

behaviour of analogous reactions^{15,16} we should expect both $\Delta \bar{V}_1$ and ΔV_2^\ddagger to be negative; the first because reaction (1) involves an increase in electrostriction, the second because reaction (2) is a bimolecular association which forms a new covalent bond. It follows that ΔV^\ddagger should also be negative and that the total reaction rate should increase with increasing pressure. The experiments have shown that it does.

(b) *Isomer Distribution*

The unusually low ratio of *ortho* to *para* isomers formed in the benzylation of toluene at atmospheric pressure (Table 3) suggests that substitution in the *ortho* position is sterically hindered,⁴ perhaps by the bulkiness of the attacking ion-pair (III). In other experiments^{2,17} it has been found that, under pressure, aromatic substitutions yield appreciably higher proportions of sterically strained isomers than they do at atmospheric pressure. For that reason we expected the *ortho*:*para* ratio to increase with increasing pressure. Surprisingly, there was no measurable change. This could mean that the influence of pressure on the steric effect is offset by other factors of the kind we have discussed in relation to the nitration of toluene² or, more probably, that the low *ortho*:*para* ratio is not really caused by steric hindrance.

¹⁵ Hamann, S. D., "Physico-Chemical Effects of Pressure." pp. 160-96. (Butterworths: London 1957.)

¹⁶ Hamann, S. D., in "High Pressure Physics and Chemistry." (Ed. R. S. Bradley.) Vol. II, pp. 163-207. (Academic Press: London 1963.)

¹⁷ Gonikberg, M. G., Prokhorova, N. I., and Litvin, E. F., *Dokl. Akad. Nauk. SSSR*, 1963, **148**, 105.