(the data are summarized below). Cuts 53 through 147 were combined to give 0.23 g. of secondary alcohol, $[\alpha]^{24}D$ $-12.00°$ ($c$ 5, $CHCl_3$). Cuts 154 and 155 were combined to give 0.25 g. of tertiary alcohol, $n^{25}D$ 1.5026, $[\alpha]^{24}D$ $-0.21°$ ($c$ 5, $CHCl_3$).

LOS ANGELES 24, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

# Stereochemistry of the Primary Carbon. VI. The Reaction of Optically Active 1-Aminobutane-1-*d* with Nitrous Acid. Mechanism of the Amine–Nitrous Acid Reaction[1]

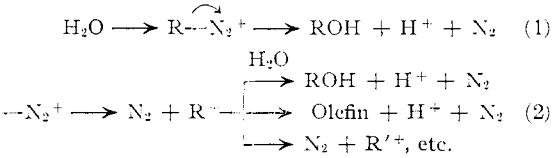
BY ANDREW STREITWIESER, JR., AND WILLIAM D. SCHAEFFER[2,3]

RECEIVED OCTOBER 2, 1956

The reaction of *n*-butylamine with sodium nitrite in acetic acid gives a mixture of esters in which the ratio of *n*-butyl acetate to *sec*-butyl acetate is 2:1 and a small amount of alkyl nitrates. The 1-butyl-1-*d*-acetate obtained from optically active 1-aminobutane-1-*d* is 69 ± 7% inverted, 31 ± 7% racemized. A mass spectral investigation of the product from 1-aminobutane-1,1-$d_2$ shows that 0% ethyl rearrangement occurs. These results in conjunction with other data lead to a complete theory for the product-determining steps of the amine–nitrous acid reaction. The fundamental tenet of this hypothesis is that the alkyldiazonium ion, the last *common* intermediate in the reaction, can undergo a number of competing reactions because of its great instability.

## Introduction

Since the first example of Piria[4] and the later extended investigations of Linnemann[5] the reaction of aliphatic primary amines with nitrous acid has been used extensively in preparative and theoretical organic chemistry. In aqueous solution, the reaction generally produces alcohols and olefins, frequently with rearrangement. Although the kinetics of the reaction has been investigated[6] it pertains only to the initial phase of the reaction of the amine with a nitrous acid moiety; the product-determining steps occur later in the reaction sequence and are not amenable to direct kinetic approaches. Analogy to the aromatic series strongly suggests that diazonium ions are intermediates in the reaction.[7] The nature of the reaction products and particularly the similarity of the many rearrangement products to products of typical carbonium ion reactions have led to the interpretation of the product-determining steps of the amine–nitrous acid reaction in terms of solvolytic displacement reactions. The commonly accepted mechanism of the reaction is a competing direct displacement (SN2) on the alkyldiazonium ion by solvent (reaction 1) and a unimolecular fission of the diazonium ion (SN1) to a carbonium ion which subsequently may react with solvent to form product, eliminate a proton to yield olefin or rearrange a hydrogen or a carbon function to a new carbonium ion which ultimately results in products of such rearrangement (reaction 2).[8-11]



$$H_2O \longrightarrow R\text{---}N_2^+ \longrightarrow ROH + H^+ + N_2 \quad (1)$$

$$R\text{---}N_2^+ \longrightarrow N_2 + R^+ \left\{ \begin{array}{l} \xrightarrow{H_2O} ROH + H^+ + N_2 \\ \longrightarrow \text{Olefin} + H^+ + N_2 \\ \longrightarrow N_2 + R'^+, \text{etc.} \end{array} \right. \quad (2)$$

In several cases the experimental observations are in accord with this hypothesis; *e.g.*, the reactions with aqueous nitrous acid of crotylamine, $\alpha$-methylallylamine, $\alpha,\alpha$-dimethylallylamine and $\gamma,\gamma$-dimethylallylamine yield, respectively, the same mixtures of isomeric allylic alcohols as the silver ion-catalyzed aqueous solvolyses of the corresponding chlorides[12,13]; cyclopropylcarbinylamine and cyclobutylamine on treatment with aqueous nitrous acid give similar mixtures of cyclobutanol, cyclopropylcarbinol and allylcarbinol.[12] However, in some other examples, this interpretation is clearly not a happy one. *n*-Propyl-, *n*-butyl- and *n*-amylamines, etc., give rather large amounts of secondary carbinol, the product of a rearrangement.[5,b,c,f,14] In solvolytic displacement reactions, rearrangement of *n*-primary to second-

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[1] Paper V, A. Streitwieser, Jr., and J. R. Wolfe, Jr., THIS JOURNAL, **79**, 903 (1957).

[2] Taken in part from the dissertation submitted by W.D.S. in partial fulfillment for the degree of Doctor of Philosophy, University of California, June, 1956.

[3] General Electric Fellow, 1955–1956.

[4] R. Piria, *Ann. chim. phys.*, [3] **22**, 173 (1848).

[5] (a) E. Linnemann, *Ann.*, **144**, 129 (1867); (b) A. Siersch, *ibid.*, **144**, 137 (1867); (c) E. Linnemann and V. v. Zotta, *ibid.*, **161**, 43 (1871); (d) **162**, 3 (1872); (e) E. Linnemann, *ibid.*, **162**, 12 (1872); (f) *Ber.*, **10**, 1111 (1877).

[6] T. W. J. Taylor, *J. Chem. Soc.*, 1099, 1897 (1928); T. W. J. Taylor and L. S. Price, *ibid.*, 2052 (1929); J. H. Dusenbury and R. E. Powell, THIS JOURNAL, **73**, 3269 (1951); A. T. Austin, E. D. Hughes, C. K. Ingold and J. H. Ridd, *ibid.*, **74**, 555 (1952); R. H. Sahasrabudey, R. Singh and Vasundhara, *J. Indian Chem. Soc.*, **31**, 69 (1954); the subject has been reviewed recently by J. C. Earl, *Research*, **3**, 120 (1950).

[7] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 295

[8] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 397; (b) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 210; (c) P. H. Hermans, "Theoretical Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1954, p. 246; (d) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1954, p. 226.

[9] F. C. Whitmore, THIS JOURNAL, **54**, 3281 (1932).

[10] P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold and P. A. D. S. Rao, *Nature*, **166**, 179 (1950).

[11] W. G. Young and R. H. DeWolfe, *Chem. Revs.*, **56**, 753 (1956).

[12] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951).

[13] W. G. Young and C.-H. Shih, unpublished results; *cf.* ref. 11.

[14] (a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934); (b) V. Meyer and F. Forster, *Ber.*, **9**, 535 (1876); (c) V. Meyer, J. Barbieri and F. Forster, *ibid.*, **10**, 130 (1877); (d) P. C. Rây and J. N. Rashkit, *J. Chem. Soc.*, **101**, 141 (1912); (e) J. D. Roberts and M. Halmann, THIS JOURNAL, **75**, 5759 (1953); (f) F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932); (g) F. C. Whitmore and R. S. Thorpe, *ibid.*, **63**, 1118 (1941).

ary compounds is observed only by the action of strong Lewis acids; *e.g.*, Friedel–Crafts reactions with aluminum halides and alkyl halides or with boron trifluoride and alcohol. These conditions are such that either the carbonium ion intermediate is formed repeatedly or the reactivity of the nucleophilic reagent is so low that reaction with the carbonium ion is slower than the rearrangement. These conditions are not likely to be met in aqueous nitrous acid. Moreover, in the reaction of optically active secondary carbinylamines, the product alcohol possesses some optical activity.[10,15] There is an apparent inconsistency in the interpretation of the net inversion of configuration observed as resulting from direct displacement by solvent (reaction 1) for the reaction of *sec*-butylamine with nitrous acid in water yields 2-butanol with 22% net inversion although in the far less nucleophilic solvent, acetic acid, 2-butyl acetate is formed with 28% net inversion.

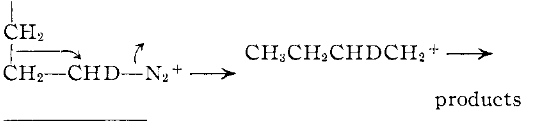
In order to specify in more detail these difficulties of the accepted mechanism, we chose to investigate the stereochemistry of a simple system in which partial rearrangement is known to occur.

## Results

Treatment of a solution of *n*-butylamine in 1 *N* hydrochloric acid with sodium nitrite is reported to yield a mixture of 25% 1-butanol, 13% 2-butanol, 5% *n*-butyl chloride, 3% *sec*-butyl chloride, 36% butenes and a trace of butyl nitrites.[14f] The reaction of *n*-butylamine with sodium nitrite in acetic acid yields butenes and a mixture of *n*-butyl acetate and *sec*-butyl acetate which contains 4–8% of butyl nitrates. Reduction of this mixture with lithium aluminum hydride yields a mixture of 65% 1-butanol and 35% 2-butanol. The ratio of primary to secondary products in acetic acid is virtually identical to that found by Whitmore and Langlois[14f] in water.

Optically active 1-aminobutane-1-*d* has been described previously.[16] The 1-butyl-1-*d* acetate obtained by treatment with sodium nitrite in acetic acid corresponded to 69 ± 7% net inversion of configuration.[17] This result is remarkably similar to that obtained from *sec*-butylamine (*vide supra*).

Roberts and Halmann[14e] have reported that the *n*-propyl alcohol obtained by treatment of *n*-propylamine with nitrous acid has undergone 8.5% of methyl group rearrangement. It was necessary to establish whether an ethyl group rearrangement in the *n*-butyl case contributed importantly to the racemization observed, *e.g.*, reaction 3. 1-Aminobutane-1,1-$d_2$[16] was treated with sodium nitrite in acetic acid and the resulting mixture of esters was converted to alcohols. The primary alcohol obtained by fractionation was compared mass spectrographically with the 1-butanol-1,1-$d_2$ used to prepare the amine. Rearrangement of an ethyl group would produce 1-butanol-2,2-$d_2$ which could be detected easily in the mass spectrum, even in rather small amount. The analysis of the cracking patterns (see Appendix) indicated that none of the rearranged alcohol was present, hence 0% ethyl rearrangement had taken place in the amine–nitrous acid reaction.



$$\mathrm{CH_3CH_2CH_2{-}CHD{-}N_2^+} \longrightarrow \mathrm{CH_3CH_2CHDCH_2^+} \longrightarrow \text{products} \quad (3)$$

It is unlikely that a significant amount of the observed racemization was due to the formation of a diazoalkane which had reacted with solvent to give racemic acetate. This reaction has been shown to be of minor importance with ethylamine[18] and is undetectable with allylic amines.[19] The mass spectral investigation of the product from 1-aminobutane-1,1-$d_2$ establishes that diazoalkane formation accounts for no more than about 1% of the reaction (see Appendix).

## Discussion

The present stereochemical results may be compared with the results of some typical solvolyses. The acetolysis of 1-butyl-1-*d* *p*-nitrobenzenesulfonate at 114° yields 1-butyl-1-*d* acetate with 85 ± 2% net inversion. In 90% nitrobenzene–10% acetic acid at 91° the product shows 59 ± 2% net inversion and in 75% dioxane–25% acetic acid at 97°, 46 ± 2% inversion.[20] In all of these cases the amount of racemization observed is comparable to that observed in the corresponding amine–nitrous acid reaction and probably is due to the intervention of intermediates of the carbonium ion type[21]; yet, *in all of these solvolyses, no trace of rearrangement to sec-butyl compounds could be detected.* It follows that the product-determining intermediates in the amine–nitrous acid reaction must differ at least in part from the intermediates in the sulfonate acetolyses. The same conclusion may be derived from the observation that the composition of the butene mixture obtained from the reaction of *sec*-butylamine differs from that obtained by solvolysis of *sec*-butyl tosylate (*vide infra*).

If the racemized product in the acetolyses of 1-butyl-1-*d* *p*-nitrobenzenesulfonate arises from a carbonium ion intermediate which has lost asymmetry, it follows that the reaction of this intermediate with acetic acid must be considerably more rapid than a rearrangement to a secondary carbonium ion; *i.e.*, the free energy of activation for rearrangement is significantly higher than that for solvolysis. It also follows that a concerted rearrangement and expulsion of the leaving group, reaction 4, also requires considerably more energy than the direct formation of a primary carbonium ion.

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(15) K. B. Wiberg, Dissertation, Columbia University, July, 1950.

(16) A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **78**, 5597 (1956).

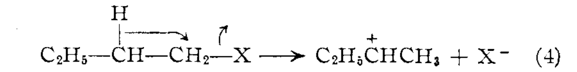
(17) This number is obtained by a direct comparison of the rotation of the product acetate with that of acetate prepared from a sample of the same 1-butanol-1-*d* from which the amine was prepared. As discussed in the earlier paper[16] the latter preparation probably went with a single inversion of configuration and no racemization.

(18) J. D. Roberts and J. A. Yancey, THIS JOURNAL, **74**, 5943 (1952).

(19) W. G. Young and D. Semenow, unpublished results; *cf.* ref. 11.

(20) A. Streitwieser, Jr., and W. D. Schaeffer, Absts. of the 129th Meeting of the American Chemical Society, Dallas, Texas, April 13, 1956, p. 52N, and unpublished results.

(21) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).



$$C_2H_5\text{—}\overset{H}{C}H\text{—}CH_2\text{—}X \longrightarrow C_2H_5\overset{+}{C}HCH_3 + X^- \quad (4)$$

In the reaction of *n*-butylamine with nitrous acid, if the *sec*-butyl products obtained are due to a process such as reaction 4 ($X = N_2^+$), it follows that the difference in free energies of activation between this process and the formation of a primary carbonium ion is much smaller than the corresponding difference in sulfonate solvolysis. To account for this change, we propose the following theory for the course of the product-determining steps in the amine–nitrous acid reaction.

Diazonium ions on the whole are rather unstable; because of the stability of the nitrogen molecule, the decomposition of an alkyldiazonium ion into nitrogen and a carbonium ion undoubtedly does not have high energy requirements and, indeed, may even be somewhat exothermic.[22] The activation energy is correspondingly rather small, perhaps of the order of 3–5 kcal./mole, compared to the corresponding dissociation of a primary alkyl sulfonate into carbonium ions for which the activation energy is about 30 kcal./mole.

*The transition state for the decomposition of an alkyldiazonium ion more closely resembles the reactant than does the transition state for solvolysis of an alkyl sulfonate.*[23] Correspondingly, the scale of energy differences for competing reactions would reasonably be expected to be compressed. Consider the following example (Fig. 1) of a system in which a competing concerted rearrangement (A′) requires 5 kcal./mole more energy than a "normal" solvolysis (A) having an activation energy of 25 kcal./mole; in the corresponding diazonium reaction for which the "normal" process (B) has an activation energy of, say, 5 kcal./mole, the rearrangement (B′) would require only 1 kcal./mole more energy to a first approximation. (In both cases the difference amounts to 20% of the activation energy of the "normal" reaction.) At room temperature, in the former case the rearrangement accounts for 0.02% of the product; in the latter case, 16%. Thus, a rearrangement which is not observed in solvolyses of halides and sulfonates can form a significant part of the product in the corresponding amine–nitrous acid reaction.

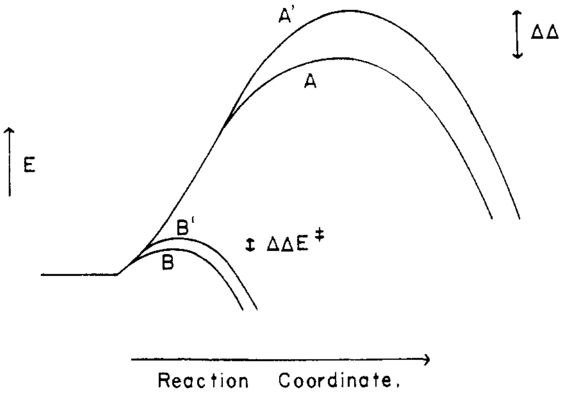
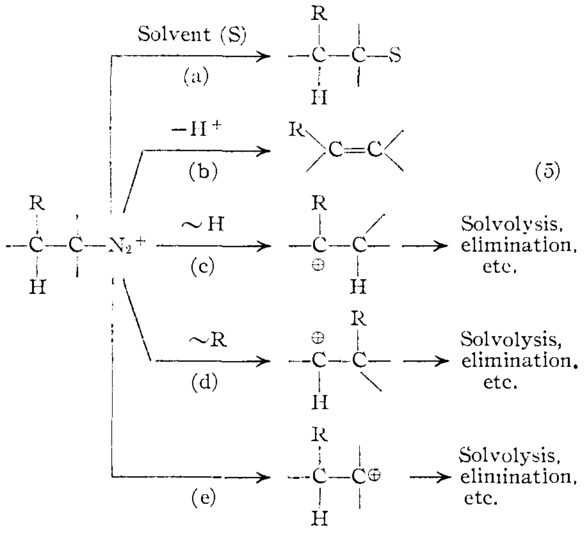


Fig. 1.—Illustrating the effect of total activation energy on the position of the transition state along a reaction coordinate and on the difference in activation energies between competing reactions.

Because of this compressed scale of energy differences, *a number of different reactions can compete more or less successfully in various systems.* These reactions, *which derive from the diazonium ion as the common intermediate,* are summarized in reaction 5. The relative importance of each reaction is more or less predictable from modern organic chemical theory and by analogy with other reactions. In the following discussion, the theory is applied to the present results.



**Reaction 5a: Direct Displacement.**—One of the reactions which can compete with normal carbonium ion formation is direct displacement by solvent. The hypothesis that the structure of the transition state resembles the reactants carries the implication that the bond to the attacking solvent molecule at the transition state for displacement is long and weak. Steric hindrance effects are reduced and relatively small stereochemical differences are to be expected between primary and secondary systems. In acetic acid, *n*-butylamine reacts with 69% inversion, *sec*-butylamine with 28% inversion (*vide supra*). Since the bond to the solvent is relatively long and weak, the extent of the inversion process is expected to be relatively insensitive to the nucleophilicity of the solvent. The similarity of the stereochemical results observed for *sec*-butylamine in water and in acetic acid may be explicable in these terms.

**Reaction 5b: Elimination.**—The olefin obtained from *sec*-butylamine in aqueous nitrous acid consists of 25% 1-butene, 19% *cis*-2-butene and 56% *trans*-2-butene (Table I). This composition would not be expected to change significantly in acetic acid. The composition of this mixture differs greatly from the mixture of butenes obtained by the acetolysis of *sec*-butyl tosylate (Table I).[24] Of particular importance is the difference in the *cis*/*trans* ratio in the two cases. The olefin in the

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(22) *Cf.* R. Huisgen and H. Reimlinger, *Ann.*, **599**, 183 (1956).

(23) Compare with ref. 21 and with G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(24) H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3614 (1955).

TABLE I

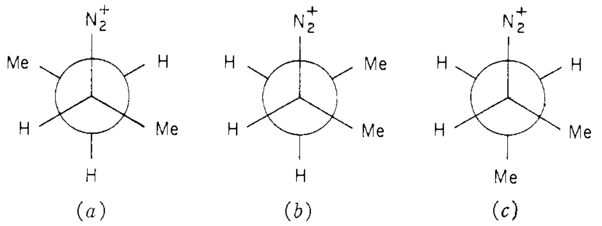
COMPOSITION OF BUTENES FROM SOLVOLYSIS AND AMINE–NITROUS ACID REACTIONS

| Reaction | Butene composition, % 1- | *cis*-2 | *trans*-2 | Ratio *trans*/*cis* |
|---|---|---|---|---|
| *s*-BuOTs + AcOH[a] | 10.3 | 43.2 | 46.5 | 1.1 |
| *s*-BuNH$_2$ + HNO$_2$[b] | (25)[c] | 19 | 56 | 2.9 |
| *n*-BuNH$_2$ + HNO$_2$[b] | 71 | 9 | 20 | 2.2 |
| Equilibrium[d] | 2 | 23 | 75 | 3.2 |

[a] At 70°; from ref. 24. [b] At room temperature. [c] By difference; direct analysis by infrared was prevented by the presence of a trace of butanol. Analysis of 2-butenes is not affected by the butanol. Less than 2% of isobutylene was present. [d] Gas at 25°; calculated from ref. 25.

*sec*-butyl tosylate and in similar solvolyses is considered to arise from a common carbonium ion intermediate because the olefin proportion and composition is the same when different leaving groups are used.[21,24,26] Consequently, the failure of this criterion with *sec*-butylamine demonstrates that at least part of the olefin formed in the amine–nitrous acid reaction does not arise from a carbonium ion intermediate.

An alternative is reaction 5b, a concerted elimination of a *trans*-hydrogen and nitrogen from the diazonium ion. Because the activation energy is presumed to be comparable to or less than the energy required for rotation about a carbon–carbon bond (3–4 kcal./mole for the central bond in *n*-butane[27]; undoubtedly more where groups bulkier than methyl are involved), the rates of such rotation will be of about the same magnitude or slower than the rate of decomposition. Hence, the relative populations of different conformations of the diazonium ion at the moment of formation will be important in determining the relative importance of possible subsequent reactions. In the case of 2-butylamine, three such conformations are important, Ia, b and c.[28] Ib is expected to be less populated than Ia and Ic.[29] Only Ia and Ib can eliminate a *trans*-3-hydrogen; hence, consistent with the observed results, *cis*-2-butene which would arise from Ib is expected to be formed in smaller amount than *trans*-2-butene which arises from Ia. In elimination from a carbonium ion, the two types of hydrogen are conformationally equivalent and comparable amounts of the *cis*- and *trans*-olefins may be anticipated. Ic, which is relatively highly populated, cannot give a 2-butene by *trans* elimination. All three conformations (*i.e.*, the entire population of diazonium ions) can give rise to 1-butene; only a fraction of the entire population of diazonium ions (that part in Ia and Ib) can generate 2-butene; therefore, even if the specific rate constant for formation of 1-butene is somewhat lower than that for the more stable 2-butenes, a relatively large amount of 1-butene is produced in the reaction (Table I).



(*a*) (*b*) (*c*)

I

This hypothesis also serves to interpret the fact that in cyclohexyl systems, equatorial amines (in which there are no *trans*-hydrogens) give essentially no olefin although axial amines generally produce large amounts of olefin.[31]

**Reactions 5c and 5d: Rearrangement.**—Rearrangement of a hydrogen or carbon function is expected when the rearranging group is *trans* to the leaving nitrogen. However, rearrangement by reaction 5c and 5d apparently occurs only when a more stable carbonium ion results. In the case of *n*-butylamine a significant fraction of the total population of diazonium ion is expected to be in conformations having a *trans*-2-hydrogen. Such a hydrogen can eliminate (reaction 5b) or migrate (reaction 5c) perhaps by way of a common hydrogen-bridged intermediate. In cases in which the population of diazonium ions in conformations having *trans*-hydrogens is too small, no rearrangement is expected. The non-occurrence of hydrogen-rearranged products from 2,2-diphenylethylamine,[32] for example, is probably due to this cause.

It should be emphasized that because the total activation energy for reaction is presumed to be small, the rearrangements 5c and 5d should not be regarded as participations in the usual sense in which a neighboring group helps to *push* out the leaving group. Rather, these reactions are perhaps better regarded as resulting from the tendency of the leaving nitrogen to *pull* over the *trans*-group.

**Reaction 5e: Carbonium Ion Formation.**—The formation of a carbonium ion by loss of nitrogen, long thought to be the principal mode of decomposition of alkyl diazonium ions, is here regarded as being only one of several possible competing reactions. In the present case, the 31% racemization observed in the 1-butyl-1-*d* acetate obtained from 1-aminobutane-1-*d* is attributed to the formation in part of primary butyl-1-*d* cations which lose their asymmetry. We would expect that carbonium ions produced in the amine–nitrous acid reaction would be "normal" and would react in the

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[25] F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. C. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, p. 475.

[26] E. D. Hughes, C. K. Ingold and U. G. Shapiro, *J. Chem. Soc.*, 1277 (1937).

[27] K. S. Pitzer, *Disc. Faraday Soc.*, **10**, 66 (1951).

[28] The notation is that of M. S. Newman, *J. Chem. Educ.*, **32**, 344 (1955).

[29] If the $N_2^+$ group (or its precursor) is regarded to a first approximation as equivalent to a methyl group, the 800 kcal./mole energy difference between *gauche* and *trans*-methyl groups (taken from *n*-butane[30]) leads to relative populations in Ia, b and c of 1.0, 0.37 and 1.0, respectively.

[30] W. G. Dauben and K. S. Pitzer in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 9.

[31] (a) J. A. Mills, *J. Chem. Soc.*, 260 (1953); (b) A. K. Bose, *Experientia*, **9**, 256 (1953); (c) W. G. Dauben, R. C. Tweit and C. Mannerskantz, THIS JOURNAL, **76**, 4420 (1954).

[32] L. Hellerman, M. L. Cohn and R. E. Hoen, *ibid.*, **50**, 1716 (1928).

same manner as carbonium ions generated from other sources.[33]

## Experimental

**Reaction of *n*-Butylamine with Sodium Nitrite and Acetic Acid.**—To a solution of 22 g. (0.30 mole) of *n*-butylamine in 200 ml. of acetic acid was added 40 g. of sodium nitrite over a period of 1 hr. at 0°. After stirring in the cold for an additional 2 hr. the mixture was allowed to warm to room temperature during 12 hr. The mixture was poured into an ice-cold solution of 200 g. of potassium hydroxide in 500 ml. of water. The resulting mixture was extracted four times with 100-ml. portions of pentane. After drying, the combined pentane extracts were distilled and yielded 13.6 ml. of material, b. 108-126°, which was a mixture of *n*-butyl acetate, *sec*-butyl acetate and *n*-butyl nitrate (identified by its intense absorption in the infrared at 6.13 $\mu$; *sec*-butyl nitrate may have been present in small amount but was not identified), which presumably arose by a reaction with nitrate ion formed by the decomposition of nitrous acid. The nitrogen analysis (found: 0.96%)[36] corresponds to the presence of 8.2%[37] butyl nitrate. The mixture was hydrolyzed by refluxing with 25 g. of potassium hydroxide and 100 ml. of water for 24 hr. The product, 9.5 ml., b. 100-117°, still showed the presence of alkyl nitrate (infrared).

The nitrate present was cleaved with lithium aluminum hydride. After refluxing 9.2 ml. of the alcohol and nitrate mixture with 2.0 g. of lithium aluminum hydride in 35 ml. of ether, 7.9 ml. of butyl alcohols was obtained, b. 100-117°. The infrared spectrum of the mixture compared to those of the pure alcohols showed the presence of 65% of *n*-butyl alcohol and 35% of *sec*-butyl alcohol.

In a similar experiment, the butenes evolved were collected in a Dry Ice trap. Analysis of the mixture by infrared[38] gave the results in Table I. No isobutylene could be detected.

**Reaction of Optically Active 1-Aminobutane-1-*d* with Sodium Nitrite in Acetic Acid.**—Eleven grams (0.15 mole) of optically active 1-aminobutane-1-*d*[16] in 100 ml. of dry acetic acid was treated with 20 g. of sodium nitrite as described above. The product, 6.5 ml., b. 112-125°, had $\alpha^{25}\text{D}$ +0.206 ± 0.004° (*l* 4) and was a mixture of approximately 69% 1-butyl-1-*d* acetate, 23% 2-butyl-1-*d* acetate and 8% of alkyl nitrate. Distillation through a concentric tube column gave 2.2 ml., b. 123-126.5°, of a mixture having $\alpha^{25}\text{D}$ +0.120 ± 0.004° (*l* 2) and consisting of approximately 80% 1-butyl-1-*d* acetate, 13% 2-butyl-1-*d* acetate and 7% alkyl nitrate. The column did not function properly in this distillation. After thorough cleaning, a second fractionation gave 0.5 ml. of product having $\alpha^{25}\text{D}$ +0.052 ± 0.004° (*l* 1) and consisting of 75% 1-butyl-1-*d* acetate and 25% *n*-decane (used as a chaser in these distillations). The compositions were estimated by comparison of the infrared spectra with standard compounds. The final product, which contained no *sec*-acetate or alkyl nitrate, corresponds to a rotation for pure 1-butyl-1-*d* acetate of +0.069 ± 0.007° (*l* 1). The rotation of acetate prepared directly from the alcohol used to prepare the amine is $\alpha^{25}\text{D}$ +0.200 ± 0.004° (*l* 2).[39] Since the preparation of the amine from alcohol probably involved one inversion and no racemization,[16] it follows that the 1-butyl-1-*d* acetate formed in the amine-nitrous acid reaction is 69 ± 7% inverted, 31 ± 7% racemized.

Using this rotation for pure 1-butyl-1-*d* acetate product, the rotation of the initial product mixture corresponds to the presence of 75% of primary acetate since the 2-butyl-1-*d* acetate present is presumed to be racemic and if the rotation due to the small amount of nitrate present is neglected. Similarly, the rotation of the product from the first fractionation corresponds to the presence of 87% of 1-butyl-1-*d* acetate. These results are in reasonable agreement with the infrared spectra, especially if the nitrate present has about the same rotation as the *n*-acetate.

**2-Butyl-1-*d* Acetate.**—This material was prepared for infrared comparison purposes. 1,2-Epoxybutane (Dow) (6.85 g., 0.095 mole) was dropped into 1.0 g. (0.0238 mole) of lithium aluminum deuteride (Metal Hydrides, Inc., Beverly, Mass.) in 75 ml. of dry ether at a rate sufficient to maintain a gentle reflux. After refluxing for an additional two hours, the product was worked up in the usual manner. Distillation gave 5.5 g. (0.073 mole, 78%) of 2-butanol-1-*d*, b. 96-99°. The infrared spectrum of this alcohol shows important differences from 2-butanol. In addition to the C-D stretching band at 4.55 $\mu$, other new bands appear at 7.84, 9.21 and 11.45 $\mu$, although the peaks at 10.37 and 12.24 $\mu$ in 2-butanol are missing. In addition, other bands are changed in shape and intensity.

Part of the alcohol was converted to the acetate with acetyl chloride and pyridine.[40] In the ester, too, there are important differences in the infrared. New bands appear at 4.56 (C-D), 9.54, 10.17 and 11.76 $\mu$; missing are the bands at 8.46, 10.04, 10.31, 11.56 and 11.95 $\mu$ present in 2-butyl acetate. There are many other differences in detail.

**Reaction of 1-Aminobutane-1,1-$d_2$ with Sodium Nitrite in Acetic Acid.**—Twenty-five grams (0.33 mole) of 1-aminobutane-1,1-$d_2$[16] in 226 ml. of dry acetic acid was treated with 45 g. of sodium nitrite as above and the products were isolated in the same manner. Distillation gave 16.0 g. (40% yield) of deuterated *n*- and *sec*-butyl acetates and nitrates. The mixture was reduced with 6.0 g. of lithium aluminum hydride in 100 ml. of ether and was refluxed for several hours. Distillation of the product through a glass

TABLE II

MASS SPECTRA OF DEUTERATED BUTYL ALCOHOLS

| Mass no. | 1-Butanol | 1-Butanol-1-*d* | 1-Butanol-1,1-$d_2$ | 1-Butanol-1,1-$d_2$ from amine |
|---|---|---|---|---|
| 27 | 39.4 | 33.4 | 39.7 | 40.9 |
| 28 | 19.4 | 19.6 | 24.8 | 25.1 |
| 29 | 24.8 | 24.2 | 28.9 | 32.6 |
| 30 | 1.4 | 9.6 | 18.5 | 18.9 |
| 31 | 72.7 | 8.0 | 13.3 | 12.3 |
| 32 | 1.4 | 68.4 | 25.4 | 26.1 |
| 33 | 7.4 | 2.7 | 66.8 | 63.6 |
| 34 | 0.2 | 7.3 | 4.5 | 4.2 |
| 35 | . . . | . . . | 7.2 | 7.0 |
| 39 | 20.4 | 15.4 | 18.1 | 19.1 |
| 40 | 5.0 | 8.7 | 11.8 | 12.6 |
| 41 | 84.1 | 54.0 | 62.6 | 66.5 |
| 42 | 28.5 | 59.8 | 70.5 | 73.1 |
| 43 | 50.7 | 51.0 | 85.9 | 100.4 |
| 44 | 4.4 | 7.1 | 11.9 | 12.3 |
| 45 | 5.5 | 5.7 | 6.8 | 7.0 |
| 46 | 0.5 | 5.4 | 2.6 | 2.8 |
| 47 | . . . | . . . | 3.8 | 4.1 |
| 48 | . . . | . . . | 0.5 | 0.7 |
| 55 | 18.4 | 4.3 | 4.8 | 6.1 |
| 56 | 100.0 | 16.9 | 18.5 | 19.0 |
| 57 | 7.9 | 100.0 | 41.5 | 59.9 |
| 58 | 0.2 | 7.9 | 100.0 | 100.0 |
| 59 | 0.2 | 0.9 | 9.6 | 9.6 |
| 60 | . . . | 0.5 | 2.6 | 2.7 |
| 61 | . . . | . . . | 0.4 | 0.4 |
| 71 | . . . | 0.2 | 1.3 | 4.6 |
| 72 | 0.6 | 0.6 | 0.4 | 0.6 |
| 73 | 1.5 | 1.0 | 1.4 | 1.5 |
| 74 | 1.3 | 0.9 | 1.0 | 1.1 |
| 75 | . . . | 1.4 | 0.4 | 0.5 |
| 76 | . . . | . . . | 1.3 | 1.1 |

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[33] This idea may be contrasted to the concept of "hot" or "high energy" carbonium ions having special characteristics which have been postulated in the decomposition of alkyldiazonium ions.[34,35]

[34] J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., THIS JOURNAL, **76**, 4501 (1954).

[35] D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957).

[36] Analysis by the Microanalytical Laboratory of the University of California.

[37] In another experiment, 4.3% of butyl nitrate was formed.

[38] Analysis was performed at the Shell Development Co., Emeryville, Calif., through the courtesy of Dr. D. P. Stevenson and Dr. J. W. Otvos.

[39] A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 379 (1957).

[40] A. Streitwieser, Jr., *ibid.*, **77**, 1117 (1955).

spiral column using 2-octanol as a chaser gave the following fractions: 1, b. 96-113°, 3.9 ml.; 2, b. 113-117°, 3.1 ml.; 3, b. 117-117.4°, 3.3 ml.; 4, b. 117.4-117.5°, 1.6 ml. The infrared spectrum of fraction 4, 1-butanol-1,1-$d_2$, indicated the absence of deuterated secondary carbinol; however, the mass spectral cracking pattern showed the presence of an impurity which is probably 2-octanol. This cracking pattern is discussed in the appendix.

**Reaction of *sec*-Butylamine with Nitrous Acid.**—The object of this experiment was the analysis of the butene mixture obtained. To a solution of 20 g. (0.27 mole) of *sec*-butylamine in 300 ml. of water and 143 ml. of 3 *N* sulfuric acid (0.216 mole) was added in portions and with stirring 52.5 g. (0.229 mole) of barium nitrite. The barium nitrite was added from a flask attached with a rubber tube. The mixture was stirred at room temperature for 20 hours and the butenes produced were passed through 20% potassium hydroxide and a potassium hydroxide tower and were collected in a Dry Ice trap. The analysis of the mixture by infrared is given in Table I.[38]

## Appendix

Cracking patterns for 1-butanol-1,1-$d_2$, and, for comparison, 1-butanol and 1-butanol-1-*d*, are given in Table II at an ionizing voltage of 75 v.[41] Column 4 contains the pattern for the 1-butanol-1,1-$d_2$ used to prepare the amine.[16] Column 5 contains the pattern for the 1-butanol-1,1-$d_2$ obtained from the reaction of the amine with nitrous acid (fraction 4). This material apparently contains an impurity (perhaps 2-octanol used as a chaser in the distillation) which contributes to some of the peaks. In the absence of this contribution and with no rearrangement of an ethyl group or loss of deuterium, the two patterns should be identical. The amount of $CH_3CH_2CD_2CH_2OH$ (II, product of an ethyl group rearrangement) present in the $CH_3CH_2CH_2CD_2OH$ (III) may be estimated in two independent ways: an important process in the electron impact of primary carbinols is the cleavage of the bond to the carbinol carbon with the formation of $CH_2OH^+$ (mass 31). To the extent that II is present in III, the 31 peak will be increased and the 33 peak lowered by a corresponding amount. Reference to Table II shows that the 33 peak is lowered (by ~5%) but the 31 peak *is not* increased by a corresponding amount; in fact, it is also lower (by 7.5%). Hence, these peaks indicate 0% rearrangement. The other fragment from the carbinol cleavage in *n*-butyl alcohol is a propyl (or isopropyl) cation, $C_3H_7^+$ (mass 43). The abnormally high 43 peak in column 5 is probably due to a contribution by the impurity. The presence of II will be manifested by an increase in the 45 peak ($C_3H_5D_2^+$). This peak is increased by only 0.2 unit which corresponds to 0.2% rearrangement but which is within the limits of the experimental uncertainties. Hence, ~0% ethyl rearrangement has occurred.

An indication may also be had of the proportion of the amine–nitrous acid reaction which proceeded through a diazobutane intermediate since an atom of deuterium would be lost in the process. The presence of an increased amount of 1-butanol-1-*d* would be shown by an increase in the 32 peak ($CHDOH^+$). The observed increase, 0.7 unit, corresponds to 1% of 1-butanol-1-*d*. This is a maximum figure because of the unknown contribution of the impurity.

**Acknowledgment.**—This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society. We wish to thank Prof. Rolf Huisgen of the University of Munich and Prof. W. G. Dauben for stimulating discussions.

BERKELEY 4, CALIFORNIA

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(41) We are indebted to Dr. D. P. Stevenson, Shell Development Co., Emeryville, Calif., for these mass spectra.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA, BERKELEY]

# Stereochemistry of the Primary Carbon. VII. The Decomposition of N-(1-Butyl-1-*d*)-N-nitrosoacetamide[1,2]

BY A. STREITWIESER, JR., AND W. D. SCHAEFFER[3]

RECEIVED SEPTEMBER 24, 1956

The thermal decomposition of optically active N-(1-butyl-1-*d*)-N-nitrosoacetamide gives an optically inactive mixture of 22% *n*-butyl acetate, 56% 1-butyl-1-*d* acetate and 22% 1-butyl-1,1-$d_2$ acetate. The decomposition of N-(1-butyl)-N-nitrosoacetamide in the presence of deuteroacetic acid gives butyl acetate containing some 1-butyl-1-*d* acetate. The results are interpreted by a mechanism which involves diazoalkane intermediates.

Methods for converting aliphatic amines to the corresponding alcohol or alcohol derivatives are rather limited. The most common method, the amine–nitrous acid reaction, generally furnishes low yields of alcohols frequently contaminated by rearrangement products. Consequently, considerable interest recently has been shown in the thermal decomposition of N-alkyl-N-nitrosoamides, the first examples of which are due to Pechmann[4] and Chancel.[5] Recent studies[6-9] have demonstrated the generality of this reaction which yields esters and olefins; from primary carbinylamines the corresponding esters are obtained in good yield with little or no rearrangement. White[9d] has inter-

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(1) Part VI, A Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **79**, 2888 (1957).

(2) Taken in part from the dissertation of W.D.S. submitted in partial fulfillment of the degree of Doctor of Philosophy at the University of California, June, 1956.

(3) General Electric Fellow, 1955–1956.

(4) H. v. Pechmann, *Ber.*, **31**, 2640 (1898).

(5) M. F. Chancel, *Bull. soc. chim. France*, [3] **13**, 125 (1895).

(6) (a) R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 (1952); (b) **575**, 197 (1952).

(7) G. Nischk and E. Muller, *ibid.*, **576**, 232 (1952).

(8) K. Heyns and W. v. Bedenberg, *Ber.*, **86**, 278 (1953).

(9) (a) E. H. White, THIS JOURNAL, **76**, 4497 (1954); (b) **77**, 6008 (1955); (c) **77**, 6011 (1955); (d) **77**, 6014 (1955).