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ORGANIC REACTIONS UNDER HIGH PRESSURE

I Pressure and Solvent Effects on the Migratory Aptitude of o-Anisyl Group

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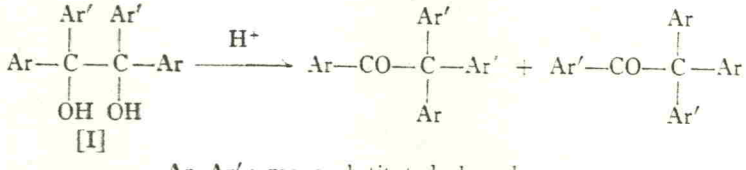
The migratory aptitude of the *o*-anisyl group in the pinacol rearrangement of 2,2′-dimethoxybenzopinacol is changed by pressure and solvents. The increasing pressure retards the migration of the *o*-anisyl group in acetic acid and acetonitrile. And the migratory aptitude increases with the changes of solvents in the order of acetic acid <acetonitrile <toluene. These observations indicate that the migration of the *o*-anisyl group brings about higher degree of desolvation than the migration of the phenyl group. This is attributable to steric inhibition of solvation and the difference of charge distribution in the two transition states.

Introduction

Bachmann[1] and Beale[2] investigated the pinacol rearrangement of symmetrically substituted benzopinacol derivatives [I] in acetic acid (equation 1) and they found that the migratory aptitudes of *p*-substituded phenyl groups are in the order of relative rates of aromatic substitution of the corresponding monosubstituted benzenes (Table 1). However, the migratory aptitude of the *o*-anisyl group was abnormally low.



(1)

[I]

Ar, Ar′ : monosubstituted phenyl group

Table 1 Migratory aptitudes of monosubstituted phenyl groups in [I]

substituents		substituents	
p-methoxyl	500	*p*-iodo	1.0
p-methyl	15.7	*p*-bromo	0.7
p-phenyl	11.5	*p*-chloro	0.66
p-*iso*-propyl	9	*o*-methoxyl	0.3

(phenyl=1)

However, no effort has been made to rationalize the reason of retardation of the *o*-anisyl migra-

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1) W. E. Bachmann and J. W. Ferguson, *J. Am. Chem. Soc.*, **56**, 2081 (1934)

2) C. H. Beale and H. H. Hatt, *ibid.*, **54**, 2045 (1932)