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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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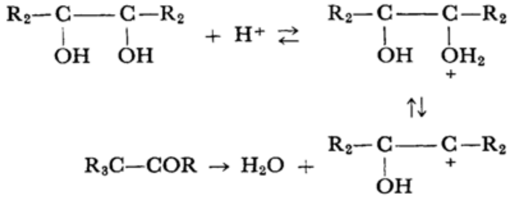
The first-order rate constants of the perchloric acid-catalyzed rearrangements of the *meso*- and *dl*-2,2′-dimethoxybenzopinacols were measured in anhydrous acetic acid. A linear correlation of the logarithm of the first-order rate constants ($\log k$) with Hammett acidity function (H_0) was obtained 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* 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:



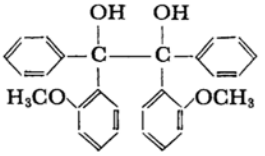
$$R_2-\underset{OH}{C}-\underset{OH}{C}-R_2 + H^+ \rightleftarrows R_2-\underset{OH}{C}-\underset{\underset{+}{OH_2}}{C}-R_2$$

$$\uparrow\downarrow$$

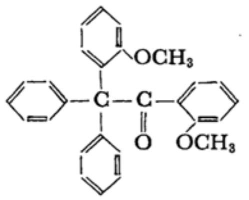
$$R_3C-COR \rightarrow H_2O + R_2-\underset{OH}{C}-\underset{+}{C}-R_2$$

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 rearrangement of the benzopinacol.3)

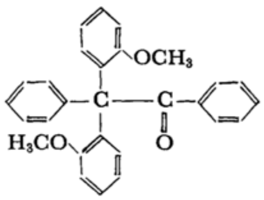
The present communication will present our findings on the kinetics of the rearrangements of the *meso*- and *dl*-2,2′-dimethoxybenzopinacols (I) to the 2-methoxybenzoyl-2-methoxyphenyldiphenylmethane (II) and benzoyldi-2-methoxyphenylmethane (III) in anhydrous acetic acid, with perchloric acid as the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

[*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).

1) For an excellent review of the pinacol rearrangement, see C. J. Collins, *Quart. Rev.*, **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).

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 m*l* of a 70—72% reagent grade commercial product to approximately 200 m*l* 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 catalyst was added to this solution. At appropirate times, 1-m*l* samples were removed and put into test tubes containing 0.0010 m*l* of a concentrated solution of potassium acetate. Each sample (0.20 m*l*) was treated by thin-layer chromatography.[2b)] Each pinacolone fraction was extracted with chloroform to a 10.0-m*l* 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)]

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)]

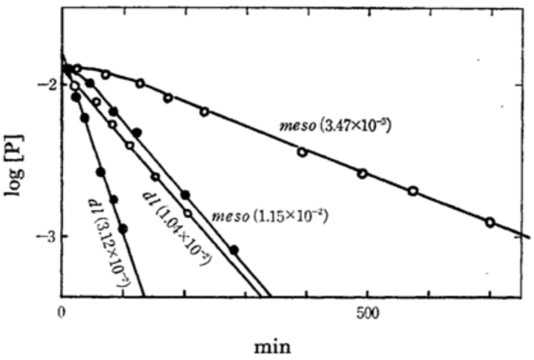


Fig. 1 First order plots of rearrangement of 2,2′-dimethoxybenzopinacol (1.36×10^{-1} mol $HClO_4$).

○ 62°C ● 72°C

TABLE 1. SUMMARY OF KINETIC DATA FOR THE PERCHLORIC ACID-CATALYZED REARRANGEMENT OF 2,2′-DIMETHOXYBENZOPINACOL IN ANHYDROUS ACETIC ACID AT 72°C

$HClO_4$ (mol×10^4)	H_0	$k\times10^2$(min^{-1})	log k	$k'\times10^{-2}$ (l/mol×min)
		(*meso*)		
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
		(*dl*)		
0.532	−2.22	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 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)]

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).

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

[*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.

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).

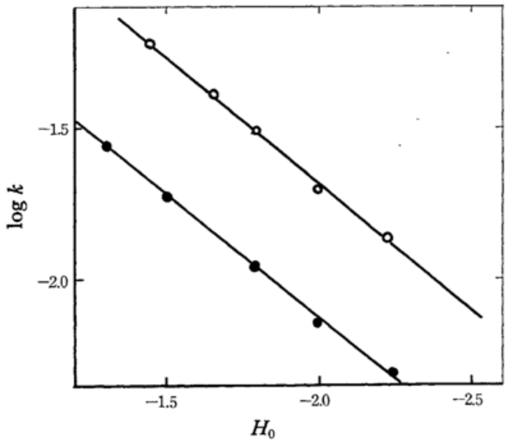

Fig. 2. Correlation of first order rate constant with the Hammett acidity function of the medium at 72°C.
○ *dl*-isomer ● *meso*-isomer

TABLE 2. THERMODYNAMICS OF ACTIVATION FOR REARRANGEMENT OF 2,2′-DIMETHOXYBENZOPINACOL IN 1.36×10^{-4} mol $HClO_4$ - ACETIC ACID

	Temp. °C	Specific rate $10^{-2}\times$ (l/mol×min)	E_a kcal/mol	$\Delta S^{\ddagger}$ a) e. u.	$\Delta F^{\ddagger}$ a) 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	0.249			

a) Computed from the equation
$$k'=(e\boldsymbol{kT}/\boldsymbol{h})\exp(-\Delta F^{\ddagger}/\boldsymbol{RT})$$
$$=(e\boldsymbol{kT}/\boldsymbol{h})\exp(-E_a/\boldsymbol{RT})\exp(\Delta S^{\ddagger}/\boldsymbol{R}).$$

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 implication 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*. Figure 3 shows that the migration aptitude of the *meso*-isomer decreases with time, while that of the *dl* increases.

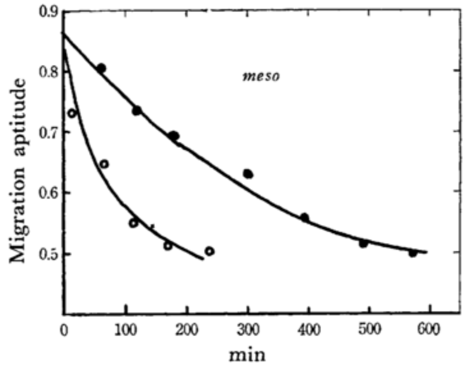

Fig. 3. Variation of migration aptitude with time (1.36×10^{-4} mol $HClO_4$).
● 62°C ○ 72°C

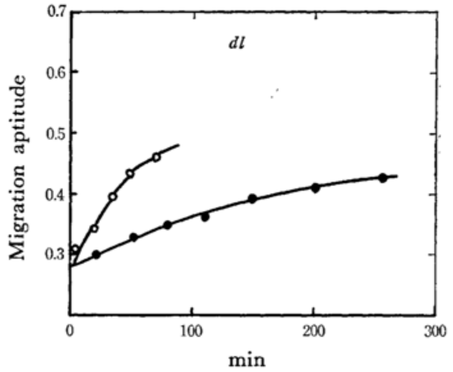

Fig. 3. Variation of migration aptitude with time (1.36×10^{-4} mol $HClO_4$).
● 62°C ○ 72°C

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 1 (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*

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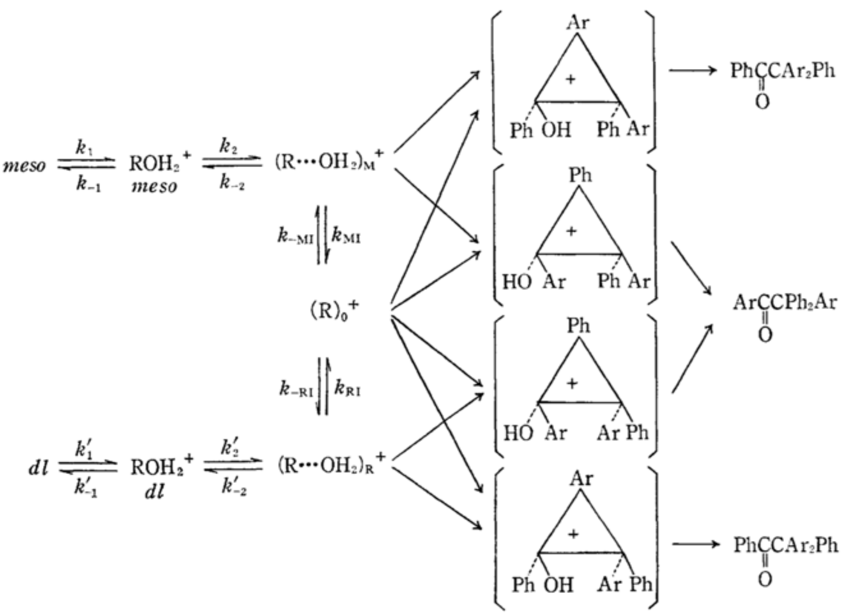
[9] J. E. Leffler and E. Grunwald, "Rate and Equilibria of Organic Reactions," John Wiley and Sons, New York and London (1963), p. 208.

*3 Migration aptitude = Aryl/Phenyl.



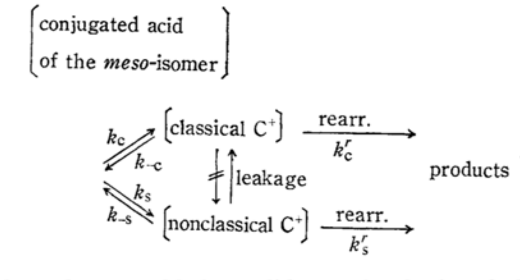
Scheme 1 {I ……Isomeisotion
R ……*dl*
M ……*meso*

intermediates without any configurational identities, such as $[\mathrm{R}]^+_{\mathrm{O}}$ and $[\mathrm{R\cdots OH_2}]^+_{\mathrm{R}}$, 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 aptutude at time 0 (in Fig. 3) reflects the value of the intrinsic migration aptitude of $[\mathrm{R\cdots OH_2}]^+_{\mathrm{M}}$ or $[\mathrm{R\cdots OH_2}]^+_{\mathrm{R}}$. 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 states of the phenyl (*o*-anisyl)-group migration *via* the *dl*-aggregate intermediate, $[\mathrm{R\cdots OH_2}]^+_{\mathrm{R}}$ (*meso*-aggregate intermediate, $[\mathrm{R\cdots OH_2}]^+_{\mathrm{M}}$) is smaller in magnitude than that *via* the *meso*-aggregate intermediate, $[\mathrm{R\cdots OH_2}]^+_{\mathrm{M}}$ (*dl*-aggreagate intermediate, $[\mathrm{R\cdots OH_2}]^+_{\mathrm{R}}$), therefore, the phenyl-group migration *via* $[\mathrm{R\cdots OH_2}]^+_{\mathrm{R}}$ may be more probable than that *via* $[\mathrm{R\cdots OH_2}]^+_{\mathrm{M}}$. 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, $[\mathrm{R\cdots OH_2}]^+_{\mathrm{M}}$, $[\mathrm{R\cdots OH_2}]^+_{\mathrm{R}}$, and $[\mathrm{R}]^+_{\mathrm{O}}$.

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, 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 liekly that $\mathrm{rate_S^{rearr}}$ and $\mathrm{rate_C^{rearr}}$ 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).

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

(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 1. The observed change in migration aptitude with time, therefore, seems to suggest that the classical carbonium ions are more favored 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) 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 bypassed mechanism *via* unstable epoxide intermediates can not be excluded.

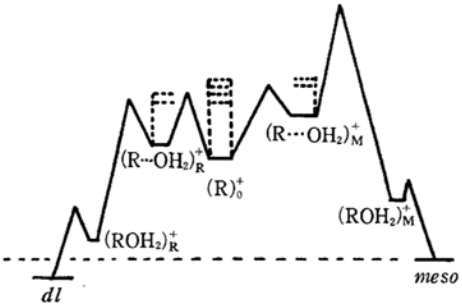

Fig. 4. Schematic energy diagram for interconversion of the diols (full line) and for formation of the products (broken line).

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 Ryozo Goto for his helfpul discussions and encouragement, and Dr. Akira Sera and Dr. Jun'ichi Hayami for their kind and valuable advice and discussions.

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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).

(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).