calcd for $C_{15}H_{17}O_3Cl_3$: C, 51.10; H, 4.82. Found: C, 51.21; H, 4.69.

B. A solution of **1** (0.300 g, 1.59 mmol) in dry CH_2Cl_2 (30 ml) was added to 1 *N* trichloroacetic acid in dry CH_2Cl_2 (1.75 ml), left for 1 min at room temperature, washed with saturated aqueous $NaHCO_3$ and H_2O, and evaporated to give a mixture (0.370 g) of **6**, **9**, **13**, and **14** which was subjected to preparative TLC, a 7:3 mixture of petroleum ether and ether being used as the eluent. Extraction of three main bands with ether (the fastest moving band contained **6** and the slowest one contained **9**) yielded **6** (0.054 g), **13** (0.120 g), and **9** (0.060 g).

Reaction of 1 with Sulfuric Acid in Water. A suspension of **1** (0.100 g) in 0.2 *N* aqueous H_2SO_4 (10 ml) was stirred at 25° for the time shown in Table III, treated with $NaHCO_3$, and then extracted with ether. Evaporation of the washed (saturated aqueous $NaHCO_3$ and H_2O) and dried ether extracts gave mixtures of **6**, **9**, **3**, and **15** (see Table III). The epimerization of **15** into **3** was shown to follow pseudo-first-order kinetics and the initial ratio between **3** and **15** was obtained by extrapolation. When pure **7** or **8** were treated under the same reaction conditions as **1**, a similar epimerization was obtained. Reactions of **1** carried out under the same conditions using more dilute (0.02 *N*) aqueous H_2SO_4 showed slower epimerization of **15** into **3**, but an almost identical extrapolated initial ratio between **3** and **15**.

A crude mixture (0.420 g), obtained from **1** (0.400 g) as described above after a reaction time of 30 min, was subjected to preparative TLC; a 7:3 mixture of petroleum ether and ether was used as the eluent and elution was repeated two times. Extraction of the two bands with ether (the slowest moving band contained **15**) afforded a mixture of **9** and **3** (0.070 g) and the trans diol **15**[21] (0.280 g) as an oil: ir λ_{OH} 2.90 μ; NMR δ 3.37 ppm (m, 2, CH_2O).

Reaction of 1 with Trichloroacetic Acid in Different Solvents. The reactions were carried out in dry benzene, cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 in carefully dried apparatus in the following way. To a solution of **1** (0.100 g, 0.53 mmol) in the solvent (10 ml) was added trichloroacetic acid (0.60 mmol) using a ca. 1 *M* solution of the acid in the same solvent. The mixture was allowed to stand for 1 min at room temperature, washed with saturated aqueous $NaHCO_3$ and H_2O, dried, and evaporated to dryness. The crude residue was dissolved in ether (20 ml) and added dropwise to a stirred suspension of $LiAlH_4$ (0.100 g) in ether (20 ml). When the addition was complete, the mixture was refluxed for 10 min and then treated with H_2O and 2 *N* aqueous NaOH. Evaporation of the dried ether yielded mixtures of **6**, **9**, **3**, and **15** which were analyzed by GLC (see Table I). Reactions of **1** carried out for each solvent under the same conditions stopping after relatively longer times (10 min) yielded the same product composition within the experimental error. However, much longer contact times showed partial rearrangements to **6** and **9**.

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