793. *Intermediates in Aralkyl Systems. Part III.*[1] *Kinetics and Mechanisms of Substitution of Diphenylmethyl Bromide by Amines in Nitromethane.*

By Y. Pocker.

The reactions of diphenylmethyl bromide with triethylamine, pyridine, aniline, and *NN*-dimethylaniline have been studied kinetically in nitromethane. Analysis of the products indicated *N*-substitution with the first three amines but *C*-substitution in the ring with *NN*-dimethylaniline. With the first three amines the upper limit to the amount of depression by common ions was found to be the entire first-order component while the second-order component was unaffected except for a general positive salt effect. With *NN*-dimethylaniline, however, there was no limit to the amount of depression by bromide ion. It is suggested that the first- and the second-order component represent S_N1 and S_N2 mechanisms respectively, and that notwithstanding the high rates of racemisation of some aralphyl halides in nitromethane, in the S_N1 component of the present system chemical capture takes place at the free carbonium ion stage. The second-order component in *NN*-dimethylaniline appears to be a bimolecular substitution at nitrogen followed by an easy rearrangement to the *C*-substituted derivative. This rearrangement proceeds through a capturable intermediate.

It is of interest to examine whether the upper limit to the amount of depression by a common ion can be used to confirm the presence of two concurrent and independent mechanisms of substitution, Thus when the S_N1 component of substitution proceeds *via* kinetically free ions, the upper limit to the amount of depression should be the entire first-order component, leaving the second-order component practically unaffected except for a general salt effect. An attempt was therefore made first to establish whether heterolysed but undissociated intermediates have to be postulated to explain the kinetics of reaction of diphenylmethyl bromide with neutral nucleophiles in nitromethane, and, secondly, to test the validity of the criterion suggested above for concurrent mechanisms in substitution reactions with non-saline nucleophiles. A detailed investigation of the reactions of diphenylmethyl bromide with various amines has now been carried out.

(1) *Reaction of Diphenylmethyl Bromide with Triethylamine.*—This reaction does not follow the simple first-order rate law. First-order rate coefficients, k_x, of disappearance of diphenylmethyl bromide, fall progressively. A set of initial first-order rate coefficients, k_i, is shown in Table 1*a* which illustrates that the first-order rate coefficients in diphenylmethyl bromide do not depend upon its concentration. The dependence on triethylamine is well represented by the equation

$$k_i = 1{\cdot}75 \times 10^{-5} + 16{\cdot}5 \times 10^{-5}[\mathrm{NEt_3}]$$

where k_i is in sec.$^{-1}$ (Table 1*a*).

When, however, the triethylamine concentration is lower than about one-twentieth of that of diphenylmethyl bromide, truly initial first-order rate coefficients cannot be directly determined from the experimental readings because of the mass-law depression. Common-ion retardation was independently established by observing the effect of added tetraethylammonium bromide on the initial rates of the forward reaction. If the process which is of first order in diphenylmethyl bromide and of zeroth order in triethylamine is represented by

$$\mathrm{Ph_2CHBr} \underset{k_{\mathrm{Br^-}}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ph_2\overset{+}{C}H} + \mathrm{Br^-} \xrightarrow{+\mathrm{NEt_3},\ k_{\mathrm{NEt_3}}} \mathrm{Ph_2CH\overset{+}{N}Et_3} + \mathrm{Br^-}$$

---

[1] Part II, Pocker, preceding paper.

and the process which is of first order in both alkyl halide and amine is represented by

$$\mathrm{NEt_3 + Ph_2CHBr \xrightarrow[S_N2]{k_2} [Et_3N^{\delta+}\ldots CHPh_2\ldots Br^{\delta-}] \longrightarrow Ph_2CH\overset{+}{N}Et_3 + Br^-}$$

then

$$k_x = \frac{k_1}{(k_{\mathrm{Br}^-}[\mathrm{Br}^-]_x/k_{\mathrm{NEt_3}}[\mathrm{NEt_3}]_x) + 1} + k_2[\mathrm{NEt_3}]_x$$

Indeed, a plot of $k_1/k_x - k_2[\mathrm{NEt_3}]_x)$ against $[\mathrm{Br}^-]_x/[\mathrm{NEt_3}]_x$ has the slope $k_{\mathrm{Br}^-}/k_{\mathrm{NEt_3}} = 1{\cdot}5$ and, as would be expected from the above equation, intercept of $+1{\cdot}0$. In the absence of added saline bromide, the progressive fall in the rate of forward reaction in any given run

TABLE 1. *Initial first-order rate coefficients, k_i (sec.$^{-1}$), of reaction between triethylamine and diphenylmethyl bromide in nitromethane at 25·0°.*

(*a*)											
$10^2[\mathrm{Ph_2CHBr}]$	2·0	2·0	2·0	2·0	2·0	2·0	10	10	10	10	10
$10^2[\mathrm{NEt_3}]$	0·20	0·50	1·0	2·0	3·0	4·0	1·0	2·0	3·0	4·0	5·0
10^5k_i	1·7	1·80	1·91	2·08	2·25	2·42	1·9	2·08	2·22	2·45	2·58

(*b*) $[\mathrm{Ph_2CHBr}] = 0{\cdot}020$M.

$10^3[\mathrm{NEt_3}]_i$	0·1	0·2	0·25	0·5	0·75	1
$10^4[\mathrm{NEt_3}]_x$	0·47	1·04	1·5	3·5	5·8	8·3
$([\mathrm{Br}^-]/[\mathrm{NEt_3}])_x$	1·13	0·924	0·667	0·429	0·293	0·205
10^5k_x	0·65	0·74	0·91	1·07	1·16	1·34
$10^5k_{1,\ \mathrm{calc.}}$	1·75	1·74	1·82	1·77	1·67	1·75

* $k_{1,\ \mathrm{calc.}} = k_x\{1{\cdot}5([\mathrm{Br}^-]/[\mathrm{NEt_3}]_x) + 1\}$

(*c*) $[\mathrm{Ph_2CHBr}] = 0{\cdot}020$M; $[\mathrm{NEt_3}] = 0{\cdot}0050$M.

$10^2[\mathrm{NEt_4ClO_4}]$	1·0	2·0	3·0	4·0	6·0
10^5k_i	1·87	1·97	2·02	2·14	2·32

(*d*) $[\mathrm{Ph_2CHBr}] = 0{\cdot}020$M, $[\mathrm{NEt_3}] = 0{\cdot}0050$M.

$10^2[\mathrm{NEt_4Br}]$	0·125	0·25	0·50	0·75	1·0
10^5k_i †	1·3	1·0	0·77	0·61	0·52

† $k_1^{\mu}/(k_i - k_2[\mathrm{NEt_3}])$ is plotted against $[\mathrm{NEt_4Br}]/[\mathrm{NEt_3}]$ in Fig. 1.

(at low ionic strength) is fairly well represented by $10^5k_1 = 1{\cdot}75$ sec.$^{-1}$ and $k_{\mathrm{Br}^-}/k_{\mathrm{NEt_3}} = 1{\cdot}5$ at 25·0°. This means that diphenylmethyltriethylammonium bromide and triethylamine hydrobromide, which are the two saline products in this reaction, have in nitromethane about the same capacity to capture the reaction intermediate as has tetraethylammonium bromide. The mass-law effect also accounts for the low first-order rate coefficients obtained when $[\mathrm{NEt_3}]/[\mathrm{Ph_2CHBr}] < \frac{1}{20}$. This effect arises because in those instances the balance of competition of the two consumers of formed carbonium ions is not what it should be when truly initial rates are determined, *i.e.*, $k_{\mathrm{Br}^-}[\mathrm{Br}^-] > k_{\mathrm{NEt_3}}[\mathrm{NEt_3}]$, leading to an increase in k_x with $[\mathrm{NEt_3}]$, similar to that encountered in S_N2C^+ behaviour.[2] As an extreme example let us take $[\mathrm{NEt_3}]/[\mathrm{Ph_2CHBr}] = 0{\cdot}01$. The first kinetically significant sample withdrawn from the reaction mixture corresponded to *ca.* 0·5% of reaction with respect to diphenylmethyl bromide which is, however, *ca.* 50% of reaction with respect to this low concentration of triethylamine. The ratio $[\mathrm{Br}^-]/[\mathrm{NEt_3}]$ for this point is *ca.* 1, and since $k_{\mathrm{Br}^-}/k_{\mathrm{NEt_3}} = 1{\cdot}5$, one obtains $k_x \sim 0{\cdot}4\ k_1$. Table 1*b* illustrates and analyses similar examples.

When $[\mathrm{NEt_3}] = 0{\cdot}005$M the contribution of the second-order component is low and the variation in k_i with added tetraethylammonium perchlorate can be analysed as being mainly due to variations in k_1. Indeed, the ionic-strength effects on k_1 are similar (Table 1*c*) to those already encountered in symmetrical exchange studies (preceding paper).

(2) *Reaction of Diphenylmethyl Bromide with Aniline.*—The stoicheiometry of this reaction is $\mathrm{Ph_2CHBr + 2PhNH_2 \longrightarrow Ph_2CH{\cdot}NHPh + PhNH_3^+\}Br^-}$. A set of initial first-order rate coefficients is shown in Table 2 which illustrates that the first-order rate coefficients in diphenylmethyl bromide do not depend upon its concentration.

---

[2] Gelles, Hughes, and Ingold, *J.*, 1954, 2924.

TABLE 2. *Initial first-order rate coefficients, k_i (sec.$^{-1}$), of reaction of diphenylmethyl bromide and aniline in nitromethane at 25·0°; effects of added tetraethylammonium bromide and perchlorate.*

(*a*)

10^2[Ph_2CHBr] ...	0·25	0·5	1·0	2·0	3·0	5·0	0·25	0·25	0·25	0·25
10^2[$PhNH_2$]	0·5	0·5	0·5	0·5	0·5	0·5	0·125	0·25	0·5	1·0
10^5k_i	2·3	2·35	2·32	2·3	2·2	2·1	1·86	2·04	2·30	2·9
10^2[Ph_2CHBr] ...	2·0	2·0	2·0	2·0	2·0	2·0	2·0			
10^2[$PhNH_2$]	0·5	1·0	2·0	3·0	4·0	5·0	10			
10^5k_i	2·3	2·86	3·95	5·05	6·15	7·25	12·7			

(*b*) [Ph_2CHBr] = 0·02M; [$PhNH_2$] = 0·005M.

10^2[NEt_4ClO_4] ...	1·0	2·0	4·0	6·0	20·0
10^5k_i	2·35	2·45	2·7	2·9	3·2

10^2[NEt_4Br]...	0·50	1·0	2·0
10^5k_i	1·65	1·37	1·1
k_{Br^-}/k_{PhNH_2} ...	0·61	0·60	0·61

(*c*) [Ph_2CHBr] = 0·020M; [NEt_4ClO_4] = 0·20M.

10^2[$PhNH_2$]	0·5	1·0	2·0
10^5k_1	3·2	3·8	5·1

[Ph_2CHBr] = 0·020M; [NEt_4Br] = 0·20M.

10^2[$PhNH_2$]	0·2	0·5	0·75	1·0	1·5	2·0
10^5k_1	0·23	0·57	0·86	1·2	1·9	2·4

FIG. 1. *Reaction of diphenylmethyl bromide with triethylamine in the presence of added tetraethylammonium bromide in nitromethane solution at* 25·0°.

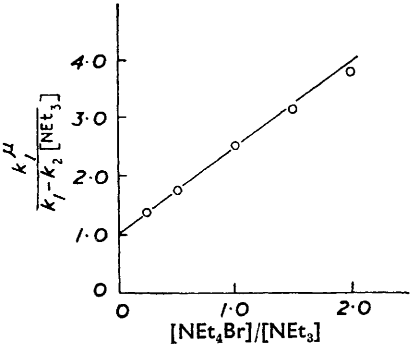
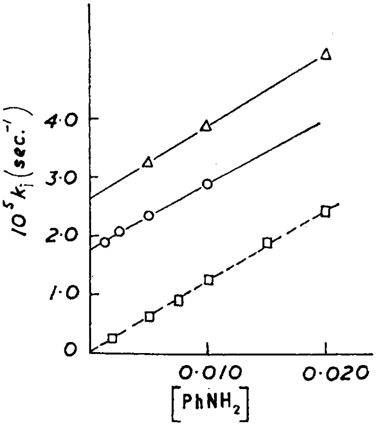


FIG. 2. *Reaction of diphenylmethyl bromide with aniline* ○; *in the presence of* 0·20M-NEt_4ClO_4 △; *and in the presence of* 0·20M-NEt_4Br □.



The dependence on aniline concentration is well expressed by the equation $k_i = k_1^\mu + k_2^\mu[PhNH_2]$. At low ionic strength $10^5k_1^\mu = 10^5k_1 = 1{\cdot}75$ sec.$^{-1}$ and $k_2^\mu = k_2 = 110 \times 10^{-5}$ sec.$^{-1}$ l. mole^{-1}. The addition of tetraethylammonium bromide depresses the initial rate of the forward reaction. The depression is well represented by the equation. The depression is well represented by the equation

$$k = \frac{k_1}{(k_{Br^-}[Br^-]/k_{PhNH_2}[PhNH_2]) + 1} + k_2[PhNH_2]$$

where at 25·0° at low ionic strength $k_{Br^-}/k_{PhNH_2} = 0{\cdot}61$. With [$NEt_4Br$] = 0·20M the first-order component is almost entirely suppressed so long as [NEt_4Br]/[$PhNH_2$] $\geqslant$ 10 and the forward reaction is almost entirely a second-order process which can be identified with the S_N2 component at an ionic strength of 0·2M-NEt_4ClO_4. Indeed, a plot of the maximally supressed rate against the concentration of aniline passes through the origin and the line is parallel to that of the unsuppressed rate at the same ionic strength (Fig. 2).

(3) *Reaction of Diphenylmethyl Bromide with Pyridine.*—This reaction was followed by the disappearance of amine during the reaction $Ph_2CHBr + C_5H_5N \longrightarrow Ph_2CH\overset{+}{N}C_5H_5\}Br^-$ Acetone–glacial acetic acid (4 : 1,v/v) was a suitable quenching medium. The acetic acid does not solidify from it even at —80°, diphenylmethyl bromide is inert in it at low

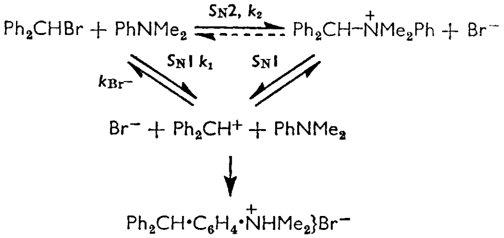
temperatures, and pyridine is quantitatively converted into acetate ions which can be satisfactorily titrated with standard perchloric acid in glacial acetic with Bromothymol Blue as indicator. A set of initial first-order rate coefficients, k_i (sec.$^{-1}$), is shown in Table 3. The dependence of k_i on pyridine concentration is satisfactorily expressed by $10^5k_i = 1{\cdot}75 + 65[C_5H_5N]$. From the depression of the initial rate by added tetraethylammonium bromide one calculates, at low ionic strength, $k_{Br^-}/_{C_5H_5N} = 3{\cdot}4$ at 25·0°. With $[NEt_4Br] = 0{\cdot}2\text{M}$ the first-order component k_1, is almost entirely suppressed at all pyridine concentrations below 0·05M and the forward reaction in this region is a second-order process: $10^5k_i = 75[C_5H_5N]$.

TABLE 3. *Initial first-order rate coefficients,* k_i *(sec.*$^{-1}$*), of reaction of diphenylmethyl bromide with pyridine in nitromethane at* 25·0°. $[Ph_2CHBr] = 0{\cdot}0097\text{M}$.

(*a*) $10^2[C_5H_5N]$	0·142	0·284	0·568	1·14	2·28	
10^5k_i	1·82	1·95	2·03	2·40	3·27	
(*b*) $10^2[C_5H_5N]$	1·14	1·14	1·14			
$10^2[NEt_4Br]$	0·237	0·593	1·18			
10^5k_i	1·76	1·36	1·14			
$k_{Br^-}/k_{C_5H_5N}$ *	3·4	3·5	3·3			
(*c*) $[NEt_4Br] = 0{\cdot}20\text{M}$						
$10^2[Ph_2CHBr]$	0·97	0·97	0·97	1·94	1·94	3·88
$10^2[C_5H_5N]$	0·50	1·0	2·0	3·0	4·0	5·0
10^5k_i	0·38	0·75	1·45	2·3	3·1	3·8

* $(k_{Br^-}/k_{C_5H_5N})([Br^-]/[C_5H_5N]) = k_1{}^{\mu}/(k_i - k_2[C_5H_5N]) - 1$

(4) *Reaction of Diphenylmethyl Bromide with* NN-*Dimethylaniline.*—This reaction was followed by the disappearance of amine during the reaction (see previous section). The first-order rate coefficients of disappearance of diphenylmethyl bromide did not show any appreciable progressive fall within any given run and it was therefore suspected that a weak electrolyte is being produced, *i.e.*, the hydrobromide of a weak tertiary amine rather than a quaternary ammonium bromide. Since the hydrobromide of a weak amine behaves on titration as an acid in acetone with respect to lacmoid the rates of " acid " production were similarly investigated (Table 4*a*). The results obtained illustrate that $-d[\text{Amine}]/dt = +dH^+/dt$ so that a *C*-substitution rather than an *N*-substitution must take place: $Ph_2CHBr + 2PhNMe_2 \longrightarrow Ph_2CH{\cdot}C_6H_4{\cdot}NMe_2 + PhN^+Me_2H\ Br^-$. This conclusion was confirmed by product analysis, the *para*-substituted diphenylmethyl derivative of *NN*-dimethylaniline being recovered in 94% yield. The dependence of the initial first-order rate coefficients of disappearance of diphenylmethyl bromide k_i (sec.$^{-1}$) on *NN*-dimethylaniline is well represented by the equation $10^5k_i = 1{\cdot}75 + 135[PhNMe_2]$. While a substitution in the *NN*-dimethylaniline ring by the electrophilic carbonium ion produced in the unimolecular component is easily visualised, the problem arises how can ring substitution proceed *via* an S_N2 transition state with respect to diphenylmethyl bromide. The products were therefore analysed at a concentration where the second-order component was 10 times larger than the first-order component and again the product was >90% *p*-diphenylmethyl-*NN*-dimethylaniline. Conceivably, the second-order component represents an S_N2 attack on nitrogen followed by an easy unimolecular rearrangement of the diphenylmethyl group to the *para*-position.



$$Ph_2CH{\cdot}C_6H_4{\cdot}\overset{+}{N}HMe_2\}Br^- + PhNMe_2 \rightleftharpoons Ph_2CH{\cdot}C_6H_4{\cdot}NMe_2 + Ph\overset{+}{N}HMe_2\}Br^-$$

If this rearrangement proceeds *via* a carbonium ion then both the first- and the second-order component should be depressed by added tetraethylammonium bromide. Indeed, this is the only reaction where tetraethylammonium bromide was found to suppress both the first- and the second-order component of substitution (Table 4*b*).

TABLE 4. *First-order rate-coefficients, k_A or k_{H^+} (sec.$^{-1}$). of reaction of diphenylmethyl bromide and* NN-*dimethylaniline in nitromethane at* 25·0°.

(*a*)						
10^2[Ph_2CHBr]	0·13	1·3	1·3	1·3	1·3	1·3
10^2[PhNMe] ...	0·15	0·15	0·45	1·13	2·26	3·39
10^5k_A	1·95	1·93	2·35	3·25	4·70	—
$10^5k_{H^+}$	1·95	1·90	2·37	3·22	4·78	6·25

(*b*)				
10^2[Ph_2CHBr]	1·3	1·3	1·3	1·3
10^2[$PhNMe_2$]...	1·13	2·26	1·13	4·51
10^2[NEt_4Br] ...	2·37	2·26	5·98	0·598
10^5k_A	1·60	1·01	0·865	0·47

k_A was calculated from $-$d[Amine]/d*t* and k_{H^+} from $+$d[R_3NH^+]/d*t*.

Discussion.—(*a*) While the stereochemical behaviour of some aralkyl halides in nitromethane indicates that in the absence of electrophilic catalysis racemisation takes place before dissociation,[3] common-ion repression experiments indicate the absence of a chemically capturable intermediate in the diphenylmethyl system before the free carbonium ion stage.

(*b*) Compelling evidence for the operation of two concurrent processes, S_N1 and S_N2, comes from observations on the rates of reactions maximally depressed by common ions.

(*c*) The capturing capacity of the various reagents employed towards the diphenylcarbonium ion, $PhNH_2$ (1·7) $>$ Br^- (1·0) $>$ NEt_3 (0·67) $>$ C_5H_5N (0·29) $>$ $PhNMe_2$, does not follow their nucleophilic power towards diphenylmethyl bromide, $Br^- > PhNMe_2 > PhNH_2 > C_5H_5N > NEt_3$, as measured by the ratios of the second-order components.

(*d*) The particularly low reactivity of NEt_3 in the S_N2 process may be due to steric hindrance.

(*e*) On a free-energy basis, the reactions where the carbonium ion reacts faster with the common ion than with amine are not strictly S_N1. They become, however, S_N1 in the limit, *i.e.*, when the concentration of reagent Y is sufficiently high that $k_Y[Y] > k_{Br^-}[Br^-]$, leading to $k_x \longrightarrow k_1$. With 2,6-lutidine the first-order rate coefficient as determined in the initial stages of reaction rises steadily and approaches the values of k_1 only at relatively high amine concentrations, but with more sterically hindered amines one observes a transition to S_N2C^+ behaviour.[4]

(*f*) The kinetics of the unimolecular component with amines embody three features: (i) the initial rates of the various substitutions are the same, (ii) the ionic strength effects are similar and positive, and (iii) common ions can depress the entire unimolecular component.

(*g*) The kinetics of the bimolecular component of substitution by amines show a positive ionic-strength effect as would accord with a reaction whose transition state is more polar than its initial state. This result should be contrasted with the negative ionic-strength effect observed in the bimolecular component of substitution by anions (preceding paper).

(*h*) The criterion used to distinguish concurrent from borderline mechanisms is limited to cases where the common-ion repression can successfully compete with the sum of forward reactions (substitutions and eliminations.)

EXPERIMENTAL

Materials.—These were prepared and purified as described previously.[5,6]

Kinetic Measurements.—Temperature control was ±0·01° at 25·0°. Reaction mixtures were prepared as indicated in the preceding paper.[1] To the reaction with triethylamine,

---

[3] Pocker, paper presented at the Informal Faraday Society meeting, Leeds, September, 1958. For abstract, see *Trans. Faraday Soc.*, 1959, **55**, 1266.

[4] Pocker, unpublished results.

[5] Pocker, *J.*, 1958, 240.

[6] Pocker, *J.*, 1959, 1179.

aliquot portions were delivered into dry acetone at −80° and titrated with standard acid with lacmoid indicator. To reactions with the weaker tertiary amines, pyridine and *NN*-dimethylaniline, aliquot portions were quenched in acetone–acetic acid (4 : 1, v/v) at −80° and titrated with standard perchloric acid dissolved in glacial acetic acid with Bromothymol Blue as indicator. In reactions where the product was the hydrobromide of a weak amine, *e.g.*, anilinium and *NN*-dimethylanilinium hydrobromide, aliquot portions were quenched in acetone at −80° and titrated with standard alkali with lacmoid indicator. An illustrative run is in Table 5.

TABLE 5. *Illustrative run.* $[\mathrm{Ph_2CHBr}]_i = 0{\cdot}020\,\mathrm{M}$. $[\mathrm{NEt_3}]_i = 0{\cdot}010\,\mathrm{M}$.

Time (sec.)	0	130	265	426	536	830	1020
$10^3(a - x)$	20·0	19·95	19·9	19·84	19·8	19·7	19·64
10^5k_x (sec.$^{-1}$)	—	1·91	1·90	1·88	1·87	1·83	1·83
Time (sec.)	1400	1760	2160	2400	3100	5400	
$10^3\ (a - x)$	19·5	19·38	19·26	19·2	19·0	18·4	
10^5k_x (sec.$^{-1}$)	1·81	1·78	1·74	1·70	1·66	1·54	

The value of k_x when $[\mathrm{Br^-}]/[\mathrm{NEt_3}] = 0$ is $k_i = 1{\cdot}91 \times 10^{-5}$ sec.$^{-1}$ $= k_1 + k_2[\mathrm{NEt_3}] = 1{\cdot}75 \times 10^{-5} + 16 \times 10^{-5}\ [0{\cdot}01]$.

The various values of k_x are well represented by the general equation given on p. 3945, if $k_{\mathrm{Br^-}}/k_{\mathrm{NEt_3}} = 1{\cdot}5$.

Isolation of Products.—Diphenylmethyltriethylammonium bromide, isolated in 88% yield * from the reaction with triethylamine, had m. p. 166° (decomp.) (Found: Br⁻, 22·8. Calc. for $\mathrm{C_{19}H_{26}NBr}$: $\mathrm{Br^-}$, 22·9%). 4-Dimethylaminotriphenylmethane, isolated in 94% yield from the reaction with dimethylaniline, had m. p. 131° (Found: C, 88·0; H, 7·6; N, 4·9. Calc. for $\mathrm{C_{21}H_{21}N}$: C, 87·8; H, 7·4; N, 4·8%). It is a weak base towards lacmoid in acetone, but liberates acetate ions in acetone–glacial acetic acid (4 : 1, v/v) which when neutralised indicate equiv. of 284. (Calc.: *M*, 287). The compound was independently synthesised (*a*) by the condensation of diphenylmethanol with *NN*-dimethylaniline in the presence of phosphoric oxide at 180°,[7a] and (*b*) from 4-dimethylaminobenzaldehyde and phenylmagnesium bromide.[7b] Recrystallised from chloroform, it had m. p. 133°, alone or mixed with a reaction sample (lit.,[7] m. p. 133°). *N*-Diphenylmethylpyridinium bromide, m. p. 204° (decomp.), was obtained in 85% yield (Found: $\mathrm{Br^-}$, 24·4. Calc. for $\mathrm{C_{18}H_{16}NBr}$: $\mathrm{Br^-}$, 24·6%).

The author thanks Professor E. D. Hughes, F.R.S., and Sir Christopher Ingold, F.R.S., for their interest, and Messrs. D. W. Hills and A. B. Spiers for technical assistance.

* This refers to conditions where $[\mathrm{NEt_3}] > [\mathrm{Ph_2CHBr}]$. However, when $[\mathrm{Ph_2CHBr}] > [\mathrm{NEt_3}]$ some triethylamine hydrobromide was also isolated. It may be that this product arises when the ratio $[\mathrm{Br^-}]/[\mathrm{NEt_3}]$ becomes so large that substitution by $\mathrm{NEt_3}$ is reduced to a point where reaction with $\mathrm{CH_2NO_2^-}$ [6] (formed in the reaction $\mathrm{CH_3NO_2 + NEt_3 \rightleftharpoons CH_2NO_2^-\}NEt_3H^+}$) is no longer negligible.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[*Received, May 29th,* 1959.]

---

[7] (*a*) Fischer, *Annalen*, 1880, **206**, 113; (*b*) Sachs and Sachs, *Ber.*, 1905, **38**, 523.