Critical Dependence of the Stability of an Overcrowded Benzylic Carbocation on the Aromatic Ring Substituent. Substituent and Solvent Effects on the Ring Opening of 1-Aryl-Substituted Epoxides. 1-(*p*-Methoxyphenyl)-2,2-dimethyl-7-oxabicyclo[4.1.0]heptane

Aldo Balsamo, Paolo Crotti, Bruno Macchia, and Franco Macchia*

Istituti di Chimica Organica e Chimica Farmaceutica, Università di Pisa, 56100 Pisa, Italy

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The reactions of 1-(*p*-methoxyphenyl)-2,2-dimethyl-7-oxabicyclo[4.1.0]heptane (5) under acidic conditions have been studied and compared with the analogous ones of the corresponding nonmethylated epoxide 12 and of the parent epoxide without substituent on the aryl group 13. Relevant differences appear both in regio- and stereoselectivity and in the amount of rearranged products. The results can be explained on the basis of the primary steric effect of the two methyl groups and of the balance between the electronic effect of the strongly electron-donating aryl group and the secondary steric effect of the methyl groups which prevents coplanarity of the aryl group and the intermediate benzylic carbenium ion. The reactions of epoxide 5 with trichloroacetic acid in low polarity aprotic solvents showed a marked dependence on solvent which can be ascribed to a nucleophilic assistance in the development of the positive charge on the benzylic carbon.

The ring opening of aryl-substituted oxiranes under acidic conditions proceeds through an intermediate or a transition state with a high degree of development of positive charge on carbon. The regio- and stereoselectivity of these ring openings and the amount of rearranged products are strictly related not only to the reaction conditions, but also to the capability of the π system to stabilize the electron-deficient center.[1] It has, in fact, been shown[1a,d,2] that the syn stereoselectivity in the acid-catalyzed hydrolysis of 1-aryl-1,2-epoxycyclohexanes almost parallels the rate of solvolysis of the corresponding 1-aryldimethylcarbinyl chlorides[3] (S$_N$1 reaction type), that is the stabilities of the related carbocations. Furthermore, in the reactions with acids an electron-donating substituent on the aryl moiety of aryloxiranes increases the percentage of rearranged products.[1d] The steric effects of the two methyl groups in 6,6-dimethyl-1-phenylcyclohexene oxide (13) prevents coplanarity of the phenyl group with the carbenium ion arising from the protonated epoxide, thus reducing in a striking way the tendency of this epoxide towards syn opening and causing a lower regioselectivity in the ring opening with respect to the nonmethylated epoxide.[1c]

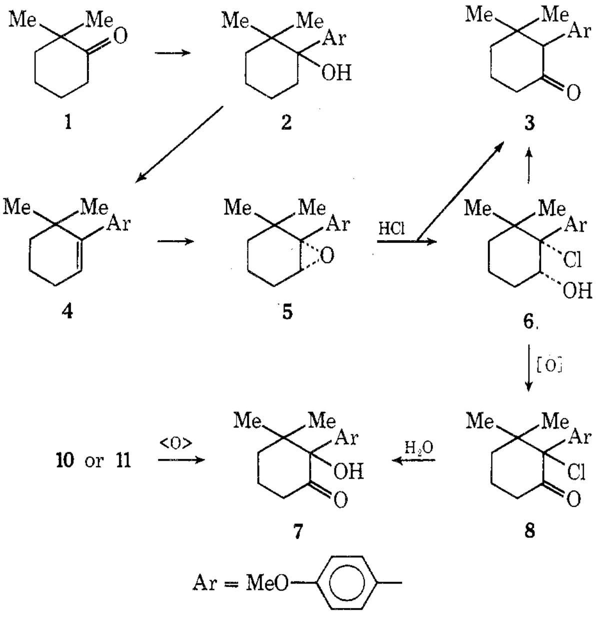
All these results imply that the syn addition products involve a benzylic carbocation in a tight ion pair which collapses to give the adduct.[1,2] Therefore aryl-substituted epoxides offer a useful tool for a study of the reactivities of carbocations by examining the stereo- and regiochemistry of their reactions with different acids under different conditions.

We have now extended our work on oxiranes to 1-(*p*-methoxyphenyl)-2,2-dimethyl-7-oxabicyclo[4.1.0]heptane (5) in order to get more information on the transmission of electronic effects of a strongly donating aryl group to a carbocation through a single bond in a case where the geometry is such as to severely hinder coplanarity.

Results

Reaction of 2,2-dimethylcyclohexanone (1) with *p*-methoxyphenyllithium gave good yield of alcohol 2, which was dehydrated to olefin 4 (Scheme I). Epoxidation of 4 yielded 5. The reaction of 5 with anhydrous HCl in benzene gave a mixture of the ketone 3 and of the cis chlorohydrin 6. No evidence for the formation of trans halohydrins was found. Treatment with alkali transformed 6 into the ketone 3. Chlorohydrin 6 on chromic oxidation in the two-phase benzene–water system gave the chloro ketone 8. However oxidation of 6, under the usual homogeneous Jones conditions,[4] gave, after short reaction times, a mixture of 6 and of the ketol 7; longer reaction times produced practically pure 7. The ketol 7 was also formed by oxidation of the diols 10 and 11 with Jones reagent in acetone. Separate experiments indicated that the replacement of chlorine by hydroxyl takes place at the chloro ketone 8 rather than at the chlorohydrin 6 stage.

Scheme I



The reaction of 5 with trichloroacetic acid in benzene afforded a mixture of 3 and of the cis trichloroacetate 9 which was hydrolyzed to the cis diol 11 (Scheme II). The secondary ester 9 is very probably not the primary product of the reaction, the tertiary ester being initially formed and rapidly transformed into the more stable secondary one 9 through an acyl shift.[1a,5] The reaction of 5 with aqueous sulfuric acid gave a mixture of the ketone 3 and of the diols 10 and 11. Table I reports the percentages of products resulting from the acid hydrolysis of 5 and of the diols 10 and 11. Table I reports the percenttained from the reaction of 5 with trichloroacetic acid in different solvents.

Table I
Products of Trichloroacetolysis and Hydrolysis of 5

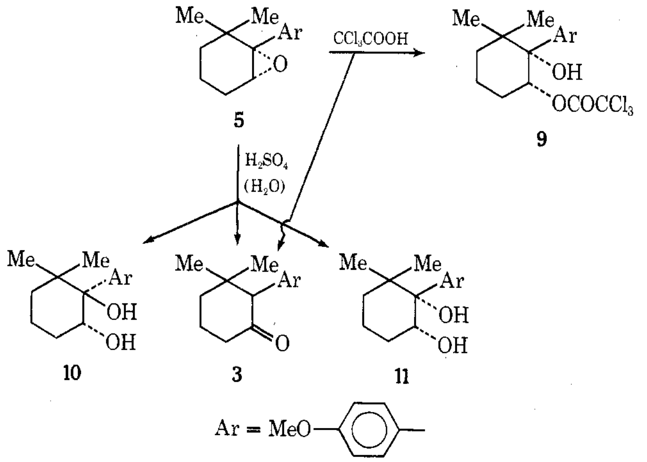
Solvent	Acid	% **3**	% **11**	% **10**
Cyclohexane	CCl_3COOH	54.5	44	1.5
CCl_4	CCl_3COOH	55	44	1
Benzene	CCl_3COOH	63.5	35.5	<1
$CHCl_3$	CCl_3COOH	76.5	23	<0.5
CH_2Cl_2	CCl_3COOH	93.9	6	<0.1
H_2O	H_2SO_4	17.5	35	47.5

Table II
Nmr Data and Wavenumber of OH Protons

	Nmr δ, ppm			Ir, cm^{-1}	
Compd	CHX ($W_{1/2}$, Hz)	CH_3		OH free	OH···X
6	4.53 (16.5)[a]	1.01	0.82		3581[c]
9	5.77 (17.0)[b]	0.88	0.85		3596[b]
10	3.95 (17)[a,d]	1.12	0.66	3625[e]	3576[a,f]
11	4.38 (16.0)[a]	0.80		3620[e]	3583[f] 3558[a]

[a] X = OH. [b] X = $OCOCCl_3$. [c] X = Cl. [d] Approximate values due to the partial overlapping of the signal with that one of the methoxy group. [e] Weak band. [f] X = aryl.

Scheme II



While the structure and configuration of the chlorohydrin **6** can be defined by its reactions (conversion into **3** by treatment with alkali and oxidation to the chloro ketone 8), those of compounds **9**, **10**, and **11** have been demonstrated, and that of **6** confirmed by nmr spectroscopy and by ir studies in 3-μ range (Table II). The chemical shifts and the half-bandwidths of the methinyl protons β to the *p*-methoxyphenyl group[1a,c,d,5-7] of the cis compounds **6**, **9**, and **11** are consistent, respectively, with their natures and with their axial positions. Furthermore the ir spectra of these compounds show the presence of strong OH···X hydrogen bonds,[1c,d,8] in accordance with their structures and configurations. These data indicate for the cis compounds a configuration with the aryl group in equatorial position. The presence in the ir spectrum of the trans diol **10** of OH···O interactions[1c,8] and the half-bandwidth of the proton α to the hydroxyl group[1a,c,5,7] suggests for this compound a twist conformation or one in which the aryl group occupies an axial position.[1c] Moreover, the ir and nmr spectra of these compounds are fully consistent with the corresponding spectra of the analogous derivatives without substituent on the phenyl group.[1c]

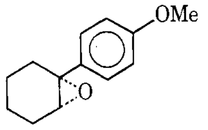
Discussion

The results obtained in the ring opening of the epoxide **5** with acid appear quite interesting when compared with the ones relative to the analogous reactions of the non-6-methylated epoxide **12**[1d] and of the parent epoxide **13** without substituent on the aryl group[1] (Table III). Previous results[1c] clearly indicated that in **13** the secondary steric effect of the methyl groups, preventing overlap between the aryl π system with the developing p orbital on the benzylic carbon atom, strongly reduced the carbocationic character of the intermediate stage, as shown by the high percentages of anti adducts, and particularly by the fact that the reaction of **13** with HCl gave 50% of the anti-Markovnikov anti adduct, which can arise only from a reaction with a high degree of A-2 character. On the other hand, in the case of epoxide **12**[1d] the unhindered nature of the aryl group and its strongly electron-donating properties favor the development of the benzylic carbocation and cause practically exclusive formation of the syn adducts through an ion-pair intermediate.

Table III
Product Compositions for the Trichloroacetolysis and Hydrolysis of Epoxides 5, 12, and 13

Epoxide	Acid	Solvent	Syn adduct	Anti adduct	Rearrt products
5	H_2SO_4	H_2O	35	47.5	17.5
12[a]	H_2SO_4	H_2O	93	3.8	3.2
13[b]	H_2SO_4	H_2O	0.7	99	0.3
5	CCl_3COOH	Benzene	35.5	<1	63.5
12[a]	CCl_3COOH	Benzene	68	0	32
13[b]	CCl_3COOH	Benzene	6	78	16

[a] Reference 1d. [b] Reference 1c.



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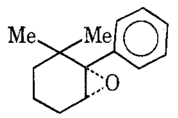

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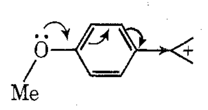
The epoxide **5** presents an intermediate situation since it possesses both features, having a hindered, but strongly activating aryl group. These features are clearly evident in the results of its ring-opening reactions. The addition of HCl (and presumably also of CCl_3COOH and of H_2O) is entirely regioselective in the Markovnikov sense. A high syn stereoselectivity is observed in the reactions of **5** with HCl and CCl_3COOH, but not in the hydrolytic opening.

These results can be explained by assuming that the electronic effect of the *p*-methoxy substituent in **5** counterbalances the reduced stabilization of the intermediate benzylic carbocation and the primary steric effects of the two methyl groups[1c] making the attack of the nucleophile on the benzylic carbon of **5** exclusive. Furthermore the high syn stereoselectivity in the ring opening of **5** with CCl_3COOH shows that a discrete cationic charge has developed on the benzylic carbon atom in such a way as to permit the ion-pair mechanism (**15a,b**) to operate in an efficient manner.[1,2,5,6] Evidently the mesomeric electron-releasing effects of the methoxy substituent prevail over the opposite inductive effect and can be transmitted to the benzylic carbon atom notwithstanding the undoubtedly serious inhibition of coplanarity of the benzylic carbocation with the aryl group. The stabilization of the cationic intermediate could result from a residual overlapping of the orbitals, or from an inductomeric electron release,[1c] as shown in **14**.



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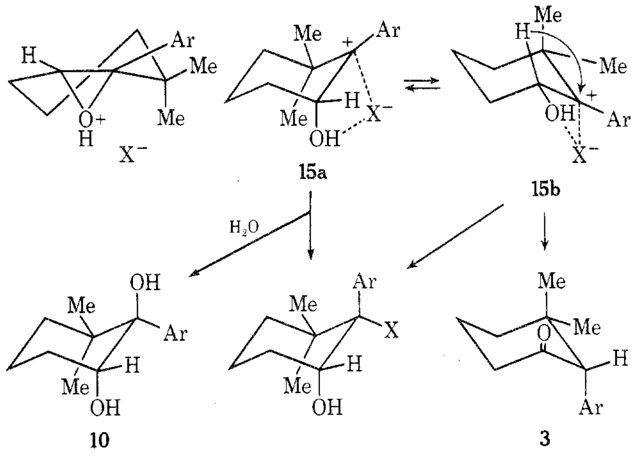
The lack of stereoselectivity in the reaction of **5** with water is probably due to the fact that the collapse of the

Scheme III



intimate ion pair **15a** is hindered by the primary steric effect of the axial OH and methyl, and in the presence of large excess of water molecules attack by H_2O rather than by X^- takes place; this attack occurs preferentially on the trans side because the mentioned steric effect (Scheme III).

The fact that **5** gives higher amounts of rearranged products than **12** and **13** can also be taken as a proof of this mechanistic proposal. It is known that the conversion of epoxides into carbonylic compounds involves transition states with a high carbocation character.[1b,9,10] As a matter of fact **5** affords more rearranged products than epoxide **13** which gives the least stable benzylic carbocation, but also more than **12** which should give the most stable cation, in apparent contrast with the premise. However, the primary steric effect of the two methyl groups in **5** retards the attack by an external nucleophile rendering the nucleophilic rearrangement more competitive. It can also be assumed that the syn interaction between OH and methyl in the ion **15a** facilitates conversion into the conformer **15b**, which is ideally disposed for the 1,2-hydride shift giving the ketone **3** (see Scheme III). The much lower amount of ketone **3** obtained in the hydrolytic reaction can again be explained on the basis of the large availability of nucleophilic molecules that can attack the ion **15a** before it passes to **15b** or, in any case, before the rearrangement stage.

A further point of interest is given by the reactions of **5** with trichloroacetic acid in several aprotic solvents (Table I). While the syn stereoselectivity of the ring opening of **5** is practically complete in all solvents, the amount of ketone **3** varies considerably. This solvent effect can be explained by assuming[1a,c] that the intermediate positive charge can be stabilized through a nucleophilic assistance by the nonprotic solvent. In fact the amount of ketone **3** is low in a solvent like cyclohexane which has very little solvating power. In chlorinated solvents the center of charge can be solvated by the external electrons of the chlorine atoms;[1a,c] the solvation effect will depend in a stringent way on the electron density on the chlorine and therefore on the order of polarization of the C–Cl bond in the solvent which is $CH_2Cl_2 > CHCl_3 > CCl_4$, and this is in accordance with the results. Also benzene can provide such an assistance by its π-electron system[1a,c,11,12] thus facilitating the formation of ketone **3**.

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 in an ~10% $CDCl_3$ solution with a JEOL C 60 HL spectrometer using TMS as an internal standard. Glpc were run on a Carlo Erba Fractovap GV apparatus with a flame ionization detector, using a dual column system with glass columns (3 mm × 2 m) packed with 1% neopentyl glycol succinate on 80–100 mesh silanized Chromosorb W; column temperature 165°, evaporator temperature 200°, detector temperature 200°; nitrogen flow 40 ml/min; retention time for **3**, 5 min, **11**, 10 min, **10**, 17 min. The ratio of chlorohydrin **6** and ketone **3** was roughly estimated through the nmr signals of the two methyl groups adjacent the phenyl group. Analytical (0.25-mm layer) and preparative (2-mm layer) tlc were performed on silica gel F 254 plates containing a fluorescent indicator; spots were detected under uv light (245 nm). A 6:4 mixture of petroleum ether and ether was always used as the eluent. All comparison between compounds were made on the basis of ir and nmr spectra, tlc, and glpc. Magnesium sulfate was always used as drying agent. Evaporations were made *in vacuo* (rotating evaporator). Petroleum ether refers to the fraction boiling at 30–50°; 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.

2,2-Dimethylcyclohexanone (1) was prepared as described before:[13] bp 170–172° (760 mm), $n^{20}{}_D$ 1.4485.

2,2-Dimethyl-1-(*p*-methoxyphenyl)cyclohexanol (2). A solution of *p*-methoxybromobenzene (16.5 g, 88 mmol) in anhydrous *n*-pentane (100 ml) was treated under N_2 with 2.3 *M* solution of *n*-butyllithium in *n*-heptane (38 ml, 88 mmol) and stirred 6 hr at room temperature. The reaction mixture was added to a solution of **1** (10.0 g, 79 mmol) in anhydrous *n*-pentane (40 ml) and anhydrous ether (20 ml), stirred at room temperature 14 hr, and refluxed for 3 hr and then treated with saturated aqueous NH_4Cl and ice. The organic layer was washed with 10% aqueous Na_2CO_3 and water, dried, and evaporated to yield a residue which on crystallization from petroleum ether gave pure **2** (11.5 g): mp 72–73.5°; ir λ_{OH} 2.82 μ; nmr δ 7.35 and 6.77 ppm (2 H each, d, J = 9 Hz, C_6H_4–). *Anal.* Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.70; H, 9.37.

6,6-Dimethyl-1-(*p*-methoxyphenyl)cyclohexene (4). **2** (3.0 g) was added to 15 ml of a freshly prepared solution of sulfuric acid and acetic acid (2:8 v/v). The mixture was shaken 10 min at room temperature and then poured into a separatory funnel containing ether (100 ml) and water (100 ml). The ether layer was washed with water, 10% aqueous Na_2CO_3, and water, dried, and evaporated to yield crude **4** (2.7 g) which was chromatographed through a 1.5 × 27 cm column of neutral Al_2O_3 (activity II). Elution with petroleum ether (250 ml) gave pure **4** (2.6 g): nmr δ 5.32 (1 H, m, HC=), 1.03 ppm (6 H, s, CH_3). *Anal.* Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.45; H, 9.17.

2,2-Dimethyl-1-(*p*-methoxyphenyl)-7-oxabicyclo[4.1.0]heptane (5). A solution of **4** (2.05 g, 9.50 mmol) in $CHCl_3$ (20 ml) was treated dropwise under stirring with a 0.245 *M* solution of peroxybenzoic acid[14] in $CHCl_3$ (43 ml, 10.5 mmol), while keeping the temperature below −6°, stirred 45 min at −6°, and then left 3 days at 5°. The reaction mixture was washed with 10% aqueous Na_2CO_3 and water, dried, and evaporated to yield a crude residue (2.1 g) which on crystallization from ethanol–water (8:2, v/v) containing a trace of KOH gave pure **5** (1.92 g). An analytical sample was obtained from petroleum ether: mp 47–49°; nmr δ 3.12 ppm (1 H, m, CHO). *Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.81; H, 8.70.

6,6-Dimethyl-1-phenyl-*c*-2-trichloroacetoxy-*r*-1-cyclohexanol (9). A solution of **5** (0.250 g, 1.08 mmol) in anhydrous benzene was treated with a 1.0 *M* solution of trichloroacetic acid in anhydrous benzene (1.19 ml, 1.19 mmol), left 4 days at room temperature, washed with saturated aqueous $NaHCO_3$ and water, and evaporated to give a solid mixture (0.27 g) of **3** and **9** (ir). Extraction of the mixture with petroleum ether at room temperature yielded a residue (0.050 g) consisting of **3**. Crystallization of the extracts at −7° from petroleum ether afforded pure **9**: mp 104–105.5°; ir λ_{CO} 5.74 μ. *Anal.* Calcd for $C_{17}H_{21}Cl_3O_4$: C, 51.60; H, 5.35. Found: C, 51.90; H, 5.31.

Compound **9** was recovered unchanged after treatment of its acetone solution with Jones reagent[4] for 15 min.

6,6-Dimethyl-1-(*p*-methoxyphenyl)-*r*-1,*c*-2-cyclohexanediol (11). A solution of **9** (0.030 g) in THF (3 ml) was treated with a 1 *M* solution of KOH in ethanol (1 ml). After 5 hr at room temperature the solution was diluted with water and extracted with ether. Evaporation of the washed and dried ether extracts yielded **9** (0.017 g), which after crystallization from petroleum ether (bp 40–70°) had mp 114–116°. *Anal.* Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.13; H, 8.72.

Reaction of 5 with Sulfuric Acid in Water. A suspension of **5** (0.500 g) in water (45 ml) and 2 *N* aqueous sulfuric acid (5 ml) was stirred 2 days at room temperature and then extracted with ether. Evaporation of the washed (water) and dried extracts yielded a solid (0.490 g) consisting of ketone **3**, diols **10** and **11** (Table I), and starting epoxide **5**. The crude reaction mixture was subjected to preparative tlc. Elution was repeated four times. Extraction of the four bands (the relative R_f were **5** > **3** > **11** > **10**) yielded **5** (0.050 g), **3,3-dimethyl-2-(*p*-methoxyphenyl)cyclohexanone (3)** (0.060 g), **11** (0.100 g), and **6,6-dimethyl-1-(*p*-methoxyphenyl)-*r*-1,*t*-2-cyclohexanediol (10)** (0.180 g).

3: mp 97–98° [from petroleum ether (bp 40–70°)]; ir λ_{CO} 5.88 μ; nmr δ 3.43 (1 H, s, CHAr), 0.83 and 0.87 ppm (3 H each, s, CH_3). *Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.60; H, 8.46.

10: mp 90–92° [from petroleum ether (bp 60–80°)]. *Anal.* Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.18; H, 8.67.

Reaction of 5 with Trichloroacetic Acid in Several Solvents. The reactions were carried out in anhydrous benzene, cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 in the following way. To a solution of **5** (0.100 g, 0.430 mmol) in the solvent was added trichloroacetic acid (0.480 mmol) using a *ca.* 1 *M* solution of the acid in the same solvent. The reaction mixture was allowed to stand 4 days at room temperature, then washed with saturated aqueous $NaHCO_3$ and water, dried, and evaporated to dryness. The crude residue was dissolved in THF (10 ml), treated with 1 *M* KOH in ethanol (4 ml), and left 4 hr at room temperature. Dilution with water, extraction with ether, and evaporation of the washed (water) and dried ether extracts gave a residue consisting of a mixture of **3**, **10**, and **11** which was analyzed by glpc (Table I).

Reaction of 5 with HCl in Benzene. Dry gaseous HCl was bubbled through a solution of **5** (0.300 g) in anhydrous benzene (30 ml) to saturation. After 1 hr at room temperature the solution was washed with water, saturated aqueous $NaHCO_3$, and water, dried, and evaporated to give a residue (0.315 g) consisting of ketone **3** and chlorohydrin **6** in a ratio of 36:64 (nmr). The crude reaction mixture was subjected to preparative tlc. Extraction of the two bands (the faster moving band contains the ketone **3**) yielded **3** (0.040 g) and **3,3-dimethyl-*c*-2-chloro-2-(*p*-methoxyphenyl)-*r*-cyclohexanol (6)** (0.180 g) which on crystallization from petroleum ether gave pure **6** (0.140 g), mp 78–80°. *Anal.* Calcd for $C_{15}H_{21}ClO_2$: C, 67.03; H, 7.88. Found: C, 67.02; H, 7.81.

Treatment of Chlorohydrin 6 with Aqueous Potassium Hydroxyde. A solution of **6** (0.020 g) in 2-propanol (6 ml) was treated with KOH (0.120 g), then refluxed for 25 min, diluted with water, and extracted with ether. Evaporation of the washed (water) and dried extracts yielded a solid residue (0.015 g) which on crystallization from petroleum ether gave pure **3** (0.010 g).

3,3-Dimethyl-2-chloro-2-(*p*-methoxyphenyl)cyclohexanone (8). A solution of **6** (0.120 g, 0.45 mmol) in anhydrous benzene (10 ml) was treated with 8 *N* chromic acid in aqueous sulfuric acid[4] (0.22 ml), stirred at room temperature for 4 hr, and then washed (water) and evaporated to give a residue (0.110 g) which on crystallization from petroleum ether at −5° yielded **8** (0.060 g): mp 58–60°; ir λ_{CO} 5.82 μ; nmr δ 0.82 and 0.89 ppm (3 H each, s, CH_3). *Anal.* Calcd for $C_{15}H_{19}ClO_2$: C, 67.53; H, 7.18. Found: C, 67.34; H, 7.23.

3,3-Dimethyl-2-hydroxy-2-(*p*-methoxyphenyl)cyclohexanone (7). A solution of **11** (0.040 g, 0.16 mmol) in acetone (4 ml) was treated with 8 *N* chromic acid in aqueous sulfuric acid[4] (0.1 ml), left 1 min at room temperature, diluted with water, and extracted with ether. Evaporation of the washed (10% aqueous Na_2CO_3, water) ether yielded a residue which on crystallization from petroleum ether yielded pure **7** (0.030 g): mp 132–136°; ir λ_{OH} 2.91, λ_{CO} 5.89 μ; nmr δ 4.15 (1 H, OH), 0.86 and 0.77 ppm (3 H each, s, CH_3). *Anal.* Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.73; H, 7.98.

Similar oxidation of **10** (0.040 g) yielded **7** (0.020 g).

Treatment of Chlorohydrin 6 with Jones Reagent. A solution of **6** (0.130 g, 0.49 mmol) in acetone (13 ml) was treated with 8 *N* chromic acid in aqueous sulfuric acid[4] (0.13 ml), left 4 min at room temperature, diluted with water, and extracted with ether. Evaporation of the washed (saturated aqueous $NaHCO_3$ and water) and dried extracts yielded a residue (0.120 g) consisting of an almost equimolar mixture of **7** and **8** (tlc). When the reaction time was longer (60 min), practically pure **7** was obtained.

Chlorohydrin **6** (0.015 g, 0.06 mmol) was recovered almost unchanged by treatment of its solution in acetone (1.5 ml) with 8 *N* aqueous sulfuric acid (0.06 ml) for 20 min; just traces of diols **10** and **11** were revealed (tlc).

When a solution of chloro ketone **8** (0.010 g, 0.04 mmol) in acetone (1 ml) was treated with 8 *N* chromic acid in aqueous sulfuric acid[4] (0.1 ml) for 1 min, an almost equimolar mixture of **7** and **8** was recovered.

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