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THE BALANCE OF STERIC AND CONJUGATIVE EFFECTS IN THE OPENING OF ARYLSUBSTITUTED OXIRANES. STEREOCHEMISTRY OF THE RING OPENING OF 1-(1'-NAPHTHYL)-1,2-EPOXYCYCLOHEXANE

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Abstract—The steric course of the ring opening of 1-(1'-naphthyl)-1,2-epoxycyclohexane (3) has been investigated and compared with that of the similar reactions of 1-phenyl-1,2-epoxycyclohexane. Reaction of 3 with KOH in DMSO-H_2O gives small yield of *trans* diol 4. Reaction of 3 with CCl_3COOH and HCl in low polarity aprotic solvents takes place with complete retention of configuration. However reaction with H_2SO_4 in H_2O is not completely stereospecific and shows a greater tendency than the phenyl substituted epoxide towards *cis* opening. Explanations of the observed stereochemical results, particularly with respect to the ability of the 1-naphthyl group to stabilize the intermediate carbocation, are discussed.

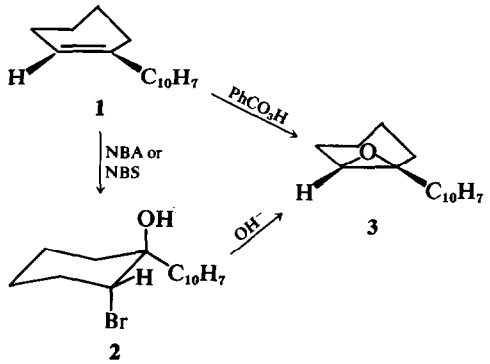
The *cis* stereochemistry that is often observed in the opening of aryl substituted oxiranes in acidic media can be interpreted[1] as a result of a reaction that implies the participation of an ion pair formed by the protonated epoxide and the anion of the acid. The stabilization of the incipient carbonium ion by the aryl group plays an important role in determining the steric course of the ring opening.

A study of the reactions of the 1-(1'-naphthyl)-1,2-epoxycyclohexane (3) was undertaken to establish if the steric interactions of the naphthyl *peri* hydrogen with the hydrogen atoms in the 2 and 6 positions of the cyclohexyl ring, which should prevent the coplanarity between the carbonium ion and the aromatic system,[2] could, in fact, modify substantially the steric results of the reactions in question.

Epoxide 3 was prepared both by direct oxidation of the olefin 1 with peroxybenzoic acid and by the dehydrohalogenation of the bromohydrin 2 which was obtained by treatment of 1 either with N-bromoacetamide (NBA) in aqueous dioxane or with N-bromosuccinimide (NBS) in moist DMSO.

The formation of 2 in the reaction of 1 with NBA and NBS is in agreement with the expectations based on the generally admitted mechanism for similar reactions[3,4] which implies the attachment of the Br^+ on the olefinic double bond to give a bromonium ion or a carbocation which later undergoes attack by the nucleophilic agent (water or DMSO[5]) on the α-benzylic carbon *trans* with respect to the halogen atom.

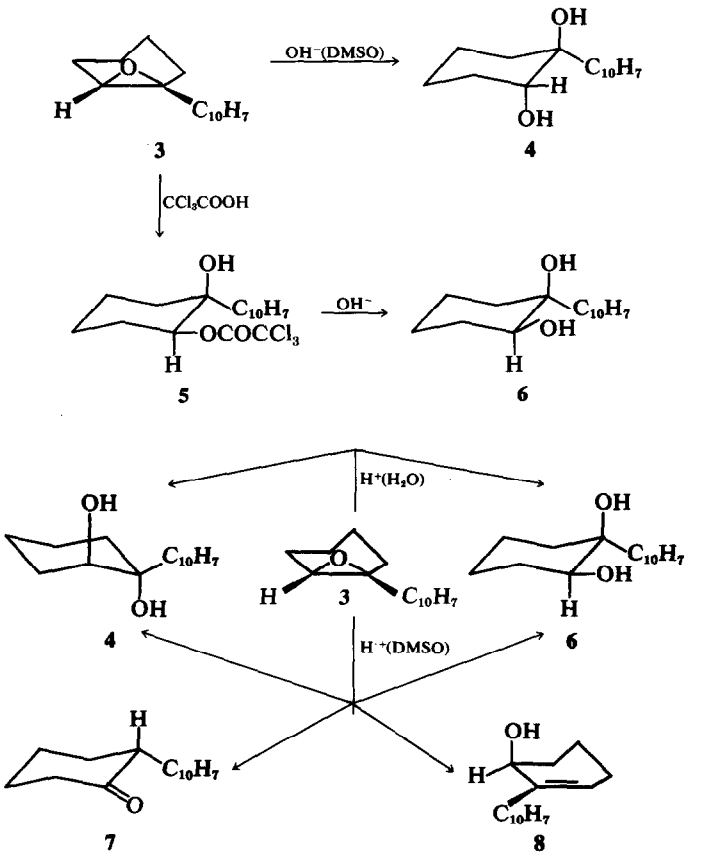
From the reaction of 3 with KOH in aqueous DMSO one obtains, even if in low yield, *trans* diol 4.



$C_{10}H_7$ = (1-naphthyl)

The reaction of 3 with trichloroacetic acid in benzene led only to the formation of the *cis* monoester 5, the secondary nature of which was demonstrated by its stability to oxidation with Jones reagent[6]; its *cis* configuration was indicated by its saponification to the *cis* diol 6.

Hydrolysis of 3 with dilute H_2SO_4 aq gave a mixture of glycols 4 and 6 in a ratio of 15:85. On the other hand reaction of 3 with H_2SO_4 in DMSO-water gave a mixture consisting of glycols 4 and 6 (ratio 75:25), 2-(1'-naphthyl)cyclohexanone (7) and 2-(1'-naphthyl)-2-cyclohexen-1-ol (8), which can be separated into its components *via* chromatography on Al_2O_3. When the reaction is conducted in anhydrous DMSO, the only products obtained are ketone 7 and the unsaturated alcohol 8 in a ratio of about 80:20. The structure of 8 is substantiated by the presence in its NMR spectrum of two one-proton signals that can be attributed to one olefinic

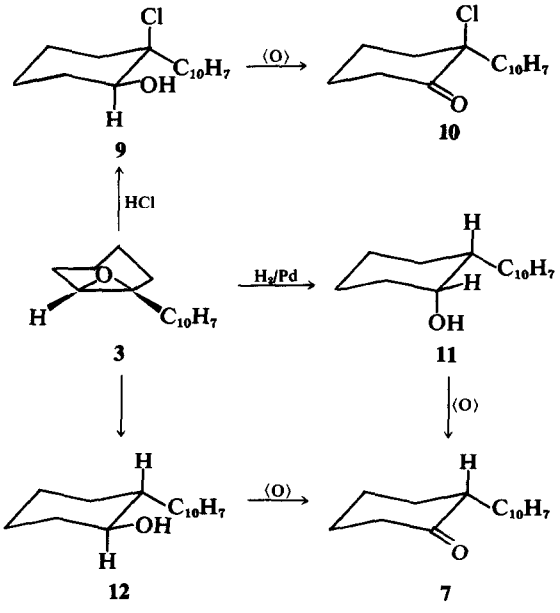


proton and one proton in α to the hydroxyl group.

Reaction of 3 with HCl in $CHCl_3$ produced, with complete retention of configuration, *cis* chlorohydrin 9, the oxidation of which gave chloroketone 10. Catalytic reduction ($Pd/CaCO_3$) of 3 gave a compound, the *cis* alcohol 11, which is different from the *trans* alcohol 12 obtained in the reaction of 1,2-epoxycyclohexane with 1-naphthyl-lithium;[7] oxidation of 11 and 12 gave the same ketone 7.

The difficulty in the opening of the epoxide 3 with KOH in aqueous DMSO is easily explained on the basis of the fact that this is an S_N2-type reaction and is therefore sensitive to steric effects.[1a,8,9] From an examination of molecular models of the two possible half-chair conformations of 3 it can be observed that in the ground state of the molecule the naphthyl group, because of the interaction of the *peri* hydrogen with the cyclohexyl hydrogens in C_2 and C_6 is forced into a conformation in which the naphthyl partially blocks the attack of the nucleophile *trans* to the oxirane ring both at the α and at the β-carbon.

The complete *cis* stereospecificity that one observes in the reaction of 3 with acids in low polarity non-protic solvents indicates that the naphthyl group has the same type of effects as the phenyl group.[1a,1c,10] These results can be explained through



a mechanism analogous to the one admitted earlier for arylderivatives.[1]

On the other hand the results of the hydrolysis of

3 in the presence of H_2SO_4 [*cis* (6) and *trans* glycol (4) in a ratio of 85:15] when compared to those relative to 1-phenyl-1,2-epoxycyclohexane[11] (*cis* and *trans* glycol in a ratio of 60:40) show that the 1-naphthyl substituent has an even greater tendency than the phenyl in promoting *cis* opening because of its greater electron-donating properties. Evidently, the steric effects of the 1-naphthyl group do not produce a deviation from coplanarity in the carbonium ion which is sufficient to affect the *cis*-*trans* ratio.[12,13]

These results are in agreement with the fact that the rate of hydrolysis is higher for (1'-naphthyl)-dimethylcarbinylchloride than for phenyldimethylcarbinylchloride.[12] These latter reactions are, in fact, S_N1-type substitutions that are particularly sensitive to the effects of the stabilization of the intermediate carbocation by the aryl group.[12,14,15]

The high ratio of *trans* to *cis* glycol obtained in the reaction of epoxide 3 with H_2SO_4 in DMSO-water confirms that DMSO is an adequate solvent to promote the acid hydrolysis of aryl substituted epoxides with inversion of the configuration.[1a,8,11,16] The formation of ketone 7 and of the unsaturated alcohol 8, together with glycols 4 and 6, in this latter reaction and its steric course can be interpreted[11,16,17] by assuming that the reaction proceeds, at least in part, by way of the intermediate formation of salts 13 and 14, similar to those which have been demonstrated to be formed as intermediates in the analogous reactions of 1-phenylcyclohexene oxide and of other epoxides.[16] These salts can on one hand be hydrolyzed to the glycols 4 and 6 on the other give 7 and 8 *via* elimination. This interpretation is in agreement with the fact that when the reaction of 3 with H_2SO_4 is conducted in anhydrous DMSO ketone 7 and alcohol 8 are the only isolated products.[11,16,17] It may however be pointed out that the products could also arise from a simple carbonium ion intermediate.

The structures, the configurations and the conformations of compounds 2, 4, 6, 9, 11, 12 have been demonstrated by the examination of the signals of the protons in the 1 and 2 positions in respect to the naphthyl group in the NMR spectra (Table 1) and through the study of the OH stretching bands in the 3 μ range in dilute solution of CCl_4 (Table 2). In the NMR spectrum of 11 and 12 the signals for the above mentioned protons have half-band widths consistent with one axial and one equatorial, and with two axial hydrogens,[1a,1d,18] respectively. In the NMR spectra of 2, 4, 6, 9 the half-band widths of the signals for the methinic β proton are consistent with an equatorial position in 2 and 4 and an axial for 6 and 9. Under the logical assumption that the naphthyl group is in the equatorial position in all of these compounds this defines their configuration and conformation, which has also been confirmed by a study of the IR spectra in dilute solution of these compounds and of the alcohols 11, 12 and 15 listed in Table 2. The spectrum of bromohydrin 2 shows a strong band at 3606 cm^{-1} which can be attributed to the tertiary OH group that forms a OH----π bond with the naphthyl group,[19,20] as is revealed by the comparison of this band with that of alcohol 15. The absence of a strong band in the vicinity of 3560 cm^{-1} in 2, expected from the interaction of the hydroxyl group with the halogen,[19,20] indicates a preference for the *trans* diaxial relationship between these two groups. The weak band at 3569 cm^{-1} is likely due to the presence of small quantities of diequatorial or twist conformer. In the spectrum of the chlorohydrin 9 the band at 3570 cm^{-1} is attributable on the other hand to the interaction of the hydroxyl group with the *cis*-vicinal chlorine. On the basis of a comparison of the

Table 1. NMR data

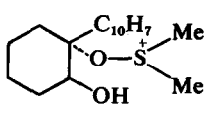
Compound	δ (ppm) H_1^a	δ (ppm) H_2^b	$W_{1/2}$(Hz) H_1^a	$W_{1/2}$(Hz) H_2^b
2	—	5·25	—	9
4	—	4·36	—	7
6	—	4·45	—	16
9	—	4·44	—	16
11	3·59	4·09	19	7
12	3·37	3·88	22	18

[a]Protons α to the naphthyl group.
[b]Protons β to the naphthyl group.

Table 2. Wave number of OH protons

Compound	$\nu_{OH\ free}$	$\nu_{OH\text{----}\pi}$	$\nu_{OH\text{----}OH}$	$\nu_{OH\text{----}X}$
2		3606[a]		3569[c]
4		3608[a,b]		
6	3618[c]	3591[b]	3561	
9				3578
11	3622[c]	3599[b]		
12		3600[b]		
15		3608[a]		

[a]Interaction between the hydroxyl and the naphthyl bonded on the same carbon atom.
[b]Interaction between the hydroxyl and the naphthyl bonded on vicinal carbon atoms.
[c]Weak band.



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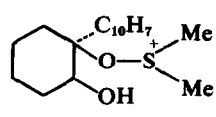

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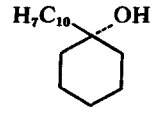

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spectra of the glycols **4** and **6** and of the alcohols **11**, **12** and **15** with those of the corresponding phenyl substituted compounds[20] the 3591 cm^{-1} band of **6** can be reasonably assigned to the interaction of the secondary OH group with the naphthyl and that at 3561 cm^{-1} to the interaction of the tertiary OH with the secondary hydroxylic *cis*-oxygen. The higher frequency weak band is attributable to a small percentage of free OH. The only band observed in the spectrum of **4** can be assigned to the unresolved stretching of the secondary and tertiary hydroxyl groups forming intramolecular hydrogen bonds with the naphthyl group.[20]

In the NMR spectra of those compounds that have an electro-negative substituent α to the naphthyl group (with the exception of **3**) the signal of one of the naphthyl protons is distinctly separated and shifted to lower field with respect to the multiplet corresponding to the other aromatic protons (Fig 1). This phenomenon must be attributed to the fact that the *peri* proton, due to its particular structural and conformational situation, can be subject to the deshielding effect of the lone pairs of the substituent in **1**.[21,22]

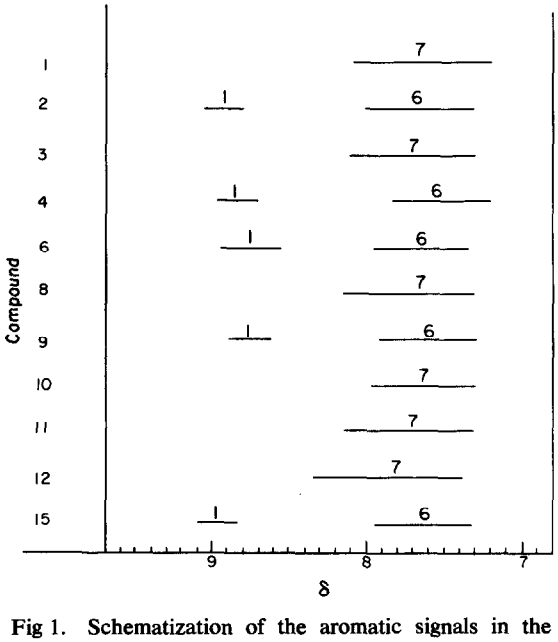

Fig 1. Schematization of the aromatic signals in the NMR spectra.

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 Model 137 and those for the determination of OH stretching bands with a Perkin-Elmer 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; the concentration of the solutions was 5.10^{-3} M or lower to prevent intramolecular association. NMR spectra were determined on *ca.* 10% $CDCl_3$ 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; temperatures: columns 200°, evaporator 245°, detectors 220°, nitrogen flow 40 ml/min. Retention times: **4**; 46 min; **6**; 35 min. All comparisons between compounds were made on the basis of their IR and NMR spectra and GLPC. $MgSO_4$ was used as drying agent. Pet 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 distilled; benzene was washed with conc H_2SO_4, refluxed over Na and distilled.

1-(1′-*Naphthyl*)*cyclohexanol* (**15**) was obtained as described before,[23] m.p. 50–52° (lit.[23] 66–68°).

1-(1′-*Naphthyl*)*cyclohexene* (**1**). **15** (20·0 g, 0·088 mole) was added to 50 ml of a freshly prepared soln of H_2SO_4 and AcOH (2:8 v/v). The mixture was shaken for 30 sec and added to ether (100 ml) and water (100 ml). The ether layer was washed with water, 10% Na_2CO_3 aq and water, dried and evaporated to give a solid residue which crystallized from EtOH to yield **1** (16·1 g), m.p. 47–48° (lit.[24] m.p. 46·5–47·5°).

trans-2-*Bromo*-1-(1′-*naphthyl*)-r-1-*cyclohexanol* (**2**). (a) A soln of **1** (0·500 g, 2·5 mmole) in 50% aqueous dioxane (v/v) (25 ml) was treated with a soln of NBA (0·379 g, 2·75 mmole) in 50% aqueous dioxane (v/v) (10 ml), warmed on a steam bath for 2–3 min, cooled immediately, poured over ice and ether extracted. Evaporation of the washed (H_2O) and dried extract gave a solid (0·350 g) which was crystallized from pet ether to yield **2** (0·200 g), m.p. 111–112°. (Found: C, 63·14; H, 5·73; Br, 25·98. $C_{16}H_{17}BrO$ requires: C, 62·96; H, 5·61; Br, 26·21%.)

(b) To a soln of **1** (0·750 g, 3·61 mmole) in DMSO (8 ml) and H_2O (0·15 ml, 8·3 mmole) cooled at 0° under an atmosphere of N_2 was added NBS (1·33 g, 7·5 mmole). The mixture was left 1 hr diluted with water and ether extracted. The organic phase was washed (H_2O), dried and evaporated. The solid residue was crystallized from pet ether to give pure **2** (0·600 g).

1-(1′-*Naphthyl*)-1,2-*epoxycyclohexane* (**3**). (a) A soln of **1** (4·0 g, 19·2 mmole) in $CHCl_3$ (20 ml) was treated under stirring with a 0·273 M soln (77·7 ml, 21·12 mmole) of peroxybenzoic acid[25] in $CHCl_3$, while keeping the temp below −3°. After 72 hr at 0°, the soln was washed with 10% Na_2CO_3aq, H_2O, dried and evaporated to give crude **3** (4·0 g). Crystallization from 2-propanol yielded pure **3** (3·4 g), m.p. 61–63° (lit.[26] m.p. 61–63°).

(b) A soln of **2** (0·200 g, 0·66 mmole) in 2-propanol was titrated with 1 N NaOHaq (phenolphthalein). The reaction was complete in 5 min with the theoretical consumption of base. The mixture was diluted with water and ether extracted. The washed (H_2O) and dried extracts gave after evaporation **3** (0·121 g).

1-(1′-*Naphthyl*)-cis-2-*trichloroacetoxy*-r-1-*cyclohexanol* (**5**). A soln of **3** (0·600 g, 2·64 mmole) in benzene (30 ml) was treated with a 1·1 M soln of trichloroacetic acid in benzene (2·61 ml, 2·87 mmole), for 12 hr, washed with sat. $NaHCO_3$aq, water and evaporated to give **5** (0·94 g). An analytical sample, prepared by crystallization from pet ether (b.p. 40–70°), had m.p. 129–130°, λ_{CO} 5·70 μ. (Found: C, 55·54; H, 4·36. $C_{18}H_{17}O_3Cl_3$ requires: C, 55·76; H, 4·42%.) The product was recovered unchanged after

treatment of its acetone soln with Jones reagent[6] for 15 min.

1-(1'-*Naphthyl*)-r-1,cis-2-*cyclohexanediol* (**6**). To a soln of **5** (0·450 g, 1·16 mmole) in THF (15 ml) was added a 1 M soln of KOH in EtOH (6 ml). After 5 hr the soln was diluted with water and ether extracted. Evaporation of the washed (H_2O) and dried ether extracts gave **6** (0·230 g), which after crystallization from pet ether (b.p. 60–80°) had m.p. 106–107°. (Found: C, 79·47; H, 7·55. $C_{16}H_{18}O_2$ requires: C, 79·31; H, 7·49%.)

1-(1'-*Naphthyl*)-r-1,trans-2-*cyclohexanediol* (**4**). A soln of **3** (0·300 g) in DMSO (8·5 ml) and 2 N KOHaq (1·5 ml) was heated 7 days at 100°, then diluted with water and extracted repeatedly with ether. The ether extracts were washed several times with water to eliminate the DMSO, dried and evaporated to give an oily residue (0·260 g) which was dissolved in benzene and chromatographed through a 1 × 20 cm column of neutral Al_2O_3 (act. II). Elution with benzene (200 ml) yielded unreacted **3** (0·200 g). Further elution with ether (200 ml) gave **4** (0·025 g) which crystallized from pet ether (b.p. 60–80°), m.p. 129–130°. (Found: C, 79·31; H, 7·57. $C_{16}H_{18}O_2$ requires: C, 79·31; H, 7·49.

If the mixture was left only 24 hr at 100° before work-up, compound **3** was recovered practically unchanged.

Reaction of **3** *with sulphuric acid in* DMSO-H_2O. A soln of **3** (0·600 g) in DMSO (3 ml) and water (10 ml) was cooled at 5°, treated with a 5° mixture of 2 N H_2SO_4aq (6 ml) and DMSO (18 ml), stirred 4 hr at room temp, diluted with water and ether extracted. The ether layer was washed with water to eliminate DMSO, dried and evaporated. The crude residue (0·570 g) was dissolved in benzene and chromatographed through a 1·5 × 35 cm column of neutral Al_2O_3 (act. II) eluting in succession with benzene (1200 ml) and 9/1 (1000 ml), 85/15 (850 ml), 8/2 (1200 ml), 75/25 (600 ml) benzene-ether. Elution with benzene gave pure **7** (0·100 g) and elution with 9/1 benzene-ether yielded 2-(1'-naphthyl)-2-cyclohexen-1-ol (**8**) (0·060 g) which crystallized from pet ether, m.p. 61–62°, λ_{OH} 3·0 μ; NMR: δ 5·87 (CH=), 4·51 ppm (CHOH). (Found: C, 85·50; H, 7·26. $C_{16}H_{16}O$ requires: C, 85·71; H, 7·14%.) Elution with 85/15 and 8/2 (560 ml) benzene-ether gave **4** (0·200 g) and then with 8/2 and 75/25 benzene-ether yielded **6** (0·060 g).

Reaction of **3** *with sulphuric acid in anhydrous* DMSO. A soln of **3** (0·500 g) in anhyd DMSO (25 ml) was cooled at 5° and treated with an equally cooled soln of 98% H_2SO_4 (0·27 ml) in anhyd DMSO (25 ml). The mixture was left 46 hr at room temp, diluted with satd $NaHCO_3$aq and ether extracted. Evaporation of the washed (H_2O) and dried organic extracts yielded a residue (0·480 g) which was chromatographed through a 1 × 35 cm column of neutral Al_2O_3 (act. II). Elution with benzene (350 ml) gave **7** (0·330 g). Further elution with 9/1 benzene-ether yielded **8** (0·090 g).

Reaction of **3** *with trichloroacetic acid in several solvents.* The reactions were carried out in anhydrous benzene, cyclohexane, CCl_4, $CHCl_3$, CH_2Cl_2 as follows. To a soln of **3** (0·100 g, 0·44 mmole) in the solvent (10 ml) was added trichloroacetic acid (0·52 mmole) using a *ca* 0·25 M soln of the acid in the same solvent. The mixture was allowed to stand for 24 hr washed with satd $NaHCO_3$aq, water, dried and evaporated to dryness. The crude residue was dissolved in THF (5 ml) treated with 1 M KOH in EtOH (2 ml) and left for 5 hr. Dilution with water, ether extraction and evaporation of the washed (H_2O) and dried ether layer gave a residue which was analyzed by GLPC and in all cases found to consist mostly of **6**; no trace of **4** was revealed.

Reaction of **3** *with sulphuric acid in water.* A suspension of **3** (0·100 g, 0·44 mmole) in water (9 ml) and 2 N H_2SO_4aq (1 ml) was stirred for 46 hr at room temp and then ether extracted. Evaporation of the washed (H_2O) and dried ether extract gave a solid residue consisting of 75% of **6** and **4** in a ratio of 85:15 and of 25% of the unreacted epoxide **3** (GLPC). Reactions carried out under the same conditions but stopping at different times showed different percentages of **3** but the same ratio of the glycols **6** and **4**.

trans-2-(1'-*Naphthyl*)-r-1-*cyclohexanol* (**12**). It was prepared by reaction of 1,2-epoxycyclohexane with 1-naphthyl-lithium according to the procedure of Cook,[7] m.p. 134–135° (lit.[7] 129–130°).

cis-2-(1'-*Naphthyl*)-r-1-*cyclohexanol* (**11**). A soln of **3** (0·700 g) in EtOH was shaken with H_2 in presence of 5% PdO_2 on $CaCO_3$ (0·400 g). When absorption stopped, the soln was filtered and evaporated to give a solid residue which after crystallization from 2-propanol yielded **11** (0·470 g), m.p. 112–113° (Found: C, 85·15; H, 8·05. $C_{16}H_{18}O$ requires: C, 84·95; H, 7·96%.)

2-(1'-*Naphthyl*)*cyclohexanone* (**7**). (a) A soln of **12** (0·226 g, 1·0 mmole) in acetone (5 ml) was treated dropwise with Jones reagent[6] (0·6 ml, 4·8 meq) and left 20 min at room temp. Dilution with water, ether extraction and evaporation of the washed (satd $NaHCO_3$aq) and dried solvent yielded **7** (0·210 g) which crystallized from pet ether (b.p. 40–70°), m.p. 85–87° (lit.[27] 83·5–85°).

(b) Similar oxidation of **11** (0·040 g) gave a crude residue (0·035 g) consisting of **7**.

Cis-2-*chloro*-2-(1'-*naphthyl*)-r-1-*cyclohexanol* (**9**). Dry gaseous HCl was bubbled through a soln of **3** (0·300 g) in dry benzene (30 ml) to saturation. After 15 min at room temp. the soln was washed with water, sat $NaHCO_3$aq, water, dried and evaporated to give **9** (0·290 g) which crystallized from pet ether (b.p. 40–70°), m.p. 91·5–92·5°. (Found: C, 73·57; H, 6·56; Cl, 13·86. $C_{16}H_{17}OCl$ requires: C, 73·70; H, 6·52; Cl, 13·62%.)

2-*Chloro*-2-(1'-*naphthyl*)*cyclohexanone* (**10**). A soln of **9** (0·400 g) in acetone (20 ml) was treated drop-wise with Jones reagent[6] (1·0 ml), left 20 min at room temp and diluted with water. Ether extraction and evaporation of the washed (H_2O, satd $NaHCO_3$ aq, H_2O) and dried extracts yielded **10** (0·380 g) which crystallized from pet ether (b.p. 40–70°), m.p. 93–94°. (Found: C, 74·55; H, 5·81. $C_{16}H_{15}OCl$ requires: C, 74·27; H, 5·80%.)

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