

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

Nucleophilic Displacement Reactions in Aromatic Systems. VI. Solvent Effects in the Reaction of 2,4-Dinitrochlorobenzene with Allylamine

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The rates of reaction of 2,4-dinitrochlorobenzene and allylamine have been measured in chloroform-ethanol mixtures, in absolute ethanol and in 2-phenylethanol. The results in the chloroform-ethanol mixtures show that any third-order term involving ethanol is negligible in magnitude in chloroform. The results in absolute ethanol can be fitted with two terms, $k_1(A)(B)$ and $k_3(A)(B)^2$. In 2-phenylethanol the results are completely comparable to those previously observed in chloroform.¹ It is also shown that, in this solvent, the reaction is accelerated by compounds containing the carbonyl group, the sulfoxide group and the sulfone group, as well as by compounds having the amino and the nitro function.

In the previous paper in this series,¹ it was shown that the reaction of 2,4-dinitrochlorobenzene with both *n*-butylamine and allylamine in chloroform, containing 0.75% ethanol as stabilizer, requires the complex rate expression

$$dD/dt = k_1(A)(B) + k_3(A)(B)^2 + k_4(A)^2(B) + k_5(A)(B)(D) + k_6(A)(B)(C) \quad (1)$$

where A is the chloride, B the amine, C added *m*-dinitrobenzene and D the product, N-allyl-2,4-dinitroaniline. It was further suggested that the last three terms in eq. 1 all represented catalyses of the product-forming reaction by nitro groups, acting as acceptors in hydrogen bond formation. The implication that other groups capable of functioning similarly in hydrogen bond formation will also catalyze the reaction is, of course, obvious.

The first objective of the present work was to consider the possibility that the first term in eq. 1, $k_1(A)(B)$, is also a third-order term and that the transition state corresponding to this term involves a molecule of ethanol acting as a hydrogen bond acceptor. This is a possibility, since all of our chloroform solutions contained a small (0.156 *M*) and constant concentration of ethanol.

An additional objective was to investigate the generality of eq. 1 and determine whether or not the large number of product-forming steps occur only when chloroform is the solvent. In this connection we have measured the rate of the reaction of 2,4-dinitrochlorobenzene with allylamine in ethanol and in 2-phenylethanol.

A final objective was to determine if compounds having functional groups, other than the nitro group, capable of participating in intermolecular hydrogen bonding would effectively catalyze the reaction between allylamine and 2,4-dinitrochlorobenzene.

Results

The rates of reaction of 2,4-dinitrochlorobenzene and allylamine in chloroform containing varying amounts of ethanol at $24.8 \pm 0.1^\circ$ are given in Table I. As in the previous paper,¹ the slopes and intercepts given in the tables are from plots of $\log A_0(B_0 - 2D)/B_0(A_0 - D)$ vs. *t*, in seconds, and the tabulated bimolecular rate constants, k_2 , are obtained from these plots. Since all of the experimental data fall almost exactly on such linear plots, this abbreviated presentation permits a reconstruction of the data. The ethanol concentrations given in Table I were determined both by vapor phase

chromatography and infrared spectroscopy. The last two measurements given in Table I are in absolute ethanol (17.04 *M*).

TABLE I

THE RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ALLYLAMINE IN CHLOROFORM-ETHANOL MIXTURES AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Ethanol, moles l. ⁻¹	Intercept	Slope $\times 10^3$	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.04982	0.2627	0.156	0.0090	0.503	0.710
.04941	.2585	0.830	.0150	.513	.740
.05000	.2594	1.84	.0110	.607	.877
.05038	.2600	6.18	.0120	1.04	1.50
.04977	.2592	10.76	.0050	1.93	2.79
.04904	.2572	14.16	.0150	2.53	3.67
.04959	.2611	17.04	.0100	3.48	4.95
.05110	.2642	17.04	.0120	3.48	4.95

The rates of reaction of 2,4-dinitrochlorobenzene with allylamine in absolute ethanol at $24.8 \pm 0.1^\circ$ are shown in Table II. These results include a set of measurements with the chloride constant and the amine concentrations varied, a series of experiments with the amine constant and the chloride varied and, finally, two experiments with added *m*-dinitrobenzene. In all cases the reactions were followed to more than 60% of completion.

TABLE II

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ALLYLAMINE IN ABSOLUTE ETHANOL AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Intercept	Slope $\times 10^3$	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.04931	0.1310	0.0050	0.683	4.86
.04959	.2611	.0100	3.48	4.95
.05110	.2642	.0120	3.48	4.95
.04955	.3976	.0150	6.89	5.31
.04884	.5245	.0200	10.17	5.49
.05089	.6589	.0130	13.47	5.57
.04860	.7856	.0200	17.67	5.91
.05014	1.0582	.0180	27.45	6.60
.02368	0.2586	.0400	4.77	5.20
.07424	.2577	.0080	2.30	4.85
.09860	.2590	.0035	1.29	4.81
.1242	.2592	.0004	0.240	5.09
.1485	.2586	— .0001	— 0.850	5.10
.1974	.2576	— .0007	— 2.92	4.90
.04974	.2585	.0150	3.42	4.95 ^a
04980	.2557	.0160	3.39	5.00 ^b

(1) S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Am. Chem. Soc.*, **81**, 5936 (1959).

^a *m*-Dinitrobenzene (0.04533 *M*) added. ^b *m*-Dinitrobenzene (0.1679 *M*) added.

The results of measurements with the same chloride and amine in 2-phenylethanol at $24.8 \pm 0.1^\circ$ are given in Table III. Values of the intercepts and slopes have not been included in this case, since all of the second-order plots pass through the origin.

TABLE III

RATES OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ALLYLAMINE IN 2-PHENYLETHANOL AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹	Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	$k_2 \times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.05082	0.1290	1.53	0.04947	0.1310	1.64
.05028	.2621	1.65	.1486	.1285	1.64
.05015	.3932	1.86	.2477	.1291	1.66
.05127	.6589	2.16	.3948	.1283	1.80

Table IV shows the effects which various added substances have on the rate of this reaction in 2-phenylethanol. The rate constant, k_6 , is an estimate for the rate of the product-forming step involving the added substance, C, and is obtained from the relationship

$$k_2^* - k_2 = k_6(C) \quad (2)$$

where k_2^* is the rate constant obtained with C added and k_2 is the rate constant for the same A_0 and B_0 but with C absent. The value used for k_2 was the average of the two values shown in Table IV.

TABLE IV

THE EFFECTS DUE TO ADDED SUBSTANCES ON THE RATE OF REACTION OF 2,4-DINITROCHLOROBENZENE AND ALLYLAMINE IN 2-PHENYLETHANOL AT $24.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	Added subst. C, mole l. ⁻¹	k_2 or k_2^* , $\times 10^4$, l. mole ⁻¹ sec. ⁻¹	k_6 , $\times 10^4$, l. mole ⁻¹ sec. ⁻¹
0.05082	0.1290	None	1.53	
.04947	.1310	None	1.64	
.05018	.1310	<i>m</i> -Dinitrobenzene, 0.2933	1.79	0.68
.05093	.1273	Benzotrifluoride, 0.4041	1.66	..
.04952	.1287	N-Allyl-2,4-dinitroaniline, 0.2687	1.97	1.4
.04985	.1308	Benzil, 0.2851	1.81	0.77
.05048	.1324	Dimethyl sulfoxide, 0.6977	3.21	2.3
.04949	.1310	Dimethyl sulfone, 0.2716	2.00	1.5

Experimental

Materials.—Baker and Adamson Reagent Grade chloroform was used without purification. This solvent contains 0.75% ethanol as a stabilizer. Absolute ethanol, obtained from the U. S. Industrial Chemicals Co., was distilled from calcium hydride before use. The chloroform-ethanol mixtures were prepared by adding absolute ethanol to the above chloroform. The exact ethanol concentrations were determined by analyzing the solutions both by vapor phase chromatography and infrared spectroscopy. Eastman Kodak Co. white label 2-phenylethanol was distilled at 8 mm. A middle fraction, b.p. 101° , was used.

The following Eastman Kodak Co., white label materials were recrystallized before use: 2,4-dinitrochlorobenzene, m.p. 51° after three crystallizations from methanol; benzil, m.p. $95-95.5^\circ$ after two crystallizations from ethanol; *m*-dinitrobenzene, m.p. $89-89.5^\circ$ after two crystallizations from ethanol.

Allylamine, from the Shell Chemical Corp., was twice distilled from calcium hydride; b.p. 53° . Benzotrifluoride was distilled at 750 mm., and a middle fraction, b.p. 99.5° , was used. Dimethyl sulfoxide, from the Stepan Chemical Co., was distilled at 6 mm.; b.p. 68° . The preparation of N-allyl-2,4-dinitroaniline has been described.¹ The melting point after three crystallizations from ethanol was $75.5-76^\circ$.

Dimethyl sulfone was prepared by oxidation of the sulfide with peracetic acid in acetic acid; m.p. $111-111.5^\circ$ from chloroform-petroleum ether.

Rate Measurements.—The procedure for the rate measurements has been described.² All aliquots were quenched by partitioning them between benzene (50 ml.) and 4 *N* nitric acid (25 ml.) and extracting the benzene solution two additional times with water.

Product Isolation Experiments. N-Allyl-2,4-dinitroaniline.—A solution of 2,4-dinitrochlorobenzene (10.13 g., 0.05 mole) in 2-phenylethanol (180 ml.) and allylamine (20 ml.) was left standing at room temperature for 24 hours. Benzene (500 ml.) was added. The benzene solution was extracted three times with water and dried over magnesium sulfate. The benzene was removed with a water-pump, and the 2-phenylethanol was distilled at 1 mm. The crude product was crystallized from ethanol; yield 10.1 g. (90.6%), m.p. $71-75^\circ$. Recrystallization from ethanol gave 8.7g. (78%), m.p. $75-77^\circ$.

In another experiment, identical with that above except that the solvent was a mixture of 2-phenylethanol (160 ml.) and dimethyl sulfoxide (20 ml.), the yield was 90.6%, m.p. $72-76^\circ$. Recrystallization gave a 78% yield, m.p. $76-77^\circ$.

Discussion

The measurements of Table I were made to determine if the $k_1(A)(B)$ term in eq. 1 involves an ethanol molecule and should be written $k_1(A)(B)(ROH)$ or, alternatively, if eq. 1 should contain an additional term, $k_7(A)(B)(ROH)$. For either possibility, it would be anticipated that the addition of more alcohol to chloroform, containing 0.75% or 0.156 *M* ethanol as stabilizer, would strongly increase the magnitude of the measured bimolecular rate constant. The data of Table I give a smooth curve when the second-order rate constants are plotted against the ethanol concentrations. For low alcohol concentrations (below 2 *M*), the measured rates are relatively insensitive to the added ethanol, and the rates do not increase rapidly until the solution is more than 6 *M* in ethanol or more than 20% by volume ethanol. At this high concentration the solvent can no longer be treated as chloroform, and all of the rate constants in eq. 1 would have new values.

Confining our attention to low ethanol concentrations, a plot of k_2 vs. ethanol concentration at constant A_0 and B_0 indicates that the rate constant for any third-order term involving ethanol is not greater than 1×10^{-6} l.²mole⁻²sec.⁻¹. This is less than one-tenth of the values previously reported¹ for k_3 , k_4 , k_5 or k_6 (eq. 1) for the allylamine-2,4-dinitrochlorobenzene reaction in chloroform. It may, therefore, be concluded that ethanol is not involved in the reactions measured in chloroform containing 0.75% ethanol.

Previous measurements of the rates of reaction of primary amines with 2,4-dinitrochlorobenzene in absolute ethanol² have demonstrated the existence of at least two product-forming steps. These results were shown to fit the rate equation

$$dD/dt = k_1(A)(B) + k_3(A)(B)^2 \quad (3)$$

which can be integrated to give

$$\frac{1}{B_0 - 2A_0} \ln \frac{A_0 B}{A B_0} - \frac{k_3}{k_1} \left[\ln \frac{B_0}{B} - \ln \frac{B_0 + \frac{k_1}{k_2}}{B + \frac{k_1}{k_2}} \right] = k_1 t + k_3 t (B_0 - 2A_0) \quad (4)$$

(2) S. D. Ross and M. Finkelstein, *J. Am. Chem. Soc.*, **79**, 6547 (1957).

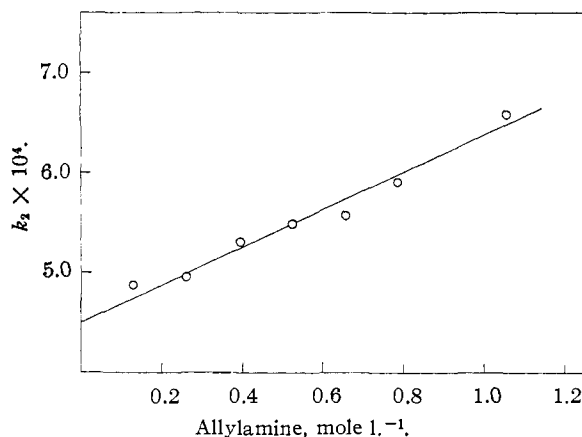


Fig. 1.—Plot of k_2 vs. B_0 for the reaction of 2,4-dinitrochlorobenzene and allylamine in absolute ethanol at $24.8 \pm 0.1^\circ$.

The results in Table II represent a more complete study of the rate of reaction of the chloride with a primary amine, allylamine, in absolute ethanol. These experiments were designed to test the adequacy of eq. 3 over a broader range of concentration changes. They were performed with the possibility in mind that the more complete rate expression, eq. 1, would prove necessary even in alcohol.

Inspection of Table II shows that, with A_0 constant and B_0 variable, k_2 increases as B_0 increases. However, with B_0 constant and A_0 increasing, there is no clear trend in the measured rate constants. Also, the addition of *m*-dinitrobenzene at constant A_0 and B_0 is without effect on k_2 .

These last two observations are to some extent limited by the sparing solubility of both 2,4-dinitrochlorobenzene and *m*-dinitrobenzene in ethanol. This prevents experiments with large changes in the initial concentrations of these two reagents. Nevertheless, the results in Table II must be taken as qualitatively supporting the adequacy of eq. 3.

For the measurements with A_0 constant at approximately 0.05 M and the initial amine concentrations varied from 0.13 to 1.0 M, a plot of k_2 vs. B_0 is linear as shown in Fig. 1. Using the method of least squares to define the best straight line through the experimental points leads to values of 4.49×10^{-4} l.mole⁻¹sec.⁻¹ for the intercept, k_1 , and $1.88 \frac{1}{2} \times 10^{-4}$ l.²mole⁻²sec.⁻¹ for the slope k_3 . More reliable values for k_1 and k_3 may be obtained by using eq. 4. The method for calculating these two rate constants has been described.³ The values that resulted were 4.25×10^{-4} l. mole⁻¹sec.⁻¹ for k_1 and 1.51×10^{-4} l.² mole⁻² sec.⁻¹ for k_3 .⁴

(3) S. D. Ross and R. C. Petersen, *J. Am. Chem. Soc.*, **80**, 2447 (1958); S. D. Ross, *ibid.*, **80**, 5319 (1958).

(4) In order to apply eq. 4 it was necessary to correct the experimental D vs. t plots so that they passed through the origin. This was done by plotting the experimental points, extrapolating to determine D at $t = 0$ and adjusting all of the experimental points by an amount equal to D at $t = 0$. It is an interesting possibility that this D at $t = 0$ results from the rapid formation of a steady state concentration of an intermediate involving A and B and having a quinoid type of structure. Such an intermediate might be titrated along with halide ion by our analytical method. Unfortunately, the times involved are too short

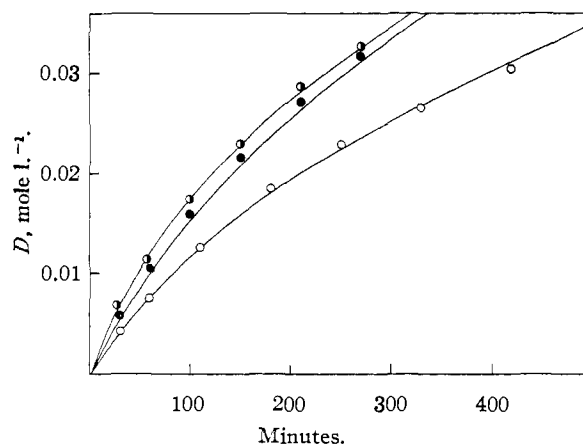


Fig. 2.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in 2-phenylethanol at $24.8 \pm 0.1^\circ$: ●, $A_0 = 0.05015$ M, $B_0 = 0.3932$ M; ●, $A_0 = 0.1486$ M, $B_0 = 0.1285$ M; ○, $A_0 = 0.05028$ M, $B_0 = 0.2621$ M.

As a further test of the adequacy of eq. 3, we have used the values of k_1 and k_3 above together with eq. 4 to calculate D vs. t curves for comparison with experimental D vs. t curves. Excellent agreement was obtained between the calculated curves and the experimental curves, corrected for D at $t = 0$, both for the experiments with A_0 constant and B_0 varied and the experiments with A_0 varied and B_0 constant. All of the experimental results can, therefore, be accommodated by eq. 3.

It is nevertheless possible that the additional terms in eq. 1 are also operating in these alcohol experiments but that their presence cannot be demonstrated experimentally because they make so small a contribution to the total reaction. This possibility is suggested by the relative magnitudes of k_1 and k_3 in chloroform and in ethanol. In chloroform the ratio, k_1/k_3 , is equal to 0.217 mole l.⁻¹. In alcohol this ratio is more than ten times larger and equal to 2.81 mole l.⁻¹. The only hope of demonstrating the presence of the k_4 term in ethanol would be in an experiment with A_0 very much larger than B_0 , but the limited solubility of 2,4-dinitrochlorobenzene does not permit such an experiment.

The results in 2-phenylethanol offer some support for the above possibility. This alcohol was chosen because it is a good solvent for 2,4-dinitrochlorobenzene and because it was hoped that its lower dielectric constant (13 at 20°)⁵ would result in a lower ratio k_1/k_3 . It is clear from Table III that k_2 increases with both increasing B_0 at constant A_0 and with increasing A_0 at constant B_0 . Equation 1 is, therefore, a more probable rate expression than eq. 3.

Since *m*-dinitrobenzene was not added in any of the experiments listed in Table III, k_6 would equal zero, and the integrated form of eq. 1 is

$$t = \frac{1}{\beta + \gamma A_0} \left[\frac{1}{(B_0 - 2A_0)} \ln \frac{A_0(B_0 - 2D)}{B_0(A_0 - D)} + \frac{\gamma}{2\beta + \gamma B_0} \ln \frac{B_0(\beta + \gamma D)}{(B_0 - 2D)\beta} \right] \quad (5)$$

and the concentrations of D at $t = 0$ are too low to permit an experimental check of this possibility.

(5) W. Hückel and U. Wenzke, *Z. physik. Chem.*, **A193**, 132 (1944).

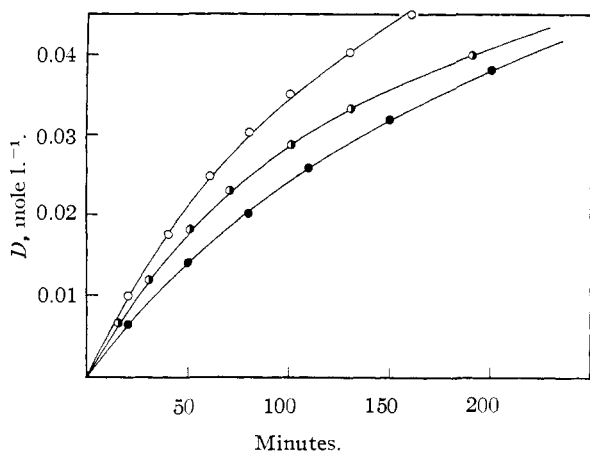


Fig. 3.— D vs. t curves for the reaction of 2,4-dinitrochlorobenzene and allylamine in 2-phenylethanol at $24.8 \pm 0.1^\circ$: \circ , $A_0 = 0.3948 M$, $B_0 = 0.1283 M$; \circ , $A_0 = 0.05127 M$, $B_0 = 0.6589 M$; \bullet , $A_0 = 0.2477 M$, $B_0 = 0.129 M$.

where $\beta = k_1 + k_3 B_0 + k_4 A_0$, and

$$\gamma = k_5 - 2k_3 - k_4$$

The ability of eq. 5 to fit the experimental data was tested by the methods described previously.¹ Preliminary values for k_1 , k_3 and k_4 were obtained from plots of k_2 vs. B_0 at constant A_0 and k_2 vs. A_0 at constant B_0 . An initial value for k_5 was obtained from the experiment in Table IV in which N-allyl-2,4-dinitroaniline, D, was added. These values were: $k_1 = 1.37 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$, $k_3 = 1.11 \times 10^{-4} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$, $k_4 = 0.74 \times 10^{-4} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$, $k_5 = 1.4 \times 10^{-4} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$.

The above rate constants and eq. 5 were used to calculate D vs. t curves for comparison with the experimental curves. The values of the rate constants were then varied by a trial and error process to obtain optimum coincidence of calculated and experimental D vs. t curves. The rate constants that finally resulted were: $k_1 = 1.35 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$, $k_3 = 1.2 \times 10^{-4} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$, $k_4 = 0.7 \times 10^{-4} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$, $k_5 = 1.3 \times 10^{-4} \text{ l.}^2 \text{ mole}^{-2} \text{ sec.}^{-1}$.

These rate constants give excellent agreement between calculated and experimental D vs. t

curves for all eight experiments in Table III. Six of these comparisons are shown in Figs. 2 and 3. The smooth lines are the calculated curves, and the circles represent experimental points. These experiments cover an almost eightfold variation in B_0 and more than a fivefold variation in A_0 . There is no combination of two rate constants, k_1 and k_3 , that will give satisfactory fits over this range of initial concentrations. It is possible that simultaneous variation of two or more of the rate constants can be made to yield a new set of values which will give satisfactory fits, but our experience in fitting these curves suggests limits of less than 10% for any of the four rate constants.

A reaction mechanism consistent with this complex kinetic pattern has been presented previously¹ and need not be repeated here. The fact that the present data obtained in 2-phenylethanol are explained by the considerations applied previously to the chloroform case lends further support and generality to the mechanism. It seems reasonable that this mechanism should be considered in all solvents, although it is clear that in some solvents, e.g., ethanol, some of the rate constants may be negligible in magnitude or totally absent.

A still further element of generality is added to this mechanism by the results in Table IV, which make it clear that this reaction can be promoted by compounds other than those containing the amino or nitro function. The carbonyl groups in benzil and the sulfoxide and sulfone linkages are all groups which are capable of participating as hydrogen bond acceptors and are all effective in accelerating the rate of reaction of 2,4-dinitrochlorobenzene with allylamine in 2-phenylethanol. In the quantities involved in the experiments of Table IV, it seems improbable that these compounds are functioning by altering the characteristics of the reaction medium. A more probable explanation is that previously offered for the accelerating effect of the nitro group.¹ Benzotrifluoride might also have been expected to catalyze the reaction. The reason for its failure to do so is not clear, but possible complicating factors lie in the difference between $\text{N}-\text{H} \cdots \text{F}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds and in steric considerations relating to the trifluoromethyl group.

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C versus O Alkylation in the Case of a Stable Cation

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The sodium salt of 2-nitropropane converted 3-bromocyclohexene to cyclohexenone whereas a C-alkylated product was obtained with tropylium bromide. It is suggested that the C-alkylation of the stable cycloheptatrienylium ion involves a reversible dissociation to give the equilibrium product.

The researches of Kornblum and co-workers¹ have led to the useful generalization postulated by

(1) (a) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955); (b) N. Kornblum and A. P. Lurie, *ibid.*, **81**, 2705 (1959).

him that in graded SN_1 - SN_2 displacement reactions involving ambident anions, for a particular anion, the greater the SN_1 character of the transition state, the more predominant is bond formation by the most electronegative atom of the ambient