430. *The Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part VI. The Effects of* p-*Alkyl Substituents on Prototropy in the Methyleneazomethine System.*

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IN Part V (preceding paper) evidence was adduced for the operation of a new type of electron-release by methyl groups in facilitating reactions which require electron-availability at the point of attack. In order to determine whether this electron-release is of an electromeric or a mesomeric type, it is necessary to ascertain whether it is able to retard side-chain reactions of the opposite type, *i.e.*, those facilitated by electron-recession from the point of attack. If the postulated tautomeric effect of the methyl group is of the electromeric type it should not be called into play in such cases, and the relative retarding effects of methyl and of higher alkyl substituents should then be strictly in accordance with their (permanent) general inductive $(+I)$ effects, *i.e.*, retardation by higher alkyl groups should be greater than that by the methyl group. If, on the other hand, the effect is of a permanent (mesomeric) character, it should be operative in retarding such reactions, provided, of course, that the necessary system be present. Since such an electron-release mechanism appears to be negligible in or absent from higher alkyl groups (cf. Part V) it would then follow, *ceterius paribus*, that the effects of alkyl substituents might be in the reverse order, *i.e.*, retardation by methyl should exceed that by higher alkyl groups. In short, for such so-called " Type B " reactions we have, possibly,

Me, $(+I)$-effect only, velocity order $H > Me > Pr^{\beta} > Bu^{\gamma}$;
Me, $(+I+M)$-effects, velocity order $H > Bu^{\gamma} > Pr^{\beta} > Me$.

The effect of alkyl substituents upon such reactions therefore constitutes a crucial test of the permanency or otherwise of the postulated new mechanism of electron-release.

This paper records the results of the application of such a test. The reaction chosen was the prototropic change in the azomethine system $p\text{-}C_6H_4R\cdot CH{:}N\cdot CH_2Ph \rightleftharpoons p\text{-}C_6H_4R\cdot CH_2\cdot N{:}CHPh$. It has been shown (Shoppee, J., 1933, 1117) that, over a wide range of substituents, this reaction is facilitated by electron-withdrawal from the triad system. It therefore constitutes a specially suitable system in which to study the relative retarding effects of alkyl substituents upon the velocity.

The data are given in Table I, which includes for comparison the results previously obtained (Shoppee, J., 1931, 1225) for a *p*-methyl substituent under identical experimental conditions. The mobility of the system $(k_1 + k_2)$ decreases in the order $Bu^{\gamma} > p\text{-}Pr^{\beta} > p\text{-}Me$, *i.e.*, the retarding effect of a *p*-methyl group is much greater than that of higher alkyl groups. Hence, in accordance with the argument developed above, the new electron-release mechanism of the methyl group must be capable of retarding this reaction, and must therefore be of a mesomeric (permanent) type. This means that the mesomeric electron-

TABLE I.

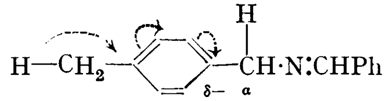
Mobility and Equilibria in the System

$$\text{(I.) } p\text{-}C_6H_4R{\cdot}CH{:}N{\cdot}CH_2Ph \underset{k_2}{\overset{k_1}{\rightleftharpoons}} p\text{-}C_6H_4R{\cdot}CH_2{\cdot}N{:}CHPh \text{ (II.)}$$

R =	H.	Me.	Pr^{β}.	Bu^{γ}.
$k_1 + k_2$(hr.$^{-1}$)	—	0·322	0·47	0·60
K	(1·0)	1·22	0·78	0·66
Equilm. % of (I)	(50·0)	45·0	56·0	60·0

release by the methyl group is largely responsible for the dipole moment of toluene. Since the mobility of the prototropic system is determined by conditions governing the ease of ionisation of the mobile hydrogen atom at C_a, the negative charge in the *p*-tolyl substituent will therefore inhibit reaction (see III). Because such mesomeric electron-release has been shown to decrease in the order methyl > higher alkyl groups, such power of inhibition will also diminish in the same order. Hence retardation by a *p-tert.*-butyl substituent will be less than that produced by a *p*-methyl group.

(III.)



EXPERIMENTAL.

Preparation of Materials.—*p-tert.*-Butylbenzaldehyde was prepared by oxidation of the corresponding benzyl bromide (10 g.) with boiling copper nitrate solution (6 g. in 100 c.c. of water) for 24 hours. Carbon dioxide was slowly bubbled into the reaction mixture to prevent further oxidation of the aldehyde. The product was extracted with ether, the extract dried, and the residue shaken with a saturated solution of sodium bisulphite. After several days the bisulphite derivative (6 g.) was filtered off, washed with a little alcohol and ether, and then decomposed by steam-distillation with 100 c.c. of dilute sulphuric acid. The distillate was extracted with ether, the extract washed first with dilute sodium bicarbonate solution and then with water, and dried over sodium sulphate. After evaporation of the ether, fractional distillation gave the aldehyde, b. p. 130°/25 mm. (3 g.). It was characterised as its p-*nitrophenylhydrazone*, m. p. 214°, after crystallisation from 96% alcohol (Found: C, 68·6; H, 6·3. $C_{17}H_{19}O_2N_3$ requires C, 68·7; H, 6·4%). Oxidation (copper nitrate without a carbon dioxide stream) gave *p-tert.*-butylbenzoic acid, m. p. 164—165° (Verley, *Bull. Soc. chim.*, 1898, **19**, 71, gives m. p. 164°).

Similar oxidation of *p-iso*propylbenzyl chloride afforded *p-iso*propylbenzaldehyde, b. p. 73°/0·5 mm. Its p-*nitrophenylhydrazone*, crystallised from 96% alcohol, has m. p. 190° (Found: C, 67·4; H, 5·9. $C_{16}H_{17}O_2N_3$ requires C, 67·6; H, 6·1%).

p-tert.-*Butylbenzylamine.* 30 G. of *p-tert.*-butylbenzyl bromide (Part IV) were heated with 24 g. of potassium phthalimide at 180° for 2—3 hours. The cooled product was extracted twice with boiling glacial acetic acid, and potassium bromide removed by filtration. The cold acetic acid solution deposited 8 g. of crystalline phthalimide (m. p. 230—231°. Found: C, 65·35; H, 3·5. Calc. for $C_8H_5O_2N$: C, 65·3; H, 3·4%); the mother-liquor was evaporated at 100°, the residue dissolved in ether, and a further quantity of phthalimide separated by filtration. The residue (27 g.), after evaporation of the ether, crystallised when rubbed with ligroin (b. p. 40—60°) and was recrystallised from this solvent; the *phthalo*-p-tert.-*butylbenzylimide*, m. p. 103° (Found: C, 77·7; H, 6·7. $C_{19}H_{19}O_2N$ requires C, 77·75; H, 6·55%), was converted by hydrazine hydrate in alcohol (Ing and Manske, J., 1926, 2348) into p-tert.-*butylbenzylamine*, b. p. 124°/16 mm. (Found: C, 81·2; H, 10·3. $C_{11}H_{17}N$ requires C, 81·0; H, 10·4%), the hydrochloride of which, when warmed with potassium cyanate, afforded the *carbamido*-derivative, m. p. 137°, after recrystallisation first from water and then from ether (Found: N, 13·7. $C_{12}H_{18}ON_2$ requires N, 13·6%). The *picrate* had m. p. 220° (decomp.) after crystallisation from aqueous alcohol (Found: C, 52·3; H, 5·0. $C_{17}H_{20}O_7N_4$ requires C, 52·0; H, 5·1%).

The Schiff's bases were prepared directly from the aldehyde and amine in the manner previously described (Shoppee, *loc. cit.*). *p-tert.*-Butylbenzylamine and benzaldehyde gave *benzylidene*-p-tert.-*butylbenzylamine*, b. p. 155—157°/0·4 mm (Found: C, 86·3; H, 8·7. $C_{18}H_{21}N$ requires C, 86·0; H, 8·5%). p-tert.-*Butylbenzylidenebenzylamine*, similarly prepared from benzylamine and *p-tert.*-butylbenzaldehyde, was difficult to purify. The sample used had

b. p. 161°/0·5 mm. (Found : C, 85·3; H, 8·2. $C_{18}H_{21}N$ requires C, 86·0; H, 8·5%). p-iso*Propylbenzylidenebenzylamine* was obtained as a colourless, viscous liquid, b. p. 155°/0·5 mm. (Found : C, 85·7; H, 8·2. $C_{17}H_{19}N$ requires C, 86·0; H, 8·1%). The azomethines are colourless, very viscous liquids which could not be crystallised. They tend to decompose when kept and were freshly distilled immediately before use in the velocity determinations.

Determination of Mobility and Equilibrium.—The method employed was identical with that previously described (Shoppee, *loc. cit.*). The following observations were used for the construction of the temperature–composition diagrams. Mixtures of the *p*-nitrophenylhydrazones of benzaldehyde (A) and *p*-*tert.*-butylbenzaldehyde (B) or *p*-*iso*propylbenzaldehyde (C) melted as follows :

Mixtures of A and B.

A, %	0	20·7	40·2	48·7	60·7	78·3	100
M. p.	210°	195·5°	178·5°	167·5°	166·25°	178·5°	190°

Mixtures of A and C.

A, %	0	11·8	19·3	27·4	39·3	43·1	58·7	76·0	100
M. p.	188°	181°	175·5°	168·5°	160°	155·5°	159·5°	174·7°	190°

Interconversion.—(i) R = Bu^{γ}. With 0·145*N*-sodium ethoxide at 82° the following data were obtained for the proportion of isomeride (II) :

Initial isomeride (I).					Initial isomeride (II).				
Time (hrs.).	Yield, %.	M. p.	(II), %.	$k_1 + k_2$ (hr.$^{-1}$).	Time (hrs.).	Yield, %.	M. p.	(II), %.	$k_1 + k_2$ (hr.$^{-1}$).
0	100	210°	0	—	8·0	97	178·5°	40	—
0·5	100	203	10	0·575	5·0	97	173·5	44	0·540
1·0	99	199	16	0·520	4·0	96	171	46	0·575
1·5	99	194·5	22	0·532	3·0	—	167·5	48·5	0·651
2·0	99	190·5	27	0·561	2·0	98	159·5	54·5	0·710
3·0	98	187	31·5	0·515	1·5	99·5	166·25	61	0·699
4·0	98	184	35	0·519	1·0	99	173	70	0·692
8·0	97	178·5	40	—	0·5	100	180·5	82	0·710
					0	100	190	100	—

Equilibrium : II (40%) $\rightleftharpoons$ I (60%) ; $k_1 + k_2$ (mean) 0·60 hr.$^{-1}$; k_1/k_2 = 0·66 ; k_1 = 0·24 ; k_2 = 0·36

The equilibrium attained by using 1·45*N*-sodium ethoxide at 85° was also determined :

1	98	179°	39·5	—	2	98	177·5	(41)	—
2	98	179·5*	40	—	1	99	178·5†	40	—

* 9·9 Mg. of this mixture + 4·5 mg. of B had m. p. 190·25°, *i.e.*, 27·0% of A (Calc. : 27·1%).

† 10·9 Mg. of this mixture + 6·8 mg. of B had m. p. 193°, *i.e.*, 24·0% of A (Calc. : 24·0%).

(ii) R = Pr^{β}. 0·145*N*-Sodium ethoxide at 82° afforded the following results, isomeride (I) being used, since this was the more readily available and the main reason for the inclusion of this derivative in the series was to confirm its position between methyl and *tert.*-butyl.

Time (hrs.).	Yield, %.†	M. p.	(II), %.	$k_1 + k_2$ (hr.$^{-1}$).	Time (hrs.).	Yield, %.†	M. p.	(II), %.	$k_1 + k_2$ (hr.$^{-1}$).
0	102·5	188°	0	—	1·5	104	173·25	22·5	0·477
0·5	(107)	181·25	11	(0·575)	2·0	105	169	27	0·475
1·0	105	176·5	17·5	0·506	3·0	102·5	165	32·5	0·447

To determine the equilibrium, 1·45 *N*-sodium ethoxide was used at 85°, 1 hour's heating giving 103% yield, m. p. 154·5,* (II) = 44%.

Equilibrium : II (44%) $\rightleftharpoons$ 1 (56%) ; $k_1 + k_2$ (mean) 0·47 hr.$^{-1}$; k_1/k_2 = 0·78 ; k_1 = 0·21 ; k_2 = 0·26.

* 5·7 Mg. of this mixture + 5·5 mg. of C had m. p. 174·5° (Calc. : 173·5°).

† Yields exceeding 100% were sometimes encountered in the earlier investigation, and are doubtless explained by slight occlusion in the precipitate (cf. *loc. cit.*, p. 704).

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