# 429. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part V. The Polar Effects of Alkyl Groups.*

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IN Part IV (preceding paper) the data for the velocity of interaction of various alkyl-substituted benzyl bromides with pyridine in dry acetone showed (i) that all alkyl substituents increased the velocity of reaction, and (ii) that, with a single *p*-alkyl substituent, the velocity decreased in the order Me > Et > $Pr^{\beta}$ > $Bu^{\gamma}$. The first of these observations clearly indicates that the accelerating effects of alkyl groups must be related to their capacity for electron-release, which will increase the ease of anionisation of the bromine atom. The second suggests that the relative magnitude of such electron-release increases in the order $CMe_3 < CHMe_2 < CH_2Me < CH_3$. This order is exactly the reverse of that anticipated on the basis of the general inductive effects (+ *I*) of alkyl groups. It seems, therefore, that the methyl group must permit additional electron-release by some mechanism which either cannot function or is greatly diminished in the higher alkyl groups.

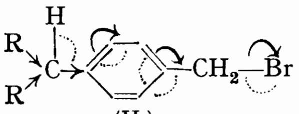
An anomaly of this kind is not observed in every type of system containing alkyl groups; *e.g.*, the order of anionic stability of alkoxide ions, $\overset{-}{\mathrm{O}}\mathrm{Me} > \overset{-}{\mathrm{O}}\mathrm{Et} > \overset{-}{\mathrm{O}}\mathrm{Pr}^{\beta} > \overset{-}{\mathrm{O}}\mathrm{Bu}^{\gamma}$ (Ingold and Shoppee, J., 1929, 447; 1930, 968), is in agreement with the generally accepted order of increasing $+ I$ effects, $\mathrm{Me} < \mathrm{Et} < \mathrm{Pr}^{\beta} < \mathrm{Bu}^{\gamma}$. The additional mechanism of electron-release by the methyl group in *p*-methylbenzyl bromide seems, therefore, to be associated with the presence of the attached conjugated system of the aromatic nucleus.

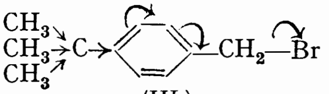
It is tentatively suggested that, *when the methyl group is attached to a conjugated system,* the duplet of electrons forming the C–H bond in this group are appreciably less " localised " than are those in a similarly placed C–C bond. This means that a methyl group, attached to the necessary system, is capable of permitting electron-release by a mechanism which, in essentials, is a type of tautomeric effect, $\mathrm{H{-}CH_2{-}C{=}C{-}C{=}C{-}}$.*

Two aspects of this hypothesis require emphasis: (1) the suggested new mechanism of electron-release is assumed to function in addition to the generally accepted inductive $(+ I)$ effect of alkyl groups; (2) the presence of the necessary system is imperative for the operation of the new mechanism.

In *p*-methylbenzyl bromide the methyl group would be able, by the new mechanism, to permit additional electron-release at the C–Br bond, thus further facilitating the anionisation of the bromine (I). In *p-tert.*-butylbenzyl bromide (III), although the inductive effect of $\mathrm{Bu}^{\gamma}$ is greater than that of Me, the new type of electron-release is no longer possible, since the new methyl groups do not form part of the necessary conjugated system owing to the intercalation of the tertiary carbon atom. Complete ignorance of the quantitative laws governing such effects makes it impossible to predict the relative importance of the inductive and of the new electron-release mechanism in the cases of ethyl and *iso*propyl substituents (II), where both types are theoretically possible. The experimental data, however, prove that, given the necessary system, the relative magnitude of total electron-release (inductive plus the new type) decreases in the order $\mathrm{Me} > \mathrm{Et} > \mathrm{Pr}^{\beta} > \mathrm{Bu}^{\gamma}$.

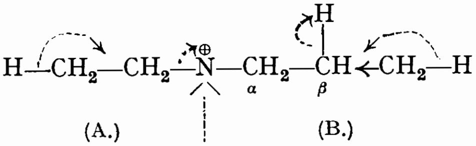

(I.)


(II.)


(III.)

We include in the necessary type of conjugated system those systems where electron-duplet displacements of the type involved in the tautomeric effect are rendered possible by fission of a group with its bond electrons, *e.g.*, $\mathrm{H{-}CH_2{-}CH_2{-}X}$, $\mathrm{H{-}CH_2{-}CH{=}CH{-}CH_2{-}X}$, $\mathrm{H{-}CH_2{-}CH_2{-}\overset{\oplus}{X}}$.

In cases where the completion of the system would require the separation, as a negative ion, of an atom or group (*e.g.*, hydrogen) which normally ionises as a positive ion, we consider that the new effect would not function, or, at least, would be too weak to be significant in comparison with the normal inductive effect of the alkyl group. The Hofmann rule on the preferential elimination of ethylene in the thermal decomposition of quaternary ammonium hydroxides (Hanhart and Ingold, J., 1927, 997, and subsequent papers) furnishes a good example of both permitted and non-permitted types of system:



(A.) (B.)

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* The original suggestion that such a polar effect is present was due to W. S. N.

For clarity, electron displacements arising from the operation of ordinary inductive effects are denoted by full arrows, and those arising from the new electron-release mechanism, by dotted arrows.

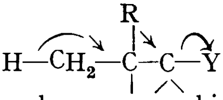
The new mechanism of electron-release would function in (A) (leading to the elimination of ethylene) since the necessary system is completed by the separation of $\overset{\oplus}{N}$ with its bond electrons. In (B) ($Pr^a$ and higher alkyl groups) conjugation with the $\overset{\oplus}{N}$ is prevented by intercalation of $C_\alpha$, and cannot be completed at $C_\beta$ because it would require the separation of hydrogen as a negative ion, and not as a positive ion as required by olefin formation. Hence the new mechanism would be ineffective in retarding cationisation of the β-hydrogen atom, which will be influenced solely by the normal inductive effect of the alkyl group attached to $C_\beta$; so ethylene is always eliminated in preference to higher alkylenes.

Since the reaction studied in this paper is one which is facilitated by electron-accession towards the side chain, the data obtained give no information as to whether such tautomeric electron-release is of an electromeric or a mesomeric (permanent) type. In Part VI (following paper), results are described which show that the new mechanism of electron-release is able to retard a reaction which is facilitated by electron-recession from the side chain to the aromatic nucleus. It must, therefore, be of a mesomeric type, arising, presumably, from a higher degree of degeneracy in the system $H{-}CH_2{-}C{=}C{-}C{=}C{-}$ than obtains in the absence of the necessary hydrogen atom.

The postulated new mechanism of electron-release by methyl groups affords a consistent explanation of many hitherto obscure points in organic chemistry.

Substitution in *p*-alkyltoluenes by electrophilic reagents is known to occur mainly in the 2-position; *e.g.*, *p-tert.*-butyltoluene affords mainly the 2-nitro-derivative (Battegay and Haeffely, *Bull. Soc. chim.*, 1924, **35**, 381; cf. Le Fèvre, Le Fèvre, and Robertson, this vol., p. 480), and the case of *p*-cymene has been quantitatively studied by Le Fèvre and his collaborators, who have shown that nitration (J., 1933, 980), sulphonation (J., 1934, 1501), and halogenation (*loc. cit.*; Ganguly and Le Fèvre, *ibid.*, p. 1697) effect monosubstitution almost exclusively in the 2-position. A similar deduction would appear to be valid for *p*-ethyltoluene (Brady and Day, *ibid.*, p. 114). Le Fèvre has already pointed out that this greater *o*-orienting power of methyl is contrary to deductions based on the generally accepted order of inductive effects of alkyl groups, and has suggested an explanation of the anomaly on the basis of the volume effects of such groups. Such a steric factor, although possibly not without significance in substitution of *p*-alkyltoluenes, can scarcely be valid in the case of quaternary salt formation between *p*-alkylbenzyl bromides and pyridine. We suggest that the greater electron-release capacity of methyl, due to its mesomeric effect, provides an equally feasible and generally applicable explanation.

The new ideas also provide a satisfactory explanation of the observed lack of reactivity of the *iso*butyl compound in all reactions of alkyl halides which necessitate the anionisation of the halogen. Examples are to be found, *inter alia*, in the interaction of alkyl iodides with triethylamine in acetone solution (Menschutkin, *Z. physikal. Chem.*, 1890, **5**, 589), with sodium phenoxide in alcohol (Segaller, J., 1913, **103**, 1154, 1421), and of alkyl bromides with potassium ethoxide (Lengfeld, *Amer. Chem. J.*, 1889, **11**, 40). A recent example is reported by Bennett and Reynolds (this vol., p. 131), who found that the relative velocity of interaction of *sec.*-butyl alcohol with hydrobromic acid is 0·97 (velocity of MeOH = 1), whereas *iso*butyl alcohol is very unreactive (0·02). Such lack of reactivity in the *iso*butyl compound cannot be understood on the basis of ordinary inductive effects since this would require a more marked effect of the same kind in *sec.*-butyl derivatives. It is clear, however, that, whereas the system necessary for the operation of the new type of electron-release is present in respect of three hydrogen atoms in the *sec.*-butyl compound $H{-}CH_2{-}CHEt{-}X$, it is much less available in the *iso*butyl derivative $H{-}CH_2{-}CHMe{-}CH_2{-}X$. The larger dipole moment of *sec.*-butyl chloride (2·12*D*) than of the *iso*- (1·97*D*) and the *n*- (1·95*D*) compound (Parts, *Z. physikal. Chem.*, 1930, **7**, *B*, 327) supports this conclusion.

The same idea also provides a consistent explanation of the ionisation of hydrogen from methyl and methylene groups in Wagner–Meerwein changes of the type  $\mathrm{H{-}CH_2{-}\overset{R}{\underset{|}{C}}{-}C{-}Y}$ (cf. Baker, "Tautomerism," p. 299 *et seq.*, for collected examples), a phenomenon which has hitherto received no satisfactory explanation.

The importance of a mesomeric type of electron-release by a methyl group upon the ease of olefin formation from aliphatic alcohols and halides, upon the electron-availability at the various positions in toluene (Ingold, Lapworth, Rothstein, and Ward, J., 1931, 1959) and alkyltoluenes, and similar problems is obvious, and it is hoped to investigate such aspects quantitatively in order to confirm the reality of this postulated polar effect.

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