

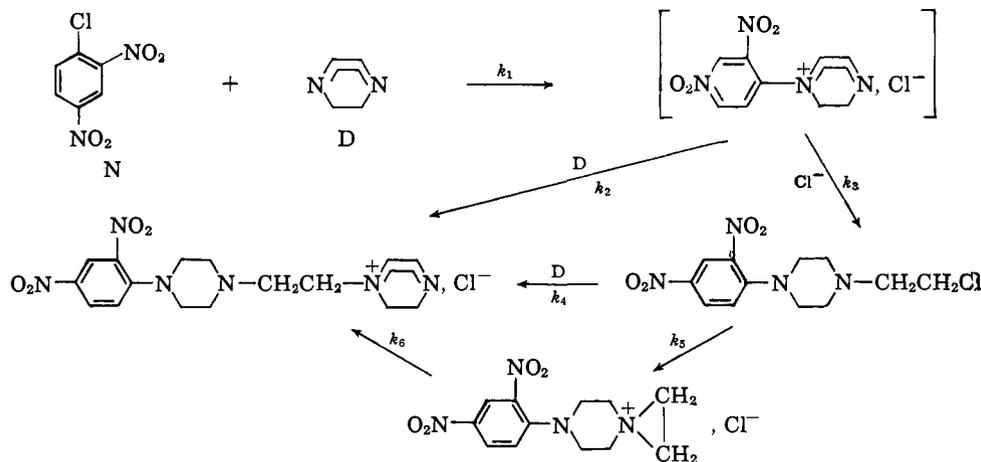
[CONTRIBUTION FROM THE RESEARCH CENTER, SPRAGUE ELECTRIC CO., N. ADAMS, MASS.]

Nucleophilic Displacement Reactions in Aromatic Systems. VIII. Rates and Mechanism for the Reaction of 2,4-Dinitrochlorobenzene with 1,4-Diazabicyclo[2.2.2]octane in Acetonitrile

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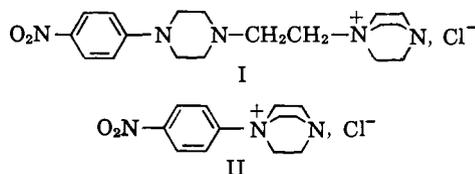
RECEIVED AUGUST 9, 1963

In acetonitrile at $50.8 \pm 0.1^\circ$ 2,4-dinitrochlorobenzene reacts with 1,4-diazabicyclo[2.2.2]octane according to the scheme



In the present work k_1 , k_4 , and k_6 have been determined and a rough estimate of the ratio k_2/k_3 has been made.

In a previous report from this Laboratory it was shown that *p*-nitrochlorobenzene reacts with 1,4-diazabicyclo[2.2.2]octane to give I.¹ Since the reaction is second order, first order in the chloride and first order

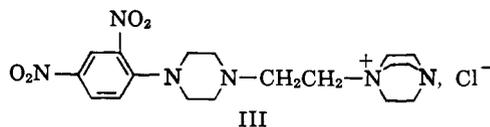


in the amine, it was suggested that II, formed in a rate-determining step, is an intermediate in this reaction and that the final product I results from a rapid nucleophilic displacement on II by another 1,4-diazabicyclo[2.2.2]octane molecule.

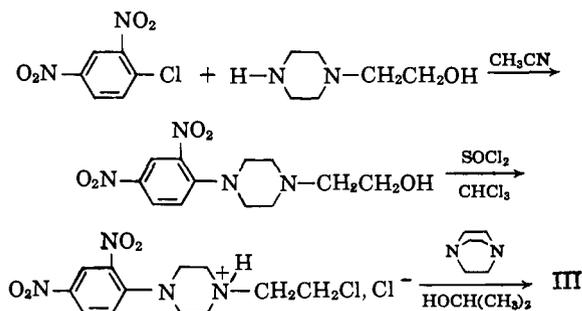
In the present study rates and products have been determined for the reaction of 2,4-dinitrochlorobenzene with 1,4-diazabicyclo[2.2.2]octane in acetonitrile at $50.8 \pm 0.1^\circ$. These results afford additional evidence for the involvement of an intermediate, comparable in structure to II, in these reactions.

Results

2,4-Dinitrochlorobenzene reacts with excess 1,4-diazabicyclo[2.2.2]octane in acetonitrile to form the salt



III, whose structure was established by synthesis using the sequence of reactions shown in the next column. Measurements of the rate in acetonitrile at 50.8° , with the amine present in excess, give good second-order plots, linear to beyond 90% reaction. As long as the amine is present in excess, it is possible to vary both the initial amine concentration and the initial halide concentration appreciably and still obtain the same



rate constant, within experimental error. These results are shown in Table I. These measurements were made by taking aliquots, quenching them by adding acid, and determining the concentration of halide ion by the Volhard method. For the results in Table I, the average rate constant is 10.3×10^{-5} l. mole⁻¹ sec.⁻¹. The maximum deviation from this average value is 7.8%, and the average deviation is 3.6%.

TABLE I
RATES, MEASURED WITH THE AMINE IN EXCESS, FOR THE REACTION OF 2,4-DINITROCHLOROBENZENE WITH 1,4-DIAZABICYCLO[2.2.2]OCTANE IN ACETONITRILE AT $50.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	$k \times 10^5$, ^a l. mole ⁻¹ sec. ⁻¹
0.0371	0.2246	9.5
.0363	.2288	10.2
.0371	.2365	10.2
.0364	.3445	9.9
.0366	.4706	9.8
.0351	.5312	10.3
.0366	.5818	10.3
.0365	.6796	10.9
.0438	.5117	10.9
.0630	.4917	10.9

^a Calculated from the rate expression: $d(\text{Cl}^-)/dt = k(N_0 - (\text{Cl}^-))(D_0 - 2(\text{Cl}^-))$, where N is 2,4-dinitrochlorobenzene and D is the amine concentration and the subscripts zero indicate initial conditions.

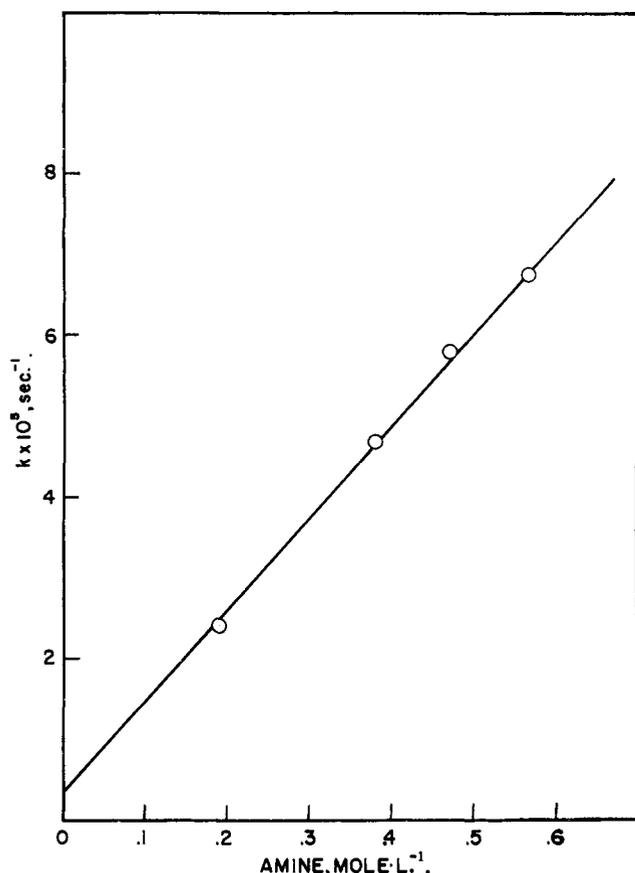
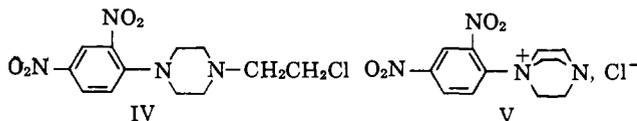


Fig. 1.—Pseudo-first-order rate constants, $k \times 10^5 \text{ sec}^{-1}$, vs. initial amine concentrations for the reaction of $1.98 \times 10^{-4} M$ 2,4-dinitrochlorobenzene with 1,4-diazabicyclo[2.2.2]octane in acetonitrile at $50.8 \pm 0.1^\circ$.

The results in Table I, although apparently satisfactory, suffer from a significant source of error. At infinite time (after ten or more half-lives) the only product present in the system is the salt III. During the course of the reaction, however, there are two products present, III and N-2,4-dinitrophenyl-N'- β -chloroethylpiperazine (IV). Both almost certainly arise from nucleophilic displacements by 1,4-diazabicyclo[2.2.2]octane and by chloride ion on the proposed intermediate for this reaction, V. When the reaction is quenched by



adding acid and the product is determined by analyzing for chloride ion by the Volhard method, only the concentration of the salt III is measured. However, if the reaction is quenched by partitioning aliquots between benzene and water and then extracting the benzene layer with dilute nitric acid, the water extract will contain III, and the acid extract will contain IV, which will liberate its halogen under basic conditions. It is thus possible to determine the concentrations of both III and IV as a function of time. As might be expected, when the initial amine concentration is high the amount of IV present at any time is small. In the experiment in Table I with $0.0351 M$ chloride and $0.5312 M$ amine, at no time during the course of the reaction does the concentration of IV exceed 4% of the combined concentrations of III and IV. At lower initial amine concentrations, as in the experiment with $0.0371 M$ chloride and $0.2246 M$ amine, there are stages in the re-

action when the concentration of IV is as much as 20% of the total product concentration. The most reliable values for the rate constant in Table I are, therefore, those at the highest initial amine concentrations, but even these suffer from the presence of some β -chloride IV during the course of the reaction and are best considered as lower limits for the value of the rate constant.

More reliable values for the rate constant can be obtained by making measurements with the chloride at very low concentrations and the amine in large excess and treating the reaction as a pseudo-first-order reaction. For these conditions it is no longer possible to measure chloride ion as a function of time using Volhard titrations, but the rate of appearance of the product can be followed by measuring the optical density at $360 m\mu$. The pseudo-first-order rate constants that resulted from these experiments are compiled in Table II, and Fig. 1 shows a plot of these rates vs. the initial amine concentrations. The second-order rate constant, obtained from the slope of the straight line in Fig. 1, is $11.3 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec}^{-1}$.

Attempts to determine the above rate constant by quenching with acid and analyzing for chloride ion in systems in which 2,4-dinitrochlorobenzene was initially in large excess gave, as might be expected, unsatisfactory results. Second-order plots were not linear over the entire course of the reaction, and points beyond 50% reaction were well below the straight line defined by the earlier points. In experiments with $0.19 M$ chloride and 0.068 – $0.071 M$ amine, the rate constants, obtained by considering only the points below 50% reaction, ranged from 4.8×10^{-5} to $5.6 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec}^{-1}$. Equally important, even after sixty half-lives the reaction liberated only 85% of the amount of chloride ion calculated for a reaction forming only III. In contrast, in those experiments in which the amine was initially present in excess the theoretical amount of chloride ion was liberated.

In these experiments N-2,4-dinitrophenyl-N'- β -chloroethylpiperazine (IV) is being formed in much larger amount, and some will persist in solution after all the 1,4-diazabicyclo[2.2.2]octane has been consumed and may be isolated from the reaction mixture as the hydrochloride. Figure 2 shows the concentrations of IV as a function of time for four experiments, two with the amine initially in excess, one with 2,4-dinitrochlorobenzene in excess, and finally one with 2,4-dinitrochlorobenzene in excess and benzyltriethylammonium chloride added to serve as an additional source of chloride ion. It is to be noted that the addition of chloride ion greatly increases the concentrations of IV, as would be expected if the amine and chloride ion were competing for the proposed intermediate in this reaction, V. As will be shown in the subsequent discussion, some information about the reaction rates may be obtained from these experiments with the chloride initially in excess.

TABLE II

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF $1.98 \times 10^{-4} M$ 2,4-DINITROCHLOROBENZENE WITH 1,4-DIAZABICYCLO[2.2.2]OCTANE IN ACETONITRILE AT 50.8°

Amine, mole l ⁻¹	$k \times 10^5, \text{ sec}^{-1}$
0.1904	2.40
.3806	4.64
.4758	5.72
.5709	6.67

Under most conditions the reaction of 2,4-dinitrochlorobenzene with 1,4-diazabicyclo[2.2.2]octane results in the formation of both III and IV with some or

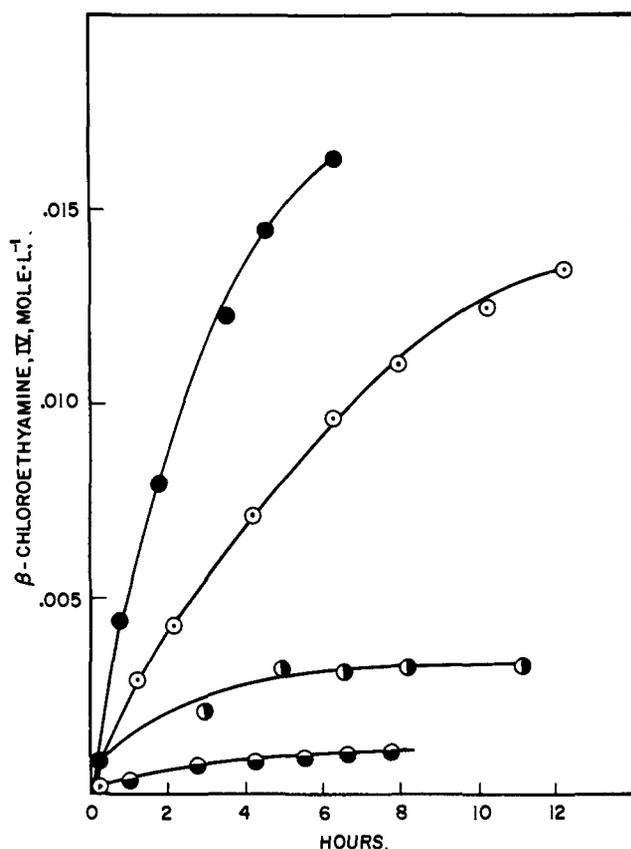
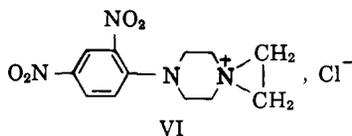


Fig. 2.—The concentration of N-2,4-dinitrophenyl-N'- β -chloroethylpiperazine (IV) vs. time for the reaction of 2,4-dinitrochlorobenzene (N) and 1,4-diazabicyclo[2.2.2]octane (D) in acetonitrile at $50.8 \pm 0.1^\circ$: \bullet , $N_0 = 0.2342 M$, $D_0 = 0.0682 M$; \circ , $0.2293 M$ benzyltriethylammonium chloride added; \ominus , $N_0 = 0.2323 M$, $D_0 = 0.0682 M$; \bullet , $N_0 = 0.0371 M$, $D_0 = 0.2246 M$; \ominus , $N_0 = 0.0351 M$, $D_0 = 0.5311 M$.

all of IV being converted to III by further reaction with more 1,4-diazabicyclo[2.2.2]octane. It was, therefore, pertinent to measure the rate at which IV reacts with 1,4-diazabicyclo[2.2.2]octane in acetonitrile at 50.8° .

The β -chloride IV is converted to III by two paths. One is a second-order, nucleophilic displacement by 1,4-diazabicyclo[2.2.2]octane on the chloride. The other involves a rate-determining, intramolecular reaction to form the cyclic immonium ion VI which is



rapidly opened by 1,4-diazabicyclo[2.2.2]octane to form III.² Individual runs give excellent first-order plots, but, as shown in Table III, the derived rate constants vary with changing initial amine concentrations.

As shown in Fig. 3, a plot of these first-order constants vs. the initial amine concentrations is linear with the intercept, $2.3 \times 10^{-5} \text{ sec.}^{-1}$, equal to the rate constant for the first-order process, and the slope, $5.9 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$, equal to the rate constant for the second-order path.

Experimental

N-2,4-Dinitrophenyl-N'-[2-(4-aza-1-azoniabicyclo[2.2.2]octane)ethyl]piperazine Chloride (III).—A solution of 2,4-dinitro-

(2) P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2971 (1947); P. D. Bartlett, J. W. Davis, S. D. Ross, and C. G. Swain, *ibid.*, **69**, 2977 (1947); S. D. Ross, *ibid.*, **69**, 2982 (1947).

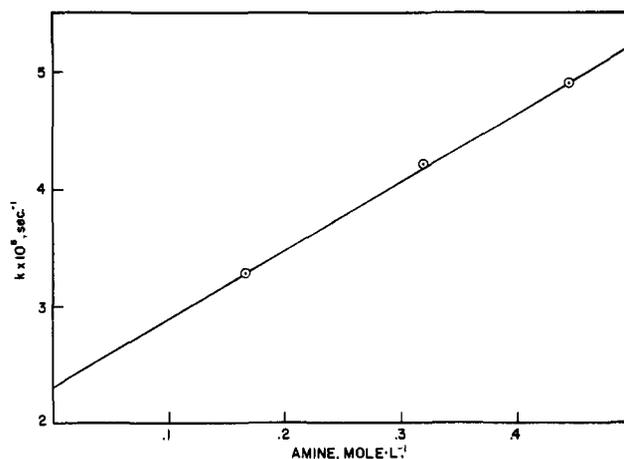


Fig. 3.—First-order rate constants, $k \times 10^5 \text{ sec.}^{-1}$, vs. initial amine concentrations for the reaction of N-2,4-dinitrophenyl-N'- β -chloroethylpiperazine with 1,4-diazabicyclo[2.2.2]octane in acetonitrile at $50.8 \pm 0.1^\circ$.

chlorobenzene (6.08 g., 0.03 mole) and 1,4-diazabicyclo[2.2.2]octane (7.85 g., 0.07 mole) in acetonitrile (100 ml.) was left standing at room temperature for 48 hr. The product, which precipitated, was filtered; yield 10 g. (78%). A sample crystallized from 2-propanol-methanol-hexane did not melt but underwent slow decomposition starting at 236° .

Anal. Calcd. for $C_{13}H_{27}N_6O_4Cl$: Cl, 8.30. Found: Cl, 8.26.

TABLE III

RATES OF REACTION OF N-2,4-DINITROPHENYL-N'- β -CHLOROETHYLPIPERAZINE WITH 1,4-DIAZABICYCLO[2.2.2]OCTANE IN ACETONITRILE AT $50.8 \pm 0.1^\circ$

Chloride, mole l. ⁻¹	Amine, mole l. ⁻¹	$k \times 10^5$, sec. ⁻¹
0.0465	0.1661	3.28
.0457	.3202	4.22
.0445	.4378	4.90

Compound III was also prepared by treating the hydrochloride of N-2,4-dinitrophenyl-N'- β -chloroethylpiperazine (IV) with 1,4-diazabicyclo[2.2.2]octane. A solution of the hydrochloride of IV (2 g., 0.0057 mole) and the amine (2.8 g., 0.025 mole) in 2-propanol (150 ml.) was refluxed 20 hr. On cooling, the product separated. It was crystallized from a mixture of 2-propanol, methanol, and hexane; yield 2.12 g. (87.3%). The infrared spectrum of this product was identical with that of the product obtained above.

Anal. Found: Cl, 8.41, 8.18.

N-2,4-Dinitrophenyl-N'- β -hydroxyethylpiperazine.—A solution of 2,4-dinitrochlorobenzene (20.3 g., 0.1 mole) and N- β -hydroxyethylpiperazine (52.1 g., 0.4 mole) in acetonitrile (275 ml.) was refluxed 6 hr. and then left standing overnight at room temperature. The solution was chilled and the solid which precipitated (12 g.) was discarded. The solvent was removed *in vacuo* from the remaining solution, and the residue was partitioned between benzene and water. The benzene layer was dried over magnesium sulfate and concentrated. Addition of hexane precipitated the product; yield 28.1 g. (95%), m.p. $100-102^\circ$.

For analysis a sample was converted to the hydrochloride, which was crystallized from a mixture of 2-propanol, methanol, and ether; m.p. $225-227^\circ$ dec.

Anal. Calcd. for $C_{12}H_{17}ClN_4O_6$: Cl, 10.65. Found: Cl, 10.68.

N-2,4-Dinitrophenyl-N'- β -chloroethylpiperazinium Hydrochloride.—Thionyl chloride (10 ml.), freshly distilled from quinoline, in chloroform (25 ml.) was added dropwise to a solution of N-2,4-dinitrophenyl-N'- β -hydroxyethylpiperazine (5 g., 0.0169 mole) in chloroform (100 ml.). The mixture was refluxed 3 hr. and then left standing for 18 hr. at room temperature. Addition of hexane precipitated the product; yield 5.9 g. (99%), m.p. 210° dec. Crystallization from methanol-ether gave 5 g. (85%) of product with unchanged melting point.

Anal. Calcd. for $C_{12}H_{16}Cl_2N_4O_6$: ionic Cl, 10.10; total Cl, 20.19. Found: ionic Cl, 10.15; total Cl, 20.14.

N-2,4-Dinitrophenyl-N'- β -chloroethylpiperazine (IV).—Anhydrous sodium carbonate (15 g., 0.14 mole) was added to a solution of the above hydrochloride (9.0 g., 0.141 mole) in ace-

tonitrile (250 ml.). The mixture was refluxed with stirring for 2 hr. After filtration to remove solid, the solvent was removed by distillation, yielding 7.3 g. of crude product, m.p. 92–95°. Crystallization from acetonitrile–ether (1:4) gave 6.05 g. (75%) of product, m.p. 96.5–97.5°.

Anal. Calcd. for $C_{12}H_{15}ClN_4O_4$: Cl, 11.71. Found: Cl, 11.62.

4-Aza-1-benzylazoniabicyclo[2.2.2]octane Bromide.—A solution of 1,4-diazabicyclo[2.2.2]octane (22.4 g., 0.2 mole) in acetone (100 ml.) was added cautiously to a solution of benzyl bromide (17.1 g., 0.1 mole) in acetone (150 ml.). Product begins to precipitate almost immediately. The reaction mixture was allowed to stand 2 hr., ether was added, and the product was filtered; yield 29 g. (98%). In a sealed tube a sample, crystallized from methanol–ether, collapsed at 212° then underwent discoloration and slow decomposition starting at 230° but was not completely decomposed even at 270°.

Anal. Calcd. for $C_{13}H_{19}N_2Br$: Br, 28.73. Found: Br, 28.47.

4-Aza-1-*m*-nitrobenzylazoniabicyclo[2.2.2]octane Bromide.—A solution of 1,4-diazabicyclo[2.2.2]octane (11.2 g., 0.1 mole) and *m*-nitrobenzyl bromide (10.8 g., 0.05 mole) in acetone (200 ml.) was refluxed 2 hr. and then cooled. Ether was added, and the crude product was filtered and crystallized from a mixture of 2-propanol, methanol, and ether; yield 15.8 g. (96%). This salt darkens at 245° but is not completely decomposed at 265°.

Anal. Calcd. for $C_{13}H_{13}BrN_3O_2$: Br, 24.35. Found: Br, 24.10.

Materials.—Anhydrous grade acetonitrile from the Eastman Kodak Co. was distilled from phosphorus pentoxide until further treatment with phosphorus pentoxide resulted in no discoloration of the reagent (usually three times) and then finally distilled from anhydrous sodium carbonate; b.p. 80–81°. It was found that rate measurements made using the solvent as received were indistinguishable from measurements made with the purified solvent. Most of the measurements were, therefore, made with the solvent as received. 1,4-Diazabicyclo[2.2.2]octane was obtained from the Houdry Process Corp. and crystallized from methanol–ether (1:1); m.p. 155–157°. Eastman Kodak Co. White Label 2,4-dinitrochlorobenzene was passed through a chromatographic column packed with alumina using benzene as solvent and then crystallized from methanol; m.p. 49–50°. Benzyltriethylammonium chloride was prepared and purified as previously described.³

Rate Measurements.—A determinate solution containing the amine and the halide was prepared at room temperature. Aliquots were withdrawn and sealed in ampoules. The concentrations given in the tables are those at the temperatures of the rate measurements and have been corrected for solvent expansion.⁴ The ampoules were placed in a constant temperature bath, withdrawn at appropriate time intervals, cooled in ice–water, and opened. The contents were added to dilute nitric acid (1:4), and chloride ion was determined by the Volhard method.

In some experiments the concentrations of both N-2,4-dinitrophenyl-N'-[2-(4-aza-1-azoniabicyclo[2.2.2]octane)ethyl]piperazine chloride (III) and N-2,4-dinitrophenyl-N'- β -chloroethylpiperazine (IV) were determined as a function of time. Aliquots were prepared and taken as above. They were first partitioned between benzene and pure water. The water extract was analyzed for chloride ion by the Volhard method. The concentration of chloride ion obtained is a measure of the concentration of III. The benzene layer was then extracted with dilute nitric acid. This extract was made basic with sodium hydroxide, refluxed 1–1.5 hr., and acidified with nitric acid. Chloride ion determined in this solution is a measure of the concentration of IV. In experiments with known mixtures of III and IV in acetonitrile it was found that the above procedure permitted the separation and determination of the two components with errors of less than 1% in each component.

Experiments in which the reaction was followed spectrophotometrically were carried out as follows. Two acetonitrile stock solutions, one $5.15 \times 10^{-3} M$ in 2,4-dinitrochlorobenzene and the other $0.9918 M$ in 1,4-diazabicyclo[2.2.2]octane, were prepared. For a rate measurement 2.0 ml. of the chloride solution was added by pipet to a 50-ml. volumetric flask containing the amount of the amine solution necessary to give the desired concentration and diluted to 50 ml. with acetonitrile; 3- to 4-ml. portions of this reaction mixture were sealed in vials and placed in the thermostat at $50.8 \pm 0.1^\circ$. At appropriate times tubes were removed, cooled in an ice–water bath, and opened; 2 ml. of solution was removed from the tube by pipet and added to a tube containing 2.0 ml. of dilute nitric acid (1:4). The optical density of this quenched solution was measured in a Zeiss PMQ II spectrophotometer at 360 $m\mu$ against a blank containing the initial amine concentration in the same solvent mixture. The pseudo-first-order rate constants were obtained from the slopes of plots of log

(O.D. _{∞} /O.D. _{t}). The optical densities at infinite time were measured after at least 10 half-lives and showed no change after still longer reaction times. In this solvent system the salt III has a maximum at 352 $m\mu$ (ϵ 10,900). At 360 $m\mu$ the extinction coefficient is 10,600. In all experiments the optical density at infinite time agreed within 5% with that calculated from the initial concentration of the chloride and the known extinction coefficient of the product at 360 $m\mu$.

Product Isolation. N-2,4-Dinitrophenyl-N'-[2-(4-aza-1-azoniabicyclo[2.2.2]octane)ethyl]piperazine Chloride (III).—A solution of 2,4-dinitrochlorobenzene (2.03 g., 0.01 mole) and 1,4-diazabicyclo[2.2.2]octane (3.37 g., 0.03 mole) in acetonitrile (50 ml.) was kept at $50.8 \pm 0.1^\circ$ for 165 hr. The solution was chilled, and crystallization was induced by scratching. The crude product which precipitated was crystallized from a mixture of 2-propanol, methanol, and hexane; yield 3.62 g. (84.8%).

Anal. Calcd. for $C_{13}H_{17}N_5O_4Cl$: Cl, 8.30. Found: Cl, 8.38.

In another experiment, this time with the chloride in excess, a solution of 2,4-dinitrochlorobenzene (6.08 g., 0.03 mole) and 1,4-diazabicyclo[2.2.2]octane (1.12 g., 0.01 mole) in acetonitrile (50 ml.) treated as above gave 1.75 g. (82%) of crude product and 1.37 g. (64.3%) of recrystallized product.

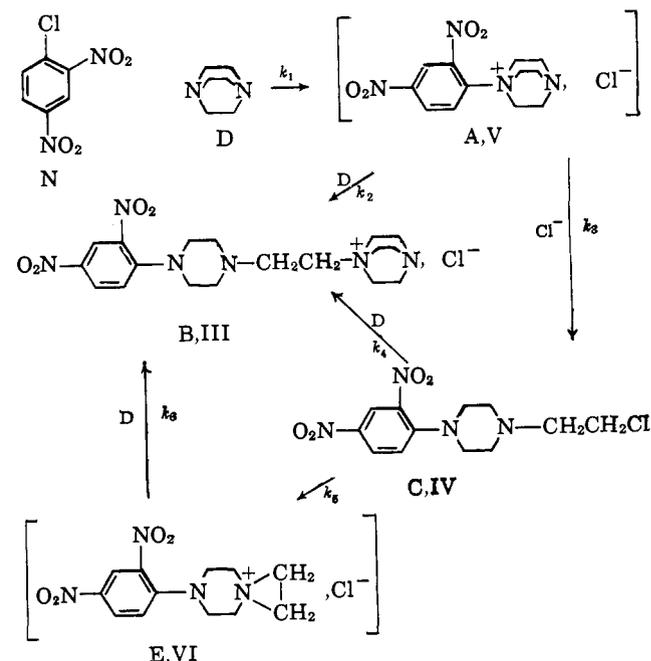
Anal. Found: Cl, 8.38.

N-2,4-Dinitrophenyl-N'- β -chloroethylpiperazine (IV).—A solution of 2,4-dinitrochlorobenzene (6.08 g., 0.03 mole) and 1,4-diazabicyclo[2.2.2]octane (1.12 g., 0.01 mole) in acetonitrile (150 ml.) was kept at $50.8 \pm 0.1^\circ$ for 71 hr. The solution was taken up in benzene (500 ml.) and extracted with four 250-ml. portions of water. This aqueous extract was discarded, and the benzene layer was extracted with four 100-ml. portions of hydrochloric acid (1:4). The water was removed from this acid extract *in vacuo* using a water bath to supply the heating. The yield of the β -chloroethylpiperazine, obtained as the hydrochloride, was 0.556 g., m.p. 210° dec. This amount of product corresponds to the conversion of 15.8% of the original 1,4-diazabicyclo[2.2.2]octane to III.

Anal. Calcd. for $C_{12}H_{16}Cl_2N_4O$: total Cl, 20.18. Found: total Cl, 20.54.

Discussion

The reaction of 2,4-dinitrochlorobenzene with excess 1,4-diazabicyclo[2.2.2]octane results ultimately in a single product, the salt III. With excess 2,4-dinitrochlorobenzene there are two final products, III and the β -chloroethylpiperazine IV. In the reaction with excess amine there may be some IV formed during the course of the reaction, but this will be converted, *via* two separate routes, to III by further reaction with the amine. A possible scheme for these transformations is



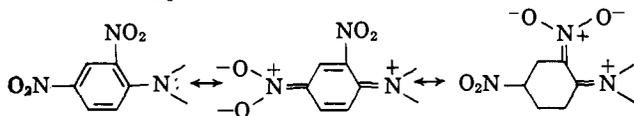
The two final products III and IV have been isolated from reaction mixtures, and their structures have been established by synthesis. The intermediate VI has not

(3) R. C. Petersen and S. D. Ross, *J. Am. Chem. Soc.*, **85**, 3164 (1963).

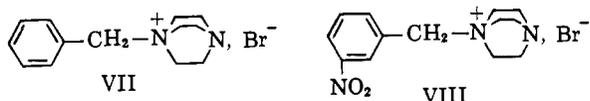
(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 28.

been isolated, but there is ample precedent for the incursion of cyclic ethylenium ion intermediates in nucleophilic displacements on β -chloroethylamines.² In acetonitrile at $50.8 \pm 0.1^\circ$, IV is converted to III both by an SN2 displacement for which the rate constant k_4 was found to be 5.9×10^{-5} l. mole⁻¹ sec.⁻¹ and by a process involving VI. In this latter path, the rate-determining step is the formation of the intermediate VI, which then reacts rapidly with 1,4-diazabicyclo[2.2.2]octane to give III. The first-order rate constant which was determined corresponds, therefore, to k_5 and is equal to 2.3×10^{-5} sec.⁻¹. It might be argued that V is also a possible intermediate for this transformation. This is, however, improbable, since it would require an intramolecular displacement by the less basic of the two available amino groups and would entail the loss of the resonance energy that results from the interaction of the free amino group with the aromatic nitro groups. This possibility for electron delocalization and stabilization is available in both IV and VI but absent in V.

The salt V is a proposed intermediate and has neither been isolated from these reactions nor been prepared independently. It might, *a priori*, have been expected as a stable product from the interaction of 2,4-dinitrochlorobenzene and 1,4-diazabicyclo[2.2.2]octane. The failure to obtain it is in all probability due to the large gain in resonance stabilization from interaction of the nitro and amino groups when the diazabicyclooctane ring system is opened, resulting in contributing structures of the type



These considerations may explain the facile opening of V and its ready conversion to III and IV. The fact that excess 1,4-diazabicyclo[2.2.2]octane reacts with benzyl bromide to give VII and with *m*-nitrobenzyl bromide to give VIII supports this explanation. Neither VII nor VIII reacts further with the amine,



for in neither case would the opening of the diazabicyclooctane ring system result in electron delocalization and stabilization.

The detailed mechanism shown above leads to the rate equation

$$d(A + B + C + E)/dt = k_1ND = k_1(N_0 - A - B - C - E)(D_0 - A - 2B - C - E) \quad (1)$$

where subscripts zero indicate initial conditions. Now if A and E are considered negligible relative to B , eq. 1 reduces to

$$d(B + C)/dt = k_1(N_0 - B - C)(D_0 - 2B - C) \quad (2)$$

Furthermore, if the amine is present in sufficient excess, C will be negligible relative to B and the applicable rate equation will be

$$dB/dt = k_1(N_0 - B)(D_0 - 2B) \quad (3)$$

Equation 3 was used in its integrated form to calculate the rate constants listed in Table I. As was mentioned earlier, the experiments in Table I do not quite meet the requirements of negligible C , as is shown by the slight upward trend in k with increasing D_0 .

The assumption that $A \ll B$ is supported by the agreement between the upper limit of the rate constants of Table I, in which B is assumed equal to the analytical value of (Cl^-) , and the value obtained from the data of Table II (Fig. 1) in which the spectrophotometric technique follows the production of B but is insensitive to A .

In the experiments summarized in Table II, the amine concentration is in every case at least 1000 times as great as the initial 2,4-dinitrochlorobenzene concentration. Here the assumption that $C \ll B$ is valid and the value of k_1 , 11.3×10^{-5} l. mole⁻¹ sec.⁻¹, that results from these experiments is, therefore, the most reliable value for this rate constant.

When the amine is not initially present in sufficient excess or when the chloride is initially present in excess, both B and C will be present in the system during all stages of the reaction, and eq. 2 must be used to determine k_1 . Since eq. 2 cannot be integrated in any useful form, it must be used in differential form. The method is subject to large uncertainties, since it requires the measurement of the slope at points along a plot of $(B + C)$ vs. t .

The data from four sets of measurements (1, $N_0 = 0.0371$, $D_0 = 0.2246$; 2, $N_0 = 0.0351$, $D_0 = 0.5312$; 3, $N_0 = 0.2323$, $D_0 = 0.0682$; 4, $N_0 = 0.2318$, $D_0 = 0.0660$) in which both B and C were determined as a function of time were used to estimate k_1 . In each case the values of $d(B + C)/dt$ were plotted against the product, $(N_0 - B - C)(D_0 - 2B - C)$, and the range of slopes for reasonable straight lines through the points was taken as a measure of k_1 . The total range of values for the rate constant is given by the value $11 \pm 2 \times 10^{-5}$ l. mole⁻¹ sec.⁻¹.

The above data should also permit an estimation of the ratio k_2/k_3 . It may be shown that

$$dB/dt = k_2AD + k_4CD + k_5C \quad (4)$$

and

$$dC/dt = k_3A(Cl^-) - k_4CD - k_5C$$

Since in eq. 4 and 5 only k_2A and k_3A are unknown, the ratio k_2/k_3 is in principle available. In practice the data do not permit a fully satisfactory determination, since slopes must be obtained from two different plots, and it may only be estimated that the ratio is approximately 0.1.

Finally it should be noted that the reaction scheme presented has included only those steps which were essential to the treatment used. The rate constant k_1 may really represent a composite of rate constants, since the formation of V may involve an intermediate. Similarly, the conversion of IV to VI is almost certainly reversible. In the present instance the formation of VI is much more rapid than its reversal to IV and $k_6 \gg k_5$.