学 位 論 文

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主 論 文

Studies on the Pinacol Rearrangement

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The Kinetics and Mechanism of the Rearrangement of
meso- and dl-2,2'-Dimethoxybenzopinacol

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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

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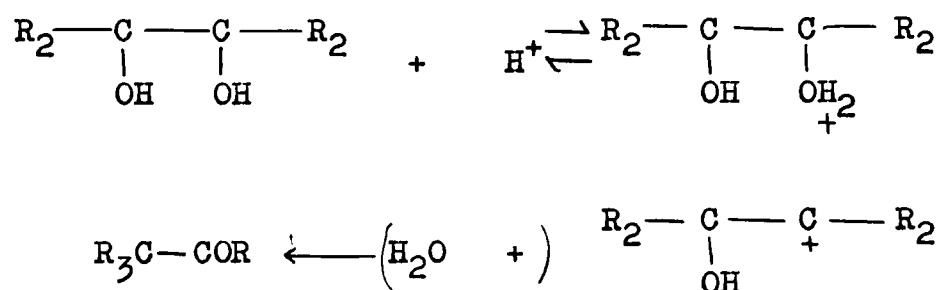
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The first-order rate constants of the perchloric

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_o) 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_o, 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

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:

$$R_2\text{---}\underset{\underset{OH}{|}}{C}\text{---}\underset{\underset{OH}{|}}{C}\text{---}R_2 \quad + \quad H^+ \underset{\longleftarrow}{\overset{\longrightarrow}{}} R_2\text{---}\underset{\underset{OH}{|}}{C}\text{---}\underset{\underset{\overset{OH_2}{+}}{|}}{C}\text{---}R_2$$

$$R_3C\text{---}COR \longleftarrow \left(H_2O \quad + \right) \quad R_2\text{---}\underset{\underset{OH}{|}}{C}\text{---}\overset{+}{C}\text{---}R_2$$

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

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[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-methoxy-phenylphenylmethane (III) in anhydrous acetic acid, with perchloric acid as the catalyst.

(I)   (II)   (III)
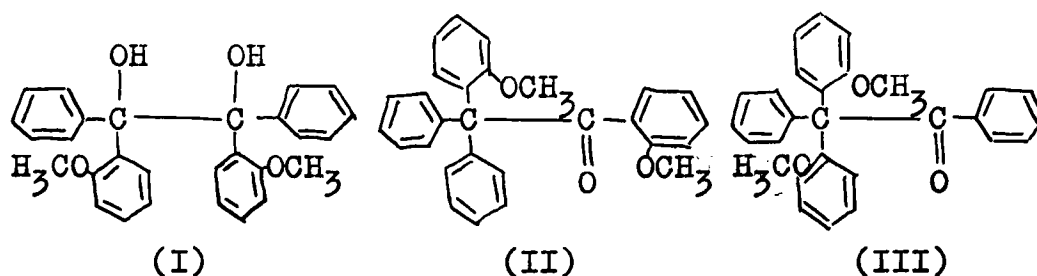
Experimental

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 distilate 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 aquous perchloric acid. The solution was then standardized by titration with a standard solution (0.0500 $\underline{N}$) 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 $\underline{M}$ of a pinacol solution was immersed in a thermostated oil bath. After half an hour, a measured volume of the catalyst 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-anisoylanisyldiphenylmethane (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]

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*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 re-arranged 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 re-action products. A similar phenomenon was observed in the rearrangements of the cis- and trans-1,2-diphenylacenaph-thene-1,2-diol.[6]

Table 1 summarizes the effects of the catalyst con-centration 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]

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

[7] $k' = k/(HClO_4)$.

[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-

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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
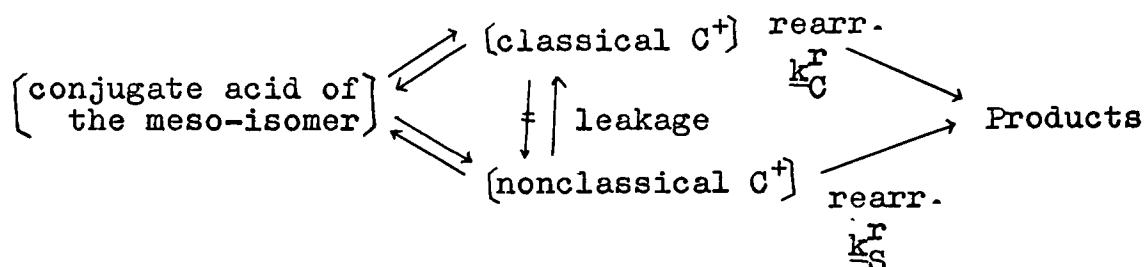
the value of the intrinsic migration aptitude of $[R\cdots OH_2]_M^+$

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 inter-

mediate, $[R\cdots OH_2]_M^+$ (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,

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[*4] The concerted mechanism implies a two-step mechanism,

while the nonclassical carbonium ion mechanism implies a

three-step mechanism, $P \rightleftharpoons PH^+ \rightleftharpoons C_N^+ \longrightarrow K$.

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

$$\left[\begin{matrix}\text{conjugate acid of} \\ \text{the meso-isomer}\end{matrix}\right] \underset{\searrow}{\overset{\nearrow}{\rightleftharpoons}} \begin{matrix}\text{(classical } C^+\text{]} \xrightarrow[k_C^r]{\text{rearr.}} \\ \not\updownarrow \text{ leakage} \\ \text{(nonclassical } C^+\text{]} \xrightarrow[k_{-S}^r]{\text{rearr.}}\end{matrix} \text{Products}$$

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 a nonclassical carbonium ion, as an inspection of

would

molecular models suggests.

v) If one assumes that either the concerted or

nonclassical mechanism is exclusively operative, the

extrapolated migration aptitude at time O 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)

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[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 Pocker[11] 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.

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[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]

Table 1

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

$HClO_4$ M X 10^4	H_o	$k \times 10^2 \, min^{-1}$ (meso)	Log k	k' 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-$HClO_4$ ACETIC ACID

	Temp. C^o	Specific Rate $\times 10^{-2}$ l/mol·min	E_a kcal/mol	$\Delta S^{\ddagger}$ e.u.	$\Delta F^{\ddagger}$ kcal/mol
	82	6.72			
dl	72	2.29	26.2	15.7	19.4
	62	0.765			
	82	2.57			
meso	72	0.846	27.1	18.4	20.1
	62	0.246			
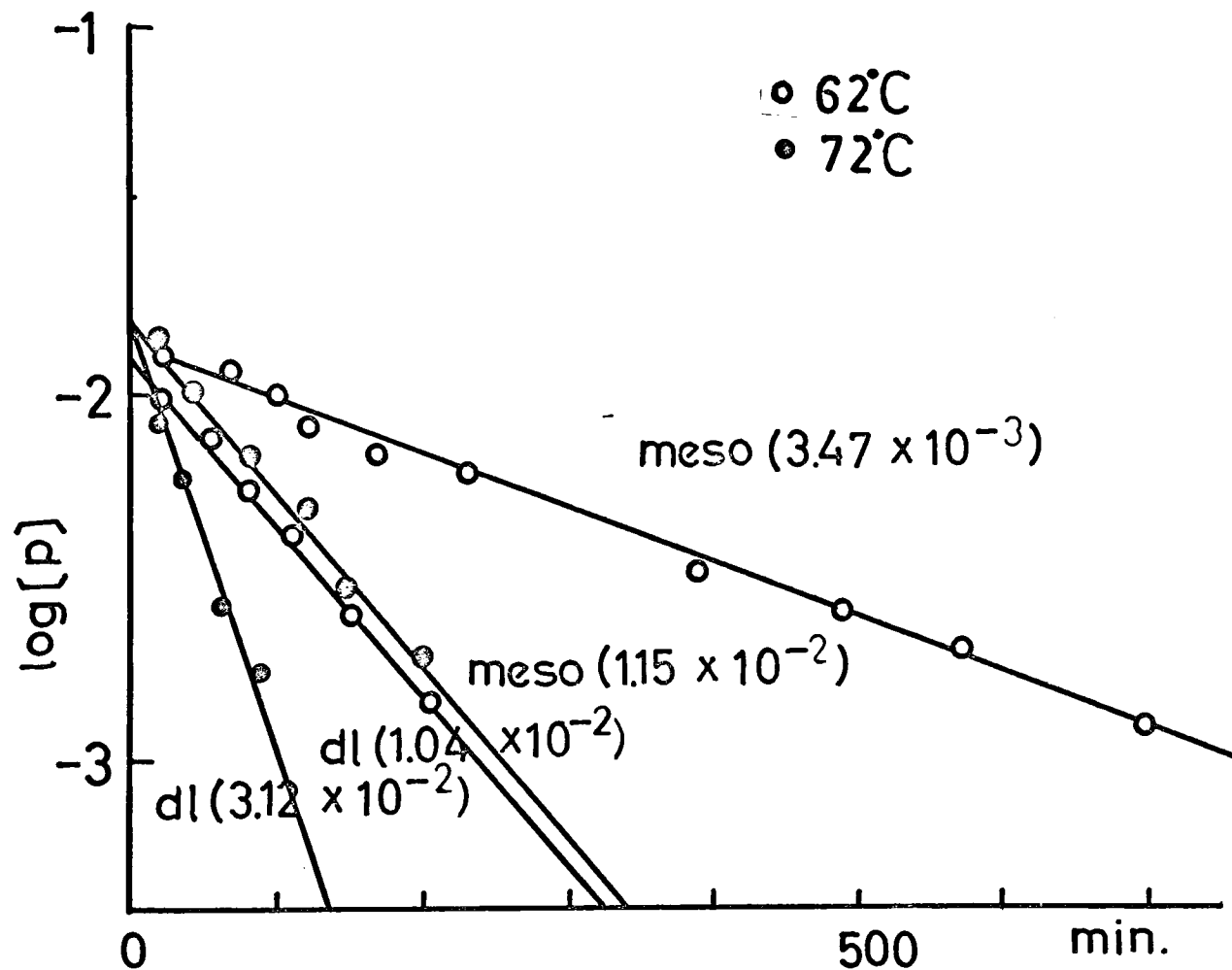
Fig.1   First order plots of rearrangement of
2,2-dimethoxybenzpinacol (1.36×10^{-4} mol-HClO$_4$)
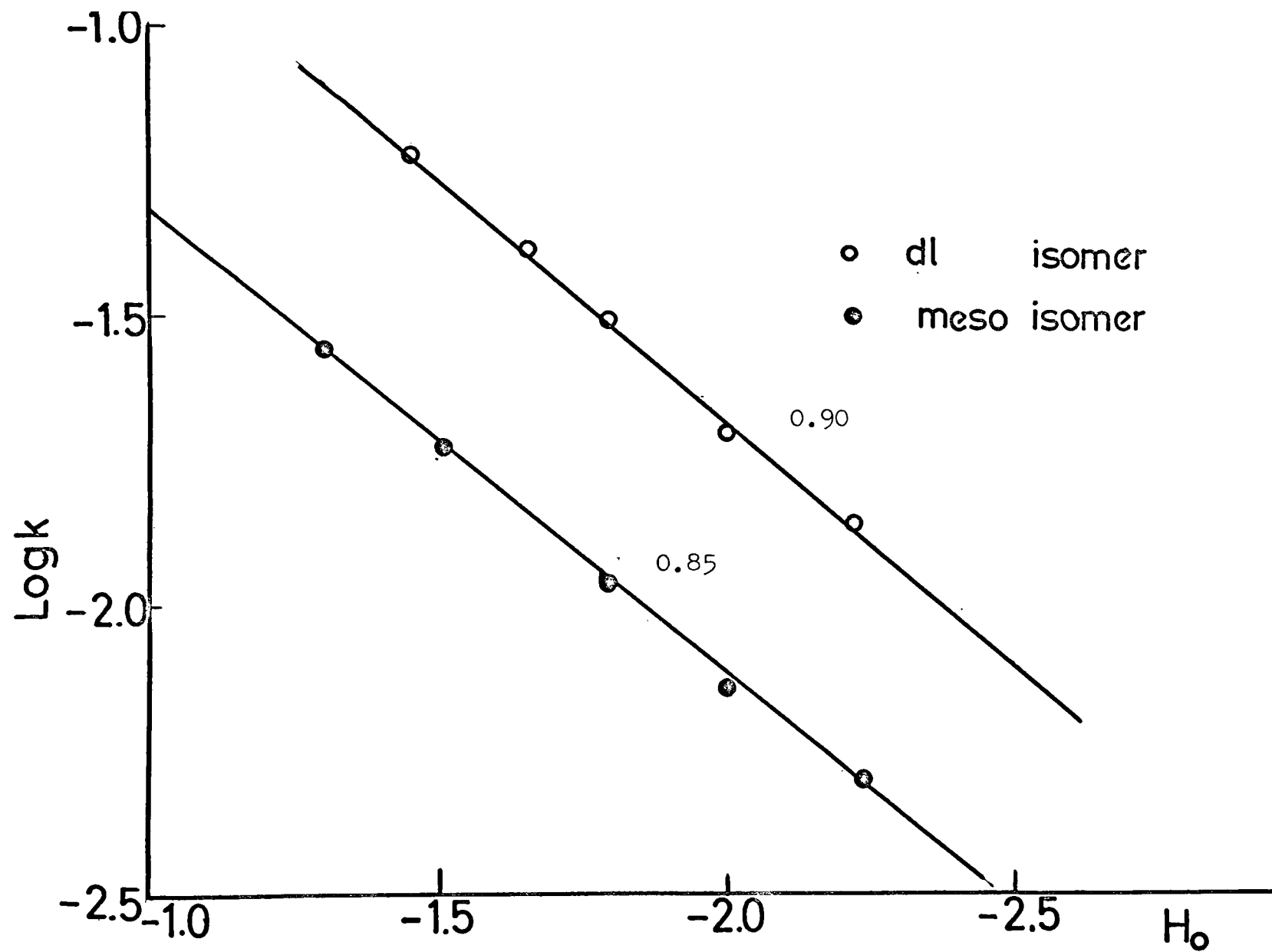
Fig.2 Correlation of first order rate constant with the Hammett
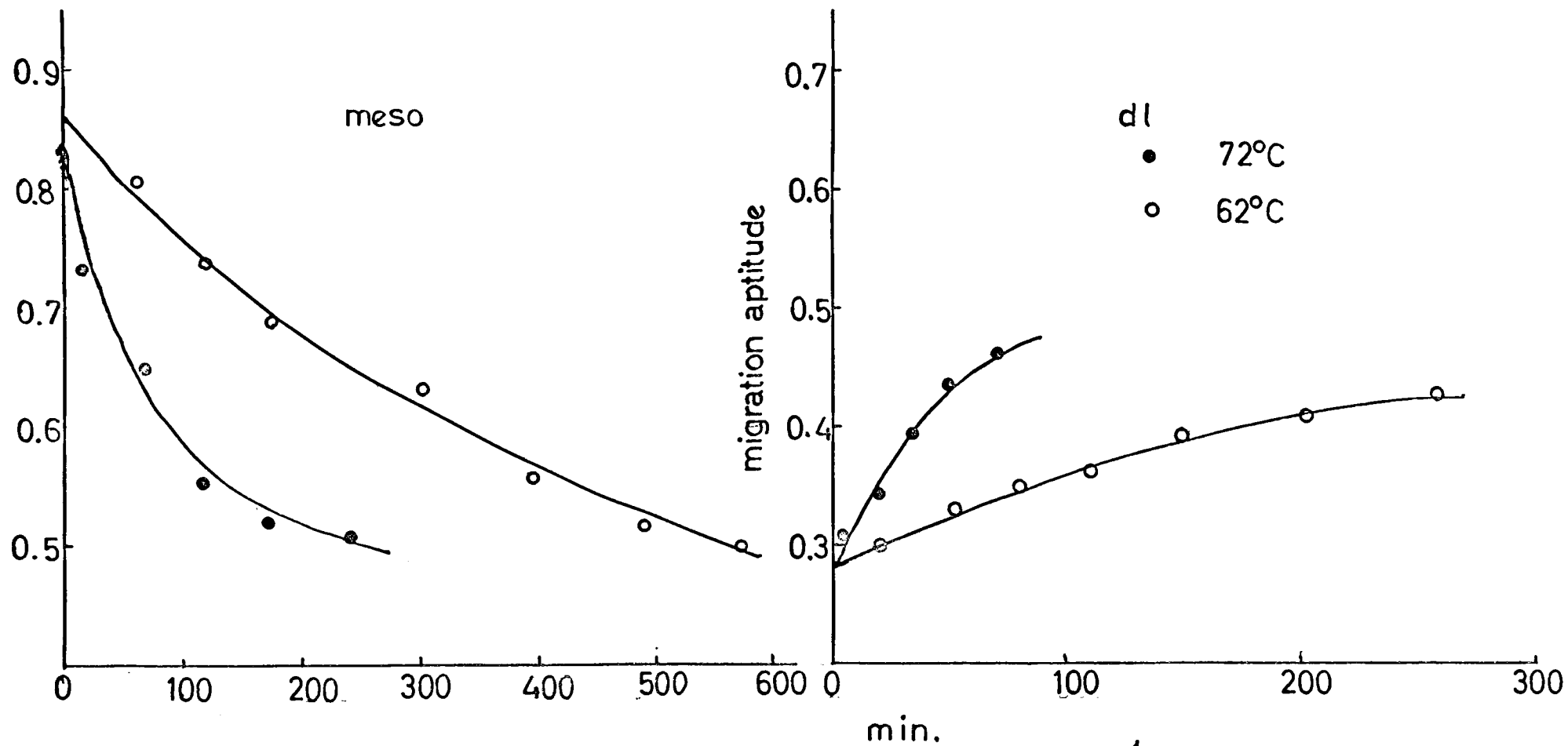acidity function of the medium at 72°C

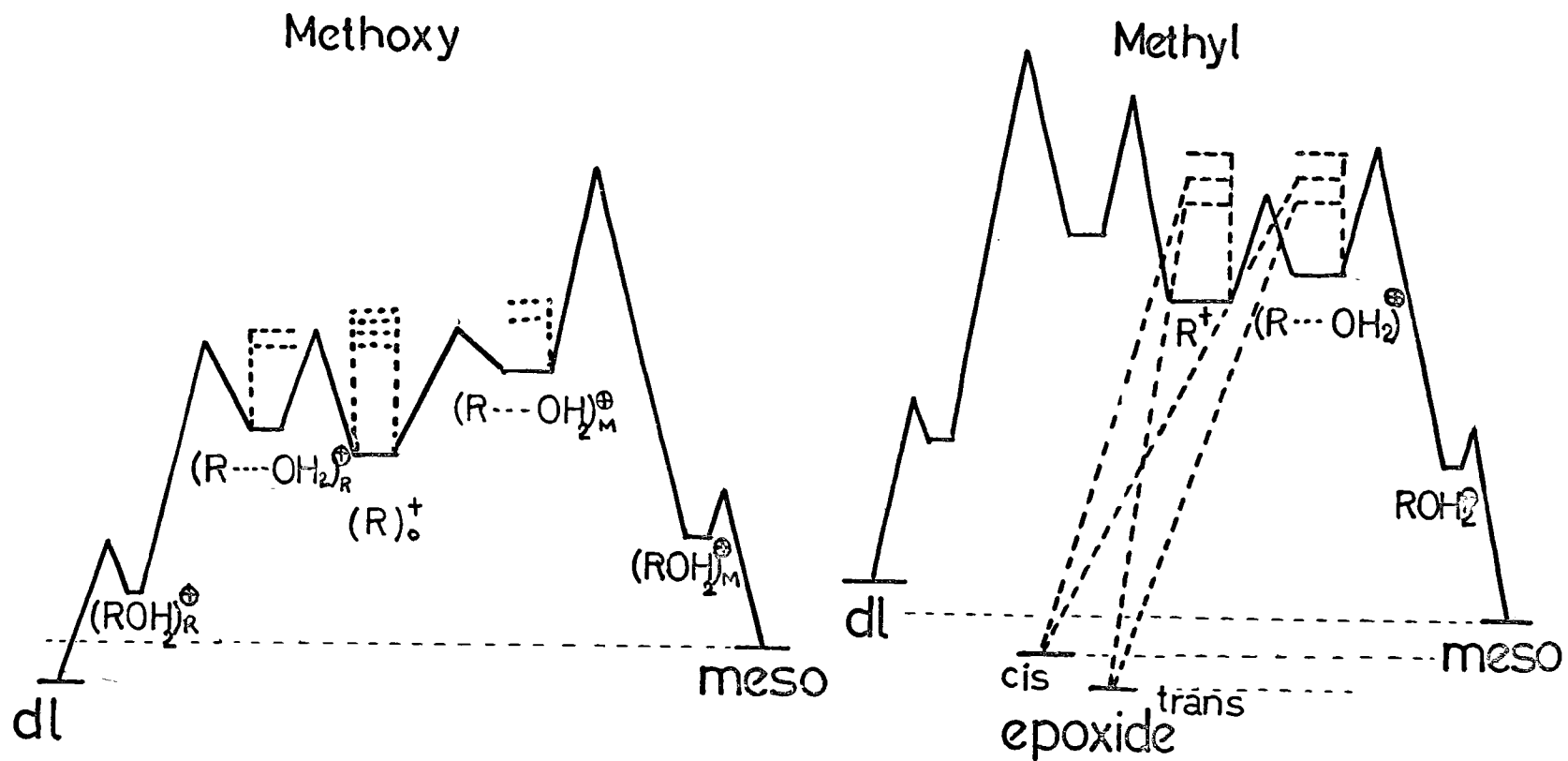Fig.3   Variation of migration aptitude with time $(1.36 \times 10^{-4} M\text{-}HClO_4)$

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

Scheme 1

主 論文

第 二 部

Studies on the Pinacol Rearrangement. V. The Rearrange-
ments of cis- and trans-1,2-Diphenyl-1,2-ditolyl-
ethylene oxides[1]

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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 $HClO_4$-anhydrous acetic acid.
Linear correlations of logarithm of the rate constants(log k)
with the Hammett acidity function of the medium(H_o) 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-

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

cally distinguishable routes as the following;

$$P_{meso} \rightleftharpoons C \longrightarrow T \longrightarrow K$$

where C and T are <u>cis-</u> and <u>trans-</u>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, there are numerous problems remained to be solved, which have been reported in the preceding papers[3]. In part IV, the rearrangements of <u>meso-</u> and <u>dl</u>-2,2'-dimethoxybenzopinacols have been investigated with respect to the character of the intermediate, the reaction processes and the migration aptitudes.
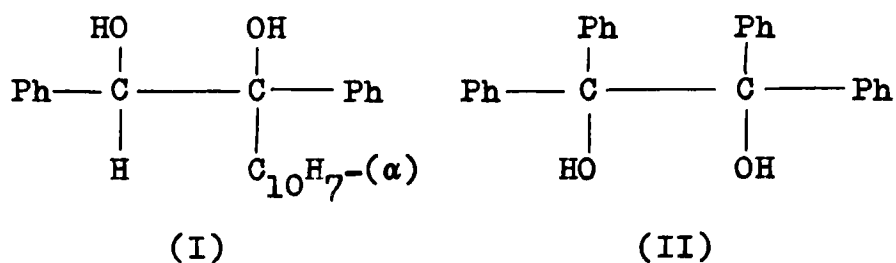
The role of the epoxide intermediate in the pinacol rearrangement has been already discussed by Wheland[4] ; he concluded that the epoxide does not play an essential role in the pinacol rearrangement. The only two examples in which the stable epoxide was recognized were the rearrangements of <u>erythro-</u>

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[2] For example, see C. J. Collins, <u>Quarterly Review</u>, <u>14</u>, 357 (1960).

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

[4] G. W. Wheland, "<u>Advanced Organic Chemistry</u>", John Wily and Sons, Inc. New York, N. Y., (1949) pp. 451—534.

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

HO   OH   Ph   Ph

Ph— C———— C——Ph   Ph— C———— C——Ph

H $C_{10}H_7$-(α)   HO   OH

(I)   (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'-dimethylbenzopinacol gave two epoxides(III) and
(IV) and pinacolone(V).

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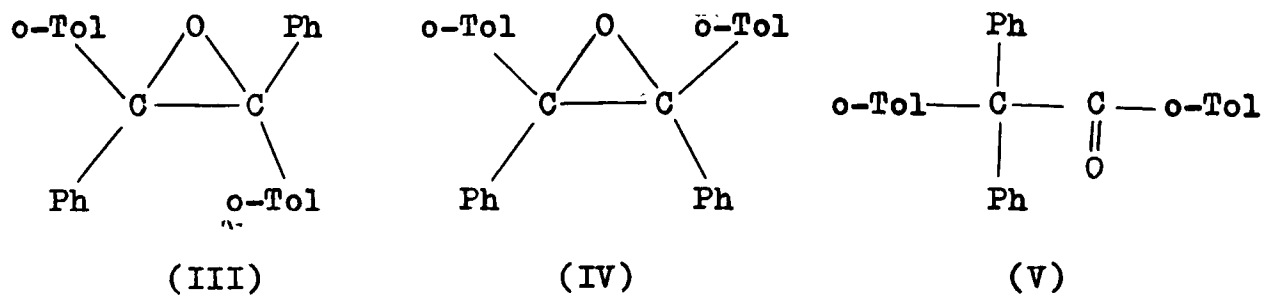
The thin layer chromatogram of the reaction products is
shown in Fig.1. The assignment of configuration(cis or trans)

[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; Rf=0.64, B; Rf=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 mag-
nitude 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) co-
incides with the above argument.

The same methyl-methyl interaction would decrease conju-
gation 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 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 qualitative and yet
unambiguous assignment of the configuration hardly is obtained
at the moment, the assignment by these data are not incon-
sistant 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 hyper-
conjugation 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, 1o37 (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 pinacol[1], would be expected, since it is known that the pinacol rearrangements studied hitherto show the first order kinetics[9]. 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_o 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), 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 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 distingushable routes as the following,

$$C \xrightarrow{\;k_1\;} T \xrightarrow{\;k_2\;} K \qquad\qquad k_T = k_2$$

$$C \xrightarrow{\;k_3\;} K \qquad\qquad k_C = k_1 + k_3$$

where C, T and K represent the _cis_-epoxide, _trans_-epoxide and the pinacolone respectively.

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

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[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

$$-d(C)/dt = k_1(C) + k_3(C) \tag{1}$$

$$d(T)/dt = k_1(C) - k_2(T) \tag{2}$$

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

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

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

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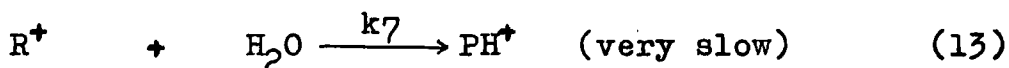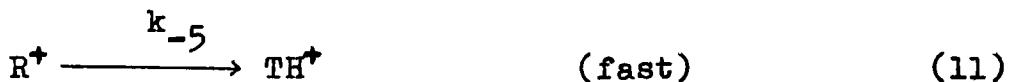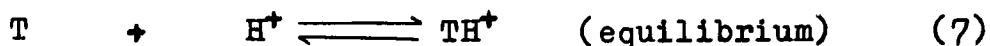$$\left. - e \exp(-k_2 t)\right\}$$

i.e.

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

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)$_o$ and (T). Table 3 summarizes the values of the experimental activation ener-gy E_a, and of the free energy $\Delta F^{\neq}$ and entropy $\Delta S^{\neq}$ of ac-tivation calculated from the values of k'$_1$, k'$_3$, k'$_C$ and k'$_T$, where k' = k_{exp}/(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.
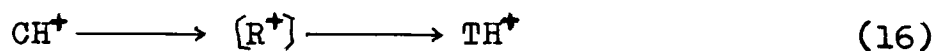
The above results suggest the two possible mecha-nisms.

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

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

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

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

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

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

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

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

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

To bring this formulation into conformity with the kinetics, it is necessary that $k_6 > k_{-5} \gg k_4 > k_5 > k_{-4}$, 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

$$TH^+ \longrightarrow [L^+] \longrightarrow K \quad + \quad H^+ \qquad (14)$$

$$CH^+ \longrightarrow [M^+] \longrightarrow K \quad + \quad H^+ \qquad (15)$$

$$CH^+ \longrightarrow [R^+] \longrightarrow TH^+ \qquad (16)$$

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.

o-Tol   Ph   Ph   Ph

    C————C   C————C

Ph   OH   o-Tol   o-Tol   OH   o-Tol

   (L⁺)   (M⁺)
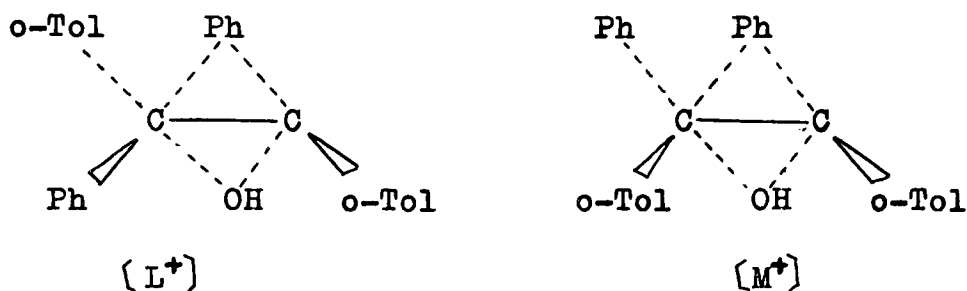
In view of the generalization that neighboring group
participation is apt to decrease with increasing phenyl
substitution of the carbon atom at which heterolysis
occurs[12], and in view of the large positive values of
$\Delta S^{\ddagger}$ and occurrance of isomerization, it is expected that
the contribution 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 sub-
stituted 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

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[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 paper[1], 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 $(R)^+_O \longrightarrow$ 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 $k^T_r > k_O$ or $k^T_r > k^O_r$ 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 paper[1].

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 aquous solution(0.04%). The mixture of benzene and hexane (1 : 2) was used as a developer.

The epoxide of Rf=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%)

The epoxide of Rf=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 solution of perchloric acid was described in the preceding paper[1].

Analytical Methods. The ordinary method by which the pinacol is estimated (oxidation with lead tetraactate) 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 Å 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 Å 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 ±0.05°, 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 aparatus[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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[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)
			8μ	11μ	12μ	λmax	$\varepsilon \times 10^{-2}$		
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 CATALIZED REARRANGEMENT OF cis- AND trans-
1,2-DIPHENYL-1,2-DITOLYLETHYLENE OXIDE IN ANHYDROUS
ACETIC ACID AT 72°C

$HClO_4$ $MOL \times 10^3$	H_o	$k \times 10^{-3}$ 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

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 ($\times 10^4$)	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	31.8		
	72	76.7		22.6	23.4
k_3'	62	96.4	31.0		
	72	328		23.2	22.2

Silica Gel

A
B

Epoxide

Pinacol + Pinacolone

Alumina

Pinacol

Pinacolone

10 20 40 60 90   160 210 380 500 660

Fig.1   (min)

Thin layer chromatogram of reaction products of
2,2'-dimethylbenzpinacol (benzene : hexane = 1 : 2)
in glacial acetic acid (2.64 x 10^{-4} mole-HClO$_4$) at 72°C
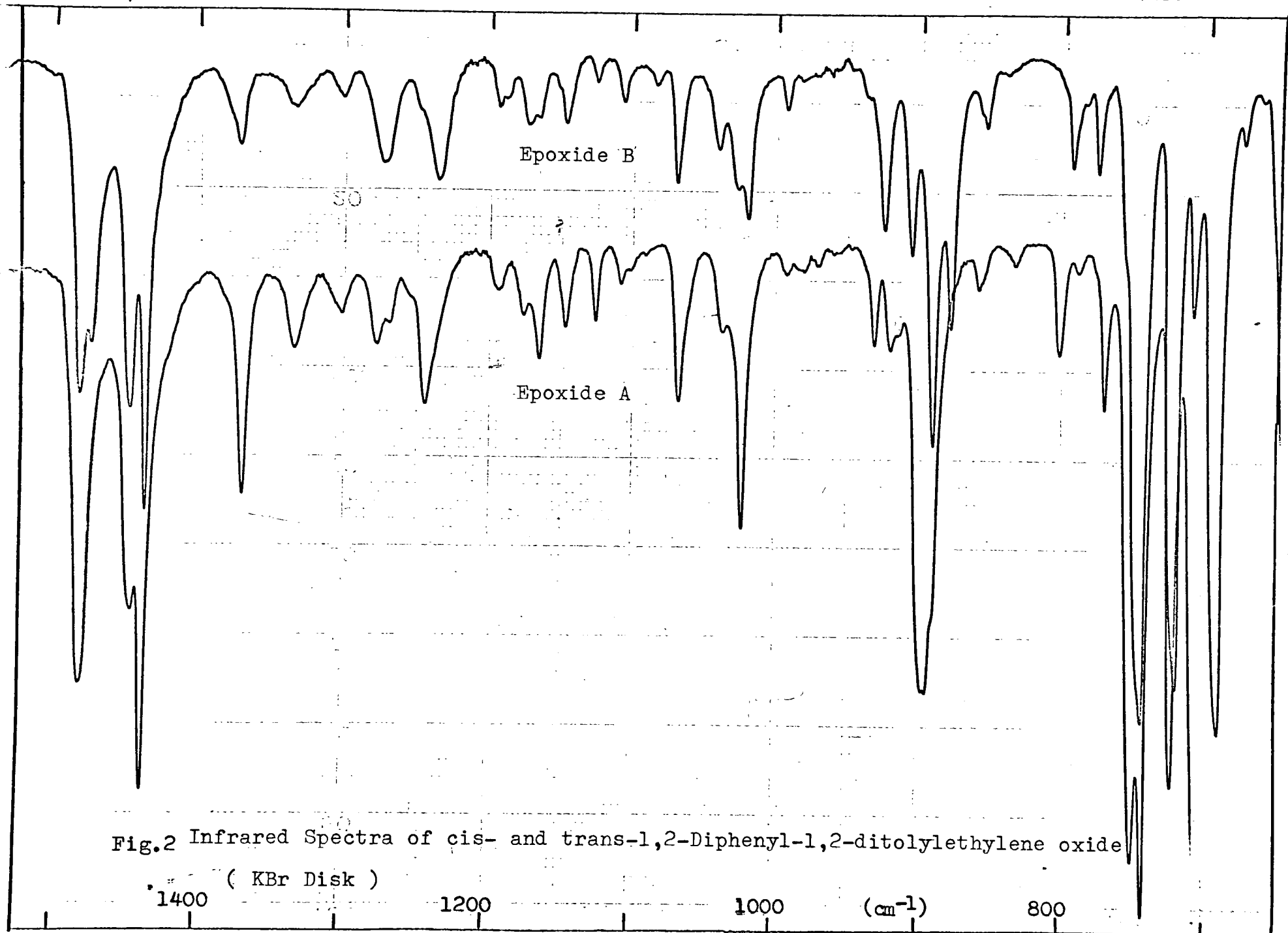
0.00942 mole Pinacol

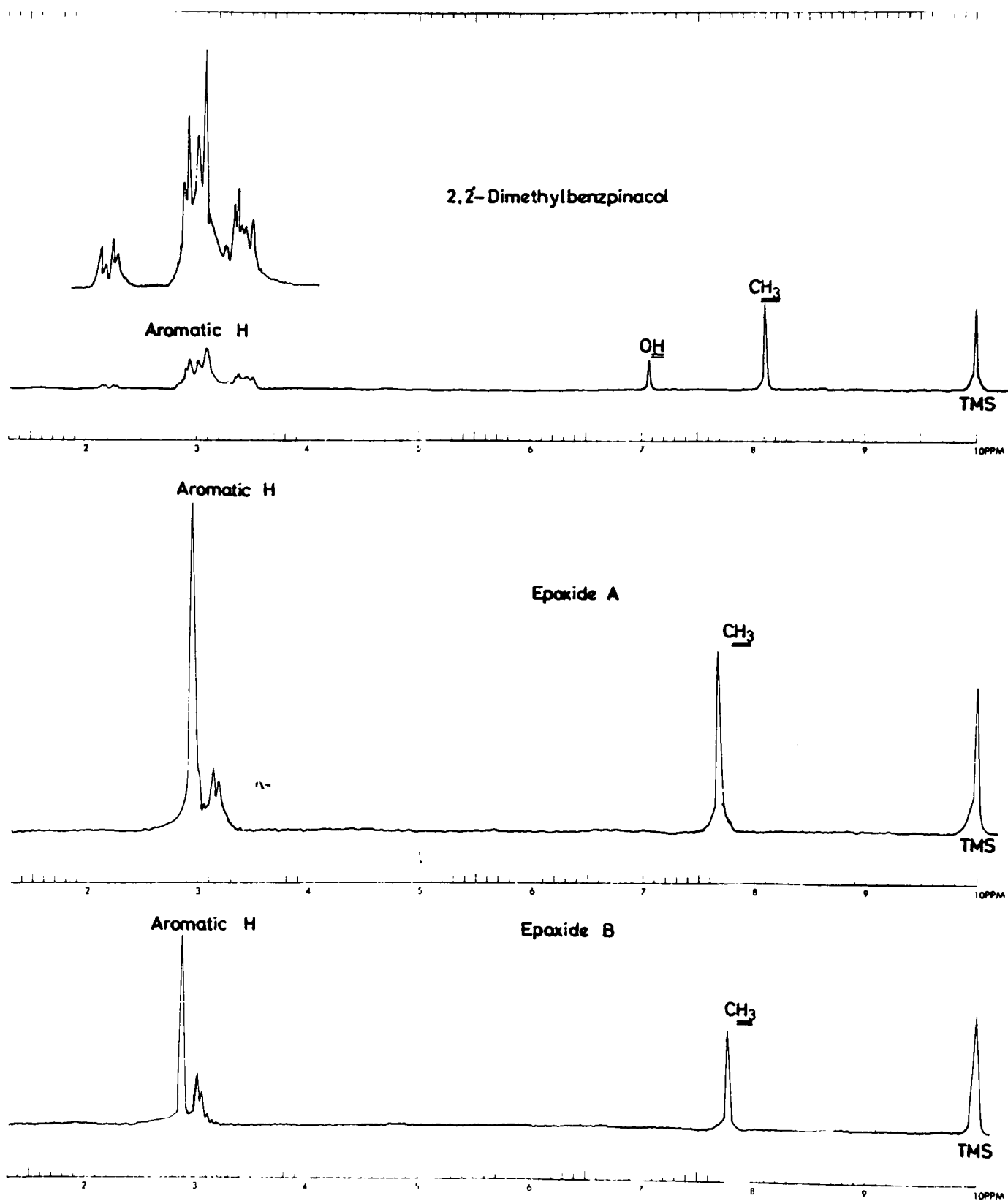Fig.2 Infrared Spectra of cis- and trans-1,2-Diphenyl-1,2-ditolylethylene oxide (KBr Disk)

2,2'-Dimethylbenzpinacol

Aromatic H

OH

CH₃

TMS

Epoxide A

Aromatic H

CH₃

TMS

Epoxide B

Aromatic H

CH₃

TMS

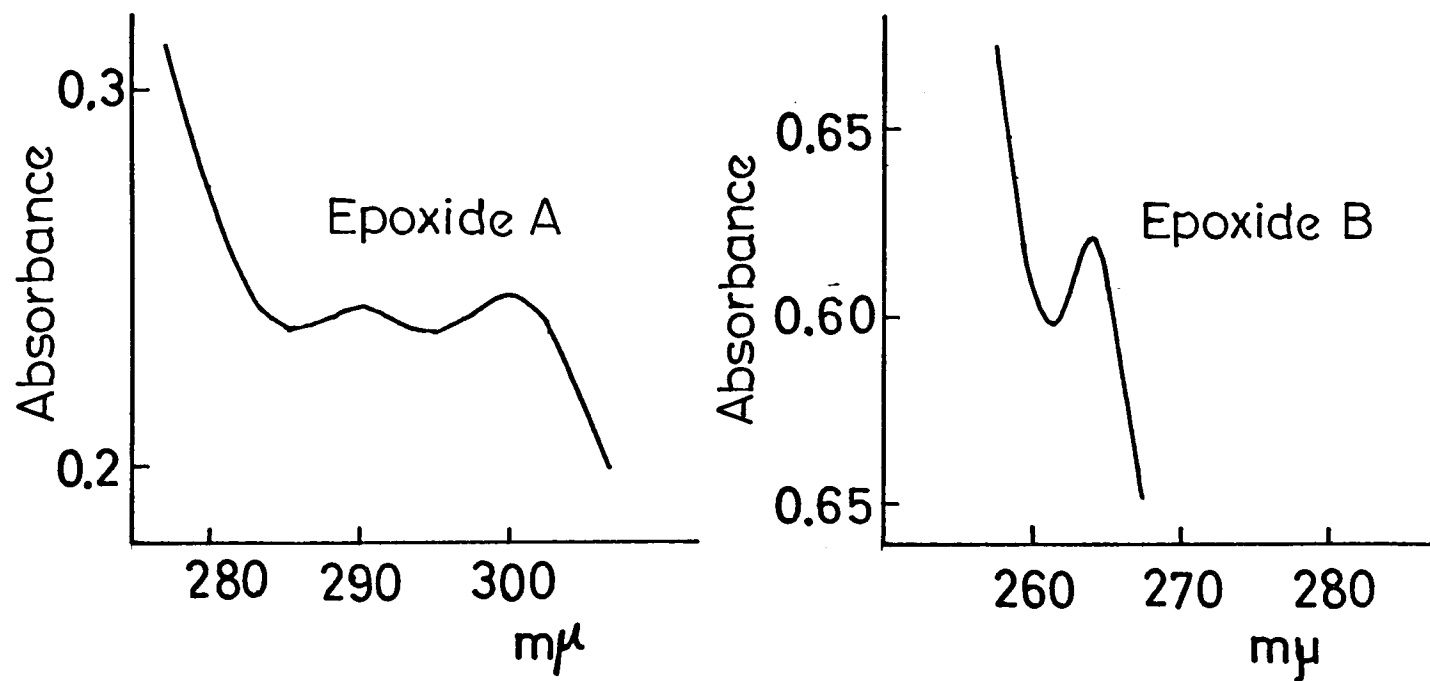Fig.3 Nmr Spectra of 2,2'-dimethylbenzopinacol, Epoxide A and Epoxide B.

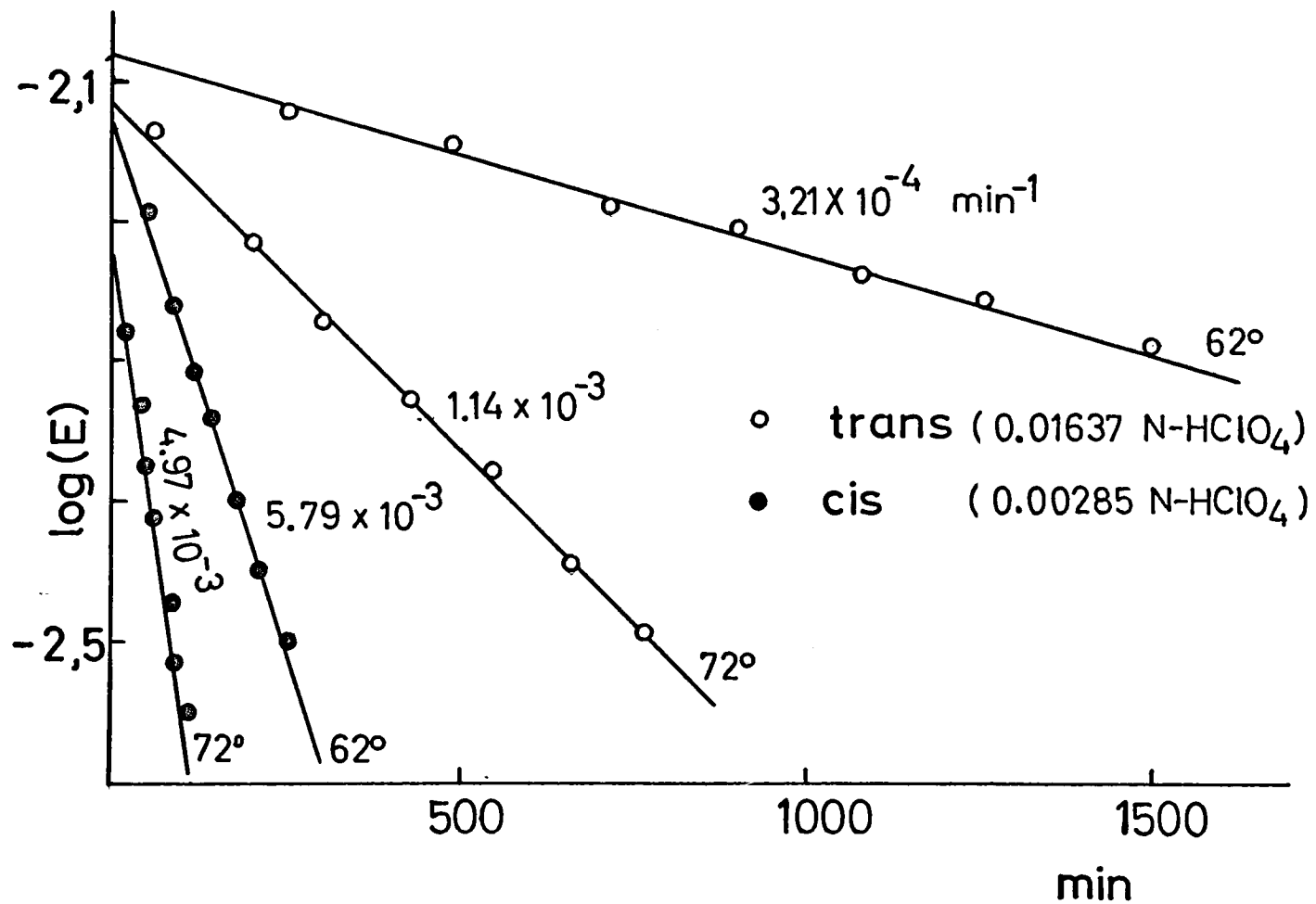Fig.4 UV Spctra of cis- and trans-1,2-Diphenyl-1,2-ditolylethylene oxide in Ethanol

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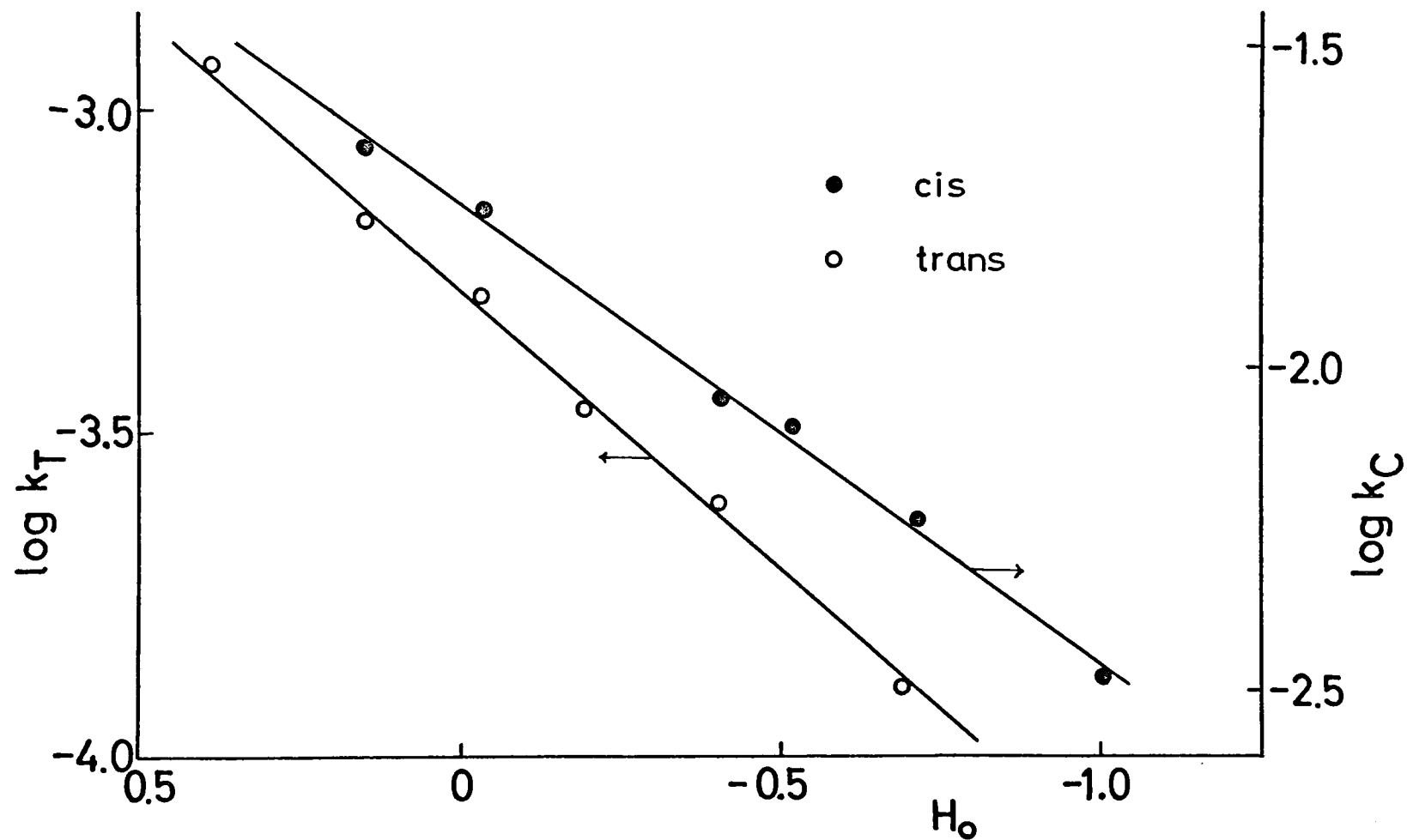
ethylene oxide

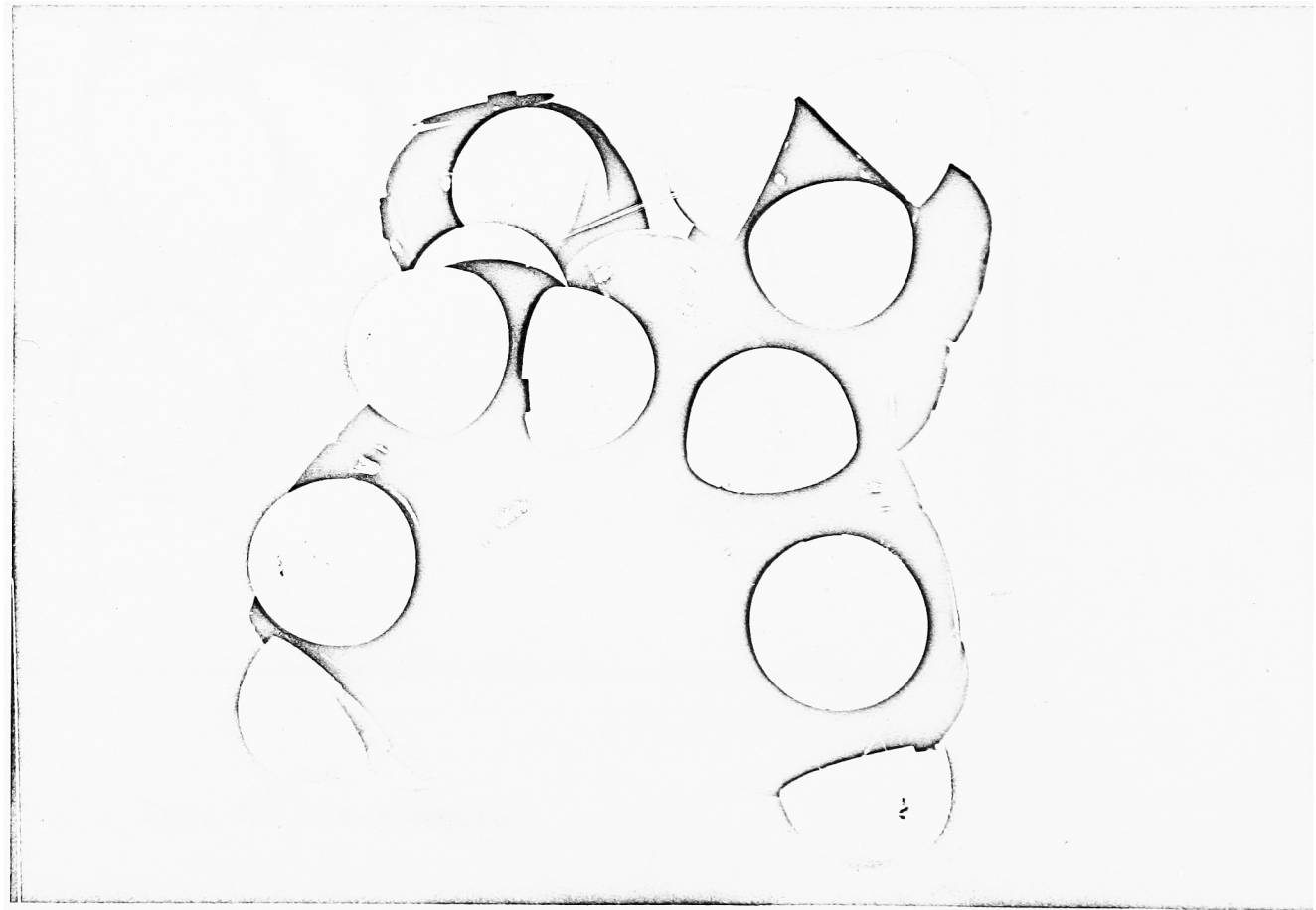Fig.6 Correlation of first order rate constant with the Hammett acidity function of the medium at 72°C
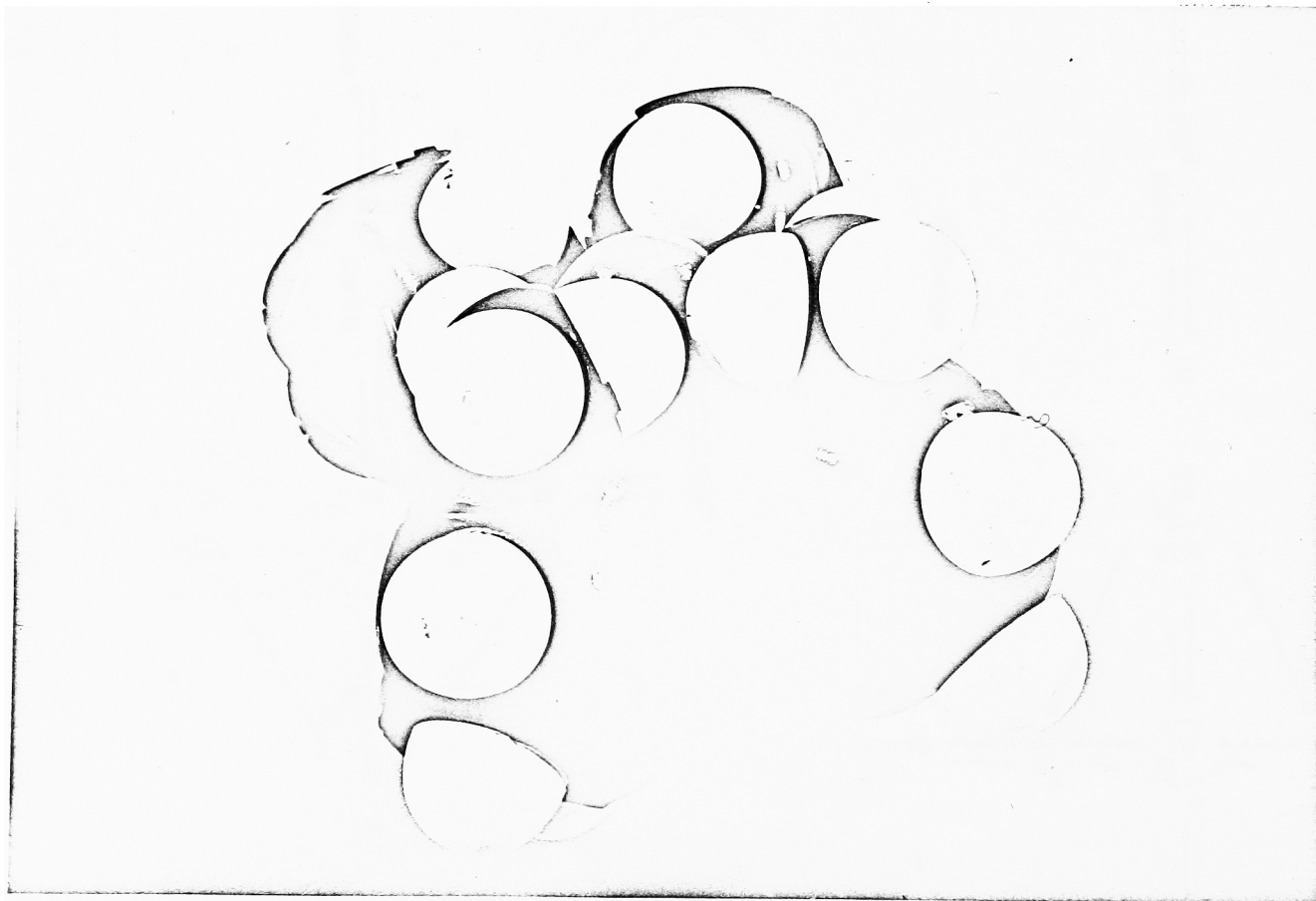
Fig. A trans-Epoxide

Fig. B cis-Epoxide

$$C \quad + \quad H^+$$

$$CH^+$$

$$P_{meso} \rightleftharpoons PH^+_{meso} \longleftarrow \{R \cdots OH_2\}^+_M \rightleftharpoons [R_o]^+ \longrightarrow K$$

$$TH^+$$

$$T \quad + \quad H^+$$

Scheme 1

$$H^+ + T \rightleftharpoons TH^+$$

$$(\ R\ )^+_T$$

$$k_o \qquad k_r$$

$$P_{meso} \rightleftharpoons PH^+_{meso} \rightleftharpoons (\ R\ )^+_o \longrightarrow K$$

$$k^o_r$$

$$(\ R\ )^+_C$$

$$H^+ + C \rightleftharpoons CT^+$$

Scheme 2