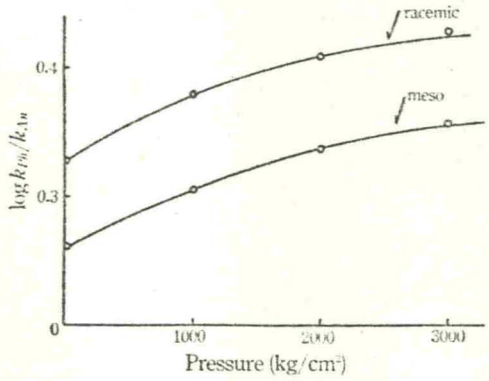

Fig. 3 Plot of log (k_{PA}/k_{A0}) *vs.* pressure obtained from the results in Table 4

Although the *o*-anisyl migration is easier compared with that in acetic acid, the pressure effect is in the same direction and magnitude as in acetic acid. From the slopes in Fig. 3, $\delta\Delta V_0^{\neq} = -3.4\pm\sim0.5$ (meso) and $-4.0\pm\sim0.5$ (racemic) m*l*/mole are obtained respectively.

The results in Tables 3 and 4 are summarized as follows.

(i) In both solvents, the migratory aptitude of the *o*-anisyl group of meso form is greater than that of racemic form.

(ii) In both solvents, the *o*-anisyl migration is retarded with increasing pressure.

(iii) A difference of the migratory aptitudes of meso and racemic form does not change with pressure. That is, the pressure effect is equal upon both isomers.

(iv) Acetonitrile facilitates the *o*-anisyl migration compared with acetic acid*4.

The isomerization of the pinacols under reaction conditions is shown in Table 5*5.

Table 5 Isomerization of the pinacols observed under reaction conditions

solvents	ordinary pressure	high pressure
acetic acid	meso⇄racemic	meso⇄racemic
acetonitrile	meso⇄racemic	meso⇄racemic
toluene	meso⇄racemic	meso⇄racemic

The facts that the migratory aptitudes are different in meso and racemic form and that the racemic pinacol does not isomerize under all the conditions used suggest that this reaction proceeds, in general, as in equation (3)*6. It may be considered, however, that some portion of meso form rearranges by the way of equation (4) under some conditions. The details of the reaction mechanisms and the reasons for

*4 A concentration of catalyst, *p*-toluenesulfonic acid, was shifted to 0.088 N, but the migratory aptitude did not change. The values at 1 atm were 5.47 (meso) and 4.06 (racemic).

*5 The isomerizations were confirmed by thin layer chromatography.

*6 In benzopinacol, Gebhart[9] suggested equation (4) on the basis of the relatively large value of $\Delta S^{\neq}$. However, taking into consideration the contribution to the entropy of activation from desolvation accompanied by the migration of the phenyl group, his suggestion seems to be uncertain or doubtful.

9) H. J. Gebhart Jr., *J. Am. Chem. Soc.*, **76**, 3925 (1954)