rapidly changed to pH of 5.0 and was again made alkaline. The solution again turned acidic on heating and continued to do so until the solution had so been treated four times with alkali. The resulting solution gave a 19.5% yield of quinuclidine picrate.

A typical diluted irradiated solution when carefully neutralized to pH 7 with potassium carbonate and then treated with piperidine (10 g.) gave upon working up in the customary manner a 2.6% yield of quinuclidine picrate.

2-Methylquinuclidine.—Ring closure was carried out on N-bromo- and N-chloro-4-*n*-propylpiperidine in a manner similar to that used in the preparation of quinuclidine. The picrate after two recrystallizations from ethanol and two from a 50-50 mixture of ligroin (60–70°) and acetone melted at 282–283° with decomposition. Prelog[8] reports 286° as the melting point for this derivative.

Ring closure of either N-bromo- or N-chloro-2-methyl-4-ethylpiperidine gave a maximum of 2% yield of 2-methylquinuclidine. The picrate from this sample after three crystallizations from acetone-ligroin (60–70°) melted at 285°. A mixture with the picrate of the sample obtained from N-halo-4-*n*-propylamine melted with no depression.

2-Ethylquinuclidine.—This compound was prepared by the ring closure of N-bromo and N-chloro-4-*n*-butylpiperidine. The picrate, after three recrystallizations from acetone–ligroin (60–70°) melted at 172° with decomposition. Prelog[8] reports a melting point of 170–171° for this derivative.

3-Methylquinuclidine.—This amine was prepared by ring closures of N-bromo- and N-chloro-3-methyl-4-ethylpiperidine. The picrate after three recrystallizations from acetone–ligroin melted at 229–230°. Prelog[8] reports a melting point of 227° for this compound.

Ring Closure of N-Chloro-2,6-dimethyl-4-ethylpiperidine.—Ring closure of N-chloro-2,6-dimethyl-4-ethylpiperidine gave only a trace of a tertiary amine picrate.

IOWA CITY, IOWA RECEIVED DECEMBER 15, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Compounds with Boron at the Bridgehead—A Study of the Steric Consequences of Planar Boron[1]

BY HERBERT C. BROWN AND EDWARD A. FLETCHER[2]

2-Ethyl-2-(hydroxymethyl)-1,3-propanediol[3] reacts with boric acid to lose the calculated quantity of water, forming the ester. The product is polymeric. The monomer is not formed from the polymer at 270° and 10^{-3} mm. It is concluded that the strain involved in accommodating the planar boron atom at the cage bridgehead (IV) must be exceedingly large. In the product each trimethylolpropane molecule must be combined with two or three different boron atoms—a relatively strain free polymer results. Triethanolamine reacts with boric acid to produce a monomeric ester, a volatile solid (VII or VIII). The product reacts with methyl iodide; the reaction follows second order kinetics, but is much slower than the corresponding reactions of simple tertiary amines. The energy of activation is 18.5 kcal. for triethanolamine borate *versus* 13.0 for triethanolamine itself. The product reacts with strong acids only at a slow, measurable rate. It is concluded from these experiments that the lone pair of the nitrogen atom cannot be free and the product must, therefore, have the "triptych" structure (VIII).

Introduction

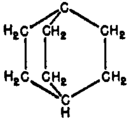
The stereochemistry of tetrahedral carbon, planar platinum and pyramidal nitrogen has been intensively investigated. The stereochemistry of planar boron, on the other hand, has received little attention. Yet there are ample indications that the planar trigonal configuration must lead to an unusual stereochemistry of considerable interest.

Thus certain major differences in the chemistry of substituted amines, R_3N, and borines, R_3B, may have their basis in the differences in configuration. For example, triisopropylamine has not yet been prepared although triisopropylboron is easily synthesized.[4] The preparation of di-*t*-butylamine has been reported but once,[5] and the synthesis involves a difficult procedure; yet tri-*t*-butylboron is easily synthesized and is highly stable.[4] It is, of course, dangerous to draw firm conclusions from evidence of this kind. Nevertheless, the differences are so great as to suggest that they cannot be the result of the minor differences in the covalent radii of boron and nitrogen. The differences are more plausibly attributed to the differences in configuration. Apparently the planar configuration of boron accommodates large bulky groups far more readily than does the pyramidal configuration of nitrogen.

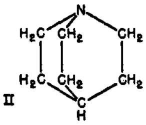
To obtain information as to the steric consequences of planar trigonal atoms, we have undertaken a number of studies of the stereochemistry of tricovalent boron. The present paper is concerned with compounds containing boron at the bridgehead.

Polymeric Trimethylolpropane Borate

Bicyclic ("cage") compounds containing normally tetrahedral atoms, such as carbon and nitrogen, at the bridgehead are well known. Bicyclo-(2.2.2)-octane (I) and quinuclidine (II) are easily prepared and highly stable, suggesting that the structures contain relatively strainless rings and the usual bond angles.[6]



I



II

The synthesis of related "cage" compounds containing boron at the bridgehead (III, IV) would presumably involve a distortion of the boron angles from their preferred 120° value to the approxi-

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[1] Studies in Stereochemistry. XVIII. This paper was presented in part before the Division of Physical and Inorganic Chemistry at the 117th Meeting of the American Chemical Society in Detroit, Michigan, April 17, 1950.

[2] E. I. du Pont de Nemours and Company Fellow at Purdue University, 1949–1950.

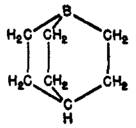
[3] We shall, for convenience, refer hereafter to this substance by its common name, trimethylolpropane.

[4] E. Krause and P. Nobbe, *Ber.*, **64B**, 2112 (1931); H. C. Brown, THIS JOURNAL, **67**, 378 (1945).

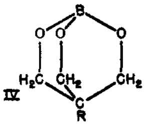
[5] F. Klages, G. Nober, F. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

[6] K. Alder, G. Stein, F. v. Buddenbrock, W. Eckardt, W. Frercks and S. Schneider, *Ann.*, **514**, 1 (1934); J. Meisenheimer, J. Neresheimer and W. Schneider, *ibid.*, **420**, 190 (1920).

mately tetrahedral value most favorable for such a "cage" compound. Bond distortions of this magnitude are not unusual; the formation of three and four-membered carbon rings involves distortions considerably greater in magnitude. Consequently, the preparation of a cage ester from trimethylolpropane and boric acid (IV, R = C_2H_5) was undertaken.



III



IV

The selection of this substance for detailed study was prompted by both practical and theoretical reasons. First, the borate esters of higher alcohols are easily prepared by merely heating together the corresponding alcohol and boric acid.[7] Second, such borate esters are readily handled in the open air with only simple precautions against moisture, whereas the organoborons are spontaneously inflammable and must be handled in inert atmospheres. Third, trimethylolpropane is easily available as a commercial product. Finally, the properties of such a "cage" compound should not only shed light on the properties of planar boron but should also permit a test of a reasonable explanation for the weakness of boric acid esters as Lewis acids.

When an equimolar mixture of trimethylolpropane and boric acid is heated under vacuum, water is evolved. Although the last fraction of water is lost only with difficulty, the calculated quantity can be removed, leaving a non-volatile product in the reaction flask whose composition is in agreement with that calculated for an ester, $[C_2H_5C(CH_2O)_3B]_x$.

The properties of the product are variable and depend on the duration and temperature of the reaction. The material is polymeric. If the temperature of an equimolar mixture is rapidly raised to 200°, a glassy product is obtained which contains 7.42% boron instead of the 7.62% calculated for complete esterification. If an equimolar mixture of the two components is maintained for an extended period, 20 hours, at a relatively low temperature, 120°, the product is a white solid. This material contains 7.37% boron, possesses a molecular weight of 550–600, and melts in the range 202–205°.

Application of the Dupire procedure,[8] azeotropic distillation of water at relatively low temperatures, yields a rubbery white material, soluble in both acetone and benzene. After several hours at room temperature this rubbery material changes to a hard solid insoluble in these solvents. This solid contains 6.87% boron, melts at 196–199° and exhibits a molecular weight of 550.

Experiments were carried out to follow the changes in composition, molecular weight and properties as an equimolar mixture of the two reactants is heated at gradually increasing temperatures. In such experiments, it was observed that the product is initially a white solid with a molecular weight in the neighborhood of 350–400, as contrasted with a value of 142 calculated for the monomeric ester. With further increase in temperature, the product becomes glassy in appearance, the theoretical amount of water is removed, and the per cent. boron in the product corresponds to the value calculated for complete esterification. At this point the molecular weight of the product is in the neighborhood of one thousand. The results of a typical study are summarized in Table I.

TABLE I

PROPERTIES OF THE REACTION PRODUCT OF TRIMETHYLOLPROPANE AND BORIC ACID

Temp., °C.	Mol. wt.	Boron, %	M.p., °C.
60	Two phase system		
100	350–400	6.4	120–140
140	550–600	6.3[a]	132–155
225	600–650	7.4	Glass
270	940	7.69[b]	Glass

[a] The low value is believed to be due to the distillation to the core of the reaction mixture of material of low boron content. The experimental set-up made it necessary to sample the product at the core. [b] Calculated for complete esterification, 7.62%.

From these experiments it appears that the strain involved in forcing the normally planar boron atom into the tetrahedral configuration required by the geometry of the "cage" is too great to permit its formation. Instead, there result relatively strain free polymeric products in which each triol unit is bonded to two, or perhaps three, different boron atoms.

It has been shown that polymeric esters, products which consist of many units held together by easily interchanged ester linkages, can be depolymerized to monomeric rings under conditions which allow the monomer to be distilled away, *i.e.*, under conditions of high temperature and low pressure.[9] However, all attempts to obtain the monomer by heating the polymeric product in a molecular still, at temperatures as high as 270° and pressures as low as 10^{-3} mm., were unsuccessful. Since boric acid esters are exceedingly readily interconvertible, this result indicates that the energy of the "cage" ester must be very much higher than the energy of the polymeric ester. An estimate of the energy may be readily made.

Assume that there is an equilibrium between polymer and monomer

$$1/n[C_2H_5C(CH_2O)_3B]_n \rightleftarrows C_2H_5C(CH_2O)_3B$$

If N_1 and N_2 represent the mole fraction of polymer and monomer, respectively, then

$$K_D = N_2/(N_1)^{1/n}$$

Since N_2 must be very small, N_1 is essentially unity, and the expression may be simplified to

$$K_D = N_2$$

By analogy with other "cage" compounds, the monomeric ester would be expected to have a normal boiling point in the neighborhood of 180°. The molar heat of vaporization may be estimated from the Trouton rule to be approximately 9500 calories, leading to a vapor pressure at 270° of approximately 5000 mm. Since no monomeric product distilled

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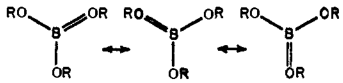
[7] J. R. Johnson and S. W. Tompkins, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 106.

[8] A. Dupire, *Compt. rend.*, **202**, 2086 (1936).

[9] J. W. Hill, THIS JOURNAL, **52**, 4110 (1930); W. H. Carothers, *ibid.*, **52**, 3292, 3470 (1930); **54**, 761 (1932).

from the reaction mixture at 10^{-3} mm. and 270°, the mole fraction of the monomer present in the reaction mixture, N_2, must be less than $10^{-3}/5 \times 10^3 = 2 \times 10^{-7}$. Therefore, $K_n < 2 \times 10^{-7}$ and $\Delta F° > +16$ kcal. The quantity 16 kcal. represents the lowest possible value for the free energy of formation of monomer from polymer, within the limits of the assumptions and approximations made.

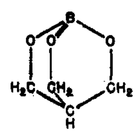
This difference in energy between the monomeric "cage" compound and the polymeric ester is exceedingly large, much larger than would have been anticipated from the relatively small distortion of the bonds. However, there is evidence that the boron–oxygen bonds in borate esters have considerable double-bond character. Such esters are considered to be hybrids of resonance structures, such as V.[10]


V

The resonance energy must greatly stabilize the borate esters, since these esters do not combine with weak organic bases such as pyridine, whereas trialkylborons readily react with amines. In the absence of resonance, the borate esters would be expected to be considerably stronger Lewis acids than the trialkylborons in view of the +I effect of alkyl groups and the −I effect of alkoxyl groups.

A rough estimate of the minimum energy involved in such resonance may be made. The heat of reaction of gaseous trimethylboron with gaseous pyridine is 17 kcal.[11] No heat is involved upon mixing tri-*n*-butyl borate and pyridine in a dewar vessel. Therefore, the resonance energy must be greater than 17 kcal. per mole.

Similar resonance structures containing double-bonds at the bridgehead (VI) would involve a violation of Bredt's rule.[12] Therefore, formation of the "cage" ester would involve not only the energy required to distort three single bonds, but also the almost complete loss of the resonance energy of borate esters. In view of the probable magnitude of these factors, the difficulties encountered in the attempted synthesis of the monomeric cage ester are not unreasonable.


VI

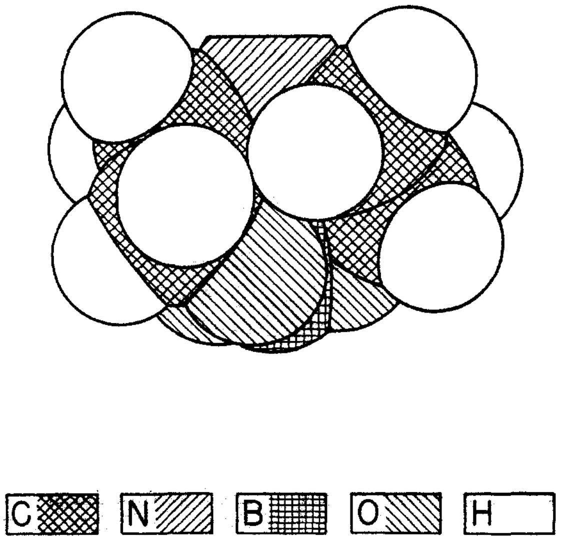


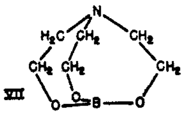
Fig. 1.—Molecular model of triethanolamine borate, "cage" structure.

Triethanolamine Borate

In contrast to the difficulties encountered with trimethylolpropane, triethanolamine reacts easily and smoothly with boric acid. The theoretical quantity of water is lost at a relatively low temperature, 150°. The product is a white, crystalline solid which can be readily purified either by vacuum sublimation or by recrystallization from acetonitrile. The crystals melt at 236.5–237.5°. Analysis and molecular weight correspond to the monomer. There can be little doubt that the reaction has proceeded in accordance with the equation

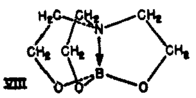
$$N(CH_2CH_2OH)_3 + (HO)_3B \longrightarrow N(CH_2CH_2O)_3B + 3H_2O$$

Two reasonable structures for the product must be considered. One is a "cage" structure (VII, Fig. 1).


VII

Here each of the three rings constituting the "cage" contains eight members. It is, therefore, not unreasonable that the planar boron atom might be accommodated with relatively little strain. Moreover, Prelog has recently demonstrated that violation of Bredt's rule is possible in rings of 8 members.[13]

In the second structure (VIII, Fig. 2), a nitrogen-boron bond is present and the boron has assumed the tetrahedral configuration.


VIII

Although this structure is relatively strain-free, the objection is pertinent that amines do not coördinate with boron in boric acid esters. Such coördination would require loss of the resonance energy.

For convenience in the following discussion, we will refer to VII as the "cage" structure of the ester and to VIII as the "triptych" structure. Evidence in support of the "triptych" structure was obtained through a study of reactions of the ester involving the lone pair of the nitrogen atom.

It had been previously demonstrated that cage amines, such as quinuclidine (II, Fig. 3) with nitrogen at the bridgehead, react much more rapidly

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[10] L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 211; S. H. Bauer and J. Y. Beach, THIS JOURNAL, **63**, 1394 (1941).

[11] H. C. Brown and G. K. Barbaras, *ibid.*, **69**, 1137 (1947).

[12] J. Bredt, H. Thiuet and J. Schmitz, *Ann.*, **437**, 1 (1928).

[13] V. Prelog, L. Ruzicka, P. Barman and L. Frenkiel, *Helv. Chim. Acta*, **31**, 92 (1948); V. Prelog, P. Barman and M. Zimmermann, *ibid.*, **32**, 1284 (1949).

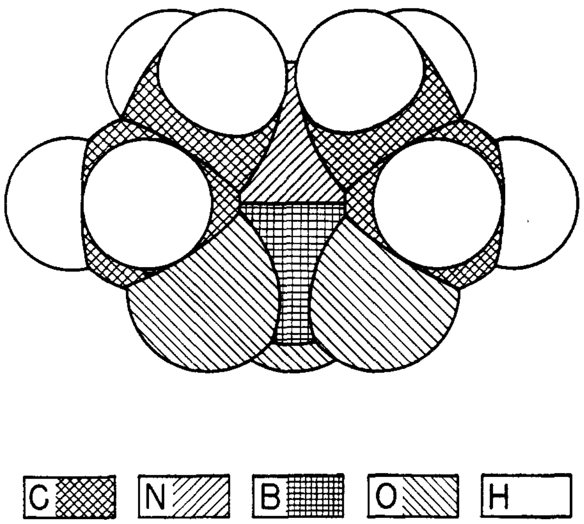

Fig. 2.—Molecular model of triethanolamine borate, "triptych" structure.

with alkyl halides than do open-chain amines, such as triethylamine.[14] The marked difference in rate is attributed to low steric interference by the "cage" structure with the approach of the alkyl halide to the nitrogen atom. Such interference is believed to be a major factor in the corresponding reactions of amines such as triethylamine.

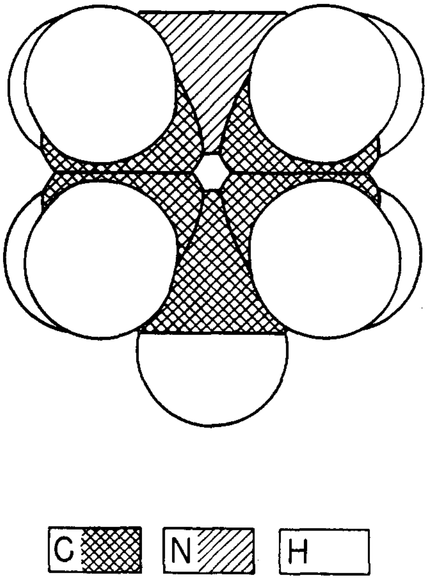

Fig. 3.—Molecular model of quinuclidine.

Accordingly, it may be postulated that the cage structure (VII) should react more readily with alkyl halides than the open-chain amine, triethanolamine itself. On the other hand, in the triptych structure (VIII), the nitrogen atom no longer possesses a lone pair of electrons. Such a structure should react exceedingly slowly, if at all.

A study was, therefore, made of the rates of reaction of methyl iodide with triethanolamine and triethanolamine borate at a number of temperatures. Acetonitrile was used as solvent. The results are summarized in Table II.

TABLE II

RATE DATA FOR THE REACTIONS OF TERTIARY AMINES WITH METHYL IODIDE IN ACETONITRILE

Amine	Temp., °C.	Rate constant, k_2, l. mole^{-1} sec.$^{-1}$	Activation energy, kcal.	log *PZ*
Triethanolamine	25	1.51×10^{-4}	13.0	5.71
	40	4.32×10^{-4}		
	55	11.16×10^{-4}		
Triethanolamine borate	25	8.57×10^{-8}	18.5	6.51
	40	3.70×10^{-7}		
	60	2.29×10^{-6}		
Pyridine	25	3.95×10^{-4}		
Triethylamine[a,b]	25	3.29×10^{-2}	9.7	5.65
Quinuclidine[a,b]	25	1.88	9.5	
Pyridine[a,c]	25	3.43×10^{-4}	13.6	6.50

[a] These values were determined in nitrobenzene solution. The rate of reaction in acetonitrile is slightly greater than in nitrobenzene. Thus, the specific rate constant for the reaction of pyridine with methyl iodide at 25° is 3.95×10^{-4} in acetonitrile as compared with the value 3.43×10^{-4} in nitrobenzene. A similar slight solvent effect is noted in the reaction between triethylamine and ethyl iodide in acetonitrile and nitrobenzene, the constants being, respectively, 2.00×10^{-4} and 1.82×10^{-4}, at 25°. [b] Ref. 12. [c] Laidler and Hinshelwood, *J. Chem. Soc.*, 852 (1938).

Both compounds react by second order kinetics, but the reaction of triethanolamine borate is very much slower than the corresponding reaction of triethanolamine. At 25° the reaction proceeds at only 1/1700 the rate of the reaction of the open chain amine. This difference is strikingly shown in Fig. 4 where the slope of each line represents the second order constant. Moreover, the energy of

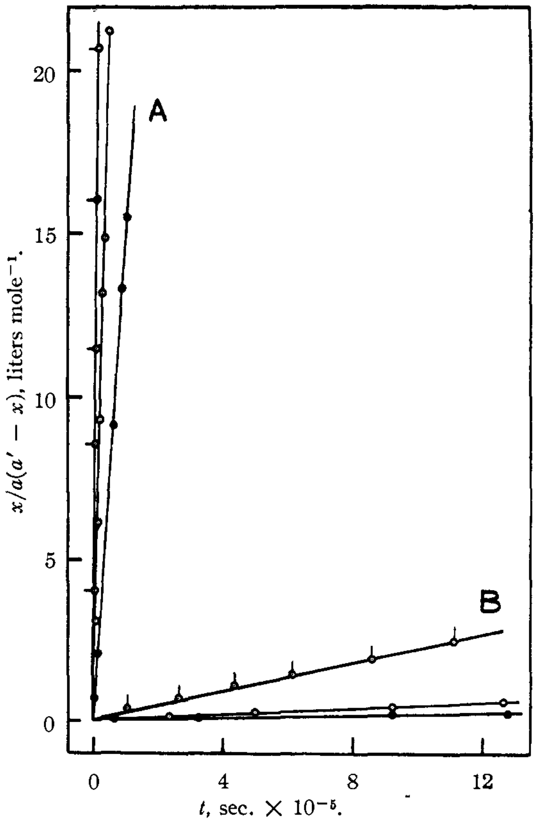

Fig. 4.—Reaction of methyl iodide with triethanolamine (A) and triethanolamine borate (B): T = 25° ●, 40° ○, 55° -○, 60° ○̍.

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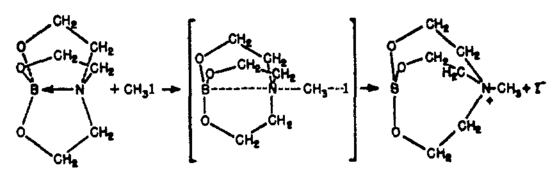
(14) H. C. Brown and N. Eldred, THIS JOURNAL, **71**, 445 (1949).

activation for the borate reaction is about 6 kcal. higher than that for the amine reaction. These results appear to eliminate the cage structure and favor the triptych structure.

This conclusion is strongly supported by observations on the reaction of triethanolamine borate with strong acids. Simple amines having a free "lone pair" react instantaneously with strong acids and can be titrated in aqueous and non-aqueous solvents with a wide variety of acids. Thus triethanolamine is easily titrated with hydrochloric acid in water, with perchloric acid in glacial acetic acid or with methanesulfonic acid in nitrobenzene. Similar attempts to titrate triethanolamine borate revealed that the reaction takes place at a slow measurable rate. In water the energy of activation for the neutralization is 14.2 kcal.; the rate is independent of acid concentration.

It is apparent that in water this slow neutralization might be the result of a slow rate-determining hydrolysis of the ester. Accordingly, a study was made of the rate of neutralization of the ester by methanesulfonic acid in nitrobenzene under strictly anhydrous conditions. Here the rate of neutralization of the ester was much slower than in water. At 25° a solution which was 0.025 *M* in triethanolamine borate and methanesulfonic acid required 32.5 minutes for 50% neutralization. Attempts were made to determine the order of the neutralization reaction in nitrobenzene. Preliminary studies pointed to a reaction first order in amine and independent of acid concentration. More detailed studies revealed that the kinetics are more complex and will probably require an extensive study for full clarification. This phase of the problem was necessarily deferred for later investigation.

In the case of the reaction of methyl iodide with triethanolamine borate, the reaction shows simple second order kinetics. It is of interest to examine possible mechanisms for the reaction which are consistent with these kinetics. Two mechanisms appear feasible. The first would involve a direct attack of the methyl iodide on the nitrogen atom. Such a mechanism would require the reaction to be first order with respect to both amine and methyl iodide.

IX 

This mechanism would be an example of an electrophilic attack on a tetrahedral atom. The possibility of such reactions has often been postulated,[15] but has never been definitely demonstrated.

In the present case an alternative mechanism, involving prior breaking of the boron-nitrogen bond, is also consistent with the kinetics. Using the symbols T and C to refer to the triptych and cage structures, respectively, we have,

$$\mathrm{T} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{C} \qquad (1)$$

$$\mathrm{C} + \mathrm{MeI} \xrightarrow{k_2} \mathrm{CMe}^{+}\mathrm{I}^{-} \qquad (2)$$

The mechanism leads to the kinetic expression

$$\text{rate} = \frac{k_1k_2[T][\mathrm{MeI}]}{k_2[\mathrm{MeI}] + k_{-1}}$$

If $k_{-1} >> k_2[\mathrm{MeI}]$, that is, if the rate constant for the reverse reaction is greater than the rate of reaction of the amine with methyl iodide, the kinetic expression becomes

$$\text{rate} = \frac{k_1k_2}{k_{-1}}[T][\mathrm{MeI}]$$

Both mechanisms presented are, therefore, consistent with the observed kinetics and it is imposrsible at this time to decide between them. Furthe- study of the reactions of triethanolamine borate is planned in the hope of obtaining evidence as to the possible existence of electrophilic displacement reactions on tetrahedral atoms.

Experimental Part

Molecular Weights.—Molecular weights were determined ebulliometrically with a Washburn and Read apparatus equipped with a Cottrell pump.[16] Pyridine dried with calcium hydride was used as the solvent. The ebullioscopic constant was taken as 2.687°/mole.[17]

Pyridine and *n*-Butyl Borate.—Equimolar quantities (0.3 mole) of pyridine and *n*-butyl borate were mixed in a half-pint dewar at room temperature, 24.4°. There was no thermal evidence for a reaction. The temperature dropped to 21.9° on mixing and then slowly approached room temperature asymptotically.

Trimethylolpropane Borate.—The triol was obtained from the Heyden Chemical Company and was purified by recrystallization from acetone and ether, m.p. 57–59°. Baker C.P. boric acid was used directly. In a typical preparation, 44.9 g. (1/3 mole) of the triol and 20.2 g. (1/3 mole) of boric acid were intimately mixed in a 500-ml. round-bottom flask. The flask was evacuated to 1 mm. and the temperature was slowly raised. After 20 hours, 17.3 g. of water (96% of the theoretical) had been lost. The product was a white solid, m.p. 202–207°. It contained 7.37% boron and exhibited a molecular weight of 629 (average value for seven determinations with individual values ranging from 587 to 668).

Triethanolamine Borate.—Triethanolamine (Carbide and Carbon Co., technical grade) was purified by vacuum distillation, b.p. 198–199.5° (8.2 mm.). Equimolar amounts of triethanolamine and boric acid, 56.2 and 23.3 g., respectively, were mixed in a 250-ml. round-bottom flask and subjected to slow evacuation to less than 1 mm., followed by gradual elevation of the temperature. Of the calculated 20.3 g. of water which should be evolved for complete esterification, 1.6 g. (7.9%) was evolved in one hour at room temperature; 13 g. (64%) was evolved after 4 more hours as the temperature was slowly raised to 96°. During the next 1.5 hours the temperature was raised rapidly to 155°, by which time 16.8 g. (83%) of the water had been lost. Finally, after 3.5 hours at 150–155°, 19.6 g. (96.6%) of water had been evolved.

The crude product was purified either by recrystallization from acetonitrile or by sublimation at 200° at reduced pressures. Yields of pure material, based on crude, were 65–74%. The purified product melted at 233.5–235°. Repeated recrystallizations from pyridine gave a product melting at 236.5–237.5°.

The product is soluble in acetonitrile, pyridine, water, alcohols, acetic acid and nitrobenzene, and insoluble in benzene, carbon tetrachloride and tetrahydrofuran. *Anal.* Calcd. for $C_6H_{12}O_3BN$: C, 45.90; B, 6.89; N, 8.92; mol. wt., 156.96. Found: C, 46.0; B, 6.82; N, 9.10; mol. wt., in acetonitrile, 150, in pyridine, 152.

Neutralization of Triethanolamine Borate by Strong Acids.—Addition of small amounts of acid to freshly prepared

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[15] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935); C. L. Arcus, A. Campbell and J. Kenyon, *Nature*, **163**, 287 (1949); *J. Chem. Soc.*, 1510 (1949).

[16] E. W. Washburn and J. W. Read, THIS JOURNAL, **41**, 729 (1919).

[17] A. L. Van Scherpenberg, *Rec. trav. chim.*, [3] **35**, 346 (1915).

solutions of triethanolamine borate in water results in an immediate change of the indicator to its acid color, followed by slow neutralization and return of the solution to the basic side. The amount of acid required for complete neutralization approaches the stoichiometric value asymptotically. The rate of the reaction was determined from the half-time. In one determination, for example, 25 ml. water, one-half of a stoichiometric amount of hydrochloric acid, and 2 drops modified methyl orange were placed in a 250-ml. beaker. A capsule containing a standard solution of borate in acetonitrile was then smashed in the beaker, and the mixture was stirred. The time interval between the rupture of the capsule and the color change of the indicator was taken as the half-time of the reaction. In a series of such runs, the half-times were independent of the initial concentrations of reactants; the rate is independent of the acid concentration. Data are given in Table III.

TABLE III

RATES OF NEUTRALIZATION OF TRIETHANOLAMINE BORATE BY HYDROCHLORIC ACID AT 25° AND 0°

Initial concentrations of reactants, mole/l. Triethanolamine borate	Hydrochloric acid	Half-time at 25°, sec.	Rate constant, k_1, at 25° sec.$^{-1}$ × 10^3	Half-time at 0°, sec.	Rate constant, k_1, at 0° sec.$^{-1}$ × 10^4
0.0357	0.0179	181	3.83	1680	4.13
.0241	.0121	184	3.77	1624	4.27
.0182	.0091	187	3.71	..	..

In glacial acetic acid, perchloric acid gives similar results. Crystal violet was used as indicator. The half time for this reaction at 25° was also determined and found to be 220 sec., $k_1 = 3.15 \times 10^{-3}$ sec.$^{-1}$.

The neutralization of the amine in nitrobenzene by methanesulfonic acid proceeded much more slowly. The reaction did not exhibit simple kinetics and will be investigated further.

Rates and Activation Energies in the Menschutkin Reaction.—Acetonitrile was used as the solvent. Equal amounts of equimolar solutions of the reactants were mixed at 25°. Samples were pipetted into thin-walled glass capsules. The sealed capsules were placed in a constant temperature bath (±0.01°). At appropriate intervals a capsule was removed from the bath, broken under dilute sulfuric acid and titrated for iodide ion. The rate constants were calculated by utilizing the integrated rate expression for a second order reaction. Rate data for a typical determination are given in Table IV.

TABLE IV

RATE OF REACTION OF TRIETHANOLAMINE WITH METHYL IODIDE AT 40°[a]

Time, sec.	Ml. $AgNO_3$, x	Rate constant,[b] k_2 l./mole sec. × 10^4	Reaction, %
7200	1.54	4.39	13.1
14400	2.68	4.29	22.7
21600	3.59	4.27	30.5
28800	4.35	4.28	36.9
36000	4.89	4.15	41.5
40920	5.34	4.26	45.3
	$11.78 = a^1$	..	..

[a] Initial concentration of reactants at zero time, a, was 0.04756 M at 40°. Each capsule contained 5.08 ml. of solution (corrected for change in volume with increase in temperature). [b] Rate constants calculated from expression $k = \frac{1}{ta}\left(\frac{x}{a^1 - x}\right)$ where x and a^1 are expressed in ml. of silver nitrate solution.

The triethanolamine for rate determinations was purified by vacuum distillation, b.p. 204° at 12.5 mm., followed by recrystallization from acetone. The highest freezing point observed was 21.15°. It was found that triethanolamine which was purified merely by distillation did not give good second order constants. The material probably contained some secondary amine although the boiling point was essentially constant. The impurity was not identified.

The rates with triethanolamine borate were determined in the same general way. These rates were extremely slow, however, proceeding at 25° to the extent of only about 8% in one month. Thus, the precision of the individual points in these runs left much to be desired. Nevertheless, fairly consistent values could be obtained by the application of the least squares method to the data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Concerted Displacement Reactions. VI. *m*- and *p*-Substituent Effects as Evidence for a Unity of Mechanism in Organic Halide Reactions(1)

BY C. GARDNER SWAIN AND WILLIAM P. LANGSDORF, JR.

The value of the Hammett reaction constant (ρ), which expresses the sign and magnitude of *m*- and *p*-substituent effects, is found to depend, in a predictable way, on four factors: the structure of the substituent, the structure of the halide, the structure of the electrophilic reagent, and the structure of the nucleophilic reagent. The solvent is relatively unimportant unless it functions in the role of either electrophilic or nucleophilic reagent. Tables are given which permit one to predict in what direction ρ will change with a given change in any of these four factors. The variation in ρ is evidence against sharply differentiated mechanistic categories, and indicates that one mechanism or interpretation is adequate for most reactions of organic halides.

The most successful quantitative correlation between the structure of chemical compounds and the rates of their reactions is the Hammett equation, which expresses the effect of *m*- and *p*-substituents in compounds containing a phenyl group.[2]

$$\log (k/k_0) = \rho\sigma$$

Here k and k_0 are corresponding rate constants with and without any substituent, ρ is a constant characteristic of the reaction and σ is a constant characteristic of the substituent.[3]

Although the reaction constant, ρ, has been tabulated for 41 different series of reactions, it is

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(1) Supported in part by a du Pont grant in aid of fundamental research. Paper presented in part at the Conference on Organic Reaction Mechanisms, Gordon Research Conferences, A. A. A. S., Colby College, N. H., July 7, 1948. For previous papers in this series, see THIS JOURNAL, **70**, 1119, 2989 (1948); **71**, 965 (1949); **72**, 2794, 4578 (1950).

(2) (a) Hammett, THIS JOURNAL, **59**, 96 (1937); (b) "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

(3) By 1940 this equation served to correlate the rates of 1763 reactions. With the 332 of these which had been measured experimentally up to that time the median deviation between calculated and observed rates was only ±15%, in spite of the fact that the variation in rate on changing from a *p*-methoxy to a *p*-nitro substituent averaged thirty-fold and exceeded a thousand-fold in several series.