Influence of Solvent on Diazoalkane–Alkyldiazonium Ion Equilibria in Amine Deaminations[1]

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Abstract: Diazotization of alkylamines and decomposition of the corresponding nitrosoamides, when effected under comparable conditions, afford hydrocarbon mixtures that are essentially identical. If the alkyl group is primary, diazoalkanes are intermediates in reactions effected in poorly solvating media; the extent of diazoalkane formation diminishes with an increase in the solvating power of the environment such that in protic media such as aqueous acetic acid there is no evidence for its intermediacy at all. Under all of the reaction conditions studied, products arise from diazonium species which are either formed by protonation of the intermediate diazoalkane (*i.e.*, carbenic decomposition of diazoalkanes does not occur) or directly from precursor nitrosoamine or nitrosoamide.
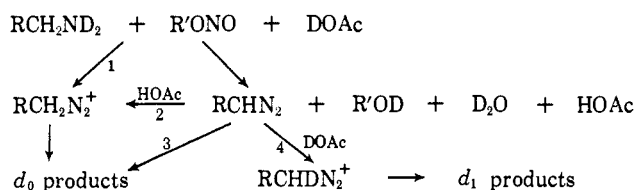
The results obtained from aprotic diazotization of isobutylamine, *e.g.*, large amounts of methylcyclopropane and minimal skeletal rearrangement, are such that two points require evaluation: (1) are diazoalkanes intermediates in aprotic diazotization of amines, such as observed from thermal decomposition of *n*-alkylnitrosoamides,[4,5] and (2) if diazoalkanes are intermediates, do they decompose thermally (*via* carbenes) under the reaction conditions or undergo protonation to diazonium species?

In order to elucidate these points diazotization of alkylamine-d_2 (RCH_2ND_2) was effected in a deuterium-labile environment (Scheme I). From the extent

Scheme I

of deuterium uptake in the products, an understanding of the reaction processes may be forthcoming. Under these conditions diazoalkane, if formed along with O-deuterated alcohol, deuterium oxide, and acetic acid, would undergo either thermal decomposition to yield deuterium-free products (route 3) or deuteration and subsequent decomposition of the diazonium ion to give monodeuterated products[6] (route 4). However, protonation could also occur (route 2) and this would also lead to nondeuterated products. On the other hand, if diazoalkanes are not intermediates, *i.e.*, only diazonium species are formed (route 1), products would be deuterium free.

Thus while d_0 products could arise *via* both cationic and carbenic processes, d_1 products could arise only *via* the cationic route (4). Occurrence of d_1 products, therefore, would be strong evidence for the intermediacy of diazoalkane. Obviously if d_1 products are formed, arising *via* protonation of the diazoalkane, d_0 products would also be observed.[7]

Results and Discussion

Diazotization of isobutylamine-d_2 (**1-d_2**) in benzene (at reflux) or mesitylene (90°) with DOAc (1 equiv) and octyl nitrite (1.1 equiv) gave hydrocarbon mixtures[8] that incorporated deuterium to the extent of 36% d_1 and 12% d_2[9] (Table I). Nmr analysis of the isobutyl acetate from the reaction in mesitylene indicated essentially the same amount of deuterium uptake and that it was present only at C-1. These results invalidate Scheme I since it does not account for occurrence of d_2 species. However, the presence of monodeuterated products is consistent with the intermediacy of diazoalkane.

The unexpected complexity of the reaction necessitated a more extensive investigation to elucidate the mechanism(s) of deuterium incorporation. In order to obtain more information diazotization was effected in several deuterium-labile solvent systems. Diazo-

(1) (a) Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged. (b) Preliminary accounts of portions of this work have been published: J. H. Bayless and L. Friedman, *J. Am. Chem. Soc.*, **89**, 147 (1967); A. T. Jurewicz and L. Friedman, *ibid.*, **89**, 149 (1967). (c) For the preceding paper in this series, see L. Friedman, and J. H. Bayless, *ibid.*, **91**, 1790 (1969).

(2) Based on the Ph.D. dissertations of A. T. J. and J. H. B., Case Institute of Technology, 1967.

(3) NASA Fellow, 1963–1966.

(4) E. H. White, *J. Am. Chem. Soc.*, **77**, 6014 (1955).

(5) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 2893 (1957).

(6) Intermediacy of diazoalkane from thermal decomposition of N-(*n*-butyl)-N-nitrosoacetamide was demonstrated by effecting the reaction in the presence of deuterioacetic acid. *n*-Butyl acetate was obtained which contained deuterium.[5]

(7) It is inconceivable that only deuteration of the diazoalkane would occur without protonation inasmuch as the system would contain acetic acid as shown in Scheme I. It is known that acetic acid adds to diazoalkanes about four times faster than deuterioacetic acid: J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 3695 (1952).

(8) Attention was focused on the hydrocarbons since their deuterium compositions are readily analyzed *via* low-voltage mass spectrometry. However, a complete study of the substitution products was also undertaken. Deuterium uptake in the substitution products (alcohols and esters) as measured by nmr is in excellent agreement with the hydrocarbon results: L. Friedman and J. H. Bayless, unpublished results.

(9) Individually trapped isomers (methylcyclopropane, 1-butene) showed essentially the same degree of deuterium incorporation. See Table II for detailed data from isobutyl-1,1-d_2-amine.

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

Run no.	Precursor[a]	Deuterium source	Solvent	Hydrocarbons—% composn[b] $\triangle$	$\diagup=$	$\diagdown$	$\diagdown$	$\diagdown\diagup$	Deuterium content,[b] mole % d_0	d_1	d_2
1	$1\text{-}d_2\text{-RONO}^c$	DOAc (1)[d]	C_6H_6	11	78	6	3	2	52	36	12
2	$1\text{-}d_2\text{-RONO}$	DOAc (1)	$t\text{-BuC}_6H_6$	12	76	7	3	2	53	36	11
3	2	D_2O (1), R'OD[e] (1)	C_6H_6	14	73	6	5	2	51	40	9
4	$2\text{-}d_2\text{-RONO}$	DOAc (3)	C_6H_6	9	77	8	4	2	70	27	3
5	2	DOAc (2)	C_6H_6	10	75	7	6	2	73	26	1
6	$1\text{-}d_2\text{-RONO}$	DOAc (1)	R'OD[e]	11	71	9	6	3	73	25	2
7	2	D_2O (1)	R'OD[e]	11	71	9	6	3	73	26	1
8	$1\text{-}d_2\text{-RONO}$	DOAc (1)	$EG\text{-}d_2$	4	65	14	11	6	65	33	2
9	2	f	$EG\text{-}d_2^f$	4	64	15	11	6	90	10	0
10	$1\text{-}d_2\text{-RONO}$		DOAc	4	65	11	14	6	96	4	0
11	2	D_2O (1), ROD (1)	DOAc	4	67	11	12	6	94	6	0
12	$1\text{-}d_2\text{-RONO}$		50% D_2O–DOAc	2	45	18	24	11	>99	<1	

[a] 5 mmol in 10 ml of solvent. [b] Via glpc and low-voltage mass spectrometry. [c] Octyl nitrite, 5.5 mmol. [d] Equivalents. [e] Hexanol-d. [f] Results independent of added reagents: D_2O, DOAc, $1\text{-}d_2$, etc.

tization of $1\text{-}d_2$ in benzene containing excess DOAc gave products containing less deuterium[10] (27% d_1, 3% d_2; run 4, Table I) relative to that obtained from aprotic diazotization. Products obtained by diazotization in ethylene glycol-d_2 ($EG\text{-}d_2$) incorporated deuterium to a similar extent (33% d_1, 2% d_2; run 8). In the more protic solvent DOAc, deuterium uptake was diminished and limited to monodeuteration,[11] while in the highly protic and polar medium D_2O–DOAc, products were essentially deuterium free (runs 10 and 12). Inasmuch as common intermediates are apparently involved in aprotic diazotization of amines and decomposition of the corresponding alkylnitrosoamides,[1c] an investigation of decomposition of N-(isobutyl)-N-nitrosoacetamide (2) in deuterium-labile environments was also undertaken.

The thermal decomposition of 2 in benzene, in the presence of 1 equiv each of D_2O and hexanol-d (used 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; run 3, Table I) as that obtained via aprotic diazotization of $1\text{-}d_2$. Furthermore, decomposition of 2 in more highly protic media resulted in less deuterium uptake (Table I); that is, the results from thermal decomposition of 2 are essentially identical with those obtained by diazotization of $1\text{-}d_2$ under similar reaction conditions.[12]

The results must be rationalized by mechanisms which accommodate the following experimental observations: (a) the incorporation of one and two deuterium atoms per molecule in products from both aprotic diazotization and from thermal decomposition of the alkylnitrosoacetamide in deuterium-labile environments and (b) a marked decrease in the extent of deuteration with an

increase of solvating power of the media and/or a decrease in the apparent pH.

The results in aprotic media are best explained by a reaction (Scheme II)[13,14] which involves the formation of covalent diazonium acetate 3[13,14] and/or diazonium-acetate ion pairs[14c,15] (3i) as the common primary intermediate(s). Thus structure 3 should prevail over 3i (charge separation is unfavorable in poorly solvating media)[16] and would give 4 via cyclic elimination[5] of acetic acid.[17] Addition of DOAc (or $(DOAc)_2$) would lead to 5 and 5i incorporating one deuterium atom at this stage. By similar processes 7 and 7i could be formed, thus incorporating two atoms of deuterium. In effect the intermediacy of free diazoalkane (4, 6) is required to accommodate the observed hydrogen–deuterium exchange phenomenon and deuterium incorporation.

Dideuterated products obviously can arise only via cationic processes (i.e., from 7i).[18] On the other hand, since d_0 and d_1 products could arise via cationic processes from 3i and 5i, respectively, and/or via carbenic processes from 4 and 6, respectively, it is not possible from these data to determine the extent of each.

The extent of carbene intermediates, i.e., via thermal decomposition of diazoalkanes, involved in amine deaminations can be determined by appropriate labeling experiments. For example, isobutyl-1,1-d_2-diazonium ion (8) could yield, by loss of nitrogen, migration of methyl, and loss of a proton, 1-butene-3,3-d_2 (9). Similarly methylcyclopropane arising di-

(10) Inasmuch as decomposition of N-(n-butyl)-N-nitrosoacetamide in cyclohexane in the presence of excess DOAc gave butyl acetate containing 74% d_0 species and only 26% d_1 species,[5] it was anticipated that less deuterium incorporation might also occur from diazotization, assuming that similar intermediates are involved in these reactions (vide infra).

(11) Diazotization of aliphatic amines in glacial acetic acid was shown to involve a maximum of 1% diazoalkane: A. Streitwieser, Jr., and W. D. Schaeffer, J. Am. Chem. Soc., 79, 2888 (1957); D. A. Semenow, C. H. Shih, and W. G. Young, ibid., 80, 5472 (1958).

(12) The only anomalous situation is the reaction conducted in ethylene glycol -d_2.

(13) (a) The possibility of diazo–diazonium ion equilibration for diazoalkanes was previously recognized but was not definitely resolved.[14] However, products from ethyl diazoacetate incorporate two deuterium atoms by this type of process: J. D. Roberts, C. M. Regan, and I. Allen, J. Am. Chem. Soc., 74, 3679 (1952).

(14) (a) K. Heyns and W. v. Bendenberg, Ann., 595, 69 (1955); (b) R. Huisgen and H. Reimlinger, ibid., 599, 161, 183 (1956); (c) R. Huisgen and C. Ruchardt, ibid., 601, 21 (1956); (d) E. H. White and C. A. Aufdermarsh, Jr., J. Am. Chem. Soc., 80, 2597 (1958); (e) ibid., 83, 1174 (1961).
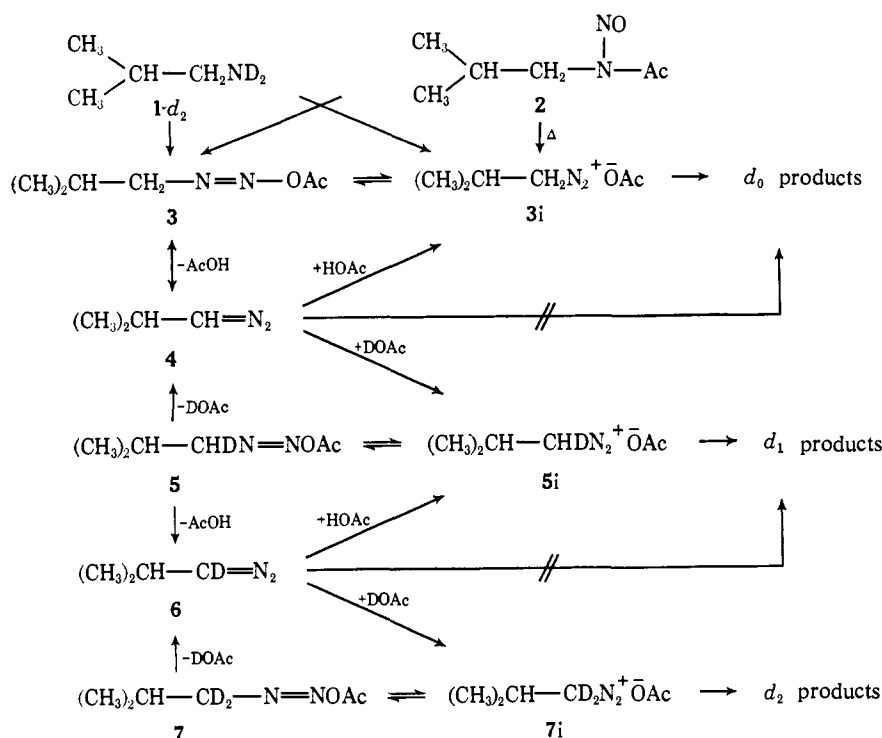
(15) R. Huisgen and C. Ruchardt, Ann., 601, 1 (1956).

(16) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 39–41.

(17) Decomposition of N-nitrosoamides of primary carbinamines gives diazoalkanes presumably via an intermediate covalent diazo ester.[4,5,14b,e]

(18) Products could be formed from the ionic species and/or from the covalent diazo esters. However, there is no way to distinguish betwene products arising from one or the other.

Scheme II

CH₃ CH—CH₂ND₂ (1-d_2)
CH₃

CH₃ CH—CH₂—N—Ac   (NO)   **2**
CH₃

(CH₃)₂CH—CH₂—N=N—OAc ⇌ (CH₃)₂CH—CH₂N₂⁺⁻OAc → d_0 products
3   **3i**

↑ -AcOH   +HOAc

(CH₃)₂CH—CH=N₂
4
+DOAc

↑ -DOAc

(CH₃)₂CH—CHDN=NOAc ⇌ (CH₃)₂CH—CHDN₂⁺⁻OAc → d_1 products
5   **5i**

↓ -AcOH   +HOAc

(CH₃)₂CH—CD=N₂
6
+DOAc

↑ -DOAc

(CH₃)₂CH—CD₂—N=NOAc ⇌ (CH₃)₂CH—CD₂N₂⁺⁻OAc → d_2 products
7   **7i**

Table II. Diazotization of Isobutyl-1,1-d_2-amine[a,b]

System	Acid–solvent	Hydrocarbon products, % composn[c] △	=<	\\\\	\/	_/	Deuterium content,[d] mol % △ d_0	d_1	d_2	\\\\ d_0	d_1	d_2	>= d_0	d_1	d_2
1	DOAc–D₂O[e]	2	44	21	24	9	0	4	96	0	3	97			
2	HOAc–H₂O[e]	3	41	21	24	11	0	5	95	0	3	97	0	16	84
3	HOAc–HCCl₃[f]	15	71	8	4	2	10	40	50	8	38	54	16	44	40
4	DOAc–HCCl₃	14	73	7	4	2	0	17	83	0	15	85	2	29	69
5	DOAc–hexanol-d[f]	11	70	10	6	3	0	9	91	0	8	92			

[a] Amine (3% d_1, 97% d_2; 1 equiv), H(D)OAc (1 equiv), and OcONO (1.1 equiv) and solvent at reflux. [b] Duplicate runs unless otherwise stated. [c] Glpc analyzed. [d] Low-voltage mass spectrometry. [e] Sodium nitrite used as diazotizing agent and reaction affected at room temperature. [f] Single run.

rectly from isobutyl-1,1-d_2-diazonium ion would also contain two deuterium atoms per molecule. If the carbene intermediate (**10**) were involved, methylcyclopropane derived from it could only contain one deuterium atom.[19] Inasmuch as significant amounts of hydrogen–deuterium exchange occur during the aprotic diazotization process, an absolute deuterium determination of the methylcyclopropane obtained is of questionable value. However, since 1-butene can only arise from isobutyl-1,1-d_2-diazonium ion via a cationic process,[20] the difference in absolute deuterium content of the 1-butene and methylcyclopropane formed from isobutyl-1,1-d_2-amine would be a measure of

(19) This technique was used in the deoxidation of n-propyl-1,1-d_2 alcohol. The cyclopropane contained 94 ± 2% d_2 and 5–6% d_1. The loss of deuterium was attributed to a 1,3 hydride shift: P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **82**, 2971 (1960).

(20) Although it is feasible that 1-butene could be formed via a carbenic intermediate, thermal decomposition of diazoisobutane in diethyl Carbitol generated *in situ* gave a hydrocarbon mixture of 64% isobutylene and 36% methylcyclopropane. Decomposition in protic solvents yielded in addition 1- and 2-butenes, which was attributed to a cationic process: L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).

carbenic intermediates and/or equilibrating methylcyclopropanes involved.

Diazotizations of isobutyl-1,1-d_2-amine-d_2 in chloroform or in DOAc–D₂O (1:1) gave hydrocarbon mixtures (product composition same as that obtained with unlabeled amine) which were separated (glpc), trapped, and analyzed. In all the solvent systems employed the deuterium content of the 1-butene and methylcyclopropane was found to be essentially identical (Table II). The extensive loss of deuterium in system 3 (Table II) is the result of protium–deuterium exchange occurring during the diazotization process. This result is in excellent agreement with the extent of deuterium incorporation (52% d_0, 36% d_1, 12% d_2) observed in the system isobutylamine-d_2–DOAc–benzene. The seemingly anomalous results of protium incorporation in diazotization of isobutyl-1,1-d_2-amine-d_2–DOAc–HCCl₃ are also best explained by a protium–deuterium exchange—a result of the experimental difficulty of creating an absolutely proton-free environment and of protium generation during olefin formation. The amount of exchange is reduced when diazotization is

Table III. Diazotization of n-Butylamine and Thermal Decomposition of N-(n-Butyl)-N-nitrosoacetamide in Deuterium-Labile Environments

Run no.	Precursor[a]	Deuterium source	Solvent	—Hydrocarbons,[b] % composn—				Hydrocarbon mixture deuterium content,[b] mole %		
				△	＼＼	＼＼	＼＿／	d_0	d_1	d_2
1	13-d_2-RONO[c]	DOAc (1)[d]	C₆H₆	3	88	6	2	57	33	10
2	14	D₂O (1), R'OD[e] (1)	C₆H₆	4	89	5	1	40	44	16
3	14	DOAc (2)	C₆H₆	3	86	8	2	62	34	4
4	13-d_2-RONO	DOAc (1)	EG-d_2	1.5	73	18	7	70	29	1
5	14	f	EG-d_2[f]	1	75	18	6	95	5	0
6	14		DOAc	1	73	18	8	94	6	0

[a] 5 mmol in 10 ml of solvent. [b] Via glpc and low-voltage mass spectrometry. [c] Octyl nitrite, 5.5 mmol. [d] The numbers in parentheses are equivalents. [e] Hexanol-d. [f] Results independent of added reagents, e.g., D₂O, DOAc, 13-d_2, etc.

Scheme III
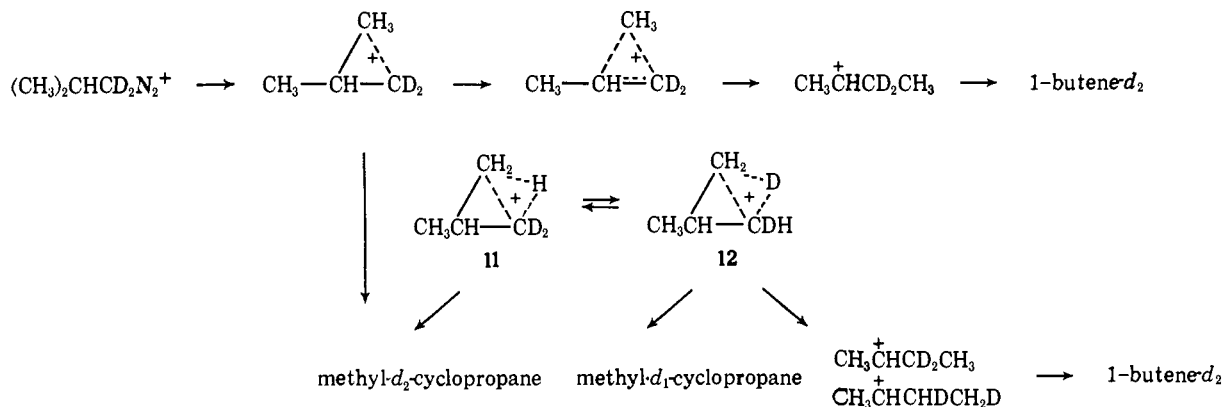
effected in excess hexanol-d (system 5) due to swamping the reaction with exchangeable deuterium (i.e., dilution of protium).

The deuterium contents of the isobutylene obtained from protic and aprotic diazotization suggest that isobutylene is formed only via a cationic intermediate.[21] Isobutylene-d_2 can only arise via cationic route, whereas the isobutylene-d_1 could feasibly result from carbenic decomposition. However, the differences between the results in protic and aprotic media are probably due to protium–deuterium exchange (Scheme II) and the isobutylene-d_1 obtained in protic media is only a result of 1,2-hydride shift followed by protium (deuterium) loss.[22]

Minor differences in the 1-butene and methylcyclopropane ($\sim$1–2% less deuterium) can be attributed to either a carbene intermediate or an equilibrating methylcyclopropane (11 to 12, Scheme III) which are capable of losing a portion of its deuterium in conversion to methylcyclopropane but not to 1-butene. The intermediacy of a carbene can be eliminated or restricted to a maximum level of involvement of ca. 0.1%.[23] However, limited involvement of a partially equilibrating deuterated (or protonated) methylcyclopropane adequately explains these small differences. Thus thermal decomposition of the diazoalkane (4, 6;[24]

(21) The deuterium content of the 2-butenes would be expected to be d_1 via either carbenoid or cationic decomposition.

(22) J. H. Bayless, A. T. Jurewicz, and L. Friedman, J. Am. Chem. Soc., 90, 4466 (1968).

(23) By considering the absolute yield of methylcyclopropane and the difference in deuterium content of methylcyclopropane and 1-butene, the maximum possible involvement of carbenic intermediates can be estimated.

(24) A measure of the minimum extent of diazoalkane formation is given by the sum of d_1 and d_2 species formed ($\sim$50%, runs 1, 2, 3, Table I). However, the actual value is undoubtedly much higher since

Scheme IV) in both protic and aprotic diazotization can be eliminated from consideration.

Reaction Scheme II also adequately accounts for the observed effect of increasing the protonicity of the medium. Inasmuch as partitioning between covalent and ionic structures is dependent on the solvent,[16] an increase in the solvating power of the medium would allow 3i to predominate and over-all deuterium uptake would be diminished. In aprotic media, excess acid would also solvate the intermediates and favor ionic species, thus resulting in a decrease in deuterium uptake.

In order to ensure that the foregoing results are not unique, diazotization of n-butylamine-d_2 (13-d_2) and decomposition of N-(n-butyl)-N-nitrosoacetamide (14) were also effected in deuterium-labile environments (Table III). In every case the results paralleled those obtained from the isobutyl system, i.e., the extent of deuterium incorporation was similar from reactions effected under comparable conditions. Therefore, reactions outlined in Scheme II explain most of the data[12] in Tables I and III and are general for diazotization of primary carbinamines and thermal decomposition of their corresponding nitrosoamides.

The exception[12] is the decomposition of alkylnitrosoamides in EG-d_2 where much less deuterium is formed in the products relative to that obtained from diazotization of the amines in EG-d_2 even though the

part of the d_0 species can be formed via collapse of cage 4 and acetic acid, and by protonation of 4 and subsequent decomposition of 3i (and/or 3). Protonation is favored, rather than deuteration, since acetic acid (arising from diazoalkane formation and from olefin formation) reacts with diazoalkanes four times faster than deuterioacetic acid.[7] Results from decomposition of optically active N-(n-butyl)-N-nitrosoacetamide in cyclohexane, i.e., loss of optical activity and extensive disproportionation of deuterium in the n-butyl acetate, indicate that essentially all of the reaction proceeds through diazoalkane intermediates.[5]

Scheme IV
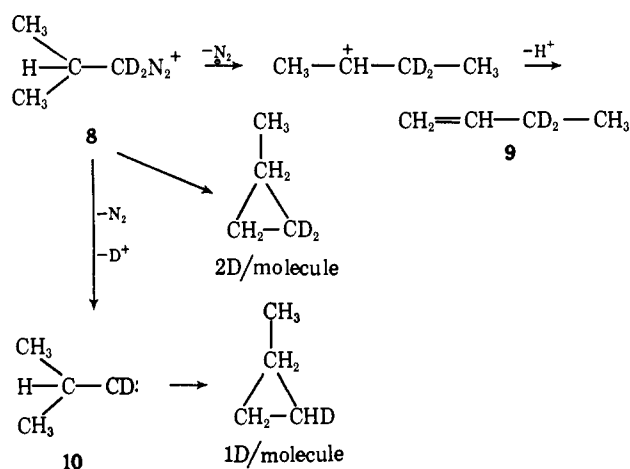
respective product compositions are identical[25] (runs 8 and 9, Table I, runs 4 and 5, Table II). The intermediacy of diazoalkane is apparently involved to a significant degree in the diazotization process in EG-d_2 which, as a result of the relatively polar and protic nature of the solvent, is rapidly deuterated to the cation leading to monodeuterated products; only a small fraction of the diazonium ion manages to survive to get to deuterated diazoalkane. The results from the decomposition of the nitrosoamides (where less deuteration occurs), on the other hand, can best be explained by proposing deuteration by EG-d_2 on nitrosyl leading directly to diazonium ion and acetic acid (eq 1).
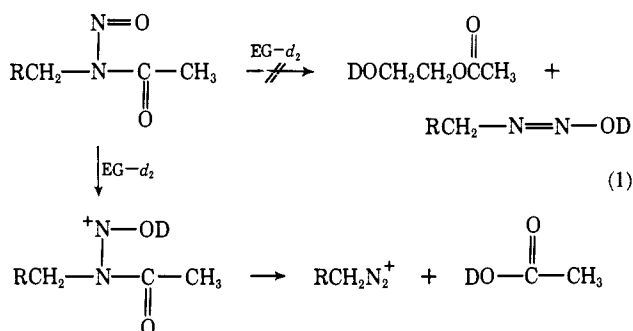
This is formally analogous to the acid-catalyzed conversion of nitrosoamine to diazonium ion.[26] The absence of hydroxyethyl acetate[27] invalidates a scheme which involves attack of EG-d_2 on carbonyl to give an alkyl diazohydroxide.[28]

The hydrocarbons (3% methylcyclopropane, 58% 1-butene, 25% trans-2-butene, 14% cis-2-butene) obtained from diazotization of sec-butylamine-d_2 with octyl nitrite and 1 equiv of DOAc incorporated deuterium to the extent of ~3% d_1.[9] This is in accord with results from decomposition of nitrosoamides of secondary carbinamines.[14d,e,29] Thus formation of diazoalkanes is at best a minor process in aprotic diazotization of sec-alkylamines. The difference between

(25) Apparently products obtained by thermal decomposition of butylnitrosoamides and by diazotization of the amines in EG-d_2 are formed from a butyldiazonium ion precursor in almost identical solvent environments. The addition of excess D_2O, AcOD, and ROD does not affect the results of the nitrosoamide decomposition. This is probably a result of the leveling effect observed in strongly hydrogen-bonded media.

primary and secondary systems could be attributed to (a) a strong α-carbon–hydrogen bond in the intermediate sec-alkyl diazo ester which would retard proton abstraction leading to diazoalkane, (b) the relative stability (i.e., relative reactivity) of the resulting diazoalkanes,[29] and/or (c) the lifetime of the secondary diazonium ion being so short that loss of an α proton no longer competes.

Experimental Section[30]

Reagents. Spectrograde solvents were employed where available. Ethylene glycol-d_2 was prepared by hydrolysis of ethylene carbonate with excess deuterium oxide.[31] Material of isotopic purity $\gtrsim 99.5\%$ (nmr) was obtained. Hexanol-d was prepared by hydrolysis of the corresponding borate ester with a 50% excess of deuterium oxide.[32] Material of isotopic purity $\gtrsim 99.5\%$ (nmr) was obtained.

N-(n-Butyl and -isobutyl)-N-nitrosoacetamides were prepared (70–80% yields) from their respective amides by reaction with dinitrogen tetroxide.[1c,4]

Isobutyl-1,1-d_2-amine.[33] Isobutyronitrile (8.3 g, 0.12 mol) was added cautiously to a stirred solution of lithium aluminum deuteride (5 g, 0.12 mol) in diethyl Carbitol,[34] and was heated at 100° for 1 hr. The mixture was cooled to 0° and hydrolyzed with n-butoxyethyl alcohol-d_1 (60 g, 0.5 mol). A rough distillation directly from the reaction flask gave isobutyl-1,1-d_2-amine (7 g, 0.10 mol), bp 62–68° (lit.[35] bp of d_0 compound 68.9°), in an 83% yield. The amine was purified through its hydrochloride salt, mp 175–176° (lit.[35] mp of d_0 compound 175°). A weak signal of methylene hydrogens was observed in the nmr spectrum. Analysis (low-voltage mass spectrometry) showed the deuterium composition to be 3% d_1 and 97% d_2.

Isobutyl-d_2- and n-Butyl-d_2-amine. Exchange of amino hydrogens on amine hydrochloride with deuterium oxide (twice) gave the amine-d_2-DCl with an isotopic purity of 99% (nmr). The free amine was obtained from the salt by treatment with saturated anhydrous potassium carbonate in D_2O.

Amine Diazotization. General Reaction Procedure. The procedure developed earlier[1c] was employed in the diazotization reactions. A solution of the amine (0.01 mol), acetic acid (0.01 mol), and octyl nitrite (0.01 mol)[36] in solvent (10 ml) was heated to reflux.[37] The olefins were trapped in heptane and glpc analyzed. Samples used for deuterium analyses were directly glpc trapped.[1c]

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(26) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961; J. H. Ridd, Quart. Rev. (London), 15, 418 (1961).

(27) In order to determine if hydroxyethyl acetate is formed, 14 was decomposed in ethylene glycol-d_2. Inasmuch as separation (glpc) of hydroxyethyl acetate and ethylene glycol was poor, it was not possible to detect quantities formed amounting to less than ~5% (based on nitrosoamide precursor). However, since the yield of products (sec-butyl acetate, 1%; n-butyl acetate, 3.4%; sec-butoxyethanol, 16%; n-butoxyethanol, 40.5%; hydrocarbons, 38%) was quantitative, none of the hydroxyethyl acetate could have been present.

(28) (a) The diazohydroxide (diazotic acid) would be expected to decompose via a cationic process to give products without incorporation of deuterium: R—N=N—OD → RN$_2^+$ + OD$^-$ → d_0 products. (b) R. A. Moss, J. Org. Chem., 31, 1082 (1966).

(29) Secondary diazoalkanes are less stable than primary.[28b]

(30) Boiling points are uncorrected. Deuterium analyses were obtained on a General Electric analytical mass spectrometer. Product composition was obtained via glpc analyses.

(31) D. J. Cram and B. Rickborn, J. Am. Chem. Soc., 83, 2178 (1961).

(32) L. Friedman, A. T. Jurewicz, and J. H. Bayless, J. Org. Chem., in press.

(33) Cf. L. Friedman and A. T. Jurewicz, ibid., 33, 1254 (1968).

(34) The diethyl Carbitol used was first distilled over lithium aluminum hydride and then passed through a column of alumina.

(35) "Dictionary of Organic Compounds," G. Harris, Ed., Vol. III, Oxford University Press, New York, N. Y., 1965, p 1897.

(36) Sodium nitrite was used when the reactions were conducted in aqueous acetic acid.

(37) Reactions in aqueous acetic acid were carried out at room temperature.