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

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

[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-

(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).

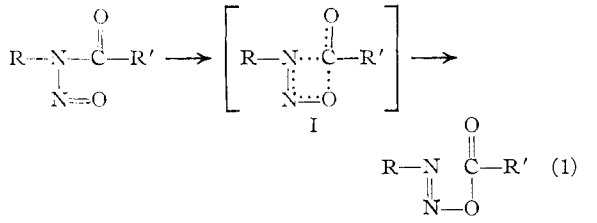
preted his stereochemical results in terms of a mechanism involving a set of cyclic transition states some of which are rather unusual and, to us, highly unlikely. It seemed clear that application of the reaction to the 1-aminobutane-1-*d* system could yield results which would be of significant interest from the standpoint of the reaction mechanism.

Results and Discussion

Optically active 1-aminobutane-1-*d*[10] was converted to N-(1-butyl-1-*d*)-N-nitrosoacetamide with acetic anhydride and nitrous acid. Since no bond to the asymmetric carbon is broken in these reactions, no loss in optical purity is expected in this sequence. The thermal decomposition of N-(*n*-butyl)-N-nitrosoacetamide in heptane solution at 85° is reported to yield 79% of *n*-butyl acetate and 16% of acetic acid.[9c] The decomposition of the deutero-nitrosoamide in cyclohexane solution at 80° gave 59% of deuterated butyl acetate having $\alpha^{25}D$ +0.005 ± 0.004° (*l* 2). 1-Butyl-1-*d* acetate of the same optical purity as the starting amine has $\alpha^{25}D$ +0.200 + 0.004° (*l* 2); hence 98 ± 2% of the optical activity has been lost. Analysis of the nitrosoamide decomposition product by comparison of its infrared spectrum with those of known mixtures showed it to consist of about 22% *n*-butyl acetate, 56% 1-butyl-1-*d* acetate and 22% 1-butyl-1,1-d_2 acetate. The analysis depended on the fact that *n*-butyl acetate is blank in the 4–5 μ region, 1-butyl-1-*d* acetate has a single intense C–D band at 4.54 μ, and 1-butyl-1,1-d_2 acetate has a C–D doublet at 4.46 and 4.63 μ, and on the differences between the three esters in the 8.5–9.0 μ region. The resulting analysis is probably better than ±5% in each component.

No mechanism involving only intramolecular transformations can account for the observed disproportionation of deuterium. A reasonable mechanism which accommodates both the complete loss of optical activity and the disproportionation of deuterium is one which involves a diazoalkane intermediate.

In the aromatic series the postulate that the first step in the decomposition of acylnitrosoarylamines involves an intramolecular rearrangement to the corresponding aryl diazoester[11] (equation 1) has been shown to be consistent with a variety of experimental observations.[12–15] Analogously the rearrangement through a transition

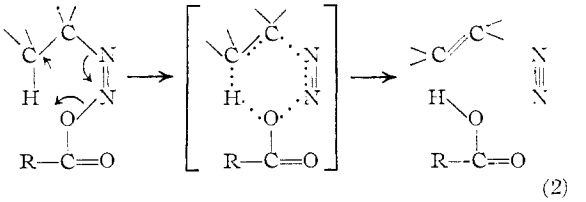


I

(1)

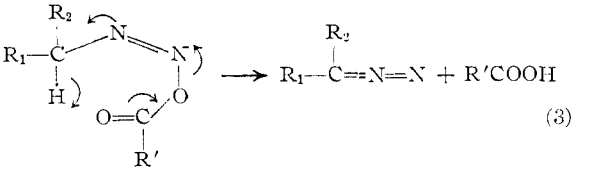
state such as I also has been postulated as the first and rate-determining step in the decomposition of aliphatic nitrosoamides.[4b,6b,9d,16,17] Huisgen and Reimlinger[17a] have recently shown that kinetic results may be accommodated readily on the basis of a rate-determining rearrangement to the diazoester; in particular, the rate pattern as a function of structure was shown to be in accord with reasonable hypotheses concerning the relative importance of steric and polar effects. Hence the reaction products may be regarded as resulting from subsequent reactions of the intermediate diazoester.

One of the subsequent reactions of the diazoester is an elimination to form olefins, nitrogen and the carboxylic acid for which the intramolecular mechanism proposed by White[9d] (reaction 2) is attractive, at least in non-polar solvents. A similar re-



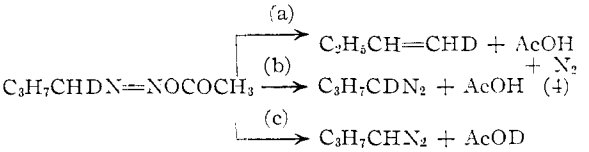
(2)

action with an α-hydrogen atom would result in the formation of a diazoalkane (reaction 3). Diazoalkanes are known to react rapidly with



(3)

carboxylic acids to form esters without rearrangement.[18,19,20] The postulate of a diazoalkane intermediate in the present case accounts for the loss of optical activity in an obvious manner. Furthermore, the deuterium migrations are readily accounted for. According to this mechanism 1-butyl-1-*d* diazoacetate can decompose by β-elimination to give acetic acid and olefin (reaction 4a), or by α-elimination to give either acetic acid and diazobutane-1-*d* (reaction 4b) or deuteroacetic acid and diazobutane (reaction 4c). The reaction



(4)

of diazobutane with acetic acid generates *n*-butyl acetate. Reaction of diazobutane-1-*d* with acetic acid or of diazobutane with deuteroacetic acid produces 1-butyl-1-*d* acetate. The reaction of diazobutane-1-*d* with deuteroacetic acid gives rise to 1-butyl-1,1-d_2 acetate.

(10) A. Streitwieser, Jr., and W. D. Schaeffer, THIS JOURNAL, **78**, 5597 (1956).
(11) R. Huisgen, *Angew. Chem.*, **62**, 369 (1950).
(12) R. Huisgen and L. Krause, *Ann.*, **574**, 157 (1951).
(13) R. Huisgen, *ibid.*, **574**, 171 (1951).
(14) D. H. Hey, J. Stuart-Webb and G. H. Williams, *J. Chem. Soc.*, 4657 (1952).
(15) D. F. DeTar, THIS JOURNAL, **73**, 1446 (1951).
(16) K. Heyns and W. v. Bedenberg, *Ann.*, **595**, 55 (1955).
(17) (a) R. Huisgen and H. Reimlinger, *ibid.*, **599**, 161 (1956); (b) **599**, 183 (1956).
(18) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 286 (1935).
(19) A. F. McKay, W. L. Ott, G. W. Teller, M. N. Buchanan and J. F. Crooker, *Can. J. Research*, **B28**, 683 (1950).
(20) D. Y. Curtin and S. M. Gerber, THIS JOURNAL, **74**, 4052 (1952).

The reaction of diazoalkanes with carboxylic acids is known to have a relatively large isotope effect; for example, the reaction of diphenyldiazomethane with acetic acid is about four times faster than the reaction with deuteroacetic acid.[21,22] Hence, if reactions 4b and 4c went at equal rates, excess deuteroacetic acid would remain at the end of the reaction (because of reaction 4a), and the product butyl acetate would manifest a net loss of some deuterium. The fact that such loss of deuterium is at most rather small suggests that the α-elimination reaction is also subject to an isotope effect; *i.e.*, reaction to 4b would seem to be faster than 4c. This point was not further investigated.

An obvious corollary of this mechanism is that the decomposition of undeuterated nitrosoamide in the presence of deuteroacetic acid should yield product ester containing some deuterium. The decomposition of N-(*n*-butyl)-N-nitrosoacetamide in cyclohexane containing 1.8 equivalents of deuteroacetic acid gave *n*-butyl acetate containing 26% of 1-butyl-1-*d* acetate; the decomposition in isopropyl ether containing 1.3 equivalents of deuteroacetic acid gave *n*-butyl acetate containing 21% of 1-butyl-1-*d* acetate.

The hypothesis also allows the interpretation of certain results in the decomposition of nitrosoamides in the presence of added salts. When N-(*n*-butyl)-N-nitrosoamide was allowed to decompose in cyclohexane in the presence of suspended sodium benzoate and calcium hydride, the ester produced was a mixture of butyl acetate and butyl benzoate. A rapid reaction of acetic acid with the sodium benzoate to form benzoic acid which reacts with the diazoester would account for the formation of butyl benzoate. The calcium hydride was used in this and in other experiments to react with the acid as produced. However, subsequent experiments demonstrated that the reaction of carboxylic acids with calcium hydride suspended in inert solvents is rather slow.

The postulate that diazoalkane intermediates are involved in the decomposition of aliphatic nitrosoamides was first offered by Heyns and Bedenberg.[8] These authors later discarded this mechanism on the basis of competition experiments[23]; for example, the thermal decomposition of a mixture of N-methyl-N-nitrosoacetamide and N-butyl-N-nitrosobutyramide without solvents gave a mixture of methyl acetate and butyl butyrate. The diazoalkane hypothesis predicts that a mixture of four esters should have resulted. Several aspects of the experimental procedure, however, seem to us to reduce the significance of these observations; *viz.*, the use of no solvent and of temperatures much higher than necessary to promote the reaction. Consequently, a competition experiment was run under conditions similar to those used generally in this investigation. When an equimolar mixture of N-ethyl-N-nitrosopropionamide and N-butyl-N-nitrosoacetamide was decomposed in hexyl ether solution at 80° for 24 hours, the product was a mixture containing comparable amounts of all four possible esters, ethyl acetate, ethyl propionate, butyl acetate and butyl propionate. A control experiment was also run in which a mixture of ethyl propionate and butyl acetate was heated in the presence of acetic acid and propionic acid in hexyl ether solution for 24 hours at 80°. The two starting esters were isolated in good yield with no evidence for the formation of ethyl acetate and butyl propionate. These results are completely consistent with the diazoalkane mechanism.

Comparison with Other Systems.—The mechanism of the nitrosoamide decomposition has been discussed by several authors, but no over-all picture has yet been presented consistent with all of the known facts. Although the present results indicate that essentially all of the decomposition of *primary* carbinyl nitrosoamides proceeds by reactions 2 and 3, the stereochemical results of White[9d] have conclusively demonstrated that these cannot be the exclusive modes of reaction in *secondary* carbinyl systems. Thus, in dioxane solution the decomposition of optically active N-(2-butyl)-N-nitrosobenzamide gave 2-butyl benzoate with about 40% retention of configuration. The intramolecular cyclic mechanism proposed by White[9d] to account for this stereochemistry would be expected, if correct, to apply at least as well to primary systems. Since our results show that the decomposition of primary alkyl nitrosoamides is actually intermolecular, the cyclic mechanism seems improbable for secondary systems.

On the other hand, the stereochemical results in secondary systems are readily accommodated by an "ion-pair" mechanism, reaction 5, analogous to that demonstrated in some decompositions of alkyl chlorosulfites.[24]

$$\mathrm{R{-}N{=}N{-}O{-}\overset{\overset{O}{\|}}{C}{-}R' \longrightarrow R^{\oplus} \cdots \ominus O_2CR' + N_2 \longrightarrow R{-}O{-}\overset{\overset{O}{\|}}{C}R' + N_2} \quad (5)$$

Reaction 5 involves a simple decomposition of the diazoester intermediate to nitrogen and a carbonium ion–carboxylate ion "ion-pair" in which the stereochemical configuration is largely preserved. Subsequent collapse of the ion-pair leads to product ester with predominant retention of configuration. Since this paper was first submitted for publication, the paper of Huisgen and Reimlinger[17b] appeared in which a similar mechanism was proposed.[25] These authors discussed the possible role of diazoalkanes without coming to definite conclusions.[26]

(21) J. D. Roberts, C. M. Regan and I. Allen, THIS JOURNAL, **74**, 3679 (1952).

(22) J. D. Roberts and C. M. Regan, *ibid.*, **74**, 3695 (1952).

(23) K. Heyns and W. v. Bedenberg, *Ann.*, **595**, 69 (1955).

(24) D. J. Cram, THIS JOURNAL, **75**, 332 (1953); C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953).

(25) In personal discussions with Professor Huisgen, it developed that both groups had independently arrived at similar mechanisms.

(26) Huisgen and Reimlinger[17b] reported some interesting experiments which demonstrated that the reaction of diazomethane with a mixture of carboxylic acids yields the same product mixture as the decomposition of a methyl nitrosoamide in the same mixture of acids. They pointed out that these results require that either diazomethane is a common intermediate in both reactions or that diazomethane reacts with carboxylic acids to give the same intermediate (a diazonium ion–carboxylate ion ion-pair) produced in the nitrosoamide decomposition. Our present demonstration that diazoalkanes *are intermediates* in the decomposition of primary alkyl nitrosoamides indicates that the former of these alternatives is correct.

TABLE I

INFRARED ANALYSES

Sample	Mole per cent. acetates: *n*-Butyl	1-Butyl-1-*d*	1-Butyl-1,1-d_2	log I_0/I Found[a]: 4.48μ	4.55μ	4.63μ	8.6μ[c]	log I_0/I Calcd.[b]: 4.55μ	4.63μ
Mixt. 1	12.7	79.9	7.4	...[d]	0.652	0.180	0.07	0.625	0.180
Mixt. 2	11.1	69.8	19.1	0.160	.554	.253	.20	.569	.254
Mixt. 3	30.2	51.8	18.0	.147	.434	.219	.19	.429	.218
Reaction product	(20.4)[e]	(56.2)[e]	(23.4)[e]	.177	.473	.267	.22		

[a] For the pure liquid in a 0.095-mm. cell. The 8.6 μ band is for a 0.025-mm. cell. [b] Calculated from the equations: $\log (I_0/I)_{4.55\mu} = 0.765N_{d_1} + 0.183N_{d_2}$; $\log (I_0/I)_{4.63\mu} = 0.154N_{d_1} + 0.768N_{d_2}$. [c] For 1-butyl-1,1-$d_2$, $\log I_0/I = 1.1$. [d] Shoulder was not resolved. [e] Calculated from the found absorbancies and the equations in (*b*). The undeuterated acetate was found by difference.

However, all of the facts are explicable by the postulate that reactions 2, 3 and 5 are *competing* modes of decomposition of the diazoester. On this basis, the racemization found in secondary systems is due in large measure to the formation of a diazoalkane intermediate. In primary carbinyl systems, carbonium ion stability is so low that reaction 5 is slow compared to the formation of diazoalkane. In the chlorosulfite decomposition the formation of carbonium ion–chloride ion "ion-pairs" also has been demonstrated to be relatively slow for primary systems.[27] As the carbonium ion stability is increased the proportion of reaction *via* reaction 5 is also increased and product with increased *retention* of configuration is expected. Thus, N-(α-phenylethyl)-N-nitrosoamides give ester with greater retention of configuration (48–70% for different amides in various solvents[9d,17b,28]) than do the secondary alkyl systems.

A further corollary of the mechanism proposed here is that in reactions 3 and 5, a carboxylic acid or carboxylate ion is formed in which both oxygens become equivalent. By use of O^{18} tracer techniques, White and Aufdermarsh have recently reported that the two oxygens do, indeed, become completely equivalent.[29]

Experimental

Thermal Decomposition of Optically Active N-(1-Butyl-1-*d*)-N-nitrosoacetamide.[30]—To a 300-ml., three-necked flask equipped with stirrer, condenser and dropping funnel and containing 5.5 g. (0.075 mole) of optically active 1-aminobutane-1-*d*, $\alpha^{25}D$ −0.013 ± 0.004° (*l* 2),[10] was added 8.0 g. (0.133 mole) of acetic acid with cooling. The ice-bath was then removed and 75 ml. of acetic anhydride was added. The mixture was stirred at room temperature for 0.5 hour and was again chilled in an ice-bath. To the cold solution was added 10.0 g. (0.126 mole) of finely divided sodium nitrite in 5.0-g. portions. Additions were made 20 minutes apart. The mixture was cooled in the ice-bath for 3 hours following the addition of the sodium nitrite, and was then allowed to warm to room temperature with stirring during the next 12 hours. The reaction mixture was then poured into 300 ml. of ice and water. After stirring for several hours at room temperature until all of the acetic anhydride had hydrolyzed, the optically active nitrosoamide was extracted into two 50-ml. portions of cyclohexane. The combined cyclohexane extracts were washed with sodium hydroxide and water and were dried with sodium sulfate.

The cyclohexane solution containing the optically active nitrosoamide was transferred to a 250-ml. flask which was arranged for magnetic stirring and which contained 2.0 g. (0.048 mole) of calcium hydride. The reaction flask was fitted with a condenser carrying a drying tube and was immersed in a thermostat at 80 ± 1°. After heating for 24 hours the inorganic salts were filtered and the filtrate was distilled through a small glass spiral column. After removal of the cyclohexane, a 5.9-ml. fraction, b. 121–125°, was collected (59% yield). Redistillation of this fraction through the same column gave 3.5 ml. of deuterobutyl acetate, b. 124–125°, having $\alpha^{25}D$ +0.005 ± 0.004° (*l* 2) and d_4^{25} 0.8836.[31]

Infrared Analyses.—1-Butyl-1-*d* acetate has a single band in the C–D region at 4.55μ. 1-Butyl-1,1-d_2 acetate has a doublet at 4.48 and 4.63μ. The spectra were taken as the pure liquids in a 0.025-mm. cell against a salt plate as reference in a Baird double beam instrument. All of the spectra reported were taken under "routine" conditions; reproducibility was satisfactory. Under the same conditions the product of the nitrosoamide decomposition above had a rather broad band in the C–D region. The spectrum in this region using a 0.095-mm. cell showed a band centered at 4.54 μ with shoulders at 4.48 and 4.63μ. Three known mixtures were made up from *n*-butyl, 1-butyl-1-*d* and 1-butyl-1,1-d_2 acetates and the spectrum of each mixture was taken in both the 0.025-mm. and 0.095-mm. cells. The latter spectra in the C–D region resembled that of the reaction product and were used to analyze for the amounts of -d_1 and -d_2 acetates present. The amount of undeuterated acetate was then obtained by difference since it is blank in this region. The 8.4–9.0μ region of the former spectra provided an independent measure of the amount of -d_2 acetate present.

In Table I are given the compositions of the three mixtures and log I_0/I for the central peaks and the shoulders of the mixtures and the reaction product. For the range of compositions used the contributions of -d_1 and -d_2 to the 4.55 and 4.63μ bands were assumed to be linear. For each band, the absorbancies found and the known compositions were used in a least squares solution of three equations in the two unknowns: $\log I_0/I = aN_{d_1} + nN_{d_2}$, in which N_{d_1} is the mole fraction of 1-butyl-1-*d* acetate; N_{d_2} is the mole fraction of 1-butyl-1,1-d_2 acetate. The resulting equations (Table I) were used to calculate the absorbancies of each band for each mixture. The agreement to the observed values was generally excellent. From the equations and the absorbancies of the nitrosoamide product, the composition was calculated (Table I). The shoulder of the 4.48μ band was not resolved in mixture 1; the other mixtures were too close in -d_2 composition to allow a valid analysis based only on these points.

The spectra reproduced in Fig. 1 show that the three esters exhibit characteristic differences in the 8.4–9.0μ region. The nature of the data does not justify a complete analysis of the entire region, but the similarity of curves D and E demonstrates the essential similarity of the reaction product to a mixture such as mixture 3. The 8.6μ band in the -d_2 acetate does not appear significantly in the others and was used to estimate the amount present. Using the base line drawn from neighboring bands, log I_0/I was determined for each of the mixtures and for the reaction product. These absorbancies are roughly proportional to the mole per cent. of -d_2 ester present and gives an analysis of about 21% for the nitrosoamide product.

The analyses are probably good to about ±5%; the average analysis is taken as 22% *n*-butyl acetate, 56%

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

(28) R. Huisgen, private communication.

(29) E. H. White and C. A. Aufdermarsh, Absts. of the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 18, 1956, p. 20-O.

(30) The procedure was adapted from that of White.[9b,c,d]

(31) This density is uncertain by about 5 units in the last place and corresponds to 0.90 ± 0.06 atom of deuterium per molecule.

1-butyl-1-*d* acetate and 22% 1-butyl-1,1-d_2 acetate for the nitrosoamide reaction product.

1-Butyl-1,1-d_2 acetate.—The preparation from 1-butanol-1,1-d_2[10] and acetyl chloride was similar to that described earlier.[32]

Thermal Decomposition of N-Butyl-N-nitrosoacetamide in the Presence of Deuteroacetic Acid.—N-Butyl-N-nitrosoacetamide was prepared from 14.6 g. (0.20 mole) of *n*-butylamine as described above. However, before hydrolyzing the acetic anhydride, the reaction mixture was divided into equal parts and each part was treated separately with ice and water. When hydrolysis was complete one fraction was extracted into cyclohexane and the other fraction was extracted into isopropyl ether.

The cyclohexane solution was dried with sodium sulfate and was transferred to a 250-ml. flask which was arranged for magnetic stirring. To the mixture was added 11.0 g. (0.180 mole) of acetic acid-*d*. The flask was fitted with a condenser and drying tube and was immersed in a thermostat at 75 ± 1°. Not all of the deuteroacetic acid dissolved immediately, but after about 2 hours of heating and stirring a homogeneous solution resulted. After heating for a total of 24 hours the reaction mixture was cooled to room temperature and was washed with sodium hydroxide and water. After drying with anhydrous sodium sulfate the mixture was distilled, collecting 8.0 g. of butyl acetate, b. 124–125°. The infrared spectrum showed the presence of a C–D band at 4.54μ, the intensity of which corresponded to the presence of about 0.26 deuterium atom per molecule.

The isopropyl ether solution prepared above was dried with anhydrous sodium sulfate. Eight grams (0.131 mole) of acetic acid-*d* was added and the mixture was decomposed as above for 30 hours at 67 ± 1°. Isolation of the product as above yielded 4.5 g. of butyl acetate, b. 124–125°, which showed the presence of a C–D band in the infrared spectrum corresponding to the presence of about 0.21 deuterium atom per molecule.

Thermal Decomposition of N-Butyl-N-nitrosoacetamide in Cyclohexane in the Presence of Sodium Benzoate and Calcium Hydride.—A solution of N-butyl-N-nitrosoacetamide in 225 ml. of cyclohexane was prepared from 14.6 g. (0.20 mole) of butylamine as described above. The solution was placed in a 500-ml. flask arranged for magnetic stirring and 4.0 g. (0.029 mole) of sodium benzoate and 2.8 g. (0.067 mole) of calcium hydride was added. The reaction flask was fitted with a condenser and drying tube and was immersed in a thermostat at 80 ± 1° for 24 hours. After cooling to room temperature the solids were removed by filtration. The filtrate was distilled and yielded, after the removal of the cyclohexane, 9.2 g. of butyl acetate (40% yield based on butylamine), b. 124–125°, and 2.0 g. of butyl benzoate (40% yield based on sodium benzoate), b. 238–245°.

Thermal Decomposition of a Mixture of N-Ethyl-N-nitrosopropionamide and N-Butyl-N-nitrosoacetamide.—Five milliliters of 70% ethylamine in water (0.075 mole) was converted to the nitrosoamide as described above with 10 ml. of propionic acid and 75 ml. of propionic anhydride. After the final hydrolysis the mixture was extracted twice with 50-ml. portions of *n*-hexyl ether.

To a solution of 8.6 g. (0.075 mole) of *n*-butylacetamide in 15 ml. of acetic acid and 75 ml. of acetic anhydride in an ice-bath was added 10 g. of sodium nitrite in two portions one-half hour apart. After stirring in the ice-bath for about 10 hours the mixture was allowed to warm slowly to room temperature with stirring. The mixture was poured into 300 ml. of ice and water and was stirred for 4 hours to hydrolyze the anhydride. The mixture was then extracted with two 50-ml. portions of hexyl ether.

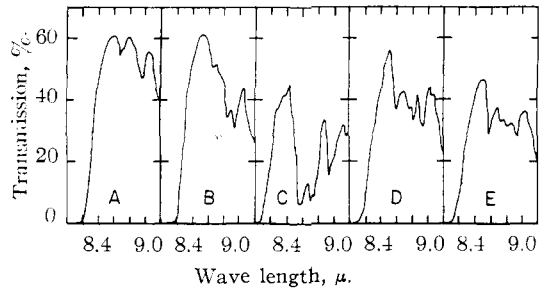


Fig. 1.—Infrared curves of butyl acetate (0.025-mm. cell): A, *n*-butyl acetate; B, 1-butyl-1-*d* acetate; C, 1-butyl-1,1-d_2 acetate; D, mixture 3; E, nitrosoamide reaction product.

The hexyl ether solutions of the two nitrosoamides were combined and were washed with water and with sodium bicarbonate. After drying with anhydrous sodium sulfate the mixture was placed in a constant temperature flask and was maintained at 80° (benzene was used as the refluxing heating bath) for 24 hours. After cooling, the mixture was washed with water and sodium bicarbonate and was dried with anhydrous sodium sulfate. The mixture was distilled until the boiling point rose to 200°. The distillate was redistilled through a spinning band column with intermittant take-off. The following fractions were taken in which the boiling points recorded are the temperatures of the thermometer at the time of take-off; 1, b. 76–81°, 2.3 ml. (ethyl acetate); 2, b. 97–102°, 2.2 ml. (ethyl acetate and ethyl propionate); 3, b. 114°, 0.3 ml.; 4, b. 121–127°, 2.2 ml. (butyl acetate and butyl propionate); 5, b. 132°, 0.3 ml.; 4, b. 142° 1.4 ml. (butyl propionate). The identifications were made by comparing the infrared spectra of the fractions with the infrared spectra of the authentic esters.

Control Stability of Esters in the Presence of Acid.—A mixture of 7.0 g. of butyl acetate (0.06 mole), 6.5 g. of ethyl propionate (0.064 mole), 0.9 g. of acetic acid (0.015 mole) and 1.1 g. of propionic acid (0.015 mole) in 200 ml. of hexyl ether was maintained for 24 hours at 80° using a constant temperature flask with benzene as the heating liquid. After cooling, the mixture was washed with water and with sodium bicarbonate and was dried with sodium sulfate. The mixture was distilled through a glass spiral column and the following fractions were collected, after redistillation of the intermediate cuts: 1, b. <96°, 0.3 ml.; 2, b. 98–103°, 7.2 ml.; 3, b. 106–120°, 1.7 ml.; 4, b. 122–128°, 5.6 ml.; 5, b. 141–170°, 1.4 ml. Fraction 1 contained no ethyl acetate and fraction 5 contained no butyl propionate (infrared). The yield of esters, b. 98–128°, is 95%.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

BERKELEY 4, CALIF.

(32) A. Streitwieser, Jr., THIS JOURNAL, **77**, 1117 (1955).