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STUDIES ON THE PINACOL REARRANGEMENT—V

THE REARRANGEMENTS OF *cis*- AND *trans*-1,2-DIPHENYL-1,2-DITOLYLETHYLENE OXIDES[1]

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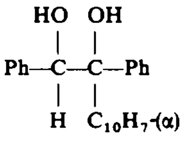
Abstract—The intermediate formation of the two epoxides was observed in the perchloric acid-catalysed rearrangement of *meso*-2,2′-dimethylbenzpinacol (P_{meso}) to 2-methylbenzoyl tolyl diphenyl methane (K) Two kinds of epoxides were separated with preparative TLC and the configuration (*cis* and *trans*) of these epoxides was inferred in the light of UV, NMR and IR spectra, dipole moment and kinetic data. The rearrangement rates of these epoxides were measured in $HClO_4$-anhydrous acetic acid. Linear correlations of logarithm of the rate constants (log k) with the Hammett acidity function of the medium (H_0) were obtained, which supports the A-1 mechanism, together with the large positive values of the entropy of activation. It is shown that the perchloric acid-catalysed rearrangement of *meso*-2,2′-dimethylbenzpinacol (P_{meso}) occurs via such many kinetically distinguishable routes as the following:

$$\begin{tikzcd}
P_{meso} \arrow[r] \arrow[rr, bend left] \arrow[rrr, bend right] & C \arrow[r] \arrow[rr, bend right] & T \arrow[r] & K
\end{tikzcd}$$

where C and T are *cis*- and *trans*-epoxide respectively. The mechanisms of the rearrangements were discussed from the data of kinetics.

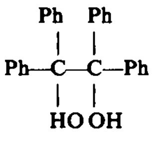
IN ITS gross aspects, the mechanism of the pinacol and related rearrangement is established.[2] However, numerous problems remain to be solved, which have been reported in preceding papers.[3] In part IV, the rearrangements of *meso*- and DL-2,2′-dimethoxybenzpinacols have been investigated with respect to the character of the intermediate, the reaction processes and the migration aptitudes.

The role of the epoxide intermediate in the pinacol rearrangement has been discussed by Wheland[4] who concluded that the epoxide does not play an essential role. The only two examples in which the stable epoxide was recognized were the rearrangements of *erythro*-1-α-naphthyl-1,2-diphenylethylene glycol (I)[5] and benzpinacol (II).[6]



$$\begin{array}{ccccc} & HO & & OH & \\ & | & & | & \\ Ph- & C & - & C & -Ph \\ & | & & | & \\ & H & & C_{10}H_7\text{-}(\alpha) & \end{array}$$

I

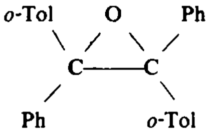


$$\begin{array}{ccccc} & Ph & & Ph & \\ & | & & | & \\ Ph- & C & - & C & -Ph \\ & | & & | & \\ & HO & & OH & \end{array}$$

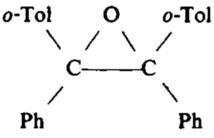
II

The present paper records the formation of stable epoxide intermediates in the rearrangement of *meso*-2,2′-dimethylbenzpinacol and the results of kinetic study of the rearrangements of these epoxides in anhydrous acetic acid with perchloric acid as catalyst.

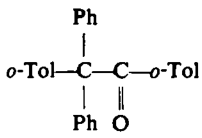
Products. The perchloric acid-catalyzed reaction of *meso*-2,2′-dimethylbenzpinacol gave two epoxides (III and IV) and pinacolone (V).



III



IV



V

The thin layer chromatogram of the reaction products is shown in Fig. 1. The assignment of the configuration (*cis* or *trans*) to these epoxides (A; $R_f = 0{\cdot}64$, B; $R_f = 0{\cdot}56$)

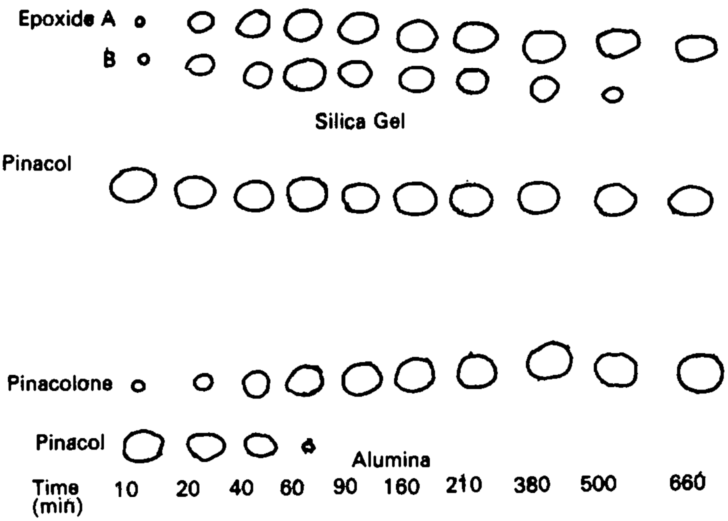


FIG. 1 The thin layer chromatogram of the reaction products of *meso*-2,2′-dimethylbenzpinacol (0·00942 mole) in $2{\cdot}64 \times 10^{-4}$ mole-$HClO_4$-acetic acid at 72°. Developer: Benzene + Hexane (1:2)

TABLE 1. IR, UV, NMR AND DIPOLE MOMENT DATA OF *cis*- AND *trans*-EPOXIDE

	R_f' [a]	IR C—O—C (cm^{-1})			UV[b]		Dipole moment[c]	NMR[d] δ Me proton
		8 μ	11 μ	12 μ	λ_{max}	$\varepsilon \times 10^{-2}$		
A	0·64	1244	895	802	300 290	3·32 3·27	1·52 D	2·54 ppm
B	0·56	1235	889	794	264	13·0	1·60 D	2·23 ppm

[a] Silica Gel G. Developer-benzene-hexane = 1:2.

[b] In EtOH soln.

[c] In benzene at 30°.

[d] In CCl_4. TMS as internal standard.

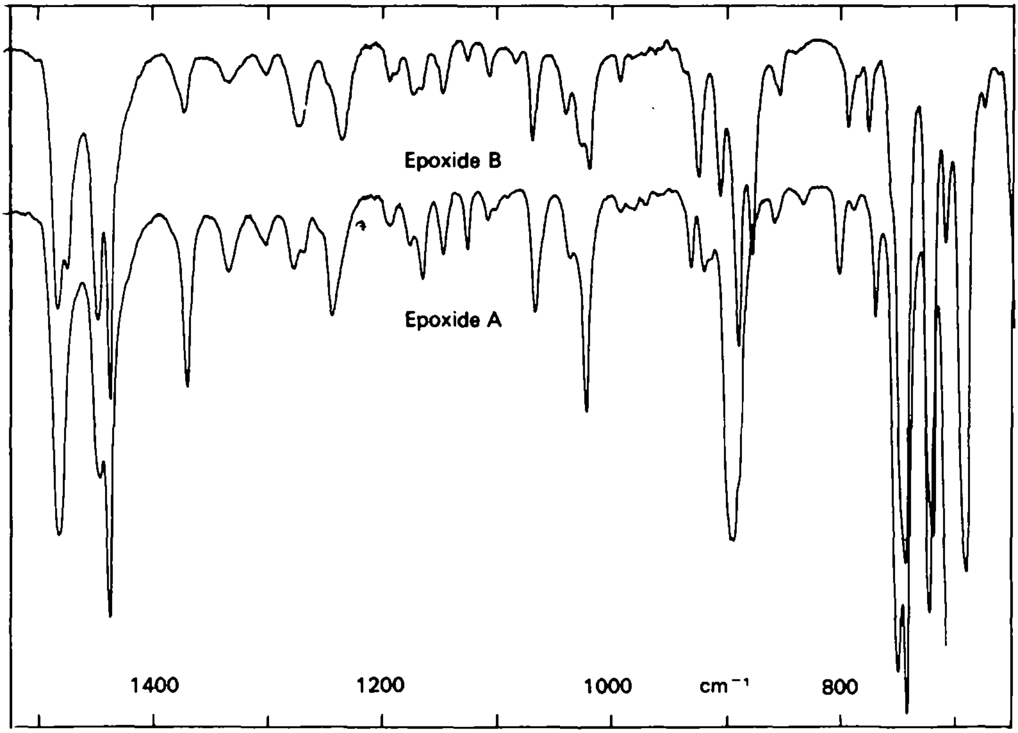


FIG. 2 IR spectra of *cis*- and *trans*-1,2-diphenyl-1,2-ditolylethylene oxides

was carried out as following. Fig. 2, Fig. 3 and Fig. 4 show IR, NMR and UV spectra of the epoxides A and B respectively. The characteristic values obtained from the above spectra are summarized in Table 1 together with the data from dipole moments.

The molecular models (Lapine Leybold models) of *cis*- and *trans*-1,2-ditolyl-1,2-diphenylethylene oxide are shown below. The other conformers show the magnitude of steric interaction and can not be constructed with this model. The examination of the molecular models indicates Me–Me steric repulsion in the *cis*-epoxide, which enforces the Me group to the more diamagnetic region compared with the *trans*. Then, the signal of the Me protons of the *cis*-isomer would be in the higher field relative to that of the *trans*-isomer.

On the other hand, the parallel arrangement of two 1,2-benzene rings of *o*-tolyl groups are distorted in the *cis*-isomer compared to that in the *trans*-isomer due to Me–Me repulsion (figures of the molecular models), which may cause a smaller negative contribution of the *o*-tolyl groups to the dipole moment of the oxirane ring. The observed difference of 0·08 Debye (experimental error $< \pm 0{\cdot}02$ Debye) coincides with the above argument.

The same Me–Me interaction would decrease conjugation of oxirane ring with

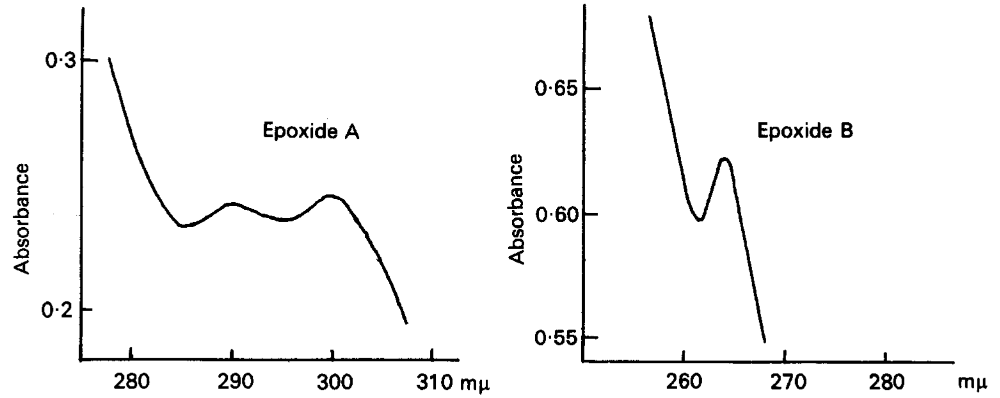


FIG. 4 UV spectra of *cis*- and *trans*-1,2-diphenyl-1,2-ditolyl-ethylene oxide in ethanol.

o-tolyl and phenyl in the *cis*-isomer in comparison with the *trans* and therefore the observed hypsochromic shift of the absorption maximum of the *cis*-isomer with respect to the *trans* would be rationalized.* A similar trend of spectrometric behaviour was reported with *cis*- and *trans*-stilbene, i.e. it is known that the hypsochromic shift of the absorption maximum of *cis*-stilbene with respect to the corresponding *trans*-isomer is due to the decrease of conjugation in the former, because the ortho H atoms would overlap.[7]

Finally, it is known that the characteristic absorption bands of C—O bond of the *cis*-epoxide appear in the regions of longer wave length with respect to the *trans*-epoxide.[8] Thus, all the data in Table 1 suggest that the epoxide A is *trans* in configuration and the epoxide B *cis*.

Although the above discussion is only qualitative the data are consistent with the chemical transformation of the epoxide B into A which suggests A to be the more stable isomer of the pair. The conclusive assignment of the configuration depends on a complete X-ray analysis.

Kinetic study. The pinacol rearrangements studied hitherto show the first order kinetics[9] but this could not be confirmed experimentally for the reaction of 2,2′-dimethylbenzpinacol because of the difficulty of the quantitative analysis of the pinacol.[1] The present communication, therefore, records the results of the kinetic study of the rearrangements of *cis*-(C)- and *trans*-(T)-1,2-diphenyl-1,2-ditolylethylene oxide and the role of the epoxide intermediates in the rearrangement of *meso*-2,2′-dimethylbenzpinacol.

The first order kinetics was observed in the rearrangements of the *cis*- and *trans*-epoxides as indicated in Fig. 5. Table 2 summarizes the effect of the catalyst concentration upon the rate constants k_C (*cis*-isomer) and k_T, (*trans*-isomer). The plots of the Hammett acidity function H_0 values[10] against log *k* (shown in Table 2) are straight lines with slopes 0·70 and 0·86 for the *cis*- and *trans*-isomer respectively (Fig. 6),

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* The possibility of steric inhibition of methyl hyperconjugation might be still uncertain.

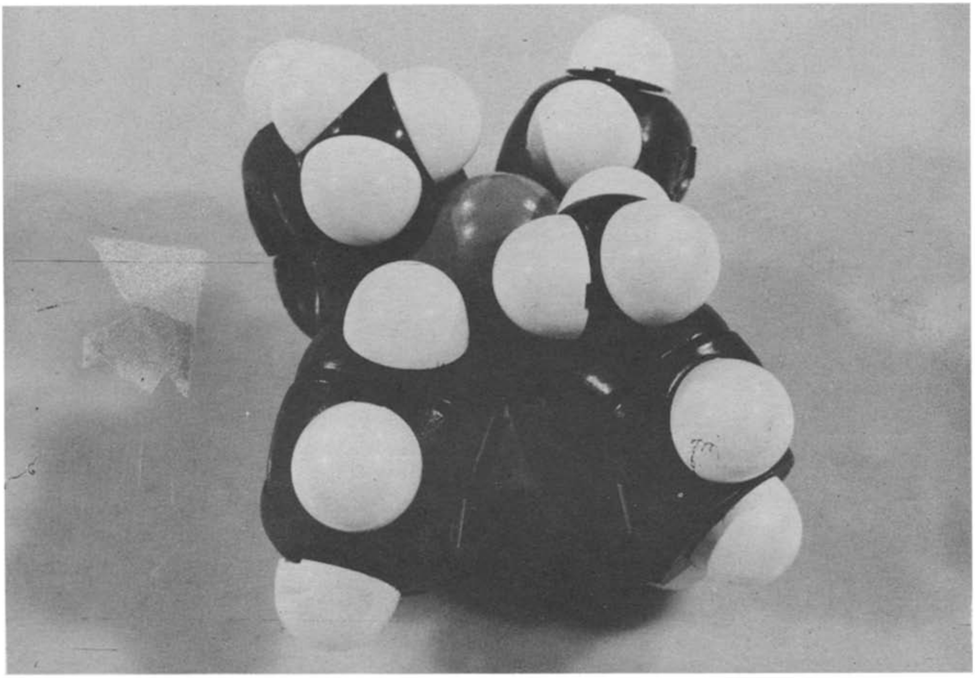


FIG. A *trans*-form.

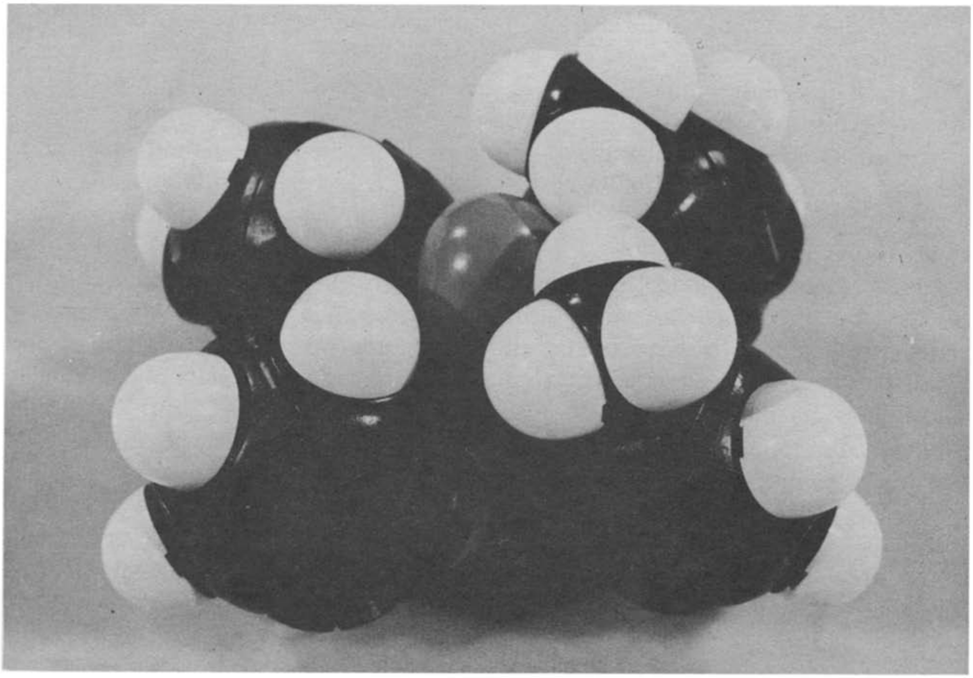
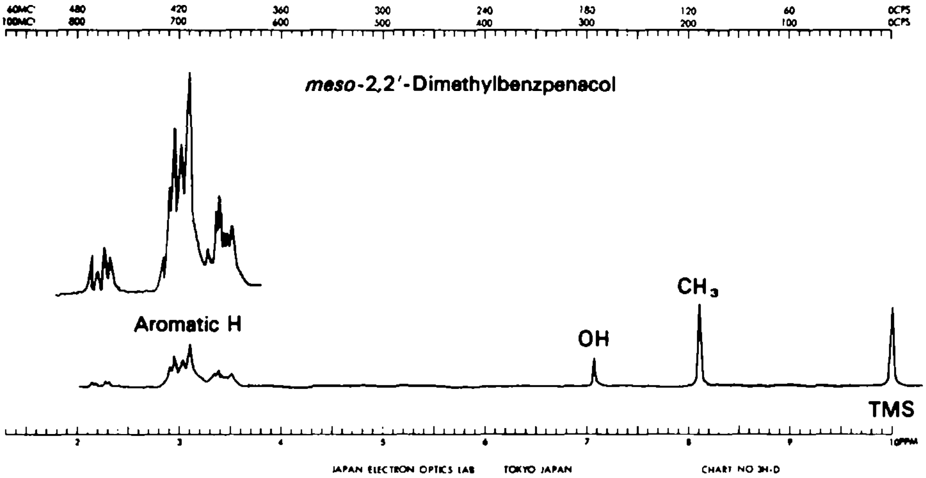


FIG. B *cis*-form.



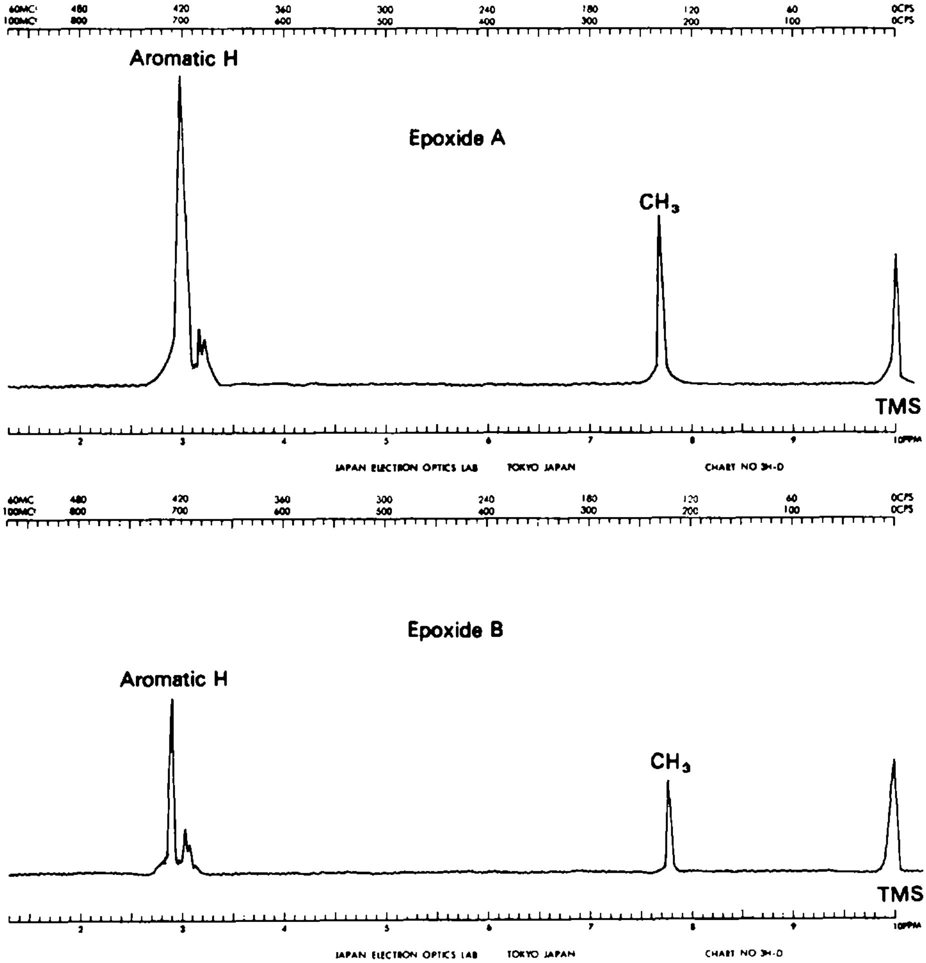


FIG. 3 PMR spectra of *cis*- and *trans*-1,2-diphenyl-1,2-ditolylethylene oxide in carbon tetrachloride.

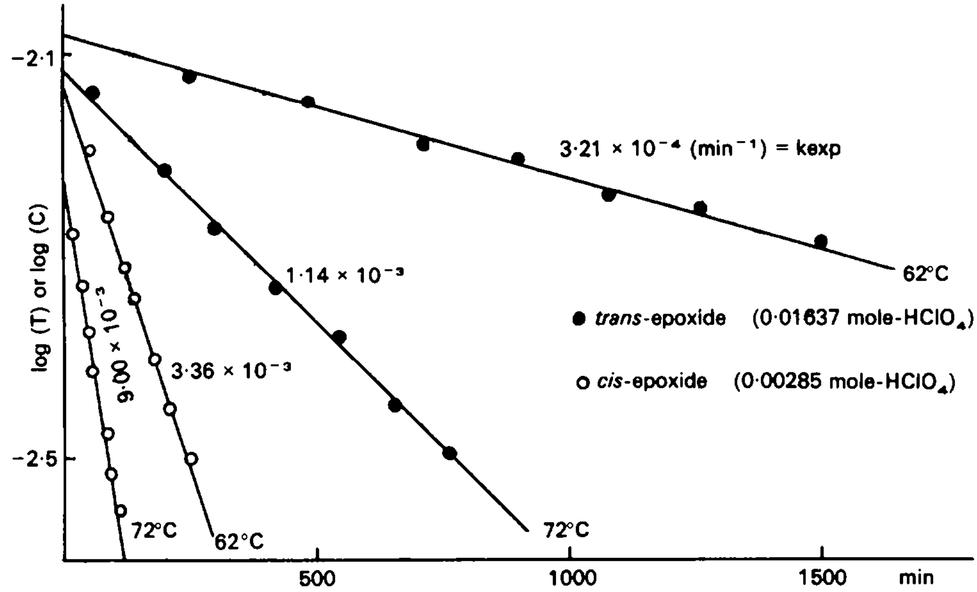


FIG. 5 The slopes of the straight lines obtained by plotting log (C) or log (T) vs. time (min) in the reaction of *cis*- and *trans*-1,2-diphenyl-1,2-ditolylethylene oxide.

which supports the A-1 mechanism according to the Zucker–Hammett hypothesis[11] together with the large positive values of the entropy of activation described below.

Mechanism. The thin layer chromatogram of the reaction products of the epoxides shows that the isomerization is from the *cis*-isomer to the *trans*- and not from the

TABLE 2. DATA OF KINETICS FOR THE PERCHLORIC ACID-CATALYSED REARRANGEMENT OF *cis*- AND *trans*-1,2-DIPHENYL-1,2-DITOLYLETHYLENE OXIDES IN ANHYDROUS ACETIC ACID AT 72°

$HClO_4$ mol × 10^3	H_0	$k \times 10^3$ min^{-1}	log *k*
		cis	
0·769	−1·00	3·37	−2·47
1·43	−0·71	5·79	−2·24
2·85	−0·41	9·00	−2·05
6·45	−0·03	17·8	−1·75
9·55	+0·15	22·2	−1·65
		trans	
2·15	−0·63	0·146	−3·84
2·72	−0·40	0·242	−3·61
4·54	−0·19	0·343	−3·47
6·45	−0·03	0·519	−3·29
9·55	+0·15	0·676	−3·17
16·37	+0·39	1·14	−2·94

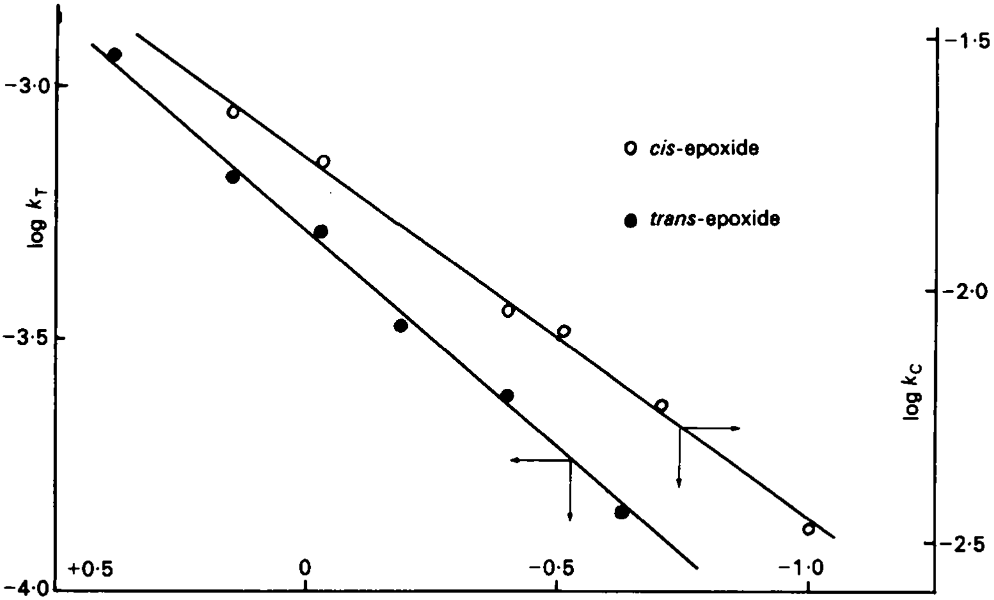


FIG. 6 Correlation of first order rate constant with the Hammett acidity function of the medium at 72°

trans to the *cis* and that both epoxides do not revert to the pinacol. Therefore, it is inferred that the rearrangement of the *cis*-epoxide occurs by two kinetically distinguishable routes as follows:

$$C \xrightarrow{k_1} T \xrightarrow{k_2} K \qquad k_T = k_2$$
$$C \xrightarrow{k_3} K \qquad k_C = k_1 + l_3$$

C, T and K are the *cis*-epoxide, the *trans*-epoxide and the pinacolone respectively.

The mathematical treatment of irreversible first order consecutive reaction C→T→K is here modified to allow for the competing simple reaction C→K. The fundamental equations are:

$$-\mathrm{d(C)}/\mathrm{d}t = k_1(\mathrm{C}) + k_3(\mathrm{C}) \qquad (1)$$

$$\mathrm{d(T)}/\mathrm{d}t = k_1(\mathrm{C}) - k_2(\mathrm{T}) \qquad (2)$$

Substitution in (2) of the value for (C) obtained by the integration of (1) yields:

$$\mathrm{d(T)}/\mathrm{d}t + k_2(\mathrm{T}) = k_1(\mathrm{C})_0 e \exp\left[-(k_1 + k_3)t\right] \qquad (3)$$

The integration of (3) and evaluation of the constant of integration for the condition that (T) = 0 when $t = 0$ yields:

$$(\mathrm{T}) = (\mathrm{C})_0 k_1/(k_2 - k_1 - k_3) \times \{e \exp\left[-(k_1 + k_3)t\right] - e \exp(-k_2 t)\} \qquad (4)$$

i.e.

$$k_1 = (\mathrm{T})/e\{\exp[-(k_1 + k_3)t] - \exp(-k_2 t)(\mathrm{C})_0\} \times (k_2 - k_1 - k_3) \qquad (5)$$

On the assumption that $k_C = k_1 + k_3$, it is possible to evaluate k_1 and k_3 with the aid of (5) and experimentally available values of k_C, $k_2 = k_T$, $(\mathrm{C})_0$ and (T). Table 3 summarizes the values of the experimental activation energy E_a, and of the free energy $\Delta F^\ddagger$ and entropy $\Delta S^\ddagger$ of activation calculated from the values of k'_1, k'_3, k'_C and k'_T, where $k' = k_{exp}/(\mathrm{HClO_4})$. According to Table 3, it is known that the *cis*-isomer rearranges 4·4 times faster than it isomerizes to the *trans*-isomer and also the *cis*-isomer rearranges about 49 times faster than the *trans*-isomer. The above results suggest two possible mechanisms.

TABLE 3. THERMODYNAMICS OF ACTIVATION FOR REACTION OF *cis*- AND *trans*-1,2-DIPHENYL-1,2-DITOLYL ETHYLENE OXIDE IN ANHYDROUS ACETIC ACID

Rate constant	Temp °C	Specific rate l/mol·min 10^2	E_a kcal/mol	$\Delta S^\ddagger$ e.u.	$\Delta F^\ddagger$ kcal/mol
$k'_2(k'_T)$	62	1·96			
	72	6·95	32·1	18·8	25·0
	82	28·1			
k'_C	62	118			
	72	405	31·2	24·2	22·1
	82	1580			
k'_1	62	21·8			
	72	76·7	31·8	22·6	23·4
k'_3	62	96·4			
	72	328	31·0	23·2	22·2

(i) The first possible mechanism can be represented as follows:

$$\mathrm{C} + \mathrm{H}^+ \rightleftharpoons \mathrm{CH}^+ \quad \text{(equilibrium)} \qquad (6)$$

$$\mathrm{T} + \mathrm{H}^+ \rightleftharpoons \mathrm{TH}^+ \quad \text{(equilibrium)} \qquad (7)$$

$$\mathrm{CH}^+ \xrightarrow{k_4} \mathrm{R}^+ \quad \text{(slow)} \qquad (8)$$

$$\mathrm{R}^+ \xrightarrow{k_{-4}} \mathrm{CH}^+ \quad \text{(slow)} \qquad (9)$$

$$\mathrm{TH}^+ \xrightarrow{k_5} \mathrm{R}^+ \quad \text{(slow)} \qquad (10)$$

$$\mathrm{R}^+ \xrightarrow{k_{-5}} \mathrm{TH}^+ \quad \text{(fast)} \qquad (11)$$

$$\mathrm{R}^+ \xrightarrow{k_6} \mathrm{K} + \mathrm{H}^+ \quad \text{(fast)} \qquad (12)$$

$$\mathrm{R}^+ + \mathrm{H_2O} \xrightarrow{k_7} \mathrm{PH}^+ \quad \text{(very slow)} \qquad (13)$$

To bring this formulation into conformity with the kinetics, it is necessary that $k_6 > k_{-5} \gg k_{-4} > k_7$ and $k_4 \gg k_5$. Here it is assumed that the unrearranged carbonium ion R^+ is a common intermediate of sufficient stability to require additional small activation energies for the formation of TH^+. (cf. Ref. 3*c*).

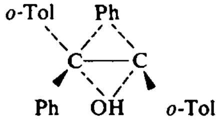
(ii) An alternate possibility that the rearrangement occurs without the formation of a carbonium ion intermediate may be represented by replacing equations 8–13 with the following:

$$TH^+ \rightarrow [L^+] \rightarrow K + H^+ \tag{14}$$

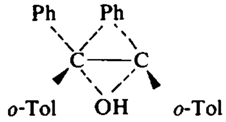
$$CH^+ \rightarrow [M^+] \rightarrow K + H^+ \tag{15}$$

$$CH^+ \rightarrow R^+ \rightarrow TH^+ \tag{16}$$

The transition complexes $[L^+]$ and $[M^+]$ would be represented by the following, and the reactions might be expected to show some evidence of neighbouring group participation. Even in this mechanism, however, the isomerization of the *cis*- epoxide to the *trans*-epoxide must be interpreted by a carbonium ion mechanism.



$[L^+]$

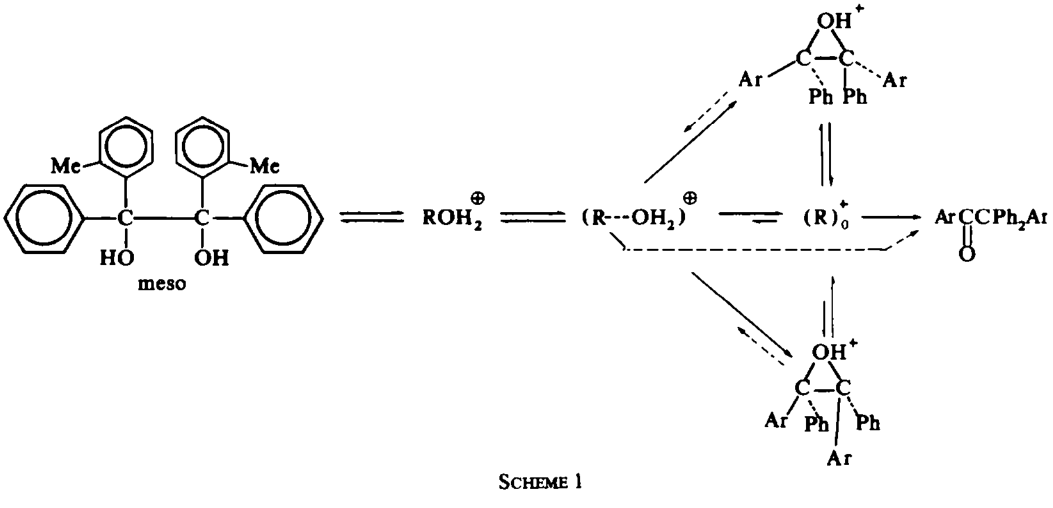


$[M^+]$

In view of the generalization that neighbouring group participation is apt to decrease with increasing phenyl substitution of the C atom at which heterolysis occurs,[12] and in view of the large positive values of $\Delta S^\ddagger$ and the occurence of isomerization, it is expected that the contribution of mechanism (i) is more important than (ii) and therefore the classical carbonium ion is an intermediate in these processes.

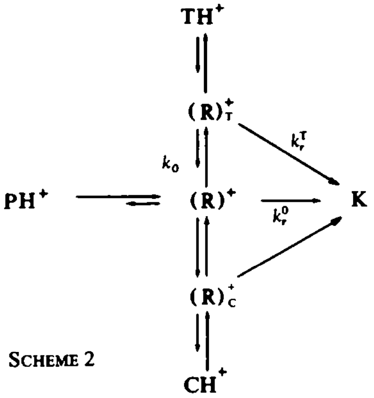
The high susceptibility to acid-catalysed hydration to the glycol which is characteristic of the phenyl substituted ethylene oxides[13] and the complete failure of the reaction in the present case suggest serious steric retardation in the hydration. The difference in the values of $\Delta S^\ddagger$ of the *cis*- and *trans*-epoxide would be ascribed to the difference in strain relief of the *cis*- and *trans*-isomer in the carbonium ion formation, which is consistent with the assignment of configuration described above.

The acid-catalysed rearrangement of *meso*-2,2'-dimethyl-benzopinacol, consequently, would be explained by the following scheme where $(R \cdots OH_2)^+$ represent



SCHEME 1

conformers of the tight carbonium aggregate in which, as postulated in the previous paper,[1] the original *meso* configuration is retained and the R···OH$_2$ bond is lengthened sufficiently to enable the rotation about the central C—C bond. The absence of the isomerisation of the *trans*-epoxide to the *cis* shows that the transformation $(R)_0^+ \rightarrow$ *cis*-epoxide is a very slow step ($k_{-5} > k_{-4}$).*



SCHEME 2

(*cis* or *trans* configuration respectively) are supposed to be retained.

In conclusion, the relative importance of the epoxide formation would be due to such factors as the degree of steric condensation in the pinacol molecule, the degree of participation of C—Ar and C—OH on the formation of the pinacolone and epoxide formed under the reaction condition.

EXPERIMENTAL

Materials. Anhydrous AcOH was obtained by the method described.[1] A comparison of the signals of the NMR in the high field (ca. 2·3 ppm) with those of the *meso*- and DL-2,2′-dialkoxybenzpinacols suggests that the present pinacol is *meso* in configuration (see Ref. 3*c* and Fig. 3). cis- (*C*) *and* trans- (T) 1,2-*Diphenyl*-1,2-*ditolylethylene oxides* were obtained by preparative TLC of the epoxides formed in the perchloric acid catalysed reaction of 2,2′-dimethylbenzpinacol. The chromatoplates used were prepared with silica gel G and uranine aqueous soln (0·04 %). A mixture of benzene and hexane (1 : 2) was used as developer and the epoxides analysed. (i) R_f = 0·64 (A), m.p. 160–161°. (Found: C, 89·47; H, 6·70. Calc. for $C_{28}H_{24}O$: C, 89·32; H, 6·43 %); (ii) R_f = 0·56 (B), m.p. 176–177°. (Found: C, 89·53; H, 6·48. Calc. for $C_{28}H_{24}O$: C, 89·32; H, 6·43 %).

The preparation of the standard stock soln of perchloric acid has been described.[1]

Analytical methods. The ordinary method by which the pinacol is estimated (oxidation with lead tetraacetate) could not be employed, because *meso*-2,2′-dimethylbenzpinacol is not oxidized quantitatively with lead tetraacetate.[3c] Therefore, in the case of the *trans*-epoxide which directly rearranges to the pinacolone, the ketone was estimated by measuring the optical density in a 1·00 cm quartz cell at a wavelength of 3290 Å. The soln required was obtained by diluting 2·00 ml of the reaction mixture to 10·00 ml with t-BuOH. The linear correlation of the optical densities with the concentrations of the ketone was obtained in the same solvent mixture. Thus, the epoxide was estimated by calculation. In the case of the *cis*-epoxide which is accompanied by formation of the *trans*-epoxide in the rearrangement, a 0·400 ml sample of the soln to be analysed by TLC and the fraction of the *cis*-epoxide was extracted with chloroform (10·00 ml) and the optical density of this soln at 2630 Å was measured. The concentration of the *cis*-epoxide in the soln was obtained with aid of the calibration line. The pinacolone was estimated by the same method as in the *trans*-epoxide, and then the concentration of the *cis*-isomer was obtained by calculation.

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* The absence of the isomerization from the *trans*-epoxide to the *cis*, however, could be explained in another way if it is assumed to be $k_r^T > k_0$ or $k_r^T > k_r^0$ and if the stereochemical identity of $(R)_C^+$ or $(R)_T^+$

Reaction rate measurement. The flask which contained the anhyd AcOH soln of the epoxide (ca. 0·01 mole) was immersed in an oil bath, the temp of which could be controlled to ±0·05°, and after 30 min, a measured volume of the catalyst was added. At appropriate times, samples were pipetted out and put into test-tubes containing 0·002 ml of conc KOAc soln. Neutralisation of the perchloric acid immediately stopped the reaction. The samples were cooled to room temp (ca. 25°) and analysed. Reaction rate constants were evaluated by the graphical method.

Spectra. The PMR of the epoxides and pinacol were observed by use of a Japan Electron Optics Lab. Model JNM-3H60 Spectrometer (60 Mc). The IR spectra were measured in KBr using a Japan Spectroscopic Model DS-402G Infrared Spectrophotometer. The UV spectra and optical densities were obtained on a Shimadzu QR-50 Spectrophotometer. The dielectric constants were measured by the heterodyne beat method with an apparatus[14] of Koizumi Laboratory (The Institute for Chemical Research, Kyoto University). The dipole moments were calculated by the Halverstadt–Kumler method.[15]

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