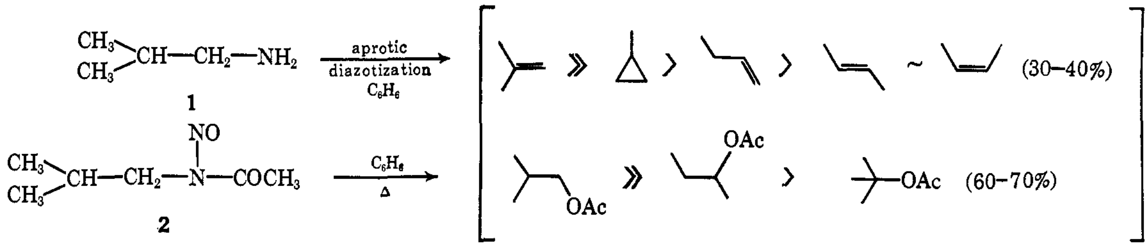
Degradation of β-Hydroxyisopropylpyridinatocobaloxime. The cobaloxime (5.0 g) was suspended in 25 ml of 1 *N* NaOH and the mixture was gently warmed. Samples of the volatile organic decomposition products were continuously withdrawn out of the gas phase and analyzed by programmed mass spectroscopy. Acetone was the only product detected. After careful neutralization with dilute H_2SO_4 the reaction mixture was fractionally distilled. Acetone, isolated in the over-all yield of 69% of the theoretical amount, was identified by gas chromatography and mass spectroscopy.

Communications to the Editor

Concerning the Mechanisms of Alkylamine Diazotization and N-Alkyl-N-nitrosoacetamide Decomposition[1]

Sir:

In attempts to determine the nature of the intermediates involved in formation of bicyclobutane by aprotic diazotization of cyclopropylcarbinylamine,[2] reactions were conducted using DOAc and amine-d_2,[3] wherein the bicyclobutane formed contained significant amounts of deuterium.[4] In order to elucidate the mechanism(s) by which this may have occurred, a study of the diazotization process was initially undertaken using isobutylamine (**1**).



Aprotic diazotization[5] of **1**-d_2 in benzene, chloroform, or mesitylene gave C-4 hydrocarbon mixtures that incorporated deuterium to the extent of ~36% d_1 and ~12% d_2.[6] Products obtained by diazotization in ethylene glycol-d_2 (EG-d_2) incorporated deuterium to a similar but somewhat smaller degree (Table I). In more protic systems such as DOAc and D_2O–DOAc, deuterium uptake was diminished[7] and limited to monodeuteration. Inasmuch as it was reported previously[5] that aprotic diazotization of amines and thermal decomposition of N-alkyl-N-nitrosoacetamides under similar conditions afford the same products, presumably *via* common intermediates, the decomposition of N-isobutyl-N-nitrosoacetamide (**2**) was also investigated in deuterium-labile media (Table I).

The decomposition of **2** in the presence of *only 1 equiv* each of D_2O and hexanol-*d*, in order to simulate as closely as possible the conditions of aprotic diazotization, *gave products which incorporated deuterium to the same extent* (51% d_0, 40% d_1, 9% d_2). Furthermore, decomposition of **2** in more highly protic media (Table I) results in less deuterium uptake.

The data must be rationalized by mechanisms which accommodate the following experimental observations for primary aliphatic systems: (a) the incorporation of one and two deuterium atoms/molecule in products from both aprotic diazotization of amines and thermal decomposition of N-alkyl-N-nitrosoacetamides in deuterium-labile environments; and (b) an increase of solvating power of the media and/or a decrease in apparent pH markedly diminishes the extent of deuteration.

The results in aprotic media are best explained by the following reaction scheme[8] which involves the formation of covalent diazonium acetate[8b,9] (**3**) as the common primary intermediate. Structure **3** should prevail over **3a** and would give **4**[10] *via* cyclic elimination of acetic acid.[7b] Addition of DOAc would lead to **5** and **5a**, incorporating one deuterium atom at this stage. By similar processes **7** and **7a** could be formed, thus incorporating two atoms of deuterium. The formation of non-, mono- and dideuterated products can occur as depicted arising from **3a**, **5a**, and **7a**, respectively.[11]

---

[1] Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged.

[2] J. Bayless, L. Friedman, J. A. Smith, F. B. Cook, and H. Shechter, *J. Am. Chem. Soc.*, **87**, 661 (1965).

[3] *I.e.*, $RND_2 + D^+ + R'ONO \longrightarrow$ products derived from $RN_2^+ + D_2O + R'OD$.

[4] Unpublished results.

[5] J. H. Bayless, F. D. Mendicino, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5790 (1965).

[6] By low-voltage mass spectrometry on total hydrocarbon fraction. Individually trapped isomers (methylcyclopropane, isobutylene, 1-butene) showed essentially the same degree of deuterium incorporation. Nmr analysis of the isobutyl acetate indicated the same amount of deuterium and that it was present only at C-1.

[7] (a) *Cf.* A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957); (b) *ibid.*, **79**, 2893 (1957).

[8] (a) The possibility of diazo–diazonium ion equilibration for diazoalkanes was previously recognized but was not definitively resolved: R. Huisgen and H. Reimlinger, *Ann.*, **599**, 183 (1956); (b) *ibid.*, **599**, 161 (1956).

[9] E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).

[10] Diazoalkanes are formed in the thermal decomposition of the N-nitrosoamides of primary carbinamines: E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1174 (1961), and references contained therein. (b) On the other hand, N-nitrosoamides of secondary carbinamines presumably decompose without the involvement of diazoalkane intermediates: E. H. White and C. A. Aufdermarsh, *ibid.*, **83**, 1179 (1961). Aprotic diazotization of *sec*-butylamine-d_2 in benzene with 1 equiv of DOAc is in agreement with this; *i.e.*, only ~3% monodeuteration is observed.

[11] Diazoester—diazonium acylate ion-pair equilibria have been postulated for the decomposition of N-nitrosoamides of secondary carbinamines.[10b]

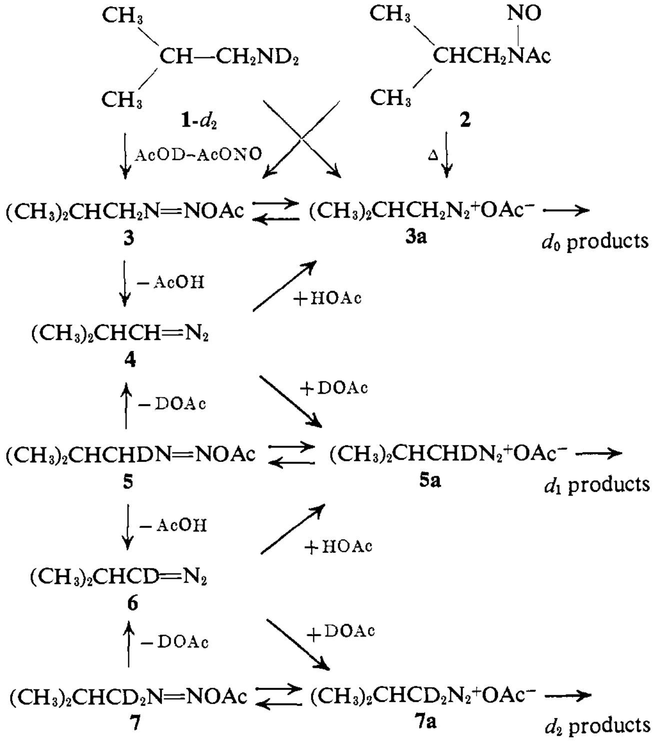
Table I. Diazotization of Isobutylamine and Thermal Decomposition of N-Isobutyl-N-nitrosoacetamide in Deuterium Labile Environments[a]

Cation precursor[b]	Deuterium source	Solvent	% composition[c] of hydrocarbon products 					Deuterium content,[c] mole % d_0	d_1	d_2
1-d_2–RONO[f]	DOAc (1)[g]	C_6H_6	11	78	6	3	2	52	36	12[d,e]
2	D_2O (1), R′OD[h] (1)	C_6H_6	14	73	6	5	2	51	40	9
1-d_2–RONO	DOAc (3)	C_6H_6	9	77	8	4	2	70	27	3
2	DOAc (2)	C_6H_6	10	75	7	6	2	73	26	1[e]
1-d_2–RONO	DOAc (1)	R′OD[h]	11	71	9	6	3	73	25	2
2	D_2O (1)	R′OD[h]	11	71	9	6	3	73	26	1
1-d_2–RONO	DOAc (1)	EG-d_2	4	65	14	11	6	65	33	2
2	*i*	EG-d_2[i]	4	64	15	11	6	90	10	0
1-d_2–RONO		DOAc	4	65	11	14	6	96	4	0
2	D_2O (1), ROD (1)	DOAc	4	67	11	12	6	94	6	0
1-d_2–RONO		50% D_2O–DOAc	2	45	18	24	11	>99	<1	

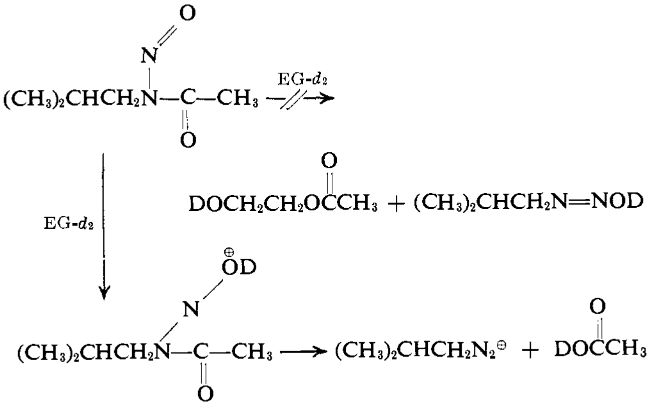
[a] Representative data. [b] 5 m*M* in 10 ml of solvent. [c] Glpc and low-voltage mass spectrometry. [d] Similar deuterium uptake was observed in hydrocarbon products from *n*-butylamine (57% d_0, 33% d_1, 10% d_2) and N-*n*-butyl-N-nitrosoacetamide (40% d_0, 44% d_1, 16% d_2). [e] A similar reaction with N-(*n*-butyl)-N-nitrosoacetamide gave *n*-butyl acetate containing 26% d_1 species.[7b] [f] Octyl nitrite, 5.5 m*M*. [g] Equivalents. [h] Hexanol-*d*. [i] These products (independent of added reagents: excess D_2O, DOAc, **1**-d_2, etc.) are formed from a butyldiazonium ion precursor in almost identical solvent environments. This is probably a result of the leveling effect observed in strongly hydrogen-bonded media.

In effect, the intermediacy of *free* diazoalkane (**4**, **6**) is required to accommodate the observed extensive deuterium–hydrogen exchange phenomena.

An increase in acid concentration would be expected to greatly decrease the probability of **3** going to **4**, and as the solvating power of the medium is increased **3a** would predominate; in each case over-all deuterium uptake would be lessened.[12] In highly polar media (D_2O–DOAc, D_2O–DCl, etc.) the lack of deuterium incorporation can be best explained by a path that involves direct conversion (protonation) of the nitrosamine to the diazonium ion.[13]



The difference observed from diazotization of **1**-d_2 and thermal decomposition of **2** in EG-d_2 are best explained by proposing deuteration (by EG-d_2) on **2**-nitrosyl leading directly to diazonium ion and acetic acid.[13] This is formally analogous to the acid-catalyzed conversion of nitrosamine to diazonium ion.[13] The absence of hydroxyethyl acetate invalidates a scheme involving a diazotic acid intermediate.[14]



Thus, the intimate details and the nature of the intermediates involved in the course of aliphatic amine diazotization and N-alkyl-N-nitrosoacetamide decomposition are subtly influenced by the nature of the reaction medium and products resulting from each arise *via* a common precursor,[15] a cationic species in presently undefined states of solvation.[16]

John H. Bayless,[17] **Lester Friedman**

Department of Chemistry, Case Institute of Technology
Cleveland, Ohio 44106

Received March 7, 1966

---

(12) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 41.

(13) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961).

(14) (a) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966). (b) Similarly, aprotic diazotization of *n*-butylamine-d_2 with DCl in benzene gave hydrocarbon products containing no deuterium (<0.1%).

(15) *Cf.* R. Huisgen and C. Rüchardt, *Ann.*, **601**, 1 (1956).

(16) *Cf.* H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 123.

(17) NASA Fellow, 1963–1966.