from a benzene-cyclohexane mixture to give 0.15 g. of white ylid, m.p. 210-212°

Anal. Calcd. for C15H18O4S2 (356.48): C, 50.53; H, 4.53; S, 26.99. Found: C, 51.20; H, 4.56; S, 27.08.

Bis(phenylsulfonyl)methylene Dimethyloxosulfonium Ylid.-A solution of 0.5 g. of 3 in 40 ml. of dimethyl sulfoxide was heated under reflux for 60 hr. Water was added to the nearly colorless mixture, and an oil slowly settled out. The clear supernatant part was decanted and on standing deposited 0.05 g. of crystalline product, m.p. 178-179°

Anal. Calcd. for $C_{15}H_{16}O_{5}S_{3}$ (372.48): C, 48.37; H, 4.33. Found: C, 48.81; H, 4.46.

Nucleophilic Displacement of Bromide by Thiosulfate Ion from **1.2-Aminobromopropanes**

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In the reaction of 2-amino-1-bromopropane hydrobromide (II) with 1 equiv. of sodium thiosulfate, the formation of only one product, 2-aminopropane-1-thiosulfuric acid (IV), is detected. Similar treatment of 1-amino-2-bromopropane hydrobromide (I) yields two products, namely, 1-aminopropane-2-thiosulfuric acid (III) and the rearranged product, IV. In order to determine whether an ethylenimonium ion is an intermediate in the formation of IV in the latter reaction, the ring opening of 2-methylethylenimine by thiosulfate ion was investigated. The direct displacement of bromide in I by thiosulfate ion without the intermediacy of the cyclic imonium ion accounts for the formation of III. The ratio of the rate constants for the intramolecular displacement vs. the intermolecular displacement was found to be 1.45.

In previous studies² of the reactions of 1,2-(tertiaryamino)haloalkanes evidence was presented that in solvolyses, dimerizations, and nucleophilic displacements, the rate-determining step in each case was the formation of the intermediate ethylenimonium ion. There

	slow	fast	
$R-CH-CH_2-X$	\rightarrow RCH	$-CH_2 \longrightarrow rin$	g opening
-	\sim	/	
Ń	Ň	∛+	
\angle	/	\backslash	
\mathbf{R}' \mathbf{R}''	Rí	Ř΄	

have been few reported investigations of such reactions in the case of (primary-amino)haloalkanes³ since the studies have been complicated by the occurrence of side reactions, especially polymerization.⁴ Also, earlier investigations^{2d,f,5} of the nucleophilic displacement and rearrangement of aminohaloalkanes have been hampered by the lack of an adequate analytical technique. The marked similarity in the physical properties of the isomeric displacement products renders the separation of isomers and the determination of the reaction product composition difficult.

The reaction of an alkyl halide with sodium thiosulfate gives an alkyl thiosulfate (Bunte salt) and, similarly, aminoalkanethiosulfuric acids can be prepared by treating sodium thiosulfate with the corresponding aminohaloalkanes. The displacement of bromide from the isomeric primary-amino bromides, 1-amino-2-bromopropane hydrobromide (I) and 2-amino-1-bromopropane hydrobromide (II), with thiosulfate ion was

CH ₃ CHCH ₂ NH ₂ ·HBr	CH₃CHCH₂Br ·HBr
Br	NH2
I	II

(1) To whom communications should be sent.

(4) H. Freundlich and W. Neumann, ibid., 87, 69 (1914).

(5) W. R. Brode and M. W. Hill, J. Am. Chem. Soc., 69, 724 (1947).

selected for study. The products anticipated from these reactions, besides sodium bromide, were the isomeric compounds, 1-aminopropane-2-thiosulfuric acid (III) and 2-aminopropane-1-thiosulfuric acid (IV).

$$\begin{array}{cccc} CH_3 & -CH & -CH_2 & -NH_2 \\ & & & & | \\ SSO_3H & & & NH_2 \\ III & & IV \end{array}$$

Experimental⁶

Bis(1-amino-2-propyl) Disulfide Dihydrochloride.--1-Amino-2-propanethiol hydrochloride (25.5 g., 0.2 mole), prepared by the method of Gabriel and Leupold⁷ according to the modification of Mylius,⁸ was dissolved in 100 ml. of water containing 20 ml. of 28% ammonia solution. To the cooled, magnetically stirred solution was added dropwise 5% aqueous hydrogen peroxide until the solution gave a negative nitroprusside test and liberated iodine from hydriodic acid. The solvent was evaporated under reduced pressure and the residue was recrystallized from methanol to give 22.8 g. (90.1% yield) of disulfide, m.p. 228-229° dec. (lit.7 m.p. 213-214° dec.)

Anal. Calcd. for C6H18Cl2N2S2: C, 28.45; H, 7.16; N, 11.06; S, 25.32. Found: C, 28.47; H, 7.28; N, 11.15; S, 25.69

Bis(2-amino-1-propyl) Disulfide Dihydrochloride.-2-Amino-1propanethiol hydrochloride⁹ (25.5 g., 0.2 mole) prepared from 2methylethylenimine was oxidized as above to give 22.7 g. (89.7%) yield) of the disulfide, m.p. 224-225° dec. (lit.⁹ m.p. 212° dec.) Anal. Calcd. for C6H18Cl2N2S2: C, 28.45; H, 7.16; N,

11.06; S, 25.32. Found: C, 28.19; H, 7.14; N, 11.02; S, 24.96.

1-Aminopropane-2-thiosulfuric Acid (III).—A solution of 7.6 g. (0.03 mole) of bis(1-amino-2-propyl) disulfide dihydrochloride and 6.24 g. (0.06 mole) of sodium bisulfite in 20 ml. of water was heated under reflux for 2.5 hr. It was cooled overnight and the product which crystallized was collected by filtration and recrystallized from water to give 2.5 g. (48.7%) of compound III, m.p. 184° dec.

Anal. Calcd. for C₃H₉NO₃S₂: C, 21.04; H, 5.30; N, 8.18; S, 37.45. Found: C, 20.96; H, 5.37; N, 8.33; S, 37.14.

^{(2) (}a) P. D. Bartlett, S. D. Ross, and C. G. Swain, J. Am. Chem. Soc., 69, 2971 (1947); (b) P. D. Bartlett, J. W. Davis, S. D. Ross, and C. G. Swain, ibid., 69, 2977 (1947); (c) P. D. Bartlett, S. D. Ross, and C. G. Swain, ibid., 71, 1415 (1949); (d) J. F. Kerwin, G. E. Ullyot, R. C. Fuson, and C. L. Zirkle, ibid., 69, 2961 (1947); (e) E. M. Schultz, C. M. Robb, and J. M. Sprague, *ibid.*, **69**, 188 1947); (f) E. M. Schultz and J. M. Sprague, *ibid.*, **70**, 48 (1948); (g) A. Gilman and F. S. Philips, *Science*, **103**, 409 (1946).

⁽³⁾ H. Freundlich, Z. physik. Chem. (Leipzig), **76**, 99 (1911); **78**, 681 (1912); **102**, 117 (1922); **122**, 39 (1926); **166A**, 161 (1933).

⁽⁶⁾ Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. The rate of heating influences the decomposition points of most aminoalkanethiosulfuric acids. Microanalyses were performed by Mr. Joseph Alicino, Metuchen, N. J. Infrared spectra were measured on a Beckman IR-5 spectrophotometer.

⁽⁷⁾ S. Gabriel and E. Leupold, Ber., 31, 2832 (1898)

⁽⁸⁾ W. Mylius, ibid., 49, 1091 (1916).

⁹⁾ M. Bose, ib id., 53, 2000 (1920).

	Reactions Followed by	N.M.R. SPECTROSCOPY
Expt.	Substrate	Nucleophile
1	0.438 g. (2 mmoles) of I in 0.5 ml. of water	0.316 g. (2 mmoles) of sodium thiosulfate pentahydrate in 0.5 ml. of water
2	0.114 g. (2 mmoles) of 2-methylethylenimine	0.296 g. (2 mmoles) of am- monium thiosulfate in 1.0 ml. of water
3	0.219 g. (1 mmole) of I in 0.5 ml. of water	1.322 g. (8.9 mmoles) of am- monium thiosulfate in 3 ml. of water
4	0.438 g. (2 mmoles) of II in 0.5 ml. of water	0.316 g. (2 mmoles) of sodium thiosulfate pentahydrate in 0.5 ml. of water
5	0.218 g. (1 mmole) of I	0.135 g. (1 mmole) of am- monium sulfite monohy- drate in 1 ml. of water
6	0.185 g. (3.24 mmoles) of 2-methylethylenimine	0.518 g. (3.86 mmoles) of am- monium sulfite monohy- drate in 2 ml. of water

TABLE I

Reaction of I with Sodium Thiosulfate.—A solution of 0.547 g. (2.5 mmoles) of I and 0.621 g. (2.5 mmoles) of sodium thiosulfate pentahydrate in 2 ml. of water was heated on a steam bath for 0.5 hr. Completion of the reaction was indicated by failure of sulfur to precipitate from an aliquot acidified with mineral acid. The solvent was removed on a rotary evaporator under reduced pressure and the residue was dried in an Abderhalden drying pistol over P_2O_5 . An infrared spectrum (KBr pellet) of the reaction products was determined.

Reaction of II with Sodium Thiosulfate.—A solution of 0.547 g. (2.5 mmoles) of II and 0.621 g. (2.5 mmoles) of sodium thiosulfate pentahydrate in 2 ml. of water was treated as in the above experiment. Similarly, an infrared spectrum was determined of the reaction products.

Reaction of 2-Methylethylenimine with Ammonium Thiosulfate.—To a stirred solution of 0.296 g. (2 mmoles) of ammonium thiosulfate in 2 ml. of water was added 0.114 g. (2 mmoles) of 2methylethylenimine. Stirring was continued for 0.5 hr. at room temperature and 0.5 hr. at $ca. 50^{\circ}$. The solvent was removed under reduced pressure, the residue was dried, and the infrared spectrum was determined.

The stability of III and IV was tested by refluxing 50 mg. of each compound in 2 ml. of water for 1 hr. Upon evaporation of

TABLE II

Concentration and Rate Data for the Reaction between 1-Amino-2-bromopropane Hydrobromide and Sodium Thiosulfate^a

101	_	[C]	_

	$ C = C _0 -$					(a[A]/at) =		
Time, hr.	$\{\mathbf{E}\}^b$	[D] ^b	[A] ^b	$[E] - [D]^{b}$	[A][C]	$d[E]/dt^{c}$	$d[A]/dt^c$	$(d[E]/dt)^{c}$
0.5	0.072	0.034	1.75	1.89	3.30	4.02		
1.0	0.145	0.073	1.54	1.78	2.74	3.50	4.02	0.519
1.5	0.209	0.111	1.45	1.68	2.43	3.14	3.58	0.439
2.0	0.268	0.149	1.38	1.58	2.18	2.95	3.29	0.335
2.5	0.327	0.187	1.35	1.49	2.01	2.81	3.09	0.283
3.0	0.384	0.22	1.28	1.40	1.79	2.61	2.82	0.212
3.5	0.44	0.256	1.21	1.30	1.57	2.51	2.65	0.142
4.0	0.49	0.293	1.18	1.22	1.44			
4.5	0.54	0.335	1.12	1,13	1.26			
5.0	0.59	0.375	1.09	1.04	1.13			

^a [A]₀ = [C]₀ = 2 M_j temperature, 36.0 ± 0.5°; $k_1 = 1.14 \pm 0.17 \times 10^{-5} \text{ sec.}^{-1}$; $k_2 = 0.79 \pm 0.12 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$. ^b Mole l.⁻¹. ^c Mole l.⁻¹ sec.⁻¹.

2-Aminopropane-1-thiosulfuric Acid (IV).—Bis(2-amino-1-propyl) disulfide dihydrochloride (7.6 g., 0.03 mole) and 6.24 g. (0.06 mole) of sodium bisulfite were treated as described above. Compound IV (4.1 g., 79.9% yield) which was obtained melted at $197-198^{\circ}$ dec.

Anal. Caled. for C₈H₉NO₃S₂: C, 21.04; H, 5.30; N, 8.18; S, 37.45. Found: C, 21.07; H, 5.37; N, 8.11; S, 37.10.

1-Amino-2-bromopropane Hydrobromide (I).—2-Hydroxypropylamine (37 g., 0.5 mole) in 250 ml. of benzene was converted into the hydrobromide salt by passing anhydrous hydrogen bromide into the solution. Thionyl bromide (156 g., 0.75 mole) in 100 ml. of benzene was slowly added to the stirred mixture. Upon completion of the addition, the mixture was warmed causing the decomposition of the bromosulfite with the evolution of sulfur dioxide. When the evolution of sulfur dioxide ceased, the solvent was removed by distillation, first at atmospheric pressure and later under reduced pressure. The residue was treated with 200 ml. of ethyl acetate and chilled overnight. The crude product was collected and recrystallized several times from isopropyl alcohol (charcoal) giving the amino bromide (25.5 g., 23.4% yield), m.p. 161–162° (lit.¹⁰ m.p. 156°).

2-Amino-1-bromopropane Hydrobromide (II).—To 49.6 g. (0.66 mole) of 2-amino-1-propanol¹¹ was cautiously added 320 ml. of 48% hydrobromic acid. The mixture was heated under reflux and the water which formed was distilled through a Vigreux column according to the method of Cortese.¹² The amino bromide (63.6 g., 43.9% yield) was recrystallized from acetonitrile and then from ethyl acetate: m.p. 112-114°.

and then from ethyl acetate; m.p. 112-114°. Anal. Calcd. for C₃H₉Br₂N: C, 16.46; H, 4.14; N, 6.40. Found: C, 16.24; H, 4.15; N, 6.50. the solutions to dryness under reduced pressure, the melting point and infrared spectrum of each compound was found to be unchanged. This ruled out the possibility of their being interconvertible under the reaction conditions.

N.m.r. Examination of the Displacement and Ring-Opening Reactions .- The displacement of bromide from the two aminobromopropanes and the ring-opening reactions were followed by measuring the rate of increase or decrease of the appropriate lines in the n.m.r. spectrum. Solutions of the two reactants (cf. Table I) were mixed in a 5-mm. n.m.r. tube, a capillary containing tetramethylsilane was added as an external reference, and the tube was rapidly transferred to the probe of the A-60 Varian Associates spectrometer which was kept at $36.5 \pm 0.5^{\circ}$. The pertinent region of the spectrum was quickly scanned. The line shapes of the methyl signals from I, II, III, and IV were the same.13 Relative peak heights were, therefore, used as a valid measure of concentration throughout the run. The n.m.r. spectrum was scanned at appropriate intervals to follow the progress of the reaction. While it was desired mainly to gain insight into the number and the nature of the products formed, the kinetics of the reaction in expt. 1 (Table I) were also determined (Table II).

An examination of the n.m.r. spectra of synthetic mixtures of III and IV showed that 2% of III was detectable in an aqueous solution of IV.

⁽¹⁰⁾ P. Elfeldt, Ber., 24, 3220 (1891).

⁽¹¹⁾ O. Vogl and M. Pohm, Monatsh., **83**, 541 (1952).

⁽¹²⁾ F. Cortese, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sone, Inc., New York, N. Y., 1943, p. 91.

⁽¹³⁾ The n.m.r. spectra were of general interest. The spectra of III and IV in D₂O at 60 Mc.p.s. are almost identical, each showing a low-field multiplet (δ 3.5-4.1) representing the CH proton and strong lines around δ 3.3 which are part of the spectrum from the CH₂ group. When the D₂O solutions were acidified with HCl, in one case the CH proton resonance broadened markedly while in the other case the CH₂ signal broadened. This results from a decrease in the rate of protolysis of the NH₃ + protons to the point that the effect of spin coupling between the NH₃ + protons and the CH or CH₂ protons is observed. In this way the isomers may readily be distinguished.

Results

In the reaction of I with sodium thiosulfate the infrared spectrum (Figure 1F) of the unpurified products indicated the presence of the two isomeric aminopropanethiosulfuric acids, III and IV. This was confirmed by the n.m.r. (expt. 1) in which the methyl signals of the two thiosulfuric acids had the same line shape. The final product composition after 24 hr., *i.e.*, the ratio of the isomeric thiosulfuric acids, was determined to be 1:1 by comparison of the C-CH₃ group heights. It



seems likely that IV arose from a rearrangement reaction involving an ethylenimonium ion as an intermediate. However, III could have arisen by two mechanisms, namely, by the direct displacement of bromide or

$$SSO_{3}^{-2}$$

$$CH_{3}-CH-CH_{2}-NH_{2} \rightarrow CH_{3}-CH-CH_{2}-NH_{2}$$

$$\downarrow$$

$$Br$$

$$SSO_{3}^{-}$$

by the ring opening of the ethylenimonium ion at the secondary carbon atom. To determine the direction

$$CH_{3} - CH - CH_{2} \rightarrow CH_{3} - CH - CH_{2} \rightarrow CH_{3} - CH - CH_{2} \rightarrow CH_{3} - CH - CH_{2} - NH_{2}$$

Br $N_{H_{2}}^{+}$ SSO_{3}^{-}

of the opening of the intermediate ion, the reaction of 2-methylethylenimine with ammonium thiosulfate was examined. The infrared spectrum of the products (Figure 1C) showed only the presence of IV. This was confirmed in the n.m.r. (expt. 2) which indicates that the intermediate ethylenimonium ion was attacked exclusively in the primary position.



That III was formed by the bimolecular displacement of bromide was further demonstrated utilizing the mass law effect. The reaction of I with thiosulfate was repeated using a 7.9 molar excess of the latter reactant (expt. 3). N.m.r. analysis indicated that the ratio of III to IV formed was 2.6:1.

It has been reported¹⁴ that in the reaction of I (impure) and sulfite, a nucleophile somewhat weaker than thiosulfate,¹⁵ only a single product was obtained which was identified as 2-aminopropane-1-sulfonic acid. This



Figure 1.—Infrared spectra (KBr pellet) of A, IV (authentic sample); B, products obtained on allowing II to react with 1 equiv. of sodium thiosulfate in water; C, products obtained on allowing 2-methylethylenimine to react with 1 equiv. of ammonium thiosulfate in water; D, III (authentic sample); E, synthetic mixture (1:1) of III and IV; and F, products obtained on allowing I to react with 1 equiv. of sodium thiosulfate in water.

reaction was repeated using pure I and ammonium sulfite (expt. 5). By following the course of the reaction using n.m.r. it was determined that indeed a single sulfonic acid was produced. Similarly, the reaction of 2-methylethylenimine with ammonium sulfite (expt. 6) gave a single product as shown by n.m.r. analysis.

The infrared spectrum of the products resulting from the reaction of II and sodium thiosulfate (Figure 1B) was identical with that of the authentic sample of IV. There was no evidence for the formation of III. That IV was the only thiosulfuric acid formed was confirmed by the n.m.r. spectrum (expt. 4). This compound could have arisen by the direct displacement of the bromide, by the ring opening of an intermediate ethylenimonium ion at the primary position, or by the simultaneous operation of both mechanisms.

$$\begin{array}{cccc} & & & & \\ & & & & \\$$

Results of the Kinetics Experiment.—The simultaneous measurement of the rates of production of III and IV by the reaction of I with thiosulfate (expt. I) using n.m.r. spectroscopy allowed direct comparison of the relative rates of bimolecular and intramolecular displacement of halide in this system (see below, where k_1 , k_2 , and k_3 are the appropriate rate constants).



⁽¹⁴⁾ P. Rumpf, Bull. soc. chim. France, [5] 5, 871 (1938).

⁽¹⁵⁾ C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (1953).

$$CH_{3} - CH - CH_{2} - NH_{2} + SSO_{3}^{-2} \xrightarrow{k_{3}}$$

$$Br$$

$$A$$

$$C$$

$$CH_{3} - CH - CH_{2} - NH_{2} + Br$$

$$-(d[A]/dt) = k_1[A] + k_3[A][C]$$
(1)

$$-(d[B]/dt) = -k_1[A] + k_2[B][C]$$
(2)

$$-(d[C]/dt) = k_2[B][C] + k_3[A][C]$$
(3)

$$(d[D]/dt) = k_2[B][C]$$
 (4)

$$(\mathbf{d}[\mathbf{E}]/\mathbf{d}t) = k_{\mathfrak{z}}[\mathbf{A}][\mathbf{C}]$$
(5)

An analytical solution is not possible since one is not justified in invoking the steady-state approximation with regard to the intermediate ethylenimonium ion.^{2a,b} Agraphical solution for obtaining k_1 and k_3 was employed instead. Values for (d[A]/dt), (d[D]/dt) and (d[E]/dt) were obtained from the respective plots of [A], [D], and [E] (determined from the n.m.r. spectrum) vs. time. The values of [C] at different times were obtained from the relationship, $[C]_t = [C]_0 - [E]_t - [D]_t$, where subscript 0 represents initial concentration and subscript t represents concentration at time t. From eq. 5 the linear plot of (d[E]/dt) vs. $[A]_t[C]_t$ gave k_3 as the gradient = 7.9 \times 10⁻⁶ l. mole⁻¹ sec.⁻¹.

From eq. 1 and 5, $-(d[A]/dt) = k_1[A] + (d[E]/dt)$, or $-(d[A]/dt) - (d[E]/dt) = k_1[A]$.

A plot of $- [(d[A]/dt) + (d[E]/dt)] vs. [A]_t$ was linear with a gradient (k_1) of 1.14×10^{-5} sec.⁻¹. Therefore, for the reaction of I with sodium thiosulfate at 36.5° the ratio

 $\frac{\text{rate of intramolecular displacement}}{\text{rate of intermolecular displacement}} = k_1/k_3 = \frac{1.14 \times 10^{-6}}{7.9 \times 10^{-6}} = 1.45 \frac{\text{sec.}^{-1}}{1. \text{ mole}^{-1} \text{ sec.}^{-1}}$

Discussion

Recently, there has been interest shown in the comparison of the rates of intra- and intermolecular displacement reactions and hydrolyses.¹⁶ The present results bear on this problem. While it is generally accepted that nucleophilic attack on 1,2-(secondary-amino)haloalkanes is preceded by the formation of an intermediate ethylenimonium ion,^{2a} most kinetic data are restricted to compounds bearing a tertiary-amino group. No similar conclusion has been reached regarding displacements occurring in primary- and secondaryamino compounds.

The work reported here indicates that ring closure occurs less readily when a primary-amino group acts as the neighboring group, allowing some direct displacement by an external nucleophile. This is probably due to the lower nucleophilicity of the primary-amino group¹⁷ since steric hindrance effects in the formation of three-membered rings are not important and are overridden by polar effects.¹⁷ If I reacted exclusively through the 2-methylethylenimonium ion, then only the rearranged thiosulfuric acid, IV, would result since it has been shown that this cyclic ion opens only at the primary carbon atom. The direction of opening of unsymmetrical cyclic imines is usually given by analogy with ordinary bimolecular nucleophilic displacement¹⁸ where the rate sequence for attack on carbon is primary > secondary > tertiary. We have shown that once the cyclic ion has been formed it is attacked exclusively in the primary position, in accordance with the above conclusion.

This is believed to be the first observation of the concurrent displacement and rearrangement occurring in the nucleophilic attack on an aminohaloalkane. The ratio of the rate constants indicates that the intramolecular displacement is dominant when thiosulfate is the nucleophile. When the weaker nucleophile, sulfite, was substituted, intramolecular displacement occurred to the exclusion of the intermolecular displacement.

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The Solvolytic Behavior of Tricyclo[3.2.1.0^{2,4}]octane Derivatives¹

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The four possible tricyclo $[3.2.1.0^{2.4}]$ octan-6-ols have been prepared and converted to their respective brosylates. Acetolysis of three of the four isomers gave identical products, *exo-exo*-tricyclo $[3.2.1.0^{2.4}]$ octan-6-yl acetate, *exo*-bicyclo [3.2.1] octa-en-6-yl acetate, and nortricyclane-3-methyl acetate. The related nortricyclane-3methyl brosylate gave qualitatively the same products. The isomerization of *endo-exo*-tricyclo $[3.2.1.0^{2.4}]$ octan-6yl brosylate to the *exo-exo* isomer during the course of solvolysis leads to the conclusion that a "norbornyl-type ion" is produced in this system. A consideration of the products and their ratios along with the kinetic data leads to a tentative scheme for the solvolysis of these compounds.

In many instances a cyclopropane ring behaves in a fashion similar to that of a double bond.³ The obser-

(1) This work was supported in part by the Army Research Office (Durham).

(3) Cf. M. T. Rogers and J. D. Roberts, J. Am. Chem. Soc., 68, 843 (1946); R. H. Eastman and S. K. Freeman, *ibid.*, 77, 6642 (1955); R. S. Mohrbacher and N. H. Cromwell, *ibid.*, 79, 401 (1957); R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. S. Hatch, J. Org. Chem., 27, 733 (1962). vation that a double bond may participate in a solvolytic reaction as with the norbornenyl tosylates⁴ and the demonstration that the cyclopropane ring in bicyclo-[3.1.0]hexane may participate in a solvolytic reaction⁵

⁽²⁾ National Science Foundation Postdoctoral Fellow, Yale University, 1962-1963.

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 Soc., 72, 5795 (1950); S. Winstein and M. Shatavsky, *ibid.*, 78, 592 (1956);
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