**183.** *Mechanism of Substitution at a Saturated Carbon Atom. Part LII.\* Polar and Steric* ortho-*Effects in Bimolecular Finkelstein Substitutions of Arylalkyl Halides.*

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This paper records rates of bimolecular replacement of chlorine by iodine in (i) benzyl chloride and methyl-substituted benzyl chlorides in acetone at 0°, and (ii) 1-phenylethyl chloride and methyl-substituted derivatives in acetone at 44·5°. In series (i), *o*- and *p*-methyl substituents accelerate the reactions. It is concluded that transmitted polar factors are here involved and that direct effects also contribute to the particularly large rate increases which are observed for *o*-methyl groups. For 1-phenylethyl chlorides, a *p*-methyl group and one *o*-methyl substituent exert effects which may be ascribed similarly to polar influences. However, the second *o*-methyl group retards reaction and this is explained by assuming the incursion of a steric retardation, since on theoretical grounds steric pressure may be expected to appear in just these structural circumstances. The magnitude of the steric effect is discussed in relation to that exhibited in solvolysis (preceding paper).

ALTHOUGH all bimolecular reactions are in principle subject to steric hindrance, large differences of sensitivity are found between one type of reaction and another, and, even for one general reaction, between systems distinguished by the changes of geometrical relation that attend the formation of the transition state. Thus the generally greater sensitivity of bimolecular nucleophilic substitution than of bimolecular elimination to steric hindrance has been attributed to the less accessible situation of the attacked carbon of the former reaction than of the attacked hydrogen of the latter. And among bimolecular substitutions, the much more noticeable steric effects in those of alkyl than in those of aryl compounds have been explained on the basis that in the latter the molecule is planar and the attack is lateral to the plane.

In this paper we deal with bimolecular substitutions of a third geometrical type, those of arylalkyl compounds, such as benzyl and 1-phenylethyl halides. We shall find that steric hindrance here exerts a relatively mild effect, essentially for the reason that the reacting atoms, those which undergo the greatest movements, are not themselves subject to substantial steric pressures : such pressures arise among the other parts of the arylalkyl group, because the mechanism demands a Walden inversion, and therefore certain atoms have to be moved across the aromatic plane, which may already be somewhat fully occupied.

As in the previous paper, we examine the interaction between α-methyl and *o*-methyl substituents in benzyl-type chlorides, employing also *p*-methyl substituents as a control on polar effects. The reaction now studied is the Finkelstein displacement of the chlorine as chloride ion by entering iodide ion in solvent acetone, a medium in which these nucleophilic substitutions are shown by their kinetics to be bimolecular processes.

The geometrical situation is somewhat similar to that which arises in unimolecular substitutions in benzyl-type halides, but with the difference that, when the tetrahedral side-chain of the initial molecule (I) goes into the bipyramidal configuration of the transition state (II), the three preserved bonds of the α-carbon atom are bent, not merely towards the aromatic plane, as in the transition state of unimolecular substitution, but completely into a plane which will be closely assimilated to the aromatic plane. Therefore, as far as these three bonds are concerned, the geometrical conditions in the bimolecular transition state will be like those in the fully formed carbonium ion of unimolecular substitution, as discussed in the preceding paper. As in that case, steric pressure between α-hydrogen and *o*-methyl, and also between α-methyl and *o*-hydrogen, is insignificant, but steric pressure between α-methyl and *o*-methyl is considerable; although it is inescapable, and therefore effective, only when *two o*-methyl groups are present. In short, steric

* Part LI, preceding paper.

retardation in the bimolecular substitutions of these halides should arise in just the structural circumstances in which it does in their unimolecular substitutions; but in bimolecular substitutions the steric retardations should be stronger than in unimolecular.



Rate-constants for the reactions of ring-methylated benzyl chlorides with potassium iodide in acetone at 0° are given in Table 1. Two reagent concentrations were employed, the higher, where possible, because the disturbance from reversibility is thus reduced, the back-reaction being restricted by the precipitation of potassium chloride, and the lower inasmuch as the large rates of some of the reactions made this necessary. The general consistency of the second-order rate-constants shows that bimolecular substitutions are under observation.

TABLE 1. *Second-order rate-constants ($k_2$ in sec.$^{-1}$ mole$^{-1}$ l.) for reactions of benzyl chlorides with potassium iodide in acetone at 0°.*

Rates (a) with [RCl] = 0·1 and [KI] = 0·02M initially.
,, (b) ,, ,, = 0·2 ,, ,, = 0·04M ,,

| | $10^5 k_2$ | | | Relative rates |
| Benzyl chloride | (a) | (b) | | [Column (a)] |
|---|---|---|---|---|
| Parent | 3·3 | 3·35 | 1 | — |
| 2-Me | 36·8 | 40·5 | 11·2 | — |
| 2 : 6-Me$_2$ | 600 | — | 182 = 11·2 × 16·2 | — |
| 4-Me | 5·1 | 5·46 | 1·55 | 1 |
| 2 : 4-Me$_2$ | 134 | 152 | 40·6 | 26 |
| 2 : 4 : 6-Me$_3$ | 950 | — | 288 | 186 = 26 × 7·1 |

An unexpected feature of these results is that, although the accelerating effect of a *p*-methyl substituent, which must be purely a transmitted polar effect, is quite small, as we should expect for a bimolecular reaction, that of an *o*-methyl substituent, even a single one, the kinetic effect of which could not possibly be steric, is considerably larger. Though it would be difficult to give a very close analysis of the figures, we assume the presence of some kind of direct polar effect of *o*-methyl groups, plausibly one deriving from an electrostatic attraction between methyl hydrogen and the semi-ionic halogen atoms in the transition state. The rate figures show no evidence of the incursion of a steric effect on the introduction of the second *o*-methyl group, and this is consistent with theoretical expectation.

The corresponding reactions of the 1-phenylethyl chlorides are slower than those of the benzyl chlorides. This is in contrast to solvolysis (preceding paper); but is to be expected if the Finkelstein substitution in acetone is bimolecular in both series of halides. In the series of 1-phenylethyl chlorides, the reaction with sodium iodide in acetone at 35—45° was shown to follow second-order kinetics by changing the initial concentrations of the reactants. The point was gone into particularly carefully in the example of 1-mesitylethyl chloride, which has been shown to undergo unimolecular racemisation in acetone (Part XLI[1]) and would therefore appear to be the case in which a unimolecular Finkelstein substitution is most probable. However, even here the reaction with sodium iodide follows second-order kinetics very approximately, the absolute rate of substitution with 0·1M-salt being of the order of 20 times greater than the unimolecular rate as given by the rate of racemisation in the presence of a similar concentration of a non-substituting salt, such as lithium perchlorate. We conclude that, with sufficient accuracy for the intended comparisons, all these substitutions are bimolecular. Some second-order rate-constants are given in Table 2.

[1] Charlton and Hughes, *J.*, 1954, 2939.

TABLE 2. *Second-order rate-constants ($k_2$ in sec.$^{-1}$ mole$^{-1}$ l.) for reactions of 1-phenylethyl chloride with sodium iodide in acetone at 44·5°.*

Initially, [RCl] = 0·05, [NaI] = 0·1M, throughout.

| 1-Phenylethyl chloride | $10^5 k_2$ | Relative rates | | |
| --- | --- | --- | --- | --- |
| Parent ........................................... | 2·49 | 1 | | — |
| 2-Me ........................................... | 80·4 | 32·3 | | — |
| 2 : 6-Me$_2$ ..................................... | 27·5 | 11·0 = 32·3 × 0·34 | | — |
| 4-Me ........................................... | 6·07 | 2·44 | | 1 |
| 2 : 4-Me$_2$ ..................................... | 249 | 100 | | 41 |
| 2 : 4 : 6-Me$_3$ ............................... | 173 | 69·5 | 28·5 = 41 × 0·69 | |

As before, we find that a *p*-methyl substituent exerts a small accelerating effect, which we explain as a transmitted polar influence. Again, the first *o*-methyl substituent produces a considerably stronger acceleration, and again we assume a transmitted polar effect, supplemented by a direct polar effect, probably one of electrostatic attraction between *o*-methyl-hydrogen and transition-state halogen. Evidently we cannot account for these rates by assuming any form of steric acceleration, because such an effect would be greatly enhanced on the introduction of the second *o*-methyl group. On the contrary, the second *o*-methyl group retards the reaction; and this we explain by assuming the incursion of a steric retardation, since on theoretical grounds we expect steric retardation to appear in just these structural circumstances.

This steric retardation must be considerable, since it more than outweighs the total polar effect of an *o*-methyl group. As a rough estimate, we may assume that the steric effect alone would reduce rate by a factor in the range 50—100, or, otherwise expressed, would raise the free energy of activation by 2—3 kcal./mole, and probably the energy of activation by a very similar amount.

We may compare these estimates for our bimolecular substitution with corresponding estimates for the unimolecular substitution discussed in the preceding paper. From Table 2 of that paper it appears that, in the unimolecular process, the steric effect of the second *o*-methyl group, if it were acting alone, would diminish the reaction rate by a factor in the range 5—10, or, in other terms, would increase the free energy of activation by 1·0—1·5 kcal./mole. It was estimated from the Arrhenius parameters that the steric factor added 1·0—1·5 kcal./mole to the energy of activation. It is consistent that in the bimolecular substitution the estimated steric effects are larger, but the interesting point is that the involved energies are only about twice as large. From this it is apparent that the flattening of bonds in the transition state of ionisation must be considerable, a conclusion of importance in relation to Bartlett's discovery that the formation of those carbonium ions which cannot be flattened is resisted by very high energy barriers.[2]

We have not attempted a calculation of the compression energy in the bimolecular transition state, because it resides largely in hydrogen–hydrogen compressions. Hitherto we have not undertaken the calculation of these, because the uncertainties arising from the imperfectly known shapes of the van der Waals surfaces of the combined hydrogen atom are proportionately greater than those which affect other calculated atom-pair energies. However, a completely stiff model of the transition state, in which α- and *o*-methyl groups are accurately centred in the aromatic plane, involves two hydrogen–hydrogen compressions, each of about 1·0 Å; and it seems entirely reasonable that these could entail an amount of energy which becomes reduced by slight adjustments in the model to the estimated compression energy of 2—3 kcal./mole.

EXPERIMENTAL

*Preparations.*—These are described in the preceding paper.

*Kinetics.*—Except for the higher concentrations of potassium iodide, the sealed-tube method was employed. The tubes were charged, with separately prepared solutions of the reactants, each in the solvent (acetone, dried finally with magnesium perchlorate), with the aid of jacketted automatic pipettes, and were preserved at −80°,* until they were put into the thermostat, with

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* For very fast reactions, the tubes were cooled before the introduction of the solution of the second reactant.

[2] Bartlett and Knox, *J. Amer. Chem. Soc.*, 1939, **61**, 3184; Bartlett and Lewis, *ibid.*, 1950, **72**, 1005.

shaking in order to speed the attainment of the reaction temperature. When the higher concentration of potassium iodide was desired, a thin-walled glass tube containing the organic halide was broken in a flask containing a solution of the salt at thermostat temperature, and aliquot portions of the reaction mixture were analysed at suitable intervals. The progress of reaction was followed by the determination of either iodide ion or chloride ion.

For the determination of iodide ion, the samples were partitioned between carbon tetrachloride and water, and the colourless aqueous extract was strongly acidified with sulphuric acid and titrated with ceric sulphate, the indicator being the *o*-phenanthroline–ferrous complex.

For the determination of chloride ion, it was necessary first to pump off the acetone rapidly, and then to partition the residue between carbon tetrachloride and water as quickly as possible. The iodide ion in the aqueous extract was next oxidised with sodium nitrite and sulphuric acid to iodine, which was extracted with carbon tetrachloride. The colourless aqueous solution was finally mixed with an equal volume of ethyl alcohol, and the chloride ion contained in it was titrated electrometrically with silver nitrate.

The iodide-ion method was usually employed on account of its greater simplicity; but it gave poor results for the reaction of 1-mesitylethyl chloride, probably because of an appreciable amount of hydrolysis of 1-mesitylethyl iodide during the analytical procedure. However, the chloride-ion method was applied in this case without difficulty.

Each of the rate-constants given in Tables 1 and 2 is the mean of either two or three consistent measurements.

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