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CONJUGATIVE AND INDUCTIVE EFFECTS IN THE RING OPENING OF 1-ARYL SUBSTITUTED OXIRANES. SOME REACTIONS OF 1-(*p*-METHOXYPHENYL)- AND 1-(*m*-METHOXYPHENYL)-1,2-EPOXYCYCLOHEXANES UNDER ACIDIC CONDITIONS

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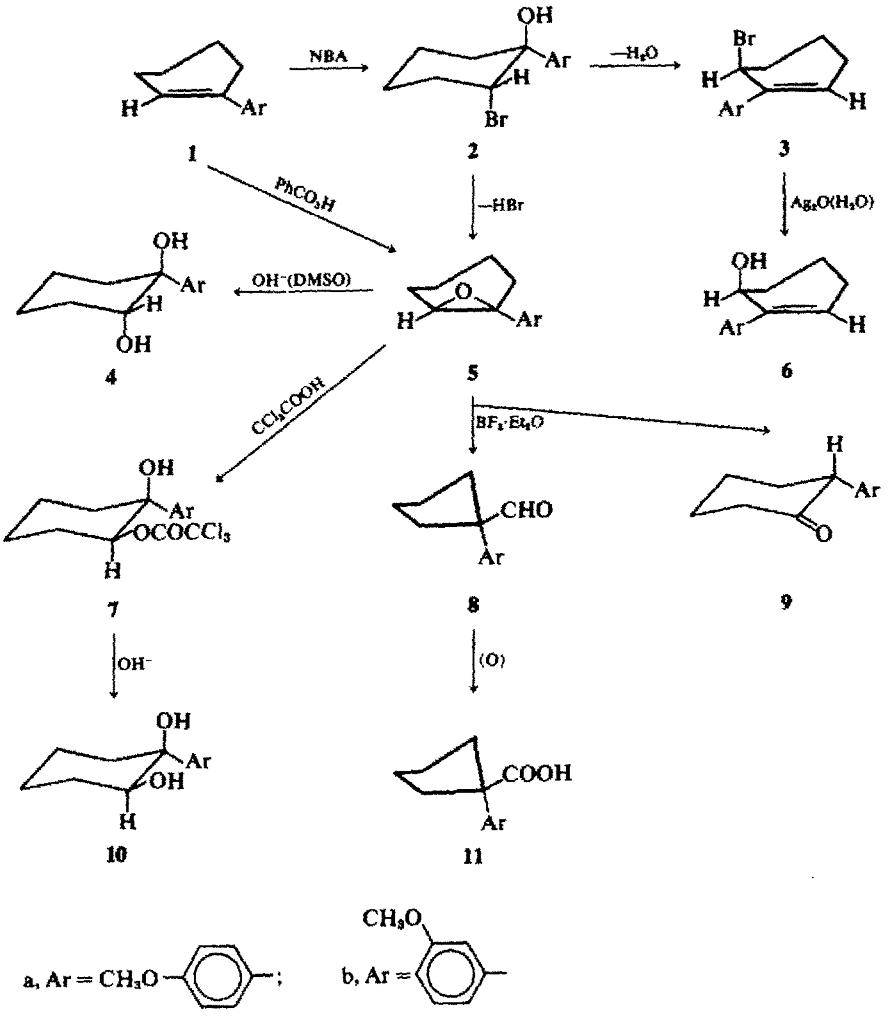
Abstract—The reactions of 1-(*p*-methoxyphenyl)- and 1-(*m*-methoxyphenyl)-1,2-epoxycyclohexanes with trichloroacetic acid in benzene and with dilute sulphuric acid have been studied and compared with those of the parent compound, 1-phenyl-1,2-epoxycyclohexane. Both the steric course of the ring opening and the amounts of rearrangement products are strictly related to the effect of the substituent in the phenyl moiety, confirming that the tendency of aryloxiranes to undergo *syn* addition is linked with the amount of charge developed at the intermediate benzylic cationic centre.

In earlier publications, the stereochemistry of the ring opening of 1-aryl substituted oxiranes under acidic conditions was shown to depend to a large extent on the structure of the epoxides and on the conditions under which the reactions are carried out; structures representing from complete retention to complete inversion of configuration can be obtained.[1-10]

In particular, it was shown that a strongly electron-withdrawing substituent (nitro group) in the para position of the phenyl ring[7] causes a net decrease in the syn stereoselectivity of the oxirane ring opening with respect to the unsubstituted epoxide.[1,3] It was suggested[7,10] that the tendency of aryl substituted epoxides towards *cis* opening is strictly related to the capability of the unsaturated system to stabilize the charge in the benzylic carbocation deriving from the protonated epoxide: the syn addition products can arise from the collapse of a tight ion pair formed by the anion of the acid and the benzylic carbocation.[1,2,4,5,7,9,10] In order to get more information on the influence of the substituent on the phenyl group in determining the steric course of the ring opening of these epoxides, it was thought of interest to prepare and study 1-(*p*-methoxyphenyl)- and 1-(*m*-methoxyphenyl)-1,2-epoxycyclohexane (**5a** and **5b**).[11] The same methoxy substituent in different positions on the phenyl ring in **5a** and **5b** should have different and opposite effects on the stereoselectivity of the ring opening of these epoxides in acidic media.[12,13] Furthermore it was thought desirable not only to compare the *syn*/*anti* product ratio, but also to evaluate the amount of rearrangement products in relation to the substituent on the phenyl ring and to the reaction conditions.

Epoxides **5a** and **5b** and pure reference compounds have been prepared in the following manner. The olefins **1a** and **1b** were converted by treatment with N-bromoacetamide in aqueous dioxane into the bromohydrins **2a** and **2b**, respectively. Alkaline dehydrohalogenation of **2a** and **2b** afforded epoxides **5a** and **5b**. Epoxide **5b** was also obtained by direct oxidation of olefin **1b** with peroxybenzoic acid. Dehydration of **2a** and **2b** led to the unsaturated bromides **3a** and **3b** (**3b** was not isolated), which on treatment with Ag_2O in aqueous dioxane gave the unsaturated alcohols **6a** and **6b**. The reaction of epoxides **5a** and **5b** with trichloroacetic acid in benzene gave the *cis* trichloroacetates **7a** and **7b** which on saponification yielded the known *cis* diols **10a** and **10b**;[14] furthermore **10a** was reconverted into **7a** by reaction with trichloroacetyl chloride. On the other hand treatment of **5a** and **5b** with KOH in aqueous DMSO[4] afforded the *trans* diols **4a** and **4b**. Reaction of epoxide **5a** with boron trifluoride-ether complex gave a mixture of aldehyde **8a** and ketone **9a** in a ratio of 26:74, while under the same conditions **5b** yielded **8b**, **9b** and **6b** in a ratio of 86:12:2; from the reaction mixtures it was possible to isolate aldehydes **8** and ketones **9** by preparative TLC on silica gel.[15] On oxidation with Jones reagent the aldehydes **8** afforded the corresponding acids **11a** and **11b**.

Some of the *p*-methoxy derivatives, namely **5a** and **2a**, are particularly unstable. Thus small amounts of water present in the solvent during the crystallization of epoxide **5a** were sufficient to convert it into the *cis* diol **10a**; **10a** was also obtained from **5a** on leaving for one day at room temp; moreover epoxide **5a** could not be chromatographed without extensive decomposition. Also bromohydrin **2a** is labile and spontaneously decom-



SCHEME 1

posed into **3a** after a few days at room temp. On the other hand, the *m*-methoxy derivatives **5b** and **2b** are stable under the same conditions. The lower stability of the *p*-methoxy derivatives must be strictly related to the strong electrodonating properties of the methoxy group in *para* position,[12,13] which facilitates reactions with cationoid intermediates.

Table 1 reports the product compositions of the reactions of the epoxides **5** with dilute aqueous sulphuric acid and of the crude reaction mixture resulting from mild hydrolysis (trace of K_2CO_3 in a mixture of benzene, MeOH and H_2O at room temp) of the reaction products of the same epoxides with trichloroacetic acid in benzene. It is remarkable that solutions of ketones **9a** and **9b** in tetrahydrofurane when treated with an ethanolic solution of potassium hydroxide at room temp were completely oxidized within a few hours to the corresponding δ-aroylvaleric acid.

The structures of compounds **3a**, **6a** and **6b** were deduced from the presence in their NMR spectra

Table 1. Products of trichloroacetolysis and hydrolysis of **5a** and **5b**

Epoxide	Solvent	Acid	10	4	6	8	9
5a	benzene	CCl_3COOH	68	—	5	<0·2	27%
5b	benzene	CCl_3COOH	95·5	—	1	2·5	1%
5a	H_2O	H_2SO_4	93	3·8	0·4	0·5	2·3%
5b	H_2O	H_2SO_4	56	44	—	—	<0·4%

of two one-proton signals that can be assigned to one olefinic proton and one proton in α to the bromine (**3a**) or to the hydroxyl group (**6a** and **6b**); in addition, the small half-band widths of the latter protons suggest a preference for conformations with pseudoaxial substituents.

The structures, configurations and conformations of compounds **2**, **4**, **7** and **10** were confirmed from their NMR and IR spectra (Table 2). The half-band widths of the methinic proton are consistent with equatorial hydrogens in compounds **2** and **4**, and with axial ones in **7** and **10**.[4,7,9,16] On the other hand the OH stretching frequencies of compounds **7** and **10** in dilute CCl_4 are in accordance with the formation of OH · · · O bonds,[14,17,18] whereas in the spectra of compounds **2** and **4** lack strong interactions of type OH · · · Br and OH · · · O respectively.[17,18]

The data in Table 1 reveal a marked difference in the course of the reactions of the *p*-methoxy (**5a**) and *m*-methoxyphenyl epoxide (**5b**) both in stereoselectivity and in the amount of rearrangement products. The hydrolysis of these epoxides in aqueous sulphuric acid gives a much higher *syn*-*anti* product ratio (96:4) for epoxide **5a** and a slightly lower one (56:44) for **5b** in comparison with the unsubstituted parent compound, 1-phenyl-1,2-epoxycyclohexane (60:40).[10] In the case of the *p*-nitro derivative the same reaction gave a *syn*-*anti* product ratio of 6:94.[7] Evidently the electron-withdrawing inductive effect of the *m*-methoxy group slightly reduces the tendency of epoxide **5b** towards *syn* addition. On the contrary the powerful resonance contribution of the *p*-methoxy group predominates over the opposite inductive effect and strongly increases the *syn*-*anti* product ratio. This is at least in qualitative agreement with the Hammett σ values relative to the substituents. It must be stressed that the percentages of *syn* opening obtained in the hydrolysis of these 1-arylsubstituted epoxycyclohexanes agree with the rates of solvolysis of the corresponding 1-aryldimethylcarbinyl chloride,[13,19] a clean S_N1-type reaction, and consequently the order of stability of the intermediate benzylic carbocations. The result clearly confirms that the tendency of aryloxiranes for *syn* addition is strictly linked with the quantity of charge developed on the cationic centre or, in other words, with the amount of breaking of the benzylic C—O bond before the attack of the nucleophile:[7,10] the extensive rupture of the C—O bond must favour the formation of tight ion pairs and *syn* attack by the nucleophile.

The complete *syn* stereoselectivity in the trichloroacetolysis of **5a** and **5b** in benzene is in accordance with our previous observations in the ring opening of aryloxiranes with acid in low polarity aprotic solvents.[1–10,20] Evidently, the low inductive effect of the *m*-methoxy group is not sufficient to affect the *syn* stereoselectivity in the reaction of **5b** under these conditions.

As far as the amount of rearrangement products (**6**, **8**, **9**) is concerned they are more abundant with the *para* than with the *meta* methoxy derivative in accordance with that expected for a transition state with a high carbocation character.[10,21–23] The lower percentage of rearrangement products in the more polar solvent (H_2O) can be ascribed to the much larger availability of nucleophilic molecules (H_2O) that can capture the carbonium ion as soon as it is formed, thus competing efficiently with the rearrangement reactions.

EXPERIMENTAL

M.ps 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 solns was

Table 2. Chemical shifts and half-band widths of the methinyl proton and wave numbers of OH protons of compounds 2, 4, 7, 10

	NMR (δ, ppm)		IR (cm^{-1})		
Compound	CHX	$W_{1/2}$ Hz	OH Free	OH · · · π	OH · · · X
2a	$4·47^a$	8·3		3609^e	$3571^{a,g}$
2b	$4·40^a$	8·5		3609^e	$3572^{a,g}$
4a	$3·71^b$	8^d		$3609^{e,f}$	
4b	$3·73^b$	8^d		$3607^{e,f}$	
7a	$5·37^c$	16·5			3595^c
7b	$5·39^c$	16·7			3595^c
10a	$3·82^b$	18^d	3618^g $(3616)^{14}$	3586^f $(3582)^{14}$	3561^b $(3560)^{14}$
10b	$3·87^b$	19^d	3622^g $(3619)^{14}$	3590^f $(3587)^{14}$	3561^b $(3553)^{14}$

[a] X = Br; [b] X = OH; [c] X = $OCOCCl_3$; [d] Approximate values due to the partial overlapping of the signal with that one of the methoxy group; [e] Interaction between the hydroxyl and the aryl bonded on the same carbon atom; [f] Interaction between the hydroxyl and the aryl bonded on vicinal carbon atoms; [g] Weak band.

$5 \cdot 10^{-3}$ M or lower to prevent intramolecular association. NMR spectra were determined an *ca.* 10% $CDCl_3$ solns 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% neopentylglycol succinate on 80–100 mesh silanized Chromosorb W (columns 175°, evaporator 210°, detectors 210°, nitrogen flow 45 ml/min). Retention times: **8a**, 3 min; **9a**, 7 min; **6a**, 8 min; **10a**, 17 min; **4a**, 23 min; **8b**, 2 min; **9b**, 6 min; **6b**, 7 min; **10b**, 14 min; **4b**, 19 min. Preparative TLC were performed on 2 mm layer silica gel plates (Merck F_{254}) containing a fluorescent indicator; spots were detected under UV light (245 nm). All comparisons between compounds were made on the basis of IR and NMR spectra and GLPC. $MgSO_4$ was used as drying agent. Evaporations were *in vacuo* (rotory evaporator). Light petroleum refers to the fraction boiling at 40–70°; benzene was washed with concentrated sulphuric acid, refluxed over sodium and rectified.

1-(p-*Methoxyphenyl*)*cyclohexene* (**1a**)-1-(*p*-Methoxyphenyl)cyclohexanol,[24] m.p. 36–37° (75·0 g, 0·372 mole) was added to 60 ml of a freshly prepared soln of sulphuric acid and acetic acid (2:8 v/v). The mixture was shaken for 30 sec and then poured in a separatory funnel containing ether (300 ml) and water (400 ml). The ether layer was washed with water, 10% Na_2CO_3 aq and water, dried and evaporated to give an oil (65 g) which was distilled to yield pure **1a** (43 g), b.p. 126–128°/0·5 mm (lit.[14] b.p. 114–118°/0·3 mm).

trans-2-*Bromo*-1-(p-*methoxyphenyl*)*cyclohexanol* (**2a**)–A soln of **1a** (4·63 g, 24·7 mmol) in 70% aqueous dioxane (v/v) (120 ml) was added to a soln of NBA (3·65 g, 26·5 mmole) in 50% aqueous dioxane (v/v) (50 ml), warmed on a steam bath for 1–2 min, cooled immediately, poured over ice and extracted with ether. The washed (H_2O) and dried extracts gave, after evaporation, a solid residue (5·8 g) which was crystallized from light petroleum to yield **2a** (4·2 g), m.p. 80–81°. (Found: C, 54·97; H, 6·09; Br, 27·95. $C_{13}H_{17}BrO_2$ requires: C, 54·75; H, 6·01; Br, 28·02%).

6-*Bromo*-1-(p-*methoxyphenyl*)*cyclohexene*(**3a**)–(a) **2a** (1·45 g) was heated under vacuum (5 mm) at 65° for 1 h to give **3a** (1·33 g) which after crystallization from light petroleum (b.p. 60–80°) had m.p. 93–94°; NMR δ 6·10 (m, 1, C$\underline{H}$=), 5·28 ppm (m, 1, $w_{1/2}$ 6·0 Hz, C$\underline{H}$Br). (Found: C, 58·63; H, 5·80; Br, 29·80. $C_{13}H_{15}BrO$ requires: C, 58·44; H, 5·66; Br, 29·91%). (b) **2a** (2·95 g) was kept 30 days at room temp to yield **3a** (2·70 g).

2-(p-*Metkoxyphenyl*)-2-*cyclohexen*-1-*ol*(**6a**)–(a) A soln of **3a** (2·2 g) in dioxane (100 ml) was treated with $CaCO_3$ (5·0 g), then with enough water to cause incipient turbidity and refluxed for 30 min. After dilution with water the reaction mixture was extracted with ether. Evaporation of the washed (H_2O) and dried ether extracts gave a solid residue (1·60 g) which was crystallized from light petroleum to yield **6a** (1·32 g), m.p. 70–71°, λ_{OH} 3·05 μ; NMR δ 6·08 (m, 1, C$\underline{H}$=), 4·63 ppm (m, 1, $w_{1/2}$ 7·8 Hz, C$\underline{H}$OH). (Found: C, 76·34; H, 7·73. $C_{13}H_{16}O_2$ requires: C, 76·44; H, 7·90%). (b) A stirred soln of **3a** (0·190 g) in dioxane (10 ml) and water (13 ml) was treated with Ag_2O (freshly prepared from 0·200 g $AgNO_3$) for 15 min, diluted with water and extracted with ether. Evaporation of the washed (H_2O) and dried extracts yielded **6a** (0·135 g).

1-(p-*Methoxyphenyl*)-1,2-*epoxycyclohexane* (**5a**)–A stirred soln of **2a** (2·80 g, 9·8 mmole) in anhydrous benzene (120 ml) was treated portionwise during one hour with potassium t-butoxide (2·20 g, 19·6 mmole), left 1 h at room temp, treated again portionwise with potassium t-butoxide (2·20 g) and stirred during 3 h at room temp. Evaporation of the washed (H_2O) benzene yielded a solid residue (m.p. 44–45°) consisting of **5a** (1·68 g) which was recrystallized from dry light petroleum at −10°, m.p. 44–45°, NMR δ 3·08 ppm (m, 1, $w_{1/2}$ 5·3 Hz, C$\underline{H}$O). (Found: C, 76·55; H, 7·71. $C_{13}H_{16}O_2$ requires: C, 76·44, H, 7·90%).

Epoxide **5a** is extremely unstable. Small amounts of water in the solvent during its recrystallization are sufficient to convert it into the *cis* diol **10a**. Analogously **10a** was obtained from **5a** when left for one day at room temp. Purification of **5a** by chromatography on neutral Al_2O_3 (act. II) was not possible owing to extensive rearrangement to carbonyl products.

1-(p-*Methoxyphenyl*)-cis-2-*trichloroacetoxycyclohexanol*(**7a**)–(a) A soln of **5a** (0·30 g, 1·47 mmole) in anhydrous benzene (30 ml) was treated with a 1·1 M soln of trichloroacetic acid (1·5 ml, 1·65 mmole) in an hydrous benzene, stored overnight at room temp, then washed with sat $NaHCO_3$, then with water, and evaporated to yield a solid residue (0·43 g) which consisted mostly of **7a** (IR and NMR) and of small quantity of carbonyl products (λ_{CO} 5·88 μ). (b) A soln of **10a** (0·50 g, 2·25 mmole) in anhydrous benzene (25 ml) and pyridine (0·36 g, 4·5 mmole) was treated with trichloroacetyl chloride (0·490 g, 2·7 mmole). After 15 min at room temp the soln was washed with dil HCl, 10% Na_2CO_3 aq, H_2O, dried and evaporated to give **7a** (0·79 g) which crystallized from light petroleum, m.p. 95–96·5°, λ_{CO} 5·73 μ. (Found: C, 48·87; H, 4·51; Cl, 28·67. $C_{15}H_{17}Cl_3O_4$ requires: C, 49·00; H, 4·66; Cl, 28·93%).

1-(p-*Methoxyphenyl*)-cis-*cyclohexane*-1,2-*diol* (**10a**)–A soln of crude **7a** (0·300 g), obtained from **5a** and trichloroacetic acid, in ethanol (30 ml) was treated with 2N KOH in ethanol (0·55 ml), refluxed 20 min, diluted with water and extracted with ether. Evaporation of the washed (H_2O) and dried soln gave a solid residue which on crystallization from light petroleum (b.p. 60–80°) yielded **10a** (0·095 g), m.p. 104–105° (lit.[14] m.p. 106–107°).

1-(p-*Methoxyphenyl*)-trans-*cyclohexane*-1,2-*diol*(**4a**)–A soln of **5a** (0·400 g) in DMSO (32 ml) and 2N KOH aq (6·5 ml) was treated 24 h at 100°, then diluted with water and extracted with ether. Evaporation of the washed (H_2O) and dried ether extracts gave a solid residue (0·38 g) which crystallized from light petroleum (b.p. 60–80°) to yield **4a** (0·23 g), m.p. 92–93°. (Found: C, 70·45; H, 8·10. $C_{13}H_{18}O_3$ requires: C, 70·24; H, 8·16%).

2-(p-*Methoxyphenyl*)*cyclohexanone* (**9a**) *and* 1-(p-*Methoxyphenyl*)-1-*formyl*-*cyclopentane* (**8a**)–A soln of **5a** (0·500 g) in anhydrous benzene (40 ml) was treated with boron trifluoride etherate (0·34 ml), left 2 min at room temp, washed with sat $NaHCO_3$, water and evaporated to give a residue (0·460 g) consisting of a mixture of **9a** and **8a** in a ratio of 74:26 (GLPC). The crude mixture was subjected to preparative TLC, a 9/1 mixture of light petroleum and ether being used as the eluent; elution was repeated once. Extraction of the two bands (the faster moving band contains aldehyde **8a**) with ether yielded **9a** (0·260 g) and **8a** (0·080 g). **9a**, m.p. 88–89° (from hexane), λ_{CO} 5·88 μ (lit.[25] m.p. 89–89·2°). **8a**, n_D^{25} 1·5473, λ_{CO} 5·81 μ. (Found: C, 75·73; H, 7·82. $C_{13}H_{16}O_2$ requires: C, 76·44; H, 7·90%); 2,4-dinitrophenylhydrazone, m.p. 140–141° (from ethanol). (Found: C, 59·10; H, 5·39; N, 14·51. $C_{19}H_{20}O_5N_4$ requires: C, 59·37; H, 5·24; N, 14·58%).

1-(p-*Methoxyphenyl*)*cyclopentanecarboxylic acid* (**11a**).

A soln of **8a** (0·050 g) in acetone (3 ml) was treated with Jones reagent[26] (0·08 ml). After 2 min, dilution with water and extraction with ether, followed by extraction of the organic layer with sat $NaHCO_3$, acidification, extraction with ether, evaporation of the dried extracts, and crystallization from hexane of the residue gave **11a** (0·027 g) m.p. 155–157°. (Found: C, 70·60; H, 7·45. $C_{13}H_{16}O_3$ requires: C, 70·89; H, 7·32%).

Treatment of **9a** *with ethanolic KOH in THF*–A soln of **9a** (0·020 g) in THF was added with 1M KOH in EtOH (2 ml), left 5 h at room temp, diluted with water and extracted with ether. Evaporation of the dried ether extracts did not yield any appreciable residue. Acidification of the aqueous layer, extraction with ether and evaporation of the washed (H_2O) and dried extracts gave δ-(*p*-methoxybenzoyl)valeric acid (0·018 g) which on crystallization from benzene-light petroleum (b.p. 60–80°) had m.p. 127–129°, λ_{CO} 5·86, 5·97 μ (lit.[27] m.p. 129°).

1-(m-*Methoxyphenyl*)*cyclohexene* (**1b**)–1-(*m*-Methoxyphenyl)cyclohexanol,[28] b.p. 100–102°/1·2 mm, n_D^{20} 1·5631 (25·0 g) was dehydrated as described for the preparation of **1a**, yielding **1b** (13·9 g), b.p. 129–130°/2 mm, n_D^{20} 1·5636 (lit.[28] 108–110°/0·5 mm, n_D^{19} 1·5680).

trans-2-*Bromo*-1-(m-*methoxyphenyl*)*cyclohexanol* (**2b**)–Treatment of **1b** (5·0 g) with NBA in aqueous dioxane, as described before for the preparation of **2a**, gave a residue which on crystallization from light petroleum yielded **2b** (4·1 g), m.p. 86–87°. (Found: C, 54·55; H, 5·82; Br, 28·22. $C_{13}H_{17}BrO_2$ requires: C, 54·75; H, 6·01; Br, 28·02%). Compound **2b** is stable and it was recovered unchanged under the conditions in which **2a** decomposes to **3a**.

2-(m-*Methoxyphenyl*)-2-*cyclohexen*-1-*ol* (**6b**)–A soln of **2b** (0·210 g) in acetic acid (8 ml) was treated with 96% H_2SO_4 (2 ml), stirred for 30 sec, diluted with water and extracted with ether. Evaporation of the washed (H_2O, 10% Na_2CO_3, H_2O) and dried ether extracts yielded a crude oily residue of **3b** (0·170 g). This residue was dissolved in dioxane (10 ml) and water (13 ml), treated with Ag_2O (freshly prepared from 0·300 g $AgNO_3$) for 15 min, diluted with water and extracted with ether. The extracts were washed with water, dried, and evaporated, to yield a residue which was chromatographed through a 1·5 × 25 cm column of neutral Al_2O_3 (act. II) eluting in succession with benzene (160 ml) and 95/5 benzene-ether (540 ml). Elution with 95/5 benzene-ether gave **6b** (0·110 g) which crystallized from light petroleum, m.p. 65–66°, λ_{OH} 3·18 μ; NMR δ 6·17 (m, 1, CH=), 4·68 ppm (m, 1, $w_{1/2}$ 8·2 Hz, $C\underline{H}OH$). (Found: C, 76·30; H, 7·87. $C_{13}H_{16}O_2$ requires: C, 76·44; H, 7·90%).

1-(m-*Methoxyphenyl*)-1,2-*epoxycyclohexane* (**5b**)–(a) A soln of **2b** (3·2 g) in 60% aqueous dioxane (160 ml) was treated with a soln of KOH (5·0 g) in water (50 ml) and stirred at room temp for 20 min. Dilution with water, extraction with ether and evaporation of the washed (H_2O) and dried extracts gave a crude residue (2·2 g) consisting of **5b** which was chromatographed through a 1·5 × 25 cm column of neutral Al_2O_3 (act. II). Elution with light petroleum (180 ml) yielded pure **5b** (1·3 g), n_D^{20} 1·5473; NMR δ 2·90 ppm (m, 1, $w_{1/2}$ 5·2 Hz, $C\underline{H}O$). (Found: C, 76·26; H, 7·78. $C_{13}H_{16}O_2$ requires: C, 76·44; H, 7·90%). (b) A soln of **1a** (0·50 g, 2·65 mmole) in $CHCl_3$ (10 ml) was treated under stirring with a 0·245 M soln of peroxybenzoic acid[29] in $CHCl_3$ (12·0 ml, 2·95 mmole), while keeping the temp below −7°. After 75 h at 0°, the soln was washed with 10% Na_2CO_3 a, water, dried and evaporated to give an oily residue which was chromatographed as described above under (a) yielded **5b** (0·24 g).

1-(m-*Methoxyphenyl*)-cis-2-*trichloroacetoxycyclohexanol* (**7b**). Treatment of **5b** (0·66 g) with trichloroacetic acid in benzene as described for the analogous reaction of **5a** yielded **7b** (1·05 g) which crystallized from light petroleum; m.p. 85–86°, λ_{CO} 5·72 μ. (Found: C, 48·75; H, 4·57; Cl, 28·78. $C_{15}H_{17}Cl_3O_4$ requires: C, 49·00; H, 4·66; Cl, 28·93%).

1-(m-*Methoxyphenyl*)-cis-*cyclohexane*-1,2-*diol* (**10b**)-**7b** (0·50 g) was saponified as described above for the preparation of **10a** yielding **10b** (0·190 g), from light petroleum (b.p. 60–80°), m.p. 95–96° (lit.[14] m.p. 95–96°).

1-(m-*Methoxyphenyl*)-trans-*cyclohexane*-1,2-*diol* (**4b**). Alkaline hydrolysis in aqueous DMSO of **5b** (1·50 g), under the same conditions used above for the similar reaction of epoxide **5a**, gave a residue which on crystallization from light petroleum (b.p. 60–80°) yielded **4b** (0·70 g), m.p. 107–108°. (Found: C, 70·47; H, 8·12. $C_{13}H_{18}O_3$ requires: C, 70·24; H, 8·16%).

2-(m-*Methoxyphenyl*)*cyclohexanone* (**9b**) *and* 1-(m-*methoxyphenyl*)-1-*formyl-cyclopentane* (**8b**). A soln of **5b** (0·68 g) in anhydrous benzene was treated with boron trifluoride etherate under the conditions used for the reaction of **5a** yielding an oily product (0·502 g) consisting of a mixture of **9b**, **8b** and **6b** in a ratio of 12:86:2. The crude mixture was subjected to preparative TLC as described above. Extraction of the two main bands (the faster moving band contains **8b**) gave **9b** (0·040 g) and **8b** (0·280 g). **9b**, λ_{CO} 5·87 μ, 2,4-dinitrophenylhydrazone, m.p. 123–124° (from ethanol) (lit.[25] m.p. 124–125°). **8b** n_D^{25} 1·5405, λ_{CO} 5·81 μ. (Found: C, 76·45; H, 7·91. $C_{13}H_{16}O_2$ requires: C, 76·44; H, 7·90%); 2,4-dinitrophenylhydrazone, m.p. 129–130° (from ethanol). (Found: C, 59·51; H, 5·36. $C_{19}H_{20}O_5N_4$ requires: C, 59·37; H, 5·24%).

Treatment of **9b** *with ethanolic KOH in THF*–A soln of **9b** (0·020 g) in THF (5 ml) was added with 1M KOH in EtOH (2 ml), left 4 hr at room temp, diluted with water and extracted with ether. Evaporation of the dried ether extracts yielded starting **9b** (0·006 g). Acidification of the aqueous layer, extraction with ether and evaporation of the washed and dried extracts gave δ-(*m*-methoxybenzoyl)valeric acid (0·012 g) which on crystallization from benzene-light petroleum (b.p. 60–80°) had m.p. 93–95°, λ_{CO} 5·85, 5·92 μ (lit.[28] m.p. 97°).

1-(m-*Methoxyphenyl*) *cyclopentanecarboxylic acid* (**11b**)–**8b** (0·100 g) was oxidized under the conditions used above for **8a** to give crude **11b** (0·092 g), m.p. 133–134° from hexane. (Found: C, 70·90; H, 7·13. $C_{13}H_{16}O_3$ requires: C, 70·89; H, 7·32%).

Trichloroacetolysis of **5a** *and* **5b** *in anhydrous benzene*–A soln of the epoxide (0·050 g, 0·25 mmole) in anhydrous benzene (5 ml) was treated with a 1·1 M soln of trichloroacetic acid in anhydrous benzene (0·25 ml), stored overnight at room temp, then washed (sat $NaHCO_3$ and H_2O) and evaporated. The crude residue was dissolved in benzene (1·7 ml) added with 2·80 ml of a freshly prepared soln of K_2CO_3 (0·312 g) in H_2O (5 ml) and MeOH (80 ml), and left 18 h at room temp. Dilution with water and ice, acidification with 2N H_2SO_4, extraction with ether and evaporation of the washed (sat $NaHCO_3$, H_2O) extracts yielded a residue which was analyzed by GLPC (see Table 1). Ketones **9** and aldehydes **8** are stable and were found unchanged under these conditions of saponification. Reactions of **5a** and **5b** with trichloroacetic acid stopped at different reaction times (1/2, 3 and 19 h) gave after saponification the same product mixtures.

Hydrolysis of **5a** *and* **5b** *with sulphuric acid in water*—A suspension of the epoxide (0·050 g) in 0·2N H_2SO_4 aq (10 ml) was stirred 24 h at room temp and then extracted with ether. Evaporation of the washed (H_2O) and dried extracts yielded a residue which was analyzed by GLPC (see Table 1).

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