ments. This is in marked contrast to the rearrangements of the analogous neopentyl derivatives.

3. The significance of this absence of rearrangement in relation to the mechanism of rearrangements is discussed.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

REARRANGEMENTS INVOLVED IN THE ACTION OF NITROUS ACID WITH NORMAL-BUTYLAMINE[1]

BY FRANK C. WHITMORE AND D. P. LANGLOIS

RECEIVED MAY 17, 1932 PUBLISHED AUGUST 5, 1932

The recorded data[2] on the reaction of nitrous acid and primary aliphatic amines make it of the utmost importance in the theory of rearrangements.[3] For instance, it can hardly be argued that a primary amine undergoes an "ionization" into R^+ and NH_2^- similar to that which is sometimes assumed as part of the mechanism of the rearrangement of carbinols (Meerwein). Moreover, this reaction results in the formation of olefins under conditions which would not cause the dehydration of even a tertiary alcohol.

n-Propylamine reacts with nitrous acid to give *n*-propyl alcohol, isopropyl alcohol and propylene.[4] Isobutylamine gives tertiary butyl alcohol[5] and isobutylene. No other organic products are mentioned. *n*-Butylamine is reported to give *n*-butyl alcohol and isobutyl alcohol.[6] Other workers report *n*-butyl alcohol, secondary butyl alcohol, *n*-butenes and dibutyl nitrosamine but *no* isobutyl alcohol.[7]

Neopentylamine gives only the rearrangement product, tertiary amyl alcohol.[8]

n-Butylamine was chosen for the present study because of the simplicity of its molecule and the disagreement in the literature regarding its behavior with nitrous acid. The amine was prepared from very pure *n*-butyl bromide obtained from highly purified *n*-butyl alcohol. The yields of products of the action of nitrous acid were as follows

[1] Presented by D. P. Langlois in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Porter, "Molecular Rearrangements," p. 140 (1928).

[3] See p. 3281.

[4] Siersch, *Ann.*, **144**, 140 (1867); Linnemann, *ibid.*, **161**, 44 (1872); *Ber.*, **10**, 1111 (1877); Meyer and Forster, *ibid.*, **9**, 535 (1876).

[5] Linnemann, *Ann.*, **162**, 24 (1872).

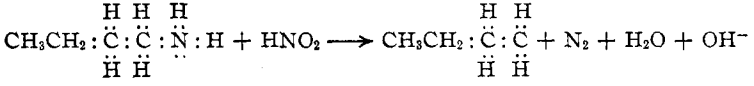
[6] Linnemann and Zotta, *ibid.*, **162**, 5 (1872); Ray and Rakshit, *J. Chem. Soc.*, **101**, 141 (1912).

[7] Meyer, Barbieri and Forster, *Ber.*, **10**, 132 (1877).

[8] Freund and Lenze, *Ber.*, **24**, 2150 (1891).

n-Butyl alcohol	25.0%
Sec.-butyl alcohol	13.2
n-Butyl chloride	5.2
Sec.-butyl chloride	2.8
n-Butenes	36.5
High boiling material	7.6
Butyl nitrites, traces	..
Total	90.3%

No trace of isobutyl alcohol, tertiary butyl alcohol or isobutylene was detected. The formation of the *n*- and *sec.*-butyl chlorides was unexpected. Their formation represents a new reaction in aliphatic chemistry and gives added evidence for the momentary existence of R^+ as an intermediate in the reaction, since it is most improbable that the alcohols were first formed and then were converted to chlorides in the barely acid solution. To get additional evidence on this new reaction, *n*-butylamine in calcium chloride solution was treated with calcium nitrite and hydrochloric acid. The increased concentration of chloride ion raised the yields of *n*- and *sec.*-butyl chlorides to 9.5 and 6.3%, respectively. The fact that the *n*-butyl chloride predominates indicates that the *n*-butenes are not intermediates in the process. Moreover, it is hardly conceivable that *n*-butenes could add hydrogen chloride under the conditions of the experiment. Further, the *n*-butenes could not have been formed by dehydration of the *n*- and *sec.*-butyl alcohols under the conditions of the experiment. The alcohols, halides and olefins are products of simultaneous reactions and are not formed from each other. Thus all evidence points to the validity of the suggested mechanism for the reaction of *n*-butylamine with nitrous acid.



The formation, from the amine nitrite, of a molecule of nitrogen, one of water, and an hydroxyl ion, each with its necessary number of electrons, leaves the end carbon of the *n*-butyl group with only six electrons. Such a product is capable of only momentary existence.[9] It unites with ions from the solution giving the observed products, *n*-butyl alcohol, chloride and nitrite. It also changes monomolecularly by (a) losing a proton to give butene-1, and (b) undergoing a shift of an electron pair and its proton to form a positive *sec.*-butyl group. This unites with ions from the solution forming *sec.*-butyl alcohol, chloride and nitrite. It also loses protons to give butene-1 and butene-2. The *sec.*-butyl ion could undergo a shift of an electron pair with a methyl to give an isobutyl ion, which could unite with ions to give isobutyl alcohol, etc., or could give isobutylene. Since no forked four-carbon products were formed, it is evident that the shift of a

[9] See p. 3277.

methyl does not take place under the conditions of these experiments. It is interesting, however, that Linnemann and Zotta, and Ray and Rakshit found such forked compounds when working at higher temperatures.

Experimental

Distillation of *n*-Butyl Alcohol.—Forty-five liters of the best commercial grade of *n*-butyl alcohol[10] was distilled through an adiabatic packed column, 8.3 meters high and 7.6 cm. in diameter.[11] At the start a reflux ratio of about 80:1 was used. After 1300 cc. of the alcohol had distilled, the refractive index became constant (n_D^{20} 1.3990). The reflux ratio was then dropped to 50:1 for the next 10 liters of distillate. The refractive index rose only 0.0001. Then 25 liters was distilled with the ratio 10:1 without any change in the refractive index. The residue of 7.5 liters was slightly brown. In all, fifty fractions were collected. The middle fractions were used in the present studies. They boiled at 116.2–116.4° (744 mm.) (Cottrell) and showed n_D^{20} 1.3991.

Preparation and Purification of *n*-Butyl Bromide.—The methods of "Organic Syntheses" [Vol. I, 1921, p. 5] were used. A 48-mole run of the purified *n*-butyl alcohol gave an 86% yield of crude *n*-butyl bromide all boiling at 95–100° (735 mm.). The crude bromide was distilled through a 150 × 2 cm. column[12] using a reflux ratio of 30:1. Three low fractions were obtained, 190 g. at 95–99°, 178 g. at 99–99.5° and 425 g. at 99.5–100°. The first two contained water. The main fraction consisted of 4.2 kg. boiling at 100° (741 mm.), n_D^{20} 1.4395. The residue was 190 g.

Preparation and Purification of *n*-Butylamine.—Two 12-liter flasks were fitted with stirrers and 8 liters of 90% alcohol placed in each. Ammonia was run in with constant stirring until the flasks had gained about 300 g. in weight. Into each flask was run 0.5 mole (68.5 g.) of *n*-butyl bromide. A slow stream of ammonia was allowed to pass through the flasks during the reaction to ensure complete saturation so that the ratio of ammonia to bromide was kept high. Altogether 11 moles of the bromide was added at the rate of 0.5 mole to each flask every four hours. This varied slightly during the night. At the end of the addition the mixture was stirred for two days longer until no bromide could be detected. It was then distilled to remove the alcohol. After about 8 liters of alcohol had been removed from the combined flasks, ammonium bromide separated and was filtered off. Eight more liters of alcohol solution was distilled off and more ammonium bromide filtered off. A total of 378 g. was obtained. About 2 liters of solution remained in the flask. To this was added 2 liters of water. The mixture was distilled to remove the last traces of alcohol. This was repeated until no alcohol remained.

Without cooling the solution there was added 12 moles of sodium hydroxide in 2 liters of water and the mixture was distilled until the lower boiling substance had come over. It was then allowed to cool. The distillate was dried over fused potassium hydroxide.

The two layers in the reaction flask were separated and the oily amine layer was dried over fused potassium hydroxide. More sodium hydroxide was added to the water layer but no more amine separated. Since extraction of a small portion of the water layer with ether showed only very small amounts of the amine, it did not seem advisable to extract the whole water layer of over 4 liters.

[10] Through the courtesy of C. L. Gabriel of the Commercial Solvents Corporation a middle cut was obtained from a batch distillation of 30,000 gallons of *n*-butanol.

[11] The construction and operation of this column have been described in detail by Fenske, Quiggle and Tongberg, *Ind. Eng. Chem.*, **24**, 408 (1932).

[12] See p. 3451.

The amine was fractionated through the 150-cm. glass-packed column.[13] Nothing came over below 76.5°, then 383.5 g. distilled at 76.5°(742 mm.). At this point the amine ceased to distil. By heating the column and increasing the heat on the flask more amine was forced up the column but the temperature began to climb rapidly, indicating the presence of dibutylamine. The yield of pure *n*-butylamine was 47%; n_D^{20} 1.4008.

Reaction of *n*-Butylamine with Nitrous Acid.—The following is a typical run. *n*-Butylamine (1 mole) was dissolved in 1 liter of water and neutralized with the calculated quantity of 6 *N* hydrochloric acid. This was placed in a round-bottomed flask fitted with a mercury-sealed stirrer, a dropping funnel and an outlet tube for gas. A solution of three moles of sodium nitrite in a minimum quantity of water was added to the cold amine hydrochloride solution. No reaction occurred in the cold.

The outlet tube was connected with the following train: a spiral condenser with a receiver cooled in an ice-bath to remove the condensable materials; two calcium chloride and one phosphorus pentoxide drying towers; a series of three 250-cc. absorption bottles containing absolute alcohol for the absorption of butenes; an absorption tower containing alkaline permanganate solution (50 g. of potassium permanganate and 20 g. of potassium hydroxide per liter) for the absorption of nitrogen oxides; and finally a large graduated carboy for collecting and measuring the nitrogen evolved. The dropping funnel of the apparatus was filled with 1 *N* hydrochloric acid.

After sealing the apparatus, the stirrer was started and the flask slowly heated until the solution boiled. A rather rapid evolution of gas occurred and considerable volatile material collected in the receiver. Heating was continued until the volume of nitrogen increased only slowly. The reaction was then stopped. A very slow stream of 1 *N* hydrochloric acid was added during the reaction to prevent the solution from becoming alkaline due to the hydrolysis of the sodium nitrite. Samples of gas were removed during the reaction from various positions along the train to test the completeness of absorption of the butenes and nitrogen oxides.

The condensed material which consisted of an oily layer and a water layer was saturated with sodium chloride and a few cc. of 1 *N* hydrochloric acid was added to remove any amine which had distilled over. The two layers were separated and the water layer extracted with ether. The ether was removed and the residue added to the oily layer, which was dried over anhydrous potassium carbonate. The amine was recovered by making the water layer alkaline with sodium hydroxide and extracting with ether. The dried oily layer was fractionated through a partial condensation column 90 × 1.2 cm.[14]

The butenes were recovered by running the alcoholic solution into warm water and collecting the evolved gas.

Reaction 1.—A total of 3.5 moles (255.5 g.) of *n*-butylamine was treated with 10.5 moles (724.5 g.) of sodium nitrite by the procedure indicated. A fractionation of the condensed material gave the following fractions.

Fraction	B. p., °C.	Pressure, mm.	n_D^{20}	Wt., g.
1	66–68	744	1.3981	7
2	68–76	744		0.5
3	76–80	744	1.4085	13
4	80–97.6	744		1.1
5	97.6–98.4	742	1.3970	26.3
6	98.4–114.6	742		1.3
7	114.6–116.2	742	1.3991	50.0
8	Higher boiling material			15.0

[13] See p. 3451.

[14] See p. 3453.

Fraction 1 was chiefly *sec.*-butyl chloride. It was identified by the method of Johnson,[15] yielding an anilide, m. p. 106–108°; mixed melting point with a pure sample of methylethylacetanilide prepared from *sec.*-butyl bromide, 106–108°. Some *sec.*-butyl nitrite was present (odor) but it was impossible to separate it by distillation since the two boiling points are so close together. A small amount of the material was refluxed for an hour with potassium carbonate solution and the aqueous solution gave a distinct test for nitrite ion.

Fraction 3 was chiefly *n*-butyl chloride. It was also identified by the method of Johnson,[15] yielding an anilide, m. p. 58–59°; mixed melting point with a pure sample of *n*-valeranilide 58–61°. The chlorine analysis of the fraction indicated the presence of some substance besides *n*-butyl chloride. Found: 33.1% Cl; calcd. for C_4H_9Cl, 38.8%. The index of refraction was high for *n*-butyl chloride. *n*-Butyl nitrite was present. Boiling some of the material with potassium carbonate solution gave nitrite ion. The odor of an organic nitrite was always obtained from material in Fractions 1 and 3.

Fraction 5 had the boiling point and index of refraction of *sec.*-butyl alcohol.

Fraction 7 was *n*-butyl alcohol. It had the correct boiling point and index of refraction. With 3,5-dinitrobenzoyl chloride it gave an ester melting at 62–64°, mixed melting point with a sample of pure *n*-butyl 3,5-dinitrobenzoate 62–64°.

Fraction 8 was unidentified but may have been the same as the dibutylnitrosamine obtained by v. Meyer.[16]

Butenes.—25.2 liters of butenes at 24° and 727 mm. was obtained from Reaction 1. Calculated to standard conditions, this gives 22.1 liters or 55.2 g.

In order to test for the presence of isobutene in the gas the method of analysis of Marcowitch and Moore[17] was used. This method depends on the relative rate of absorption of isobutene and the *n*-butenes in 68% sulfuric acid. No attempt was made to distinguish between the *n*-butenes.

The apparatus consisted of an Orsat absorption pipet and a gas-measuring buret. The rate of absorption was determined by measuring the decrease in volume of the gas standing in contact with the acid for five-minute periods.[18]

Samples of isobutene and the *n*-butenes were prepared according to the method of Davis[19] and the rate of absorption of a 50% mixture of each gas with air was determined. The result is plotted on Fig. 1. The isobutene is quantitatively absorbed in twenty minutes while only 15% of the *n*-butenes is absorbed in the same time. Synthetic mixtures of isobutene with the *n*-butenes were then prepared and the rate of absorption determined as before. These results are also plotted on Fig. 1. The curves for the mixtures show a rapid absorption for the first five or ten minutes and then a sharp decrease in the rate until a final slow constant rate is obtained. From a consideration of the curves for the pure butenes it is evident that the final slow rate of absorption is due to the *n*-butenes and that they have been absorbed at this constant rate from the beginning. We can then calculate the percentage of isobutene in the mixture by taking the total absorption and subtracting from it the quantity of *n*-butenes absorbed. This latter factor is obtained by taking the amount of gas absorbed in five minutes as indicated by the final slope of the line and multiplying by the number of five-minute intervals. This may be read directly from the graph by extending the straight line portion of the curve until it intersects the ordinate axis, taking the percentage of isobutene to be that corresponding to the intersection on the axis. In this manner results with a precision of

[15] Johnson, THIS JOURNAL, **53**, 1063 (1931).

[16] V. Meyer, *Ber.*, **10**, 132 (1877).

[17] Marcowitch and Moore, *Natl. Pet. News*, Oct. 14 and 21, 1931.

[18] Fresh acid was introduced after every third run.

[19] See THIS JOURNAL, **50**, 2778 (1928).

about 1% can be obtained. The following results were calculated for the curves in Fig. 1.

Curve	Gas mixture *n*-Butenes, cc.	Gas mixture Isobutene, cc.	Isobutene taken, %	Isobutene calcd., %
2	78.1	3.7	4.9	5.2
3	48.0	4.0	7.7	7.6
4	86.0	12.6	12.8	13.2
5	51.7	22.7	30.5	29.8
6	60.1	29.1	32.6	30.7

Figure 2 represents the absorption curve of the butenes obtained from Reaction 1. It is practically identical with the curve for *n*-butenes given in Fig. 1. There is a slightly

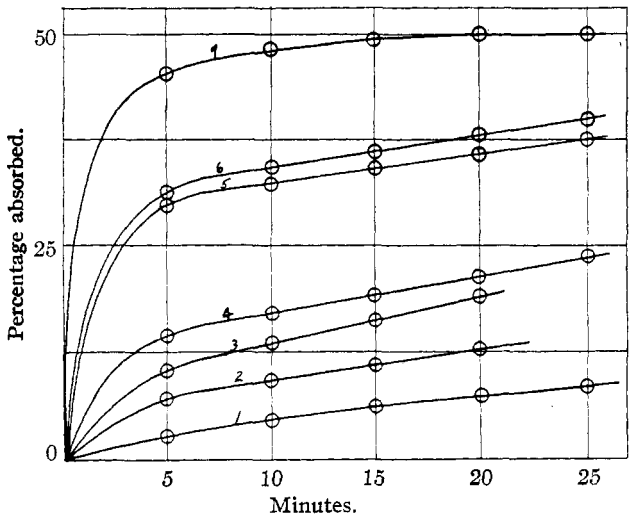


Fig. 1.—1, 50% *n*-butenes, 50% air; 2, 4.9% isobutene; 3, 7.7% isobutene; 4, 12.8% isobutene; 5, 30.5% isobutene; 6, 32.6% isobutene; 7, 50% isobutene, 50% air. 2–6, isobutene + *n*-butenes = 100%.

greater absorption during the first five minutes than during the subsequent five-minute intervals which amounts to about 0.5%. This behavior is also shown by the curve for

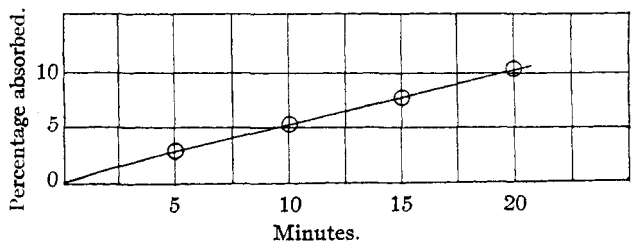


Fig. 2.—79% butenes, 21% air.

the *n*-butenes, so that it is evident that isobutene is not present in amounts greater than 1% in the gas from Reaction 1.

The dibromide was prepared by passing the butene into bromine in carbon tetrachloride. The product was fractionated through a 62 × 2.3 cm. packed total reflux column.[20] Only one fraction was obtained boiling at 153–158° at 728 mm. Apparently no isobutylene dibromide (b. p. 148°) was present.

No tertiary butyl alcohol, isobutyl alcohol or isobutylene could be detected.

Reaction 2.—This reaction was carried out in the presence of a higher concentration of chloride ion. One mole of *n*-butylamine in a solution of 1.5 moles of calcium chloride was treated with 1 mole of calcium nitrite. (The latter was used instead of sodium nitrite to prevent the precipitation of part of the chloride ion as sodium chloride.) The usual procedure was used and the products of reaction were separated and identified as in Reaction 1.

	Weight, g.	Yield based on amine consumed, %
n-Butyl chloride	4.4	9.5
Sec.-butyl chloride	2.9	6.3
Mixture of *n*- and *sec.*-butyl alcohols	14.7	39.6
n-Butenes	10.5	37.6
		93.0

Unreacted amine recovered, 36.1 g. (0.5 mole). No isobutyl alcohol, *tert.*-butyl alcohol or isobutylene was detected.

Reaction 3.—This reaction was carried out in the presence of freshly precipitated copper. Half a mole of *n*-butylamine (36.5 g.) in the presence of 60 g. of moist freshly precipitated copper was treated with 1.5 moles of sodium nitrite by the usual procedure. The copper reacted readily to give cuprous chloride but most of the amine was recovered unchanged.

Oily material	5.4 g.	
n-Butenes	5.32 g.	(43.6% yield based on amine consumed)
Unreacted amine recovered	21 g.	(0.29 mole)

Summary

1. *n*-Butylamine reacts with nitrous acid to give the alcohols and chlorides and traces of nitrites of *n*- and *sec.*-butyl together with butene-1 and -2. No branched chain butyl compounds have been detected.

2. The relation of these facts to the mechanism of rearrangements is discussed.

STATE COLLEGE, PENNSYLVANIA

[20] See p. 3451.