

Pressure Effect: From the value of $\partial \Delta V^{\ddagger} / \partial P$, the volume of transition state [III] is larger than that of [IV] by about 3~4 ml/mole in acetic acid and acetonitrile at 1 atm. As mentioned in the introduction, these differences should not be present in pinacol molecule itself, but rather in solvated species. Moreover, the fact that the pressure effect upon two isomers is equal indicates that the volumes of transition states are not affected by the configuration of nonparticipating substituents.

Solvent Effect: Some desolvation will be expected to occur during the rearrangement of an aryl group, because of both steric and electronic changes in the molecule. The large configurational transformation of the pinacol molecule should require the reorganization of solvation sphere, because the solvent molecules should rearrange their packing for the purely sterical reasons to accommodate the changed shape of the reacting molecules. An alternative way to state this interpretation is to say that the solvent molecules attached to positively charged part of the reactant or to methoxyl oxygen atom (especially in acetic acid), are excluded by an attacking aryl group. For they interfere its approach. Moreover, the spreading of positive charge over the migrating aryl group should cause the loosening of the electrostatic interaction between the solvent and the reactant species. The degree of desolvation should be larger in *o*-anisyl migration than in phenyl¹⁰⁾. For the *o*-methoxyl group—its position is close to the reaction center and hence the repulsion between the substituents must be larger—should require a larger transformation of the geometrical shape of the reacting molecule. And also the positive charge might spread over this substituent for its electron releasing nature.

The experimental results in toluene make this interpretation plausible. The migratory aptitudes of the *o*-anisyl group in toluene are 6.40 (meso) and 6.00 (racemic), respectively, at 1 atm (77.4°C, *p*-toluenesulfonic acid 0.0096 N). These large values should be expected from the low solvating power of toluene. That is, in toluene because of its low solvating power, the destabilization of the transition states [VIII]~[XI] by desolvation might be small. Accordingly, the free energy difference between [VIII] or [X] and [IX] or [XI] should become smaller than in more polar solvents, acetic acid and acetonitrile. Although higher degree of desolvation is considered to cause the abnormally low migratory aptitude of the *o*-anisyl group, the difference in charge distribution in the two transition states [IX] or [XI] and [VIII] or [X] is not the sole reason for this higher degree of desolvation. If it is the only one reason, the migratory aptitude of the *o*-anisyl group should become smallest in acetonitrile which has the largest dielectric constant 37.5 (20°C). However, in practice, the migration of the *o*-anisyl group is retarded most highly in acetic acid. Accordingly, the higher degree of desolvation in the transition state [IX] or [XI] compared with [VIII] or [X] must be attributed mainly to steric factors: steric inhibition of solvation by the *o*-methoxyl group.

From the above discussion, we are now strongly inclined to maintain that besides the stability of the reacting molecule itself the difference in solvation of transition states must be considered in discussing the low migratory aptitude of the *o*-anisyl group in the pinacol rearrangement of meso and racemic 2,2'-dimethoxybenzopinacol.

10) That an *o*-substitution causes steric inhibition of solvation has been reported, e.g. (a) N. B. Chapman, J. Shorter and J. H. P. Utkey, *J. Chem. Soc.*, 1963, 1291 (b) W. J. leNoble, *J. Am. Chem. Soc.*, 85, 1470 (1963)

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