
學位論文

松本澄

主 論 文

Studies on the Pinacol Rearrangement

第一節. Studies on the Pinacol Rearrangement. IV.
The Kinetics and Mechanism of the Rearrangement of
meso- and dl-2,2'-Dimethoxybenzopinacol

第二節. Studies on the Pinacol Rearrangement. V.
The Rearrangements of cis- and trans-1,2-Diphenyl-
1,2-ditolylethylene oxides

主 論 文

第 一 部

Studies of the Pinacol Rearrangement. IV.^{*1} The
Kinetics and Mechanism of the Rearrangement of meso-
and dl-2,2'-Dimethoxybenzopinacol

Kiyoshi MATSUMOTO

Department of Chemistry, Faculty of Science,
Kyoto University, Sakyo-ku, Kyoto.

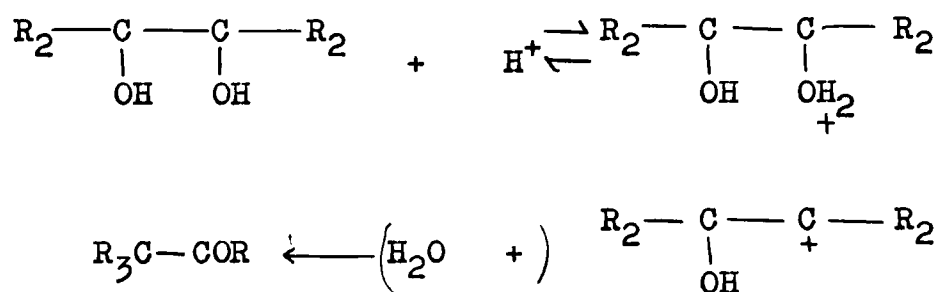
(Received October 6, 1967)

The first-order rate constants of the perchloric acid-catalyzed rearrangements of the meso- and dl-2,2'-dimethoxybenzopinacols were measured in anhydrous acetic acid. A linear correlation of the logarithm of the first-order rate constants ($\log k$) with Hammett acidity function (H_0) was obtained in each case. The large positive values of the entropy of activation support the A-1 mechanism, which is also supported by the linearities of $\log k$ with H_0 , suggesting that the classical carbonium ion is an intermediate in these processes. The migration aptitude of the meso-isomer decreases with time, while that of dl

^{*1} Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967. Part III: K. Matsumoto, R. Goto, T. Asano and H. Wada, Nippon Kagaku Zasshi(J. Chem. Soc. Japan, Pure Chem. Sect.), 88, 92 (1967).

increases. On the basis of this information, the mechanism of the rearrangement was discussed.

The pinacol rearrangement is one of the most classical reactions, therefore, a large amount of information about it and about related rearrangements has been reported.¹⁾ Collins has reviewed the evidence on the mechanisms of the pinacol rearrangement and has concluded that it supports the general scheme:



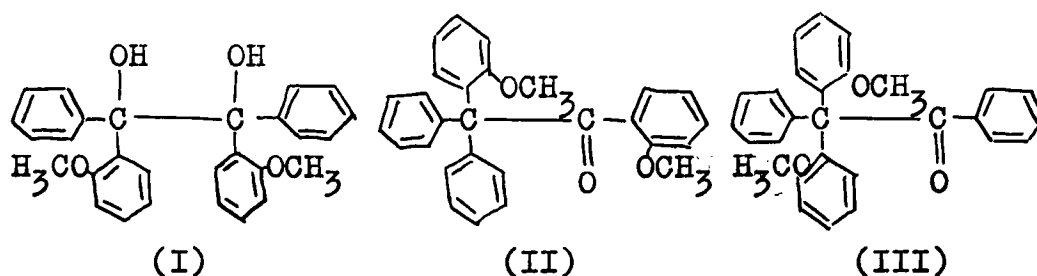
However, there are numerous detailed aspects of these reactions which have been inadequately investigated.²⁾ The kinetics of the reactions of the tetraarylpinacols have received particularly little attention except for the

1) For an excellent review of the pinacol rearrangement, see C. J. Collins, Quart. Review, 14 357 (1960).

2) a) R. Goto, K. Matsumoto and A. Sera, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.), 87, 93 (1966). b) ibid., 87, 1076 (1966). c) ibid., 88, 92 (1967).

rearrangement of the benzopinacol.³⁾

The present communication will present our findings on the kinetics of the rearrangements of the meso- and dl-2,2'-dimethoxybenzopinacols (I) to the 2-methoxybenzoyl-2-methoxyphenyldiphenylmethane (II) and benzoyldi-2-methoxyphenylphenylmethane (III) in anhydrous acetic acid, with perchloric acid as the catalyst.



Experimental

Materials. Anhydrous Acetic Acid; Glacial acetic acid (commercial, extra pure) was refluxed with acetic anhydride and distilled through a 1-m column packed with glass tubes (1 cm long). The first 20% of the distillate was rejected, and the fraction of the 117.0—118.3°C boiling range was collected. This fraction was redistilled, after which the fraction of the 117.8—118.1°C boiling range was collected.

³⁾ H. J. Gebhart and K. H. Adams, J. Am. Chem. Soc., 76, 3925 (1954).

The methods of preparing and purifying meso- and dl-2,2'-dimethoxybenzopinacol have already been reported.^{2c)}

A standard stock solution of perchloric acid was prepared by the addition of 1.00 ml of a 70—72% reagent grade commercial product to approximately 200 ml of anhydrous acetic acid containing a stoichiometric amount of the redistilled acetic anhydride required to react with the water of the aqueous perchloric acid. The solution was then standardized by titration with a standard solution (0.0500 N) of sodium acetate in glacial acetic acid, using bromophenol blue as an indicator.⁴⁾

Analytical Method. Since the oxidation method with lead tetraacetate is not accurate for 2,2'-disubstituted-benzopinacol,^{2c)} the optical densities of the pinacolones were measured and the concentration of the pinacol remaining was calculated.

Reaction-rate Measurements. A reaction flask containing about 0.01 M of a pinacol solution was immersed in a thermostated oil bath. After half an hour, a measured volume of the catalyst¹ was added to this solution. At appropriate times, 1-ml samples were removed and put into

⁴⁾ S. Winstein, E. Grunwald and L. L. Ingraham, J. Am. Chem. Soc., 70, 821 (1939).

test tubes containing 0.0010 ml of a concentrated solution of potassium acetate. Each sample (0.20 ml) was treated by thin-layer chromatography.^{2b)} Each pinacolone fraction was extracted with chloroform to a 10.0-ml solution. Measurements of the optical densities of these solutions gave the concentrations of the pinacol remaining.*² A straight line correlating the concentrations of the pinacolone, (II) or (III), with the optical densities at 2820 or 2765 Å was used to obtain the concentrations of the pinacolones. The reaction-rate constants were evaluated by the graphical method.

Results and discussion

Products. The meso- and dl-2,2'-dimethoxybenzopinacols rearranged to produce o-anisoylanisylldiphenylmethane (II) and benzoyldi-o-anisylphenylmethane (III), which have absorption maxima at 282 mμ and 276 mμ respectively in chloroform. The thin-layer chromatography showed that the meso-isomer isomerizes to the dl, while neither pinacol forms a stable epoxide intermediate.^{3, 5)}

*² The experimental errors of the analysis were ca. 3—5%. The meso-isomer formed the dl-isomer in addition to the ketones. The dl produced only the ketones.

5) K. Matsumoto, unpublished work.

Kinetics. We have much evidence that the pinacol rearrangement shows first-order kinetics, as was observed in the present case (cf. Fig. 1). The dl-isomer is rearranged about three times as fast as the meso. In the case of the meso-isomer, a slight curvature was evident. This curvature corresponded to acceleration as the reaction proceeded. This deviation may be due to the contribution of the isomerization of the meso-isomer to the dl, which was observed in the thin-layer chromatography of the reaction products. A similar phenomenon was observed in the rearrangements of the cis- and trans-1,2-diphenylacenaphthene-1,2-diol.⁶⁾

Table 1 summarizes the effects of the catalyst concentration upon the rate constant.⁷⁾ The plots of the Hammett acidity function values shown in Table 1 against log k are two straight lines with slopes of 0.90 and 0.85 for the dl- and meso-isomer respectively (Fig. 2). These correlations support the A-1 (acid-catalyzed first-order reaction) mechanism, according to the original form of the Zucker-Hammett hypothesis.⁸⁾

6) P. D. Bartlett and R. F. Brown, J. Am. Chem. Soc., 62, 2927 (1940).

7) $k' = k/(\text{HClO}_4)$.

8) F. A. Long and M. A. Paul, Chem. Revs., 57, 935 (1957).

The values of the experimental activation energy, E_a , and of the free energy, $\Delta F^\ddagger$, and entropy, $\Delta S^\ddagger$, of the activation were calculated from the specific rate constants k' (Table 2).

Variation of Migration Aptitude with Time. Although the molecular rearrangements of tetraarylpinacols to pinacolones have been studied extensively with respect to the relative migration aptitudes of the aryl groups, most of the foregoing data were obtained without any knowledge of whether the configuration of the pinacols was meso or dl. In the rearrangement of p, p'-disubstituted benzopinacol, which probably rearranges via long-lived carbonium ion intermediates, the rate of the interconversion of the different rotational isomers is rapid in comparison with the rate of aryl-group migration, and a Hammett-type $\rho\sigma^+$ correlation is observed.⁹⁾ In the rearrangement of such sterically-condensed glycols as o,o'-disubstituted benzopinacols, however, the rate of the interconversion of the rotational isomers of the carbonium ions may be comparable with the rate of aryl-group migration. Thus, it is expected that the migration aptitude^{*3} would vary with time, as was observed in the present case (shown in Fig. 3). The im-

9) J. E. Leffler and E. Grunwald, "Rate and Equilibria of Organic Reactions," John Wiley and Sons, New York and London (1963), p. 208.

*3 Migration aptitude = Aryl/Phenyl.

plication of the variation of the migration aptitude of the meso-isomer with time is more complicated because of the isomerization of the meso-isomer to the dl. Fig. 3 shows that the migration aptitude of the meso-isomer decreases with time, while that of the dl increases.

It seems that the isomerization of the meso-isomer to the dl and the change in the migration aptitude with time can reasonably be interpreted on the basis of the kinetic consideration, when the rate constants of the aryl-group migration are assumed to be roughly comparable with the rate constants, k_{MI} , k_{MI} , k_{RI} , k_{RI} , and k'_{-2} , k_{-2} being much smaller in Scheme I (where $[R \cdots OH_2]^+_M$, $[R \cdots OH_2]^+_R$, and $[R]^+_O$ are two carbonium aggregate intermediates which retain meso (M) and dl (R) configurations, and an open carbonium ion (O) intermediate respectively). The decrease in the migration aptitude with time in the reaction of the meso-isomer may be interpreted by assuming the contribution of the aryl-group migration via intermediates without any configurational identities, such as $[R]^+_O$ and $[R \cdots OH_2]^+_R$, intervening through isomerization. The increase in the migration aptitude with time in the reaction of the dl-isomer can be explained in a similar way.

It is a sound assumption that the extrapolated value of the migration aptitude at time 0 (in Fig. 3) reflects

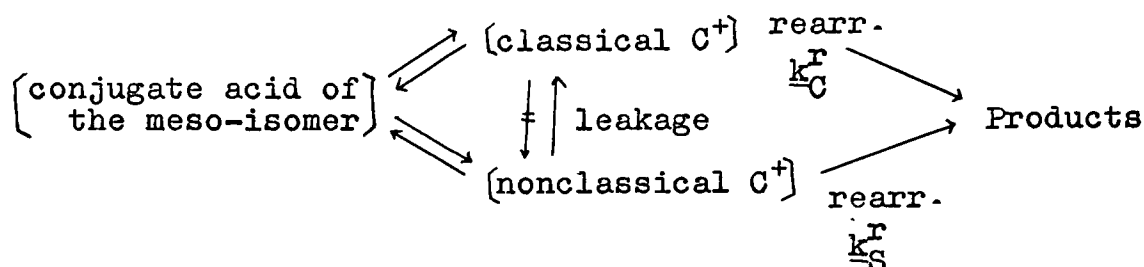
the value of the intrinsic migration aptitude of $\{R\cdots OH_2\}_M^+$ or $\{R\cdots OH_2\}_R^+$. The difference between these two intrinsic migration aptitudes (0.3 and 0.85) may be explained in terms of the difference in the magnitude of the eclipsing effects in the transition states of the aryl-group migrations (see Scheme 1). An inspection of the model will reveal that the eclipsing effects in the transition of the phenyl (o-anisyl)-group migration via the dl-aggregate intermediate, $\{R\cdots OH_2\}_R^+$ (meso-aggregate intermediate, $\{R\cdots OH_2\}_M^+$) is smaller in magnitude than that via the meso-aggregate intermediate, $\{R\cdots OH_2\}_M^+$ (dl-aggregate intermediate, $\{R\cdots OH_2\}_R^+$), therefore, the phenyl-group migration via $\{R\cdots OH_2\}_R^+$ may be more probable than that via $\{R\cdots OH_2\}_M^+$. Thus, the diminished difference in the observed migration aptitudes of the meso- and dl-isomers may reasonably be interpreted in terms of the interconversion among the intermediates, $\{R\cdots OH_2\}_M^+$, $\{R\cdots OH_2\}_R^+$, and $\{R\}_O^+$.

Although the possibility of a contribution of the concerted mechanism and/or of the nonclassical carbonium ion mechanism^{*4} could not be excluded by the present results,

^{*4} The concerted mechanism implies a two-step mechanism, while the nonclassical carbonium ion mechanism implies a three-step mechanism, $P \rightleftharpoons PH^+ \rightleftharpoons C_N^+ \rightarrow K$.

the classical carbonium ion mechanism can be explained as follows:

i) A considerable amount of the isomerization of the meso-isomer to the dl was observed.^{2b)} If $k_S > k_C$ (a rate enhancement is observed by neighboring group participation) in the following chart, $k_S > k_C$ would be valid on the



basis of the principle of the microscopic reversibility. Since it is likely that $\text{rate}_S^{\text{rearr}}$ and $\text{rate}_C^{\text{rearr}}$ are not very different, the return of the meso-isomer to the meso-isomer may be effected to be much more predominant than the return of the meso-isomer to the dl-isomer in addition to the meso-isomer. This is not, however, in accord with the observed results. Therefore, the case $k_S < k_C$ would be valid, showing a smaller contribution of nonclassical carbonium ions.

ii) The large positive values of the entropy of activation is in accord with the classical carbonium ions if the contribution of the entropy of desolvation in the transition state is assumed to be small (Table 2).

iii) It is known that, in general, the neighboring group participation tends to decrease with an increase in

the phenyl substitution of the carbon atom at which heterolysis occurs.¹⁰⁾

iv) In such a sterically-condensed system as 2,2'-dimethoxybenzopinacol, a classical carbonium ion would give more chances for a decrease in the steric interaction than ^{would} a nonclassical carbonium ion, as an inspection of molecular models suggests.

v) If one assumes that either the concerted or nonclassical mechanism is exclusively operative, the extrapolated migration aptitude at time 0 in Fig. 3 would be observed, since the transition states or intermediates are considered to have structures similar to those of the transition states of aryl-group migration described in Scheme I. The observed change in migration aptitude with time, therefore, seems to suggest that the classical carbonium ions are more favoured as intermediates.

In conclusion, again, the contribution of the concerted mechanism and/or the nonclassical carbonium ion mechanism would be small, if not entirely absent.

The slightly larger rate constant (ca. three times)

¹⁰⁾ S. Winstein and E. Grunwald, J. Am. Chem. Soc., 70, 828 (1948), S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, ibid., 74, 1113 (1952).

of the dl-isomer compared with the meso may be considered to be due to the conformational predominance of the meso-pinacol with a trans arrangement of the hydroxyl groups, while the dl has a cis.^{2c)}

Although the low migration aptitude (< 1) of the o-anisyl group is usually ascribed to steric hindrance,^{2b)} it has been suggested by Pocker¹¹⁾ that it could be due to the interaction of the o-anisyl oxygen with a developing carbonium ion.¹²⁾ However, this suggestion is not in accord with the large positive values of the entropy of activation which follow if the degree of desolvation in the transition state is assumed to be small. The abnormally low migration aptitude of the o-anisyl group may instead be ascribed to steric hindrance by the solvated methoxy group.¹³⁾

Though the epoxide intermediates were not detected by thin-layer chromatography, the by-passed mechanism via unstable epoxide intermediates can not be excluded.

11) Y. Pocker in "Molecular Rearrangements," P. de Mayo ed., Interscience Pub., New York and London (1963), p. 22.

12) S. Winstein, Experientia, Suppl. No. 2, 153 (1955).

13) For this problem, see R. Goto, T. Asano, K. Matsumoto and A. Sera, The Review of physical Chemistry of Japan, 37, 16 (1967).

The conclusions as to the fates of the carbonium ions are summarized qualitatively in a plot of the free energy against the reaction co-ordinate (Fig. 4). From the evidence for the strong hydrogen bonding in the dl-isomer, it may be assumed that the dl-isomer is more stable than the meso in the ground state.^{2c)}

The author wishes to thank Professor Ryoze Goto for his helpful discussions and encouragement, and Dr. Akira Sera and Dr. Jun'ichi Hayami for their kind and valuable advice and discussions.

Table 1

Summary of Kinetic Data for the Perchloric Acid-catalyzed Rearrangement of 2,2'-Dimethoxybenz-pinacol in Anhydrous Acetic Acid at 72°C

HClO_4 $\text{M} \times 10^4$	H_o	$k \times 10^2 \text{ min}^{-1}$ (meso)	Log k	$k' \text{ l/mol.l}$ $\times 10^{-2}$
0.518	-2.23	0.502	-2.30	0.969
0.857	-2.00	0.724	-2.14	0.845
1.36	-1.79	1.15	-1.96	0.846
2.60	-1.50	1.94	-1.72	0.746
3.98	-1.30	2.81	-1.55	0.706
0.532	-2.22	(dl) 1.38	-1.86	2.71
0.863	-2.00	1.99	-1.70	2.32
1.36	-1.79	3.12	-1.51	2.28
1.87	-1.65	4.14	-1.39	2.21
2.87	-1.45	6.03	-1.22	2.10

Table 2

THERMODYNAMICS OF ACTIVATION FOR REARRANGEMENT OF 2,2'-DIMETHOXYBENZ-
PINACOL IN 1.36×10^{-4} mol-HClO₄ ACETIC ACID

	Temp. C°	Specific Rate $\times 10^{-2}$ l/mol·min	E _a kcal/mol	$\Delta S^\ddagger$ e.u.	$\Delta F^\ddagger$ kcal/mol
dl	82	6.72			
	72	2.29	26.2	15.7	19.4
	62	0.765			
meso	82	2.57			
	72	0.846	27.1	18.4	20.1
	62	0.246			

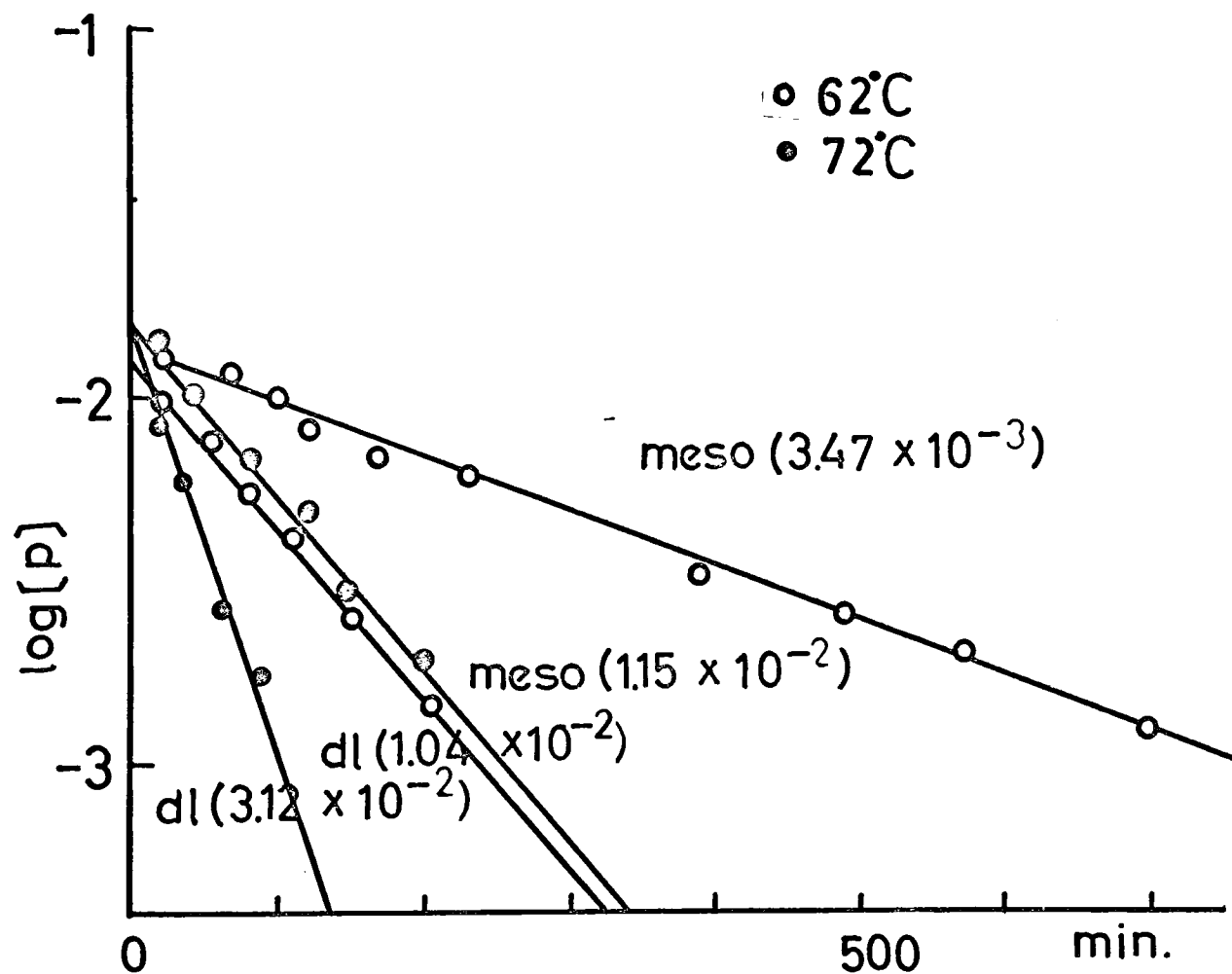


Fig.1 First order plots of rearrangement of 2,2-dimethoxybenzpinacol (1.36×10^{-4} mol- HClO_4)

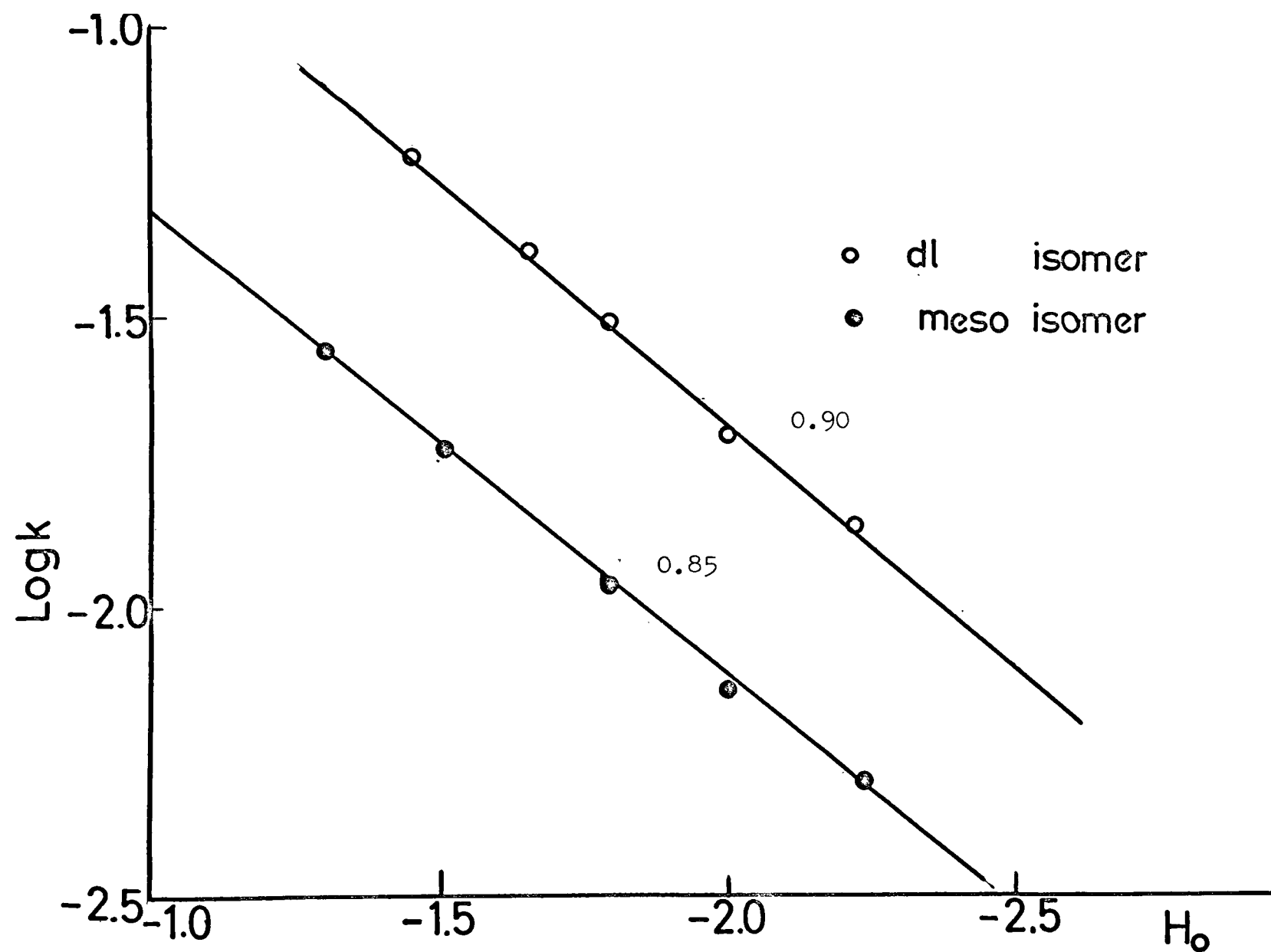


Fig.2 Correlation of first order rate constant with the Hammett acidity function of the medium at 72°C

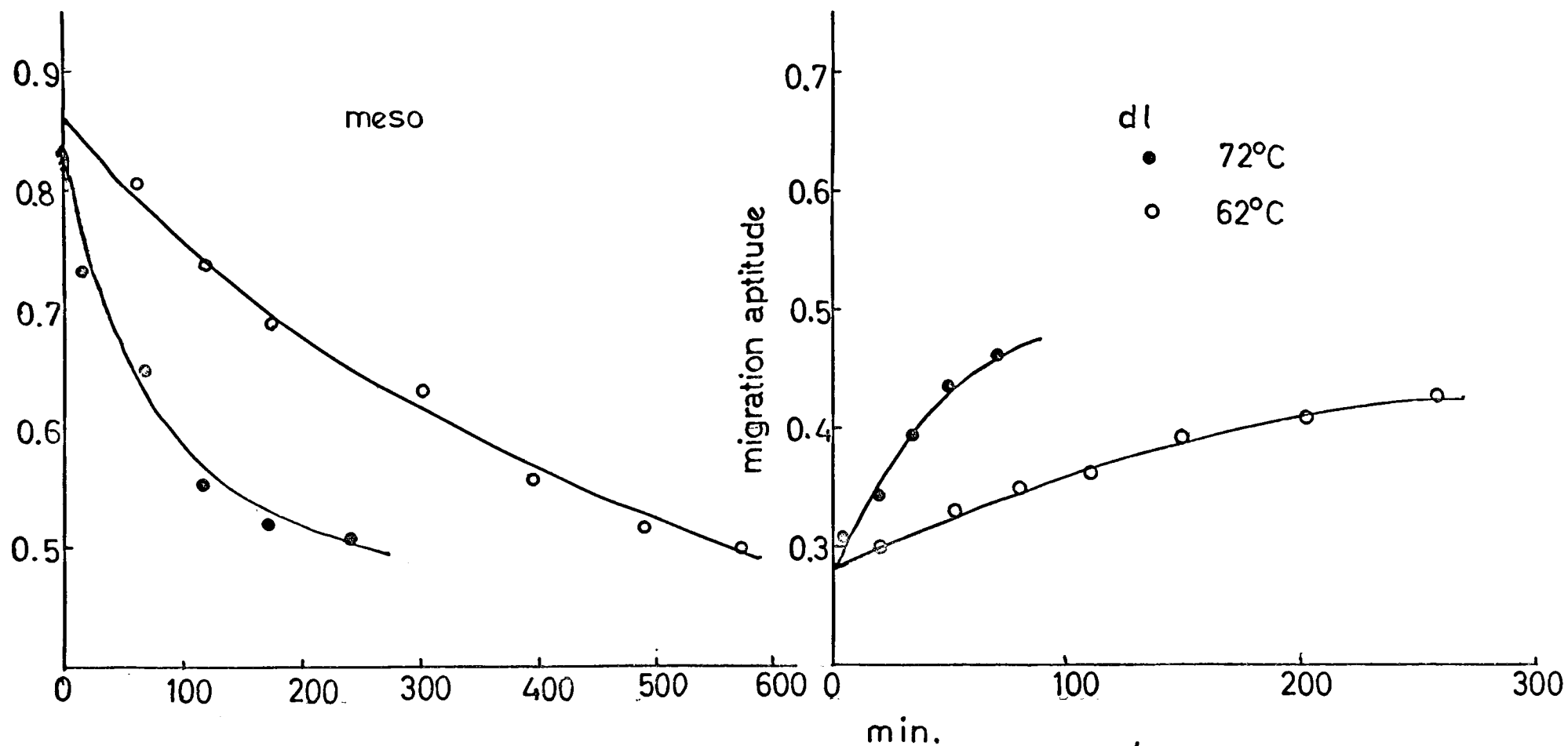


Fig.3 Variation of migration aptitude with time (1.36×10^{-4} M- HClO_4)

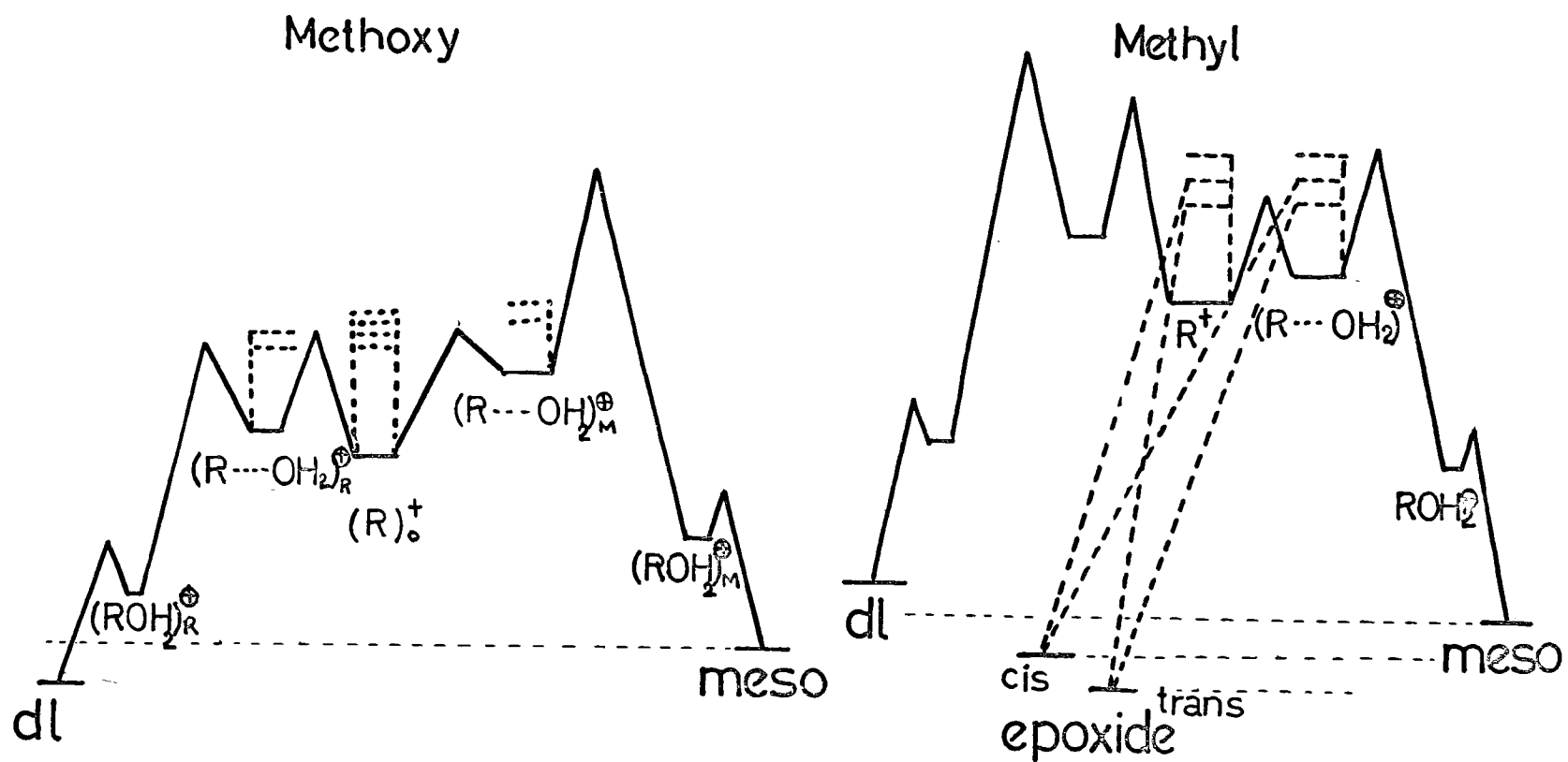
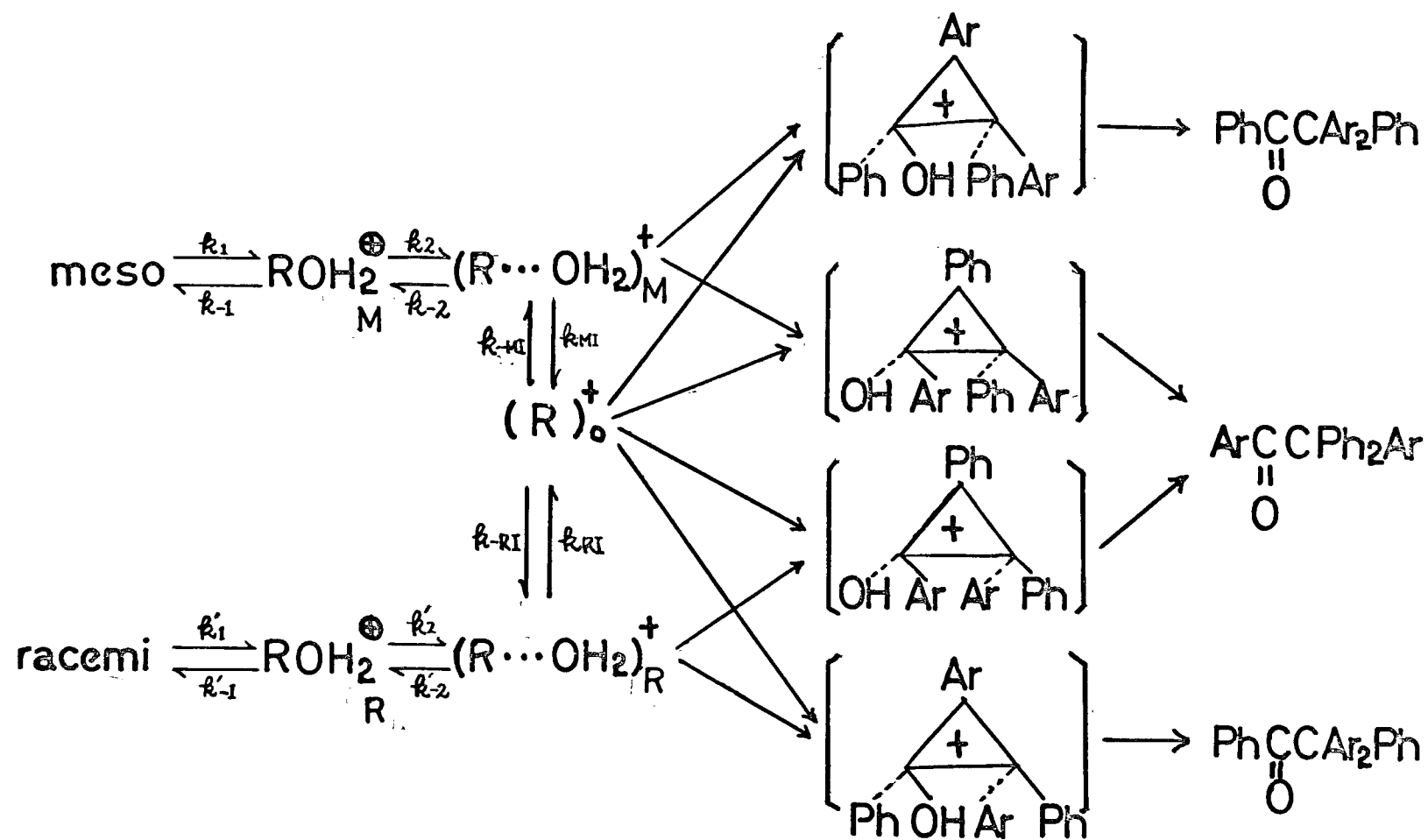


Fig.4 Schematic energy diagram for (inter)conversion of the diols(tull line) and for formation of the products(broken line)



Scheme 1.

主 論 文
第 二 部

Studies on the Pinacol Rearrangement. V. The Rearrangements of cis- and trans-1,2-Diphenyl-1,2-ditolylethylene oxides¹

Kiyoshi MATSUMOTO

Department of Chemistry, Faculty of Science,

Kyoto University, Sakyo-ku, Kyoto, Japan.

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Abstract — The intermediate formation of the two epoxides was observed in the perchloric acid-catalyzed rearrangement of meso-2,2'-dimethylbenzopinacol(P_{meso}) to 2-methylbenzoyl tolyl diphenyl methane(K) in acetic acid. Two kinds of epoxides were separated with preparative thin layer chromatography and the configurations(cis and trans) of these epoxides were inferred in the light of UV spectra, NMR spectra, IR spectra, dipole moment and kinetic data. The rearrangement rates of these epoxides were measured in HClO₄-anhydrous acetic acid. Linear correlations of logarithm of the rate constants(log k) with the Hammett acidity function of the medium(H₀) 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-catalyzed rearrangement of meso-2,2'-dimethylbenzopinacol(P_{meso}) occurs via such many kineti-

¹ Part IV; Bull. Chem. Soc. Japan, 41, in press (1968).

cally distinguishable routes as the following;



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 established². However, there are numerous problems remained to be solved, which have been reported in the preceding papers³. In part IV, the rearrangements of meso- and dl-2,2'-dimethoxybenzopinacols have been investigated with respect to the character of the intermediate, the reaction processes and the migration aptitudes.

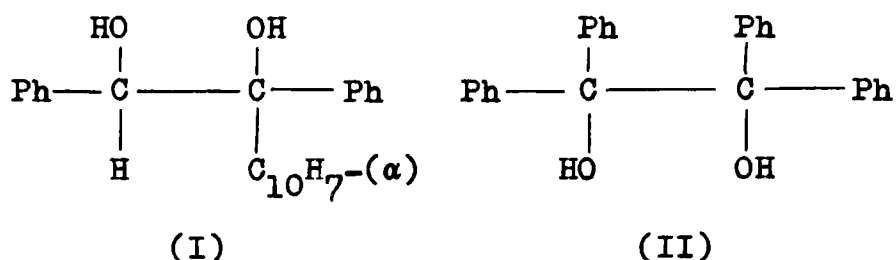
The role of the epoxide intermediate in the pinacol rearrangement has been already discussed by Wheland⁴; he concluded that the epoxide does not play an essential role in the pinacol rearrangement. The only two examples in which the stable epoxide was recognized were the rearrangements of erythro-

² For example, see C. J. Collins, Quarterly Review, 14, 357 (1960).

³ a) R. Goto, K. Matsumoto and A. Sera, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.), 87, 93 (1966).
b) ibid., 87, 1076 (1966). c) ibid., 88, 92 (1967).

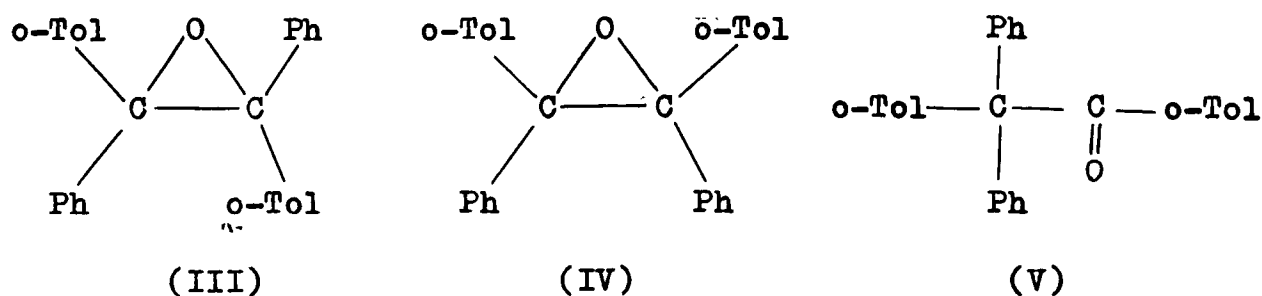
⁴ G. W. Wheland, "Advanced Organic Chemistry", John Wiley and Sons, Inc. New York, N. Y., (1949) pp. 451—534.

-1- α -naphthyl-1,2-diphenylethylene glycol(I)⁵ and benzo-pinacol(II)⁶.



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).



The thin layer chromatogram of the reaction products is shown in Fig.1. The assignment of configuration(cis or trans)

⁵ A. Mackenzie and R. Roger, J. Chem. Soc., 125, 853 (1924).

⁶ H. J. Gebhart and K. H. Adams, J. Am. Chem. Soc., 76 3925 (1954).

to these epoxides(A; $R_f=0.64$, B; $R_f=0.56$) was carried out as following. Fig.2, Fig.3 and Fig.4 show IR spectra, NMR spectra and UV spectra of the epoxides A and B respectively. The characteristic values obtained with the above spectra are summarized in Table 1 together with the data of dipole moment.

The molecular models(LAPINE LEYBOLD MODEL) of cis- and trans-1,2-ditolyl-1,2-diphenylethylene oxide are shown below. (Fig.A and Fig.B). The other conformers show the great magnitude of steric interaction and can not be constructed with this model. The examination of the molecular models of cis- and trans-epoxides indicates methyl group-methyl group steric repulsion in the cis-epoxide, which enforces methyl group to the more diamagnetic region compared with the trans. Then, the signal of the methyl 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 cis-isomer compared to that in the trans-isomer due to methyl group-methyl group repulsion(see, 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 ± 0.02 Debye) coincides with the above argument.

The same methyl-methyl interaction would decrease conjugation of oxirane ring with 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^{*1}. Same trend of the 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 hydrogen atoms would overlap⁷.

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-epoxide⁸. 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 qualitative and yet unambiguous assignment of the configuration hardly is obtained at the moment, the assignment by these data are not inconsistent with one another. Also the chemical transformation of the epoxide B into A suggests the epoxide A to be the

^{*1} The possibility of steric inhibition of methyl hyperconjugation might be still uncertain.

⁷ G. Riezebos and E. Havinga, Rec. trav. chem., 80, 446 (1961); F. Ramirez and A. F. Kirby, J. Am. Chem. Soc., 76, 1037 (1954).

⁸ A. Fujino and M. Yamaguchi, Kagaku no Ryoiki (Journal of Japanese Chemistry), Extra Number 28, 102 (1958).

more stable isomer of the pair.

The conclusive assignment of the configuration should wait a complete X ray analysis.

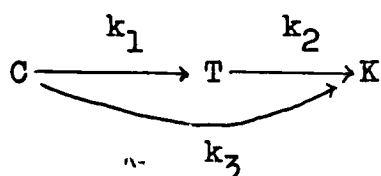
Kinetic Study. The first order character of the reaction of meso-2,2'-dimethylbenzopinacol, which could not be confirmed experimentally because of the difficulty of the quantitative analysis of the pinacol¹, would be expected, since it is known that the pinacol rearrangements studied hitherto show the first order kinetics⁹. 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'-dimethylbenzopinacol.

The first order kinetics were 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 and k_T . (k_C ; rate constant of the

⁹ P. D. Bartlett and R. F. Brown, J. Am. Chem. Soc., 62, 2927 (1940); R. F. Brown, ibid., 74, 428, 432(1952); 76, 1279 (1954); R. Criegee and K. H. Plate, Ber., 72, 178(1938); J. F. Duncan and K. R. Lynn, J. Chem. Soc., 1956 3512,3519, 3674; J. B. Ley and C. A. Vernon, ibid., 1957, 2487; N. C. Deno and C. Perizzolo, J. Am. Chem. Soc., 79 1435(1957); W. B. Smith, et al., ibid., 81, 997(1959); 83, 2190(1961); C. J. Collins, et al., ibid., 81, 460(1959); M. Stiles and R. P. Mayer, ibid., 81, 1497(1959); C. A. Bunton, et al., J. Chem. Soc., 1958, 403; 1963, 5854, 5861.

reaction of the cis-isomer, k_T : that of the trans-isomer). The plots of the Hammett acidity function H_0 values¹⁰ 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), which supports the A-1 mechanism according to the Zucker-Hammett hypothesis¹¹ together with the large positive values of the entropy of activation described below.

Mechanism. The investigation of the thin layer chromatogram of the reaction products of the epoxides shows that the isomerization of the cis-isomer to the trans-isomer occurs, not of the trans to the cis and 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 the following,



$$k_T = k_2$$

$$k_C = k_1 + k_3$$

where C, T and K represent the cis-epoxide, trans-epoxide and the pinacolone respectively.

The mathematical treatment of irreversible first order consecutive reaction $C \rightarrow T \rightarrow K$ is here modified to allow for the competing simple reaction $C \rightarrow K$. The fun-

¹⁰ F. J. Ludwig and K. H. Adams, J. Am. Chem. Soc., 76, 3853(1954).

¹¹ F. A. Long and M. A. Paul, Chem. Rev., 57, 935(1957).

damental equations are

$$-d(C)/dt = k_1(C) + k_3(C) \quad (1)$$

$$d(T)/dt = k_1(C) - k_2(T) \quad (2)$$

Substitution into (2) of the value of (C) obtained by the integration of (1) yields

$$d(T)/dt + k_2(T) = k_1(C)_0 e \exp[-(k_1 + k_3)t] \quad (3)$$

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

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

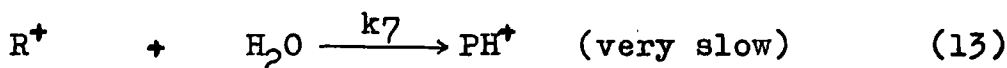
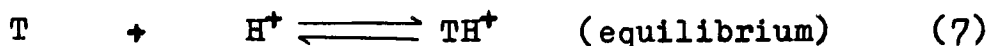
i.e.

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

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 , $k_2 = k_T$, $(C)_0$ 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 $k' = k_{\text{exp}} / (\text{HClO}_4)$. 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.

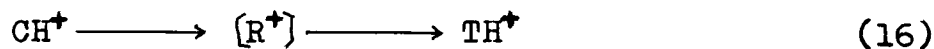
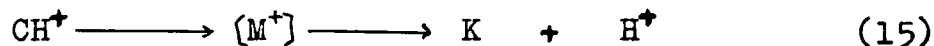
The above results suggest the two possible mechanisms.

i) The first possible mechanism can be represented as the following.



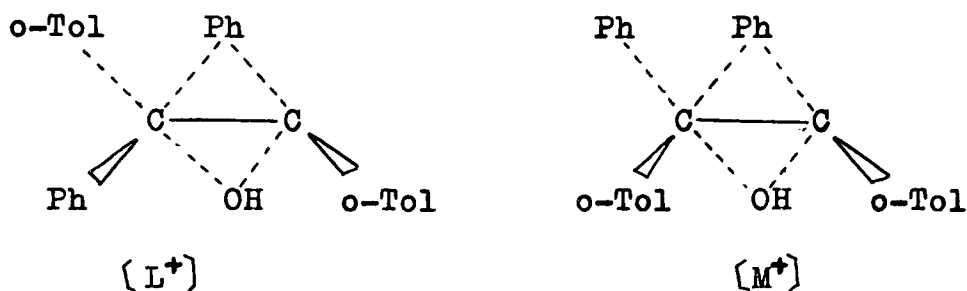
To bring this formulation into conformity with the kinetics, it is necessary that $k_6 > k_{-5} \gg k_4 > k_5 > k_{-4}, k_7$. Here, it is assumed that the unrearranged carbonium ion R^+ is a common intermediate of sufficient stability to require additional small activation energies for the formation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

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



The transition complexes $[L^+]$ and $[M^+]$ would be represented by the following, and the reactions might be expected to show some evidence of neighboring 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.



In view of the generalization that neighboring group participation is apt to decrease with increasing phenyl substitution of the carbon atom at which heterolysis occurs¹², and in view of the large positive values of $\Delta S^\ddagger$ and occurrence of isomerization, it is expected that the contribution of mechanism(i) is more important than mechanism(ii) and therefore the classical carbonium ion is an intermediate in these processes.

The high susceptibility to acid-catalyzed hydration to the glycol which is characteristic of the phenyl substituted ethylene oxides¹³ 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

¹² S. Winstein and E. Grunwald, J. Am. Chem. Soc., 70, 928(1948); S. Winstein et al., ibid., 74, 1113(1952).

¹³ J. L. Lane and D. R. Walters, ibid., 73, 4234(1951).

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'-dimethylbenzopinacol, consequently, would be explained by the following scheme(Scheme 1), where $(R \cdots OH_2)_M^+$ represent conformers of tight carbonium ion aggregate in which, as postulated in the previous paper¹, the original meso configuration is retained and $R \cdots OH_2$ bond is lengthened enough to enable the rotation about the central C—C bond. The absence of the isomerization of the trans-epoxide to the cis shows that the transformation $(R)_O^+ \longrightarrow \text{cis-epoxide}$ is a very slow step($k_{-5} > k_{-4}$)^{*2}.

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.

^{*2} 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 $k_R^T > k_O$ or $k_R^T > k_R^O$ and if the stereochemical identity of $(R)_C^+$ or $(R)_T^+$ (cis or trans configuration respectively) are supposed to be retained(Scheme 2).

Experimental

Materials. Anhydrous acetic acid was obtained by the method of purification described in the previous paper¹.

The comparison of the features of the signals of NMR in the high field (ca. 2.3 ppm) with those of meso- and dl-2,2'-dialkoxybenzopinacol suggests that the present pinacol is meso in configuration^{3c}. (see ref. 3c and Fig.3).

cis-(C) and trans-(T) 1,2-Diphenyl-1,2-ditolylethylene oxides were obtained with the preparative thin layer chromatography of the epoxides formed in the perchloric acid catalyzed reaction of 2,2'-dimethylbenzopinacol. The chromatoplates used were prepared with Silica Gel G and uranine aqueous solution (0.04%). The mixture of benzene and hexane (1 : 2) was used as a developer.

The epoxide of R_f=0.64 (A): m.p. 160 -- 161°. (Found: C, 89.47; H, 6.70%. Calc. for C₂₈H₂₄O : C, 89.32; H, 6.43%)

The epoxide of R_f=0.56 (B): m.p. 176 -- 177°. (Found: C, 89.53; H, 6.48%. Calc. for C₂₈H₂₄O: C, 89.32; H, 6.43%).

The preparation of the standard stock solution of perchloric acid was described in the preceding paper¹.

Analytical Methods. The ordinary method by which the pinacol is estimated (oxidation with lead tetraacetate) could not be employed, because meso-2,2'-dimethylbenzopinacol was not oxidized quantitatively with lead tetraacetate^{3c}. Therefore, the following methods were used. 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 $3290 \text{ \AA}$ of the solution obtained by the dilution of 2.00 ml of the reaction mixture to 10.00 ml with t-butyl alcohol. 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 the calculation. In the case of the cis-epoxide which is accompanied with the formation of the trans-epoxide in the rearrangement, a 0.400 ml sample of the solution to be analyzed on the thin layer chromatography and the fraction of the cis-epoxide was extracted with chloroform to 10.00 ml and the optical density of this solution at $2630 \text{ \AA}$ was measured. The concentration of the cis-epoxide in the solution 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.

Reaction Rate Measurement. The flask which contained the anhydrous acetic acid solution of the epoxide(0.01 mole) was immersed in an oil bath, the temperature of which could be controlled to $\pm 0.05^\circ$, and after 30 min, the measured volume of the catalyst was added. At the appropriate times, the sample were pipetted out and put into the test-tubes containing 0.002 ml of the concentrated solution of potassium acetate. The neutralization of the perchloric acid immediately stopped the reaction. The samples were cooled to room temperature(ca. 25°) and analysed. Reaction rate

constants were evaluated by the graphical method.

NMR spectra. The proton magnetic resonances of the epoxides and pinacol were observed by the use of a Japan Electron Optics Lab. Model JNM-3H60 Spectrometer(60 Mc).

IR Spectra. The infrared spectra were measured in KBr by using a Japan Spectroscopic Model DS-402G Infrared Spectrophotometer.

UV Spectra. The spectra and optical densities were obtained on a Shimadzu QR-50 Specrophotometer.

Dipole Moments. The dielectric constants were measured by the heterodyne beat method with an apparatus¹⁴ of Koizumi Laboratory(The Institute for Chemical Research, Kyoto University). The dipole moments were calculated by the Halverstadt-Kumler method¹⁵.

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¹⁴ N. Koizumi, F. Tsuji and H. Okamoto, Bull. of Inst. for Chem. Research(Kyoto Univ.), 43, 388 (1965).

¹⁵ L. F. Halverstadt and W. D. Kumler, J. Am. Chem. Soc., 64, 2988 (1942).

Table 1 IR UV NMR and Dipole Moment data of cis- and trans-epoxide

epoxide	R _f ^{a)}	mp	IR C—O—C (ν cm ⁻¹)			U V ^{b)}		Dipole ^{c)} moment (D)	NMR ^{d)} methyl proton (ppm)
			8 μ	11 μ	12 μ	$\lambda_{\max}$	$\epsilon \times 10^{-2}$		
A	0.64	160 ~ 161	1244	895	802	290 300	3.27 3.32	1.52	2.54
B	0.56	176 ~ 177	1235	889	794	264	13.4	1.60	2.23

a) Silica Gel G . Benzene : Hexane = 1 : 2 .

b) in ethanol .

c) in benzene at 30° .

d) in carbon tetrachloride.

Table 2 SUMMARY OF KINETIC DATA FOR THE PERCHLORIC
ACID CATALYZED REARRANGEMENT OF cis- AND trans-
1,2-DIPHENYL-1,2-DITOLYLETHYLENE OXIDE IN ANHYDROUS
ACETIC ACID AT 72°C

HClO ₄ MOL X 10 ³	H ₀	k x 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

Table 3 THERMODYNAMICS OF ACTIVATION FOR REACTION OF cis- AND trans-
1,2-DIPHENYL-1,2-DITOLYLETHYLENE OXIDE IN GLACIAL ACETIC ACID

Rate Constant	Temp. °C	Specific Rate l/mol·min (x 10 ²)	E _a kcal/mol	ΔS [‡] e.u.	ΔF [‡] kcal/mol
k ₂ (k' _T)	62	1.96	32.1	18.8	25.0
	72	6.95			
	82	28.1			
k' _C	62	118	31.2	24.2	22.1
	72	405			
	82	1580			
k' ₁	62	21.8	31.8	22.6	23.4
	72	76.7			
k' ₃	62	96.4	31.0	23.2	22.2
	72	328			

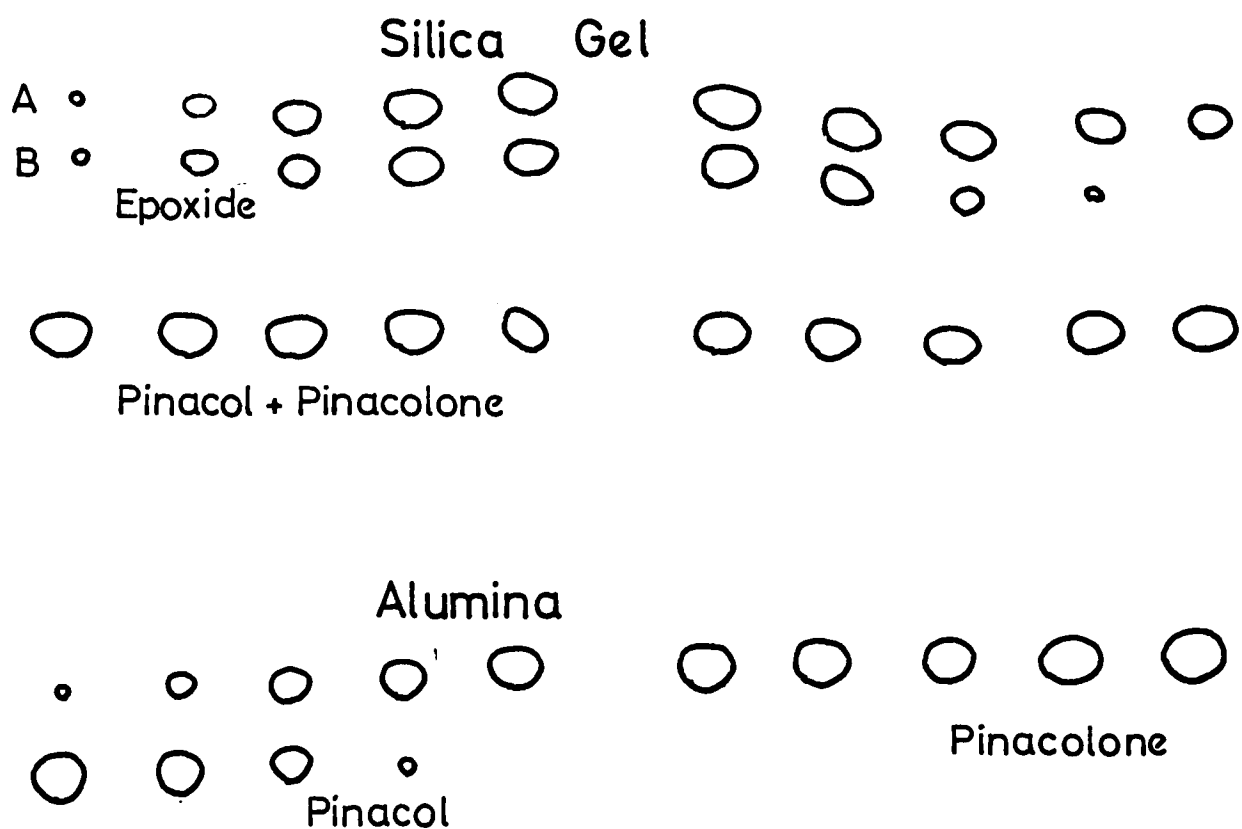
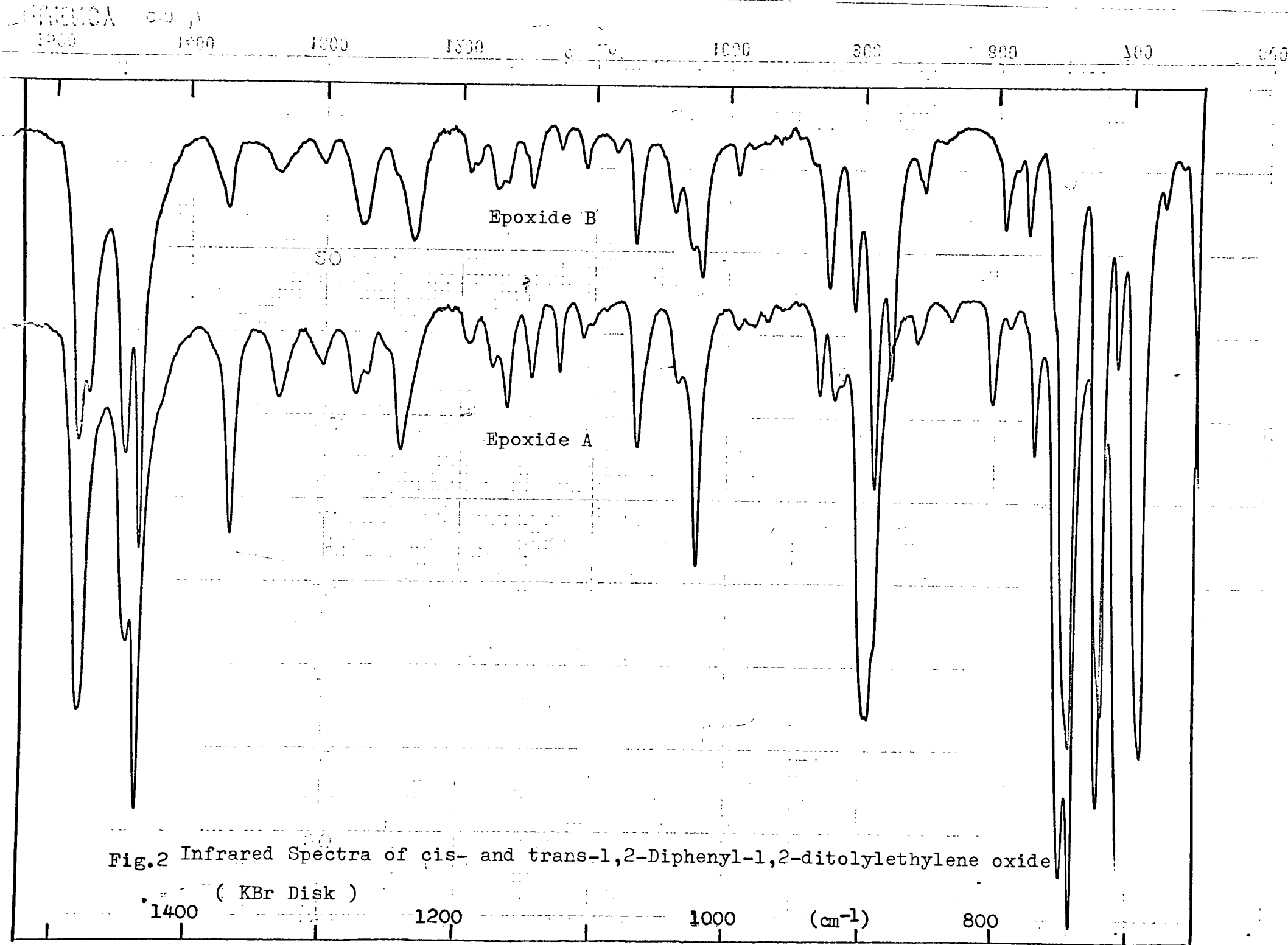


Fig.1

Thin layer chromatogram of reaction products of
 2,2'-dimethylbenzpinacol (benzene : hexane=1 : 2)
 in glacial acetic acid (2.64×10^{-4} mole- HClO_4) at 72°C
 0.00942 mole Pinacol



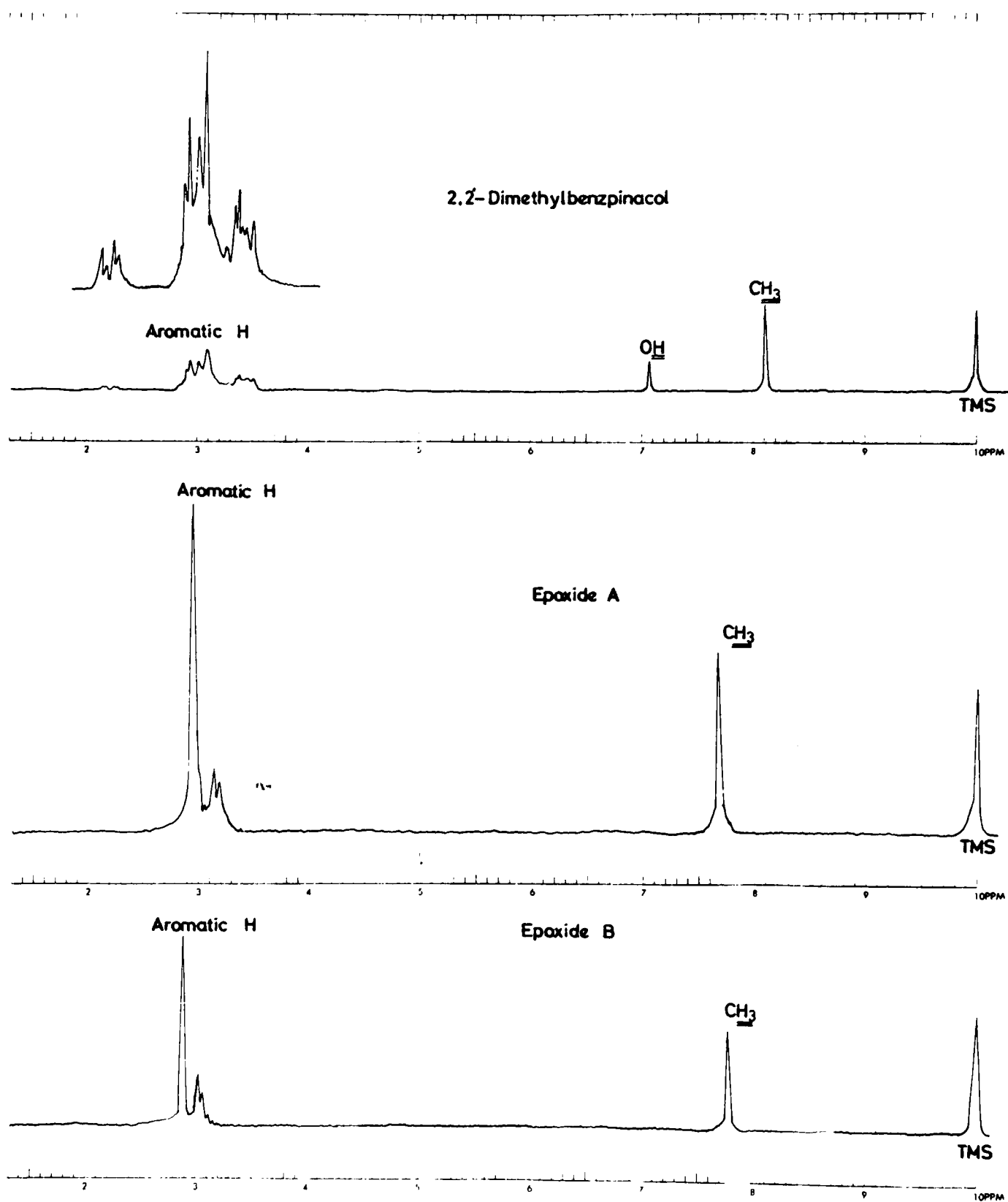


Fig.3 Nmr Spectra of 2,2'-dimethylbenzopinacol, Epoxide A and Epoxide B.

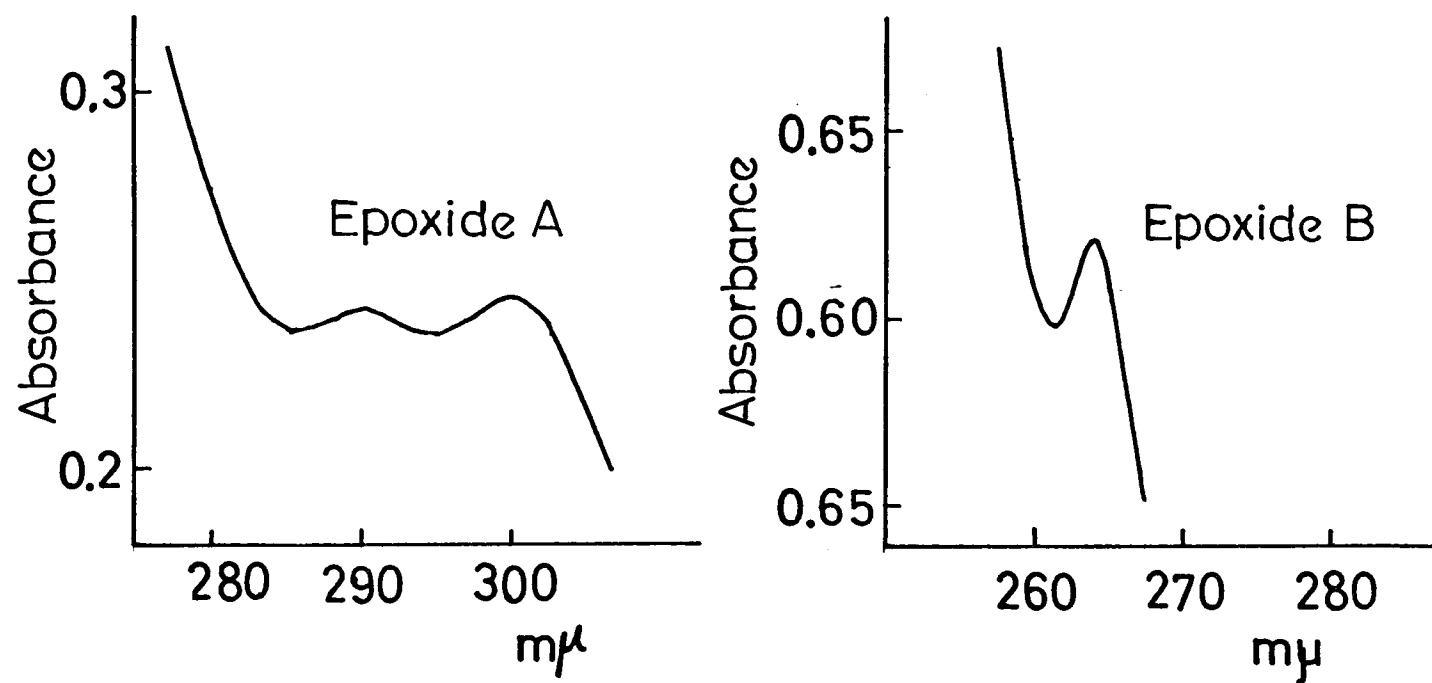


Fig.4 UV Spectra of cis- and trans-1,2-Diphenyl-1,2-ditolylethylene oxide in Ethanol

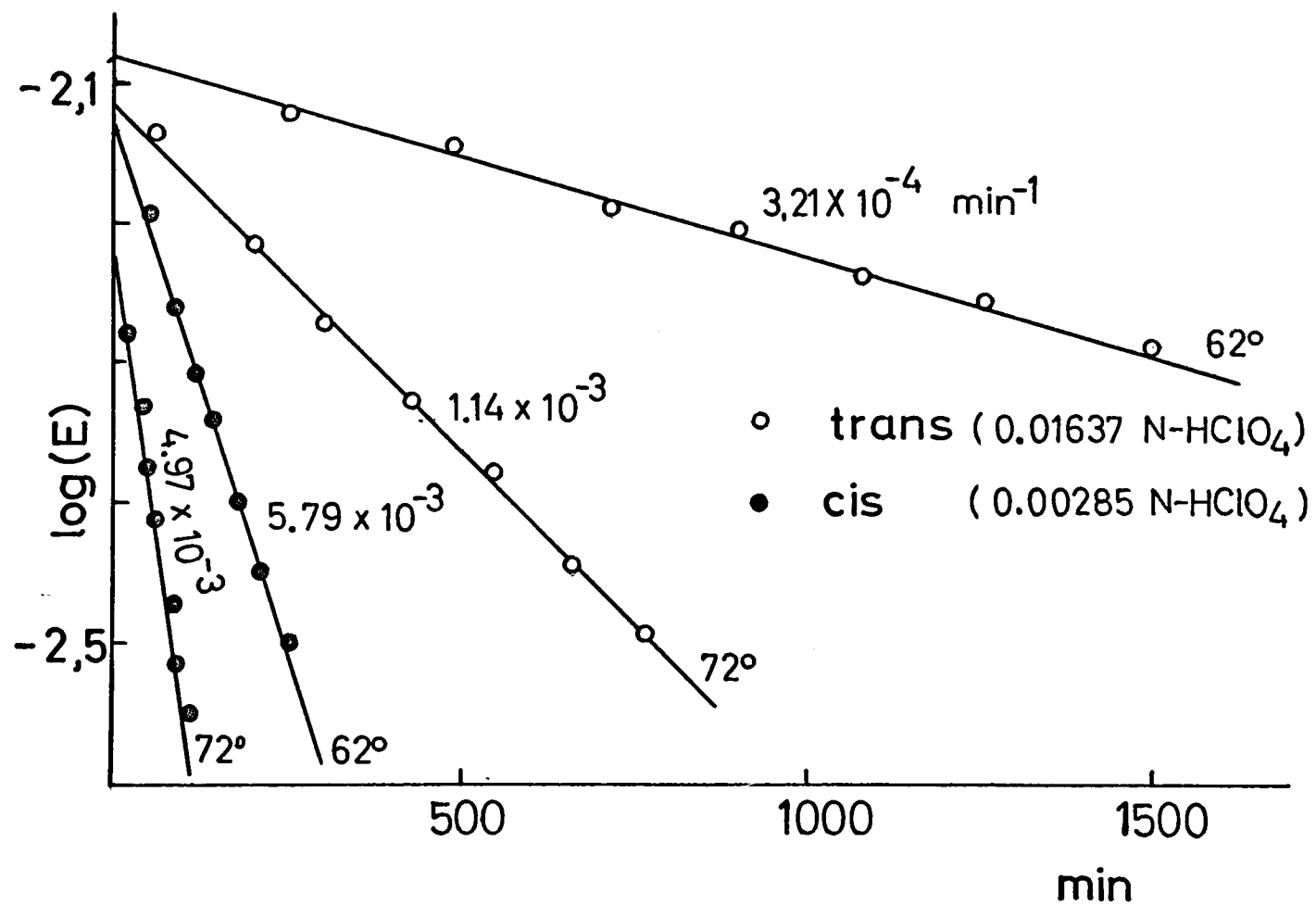


Fig.5 First order plots of reaction of cis- and trans-1,2-diphenyl-1,2-ditolyl-ethylene oxide

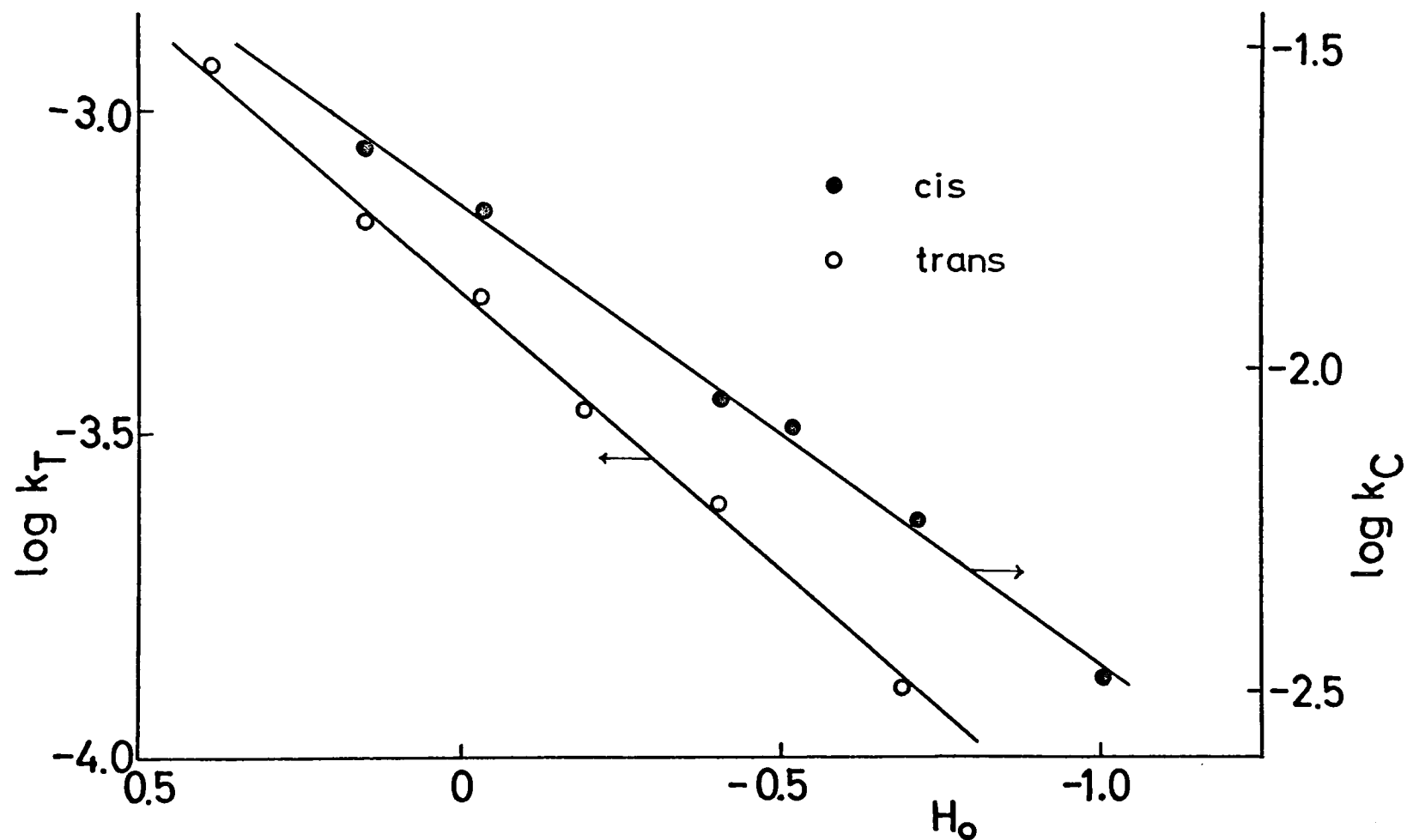


Fig.6 Correlation of first order rate constant with the Hammett acidity function of the medium at 72°C

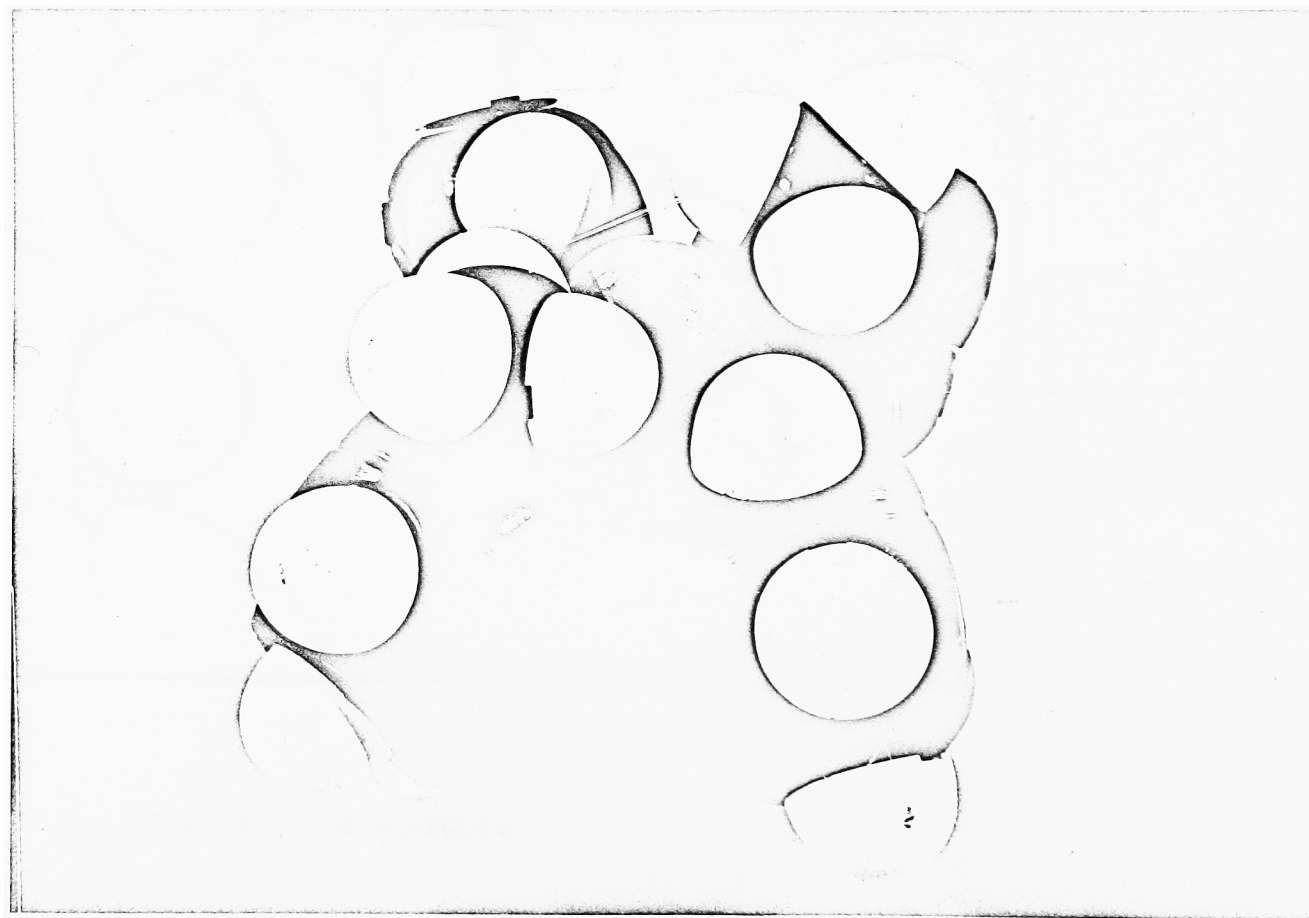


Fig. A trans-Epoxyde

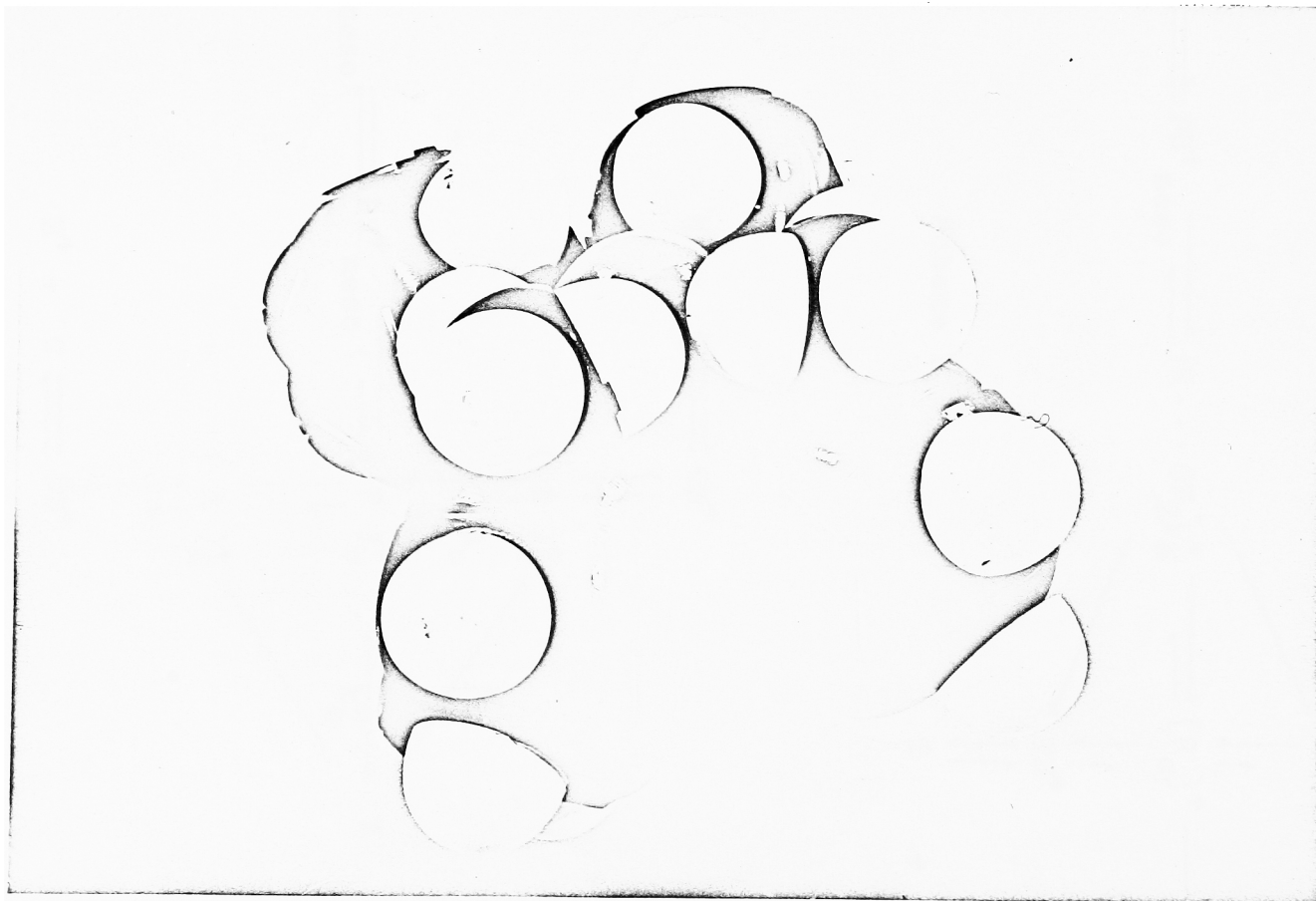


Fig. B cis-Epoxide

