88. *Steric Relations between Ionisation of Aralkyl Chlorides and Dissociation of Anilinium Ions. Part II.**

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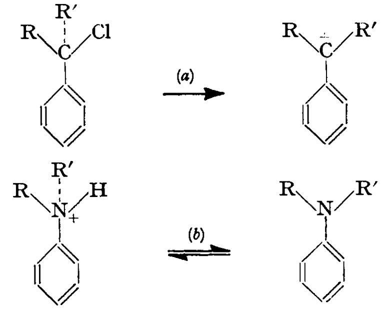
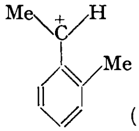
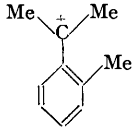
Rates of ethanolysis of several tertiary aralkyl chlorides RR'CAr•Cl have been determined and compared with the dissociation constants of the corresponding anilinium ions RR'NArH$^+$. The comparison supports the view [1] that ionisation of the chlorides and dissociation of the anilinium ions effect changes of intramolecular conformation which increase intramolecular steric interaction.

IONISATION process (*a*) and dissociation (*b*) (see formulæ) incur similar changes in intramolecular conformation and, therefore, are probably affected by similar changes in steric interaction : aralkyl chloride and anilinium ion, being comparatively free from mesomeric phenomena, will prefer those conformations in which R and R', should these be bulky groups, avoid the plane of the benzene ring whereas these groups must be in or near this plane in the benzyl cation and in the amine if these are to have maximum resonance energy. Thus both reactions are expected to be hindered by the increase in steric interaction as R and R' approach the plane of the ring and by loss of resonance energy in the benzyl cation and in the amine if these, for steric reasons, are not approximately planar. Consequently, in a series of chlorides and amines in which the members differ mainly in the magnitude of this steric effect, the more basic amines will be those corresponding to the less reactive chlorides and *vice versa*. In Part I secondary aralkyl chlorides R•CHArCl and the corresponding secondary amines R•NHAr were shown to be so related. This relation, which is the opposite of that which usually obtains in the absence of this steric effect, is now shown to obtain between tertiary aralkyl chlorides RR'CArCl (R and R' = alkyl) and the corresponding tertiary amines RR'NAr.





(I)



(II)

Rates of ethanolysis of the chlorides in absolute ethanol were determined at two temperatures; the results are assembled in Table 1 and show that, in general, increased reactivity is caused by diminution in activation energy (E) and that the action constant (A) varies so as to compensate partly for the change in E.

TABLE 1. *Constants of Arrhenius equation,* $k = A\mathrm{e}^{-E/\mathbf{R}T}$, *for the formation of hydrogen chloride by the ethanolysis of the chlorides.*

	$10^7k_{0\cdot0}$ (sec.$^{-1}$)	$10^5k_{25\cdot0}$ (sec.$^{-1}$)	E (kcal./mole)	$10^{-12}A$ (sec.$^{-1}$)
Ph•CMe$_2$Cl	147	34·7	21·4	1·5
Ph•CMeEtCl	34·2	9·72	22·8	4·7
Ph•CEt$_2$Cl	2·82	1·15	25·3	35·5
Ph•CPr$_2$Cl	9·58	3·48	24·5	28·2
Ph•CBu$_2$Cl	11·4	3·98	24·2	13·6
o-C$_6$H$_4$Me•CMe$_2$Cl ...	512	127	21·9	13·2
o-C$_6$H$_4$Me•CEt$_2$Cl	24·3	9·15	24·7	115

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* Part I, *J.*, 1954, 2405.

[1] Baddeley, Chadwick, and Taylor, *J.*, 1954, 2405.

The most noticeable feature is the *decrease* in reactivity as each methyl group of 2-chloro-2-phenylpropane is replaced by ethyl. It is not caused by change in inductive, inductomeric, or hyperconjugative effect since, as illustrated by comparison of the first and the third set of data in Table 4, the same change of alkyl group in tertiary alkyl chlorides provides a small *increase* in the rate of unimolecular solvolysis. Consideration of the change of intramolecular steric interaction which affects ionisation of the aralkyl chlorides provides an explanation : in these chlorides, steric interaction of alkyl groups and the benzene ring orients the former at a distance from the plane of the latter and ionisation is therefore energetically hindered by the increase in steric interaction as the alkyl groups move towards the plane of the ring to provide maximum resonance stabilisation of the resulting carbonium ion. Differences (i), (ii), and (iii) of Table 2 show that replacement of a methyl by an ethyl group (Ph·CRMeCl $\longrightarrow$ Ph·CREtCl) increases the energy of activation of ionisation by an amount which is small (0·3 kcal./mole) when R = H and increases to 1·4 and 2·5 kcal./mole when R is Me and Et respectively. These increments indicate that repulsive forces between R and the neighbouring ethyl group tend to orient the latter with its terminal methyl group close to the benzene ring and that this effect increases in the order $R = H < Me < Et$. This " buttressing-effect " has been discerned previously in the dissociation constants and heats of formation (ΔH) of addition compounds of aliphatic amines with trimethylboron :[2] $RR'R''N + BMe_3 \rightleftharpoons RR'R''\overset{+}{N}\cdot\overset{-}{B}Me_3$; compare differences (i) and (v), and (iv) and (vi), of Table 2. Whereas the steric effects of methyl and ethyl groups are very similar in the addition compounds obtained from methyl- and ethyl-amine severally, they are very different in those from dimethyl- and diethyl-amine. In the latter, each ethyl group is " buttressed " by the other and thus their terminal methyl groups are pressed closer to the trimethylboron moiety.

TABLE 2.

	E		*E*		*E*
(i) Ph·CHEtCl	20·7	(ii) Ph·CMeEtCl	22·8	(iii) Ph·CEtEtCl	25·3
Ph·CHMeCl	20·4	Ph·CMeMeCl	21·4	Ph·CEtMeCl	22·8
	0·3		1·4		2·5
	E		ΔH		ΔH
(iv) $Ph\cdot CEt_2Cl$	25·3	(v) $Me_2\overset{-}{B}\cdot\overset{+}{N}H_2Et$	−18·00	(vi) $Me_3\overset{-}{B}\cdot\overset{+}{N}HEt_2$	−16·31
$Ph\cdot CMe_2Cl$	21·4	$Me_3\overset{-}{B}\cdot\overset{+}{N}H_2Me$	−17·62	$Me_3\overset{-}{B}\cdot\overset{+}{N}HMe_2$ ...	−19·26
	3·9		− 0·38		2·95

Whereas the energies of activation for solvolysis of $Ph\cdot CMe_2Cl$ and $Ph\cdot CEt_2Cl$ differ by 3·9 kcal./mole, those for o-$C_6H_4Me\cdot CMe_2Cl$ and o-$C_6H_4Me\cdot CEt_2Cl$ differ by only 2·8. This partial neutralisation of the difference between the steric effects of methyl and ethyl groups by the *o*-methyl group is probably caused by this group's giving added importance to the steric effect of that part of the side-chain alkyl group which is directly attached to the seat of reaction.

The above arguments in which difference between the effect of methyl and ethyl groups on the reactivity of aralkyl chlorides is attributed to steric causes is supported by comparison of the logarithms of the velocity constants for solvolysis of the chlorides Ar·CRR'Cl with the values of pK_a for the structurally related amines Ar·NRR' (see Table 4, first and second sets). It shows, what must be expected from steric considerations, that the most basic amines are those which correspond to the least reactive chlorides and *vice versa*. An obvious exception arises on introduction of an *o*-methyl group since this affords chlorides and amines of comparatively high reactivity and basic strength respectively. Thus, as must be expected, the *o*-methyl group exerts an electronic as well as a steric effect. The latter is revealed by (*a*) the fact that o-$C_6H_4Me\cdot CMe_2Cl$ is *more* reactive than o-$C_6H_4Me\cdot CEt_2Cl$ whereas o-$C_6H_4Me\cdot NMe_2$ is *less* basic than o-$C_6H_4Me\cdot NEt_2$, and

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[2] Brown *et al.*, *J. Amer. Chem. Soc.*, 1944, **66**, 435; 1947, **69**, 1332; 1951, **73**, 2464.

(*b*) the data assembled in Table **3**. They show that introduction of an *o*-methyl group into 1-phenylethyl chloride gives a **34**-fold increase in rate and a diminution of **2·8** kcal./mole in the energy of activation (consequences of the inductive and hyperconjugative effects of the methyl group), whereas introduction of *o*-methyl group into 2-chloro-2-phenylpropane affords little more than a **3**-fold increase in rate and no diminution in the energy of activation. In this instance the electronic effects of the methyl group are essentially neutralised by a comparatively large steric effect [cf. (I) and (II)].

TABLE 3.

	$10^9k_{0\cdot0}$ (sec.$^{-1}$)	E (kcal./mole)		$10^7k_{0\cdot0}$ (sec.$^{-1}$)	E (kcal./mole)
o-C_6H_4Me·CHMeCl ...	110	22·8	*o*-C_6H_4Me·CMe_2Cl	512	21·9
Ph·CHMeCl	3·23	25·6	Ph·CMe_2Cl	147	21·4

TABLE 4.

	log $k_{0\cdot0}$	Ref. *a*	pK_a	Ref. *b*	log $k_{25\cdot0}$	Ref. *c*	pK_a
Ph·CMe_2Cl	2·17	Ph·NMe_2	5·06	Me·CMe_2Cl	2·17	H·NMe_2 ...	10·71
Ph·CMeEtCl	1·53	Ph·NMeEt	5·98	Me·CMeEtCl ...	2·40	H·NMeEt ...	—
Ph·CEt_2Cl	0·45	Ph·NEt_2	6·56	Me·CEt_2Cl	2·60	H·NEt_2 ...	10·98
Ph·CPrCl	0·98	Ph·NPr_2	5·59				
Ph·CBu_2Cl	1·06	Ph·NBu_2	5·7				
o-C_6H_4Me·CMe_2Cl ...	2·71	*o*-C_6H_4Me·NMe_2 ...	5·86				
o-C_6H_4Me·CEt_2Cl ...	1·39	*o*-C_6H_4Me·NEt_2 ...	7·18				

[a] In aqueous solution : Vexlearschi and Rumpf, *Compt. rend.*, 1949, **229**, 1152. [b] In 80% aqueous ethanol : Hughes, *Quart. Rev.*, 1951, **5**, 257. [c] In aqueous solution : Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1930, **52**, 5115; 1932, **54**, 3469.

Further lengthening of the alkyl group to include *n*-propyl and *n*-butyl groups (see Tables 1 and 4) seems to afford steric effects which are smaller than that of the ethyl group : the resulting chlorides have comparatively high reactivity and the corresponding amines have comparatively low basic strength.

EXPERIMENTAL

Materials.—Chlorides. Dry hydrogen chloride was passed for 3 hr. though an ice-cold solution of 2-phenylpropan-2-ol (5 g.) in light petroleum (25 c.c.). An aqueous layer separated; the organic layer was decanted and dried ($CaCl_2$), and the solvent was volatilised at 25—30° under reduced pressure. The residue was mainly 2-phenyl-2-chloropropane (Found : Cl, 22·6. Calc. for $C_9H_{11}Cl$: 23·0%). The other tertiary aralkyl chlorides were similarly obtained and contained 94—98% of the calculated amount of chlorine. The required dialkylphenylmethanols RR′CPh·OH were obtained as previously described.[3] 2-*o*-Tolylpropan-2-ol, m. p. 43°, was obtained in the manner described by Hirschberg,[4] and 3-o-*tolylpentan*-3-*ol*, b. p. 125—126°/22 mm. (Found : C, 80·8; H, 10·1. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%), was similarly obtained by reaction of *o*-tolylmagnesium bromide with diethyl ketone.

Solvent.—One batch of ethanol which had been purified by the process described by Lund and Bjerrum[5] was used throughout.

Determination of Rates of Solvolysis of the Chlorides.—This was effected by the sampling method described by Hughes, Ingold, and Taher.[6] Freshly prepared samples of the chlorides were used immediately after removal of the solvent in which they had been prepared. Distillation of the chlorides under reduced pressure gave distillates which contained much less halogen than was required. Before and after distillation the chlorides provided rates of ethanolysis which did not differ by more than the experimental error (*ca.* 3%). Duplicate determinations were made in every case.

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[3] Klages, *Ber.*, 1902, **35**, 2637, 3507; 1903, **36**, 3692; Gilman and Adams, *J. Amer. Chem. Soc.*, 1925, **47**, 2818; Gilman, Fothergill, and Parker, *Rec. Trav. chim.*, 1929, **48**, 750.

[4] Hirschberg, *J. Amer. Chem. Soc.*, 1949, **71**, 3241.

[5] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[6] Hughes, Ingold, and Taher, *J.*, 1940, 949.