#### [CONTRIBUTION NO. 1263 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

# The Chemistry of the N-Alkyl-N-nitrosoamides. II. A New Method for the Deamination of Aliphatic Amines

## BY EMIL H. WHITE

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A new method for the deamination of aliphatic amines has been developed. The steps involved are acylation of the amine, nitrosation of the amide and thermal elimination of nitrogen from the resulting N-alkyl-N-nitrosoamide to form the corresponding ester. The new method gives much better yields than does the conventional amine deamination, and the products are obtained relatively free of isomers. The analogous N-nitrosourethans, N-nitrosoulfonamides and N-nitroamides also have been found to rearrange under similar conditions to yield the corresponding esters.

The conversion of aliphatic amines into alcohols or their derivatives is a reaction which has not been extensively used, since the only method hitherto available—the deamination with nitrous acid furnishes low yields of alcohols badly contaminated with isomers (Table I). A new method for this conversion, based on the facile elimination of nitro-

#### TABLE I

PRODUCTS OF NITROUS ACID DEAMINATION								
Reactants	Alcohols, %	Olefins, %						
<i>n</i> -Butylamine <sup><i>a</i></sup>	n-Butyl, 25 sec-Butyl, 13 <sup>b</sup>	Butenes, 37						
Isobutylamine <sup>c</sup>	Isobutyl, 20 <i>t</i> -Butyl, 60							
Isobutylamine <sup>d</sup>	Isobutyl, 5 t-Butyl, 20 sec-Butyl, 3							
sec-Butylamine <sup>e</sup>	sec-Butyl, 20							

<sup>a</sup> F. C. Whitmore and D. P. Langlois, THIS JOURNAL, 54, 3441 (1932). <sup>b</sup> 1-Chlorobutane (5%) and 2-chlorobutane (3%) were also obtained. <sup>c</sup> M. L. Henry, *Compt. rend.*, 145, 899 (1907). <sup>d</sup> Experimental section. <sup>e</sup> K. B. Wiberg, Ph.D. Thesis, Columbia University, 1950 (*ca.* 2.5 g. of alcohol from 12.6 g. of amine).

gen from the N-alkyl-N-nitrosamides (I), has been developed. The steps involved in this procedure are acylation of the amine, nitrosation of the amide and thermal elimination of nitrogen from the resulting N-alkyl-N-nitrosoamide.

$$\begin{array}{ccccccccc} H & O & O = N & O \\ & & & & & \\ RNH_2 \longrightarrow RN - C - R' \longrightarrow R - N - C - R' \longrightarrow \\ & I & O \\ & & & I \\ ROCR' + N_2 \end{array}$$

The esters from the last step are obtained relatively isomer-free and in good yield (Table II, runs 1, 6, 10, 17 and 19). A comparison of the data of Tables I and II illustrates the superiority of the new method.

Since acylation procedures are well known and the nitrosation procedures are reported elsewhere,<sup>1</sup> this paper will deal principally with the nitrogen elimination from I.

The first N-alkyl-N-nitrosoamides were prepared by Pechmann<sup>2a</sup> in 1894 and by Chancel<sup>2</sup> in 1895. Chancel and later Pechmann,<sup>2b</sup> reported that the decomposition of nitrosoamides yielded esters, but neither studied the reaction further. Sub-

(1) E. H. White, THIS JOURNAL, 77, 6008 (1955).

(2) (a) H. v. Pechmann, Ber., 27, 1888 (1894); M. F. Chancel, Bull. soc. chim. France, [3] 13, 125 (1895).
(b) H. v. Pechmann, Ber., 31, 2640 (1898). sequent workers have been concerned mainly with the use of nitrosoamides as derivatives<sup>3</sup> or for the preparation of diazoalkanes.<sup>4</sup> In view of the potentialities of this method of deamination, the work reported in this paper was undertaken in 1952.5 Since that time, a number of related cases have been reported. N-Nitrosolactams have been shown to eliminate nitrogen, forming a number of products including the corresponding lactones6; a Nnitrosourethan has been reported to yield the corresponding carbonate under certain conditions7; a N-nitrososulfonamide has been reported to yield the corresponding sulfate<sup>8</sup>; and finally, two N-alkyl-N-nitrosoamides have been shown to yield the corresponding esters when decomposed in the pure liquid state.9

#### Results

A study of the thermal elimination of nitrogen from the nitrosoamides I has shown that two competing reactions occur, which in typical cases account quantitatively for the starting material used.  $RN(NO)COR' \longrightarrow ROOCR' + N$ 

$$\begin{array}{c|c} N(NO)COR' & \longrightarrow & ROOCR' + N_2 \\ I & & & (1) \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

The relative importance of the two reactions depends upon the temperature, solvent, etc.; the reaction, therefore, will be discussed in terms of these variables.

Effect of the Alkyl Group (R).—The highest yields of esters are obtained from amides of primary carbinamines (R"CH<sub>2</sub>NH<sub>2</sub>) (runs 1, 5, 10 and 18). For example, N-(*n*-butyl)-N-nitroso-3,5-dinitrobenzamide in hexane at 69° (15 hr.) yielded *n*-butyl 3,5-dinitrobenzoate (81–84%), 3,5-dinitrobenzoic acid (16–18%), 1-butene,<sup>9a</sup> and nitrogen (1 mole). The crude ester obtained was quite pure, m.p. 62–

(3) J. V. Braun, ibid., 70B, 979 (1937).

(4) C. Paal and H. Apitzsch, *ibid.*, **32**, 78 (1899); H. J. Backer, J. Chem. Soc., **101**, 592 (1912); F. W. Bollinger, F. N. Hayes and S. Siegel, THIS JOURNAL, **72**, 5592 (1950).

(5) E. H. White, *ibid.*, **76**, 4497 (1954).
(6) R. Huisgen and J. Reinertshofer, *Ann.*, **575**, 174 and 197 (1952).
See also G. Nischk and E. Müller, *ibid.*, **576**, 232 (1952).

(7) C. D. Gutsche and H. E. Johnson, THIS JOURNAL, 76, 1776 (1954).
(8) Th. J. de Boer and H. J. Backer, Proc. Koninkl. Ned. Akad. Wetenschap., 55B, 444 (1954).

(9) K. Heyns and W. v. Bebenburg, Ber., 86, 278 (1953).

(9a) The infrared spectrum showed no 2-butene; in the other runs, the gases were qualitatively identified from the spectra. Quantitatively, the olefin yields were assumed to equal the acid yields (path b), since no polymers or tars were found and since the acyl moiety is quantitatively accounted for, in each case, by the ester and acid. This assumption was verified in run 23 by titration of the cyclohexene formed with perbenzoic acid. Found: acid 38%; olefin 35%.

#### TABLE II

		I RODUCID OF	THE IVIIROUGH DE	and Alto	N FROM 1	1				
				-	Yields <sup>a</sup>		)	Isomer distribution # %		70
Run	R	R'	Solvent	°C.	Ester,¢	Acid, %	п	but iso	yl esters sec	terl
1	n-Butyl	3,5-Dinitro-	Hexane	69	83	17	99		1	
$^{2}$		phenyl	Heptane	75	82		99		1	
3			Decalin	$192^d$	30	40	96		4	
4			Acetic acid <sup>e</sup>	70	13		78		22	
5	n-Butyl	Methyl	Heptane <sup>c</sup>	85	79	16				
6			CCl <sub>4</sub>	77	$67^{\circ}$	18	99		1	
7			Dioxane	95	78	19				
8			<i>p</i> -Xylene	95		21				
9			CHCl <sub>3</sub>	61		21				
10	Isobutyl	3,5-Dinitro-	Hexane	69	66	33		95.5	$3.5^{f}$	1
11		phenyl	Heptane	98	61	• •		91.5	7.5	1
12			Decalin	115	44	49		87	11	2
13			Acetonitrile $+$							
			Na <sub>2</sub> CO <sub>3</sub> <sup>g</sup>	81	30			91	7	2
14			Acetonitrile	81	11	53		45	25	30
15			Acetic acid®	25	8			45	15	40
16			Dioxane	80	64	35		91	8	1
17	Isobutyl	Methyl	Heptane	90		33				
18			$CC1_4$ °	77	62	37		94	4.5	1.5
19			Pyridine	85		35				
20	sec-Butyl	3,5-Dinitro-								
		phenyl	CCl <sub>4</sub>	30	26	59			100	
21	sec-Butyl	Phenyl	Pentane	25	23	64			100	
22	sec-Butyl	Methyl	$CC1_4$	60		67			100	
23	Cyclohexyl	Methyl	Pentane	36	50	38				
24	Cyclohexyl	Ethoxyl	CC14	70	36	43				
25	α-Phenyl ethyl	Methyl	Pentane	36	35	• •				
26			Dioxane	45	32	55				
a Vi	alde for rune 1-10 we	re based on I that	so for runs 20-26 w	ere hased	on the at	nidence	linth	a two sta	n nrooper c	fuitroon

PRODUCTS OF THE NITROGEN ELIMINATION FROM R-N-C-R'

N = 0

<sup>a</sup> Yields for runs 1–19 were based on I, those for runs 20–26 were based on the amide used in the two-step process of nitrosation and rearrangement (the nitrosoamides were unstable in the latter cases, and not isolated). No attempts were made to isolate products in those runs for which no yield data are given. For olefin yields, see footnote 9. <sup>b</sup> Isomer distribution determined by comparison of the infrared spectra with those of standard mixtures of the authentic esters. The errors for runs 1, 2, 6, 10, 11, 12, 18 =  $\pm 1\%$ ; (*tert* error  $\pm 0.5\%$ ); for runs 3, 4, 13, 16 =  $\pm 2\%$ ; (*tert* error  $\pm 1\%$ ); and for runs 14 and 15 *ca*.  $\pm 5\%$ . <sup>c</sup> Yields determined by saponification for runs 5, 7 and 18 and gravimetrically for the remaining runs. <sup>d</sup> The only run in which tar formation occurred. <sup>e</sup> The ester yields refer to the dinitrobenzoates. Acid interchange could not have been important in these runs, since *n*-butyl 3,5-dinitrobenzoate was recovered in 95\% yield after being subjected to the same reaction conditions. In addition to the normal products, the corresponding amide was formed in these runs, 20% in run 4 and 25\% in run 15. <sup>f</sup> This unusual formation of the secondary isomer was noted in other reactions of isobutyl derivatives; these results will be reported later. <sup>e</sup> An unidentified product was also obtained in this run.

 $63^{\circ}$ , trace at  $68^{\circ 10}$  (authentic sample,  $63.5-64^{\circ}$ , lit.<sup>11</sup>  $64^{\circ}$ ). The infrared spectrum was superimposable on that of authentic *n*-butyl 3,5-dinitrobenzoate, and a comparison with the spectra of mixtures of the normal and *sec*-butyl isomers showed that less than 1% of the secondary isomer could have been formed. The actual formation of traces of *sec*-butyl 3,5-dinitrobenzoate was indicated by the infrared spectrum of the leading fraction (enriched in the secondary isomer) from the chromatography of the crude ester on neutral alumina.

The yields of esters are lower from amides of secondary aliphatic carbinamines (runs 20, 21 and 22), with olefin and acid yields proportionately higher

(10) The high melting crystals were found to be adducts formed by the ester with trace amounts of hydrocarbons from the stopcock grease used. The adduct from the ester and pure hexadecane was a crystalline material, m.p.  $69-69.5^{\circ}$ . Even in a carefully cleaned vessel, the ester from the nitrogen elimination contained a trace of the adduct, suggesting that a small portion of the olefin had polymerized.

(11) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 226. (path b). Cyclohexyl and  $\alpha$ -phenylethyl derivatives give intermediate yields (runs 23–26), whereas amides of tertiary carbinamines give quite low yields of the corresponding esters.<sup>12</sup> Stereochemically, esters are formed from nitrosoamides of optically active secondary carbinamines with either partial retention or partial inversion of configuration, depending on the reaction conditions.<sup>13</sup>

Effect of the Acyl Group.—The ester yields and isomer distributions were essentially the same for the nitrosoacetamides, benzamides and dinitrobenzamides used (Table II). The yields from the nitrosourethans<sup>14</sup> and the nitrososulfon-(12) To be reported later.

 (13) The stereochemistry of this reaction is reported in paper III, THIS JOURNAL, 77, 6014 (1955).

(14) The reaction of nitrosourethans with bases is often used to prepare diazoalkanes; in some cases, however, carbonyl containing byproducts have been detected as well (D. Y. Curtin and S. M. Gerber, THIS JOURNAL, **74**, 4052 (1952)) and in others, dialkyl carbonates have been isolated (F. W. Bollinger, F. N. Hayes and S. Siegel, *ibid.*, **72**, 5592 (1950)). In all probability, these by-products are the dialkyl carbonates expected from the thermal nitrogen elimination reaction reported in this paper (path a, R' = OEt). See also footnote 7. amides (vide infra) were slightly lower however.

Effect of the Solvent.—The highest yields and the purest esters are obtained from the nitrogen elimination in relatively non-polar solvents; a number of these solvents were used with essentially the same results (Table II). In the more polar solvents, the acids formed in the elimination step (path b) are more important than the solvents in determining the yields and amount of isomerization. The effect of the solvent itself was determined by carrying out the reaction in the presence of anhy-drous sodium carbonate.<sup>15</sup> Under these conditions, the isomer distribution was not appreciably different from that observed in non-polar solvents (compare runs 13 and 14). In acetic acid and in acetonitrile (in the absence of sodium carbonate) some denitrosation to the amide occurs, the yield of ester is low (path a), and the proportion of isomerized ester is high (runs 4, 14 and 15). The relative rates of nitrogen elimination in the solvents tested were in the order acetic acid > dioxane > hexane.

Effect of Temperature.—The nitrosoamides of primary carbinamines eliminate nitrogen at ca.  $60-80^{\circ}$ , those of aliphatic secondary carbinamines at ca.  $20-30^{\circ}$ , and those of  $\alpha$ -phenylethylamine at ca.  $50^{\circ}$  (ca. 10-15 hr. required). The highest yields and the purest esters are obtained at the lowest practicable temperatures (compare runs 1 and 3; 10, 11 and 12).

Miscellaneous Applications.—A number of analogs of the nitrosoamides undergo similar elimination reactions. (i) N-(n-Butyl)-N-nitroacetamide in carbon tetrachloride at 77° (15 hr.) yielded nbutyl acetate (75%), acetic acid and 1-butene (23%), and nitrous oxide (compare with runs 5 and 6).

Path b, equation 1 R—N—CR' 
$$\rightarrow$$
 ROCR' + N<sub>2</sub>O

(ii) N - (n - butyl) - N - nitroso - p - toluenesulfonamide(plus one mole of sodium carbonate) in hexane at69° (15 hr.) yielded*n*-butyl*p*-toluenesulfonate(55%) and sec-butyl*p*-toluenesulfonate (7%). In

the absence of sodium carbonate, the reaction was markedly affected by the toluenesulfonic acid formed (path b). In this case, mixed butyl ptoluenesulfonates (25%), p-toluenesulfonic acid and butene (21%), and N-(*n*-butyl)-p-toluenesulfonamide (25%) were formed. (iii) N-Cyclohexyl-Nnitrosourethan in carbon tetrachloride at 77° (3 hr.) yielded cyclohexyl ethyl carbonate,<sup>14</sup> cyclohexene, carbon dioxide, ethanol and nitrogen (run 24).

$$\begin{array}{cccc} O = N & O & O \\ & & \parallel \\ Path b, equation 1 & \longrightarrow RN-COR' \longrightarrow ROCOR' + N_2 \end{array}$$

Application of the new method to several other

(15) In non-polar solvents, sodium carbonate had no effect on either the yields of esters or on the distribution of isomers. derivatives yielded different results. Methyl Nbenzoyl-N-nitrosoalanate yielded only methyl  $\alpha$ diazopropionate and benzoic acid; whereas both Nmethyl-N-nitrosourea and N-nitrosoacetanilide<sup>16</sup> in

$$\begin{array}{ccc} & \stackrel{O=N}{\underset{\parallel}{H}} & \stackrel{O}{\underset{\parallel}{H}} \\ & \stackrel{H}{\underset{\parallel}{H}} & \stackrel{O}{\underset{\parallel}{H}} \\ & \stackrel{MeC-NCC_{6}H_{5}}{\underset{\parallel}{\longrightarrow}} & \stackrel{MeC=\stackrel{+}{\underset{\parallel}{N}} = \bar{N} + C_{6}H_{5}CO_{2}H \\ & \stackrel{I}{\underset{\parallel}{H}} \\ & \stackrel{I}{\underset{\parallel}{H}} \\ & \stackrel{O=N}{\underset{\parallel}{H}} \\ & \stackrel{I}{\underset{\parallel}{H}} \\ & \stackrel{I}{\underset{\parallel}{H}} \\ & \stackrel{I}{\underset{\parallel}{H}} \\ \end{array}$$

refluxing carbon tetrachloride yielded complex mixtures of products containing none of the expected ester.

#### Experimental

**Preparation of Nitrosoamides.**—The N-nitrosoamides described in this paper were prepared by the methods given earlier.<sup>1</sup>

Nitrogen Elimination from I.—A solution of N-(isobutyl)-N-nitroso-3,5-dinitrobenzamide (1.154 g., 3.90 mmoles) in 500 ml. of hexane was refluxed with stirring for 15 hr. The butenes were collected by bubbling the effluent gases through carbon tetrachloride traps.<sup>9</sup> The reaction mixture was cooled and the 3,5-dinitrobenzoic acid filtered (0.268 g., 1.27 mmoles, 33%). The hexane solution was washed with aqueous sodium hydroxide, dried and evaporated to dryness to yield 0.685 g. (2.56 mmoles, 66%) of crude isobutyl 3,5-dinitrobenzoate, m.p. 84–85° (authentic sample 86– 87°, IIt.<sup>11</sup> 86°). The isomer distribution was determined for this product by the method given below.

In general, for the nitrogen elimination from I, a solution of the nitrosoamide in the appropriate solvent was maintained at the lowest temperature at which nitrogen evolution occurred, until the evolution had ceased. If sodium carbonate was not used, the acid formed was titrated with standard base, the organic phase separated, washed with water and then dried. The solvent was removed<sup>17</sup> (*in vacuo* if possible) and the product distilled or recrystallized, depending on its properties. During the course of this work, infrared spectra were taken of the esters (before purification) dissolved in carbon tetrachloride (0.3 M). The isomer contents were determined by comparing these spectra with infrared spectra of mixtures of the esters of known composition.

A Procedure for the Deamination Omitting the Isolation of Intermediates-Preparation of Acetamides.—One mole of the amine was chilled to  $-80^{\circ}$  and acetic acid<sup>18</sup> slowly added (1.5 moles). The flask was removed from the cooling bath, one mole of acetic anhydride added, and after the exothermic reaction had subsided, the acetic acid was removed by distillation. The crude amide was nitrosated using any of the methods reported earlier,<sup>1</sup> and the elimination of nitrogen carried out as described in the previous section. By this procedure, redistilled *n*-butyl acetate  $(n^{25}D 1.3919, \text{lit.})^{19} n^{25}D 1.3914)$  was obtained by the threestep reaction from *n*-butylamine in 56% yield. N-(n-Butyl)-N-nitroacetamide.<sup>20</sup>—A solution of 90%

N-(*n*-Butyl)-N-nitroacetamide.<sup>20</sup>—A solution of 90% nitric acid (50 ml., d. 1.50) in acetic anhydride (100 ml.) was prepared at  $-15^{\circ}$ , N-(*n*-butyl)-acetamide<sup>21</sup> (21.5 g., 0.187 mole) was added slowly, and the mixture allowed to stand at 4° for 10 hr. The solution was poured into a mixture of ice and water, the product extracted with pentane, and the extract washed with a sodium carbonate solution (10%), with water, and then dried. The pentane was removed under vacuum and the yellow oil distilled, b.p. 45-47° at 0.5 mm. (21.4 g., 0.134 mole, 71.5%),  $n^{25}$ p 1.4542. Infrared spectrum: C=O, 5.79  $\mu$ ; NO<sub>2</sub>, 6.34  $\mu$ . Anal.

(16) W. A. Waters, J. Chem. Soc., 113 (1937).

(17) In the case of a volatile ester and a water-miscible solvent, pentane was added and the other solvent extracted out with water.

(18) The acetic acid is used to moderate the otherwise violent reaction of acetic anhydride with the amine.

(19) J. C. Munch, THIS JOURNAL, 48, 997 (1926).

(20) This procedure is a modification of that used by W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton and C. E. Maxwell, *ibid.*, **72**, 3132 (1950).

(21) Prepared by the general method given in the preceding section, and distilled, n<sup>24</sup>D 1.4385. R. H. Wiley, O. H. Borum and L. L. Bennett, *ibid.*, **71**, 2899 (1949) report n<sup>25</sup>D 1.4388. Calcd. for  $C_6H_{12}O_3N_2$ : C, 44.99; H, 7.55; N, 17.49. Found: C, 45.07; H, 7.71; N, 17.53.

The elimination of nitrous oxide was carried out using the procedure given above for the nitrosoamides.

The Reaction of Isobutylamine with Nitrous Acid.—Isobutylamine (14.9 g., 0.204 mole) was added to 300 ml. of 0.8 N sulfuric acid (0.24 mole) at 0° and a solution of sodium nitrite (25 g., 0.36 mole) in 50 ml. of water was slowly added. After one day, 25 ml. of 1.0 N sulfuric acid was added, and after an additional day at 0°, the solution was saturated with sodium chloride and the alcohols extracted with ether (the aqueous solution yielded 1.9 g. of unreacted amine, 0.026 mole, 13%). The ether solution was washed with dilute sodium hydroxide solution (5%), the solution was dried, and the ether removed through a small column. The mixture of alcohols was distilled at 1 atm., the fraction boiling from 65 to 120° weighed 2.9 g. (0.04 mole, 22%) based on the amine which had reacted). The infrared spectrum indicated that the alcohols were contaminated with small amounts of nitroalkanes and nitrates. The isomer distribution given in Table I was determined by comparing the infrared spectrum of the product with the spectra of mixtures of the authentic alcohols. This isomer distribution was confirmed by the infrared spectrum of the 3,5-dinitrobenzoates prepared by treating the alcohol mixture with 3,5-dinitrobenzoyl chloride in an excess of pyridine. The analyses given are good to within ca. 5%.

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## The Chemistry of the N-Alkyl-N-nitrosoamides. III. Mechanism of the Nitrogen Elimination Reaction<sup>1</sup>

### BY EMIL H. WHITE

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A two-stage mechanism is proposed for the rearrangement of a N-alkyl-N-nitrosoamide into the corresponding ester. The formation of a diazo ester represents the first stage, and the elimination of nitrogen from the diazo ester *via* a SNi reaction, the second. Studies with optically active nitrosoamides have shown that, depending on the reaction conditions, the products from the second stage may be formed by intramolecular retention, intramolecular inversion or intermolecular inversion reactions.

In the preceding paper<sup>2</sup> it was shown that, stoichiometrically, the elimination of nitrogen from the N-alkyl-N-nitrosoamides occurs according to equation 1.

A single-stage mechanism does not seem possible for this intramolecular reaction; the following mechanism, based upon reactions of the analogous N-nitroamides and the N-aryl-N-nitrosoamides, satisfactorily accounts for the main features of the reaction.

$$\begin{array}{c} N = O \\ \vdots & \uparrow \downarrow \\ R - N & \hline C - R' \longrightarrow \begin{bmatrix} O \\ \parallel \\ RN = NOCR' \end{bmatrix} \longrightarrow \\ 0 & I \\ O & products (eq. 1) \quad (2) \end{array}$$

Formation of the Diazo Ester (I).—In the aromatic series, the formation of a diazo ester from the corresponding nitrosoamide has long been assumed to be the first step in the modified biaryl synthesis.<sup>3</sup> Recent kinetic studies by Huisgen<sup>4</sup> and Hey<sup>5</sup> have confirmed this view. Aliphatic dia-

$$\begin{array}{c} N = O \\ \downarrow & \uparrow^{\downarrow} \\ Ar - N \xrightarrow{\uparrow} C - R \xrightarrow{\downarrow} \begin{bmatrix} O \\ H \\ Ar N = NOCR \end{bmatrix} \xrightarrow{C_6 H_6} \\ \downarrow \\ O \\ Ar - C_6 H_5 + N_2 + RCO_2 H \quad (3) \end{array}$$

(1) Presented at the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, March 30, 1955.

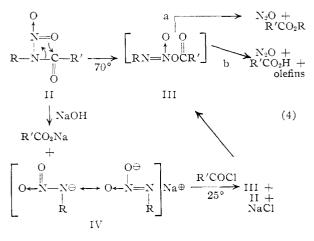
(2) E. H. White, THIS JOURNAL, 77, 6011 (1955).

(3) W. E. Bachmann and R. A. Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 228.

(4) R. Huisgen, Ann., 574, 184 (1951), and four earlier papers.
(5) D. H. Hey, J. Stuart-Webb and G. H. Williams, J. Chem. Soc., 4657 (1952).

zonium salts and diazo esters have never been isolated; however, indirect evidence for the intermediate formation of a diazo ester in the reactions of aliphatic nitrosoamides was obtained from a study of the corresponding N-nitroamides.

N-Nitroamides and N-nitrosoamides under the same reaction conditions eliminate nitrous oxide and nitrogen, respectively, to form olefins and esters in approximately the same yields.<sup>2</sup> The mechanisms for the two reactions are probably very similar; that proposed for the N-nitroamides is given in the upper line of equation 4.



The unstable intermediate in this case (III) can be obtained by an independent route. The N-nitroamide was saponified to yield the sodium salt of a N-nitroamine IV. Acylation of this salt can occur either on nitrogen or on oxygen, *i.e.*, to yield II or III. N-Nitroamides II are stable under the reaction conditions employed in the last step, whereas the intermediate III should eliminate nitrous oxide