obtained by reduction of the tosylate exhibited only the shorter RT peak (cis).

3-Hydroxymethylenenorcarane (22, 23). The residue from methylenation of **8** gave only one peak on the vpc column used for kinetic analysis, but on an 8 m × 1.6 mm Carbowax 4M column at 150° showed two imperfectly separated peaks with areas of 45 and 55% (in order of RT). The tosylate prepared from a sample of this mixture was reduced by lithium aluminum hydride to give a mixture

of *cis-* (45%) and *trans*-3-methylnorcarane (55%), analyzed on the capillary column described above.

Rates and Salt Effects in the Reactions of Phenacyl Bromide with N-Ethylaniline and Triethylamine in Chloroform

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Abstract: Measurements of the rate of reaction of phenacyl bromide and N-ethylaniline in chloroform are fitted best by a rate equation involving two terms, one first order in amine and first order in bromide and the other second order in amine and first order in bromide. The reaction is subject to a strong, positive, neutral salt effect, and with a neutral salt added the reaction is bimolecular. The reaction of phenacyl bromide with triethylamine in chloroform also shows a positive salt effect and is bimolecular even in the absence of the neutral salt. The significance of these observations has been discussed.

The remarkable ease with which α-halo ketones undergo SN2 displacements was reported as early as 1909 by Slator and Twiss[1] and has been a subject of active investigation ever since. This enhanced reactivity has been attributed to inductive electron withdrawal by the carbonyl group,[2] to a mechanism involving an intermediate in which the nucleophile is covalently bonded to the carbonyl carbon,[3] to the electrostatic effect exerted by the carbonyl group on the approaching nucleophile,[4] and to orbital overlap with the nucleophile, either by the π-molecular orbital of the C–C–O system[5] or the p orbital of the carbonyl carbon.[6] The stereochemical implications of this last proposal have been explored in a well-designed experiment by Bartlett and Trachtenberg.[7] Although the results strongly support the orbital-overlap mechanism, they do not eliminate Pearson's[4] hypothesis.

The rates of reaction of phenacyl halides with amines are of special interest because of the many perturbations of second-order kinetics that are potentially possible. With strongly basic amines some of the diphenacyl halide formation observed in the reaction with ethoxide ion becomes possible.[8] With a primary amine competing azine formation has been observed in the reaction of 2-(bromoacetyl) naphthalene with isopropylamine.[9] In this same study it was found that the data were fitted best by eq 1

$$\frac{dx}{dt} = k(A_0 - X)(B_0 - nX) \tag{1}$$

where A_0 is the initial halide concentration, B_0 the initial amine concentration, and n has a value intermediate between 1 and 2 rather than the expected value of 2. In reactions with amines the starting materials are neutral molecules, but the product includes a salt, either an amine hydrohalide or a quaternary ammonium salt. The transition state might, therefore, be expected to show extensive charge separation and to have ionic or zwitterionic characteristics. This could manifest itself in the observation of significant neutral salt effects. Finally, in the reactions with primary and secondary amines the transition from reactants to products necessarily involves a proton transfer at some stage of the process. The implications of this proton transfer step, even if not rate determining, are important in rate studies but have not been fully explored.

In the present study the rates of reaction of phenacyl bromide with N-ethylaniline were measured in methanol, in chloroform, and in 50% chloroform–50% carbon tetrachloride at 24.6 ± 0.1°. For purposes of comparison measurements were also made of the rates of reaction of phenacyl bromide with triethylamine and of benzyl bromide with N-ethylaniline and with triethylamine, all in chloroform. In addition the effect of added neutral salts on these reaction rates was investigated.

Results

The rate of reaction of phenacyl bromide and N-ethylaniline in chloroform, stabilized with 0.75% eth-

(1) A. Slator and D. F. Twiss, *J. Chem. Soc.*, 95, 93 (1909).

(2) E. D. Hughes, *Trans. Faraday Soc.*, 37, 603 (1941); *Quart. Rev. (London)*, 5, 245 (1951).

(3) J. W. Baker, *J. Chem. Soc.*, 445 (1938).

(4) R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Am. Chem. Soc.*, 74, 5130 (1952).

(5) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p 73.

(6) Suggested by S. Winstein at the International Colloquium on Molecular Rearrangements and Walden Inversion, Montpellier, France, 1950.

(7) P. D. Bartlett and E. N. Trachtenberg, *J. Am. Chem. Soc.*, 80, 5808 (1958).

(8) H. H. Wasserman, N. E. Aubrey, and H. E. Zimmerman, *ibid.*, 75, 96 (1953).
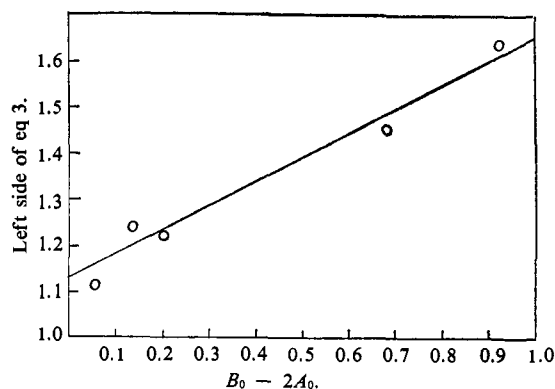
(9) A. J. Taylor, *J. Chem. Soc.*, B, 904 (1967).

Figure 1. Plot of eq 3.

anol, was measured at 24.6 ± 0.1°. The reaction is a clean one, and the product, N-phenacyl-N-ethylaniline, can be isolated in almost 90% yield. Measurements were made at a single phenacyl bromide concentration, but the amine concentration was varied more than sixfold. Bimolecular plots, using the integrated form of eq 1 with $n = 2$, show slight upward curvature, particularly for points at high percentage reaction. The results shown in Table I, column 3, were obtained by stressing the points below 40% reaction, since in all cases a good straight line could be drawn through these points.

Table I. Rates of Reaction of Phenacyl Bromide with N-Ethylaniline in Chloroform at 24.6 ± 0.1°

Bromide, mol l.$^{-1}$	Amine, mol l.$^{-1}$	k_2, l. mol^{-1} hr^{-1}	k_2 at $\mu = 0$, l. mol^{-1} hr^{-1}
0.05065	0.1573	0.0446	0.0256
0.05052	0.1583	0.0442	0.0352
0.05052	0.2370	0.0424	0.0272
0.05052	0.3024	0.0469	0.0324
0.05018	0.7837	0.0529	0.0411
0.05067	1.0248	0.0564	0.0452

The average value for the rate constants in column 3 is 0.0479 l. mol^{-1} hr^{-1}. The maximum deviation from this average value is almost 18%, and the average deviation is more than 9%. The rate constants show a definite tendency to increase with increasing initial amine concentration, B_0, and a plot of k_2 vs. B_0 is reasonably linear. The measurements would, therefore, be better fitted by eq 2. Using the initial amine concentrations, the rate constants of column 3 and the method of least squares, values of 0.0414 l. mol^{-1} hr^{-1} and 0.0146 l.^{2} mol^{-2} hr^{-1}, respectively, were obtained for k_2 and k_3 in eq 2.

$$\frac{dx}{dt} = k_2(A_0 - x)(B_0 - 2x) + k_3(A_0 - x)(B_0 - 2x)^2 \quad (2)$$

As will be shown later this reaction is subject to a strong, positive neutral salt effect. The bimolecular rate constants that have thus far been used refer, at best, to some indeterminate ionic strength, and it is even possible, although unlikely, that the variations shown in column 3 are entirely due to differences in ionic strength. To obviate this difficulty the bimolecular rate constants were determined at zero ionic strength.

This was done by plotting x vs. t for each run in Table I. Slopes were determined at regular intervals along these plots and were used to calculate the instantaneous bimolecular rate constants. For each run log k_2 was plotted against $\mu^{1/2}$, and in every case a good linear plot, permitting a facile extrapolation to $\mu = 0$, was obtained. The resulting bimolecular rate constants at $\mu = 0$ are shown in column 4 of Table I.

It is clear that the values for k_2 at $\mu = 0$ increase with increasing B_0 and that once again eq 2 is the more appropriate rate equation. The data from a plot of k_2 at $\mu = 0$ vs. B_0, treated by the method of least squares, gave values of 0.0255 l. mol^{-1} hr^{-1} for k_2 and 0.0203 l.^{2} mol^{-2} hr^{-1} for k_3.

Finally, eq 2 was used in its integrated form, eq 3 below, to determine k_2 and k_3.[10] The time chosen in

$$\frac{1}{B_0 - 2A_0} \ln \frac{A_0 B}{A B_0} - \frac{k_3}{k_2} \times$$

$$\left[\ln \frac{B_0}{B} - \ln \frac{B_0 + \frac{k_2}{k_3}}{B + \frac{k_2}{k_3}} \right] = k_2 t + k_3 t (B_0 - 2A_0) \quad (3)$$

fitting eq 3 was 25 hr, and the values that resulted were 0.0454 l. mol^{-1} hr^{-1} for k_2 and 0.0206 l.^{2} mol^{-2} hr^{-1} for k_3. An indication of the quality of the fit obtained is given by Figure 1, where the the y axis is the sum of the terms on the left side of eq 3 and the x axis is $B_0 - 2A_0$. The intercept in Figure 1 corresponds to $k_2 \times 25$ hr and the slope to $k_3 \times 25$ hr.

In this case, too, the value of k_2 obtained is the rate constant for some indeterminate ionic strength. The value obtained for k_2 from the data extrapolated to zero ionic strength is the most reliable, since it corresponds to the value of the rate constant in a well-defined ionic atmosphere. As will be demonstrated later, the value of k_3 is not significantly increased by an increase in the ionic strength of the solution. Therefore, all the values obtained for k_3, particularly those from the last two treatments, are in reasonable or excellent agreement. It is concluded, therefore, that the data cannot be fitted properly with eq 1 and that a rate equation having two terms, one second order and one third order, better accommodates the data.

Table II records the results of measurements of the

Table II. Rates of Reaction of Phenacyl Bromide and N-Ethylaniline in the Presence of Initially Added 0.05722 M Benzyltriethylammonium Nitrate in Chloroform at 24.6 ± 0.1°

Bromide, mol l.$^{-1}$	Amine, mol l.$^{-1}$	k_2, l. mol^{-1} hr^{-1}
0.05048	0.1588	0.323
0.05038	0.3155	0.324
0.05040	0.3160	0.318
0.05051	0.7857	0.324

rate of the same reaction in the presence of an initially added neutral salt, 0.05722 M benzyltriethylammonium nitrate. Once again the measurements were at a constant bromide concentration and varied amine con-

(10) For details on the application of eq 3 to the determination of k_2 and k_3, see S. D. Ross and R. C. Petersen, J. Am. Chem. Soc., 80, 2447 (1958).

centrations. In this case the bimolecular plots showed very slight downward curvature at very high percentage reaction, and once again the earlier points were stressed in determining the rate constants. That the addition of a neutral salt has a very striking effect on this reaction is clear from the rate constants shown in Table II. The reaction is now an order of magnitude faster, but, more important, the rate constants obtained do not increase with increasing B_0. The average rate constant is 0.323 l. mol^{-1} hr^{-1}. The maximum deviation from this average value is 1.5% and the average deviation is 0.5%. Thus in the presence of a neutral salt the third-order process does not contribute significantly to product formation, and the reaction can be treated as a simple bimolecular reaction. It follows, also, that in this reaction the second-order process is subject to a strong, positive salt effect, while the third-order process is relatively unaffected by the addition of a neutral salt.

Table III assembles the results of measurements of the rate of reaction of phenacyl bromide with N-ethyl-aniline in the presence of various additives. The measurements were all in chloroform, stabilized with 0.75% ethanol, at 24.6 ± 0.1°. Included are an experiment with benzyltriethylammonium nitrate added at a lower concentration than in the data reported in Table II, and an experiment with added N-ethylaniline hydrobromide, a product of the reaction between phenacyl bromide and the aniline. The hydrobromide, which is probably only slightly dissociated in chloroform, accelerates the reaction but to a much lesser extent than an equivalent concentration of a quaternary ammonium salt.

Table III. Rates of Reaction of Phenacyl Bromide and N-Ethylaniline in the Presence of Various Additives in Chloroform at 24.6 ± 0.1°

Bromide, mol l.$^{-1}$	Amine, mol l.$^{-1}$	Additive	Amt, mol l.$^{-1}$	k_2, l. mol^{-1} hr^{-1}
0.05038	0.1569	Benzyltriethyl-ammonium nitrate	0.02677	0.133
0.05022	0.1573	N-Ethylaniline hydrobromide	0.02659	0.0579
0.05043	0.7840	Tetraethylammonium nitrate	0.05724	0.335
0.05056	0.7853	Benzyltriethyl-ammonium nitrate and N-phenacyl-N-ethylaniline	0.05727 0.05054	0.306
0.05049	0.1571	Benzyltriethyl-ammonium nitrate and N-phenacyl-N-ethylaniline	0.05721 0.05194	0.295

The remaining experiments in Table III were designed to explain the slight downward curvature in the bimolecular plots of the measurements reported in Table II. It is not due to reversibility of the reaction, since in a separate experiment it was demonstrated that the aniline hydrobromide does not react measurably with N-phenacyl-N-ethylaniline in chloroform. It is also not due to reaction of bromide ion with benzyltriethyl-ammonium nitrate to give benzyl bromide, and this, too, was confirmed in a separate experiment. This last result is corroborated by the experiment with added tetraethylammonium nitrate, which gives a rate constant which is not significantly different from that
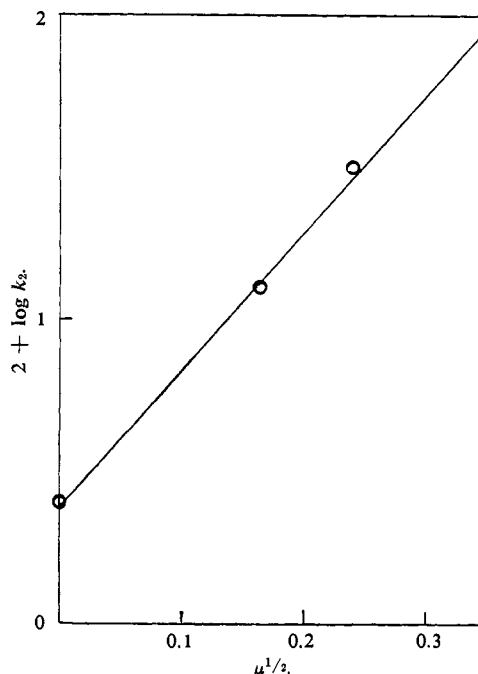

Figure 2. Plot of 2 + log k_2 vs. $\mu^{1/2}$.

observed with the same concentration of the benzyltri-ethylammonium salt. A reasonable explanation is afforded by the last two experiments in Table III. Measurements with both benzyltriethylammonium nitrate and N-phenacyl-N-ethylaniline added initially give bimolecular rate constants which are lower than those obtained when only the salt was added. These rate constants were calculated using eq 1 with $n = 2$. When appreciable amounts of N-phenacyl-N-ethyl-aniline are present, some of the protons produced in the reaction are bound by this compound as well as by N-ethylaniline. At this stage of the reaction the correct form of eq 1 should have n equal to a number somewhat less than 2, and use of the equation with $n = 2$ results in some slight downward curvature at high percentage reactions.

The results described afford three values for k_2, one at $\mu = 0$ obtained from the data of Table I, one at $\mu = 0.05722$ M obtained from the average of the values given in Table II, and one at $\mu = 0.02677$ M from the single measurement in Table III. A plot of log k_2 vs. $\mu^{1/2}$, using the above data, permits a test of the self-consistency of the data and its treatment, and this is shown in Figure 2.

The rate of this reaction was also measured in 50% chloroform–50% carbon tetrachloride at 24.6 ± 0.1°. Bimolecular plots showed strong upward curvature, and again the rate constants were determined at $\mu = 0$ using x vs. t plots and the procedure already described. Plots of k_2 vs. $\mu^{1/2}$ were in every case linear. The results are shown in Table IV.

The rate constants shown in Table IV are reasonably constant. The average value is 0.0198 l. mol^{-1} hr^{-1}; the maximum deviation is 9.4% and the average deviation is 4.7%. The values, however, show a slight but definite trend, with k_2 increasing as B_0 increases. This effect, even if real, would mean that k_3 in this reaction would have a value of only approximately 2 × 10^{-4} l.^{2} mol^{-2} hr^{-1}, and this was not pursued further.

Table IV. Rates of Reaction of Phenacyl Bromide and
N-Ethylaniline in 50% Chloroform–50% Carbon
Tetrachloride at 24.6 ± 0.1°

Bromide, mol l.$^{-1}$	Amine, mol l.$^{-1}$	k_2 at $\mu = 0$, l. mol^{-1} hr^{-1}
0.05042	0.2363	0.0189
0.05077	0.3937	0.0191
0.05040	0.5927	0.0194
0.05047	0.7881	0.0216

Measurements of the rate of this reaction in methanol give excellent bimolecular plots with all points on the straight line. There is no trend in the values of the rate constants with increasing B_0, and it is concluded that in this solvent the reaction is bimolecular. The results are summarized in Table V.

Table V. Rates of Reaction of Phenacyl Bromide with
N-Ethylaniline in Methanol at 24.6 ± 0.1°

Bromide, mol l.$^{-1}$	Amine, mol l.$^{-1}$	k_2, l. mol^{-1} hr^{-1}
0.05035	0.1539	0.817
0.05067	0.3041	0.791
0.05071	0.6004	0.908
0.04999	0.7862	0.875

The reaction of phenacyl bromide with triethylamine in chloroform presents a very different picture. To begin with the reaction is some 60 times faster than the reaction with N-ethylaniline. The reaction is bimolecular within experimental error, and there is no indication that a third-order process is involved. The reaction does show a positive, neutral salt effect, but its magnitude is small. The addition of 0.05728 M benzyltriethylammonium nitrate increased the rate constant less than twofold. In the reaction with N-ethylaniline this salt concentration increased the rate constant almost 13-fold. These results are summarized in Table VI. The reported rate constants were determined using eq 1 with $n = 1$.

Table VI. Rates of Reaction of Phenacyl Bromide with
Triethylamine, with and without Added Benzyltriethylammonium
Nitrate in Chloroform at 24.6 ± 0.1°

Bromide, mol l.$^{-1}$	Amine, mol. l.$^{-1}$	Salt, mol l.$^{-1}$	k_2, l. mol^{-1} hr^{-1}
0.05051	0.05342	0	1.56
0.05049	0.1427	0	1.46
0.05061	0.2856	0	1.51
0.1010	0.1428	0	1.61
0.05042	0.1434	0.05728	2.51
0.05056	0.1426	0.01515	1.81

For purposes of comparison a limited number of measurements were made of the rates of reaction of benzyl bromide with both N-ethylaniline and triethylamine in chloroform at 24.6 ± 0.1°. In the reaction with N-ethylaniline three measurements were made, all with the bromide at 0.083 M and with the amine at 0.24 M, with the amine at 0.39 M, and with the amine at 0.39 and 0.026 M benzyltriethylammonium nitrate added. Bimolecular plots showed strong upward curvature. The rate constant at $\mu = 0$ was determined

as before, using the data from all three experiments, and it had the value of 0.31 l. mol^{-1} hr^{-1}. The initial rate in the run with added salt was 0.7 l. mol^{-1} hr^{-1}. The salt effect is appreciable in magnitude but smaller than that observed with phenacyl bromide.

The reaction with triethylamine showed very similar characteristics, and the data were treated as above. Two measurements were made, one with the bromide at 0.051 M and the amine at 0.107 M and the other with the bromide at 0.085 M and the amine at 0.144 M. These gave a value of 4.2 l. mol^{-1} hr^{-1} for the rate constant at $\mu = 0$. It is to be noted that benzyl bromide reacts more rapidly with both amines than does phenacyl bromide. With N-ethylaniline the rate constant is more than ten times as large and with triethylamine almost three times greater.

Experimental Section

Materials. Chloroform, carbon tetrachloride, and methanol were reagent grade chemicals used without further purification. The chloroform contained 0.75% ethanol as stabilizer.

Eastman Kodak White Label triethylamine was refluxed several hours over calcium hydride, distilled, and then redistilled from sodium hydroxide through a Vigreux column. A middle cut, bp 88–89°, was used.

Eastman Kodak White Label N-ethylaniline was distilled from zinc dust at water pump pressure. A middle fraction from this distillation was redistilled from zinc dust under nitrogen and stored under nitrogen. Its boiling point was 84° (12 mm).

Phenacyl bromide, obtained from Columbia Organic Chemicals Co., Inc., was crystallized four times from hexane, mp 48–49°.

N-Ethylaniline hydrobromide was prepared by adding aqueous hydrobromic acid to N-ethylaniline. Concentration at the water pump and crystallization of the residue from ethanol–ether gave white crystals, mp 167–169°.

Benzyltriethylammonium nitrate[11] was prepared either by treating benzyltriethylammonium chloride with silver nitrate or by converting benzyltriethylammonium bromide to the hydroxide with silver oxide and then neutralizing with nitric acid, mp 106–108° from ethanol–ether.

Tetraethylammonium nitrate was prepared by treating a solution of the bromide, acidified with dilute nitric acid, with silver nitrate solution. The water was removed *in vacuo*, and the salt was crystallized twice from isopropyl alcohol–ether.

Rate Measurements. Separate, determinate solutions of the amine and the bromide in solvent, containing the appropriate salt when added, were made up at the temperature of the measurements. The solutions were mixed at zero time, and aliquots were withdrawn at appropriate time intervals and partitioned between benzene and water. The aqueous layer was analyzed for bromide ion by the Volhard method.

Tests for Reaction Reversibility. A chloroform solution containing N-ethylaniline hydrobromide (0.04978 M), N-phenacyl-N-ethylaniline (0.05270 M), and benzyltriethylammonium nitrate (0.04013 M) was maintained at 24.6° for 48 hr. Periodic analysis showed no decrease in ionic bromide.

A chloroform solution of N-ethylaniline hydrobromide (0.03909 M) and benzyltriethylammonium nitrate (0.06475 M) was kept at 24.6° for 79 hr. Periodic analysis showed no decrease in ionic bromide.

Product Isolation. Phenacyl Bromide–N-Ethylaniline. To a solution of phenacyl bromide (10 g, 0.05 mol) in chloroform (200 ml) was added N-ethylaniline (25 ml). After 45 hr at 24.6° the solution was extracted three times with water. The chloroform solution was dried over magnesium sulfate and concentrated at the water pump. Crystallization from ethanol gave two crops of yellow crystals: 10.7 g (89.4%), mp 92–94°; mp 95–96° after recrystallization from ethanol. There was no depression on mix melting with authentic N-phenacyl-N-ethylaniline,[12] and the two samples gave identical infrared spectra. The same product (85.3% yield) was obtained with methanol as the solvent.

(11) S. D. Ross and M. Finkelstein, *J. Amer. Chem. Soc.*, **79**, 6547 (1957).
(12) A. F. Crowther, F. G. Mann, and D. Purdie, *J. Chem. Soc.*, 58 (1943).

Phenacyl Bromide–Triethylamine. A solution of phenacyl bromide (2.49 g, 0.0125 mol) and triethylamine (5 ml, 0.036 mol) in chloroform (100 ml) was kept at 24.6° for 94 hr. The solution was concentrated *in vacuo*, and ether was added to precipitate the product. Crystallization from ethanol-ether gave two crops: 3.44 g (92%); mp 65–68°.

Anal. Calcd for $C_{14}H_{22}BrNO$; Br, 26.62. Found: Br, 26.72. Phenacyltriethylammonium bromide prepared in ether solution has been reported to have a melting point of 150–151°.[13] Repetition of this procedure in this laboratory gave a 78% yield of product which melted at 64–68° after crystallization from acetone and showed no melting point depression on mix melting with the product obtained in chloroform.

Benzyl Bromide–N-Ethylaniline. A solution of benzyl bromide (1.43 g, 0.0084 mol) and N-ethylaniline (2.87 g, 0.024 mol) in chloroform (100 ml) was kept at 24.6° for 48 hr. The solution was taken up in benzene (400 ml) and extracted with water. The benzene and chloroform were removed, and the residue was distilled at 10 mm with a bath temperature of 80° to remove excess N-ethylaniline. An ethanol solution of picric acid (2.3 g, 0.01 mol) was added to precipitate the product as the picrate. The yield was 2.9 g (78.8%); mp 118–120° after crystallization first from chloroform–hexane and then from ethanol. Admixture with picric acid strongly depressed the melting point.

Discussion

The significant and perhaps unanticipated observations in the present study all relate to the reaction of phenacyl bromide with N-ethylaniline in chloroform. The salient facts are that the rate data for this reaction cannot be fitted properly with the usual bimolecular equation and that eq 2, which contains both a second-order term and a third-order term, is required. This implies that there are two product-forming transition states, one involving one bromide molecule and one amine molecule and the other one bromide molecule and two amine molecules.

Equally striking is the observation that the rate of the reaction can be increased tenfold by adding a neutral salt at a concentration equivalent to that of the starting bromide. In addition, with the salt added, eq 2 is no longer needed to fit the rate data, which now adequately obey the bimolecular rate equation. Thus with a neutral salt added, only a single product-forming transition state, involving one bromide molecule and one amine molecule, need be considered.

Salt effects of this magnitude are common in reactions involving ions and can be attributed to decreases in the activity coefficients of ions with increasing ionic strength of the solution. The starting materials for the present reaction are, however, neutral molecules. Nevertheless, a salt effect is possible, and its observation may also provide some information about the transition state. The rate of the reaction with a neutral salt present may be expressed by eq 4 where A and B are the

$$V = k_2AB\frac{f_Af_B}{fx} \qquad (4)$$

amine and the bromide, f_A and f_B the corresponding activity coefficients and fx the activity coefficient of the transition state. Since A and B are neutral molecules, f_A and f_B are insensitive to changes in ionic strength. The products of this reaction eventually include a salt, N-ethylaniline hydrobromide. The transition state can, therefore, have little charge separation, extensive charge separation or the actual characteristics of an ion

(13) F. Krohnke and K. Fasold, *Ber.*, **67B**, 656 (1934).

or ions, depending on how far along the path from reactants to products it occurs. In the present case the transition state must be close to products, since fx must be decreasing as the ionic strength of the solution increases.

These observations require a transition state in which the C–Br and N–H bonds are largely broken and the C–N bond is extensively formed. These requirements can be met, perhaps equally well, by the mechanisms proposed by Pearson,[4] Dewar,[5] or Winstein.[6] In the reaction with potassium iodide in acetone phenacyl chloride reacts more than 12,000 times faster than 2-phenylethyl chloride and more than 60 times faster than benzyl chloride.[14] In the reaction with N-ethylaniline in chloroform it is benzyl bromide that reacts more rapidly than phenacyl bromide by a factor of more than tenfold. For this reaction the incentive for involving an orbital-overlap mechanism may be less compelling.

The transition state involving two amine molecules affords an even wider range of structural possibilities. In the presence of a neutral salt this transition state does not contribute to product formation, and it may be concluded that its activity coefficient is relatively insensitive to the ionic strength of the medium. This would be the case, if for this reaction path, the transition state lies close to reactants. It would be consistent with the present observations if this route to product had a lower enthalpy of activation but a much less favorable entropy of activation.

It is unlikely that this reaction involves a discrete intermediate and that the second amine molecule catalyzed the decomposition of this intermediate to products. A preequilibrium involving either two amine molecules or an amine molecule and a bromide molecule is possible. The former equilibrium would be a form of base catalysis and could be represented as

I
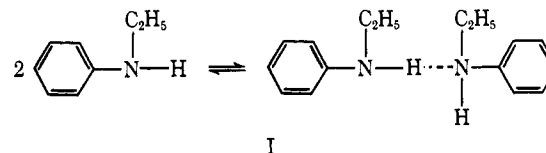
with I being a more effective nucleophile than the amine itself. The latter possibility

II
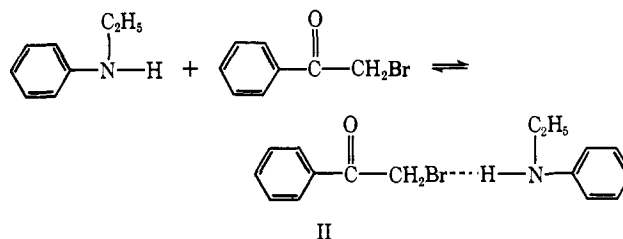
would correspond to electrophilic catalysis, with the bromine in II being more readily displaced than the bromine in phenacyl bromide itself. The fact that no third-order reaction manifests itself in the reaction with triethylamine, which lacks the hydrogen required for either of the above equilibria, is consistent with either possibility.

(14) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 232 (1924).