Aprotic Diazotization of Aliphatic Amines. Hydrocarbon Products and Reaction Parameters[1]

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Abstract: From reaction of isobutylamine with isoamyl nitrite in aprotic media only moderate amounts of gaseous products are obtained consisting mainly of nitrous oxide and small amounts of hydrocarbons and nitrogen. However, in protic media the amount of hydrocarbons and nitrogen increase with a concomitant decrease in nitrous oxide. In the presence of 1 equiv of acetic acid, the reaction in aprotic media is highly efficient in that hydrocarbons and counterion-derived products are obtained in high yield and nitrous oxide formation is negligible. The hydrocarbon mixtures obtained from diazotization of isobutylamine with alkyl nitrite–acetic acid in "aprotic media," *e.g.*, diethyl Carbitol, chloroform, and *n*-amyl alcohol, contain appreciable amounts of methylcyclopropane (10–15%). In "protic media," such as ethylene glycol and water, the amount of skeletal rearranged olefins (1- and 2-butenes) increase at the expense of methylcyclopropane. The results are similar to those obtained from decomposition of diazoisobutane and N-nitroso- and N-nitroacetamides and -urethans in aprotic and protic media, respectively. It is proposed that all products arise *via* cationic processes.

Preparation of diazoalkanes by direct diazotization with aqueous nitrous acid is only possible when the amine bears a negative substituent on the α-carbon atom,[3] for example, the preparation of diazoacetic ester from aminoacetic ester.[4] Diazoalkanes cannot be

$$EtO_2CCH_2NH_2 \xrightarrow[H_2O]{HONO} EtO_2CCH_2N_2^+ \xrightarrow{-H^+} EtO_2CCH{=}N_2$$

prepared from simple alkylamines by this method since the intermediate diazonium species decompose with loss of nitrogen faster than deprotonation and isolation can occur.

Recently it was reported that arylamines can be diazotized with amyl nitrite in benzene to give biaryls.[5] Thus it was anticipated that aliphatic amines[5b] could similarly react with alkyl nitrites to generate the corresponding diazoalkane, water, and alcohol (Scheme I). In effect, this would constitute a direct preparation of diazoalkanes from amines.

Scheme I

$$RCH_2NH_2 + R'ONO \longrightarrow RCH_2NH_2^+NO + R'O^-$$

$$RCH_2NH_2^+NO + R'O^- \longrightarrow RCH_2NHNO + R'OH$$

$$RCH_2NHNO \longrightarrow RCH_2{-}N{=}N{-}OH$$

$$RCH_2{-}N{=}N{-}OH \longrightarrow RCH{=}N_2 + H_2O$$

In the reaction sequence amine displaces alkoxide from alkyl nitrite to yield a protonated nitrosoamine which, by proton transfer, gives the nitrosoamine[3] and alcohol. Rearrangement of the nitrosoamine to the diazohydroxide followed by loss of water then would yield diazoalkane.

Results and Discussion

Reaction of Alkylamines with Amyl Nitrite. Diazotization of isobutylamine[6-8] with isoamyl nitrite[9] was attempted in diethyl Carbitol (bis(2-ethoxyethyl) ether, an aprotic solvent) at 170°.[8] Under these conditions it was expected that the diazoisobutane would thermally decompose (*via* a carbenic process) to give nitrogen and C_4 hydrocarbons.[6,7] Approximately 25% of the expected volume[10] of gaseous products was obtained which consisted of nitrous oxide, nitrogen, and hydrocarbons (N_2O/hydrocarbons $\simeq$ 0.8) (Table I). The hydrocarbon mixture (14% methylcyclopropane, 68% isobutylene, 8% 1-butene, and 10% 2-butenes) was considerably different from that (35% methylcyclopropane, 64% isobutylene, 1% 1- and 2-butenes) obtained by decomposition of diazoisobutane in diethyl Carbitol.[7] The relatively large amounts of both methylcyclopropane[6] and skeletal rearranged olefins (1- and 2-butenes) could be attributed to carbenic (thermal) decomposition of diazoisobutane and concomitant cationic processes, respectively.

Since the reaction in the aprotic solvent was poor, reaction was attempted in the hydroxylic solvent, butyl Cellosolve (2-*n*-butoxyethanol). While the volume of gaseous products (~40% of that expected)[10] was higher, the relative amount of nitrous oxide (N_2O/hydrocarbons $\simeq$ 0.5) was lower. However, the hydrocarbon composition was similar to that obtained in diethyl Carbitol. In view of these results, *i.e.*, increased

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[1] (a) Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged. (b) Preliminary account of portions of this work have been reported: J. H. Bayless, F. D. Mendicino, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5790 (1965).

[2] (a) Based on the Ph.D. Thesis of J. H. B., Case Institute of Technology, 1967. (b) NASA Fellow, 1963–1966.

[3] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961.

[4] T. Curtius, *Chem. Ber.*, **16**, 2030 (1883).

[5] (a) J. I. G. Cadogan, *J. Chem. Soc.*, 4257 (1962); J. I. G. Cadogan, D. A. Roy, and D. M. Smith, *ibid.*, 1249 (1966), and references contained therein; L. Friedman and J. F. Chlebowski, *J. Org. Chem.*, **33**, 1633 (1968). (b) For the reaction of vinylamines with isoamyl nitrite, see D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Am. Chem. Soc.*, **87**, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, 874 (1965).

[6] Isobutylamine was employed since the expected diazoisobutane would give a large amount of methylcyclopropane *via* thermal decomposition.[7] Thus it was assumed that the amount of methylcyclopropane formed would be a measure indicative of diazoalkane formation.[8]

[7] (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) L. Friedman, Ph.D. Thesis, Ohio State University, 1959.

[8] F. D. Mendicino, Case Undergraduate Participant, Senior Thesis, Case Institute of Technology, 1962.

[9] "Amyl" nitrite (actually isoamyl nitrite) was obtained from Mallinckrodt Chemical Works.

[10] Thermal decomposition of diazoisobutane (1 mol) gives 2 mol of gaseous products: 1 mol of nitrogen and 1 mol of C_4 hydrocarbons.

Table I. Reactions of Alkylamines with Amyl Nitrite[a]

Solvent	Reactants[b] AcOH: AmONO	Temp, °C	Volatile[c] products, ml	N_2O/hydrocarbons	Hydrocarbons, % composition[d]				
									
				Isobutylamine					
Diethyl Carbitol	0:1	160	105	0.82	14	68	8.0	5.4	4.6
Diethyl Carbitol	1:1	100	315	0.01	12	73	8.3	4.6	2.2
Dioxane	1:1	98	335	0.004	12	74	7.5	4.5	2.4
Benzene	1:1	80	320	0.003	12	72	8.5	4.5	3.3
Chloroform	1:1	61	320	0.000	15	72	7.0	4.2	1.8
Butyl Cellosolve	0:1[e]	150	85	28	9.0	62	15	7.9	4.1
Butyl Cellosolve	0:1	150	200	0.54	9.9	63	14	8.6	4.7
Butyl Cellosolve	1:1	150	370	0.07	9.9	69	11	7.1	3.7
Ethylene glycol	0:1	160	278	0.12	3.9	63	15	14	4.6
Ethylene glycol	1:1	160	340	0.02	4.0	61	16	12	6.7
				n-Butylamine					
Benzene	1:1	80	290	0.02	3.3		85	7.6	4.4
Glyme	1:1	80	290	0.02	3.4		85	7.5	4.0
				sec-Butylamine					
Benzene	1:1	80	370	0.10	3.3		55	24	17
Glyme	1:1	80	370	0.006	5.4		47	29	17

[a] 10 mmol of amine, 10 mmol of amyl nitrite, 20 ml of solvent, except where indicated otherwise. [b] Equivalents. [c] Theoretical volume of nitrogen and hydrocarbons derived from diazoalkanes would be 490 ml (under these conditions), typical data. Reproducibility to ±3 ml. [d] Typical data. Reproducibility to about ±0.5%. [e] In the presence of 10 mmol of sodium butoxyethoxide.

amount of volatile products and reduced amount of nitrous oxide, diazotization was effected in the more protic (*i.e.*, acidic) solvent ethylene glycol.[11] The formation of volatile products was further enhanced (~55%)[10] while nitrous oxide formation was decreased (N_2O/hydrocarbons $\simeq$ 0.1) and the hydrocarbon composition (3.9% methylcyclopropane, 63% isobutylene, 15% 1-butene, 19% 2-butenes) was essentially identical with that obtained by decomposition of diazoisobutane in ethylene glycol[7] (Table I). Thus from the composition of the hydrocarbon mixture the intermediacy of diazoisobutane could be rationalized. The differences in product composition are a result of the effect of environment (solvent)[12] on the chemistry of the product-forming precursors. Since the diazotization reaction was enhanced in hydroxylic media (possibly as a result of hydrogen bonding of the amine) it was reasoned that the reaction might be even further improved if the amine were neutralized with a weak acid. Thus diazotization was initially attempted in ethylene glycol and butyl Cellosolve in the presence of 1 equiv of acetic acid. The amount of volatile products was significantly increased to 70–75%,[10] nitrous oxide formation was negligible (N_2/hydrocarbons ~0.02–0.07), and surprisingly the hydrocarbon composition was essentially identical with that obtained in the absence of acetic acid (Table I).

Diazotization in the presence of 1 equiv of acetic acid was then extended to aprotic solvents such as diethyl Carbitol, dioxane, benzene, chloroform, etc. In each case the yield of volatile products was enhanced (~65%),[10] hydrocarbon composition was essentially identical with that obtained in the absence of acetic acid, and nitrous oxide formation was negligible (Table I).

Similar results were also obtained from diazotization of *n*- and *sec*-butylamines with amyl nitrite–acetic acid in aprotic media (benzene, glyme) in that (a) large amounts of volatile products were obtained which consisted almost entirely of nitrogen and hydrocarbons and (b) the ratios of methylcyclopropane and butenes were consistent, in part, with the intermediacy of the respective diazoalkanes.

Thus diazotization of alkylamines with amyl nitrite in "aprotic" and "protic" media is a highly efficient process in the presence of 1 equiv of acetic acid.[13]

Since the basic amine was obviously implicated in the formation of nitrous oxide, the reaction of isobutylamine with amyl nitrite was conducted in butyl Cellosolve in the presence of sodium butoxyethoxide. The amount of volatile products was markedly reduced (~18%)[10] and consisted principally of nitrous oxide (N_2O/hydrocarbons $\simeq$ 28). The composition of the hydrocarbon portion of the mixture, however, was essentially identical with that obtained previously.[12]

Mechanism of Nitrous Oxide Formation. There is no logical path by which nitrous oxide can be formed *via* diazotization (Scheme I). Inasmuch as acid retards nitrous oxide formation while strong base favors its formation, it is proposed that base[14] (*e.g.*, amine, sodium alkoxide) abstracts an α proton from amyl nitrite to give an anion which eliminates nitrosyl anion (NO^-)[15] and aldehyde (Scheme II). Nitrosyl anion yields, *via* protonation followed by dimerization, hypo-

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[11] H. Shigematsu, Y. Nishikawa, and Y. Ishii, *Kogyo Kagaku Zasshi*, **65**, 945 (1962).

[12] For the effect of environment on the course of the reaction, see (a) J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Am. Chem. Soc.*, **91**, 4466 (1968); (b) L. Friedman, A. T. Jurewicz, and J. H. Bayless, *ibid.*, 1795 (1969).

[13] Diazotization with alkali nitrites in aqueous media obviously requires acid.[3] However, under these conditions diazotization is inefficient and, in order to obtain good yields, a large excess of nitrosating reagent (*e.g.*, $NaNO_2$) and acid is required. *Cf.* G. J. Karabatsos, N. Hsi, and S. Meyerson, *ibid.*, **88**, 5649 (1966).

[14] The fact that diazotization of aryl-[5a] and vinylamines[5b] can be effected in aprotic media without added acid is attributed to their lower basicity relative to aliphatic amines.

[15] L. Friedman and F. D. Mendicino, Abstracts of Papers, 145th National Meeting of the American Chemical Society, New York, N. Y., 1963, p 86Q.

nitrous acid[16] which undergoes dehydration[16,17] to nitrous oxide.

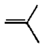
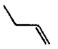
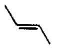
Scheme II

$$RCH_2ONO + B^- \longrightarrow RCH^-ONO + BH$$
$$RCH^-ONO \longrightarrow RCHO + NO^-$$
$$NO^- + BH \longrightarrow NOH + B^-$$
$$2NOH \longrightarrow H_2N_2O_2 \longrightarrow N_2O + H_2O$$

This is supported by the fact that (a) nitrous oxide is formed in near quantitative yield by the action of hot sodium amyloxide solution on amyl nitrite[8] and (b) that carbonyl compounds (ir) were present in the mother liquors from reactions of isobutylamine with amyl nitrite.[8]

Dependence of Hydrocarbon Yield on Amount of Acid (Proton Donor). In order to determine the minimum amount of acid required to effect satisfactory diazotization, reaction of isobutylamine with 1.1 equiv of octyl nitrite[18] and varied amounts of acetic acid was carried out in refluxing chloroform[19] (Table II). Hydrocarbon yields were maximized when 1-2 equiv of acid was employed. Hydrocarbon composition, however, is essentially independent of the amount of acetic acid or other acids present.[20]

Table II. Aprotic Diazotization of Isobutylamine in Chloroform.[a] Effect of Acetic Acid on Hydrocarbon Yield

		Hydrocarbons,[b] % composition				
Acid, equiv	Yield, %					
0	~0					
0.25	13	15	72	7.3	4.2	1.4
0.5	28	15	72	6.8	4.0	1.8
1.0	35	15	72	7.0	4.2	1.8
2.0	41	13	74	6.9	4.5	2.1
3.0	36	11	75	7.1	4.7	1.8

[a] 5.0 mmol of amine, 5.5 mmol of octyl nitrite, 10 ml of solvent at reflux. [b] Analyzed by glpc.

In view of these results a standard diazotization procedure was adopted in order to minimize the number of variables: amine (1 equiv), acetic acid (1 equiv), and alkyl nitrite (1.1 equiv) in solvent[21] (2 ml/mmol of amine). This mode of diazotization when carried out in aprotic[22] media is defined as "aprotic diazotization."

Dependence of Hydrocarbon Composition on Solvent. Isobutylamine was diazotized in several polar and nonpolar solvents in order to determine the extent of solvent effects on the course of hydrocarbon formation. In nonpolar, "aprotic"[22] solvents, *e.g.*, cyclohexane, chloroform, *t*-amyl alcohol, the hydrocarbon mixtures (~30-35% yield)[23] were similar and contained 10-14% methylcyclopropane, 72-78% isobutylene, 7-9% 1-butene, 2-5% *trans*-2-butene, and 1.5-2.5% *cis*-2-butene (Table III). In the more protic solvent diethylene glycol hydrocarbon mixture (28% yield) consisting of 7.8% methylcyclopropane, 59% isobutylene, 15% 1-butene, 11% *trans*-2-butene, and 6.8% *cis*-2-butene was obtained. In aqueous perchloric acid (using sodium nitrite) the hydrocarbons (11% yield)[24] were largely the skeletal rearranged olefins (the 1- and 2-butenes) (61%) accompanied by less than 1% methylcyclopropane.

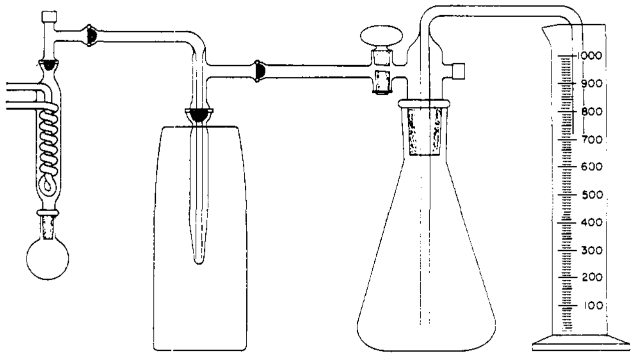


Figure 1. Reaction apparatus.

Apparently relatively nonpolar solvents have little effect on the hydrocarbon compositions (runs 1-12). However, as the polar and protic character is increased (runs 13-17) there is a marked reduction in the amount of methylcyclopropane and isobutylene and a concomitant increase in the amount of skeletal rearranged olefins (Table III). The trend on going from aprotic to protic media is a decrease in the amount of methylcyclopropane and an increase in the amount of skeletal rearranged olefins. This is a consequence of the greater solvating power of the medium.[11]

Comparison of Hydrocarbons from Decomposition of N-(Isobutyl)-N-nitroso- and -nitrourethan and -acetamides and Aprotic Diazotization of Isobutylamine. Since aprotic diazotization of alkylamines is effected in the presence of acetic acid, the possible intermediacy of a diazo ester was considered. Diazo esters are intermediates from decomposition of alkylnitrosoamides[25-27] and, therefore, N-(isobutyl)-N-nitrosoacetamide was decomposed in aprotic media (*e.g.*, benzene, chloroform) in order to obtain comparative data (Table IV). The hydrocarbon compositions were essentially identical with that obtained from aprotic diazotization of isobutylamine. This is further evidence[28] that com-

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[16] C. C. Addison and J. Lewis, *Quart. Rev.* (London), **9**, 115 (1955).

[17] E. Zintl and A. Harder, *Chem. Ber.*, **66**, 760 (1933).

[18] Results are independent of alkyl nitrite employed, *e.g.*, isoamyl,[9] *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl. Octyl nitrite was employed to facilitate analysis of substitution products.

[19] Chloroform was chosen since the maximum amount of methylcyclopropane and minimum amount of skeletal rearrangement was obtained in this solvent.

[20] Providing that the relative concentration of the solute acid is low.

[21] An increase in solvent volume does not alter the results. However, significant reductions in volume markedly change hydrocarbon product compositions (more rearrangement) since the gross protonicity of the reaction medium increases. See, for example, A. T. Jurewicz, J. H. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5788 (1965).

[22] Aprotic media are solvents or solvent systems that are not proton donors insofar as the reaction intermediates are concerned.

[23] The yield of nitrogen is essentially quantitative, *i.e.*, conversion of amine to nitrogen and alkyl products (hydrocarbons and substitution products) is essentially complete. For a preliminary account of the influence of reaction conditions on the substitution products, see ref 12a.

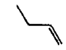
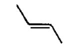
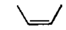
[24] The low yield is a result of poor conversion of the amine; *cf.* ref 13.

[25] Alkyl nitrites are insoluble in aqueous systems.

[26] (a) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008, 6011, 6014 (1955); (b) K. Heyns and W. V. Bendenberg, *Ann.*, **595**, 69 (1955); R. Huisgen and H. Reimlinger, *ibid.*, **599**, 161, 183 (1956); R. Huisgen and C. Ruchardt, *ibid.*, **601**, 21 (1956); E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **80**, 2597 (1958).

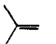
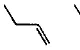
[27] E. H. White and C. A. Aufdermarsh, *ibid.*, **83**, 1174 (1961); (b) *ibid.*, **83**, 1179 (1961).

Table III. Diazotization of Isobutylamine[a] in Aprotic and Protic Solvents

					Hydrocarbons, % composition[d]				
Run	Solvent	Temp,[b] °C	ε[c]	Yield, %[d]					
1	Cyclohexane	Reflux	1.9	35	10	78	6.9	3.4	1.6
2	Benzene	Reflux	2.3	37	11	76	6.9	4.2	2.0
3	Diethyl Carbitol	100	~5[e]	28	12	73	8.3	4.6	2.2
4	Diglyme	85	~5[e]	20	10	75	8.0	4.6	2.3
5	Glyme	Reflux	3.5–6.8	35	10	76	7.7	4.1	2.2
6	Chloroform	Reflux	4.7	33	15	72	7.1	4.1	1.8
7	Carbon tetrachloride	Reflux	2.2	30	11	76	7.3	3.5	1.6
8	1,1-Dichloroethane	Reflux	10	32	11	78	7.6	2.0	1.5
9	Tetrachloroethylene	100	2.4[f]	33	12	73	8.0	4.3	2.2
10	1,2-Dichloroethane	100	10	32	11	72	8.9	5.3	2.5
11	Tetrachloroethane	100	8.0[f]	30	14	69[g]	9.4	5.2	2.1
12	*t*-Amyl alcohol	100	~12[e]	32	10	68	11	6.6	3.9
13	Diethylene glycol	120		28	7.8	59	15	11	6.8
14	Acetic acid	Reflux	6.2[h]	20	4.5	62	12	14	7.1
15	Ethylene glycol	110	38	25	4.0	61	16	12	6.7
16	Acetic acid–water (50:50)	Reflux		12	2.5	42	20	25	11
17	Water[i,j]	Reflux	79	11	0.8	38	14	32	15

[a] 5.0 mmol of amine, 5.0 mmol of acetic acid, 5.5 mmol of alkyl nitrite (ref 18), 10 ml of solvent. [b] Bath temperature, except where otherwise noted. In most cases, this temperature exceeds reflux temperature. [c] Dielectric constant. Values taken from C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965), except where otherwise noted. [d] Determined *via* glpc. [e] Estimated from dielectric constants of comparable solvent; *cf.* reference in footnote *c*. [f] International Critical Tables. [g] The solvent readily undergoes elimination in the presence of amine. Hence, hydrogen chloride may have been formed in the reaction and this would add to isobutylene and the 2-butenes, thus apparently increasing the relative amount of methylcyclopropane and 1-butene. [h] The dielectric constant does not give a good correlation of the solvating power of acetic acid; *cf.* reference in footnote *c*. [i] 5.0 mmol of isobutylammonium perchlorate, 10 mmol of sodium nitrite, 10 ml of 10% perchloric acid at 100°. [j] Compare L. G. Cannell and R. W. Taft, *J. Am. Chem. Soc.*, **78**, 5812 (1956).

Table IV. Thermal Decomposition of N-(Isobutyl)-N-nitroso- and -N-nitroacetamides and -urethans[a]

		Hydrocarbons, % composition[d]				
Solvent	Yield, %					
	Nitrosoacetamide					
Chloroform	15	12	72	7.6	5.5	2.3
Benzene	25	13	72	7.4	4.9	2.1
Cyclohexane	10	13	76	6.5	3.4	1.3
	Nitrosourethan					
Benzene	7[b]	13	76	5.5	3.5	2.0
Diethyl Carbitol	20	11	86	1.5	1.0	0.4
	Nitroacetamide					
Benzene[c]	32	9.1	79	5.9	4.2	1.7
Diethyl Carbitol[d]	27	13	75	7.7	2.7	1.9
	Nitrourethan					
Benzene[c]	<5[c]	14	67	7.6	5.8	3.6
Diethyl Carbitol	35	14	64	9.7	6.1	3.5
	Diazotization of Isobutylamine[d]					
Benzene	38	12	73	8.2	4.6	2.5
Diethyl Carbitol	28	12	73	8.2	4.6	2.2

[a] 5.0 mmol of substrate, 10 ml of solvent at reflux. [b] Low yields are a result of incomplete reaction. However, olefin compositions are invariant with reaction time. The urethans are more stable than the acetamides and require longer reaction time. Reactions were run for ~48 hr. [c] Nitrous oxide formed (infrared spectrum identical with that of authentic sample); *cf.* ref 31. [d] Included for comparison. Data taken from Table III.

mon intermediates may be involved in these reactions. Since decomposition of *n*-alkylnitrosoamides in aprotic media yields diazoalkanes as intermediates,[28,29] it might be expected that diazoalkanes could also be formed as an intermediate by aprotic diazotization of the corresponding amine (under comparable conditions).[12,30]

Decomposition[31] of N-(isobutyl)-N-nitroacetamide and N-(isobutyl)-N-nitroso- and -nitrourethans in aprotic media also gave similar hydrocarbon compositions (Table IV). Thus all of these precursors apparently generate similar primary intermediates, presumably RN=NOCOR′, RN=NOCOOR′, etc.

Diazotization of Neopentylamine in Benzene. The formation of relatively large amounts of methylcyclopropane and isobutylene and small amounts of skeletal rearranged olefins from aprotic diazotization of isobutylamine is consistent with, but not proof of, partial carbenic participation[7] and, hence, with the intermediacy of diazoisobutane.

Aprotic diazotization of neopentylamine, in principle, could give more information by comparison of the hydrocarbon composition with that obtained from decomposition of 2,2-dimethylpropanal tosylhydrazone anion in diethyl Carbitol—a carbenic process since the differences in product composition (*i.e.*, dimethylcyclopropane formation) from carbenic and cationic precursors are more exaggerated. In the former case 1,1-dimethylcyclopropane is the principal product[7] (~95%) while in the latter case it is barely detectable. However, aprotic diazotization gave a hydrocarbon mixture containing less than 0.5% 1,1-dimethylcyclopropane (Table V). In this instance, on the basis of cyclopro-

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(28) R. Hulsgen and C. Ruchardt, *Ann.*, **601**, 1 (1956).

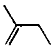
(29) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2893 (1957).

(30) This was recently demonstrated: J. H. Bayless and L. Friedman, *ibid.*, **89**, 147 (1967); see also ref 12b.

(31) The kinetics and products from the thermal decomposition of several N-alkyl-N-nitroamides and carbamates was recently reported by E. H. White and L. A. Dolak, *ibid.*, **88**, 3790 (1966).

pane formation, a carbenic process is at best a negligible factor.[32]

Table V. Comparison of Aprotic Diazotization of Neopentylamine with Thermal Decomposition of Diazoneopentane

Precursor	Aprotic solvent	Yield, %	Hydrocarbons, % composition 		
Neopentylamine[a]	Benzene	70	<0.5	55	45
Diazoneopentane[b]	Diethyl Carbitol	85	92	2	6

[a] 5.0 mmol of acetic acid, 5.5 mmol of octyl nitrite, 10 ml of benzene at reflux. [b] Data taken from ref 7. Diazoneopentane generated *in situ via* thermolysis of 2,2-dimethylpropanal tosylhydrazone anion.

Minor differences are also found in the amounts of cyclopropane formed by diazotization of *sec*-butylamine and by thermal decomposition of the corresponding diazoalkane (Table VI). More methylcyclopropane (~3-5%) is obtained from aprotic diazotization of *sec*-butylamine than that (0.5%) obtained from carbenic decomposition of 2-diazobutane.[33] In fact, decomposition of the latter compound in ethylene glycol (wherein cationic processes predominate)[7,12] gives more methylcyclopropane (1.4%) than that obtained in diethyl Carbitol. Thus it appears that from the results obtained with *sec*-butylamine and neopentylamine that carbenic processes are not involved.[34,35]

Table VI. Comparison of Aprotic Diazotization of *sec*-Butylamine and Decomposition of 2-Diazobutane

Precursor	Solvent	Hydrocarbons, % composition 			
sec-Butylamine[a]	Benzene	3.3	55	24	17
	Glyme	5.4	47	29	17
2-Diazobutane[b]	Diethyl Carbitol	0.5	5	67	28
	Ethylene glycol	1.4	31	37	28

[a] Taken from Table I. [b] Taken from ref 7. Diazoalkane generated *in situ via* thermal decomposition of 2-butanone tosylhydrazone anion.

Experimental Section

Reagents. Spectrograde solvents were employed where available. Others were purified by distillation and the center cut was collected. Deuterated solvents were prepared as described recently.[36] Isoamyl nitrite ("amyl nitrite") was purchased from Mallinckrodt Chemical Works. Octyl nitrite was purchased from Eastman Organic Chemicals (Distillation Products Industries, Rochester, N. Y.). The alkylamines were purchased and were shown to be free of isomers (glpc).

Analytical Procedure. Hydrocarbons were identified and analyzed *via* glpc. Identification of each of the glpc peaks separated on 30 ft 0.25 in. o.d. (aluminum tube) silver nitrate (12%), benzyl cyanide (25%) on acid-washed Chromosorb P (30–60 mesh) (ASTM Designation D 1717-617) at 25°, 10 psi of helium, was obtained by comparison with authentic samples and by infrared, nmr, and/or mass spectral analysis.

Intermediates. **N-(*n*-Butyl-, -*sec*-butyl-, -isobutyl-, and -isopropyl)-N-nitrosoacetamides** were prepared (70–85% yields) from their respective amides by reaction with dinitrogen tetroxide.[26a] These compounds were not distilled due to their instability but were shown to be pure on the basis of their respective infrared and nmr spectra. No NH stretch was observed in the infrared or amide (NH) protons in the nmr. In the infrared spectra bands for carbonyl and nitroso stretch agreed with these reported in the literature.[26a] The new compounds (N-*sec*-butyl- and N-isopropyl-N-nitrosoacetamide) gave satisfactory elemental analyses.

N-(Isobutyl)-N-nitrosourethan (crude, $n^{30}D$ 1.4326, NH stretch absent in ir) was prepared (68%) from isobutylurethan by reaction with nitric acid and sodium nitrite.[37]

N-(Isobutyl)-N-nitroacetamide (crude, $n^{25}D$ 1.4500, NH stretch absent in ir) was prepared in 41% yield from isobutylacetamide by reaction with concentrated nitric acid following the procedure given for the preparation of the *n*-butyl derivative.[26a]

N-(Isobutyl)-N-nitrourethan (crude, $n^{20}D$ 1.4435, NH stretch absent in ir) was prepared in 82% yield as described[38] from isobutylurethan by reaction with fuming nitric acid at −13°.

General Procedure. Amine (0.005 mol), acid (0.005 mol), and solvent (10 ml) were mixed in a 50-ml flask fitted with a side arm (10 mm) capped with a rubber septum. The flask was attached to the trap system (Figure 1), alkyl nitrite (0.0055 mol) was added through the septum with a syringe, and the flask was heated with stirring (Teflon coated, magnetic stir bar) in a hot (80–100°) silicone oil bath on a stirrer hot plate. Vigorous reaction occurred after an induction period of about 1–2 min and continued for about 20–30 min (nitrogen and hydrocarbons are rapidly evolved). After reaction had ceased, the nitrogen trap was disconnected and dry nitrogen was bubbled through the hot mixture (30 min) to displace dissolved hydrocarbons. The cold trap was disconnected and the reaction flask cooled to room temperature. Internal standard (usually *n*-pentane) was then added to the hydrocarbons (trapped in heptane at −70°) and the mixture analyzed *via* glpc.

Acetic acid was the most commonly employed proton source for the diazotization. However, in experiments with other counterions (Cl^- and Br^-) amine hydrohalides were employed. These were prepared by bubbling anhydrous hydrogen chloride or hydrogen bromide through a cold (0°) solution of the amine in ether. The precipitate was collected, washed with ether, and dried *in vacuo*.

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[32] It was conclusively demonstrated that 1,1-dimethylcyclopropane formed by decomposition of 2,2-dimethylproposal tosylhydrazone anion arises almost exclusively *via* carbenoid processes: J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, *J. Am. Chem. Soc.*, **90**, 531 (1968).

[33] Methylcyclopropane was not observed from dehydrohalogenation of *sec*-butyl halides with phenylsodium (a carbenoid process): L. Friedman and J. F. Berger, *ibid.*, **83**, 492 (1961).

[34] These results are not inconsistent in view of the many recent authenticated examples of cyclopropane formation *via* cationic processes,[31,35] *e.g.*, deoxidation of alcohols,[35a,b] protic diazotization of amines,[35b,c] and anodic oxidation of carboxylic acids.[35d] In fact, formation of cyclopropanes *via* "cationic processes" has been sporadically observed in terpene chemistry since the turn of the century.[35e] Involvement of "cyclopropane intermediates" was postulated, but not proven, by many investigators to explain extensively rearranged products.[35d]

[35] (a) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **84**, 3962 (1962); P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962); W. A. Sanderson and H. S. Masher, *ibid.*, **88**, 4185 (1966); (b) P. S. Skell and I. Starer, *ibid.*, **82**, 2971 (1960); (c) M. S. Silver, *ibid.*, **82**, 2971 (1960); M. S. Silver, *J. Org. Chem.*, **28**, 1686 (1963); O. E. Edwards and M. Lesage, *Can. J. Chem.*, **41**, 1592 (1963); M. Hanach and H. Schneider, *Tetrahedron*, **20**, 1863 (1964); W. G. Dauben and P. Laug, *ibid.*, **20**, 1259 (1964); A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964); (d) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *ibid.*, **82**, 2645 (1960); J. G. Traynham and J. S. Dehn, *ibid.*, **89**, 2139 (1967); (e) for example, G. Wagner, St. Moycho, and Fr. Zienkowski, *Chem. Ber.*, 37, 1032 (1904); O. Aschan, *Ann.*, **387**, 1 (1912); J. Bredt, *J. Prakt. Chem.*, **98**, 96 (1918); M. Bredt-Savelsberg, *Chem. Ber.*, **56**, 554 (1923); J. Bredt, *J. Prakt. Chem.*, **131**, 137 (1931); H. Kamppa and G. A. Nyman, *Ann.*, **535**, 252 (1938); G. A. Nyman and A. M. Kuvaja, *ibid.*, **538**, 68 (1939); W. Huckel and G. Meinhardt, *Chem. Ber.*, **90**, 2025 (1957); C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Nature*, **190**, 725 (1961); E. U. Emoven, *J. Chem. Soc., B*, 588 (1966).

[36] L. Friedman, J. H. Bayless, and A. T. Jurewicz, *J. Org. Chem.*, in press.

[37] A. L. Wilds and A. L. Meader, Jr., *ibid.*, **13**, 771 (1948).

[38] E. H. White and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **83**, 1191 (1961).