Synthesis of 1,3-Diol Derivatives from Sterically Overcrowded Oxiranes. Ring-opening Reactions of 1-t-Butyl-1,2-epoxycyclohexane.

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The acid-catalysed ring-opening reactions of 1-t-butyl-1,2-epoxycyclohexane (**1**) (methanolysis, hydrolysis, and trichloroacetolysis in non-protic solvents) lead to very complex mixtures. In these reactions, in addition to the usual 1,2-primary addition products, and to the non-addition products in which the t-butyl skeleton is still present, considerable amounts of other products are formed. These compounds include 1,3-secondary addition products and other rearranged non-addition products which arise by rearrangement of the original skeleton of (**1**), by methyl group migration; the aldehyde (**20**) which is lacking both the t-butyl group and the cyclohexane skeleton is also obtained. However, the opening reactions of (**1**) in acid media are highly regioselective, most of the reaction products arising from C–O breaking on the tertiary carbon. The structures and the configurations of all the reaction products have been well established by a study of their i.r. and n.m.r. data; however, in some cases the structures and the configurations were confirmed either through unequivocal syntheses and/or chemical correlations. The stereoselectivity of the trichloroacetolysis reactions of (**1**) is not completely *anti*, even if the amounts of 1,2 adducts formed are somewhat small, and the *syn*/*anti* ratio increases with the polarity of the solvent. The results obtained were rationalized through a mechanism analogous to that previously proposed for 2-aryl- and 2-ethynyl-oxiranes in which different kinds of carbenium ion species are involved.

The ring opening of 1,2-epoxides in acid media implies a preliminary protonation of the oxirane oxygen to an oxonium ion followed by a partial or complete cleavage of a carbon–oxygen bond.[1–4] The carbenium-ion type species formed can lead either to the normal 1,2-adducts by the attack of nucleophiles, or to several different types of elimination and/or rearrangement products depending both on the structure of the epoxide and on the reaction conditions.[1–4] When aryl groups, double bonds, or other unsaturated systems are directly linked to the oxirane ring, the steric course of 1,2-adduct formation is highly variable,[1–3,5] ranging from almost complete *anti* ring opening to nearly complete *syn* stereoselectivity.[1–3,5] For 2-aryloxiranes, the amounts of *syn* addition products were shown to be closely related to the ability of the aromatic moiety to stabilize the benzylic carbocationic structures formed.[5] In contrast, the reactions of aliphatic or cycloaliphatic oxiranes under acidic conditions normally occur with complete *anti* stereoselectivity,[1,6] even if, as in the case of 1,2-epoxy-1-methylcyclohexane (**2**), a small percentage of *syn* addition was observed.[6] The presence of *syn* products in these latter reactions has been related to the relative ability of the methyl group to stabilize an adjacent tertiary carbocationic centre through an inductive or hyperconjugative mechanism.[4,6]

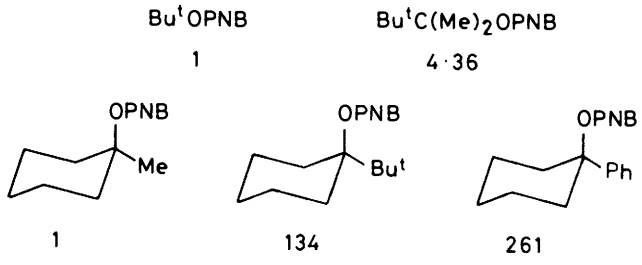
The difference in the inductive and the hyperconjugative effects of various alkyl groups such as methyl and t-butyl are relatively small, as can be seen from the σ_p^+ and σ_m^+ values of these groups.[7] However, on the assumption that $\sigma_p^+ - \sigma_m^+$ can be used as a crude measure of the direct resonance effect of a substituent,[8] these differences ($\sigma_p^+ - \sigma_m^+$) suggest that the hyperconjugative contribution of the methyl is higher than that of the t-butyl group (Table 1). These differences, even if small, in the electronic effects of these two groups can be significant when the two groups are relatively far from the reaction centre[9] as, for example, in the hydrolysis of alkylphenyldimethyl chlorides.[9] However, when we consider solvolysis or other reactions in which the alkyl group is directly linked to the reaction centre, the different steric requirements of the alkyl group can predominate; other effects (inductive and/or conjugative ones) should be relatively less important.[10,11] The replacement of a methyl group by a t-butyl group in the solvolysis of simple aliphatic tertiary *p*-nitrobenzoates (2-propyl) results in a rate enhancement by a factor of 4.36.[10,12] This increase is due to the relief of strain accompanying the ionization process of the sterically more crowded t-butyl derivative (steric assistance to ionization).[10,11] On passing to the more rigid cyclohexyl system this effect is known to be larger;[10] thus, in the solvolysis of 1-alkylcyclohexyl *p*-nitrobenzoate replacement of a methyl by a t-butyl substituent increased the rate by a factor of 134.[10,11,13] It is interesting to note that the solvolysis rate of the corresponding phenyl derivative,[14] exhibits an enhancement of 261 with respect to the methyl derivative, but is only just twice that of the t-butyl derivative. As pointed out above, the presence of a phenyl substituent on an oxirane ring can substantially modify the steric course of the ring opening.[1,2,5]

As part of our research programme on the mechanism and

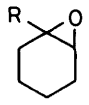
Table 1. Selected substituent constants[a]

Substituent	σ_p^+	σ_m^+	$\sigma_p^+ - \sigma_m^+$
Me	−0.311	−0.066	−0.245
Bu^t	−0.256	−0.059	−0.197

[a] Ref. 7.

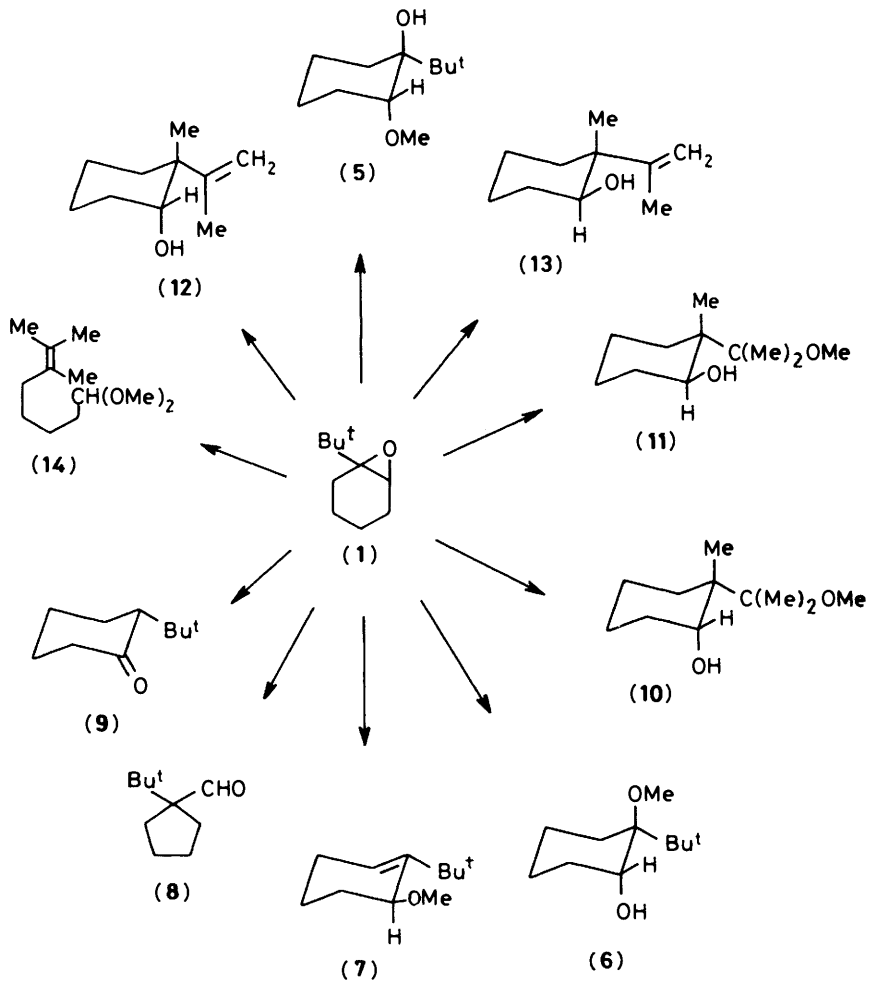


the stereochemistry of the reactions of substituted oxiranes,[3,4] we have studied 1-t-butyl-1,2-epoxycyclohexane (**1**) which is structurally analogous to the epoxides (**2**),[6] (**3**),[4,5] and (**4**).[15] The steric requirements of the t-butyl group, exalted by its substitution at a tertiary carbon in a cyclohexane system, together with its hyperconjugative ability, and the possibility of 1,2-shifts in the intermediate carbenium ion all suggested that the chemical behaviour of the t-butyl epoxide (**1**) was likely to be different from that of the corresponding methyl epoxide (**2**).[6] Further, it was thought that the reactions of the epoxide (**1**) could lead to products of noteworthy synthetic interest.



(**1**) R = Bu^t
(**2**) R = Me
(**3**) R = Ph
(**4**) R = $SiMe_3$

Whereas the reaction of the epoxide (**1**) with sodium methoxide in methanol yielded exclusively the tertiary *trans*-methoxy-alcohol (**5**), acid-catalysed methanolyses led to a complex mixture of products (see Scheme 1 and Table 2). However, the acid-catalysed oxirane ring opening is largely regioselective, all the reaction products but the methoxy-alcohol (**5**) arising from C–O breaking on the tertiary carbon. In these reactions, in addition to the usual primary 1,2-addition products, (**5**) and (**6**), and to the non-addition products in which



Scheme 1.

Table 2. Product composition in the ring opening of the epoxide (**1**) in acidic methanol

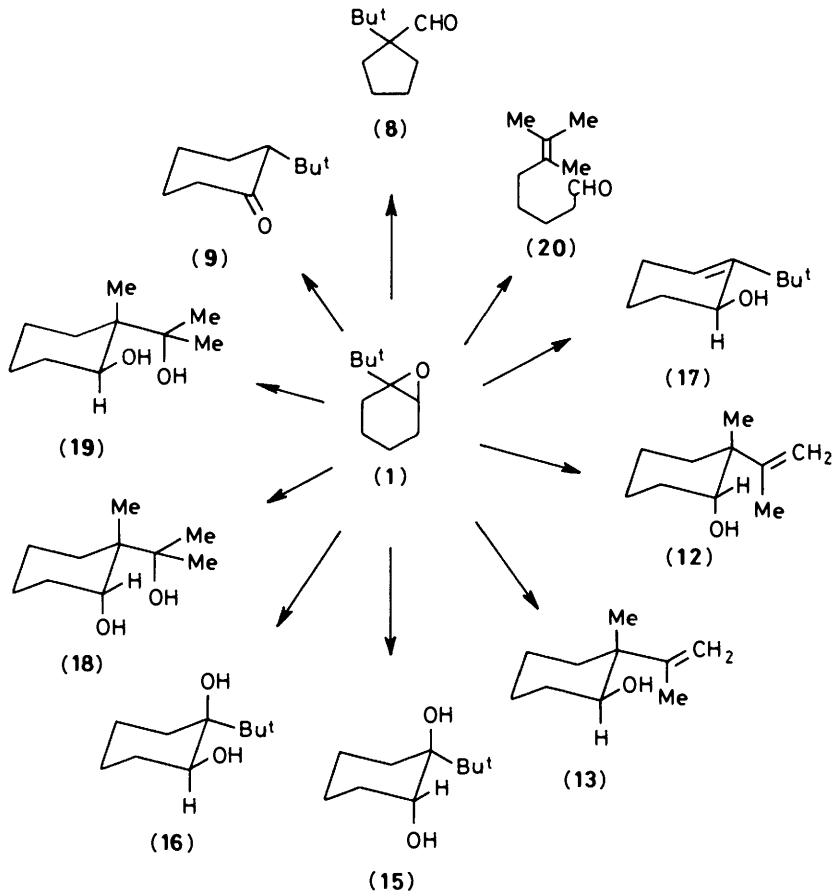
Reagents		(5)	(6)	(7)[a]	(8)	(9)	(10)	(11)	(12)	(13)	(14)[b]
MeOH	H_2SO_4	12.0	18.5	25.2	1.5	1.7	23.1	1.8	9.3	1.9	5.0
MeOH–$LiClO_4$[c]	TsOH	5.3	10.4	18.7	2.5	2.1	29.0	3.2	11.2	3.7	13.9
MeOH–CH_2Cl_2[d]	TsOH	0.9	2.2	30.3	16.6	7.0	4.9	0.3	7.2	2.2	20.5[e]

[a] The alcohol (**17**) is the primary reaction product. [b] The aldehyde (**20**) is the primary reaction product. [c] 0.5M-Solution. [d] Molar ratio epoxide:acid:MeOH 1:0.1:6. [e] Free aldehyde (**20**) is also present (7.9%).

Table 3. Product composition in the trichloroacetolysis and hydrolysis of the epoxide (**1**).

Reagents		(8)	(9)	(17)	(12)	(13)	(20)	(15)	(16)	(18)	(19)	*syn/anti ratio*
Cyclohexane	TCA	10.1	4.8	32.3	3.8	1.0	13.8	32.1[a]	0.5[a]	1.3[a,b]		1.6/98.4
CCl_4	TCA	10.7	3.0	36.8	5.1	2.5	13.0	26.0[a]	1.2[a]	1.5[a,b]		4.5/95.5
Benzene	TCA	11.7	1.2	45.2	8.0	4.6	21.0	4.0[a]	1.6[a]	2.5[a,b]		28.6/71.4
$CHCl_3$	TCA	16.3	1.6	46.0	6.6	3.7	21.5	1.6[a]	1.0[a]	1.3[a,b]		38.5/61.5
CH_2Cl_2	TCA	23.0	2.1	8.7	8.5	4.0	42.4	0.6[a]	0.8[a]	7.5[a]	2.0[a]	57.2/42.8
H_2O	H_2SO_4	1.2	0.2	13.3	9.4	3.0		6.6		60.8	6.0	

[a] After saponification of the crude reaction mixture. [b] The ratio between (**18**) and (**19**) was not determined.



Scheme 2.

the t-butyl skeleton is still present, (**7**) and (**9**), considerable amounts of other products are formed; namely, the 1,3-secondary addition products, (**10**) and (**11**), and other rearranged non-addition products, (**12**) and (**13**), which can be assumed to arise by rearrangement of the original skeleton of (**1**) by methyl group migration. Furthermore, small amounts of the dimethyl-acetal (**14**) of the aldehyde (**20**),[16]* which lacks both the t-butyl and the cyclohexane skeleton, were found in the reaction mixture. The acid hydrolysis of (**1**) yielded a mixture (Table 3) consisting mainly of the *cis*- (**18**) and *trans*-1,3-diols (**19**) accompanied by minor amounts of the primary *trans*-1,2-diol (**15**). The ring-opening reactions of (**1**) have also been carried out with trichloroacetic acid in several non-protic solvents affording mixtures of the monotrichloroacetates of the 1,2-diols (**15**) and (**16**), and of the 1,3-diols (**18**) and (**19**), detected and characterized after saponification to the corresponding diols (**15**), (**16**), (**18**), and (**19**), together with the aldehyde (**20**)[16] and other rearrangement products detected, too, in the acid hydrolysis (see Scheme 2 and Table 3). In the trichloroacetolyses, the non-diol derivatives predominate, but their yields vary considerably depending on the solvent.

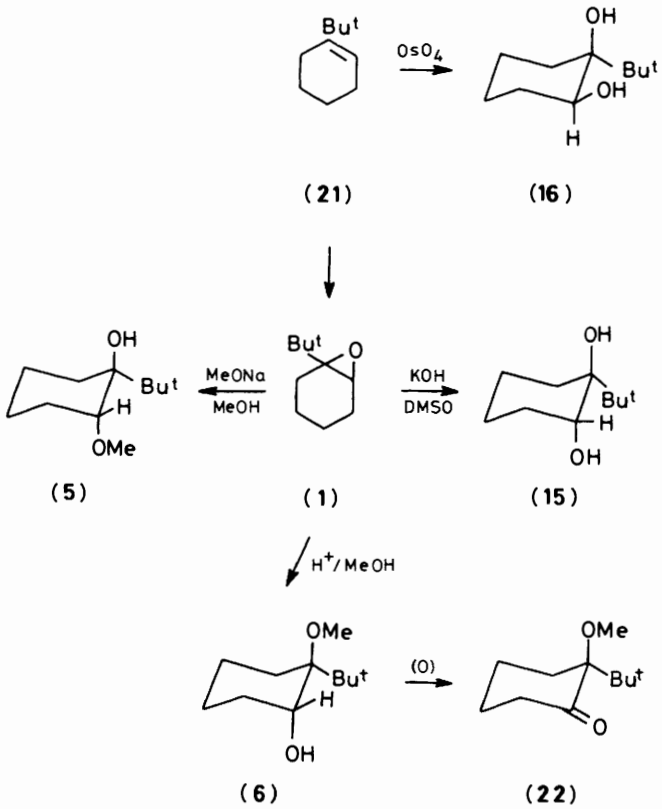
Most of the products obtained have had their structures and configurations established on the basis of i.r. and ^1H n.m.r. spectral evidence. However, in some cases the structures and the configurations of the products were confirmed either *via* alternative unequivocal syntheses and/or chemical correlations. The configurations of the t-butyl diols (**15**) and (**16**), and of the t-butyl methoxy-ethers (**5**) and (**6**) can be inferred on the basis of the values of the half-bandwidth of the methine proton[2,17,18] β

* The formation and the structural identification of the aldehyde (**20**), a structural analogue of citronellal, and of its dimethyl acetal (**14**) in the acid-catalysed reactions of the epoxide (**1**), has been previously reported and discussed in a separate paper.[16]

Table 4. I.r. data for *cis*- and *trans*-1,2- and 1,3-diols and 1,2- and 1,3-methoxy alcohols.

Compd.	$\nu_{max.}/cm^{-1}$ OH_{free}	$\nu_{max.}/cm^{-1}$ OH···O
(5)	3 630	
(6)	3 625	
(10)		3 447
(11)		3 483
(15)	3 626	
(16)	3 621	3 588
(18)	3 619	3 498
(19)	3 613	3 516

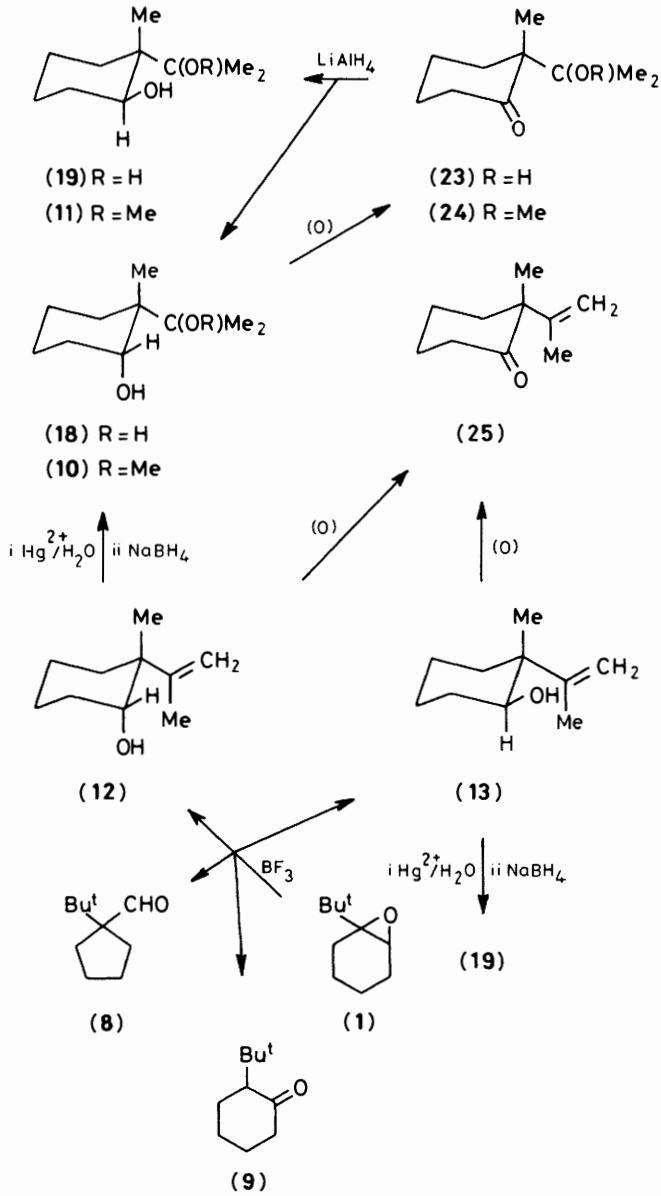
to the t-butyl group. The structure of the methoxy-alcohol (**5**) was deduced, and its configuration confirmed, by its formation in a slow base-catalysed methanolysis of (**1**) (Scheme 3) *via* an



Scheme 3.

S_N2-type mechanism which favours the attack of the nucleophile from the *anti* side on the less hindered carbon.[2,19,20] Further, whilst the methoxy-alcohol (**5**) is stable to oxidation, (**6**) gives the ketone (**22**). The structures and configurations of the 1,2-diols (**15**) and (**16**) were also confirmed by their method of preparation (Scheme 3). Thus, the *trans* diol (**15**) was formed in the base-catalysed hydrolysis[2,19,20] of (**1**), whereas the *cis*-diol (**16**) was obtained in the OsO_4-catalysed *cis*-dihydroxylation[21,22] of the olefin (**21**). Also the i.r. spectra of (**5**), (**6**), (**15**), and (**16**) in dilute solution of CCl_4 in the 3000—3 600 cm^{-1} range confirm their configurations; only the *cis*-compound (**16**) shows absorption arising from OH···O interaction[2,18,23,24] (Table 4).

Only the *cis* forms, that is the ones in which the $Me_2C(OR)$ and the OH are on the same side, (**18**) and (**10**) respectively, of the two epimeric couples of 1,3-diols, (**18**) and (**19**), and of 1,3-methoxyalcohols, (**10**) and (**11**), were obtained in substantial amounts from the reaction mixtures of the acid-catalysed ring opening of (**1**). However, oxidation of (**18**) and (**10**) (Scheme 4)



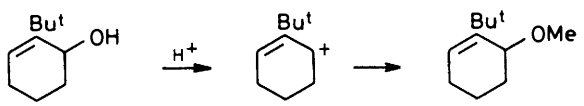
Scheme 4.

afforded the ketones (**23**) and (**24**) respectively. LAH reduction of these ketones led to a mixture of the corresponding *cis*- and *trans*-derivatives (**18**) and (**19**), and (**10**) and (**11**). Their relative configurations could have been assigned from the half-band widths of the methynic proton in C-1 [$W_{\frac{1}{2}}$ 4.0, 18.0, 6.0, and 16.0 Hz for (**18**), (**19**), (**10**), and (**11**) respectively] assuming that both the bulky 1-hydroxy- and 1-methoxy-1-methylethyl groups occupy an equatorial position in the preferred conformation of these compounds. However, the presence of a strong band due to an intramolecular OH···O interaction[23–25] in the i.r. spectra in a dilute solution in CCl_4 of (**18**) and (**10**), in which the secondary OH was found to be axial by n.m.r. data as

described above, definitely defines the equatorial position of the 1-hydroxy- and of the 1-methoxy-1-methylethyl group and therefore the configuration of (**18**) and (**10**) and of their epimers (**19**) and (**11**).

The 2-methyl-2-prop-2-enylcyclohexanols (**12**) and (**13**) were obtained in good yield together with the aldehyde (**8**) (characterized through its n.m.r. spectrum and its 2,4-DNP derivative) and minor amount of the known ketone (**9**)[26] by treatment of (**1**) with BF_3·Et_2O complex in CH_2Cl_2. Oxidation of the epimers (**12**) and (**13**) afforded the ketone (**25**). The relative configuration of (**12**) and (**13**) could have been derived also in the present case by the half-bandwidth of the methynic proton [$W_{\frac{1}{2}}$ 6.7 and 15.8 Hz for (**12**) and (**13**) respectively], assuming that the prop-2-enyl group is the largest one and occupies the equatorial position in the preferred conformation. However, this assumption was not necessarily obvious because of the relatively low *A* value reported for the vinyl group (1.68 kcal/mol),[27] slightly smaller than the value for the methyl; the vinyl group might be expected to be closely related to the prop-2-enyl group from a conformational point of view. The problem of the conformation of (**12**) and (**13**) was unequivocally solved through their conversion into the corresponding 1,3-diols *cis* (**18**) and *trans* (**19**) by hydroxymercuriation–demercuriation of the double bond (Scheme 4).

It is clear from the mechanistic discussion, that compound (**7**) cannot be a primary reaction product of the acid methanolysis of (**1**), its genesis either being *via* acid dehydration of (**5**) or by protonation of the unsaturated alcohol (**17**) to form the allyl carbenium ion (**26**) which then reacts with methanol to yield (**7**). However, whereas (**5**) is stable under the reaction conditions, (**17**) is easily converted into (**7**) in methanol at room temperature in the presence of a catalytic amount of acid (Scheme 5). The dimethylacetal (**14**) is likewise not the primary



(**16**) (**26**) (**7**)

Scheme 5.

reaction product, but it is very probably formed from the aldehyde (**20**) under the reaction conditions.[16]

The most striking feature in the reactions of the epoxide (**1**) (see Tables 2 and 3) is the formation of substantial amounts of rearranged compounds in which the t-butyl skeleton is no longer present. A further point of interest is the formation, in some cases as the main product, either of the aldehyde (**20**), or of its dimethyl acetal (**14**) in the reactions in methanol, in which both the cyclohexyl and the t-butyl moieties are lost.[16]

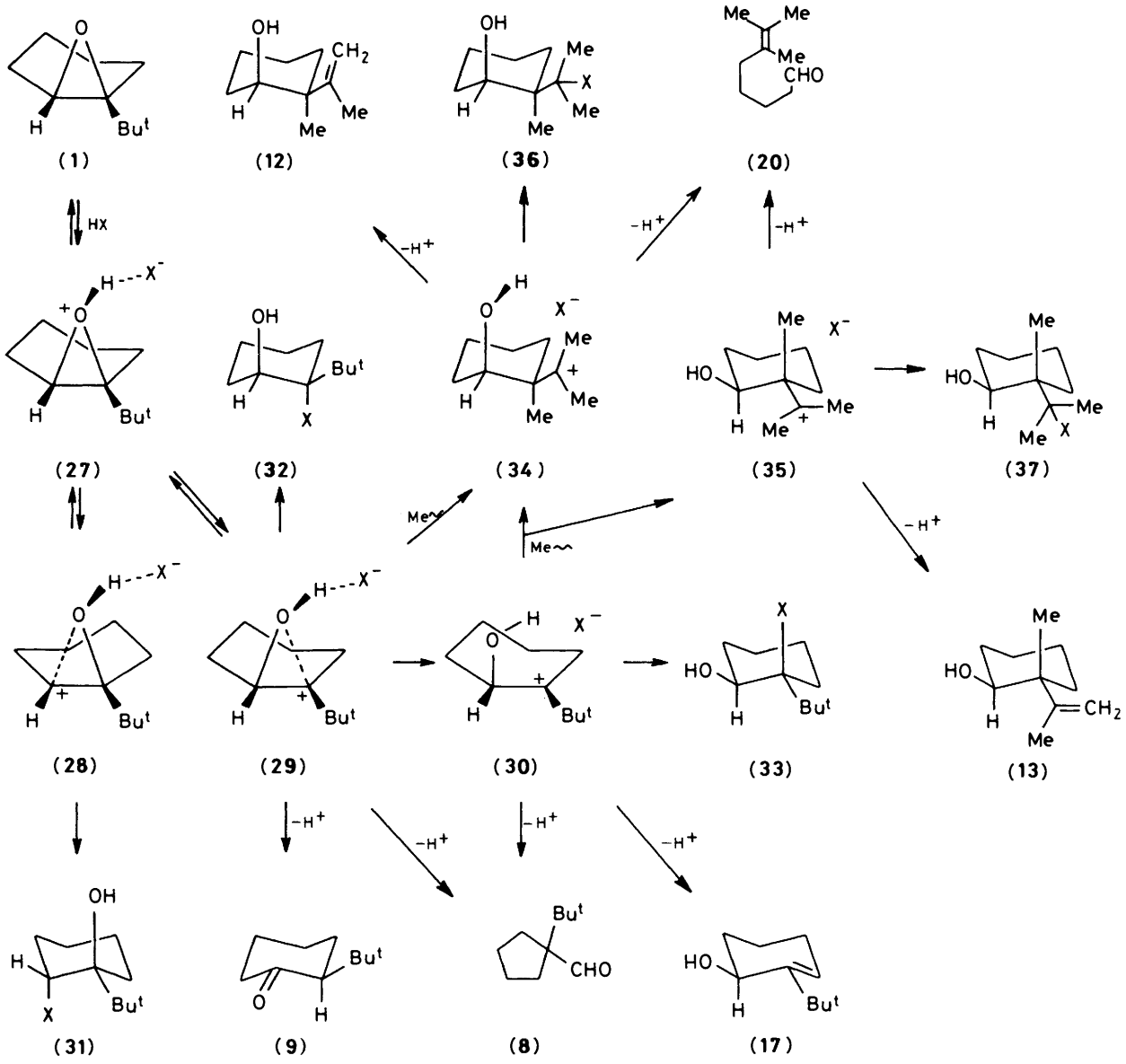
The amounts of 1,2-adducts formed in the trichloroacetolysis reactions are quite low; however, the formation of these products is not completely *anti*-stereoselective. Significant amounts of the *syn* 1,2-adduct are formed and the *syn*/*anti* ratio increases with the solvating power of the medium; concurrently the overall yield of 1,2-adducts decreases, whereas that of rearrangement compounds increases. In addition, the relative percentages of the different types of compounds vary noticeably depending on the reaction conditions (type of nucleophile, solvent, polarity of the solvent, *etc.*).

The results obtained in the acid-catalysed reactions of (**1**), and in particular the formation of marked amounts of products with rearranged skeletons, suggest the intervention, in the ring opening of the epoxide (**1**), of intermediate structures with discrete carbocationic character. A rationalization of the products formed, and in general of the results, can be attempted in terms of a mechanism, previously proposed for the ring opening of 2-aryl-[2,5,18] or other 2-substituted oxiranes[3,4] in acid media, in which different kinds of carbenium ion species are involved (see Scheme 6, there are no conformational implications in the formulae). This mechanism is connected with the 'ion-dipole pairs' mechanism,[28] an analogue of the Winstein ion-pair scheme of nucleophilic substitutions and eliminations.[29–31] According to this mechanism, the protonated epoxide (**27**) can lead to intramolecular intimate ion/dipole pairs (**28**) and (**29**) which on attack of the nucleophile X^- (written as an anion for convenience) from the rear-side, because of the strong shielding at the front, can afford the *anti* adducts (**31**) and (**32**) respectively. On the other hand, the tertiary ion/dipole pair (**29**) can evolve to a more carbocationic species (**30**) which can be related to a solvent separated ion-dipole pair;[28] collapse of this species (**30**) with the nucleophile X^- on the tertiary centre affords the *syn*-adduct (**33**). The carbocationic species (**29**) and (**30**) can undergo methyl migration to give the new tertiary carbenium ions (**34**) and (**35**).* These species (**34**) and (**35**) can either lose a proton to give the rearranged unsaturated alcohols (**12**) and (**13**) respectively, or react with the nucleophile to give the corresponding 1,3-adducts (**36**) and (**37**). Furthermore, the carbocations (**34**) and (**35**) can give, *via* a retro-Prins fragmentation with cleavage of the cyclohexylic C–C bond, the aldehyde (**20**).[16] Both the carbocationic species of type (**29**) and (**30**) also afforded the usual rearranged products (**8**), (**9**), and (**17**) in which the t-butyl moiety remains unchanged.

The high regioselectivity observed in the ring-opening reactions of (**1**), that is the formation of very large amounts of products derived from the breaking of the tertiary C–O bond, can be ascribed to the preferential formation of the ion/dipole pair (**29**) owing to the presence of the tertiary carbocationic centre. Further support in favour of the formation of (**29**) is the marked decrease in strain accompanying the ionization of the sterically crowded tertiary C–O bond.[11] The presence of substantial amounts of products derived from (**34**) and (**35**) underlines the facility with which the tertiary carbenium ion species, either (**29**) or (**30**), rearrange to other tertiary carbocations (**34**) and (**35**). As previously suggested,[16] the driving force of these rearrangements could be the higher stability of the carbenium ions (**34**) and (**35**) compared with (**29**) and (**30**), the electron-withdrawing oxirane oxygen being further from the electron-deficient carbon in the former.

The relatively small amounts of non-addition products and the large amounts of adducts with both unrearranged and rearranged skeletons found in reactions carried out in nucleophilic protic solvents (H_2O and MeOH) can be explained in terms of the abundant availability of the nucleophile which can capture the carbocationic structures.[34] Methanolyses carried out in CH_2Cl_2 with only a limited excess of nucleophile

* The two methyl shifted carbenium ions (**34**) and (**35**) can be assumed to be formed by migration of the methyl at the *migration terminus*,[32] respectively with inversion and retention of the configuration compared with the configuration of the starting structures (**29**) and (**30**). The migration of a methyl group in the intimate ion/dipole pair (**29**) in which an interaction between the former oxirane oxygen and the carbenium ion still occurs, would, very likely, proceed with a discrete degree of concertedness leading to the carbenium ion (**34**), inversion of configuration occurring at the *migration terminus*.[32,33] In contrast the migration of the methyl group from the carbenium ion (**30**) or from other carbocationic species which have lost completely or almost completely the 'memory' of the starting configuration at the *migration terminus* may occur either with inversion or retention of the configuration to afford the carbenium ions (**34**) and (**35**) respectively. It may be pointed out that the products arising from the carbenium ion (**34**), formed with inversion of the configuration at the *migration terminus*, largely predominate compared with the ones occurring from the carbenium ion (**35**) formed with retention of the configuration.



Scheme 6.

give larger amounts of the non-addition products. In such reactions, discrete amounts of the primary 1,2-adducts of type (**31**) and (**32**) are formed; however, as the polarity of the medium is increased by the addition of salt, the 1,2-adducts (**31**) and (**32**) decrease in favour of the rearranged products lacking the t-butyl function; these arise from the rearranged carbenium ions (**34**) and (**35**). Such products, in particular the 1,3-adduct of type (**36**) [(**18**)], largely predominate in reactions in water.

The trichloroacetolysis reactions of (**1**) in non-protic solvents show a marked dependence on both the polarity and the solvating power of the medium. In cyclohexane both the *anti* primary 1,2-adducts, (**31**) and/or (**32**), are formed together with the unsaturated alcohol (**17**), the aldehydes (**8**) and (**20**), and smaller quantities of other products including the *syn* 1,2-adduct (**33**). With an increase in the solvating power of the solvent on passing from cyclohexane to CH_2Cl_2, the quantity of the *anti* 1,2-adducts, (**31**) and/or (**32**), decreases dramatically (from 32.1 to 0.6%), whereas the products in which the t-butyl function is lacking, increase; in particular the yield of the aldehyde (**20**) passes from 13.8 to 42.4% in the same solvent series. Evidently, as in the reactions in protic solvents, an increase of the solvating power of the medium favours the pathways leading to the rearranged carbenium ions (**34**) and (**35**) and, therefore, the formation of the products which derive from them. As stated above, the trichloroacetolysis reactions are not completely *anti*-stereoselective; small but significant amounts of the *syn* 1,2-adduct (**33**) are formed. This means that a carbocationic species of type (**30**) must, at least to a limited extent, be directly involved in these reactions. In the trichloroacetolysis reactions of (**1**) a definite dependence of the *syn*/*anti* ratio on the solvent is observed in the solvent series: cyclohexane, CCl_4, benzene, $CHCl_3$, CH_2Cl_2, as previously reported for the analogous reactions of 1-aryl- and 1-ethynyl-1,2-epoxycyclohexanes.[3,5c] However, in the present case, the increase in the *syn*/*anti* ratio seems to be due much more to a net decrease in the *anti* adduct than to a real increase in the *syn* adduct.

The most outstanding difference between the epoxide (**1**) and the trimethylsilyl substituted compound (**4**)[15] is that in the ring-opening reactions in acid media, considerable amounts of non-

addition and rearrangement products are obtained for the former compound and none for the latter. Moreover, the reactions of (**4**) are completely *anti* stereoselective, while those of (**1**) give rise to *syn* adducts as well even if only in low yield. As a consequence, the reactions of the epoxide (**1**) seem to proceed *via* transition states with carbocation character markedly higher than those for the corresponding trimethylsilyl substituted epoxide (**4**).[15]

Experimental

M.p.s were determined on a Kofler apparatus and are uncorrected. I.r. spectra for comparison between compounds were taken for Nujol mulls on a Perkin-Elmer Infracord Model 137, and those for the determination of OH stretching bands were taken with a Perkin-Elmer 257 double-beam grating spectrophotometer in dried (P_2O_5) CCl_4 with the indene band at 3 110 cm^{-1} as calibration standard; a quartz cell of 2-cm optical length was employed, and the concentration of the solution was 5×10^{-3}M or lower to prevent intermolecular association. ^1H N.m.r. spectra were determined on 10% $CDCl_3$ solutions with a Varian EM 360 spectrometer using $SiMe_4$ as internal standard. G.l.c. analyses of all the mixtures obtained by hydrolysis, methanolysis, and trichloroacetolysis of the epoxide (**1**) were run on a Carlo Erba Fractovap 2300 apparatus with a flame-ionization detector and a glass column (2 m × 2.5 mm) packed with 10% diethylene glycol succinate on 80—100 mesh silanized Chromosorb W [column: low isotherm 100 °C (6 min), high isotherm 190 °C, increasing temperature 3 °C/min; evaporator and detector 275 °C; nitrogen flow 30 ml/min]; the order of increasing retention times was (**7**) < (**8**) < (**9**) < (**14**) < (**12**) < (**5**) < (**13**) < (**11**) < (**6**) (methanolysis reactions), (**8**) < (**9**) < (**20**) < (**17**) < (**12**) < (**13**) < (**16**) < (**15**) < (**18**) and (**19**) (trichloroacetolysis and hydrolysis reactions). Compounds (**18**) and (**19**) failed to separate under these conditions and so their relative ratios in the hydrolysis and the trichloroacetolysis in CH_2Cl_2 were determined on a Dani Gas Cromatograph 3800 apparatus with a flame-ionization detector and a SE 30 capillary glass column (20 m × 0.2 mm) (column: 150 °C, evaporator and detector 200 °C; nitrogen flow 2 ml/min); the order of increasing retention times was (**19**) < (**18**). Preparative t.l.c. was performed on 2-mm layer silica gel plates (Merck F_{254}) containing a fluorescent indicator: the t.l.c. plates were visualized first by u.v. light (254 nm) and then by spraying with 0.2M-$K_2Cr_2O_7$ in 40% aqueous sulphuric acid followed by gentle heating. All comparisons between compounds were made on the basis of i.r. and n.m.r. spectra and g.l.c. Magnesium sulphate was always used as the drying agent. Light petroleum refers to the fraction with b.p. 30—50 °C. Evaporations were carried out under reduced pressure (rotating evaporator). Cyclohexane, CCl_4, $CHCl_3$, and CH_2Cl_2 were refluxed over and redistilled from P_2O_5. Benzene was washed with concentrated sulphuric acid, kept at reflux over sodium and distilled.

1-*t-Butylcyclohexene* (**21**).—*cis*-2-t-Butylcyclohexanol (33.5 g) prepared as previously described,[26] m.p. 56—57 °C (lit.,[26] m.p. 56.8—57.7 °C) was added to a freshly prepared solution of sulphuric acid in glacial acetic acid (2:8 v/v; 200 ml). The reaction mixture was stirred at room temperature for 24 h and then poured into a separating funnel containing light petroleum (150 ml) and water (300 ml). The organic layer was separated, washed (water, 10% aqueous sodium carbonate, and water), dried, and evaporated to give a liquid (30 g) which was distilled to yield pure compound (**21**) (16.6 g), b.p. 70—71 °C (60 mmHg) [lit.,[35] b.p. 169—170 °C (749 mmHg); lit.,[26] 166.5 °C (735 mmHg)].

2-*t-Butylcyclohexanone* (**9**). This was prepared as previously described.[26]

1,2-*Epoxy*-1-*t-butylcyclohexane* (**1**). This compound was prepared as previously described.[16]

t-2-*Methoxy*-1-*t-butylcyclohexan*-r-1-*ol* (**5**).—A solution of compound (**1**) (0.50 g, 3.24 mmol) in anhydrous methanol (10 ml) was added dropwise to a stirred solution of MeONa (15.1 g) in anhydrous methanol (50 ml) and the resulting mixture was maintained at gentle reflux for 10 days. Evaporation of the washed (water) ether extracts yielded a residue (0.40 g) mainly consisting of the ether (**5**) which was subjected to preparative t.l.c. (a 9:1 mixture of light petroleum and ether was used as the eluant: elution was repeated twice). Extraction (CH_2Cl_2) of the band with R_F 0.50 yielded pure (**5**) (0.14 g) (g.l.c.) as a liquid; $\nu_{max.}$(CCl_4) see Table 4; δ 3.27 (1 H, m, $W_{\frac{1}{2}}$ 6.0 Hz, the signal is partially overlapped with that of the methoxy group, C*H*OMe), 0.96 (9 H, s, Bu^t) (Found: C, 70.8; H, 11.55. $C_{11}H_{22}O_2$ requires C, 70.91; H, 11.90%). Compound (**5**) was not oxidized by Jones reagent.[36]

Reactions of the Oxide (**1**) *with* 0.1M-*Sulphuric Acid in Anhydrous Methanol*.—A solution of (**1**) (0.50 g) in 0.1M-H_2SO_4–MeOH (50 ml) was stirred at room temperature for 15 min and then diluted with saturated aqueous sodium hydrogen carbonate and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded a liquid residue (0.49 g) (g.l.c., see Table 2) which was subjected to preparative t.l.c. [light petroleum–ether (9:1) was used as the eluant (× 2)]. Many bands were observed and extracted (CH_2Cl_2) to give the following: 2-*methyl*-c-2-(1-*methyl*-1-*methoxyethyl*)*cyclohexan*-r-1-*ol* (**10**) (R_F 0.21; 0.070 g) as a liquid; $\nu_{max.}$ see Table 4; δ 3.53 (1 H, m, $W_{\frac{1}{2}}$ 6.0 Hz, C*H*OH), 3.23 (3 H, s, OMe), 1.30, 1.10, and 0.83 (9 H, 3 s, 3 Me) (Found: C, 70.55; H, 11.85. $C_{11}H_{22}O_2$ requires C, 70.91; H, 11.90%). t-2-*Methoxy*-2-*t-butylcyclohexan*-r-1-*ol* (**10**) (R_F 0.21; 0.070 g) as a liquid; $\nu_{max.}$ see Table 4; δ 3.53 (1 Table 4; δ 4.10 (1 H, m, $W_{\frac{1}{2}}$ 8.0 Hz, C*H*OH), 3.36 (3 H, s, OMe), and 1.03 (9 H, s, Bu^t) (Found: C, 71.1; H, 11.6. $C_{11}H_{22}O_2$ requires C, 70.91; H, 11.90%). c-2-*Isopropenyl*-2-*Methylcyclohexan*-r-1-*ol* (**12**) (R_F 0.50; 0.030 g) as a solid, m.p. 37—38 °C; $\nu_{max.}$ 3 335 cm^{-1}; δ 4.96 (2 H, m, =C*H*$_2$), 3.73 (1 H, m, $W_{\frac{1}{2}}$ 6.0 Hz, C*H*OH), 1.78 (3 H, s, =CMe), 1.05 (3 H, s, Me) (Found: C, 77.75; H, 11.8. $C_{10}H_{18}O$ requires C, 77.86; H, 11.76%. Compound (**5**) (R_F 0.58; 0.038 g). 6,7-*Dimethyloct*-6-*enal dimethyl acetal* (**14**) (R_F 0.75, 0.020 g) as a liquid.[16] 3-*Methoxy*-2-*t-butylcyclohexene* (**7**) (R_F 0.83; 0.070 g) as a liquid; $\nu_{max.}$ 1 075 cm^{-1}; δ 5.70 (1 H, m, =CH), 3.66 (1 H, m, C*H*OMe), 3.26 (3 H, s, OMe), 1.03 (9 H, s, Bu^t) (Found: C, 78.85; H, 11.65. $C_{11}H_{20}O$ requires C, 78.51; H, 11.98%).

2-*Methoxy*-2-*t-butylcyclohexanone* (**22**).—A solution of compound (**6**) (0.050 g, 0.26 mmol) in acetone (5 ml) was treated dropwise with Jones reagent[36] (0.07 ml, 0.58 mequiv.). After 10 min at room temperature the mixture was diluted with water and extracted with ether. Evaporation of the washed (water, saturated aqueous sodium hydrogen carbonate, and water) and dried ether extracts gave an oily residue consisting of pure (**22**) (g.l.c.) (0.045 g); $\nu_{max.}$ 1 700 cm^{-1}; δ 3.29 (3 H, s, OMe) and 1.00 (9 H, s, Bu^t) (Found: C, 71.55; H. 11.3. $C_{11}H_{20}O_2$ requires C, 71.69; H, 10.93%).

Reduction of the Ketone (**22**) *with* $NaBH_4$, $LiAlH_4$, *Borane-Methyl Sulphide Complex* (*BMS*).—Three 0.010-g portions of the oxide (**22**) were treated respectively with $NaBH_4$ (0.020 g) in EtOH (5 ml), $LiAlH_4$ (0.020 g), and BMS (0.01 ml) in anhydrous ether (10 ml). G.l.c. analysis of each crude reaction product showed the hydroxy ether *trans* (**6**) as the chief product. A further small peak indicated, presumably, the presence of the *cis* isomer; however it was not possible to separate this product owing to the small amount present.

1-*t-Butylcyclohexane*-r-1,t-2-*diol* (**15**).—Aqueous 2M-KOH (8 ml) was added to a solution of epoxide (**1**) (0.30 g) in DMSO (30 ml) and the resulting mixture was heated at 100 °C for 7 days. The mixture was cooled, diluted with water and the suspension extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded a crude semisolid (0.22 g) which was recrystallized from light petroleum to give pure (**15**) (0.11 g), m.p. 124—125 °C; $\nu_{max.}$ see Table 4; δ 3.90 (1 H, m, $W_{\frac{1}{2}}$ 6.0 Hz, C*H*OH), 1.00 (9 H, s, Bu^t) (Found: C, 69.45; H, 11.35. $C_{10}H_{20}O_2$ requires C, 69.72; H, 11.70%).

Reaction of the Epoxide (**1**) *with* 0.1M-*Sulphuric Acid*.—A suspension of the epoxide (**1**) (0.30 g) in 0.1M-aqueous sulphuric acid (30 ml) was stirred for 24 h at room temperature. After this time the reaction mixture was treated with solid sodium hydrogen carbonate and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded a solid residue (0.26 g) (g.l.c., see Table 3) which was recrystallized from light petroleum to give pure c-2-(1-*hydroxy*-1-*methylethyl*)-2-*methylcyclohexan*-r-1-*ol* (**18**) (0.110 g), m.p. 122—123 °C; $\nu_{max.}$ see Table 4; δ 3.96 (1 H, m, $W_{\frac{1}{2}}$ 4.0 Hz, C*H*OH), and 1.33, 1.13, and 0.83 (9 H, 3 s, 3 Me) (Found: C, 69.85; H, 11.5. $C_{10}H_{20}O_2$ requires C, 69.72; H, 11.70%). The mother liquor was evaporated and the residue (0.10 g) was subjected to preparative t.l.c. [light petroleum–ether (9:1) was used as eluant (×4)]. Extraction of the band with the lowest R_F yielded pure (**15**) (0.005 g), while extraction of the band with the highest R_F afforded (**17**) (0.020 g) (see below).

1-*t-Butylcyclohexane*-r-1,c-2-*diol* (**16**).—A mixture of *N*-methylmorpholine *N*-oxide monohydrate[21] (1.5 g, 11.2 mmol), water (5 ml), acetone (1 ml), and OsO_4 (0.010 g) in t-butyl alcohol (1 ml) was treated with compound (**21**) (1.3 g, 9.4 mmol) in acetone (2 ml). The resulting reaction mixture was stirred at room temperature for 3 days and then gently refluxed for 14 h. After cooling, the reaction mixture was added to a slurry of sodium hydrogen sulphite (0.10 g), magnesium silicate (1.2 g), and water (12 ml), and stirred for 30 min. The magnesium silicate was filtered off and the filtrate acidified (pH 2) with 0.5M-aqueous sulphuric acid, and extracted with ether. Evaporation of the washed (saturated aqueous sodium hydrogen carbonate, and water) and dried ether extracts yielded (**16**) as a solid residue (0.45 g). Recrystallization from light petroleum gave pure compound (**16**) (0.25 g), m.p. 115—116 °C; $\nu_{max.}$ see Table 4; δ 3.83 (1 H, m, $W_{\frac{1}{2}}$ 18.0 Hz, C*H*OH), 1.03 (9 H, s, Bu^t) (Found: C, 69.95; H, 11.65. $C_{10}H_{20}O_2$ requires C, 69.72; H, 11.70%).

Reaction of the Epoxide (**1**) *with Trichloroacetic Acid in Anhydrous* CH_2Cl_2.—A solution of the epoxide (**1**) (1.3 g, 8.4 mmol) in anhydrous CH_2Cl_2 (130 ml) was treated with a 1M-solution of trichloroacetic acid in anhydrous CH_2Cl_2 (9.1 ml) and the resulting mixture was left 15 min at room temperature. Evaporation of the washed (saturated aqueous sodium hydrogen carbonate, and water) and dried organic solution yielded an oily residue which on g.l.c. analysis showed the complex composition reported in Table 3. A first portion (0.60 g) of the crude reaction product was subjected to preparative t.l.c. [light petroleum–ether (9:1) was used as the eluant (×2)]. Many bands were observed and successively extracted (CH_2Cl_2) to give the following: extraction of the band with R_F 0.23 yielded an oily residue (0.020 g) consisting (g.l.c. and n.m.r.) of a mixture of the isopropenyl alcohols (**12**) and (**13**) (see below); 2-*t-butylcyclohex*-2-*en*-1-*ol* (**17**) (R_F 0.32; 0.040 g) as a liquid: $\nu_{max.}$ 3 367 cm^{-1}; δ 5.66 (1 H, m, =CH), 4.30 (1 H, m, C*H*OH), and 1.13 (9 H, s, Bu^t) (Found: C, 77.5; H, 11.45. $C_{10}H_{18}O$ requires C, 77.86; H, 11.68%); 6,7-*dimethyloct*-6-*enal* (**20**)[16] (R_F 0.45; 0.24 g) as a liquid.[16] Extraction of the band with R_F 0.54 afforded an oily residue (0.010 g) which on g.l.c. analysis was shown to be the ketone (**9**) slightly impure due to the presence of the aldehyde (**8**) (see below). Extraction of the band with R_F 0.68 afforded a liquid (0.060 g) which was further purified through semi-preparative t.l.c. on 0.5 mm layer silica gel plates [light petroleum–ether (9:1) as the eluant (×2)]; extraction of the band with the lower R_F afforded pure 1-*t-butylcyclopentane*-1-*carbaldehyde* (**8**) (0.030 g) as a liquid; $\nu_{max.}$ 1 712 cm^{-1}; δ 9.86 (1 H, s, CHO) and 0.96 (9 H, s, Bu^t). Addition of (**8**) (0.010 g) to an EtOH–H_2SO_4 solution of 2,4-dinitrophenylhydrazine[37] afforded the 2,4-DNP of (**8**), m.p. 155—156 °C (Found: C, 58.0; H, 6.85; N, 16.1. $C_{16}H_{22}N_4O_4$ requires C, 57.47; H, 6.63; N, 16.76%). A second portion (0.55 g) of the trichloroacetolysis crude reaction product in THF (40 ml) was hydrolysed by treatment with 1M-KOH ethanolic solution (13 ml) and then left for 5 h at room temperature. Evaporation of the washed (water) and dried ether extracts yielded an oily residue (0.50 g) which was subjected to preparative t.l.c. [light petroleum–ether (9:1) as the eluant (×2)]. Many bands were detected, but only two yielded significant amounts of products: extraction of the band with R_F 0.16 yielded a semisolid product (0.030 g) which on addition of light petroleum at −20 °C gave pure t-2-(1-*hydroxy*-1-*methylethyl*)-2-*methylcyclohexan*-r-1-*ol* (**19**) (0.008 g) as a solid, m.p. 74—76 °C; $\nu_{max.}$ see Table 4; δ 4.00 (1 H, m, $W_{\frac{1}{2}}$ 18.0 Hz, C*H*OH), and 1.33, 1.15, and 1.03 (9 H, 3 s, 3 CH_3) (Found: C, 69.6; H, 11.45. $C_{10}H_{20}O_2$ requires C, 69.72; H, 11.70%). The mother liquors yielded the *cis*-1,3-diol (**18**) (0.015 g). Extraction of the band with R_F 0.38 yielded the alcohol (**17**) (0.025 g).

Treatment of the Alcohol (**17**) *with* 0.1M-H_2SO_4–MeOH.—The alcohol (**17**) (0.020 g) was added to 0.1M-H_2SO_4 in anhydrous methanol and the resulting mixture was stirred 15 min at room temperature. After dilution with water and extraction with ether, the combined ether extracts were washed (water, saturated aqueous sodium hydrogen carbonate, and water), dried, and evaporated to give pure (**7**) as an oily residue (0.010 g) (g.l.c. and n.m.r.).

Reaction of the Epoxide (**1**) *with Trichloroacetic Acid in Anhydrous Cyclohexane*.—A solution of the epoxide (**1**) (0.52 g, 3.42 mmol) in anhydrous cyclohexane (50 ml) was treated with 1M-solution of trichloroacetic acid in anhydrous cyclohexane (3.80 ml) and the resulting mixture was left overnight at room temperature. The organic solution was washed (saturated aqueous sodium hydrogen carbonate and water), dried, and evaporated: the crude reaction product was dissolved in THF (40 ml), treated with 1M-ethanolic KOH (13 ml) and left at room temperature for 5 h; it was then diluted with water and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded an oily residue (0.51 g) which was subjected to preparative t.l.c. [light petroleum–ether 9:1 was used as the eluant (×2)]. Many bands were detected and successively extracted to give the following: (**15**) (R_F 0.15; 0.040 g), (**17**) (R_F 0.38; 0.060 g), (**9**) (R_F 0.53; 0.015 g), and (**1**) (R_F 0.69; 0.10 g).

2-(1-*Hydroxy*-1-*methylethyl*)-2-*methylcyclohexanone* (**23**).—A stirred solution of (**18**) (0.20 g, 1.16 mmol) in acetone (20 ml) was treated dropwise with Jones reagent[36] (0.29 ml). After 5 min at room temperature, the mixture was diluted with water and extracted with ether. Evaporation of the washed (water, saturated aqueous sodium hydrogen carbonate, and water), and dried ether extracts gave pure (**23**) (0.18 g) as an oil: $\nu_{max.}$ 1 680 cm^{-1}; δ 1.27, 1.23, and 1.10 (9 H, 3 s, 3 Me) (Found: C, 70.92; H, 10.54. $C_{10}H_{18}O_2$ requires C, 70.54; H, 10.65%).

Reduction of the Ketone (**23**) *with* $LiAlH_4$.—A stirred solution of the ketone (**23**) (0.15 g) in anhydrous ether (20 ml) was treated with $LiAlH_4$ (0.15 g) added in small portions, and the resulting suspension was refluxed for 1 h. The mixture was cooled, diluted

with ether, and the excess of hydride decomposed with water and 10% aqueous sodium hydroxide; evaporation of the filtered and dried ether solution gave a solid residue (0.13 g), consisting of a mixture of the two diols (**18**) and (**19**) in the ratio 60:40 (g.l.c.), which was subjected to semipreparative t.l.c. on 0.5 mm layer silica gel plate [light petroleum–ether (7:3) was used as the eluant (×4)]. Extraction (CH_2Cl_2) of the two main bands, the faster moving band contained (**19**), afforded (**18**) (0.030 g) and (**19**) (0.030 g).

2-(1-*Methoxy*-1-*methylethyl*)-2-*methylcyclohexanone* (**24**).—The methoxy alcohol (**10**) (0.20 g, 1.16 mmol) in acetone (20 ml) was treated with Jones reagent[36] (0.28 ml) as previously described for the preparation of (**23**) to give pure (**24**) (0.12 g) as a liquid; $\nu_{max.}$ 1 692 cm^{-1}; δ 3.17 (3 H, s, OMe), 1.17 (6 H, s, Bu^t), and 1.03 (3 H, s, Me) (Found: C, 69.3; H, 11.65. $C_{10}H_{20}O_2$ requires C, 69.72; H, 11.70%).

Reduction of the Ketone (**24**) *with* $LiAlH_4$.—A stirred solution of the ketone (**24**) (0.10 g) in anhydrous ether (10 ml) was treated with $LiAlH_4$ (0.10 g). Work-up gave an oily residue (0.090 g) consisting of the two methoxyalcohols (**10**) and (**11**) in the ratio 66:34 which was subjected to semi-preparative t.l.c. on a 0.5 mm layer silica gel plate [light petroleum was used as the eluant (×10)]. Extraction (CH_2Cl_2) of the two main bands, only slightly separated, the faster moving band contained (**10**), afforded (**10**) (0.045 g), and 2-*methyl*-t-2-(1-*methoxy*-1-*methylethyl*)*cyclohexan*-r-1-*ol* (**11**) (0.020 g) as an oil; $\nu_{max.}$ see Table 4; δ 3.87 (1 H, m, $W_{\frac{1}{2}}$ 16.0 Hz, C*H*OH), 3.22 (3 H, s, OMe), and 1.27, 1.10, and 1.01 (9 H, 3 s, 3 Me) (Found: C, 68.85; H, 12.6. $C_{10}H_{22}O_2$ requires C, 68.91: H, 12.72%).

Reaction of the Epoxide (**1**) *with* $BF_3{\cdot}Et_2O$ *in* CH_2Cl_2.—A solution of the epoxide (**1**) (0.50 g, 3.25 mmol) in anhydrous CH_2Cl_2 (50 ml) was treated at 0 °C with $BF_3{\cdot}Et_2O$ (0.45 ml, 3.55 mmol) and the reaction mixture was further stirred for 60 s at 0 °C and then poured into a separatory funnel containing ice and saturated aqueous sodium hydrogen carbonate. The organic layer was separated, washed (saturated aqueous sodium hydrogen carbonate, and water), filtered, and evaporated to yield an oily residue (0.49 g) consisting of the aldehyde (**8**) (26%), the ketone (**9**) (3%), and the two isopropenyl alcohols *cis* (**12**) (36%) and *trans* (**13**) (35%, see below) (g.l.c.). This crude reaction product was subjected to preparative t.l.c. [a 95:5 mixture of light petroleum and ether was used as the eluant (×2)]; extraction of the three main bands, the faster moving band contained (**8**) and the slower one contained (**13**), afforded (**8**) (0.070 g), (**12**) (0.080 g) and t-2-*isopropenyl*-2-*methylcyclohexan*-r-1-*ol* (**13**) (0.060 g) as a liquid; $\nu_{max.}$ 3 378 cm^{-1}; δ 5.00 (2 H, s, $=CH_2$), 3.73 (1 H, m, $W_{\frac{1}{2}}$ 15.0 Hz, C*H*OH), 1.83 (3 H, s, CH_3-C=), and 1.07 (3 H, s, Me) (Found: C, 77.55; H, 11.45 $C_{10}H_{18}O$ requires C, 77.86; H, 11.76%).

2-*Isopropenyl*-2-*methylcyclohexanone* (**25**).—Treatment of a stirred solution of the alcohol (**12**) (0.040 g) in acetone (5 ml) with Jones reagent,[36] gave, after work-up as described above for the preparation of (**23**), an oily residue (0.020 g) consisting of pure (**25**); $\nu_{max.}$ 1 712 cm^{-1}; δ 5.00, 4.80 (2 H, 2 s, $=CH_2$), 1.70 (3 H, s, Me-C=), and 1.10 (3 H, s, Me). A sample of (**25**) was added to a EtOH–H_2SO_4 solution of 2,4-dinitrophenylhydrazine[37] affording the 2,4-DNP of (**25**), m.p. 135—136 °C (Found: C, 54.2; H, 5.75; N, 16.25. $C_{16}H_{20}N_4O_4$ requires C, 54.85; H, 5.71; N, 16.00%).

Analogous treatment of (**13**) (0.040 g) yielded a crude product (0.018 g) which was shown to be the ketone (**25**).

Hydroxymercuriation–demercuriation of (**12**).—A solution of the alcohol (**12**) (0.060 g, 0.39 mmol) in a 1:1 (v/v) THF–water was treated with $Hg(CF_3CO_2)_2$ (0.179 g, 0.42 mmol) and stirred at room temperature 24 h. Then 4M-aqueous sodium hydroxide (0.6 ml) and $NaBH_4$ (0.050 g) were added and stirring was continued for 10 min; the reaction mixture was diluted with water and extracted with ether. Evaporation of the washed (water) and dried ether extracts yielded an oily residue (0.040 g) consisting of the *cis*-1,3-diol (**18**) together with the starting product (n.m.r. and g.l.c.).

Analogous treatment of (**13**) afforded a crude reaction product consisting of *trans* 1,3-diol (**19**) and the starting material (n.m.r. and g.l.c.).

Acid-catalysed Reactions of the Epoxide (**1**) *in Water and Methanol.*—A suspension (water) or a solution (methanol) of the oxide (**1**) (0.10 g, 0.64 mmol) in a 0.1M-solution of the acid (H_2SO_4) in the solvent (10 ml) was stirred at 25 °C for 24 h (reaction in water), and 15 min (reaction in methanol), quenched with solid sodium hydrogen carbonate and saturated aqueous sodium hydrogen carbonate, and thoroughly extracted with ether. Evaporation of the washed (water) ether extracts yielded mixtures consisting of the *trans* 1,2,-diol (**15**), the *cis* 1,3-diol (**18**), and the *trans* 1,3-diol (**19**) (reaction in water), and of the *trans* 1,2-hydroxy-ethers (**5**) and (**6**), the 1,3-hydroxy-ethers *cis* (**10**) and *trans* (**11**) (reaction in methanol), together with differing amounts of the rearrangement and non-addition products (**8**), (**9**), (**12**), (**13**), and (**17**) (reaction in water), and (**7**), (**8**), (**9**), (**12**), (**13**), and (**14**) (reaction in methanol) which were analysed by g.l.c. (see Tables 2 and 3). The reaction of the oxide (**1**) in methanol was also performed in the presence of anhydrous $LiClO_4$ (0.5M) using toluene-*p*-sulphonic acid monohydrate as the acid, to give the results shown in Table 2.

The solvolysis addition products and the rearrangement and the non-addition products of these reactions were completely stable under the reaction conditions used.

Reaction of the Epoxide (**1**) *with Methanol in* CH_2Cl_2 *in the Presence of Toluene*-p-*sulphonic Acid.*—The epoxide (**1**) (0.30 g, 1.94 mmol) was dissolved in a solution of toluene-*p*-sulphonic acid monohydrate and methanol in a molar ratio (epoxide/acid/methanol) of 1:0.1:6 in anhydrous CH_2Cl_2 (30 ml) at 25 °C. The resulting mixture was left 15 min at the same temperature and then treated with solid sodium hydrogen carbonate and saturated aqueous sodium hydrogen carbonate. Evaporation of the washed (water) and filtered organic solution gave an oily residue (0.29 g) which was analysed by g.l.c. (see Table 2) and at the same time subjected to preparative t.l.c. [light petroleum–ether (9:1) was used as the eluant (×2)]. Extraction (CH_2Cl_2) of the two well separated bands, the faster moving band contained (**7**), afforded (**7**) (0.050 g) and (**14**) (0.035 g).

Reactions of the Epoxide (**1**) *with Trichloroacetic acid in Various Solvents.*—The reactions were carried out in anhydrous benzene, cyclohexane, carbon tetrachloride, chloroform, and methylene dichloride in the following way. A solution of the epoxide (**1**) (0.10 g, 0.64 mmol) in the solvent (10 ml) at 25 °C was treated with a 1M-solution of trichloroacetic acid in the same solvent (0.71 ml), and stirred for 3 h (reaction in cyclohexane and carbon tetrachloride), for 30 min (reaction in benzene and chloroform) and for 15 min (reaction in methylene dichloride) at the same temperature. Evaporation of the washed (saturated aqueous sodium hydrogen carbonate, and water) organic solution yielded crude products consisting of mixtures of monotrichloroacetates of 1,2- and 1,3-diols (not detected by g.l.c.) and of the rearrangement and non-addition products (**8**), (**9**), (**12**), (**13**), (**17**), and (**20**) which were analysed by g.l.c. The 1,2-diols, (**15**) and (**16**), and the 1,3-diols, (**18**) and (**19**), were determined only after hydrolysis of the corresponding

monotrichloroacetates which was carried out in the following way. The trichloroacetolysis crude product was dissolved in freshly distilled THF (8 ml), treated with 1M-KOH in ethanol (2.5 ml), and left 5 h at room temperature. Dilution with water, extraction with ether and evaporation of the washed (water) and dried ether extracts yielded a mixture of (**15**), (**16**), (**18**), and (**19**) together with the rearrangement products above mentioned, partly decomposed by the alkaline conditions used in the hydrolysis (g.l.c.). The relative ratio between (**18**) and (**19**) was not calculated in the case of the reaction carried out in cyclohexane, carbon tetrachloride, benzene, and chloroform owing to their too small overall amounts: in these cases only the total amounts of (**18**) and (**19**) are reported in Table 3. The reaction of the epoxide (**1**) in each solvent carried out under the same conditions, but stopping after a longer reaction time of contact with the acid, yielded the same product composition within the experimental error. Experiments were carried out in order to verify if the diols (**15**), (**16**), (**18**), and (**19**) are stable under the saponification conditions and if the method of saponification used does not alter the stereoselectivity of the reactions.

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