propionic acid-d_1 gave propionitrile-2,2-d_2 (6 g, 0.11 mol), bp 95–99°, n^{27}D 1.3652 (lit.[25] bp of d_0 compound 97°; n^{25}D 1.3659), in 53% yield.

n-Propylamine-2,2-d_2. Reduction[26] of propionitrile-2,2-d_2 (6 g, 0.11 mol) with lithium aluminum hydride (5 g, 0.13 mol) afforded a 55% yield of n-propylamine-2,2-d_2 (3.5 g, 0.06 mol), bp 50–54° (lit.[26] bp of d_0 compound 49°). The amine was purified through its hydrochloride, mp 156–158° (lit.[26] mp of d_0 compound 157–158°). Low-voltage mass spectrometry showed the deuterium composition to be 7% d_1 and 93% d_2.

Reaction Procedure. The procedure developed earlier[33] was employed in the diazotization reactons. A solution of the amine (0.01 mol), acetic acid (0.01 mol), and octyl nitrite (0.011 mol)[34] in chloroform (10 ml) was heated to reflux.[35] The olefins were trapped in heptane and glpc analyzed. The samples used for deuterium analysis were directly glpc trapped.

Acknowledgment. The authors are deeply indebted to Professor C. J. Collins for his most helpful comments and suggestions in interpreting the data.

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[33] L. Friedman and J. H. Bayless, *J. Am. Chem. Soc.*, **91**, 1790 (1969).

[34] Sodium nitrite was used when the reactions were effected in aqueous acetic acid and 35% perchloric acid.

[35] Reactions in aqueous acetic acid and 35% perchloric acid were carried out at room temperature.

Hydrocarbon Forming Pathways from Amine Diazotizations[1]

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Abstract: Diazotization of several deuterium-labeled isobutyl- and *sec*-butylamines in protic and aprotic solvents gave hydrocarbon mixtures containing methylcyclopropane. The deuterium contents of the methylcyclopropanes suggest that a minor amount (~2%) of the methylcyclopropane arises *via* a partially equilibrating protonated methylcyclopropane. From the deuterium content of isobutylene it is possible to calculate the extent of hydride shift to *t*-butyl cation in its formation. Rearrangement (1,2-hydride shift) of *sec*-butyl cation obtained from isobutylamine *via* a 1,2-methyl shift was found to be solvent dependent. Possible explanations for this phenomenon are considered.

It has been recently demonstrated[3] that protic diazotization of methyl-substituted deuterium-labeled propylamines gave alcohols without involving the intermediacy of protonated cyclopropanes. This conclusion was based upon the positions of the deuterium label in the products. Furthermore, it was stated that there was no evidence for an edge-protonated methylcyclopropane and that the "methyl bridged species, if present, can be detected only by formation of methylcyclopropane."[3a]

In an attempt[4] to elucidate the processes occurring *prior* to loss of nitrogen from alkyldiazonium ions it was found that some of the reactions *following* loss of nitrogen from isobutyl-1,1-d_2-amine (**1**) could be interpreted as going *via* a *partially* equilibrating protonated methylcyclopropane.[5] A more thorough investigation of the isobutyl system was thus warranted to verify this interpretation. In principle, this could be accomplished by determining the deuterium contents of the hydrocarbon products formed *via* the protic and aprotic diazotization of 2-methyl-d_3-propyl-2,3,3,3-d_4-amine (**2**) and isobutyl-2-d_1-amine (**3**). In addition, it was of interest to see the effect that such isotopic labeling would have on hydrocarbon product composition.

Results and Discussion

Diazotization of **2** and **3** gave essentially the same hydrocarbon composition (Table I) as that obtained from unlabeled isobutylamine when identical reaction conditions were employed. The absence of a significant deuterium isotope effect is somewhat surprising in light of the results obtained from deuterated *t*-pentylamine[6] and from partially deuterated neopentyldiazonium ion.[7,8]

The deuterium contents of the hydrocarbon products from the diazotization of **2** are given in Table II. The slight retention (2–4%) of deuterium in methylcyclopropane corresponds with the small difference in deuterium between 1-butene and methylcyclopropane obtained from **1**.[4] This can also be attributed to the limited involvement of a partially equilibrating protonated methylcyclopropane or less likely carbenic intermediates.[9]

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[1] (a) Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged. (b) A preliminary account of portions of this work have been published: J. H. Bayless, A. T. Jurewicz, and L. Friedman, *J. Am. Chem. Soc.*, **90**, 4466 (1968). (c) For the preceding paper in this series, see L. Friedman and A. T. Jurewicz, *ibid.*, **90**, 1800 (1968).

[2] Taken from the Ph.D. thesis of A. T. J., Case Institute of Technology, June 1967.

[3] (a) G. J. Karabatsos, N. Hsi, and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 5649 (1966); (b) G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, *ibid.*, **88**, 5651 (1966).

[4] (a) A. T. Jurewicz and L. Friedman, *ibid.*, **89**, 149 (1967); (b) J. H. Bayless and L. Friedman, *J. Am. Chem. Soc.*, **89**, 147 (1967).

[5] We have been studying the diazotization of aliphatic amines under widely varying reaction conditions and our results from several deuterium-labeled iso- and *sec*-butylamines are generally in good agreement with the conclusions of Karabatsos, Hsi, and Meyerson.[3a] The differences are mainly concerned with minor reaction pathways.

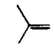
[6] M. S. Silver, *J. Am. Chem. Soc.*, **83**, 3487 (1961).

[7] J. H. Bayless, Ph.D. Thesis, Case Institute of Technology, June 1967.

[8] The small variations in product composition (Table I) could be attributed to deuterium isotope effects. Since five hydrocarbons are formed wide variations in product composition are not anticipated.

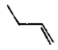
[9] Carbenes are not expected to be intermediates in media such as glacial and aqueous acetic acid because of the highly acidic nature of these solvents. This expectation is in good agreement with minor amounts of deuterium pickup in glacial acetic acid and the absence of deuterium pickup in aqueous acetic acid in the products from diazotization of isobutyl-d_2-amine: J. H. Bayless and L. Friedman, *J. Am. Chem. Soc.*, **89**, 147 (1967). By analogy, carbenoid involvement is not expected to be a major pathway in aprotic diazotization.

Table I. Diazotization of Isobutylamine[a]

	Hydrocarbons, % composition[b,c]				
Solvent					
$HCCl_3$	15 ± 0.6	72 ± 2	4 ± 1	2 ± 0.5	7 ± 0.5
HOAc[d]	4.5 ± 0.5	62 ± 1	14 ± 1	7 ± 0.5	12 ± 1
HOAc-H_2O[d]	2.5 ± 0.5	42 ± 2	25 ± 1	15 ± 2	20 ± 0.5

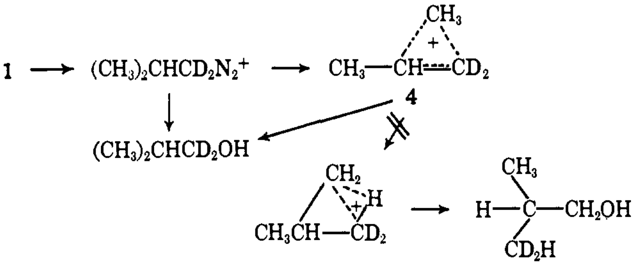
[a] 5.0 mmol of amine, 5.0 mmol of acetic acid, 5.5 mmol of alkyl nitrite in 10 ml of solvent. [b] Determined *via* glpc. [c] The deviations in product composition are for **2** and **3** from the product composition of unlabeled amine (*cf.* ref 7). [d] Sodium nitrite used.

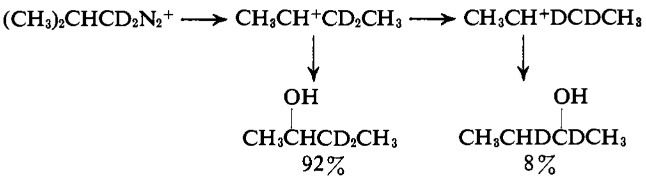
Table II. Diazotization of 2-Methyl-d_3-*n*-propyl-2,3,3,3-d_4-amine[a,b]

	Deuterium content,[c] mol %							
								
Acid–solvent	d_6	d_7	d_6	d_7	d_6	d_7	d_6	d_7
HOAc–$HCCl_3$[d]	96.2	3.8	76.4	23.6	0	100	100	0
HOAc[e]	97.5	2.5	76	24	2	98		
HOAc–H_2O[f]	98	2.0	76	24	2.4	97.6	100	0

[a] Amine (6.7% d_6, 93.3% d_7; 1 equiv), HOAc (1 equiv), OcONO (1.1 equiv), and solvent at reflux. [b] Duplicate runs unless specified. [c] Low-voltage spectrometry. The deuterium content corrected for d_6 in starting amine. [d] Double trapped. [e] Single run. [f] Sodium nitrite used as diazotizing agent and reaction effected at room temperature.

Equilibrating protonated cyclopropanes were eliminated as precursors for substitution products based on the data obtained from diazotization of isobutyl-1,1-d_2-ammonium perchlorate, since no scrambling of deuterium in the isobutyl alcohol was observed.[3a] However, a bridged methyl species (**4**) was postulated to account for methylcyclopropane formation, and which rearranges (to the more stable secondary cation) faster than it equilibrates. Further rearrangement (~7.7% 1,2-hydride shift) of the resulting *sec*-butyl cation occurs.[3a] This same phenomenon was detected in *trans*-2-butene derived from diazotization of **2** in aqueous acetic acid (Table II). The extent of rearrangement, ~7%,[10] is in good agreement with the results of Karabatsos and coworkers.[3a] A decrease in rearrangement of the *sec*-butyl cation occurs in acetic acid (~6%), and none occurs in chloroform. Two possible explanations account for these results. The first is that in aprotic systems **6**, as well as its gegenion, are not solvent stabilized, and therefore deprotonation will occur before further rearrangement. In aqueous acetic acid the ions are stabilized, and as a consequence **6** could partially rearrange to **7** before collapsing to 2-butene. The other possibility is that **5** could give olefins directly without loss of deuterium. This mode of decomposition would probably be more important in aprotic solvents where the *sec*-butyl cation is not solvent stabilized.[11]

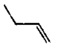




Methyl migration, followed by loss of a methyl deuterium, gives 1-butene.[12] The deuterium content of 1-butene (100% d_6) is consistent with this.

The deuterium content of isobutylene (Table II) from diazotization of **2** is an additional measure of hydride rearrangement to *t*-butyl cation.[13a] While the extent of hydride rearrangement is markedly solvent dependent (it increases with increasing solvation), the extent of the deuterium content of the isobutylene derived from **2** appears to be solvent independent. A

Table III. Diazotization of Isobutyl-2-d_1-amine[a,b]

	Deuterium content,[c] mol %							
								
Acid–solvent	d_0	d_1	d_0	d_1	d_0	d_1	d_0	d_1
HOAc–$HCCl_3$[d]	0	100	0	100	46	54		
HCl–$HCCl_3$					46	54		
HOAc–H_2O[e]					45.5	54.5	3	97

[a] Amine (13.4% d_0, 86.6% d_1; 1 equiv), HOAc (1 equiv), and OcONO (1.1 equiv) and solvent at reflux. [b] Duplicate runs unless otherwise stated. [c] Low-voltage mass spectrometry. The deuterium content corrected for d_0 in the starting amine. [d] Single run. [e] Sodium nitrite used; reaction effected at room temperature.

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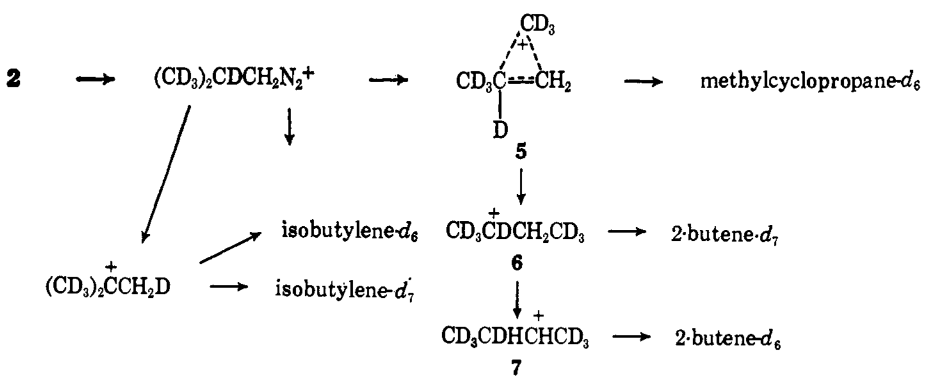
(10) This calculation was made by considering the partitioning of a *sec*-butyl cation, in this system, to 1-butene and 2-butenes. No deuterium isotope effect was used, and it was assumed that the rearranged *sec*-butyl cation ($CD_3CDHC^+DCD_3$) loses deuterium as readily as hydrogen to form 2-butenes. Using a k_H/k_D of 1.1 only changes this value by 0.6%.

(11) Acylation of cyclopropane gave a 33% yield of 3-methyl-3-buten-2-one. Deprotonation of a protonated cyclopropane intermediate to give this olefin was postulated: H. Hart and R. H. Schlosberg, *J. Am. Chem. Soc.*, **88**, 5030 (1966). Similarly deprotonation of protonated cyclopropanes was suggested to explain the deuterium contents of propenes from diazotizations of propyl-2,2-d_2- and -3,3,3-d_3-*n*-amines: see ref 1c.

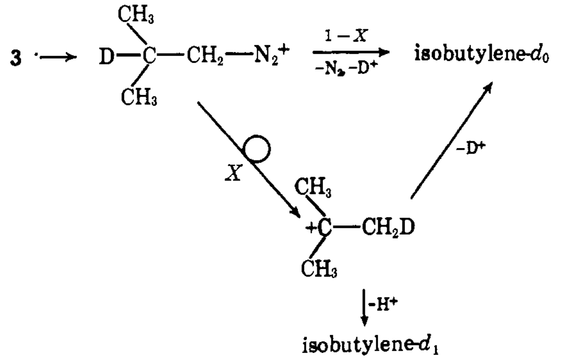
(12) This occurs regardless of the amount of subsequent rearrangements of the *sec*-butyl cation.

(13) (a) The formation of *t*-butyl products is another. (b) The deuterium contents of isobutylene from diazotization of isobutyl-1,1-d_2-amine in all media were not identical[4]; however, this is due to the protium–deuterium exchange on α carbon that occurs in the diazotization process.[4,9] Since no deuterium pickup is observed in aqueous acetic acid[4,9] the loss of deuterium from isobutyl-1,1-d_2 amine in this solvent is due to hydride migration, followed by deprotonation, to form isobutylene.



study on isobutyl-2-d_1-amine (**3**) was initiated to see if this were a general phenomenon.[13b] The deuterium contents of the isobutylene obtained from both protic and aprotic diazotization of **3** were also solvent independent (Table III). From these and the aforementioned results the extent of hydride shift in isobutylene formation can be estimated.

All the calculations of hydride shift were based on the loss of deuterium or hydrogen[14] and a hydrogen–deuterium isotope effect of 1.12–1.13 per deuterium atom was employed in calculating the expected isotopic composition of isobutylene resulting from *t*-butyl cation.[15] A sample calculation follows. The observed



mole fraction, d_{n-1}, of the isobutylene that lost deuterium is

$$d_{n-1} = (1 - d_n) = (1 - X) + \frac{nX}{n + m(k_\mathrm{H}/k_\mathrm{D})^n}$$

where *n* and *m* are the number of deuterium and hydrogen atoms, respectively, in the cation (*i.e.*, in the starting amine), *X* is the extent of hydride shift, and $n/[n + m(k_\mathrm{H}/k_\mathrm{D})^n]$ is the mole fraction expected for 100% hydride shift.[16] Thus

$$X = [1 - d_{n-1}]\left[\frac{n}{m(k_\mathrm{H}/k_\mathrm{D})^n} + 1\right] = d_n\left[\frac{n}{m(k_\mathrm{H}/k_\mathrm{D})^n} + 1\right]$$

The value of *X* for isobutylene obtained from **3** is 0.6 and therefore 60% of the isobutylene is formed from the *t*-butyl cation. A similar calculation on **2** gave essentially identical results (Table IV).[17,18] The larger extent of hydride shift from **1**[19] suggests that an isotope effect (~1.2) exists for 1,2-hydrogen migration.

Table IV. Isobutyldiazonium Ion Extent of Hydride Shift

Amine precursor	Deuterium content, mol[a,b] % Isobutylene d_{n-1}	d_n	Hydride shift, % Un-cor[c]	Cor[d]
$(CH_3)_2CHCD_2NH_2$ (**1**)	13.5	86.5	61	73[e]
$(CH_3)_2CDCH_2NH_2$ (**3**)	46	54	63	60[e]
$(CD_3)_2CDCH_2NH_2$ (**2**)	76	24	108	60.5 ± 1.5

[a] Low-voltage mass spectrometry, corrected for isotopic content of amine precursor. [b] Values from typical runs in protic and aprotic media. [c] Calculated using statistical factors only. [d] Calculated using a $k_\mathrm{H}/k_\mathrm{D}$ (multiplicative) of 1.12–1.13/deuterium atom, *i.e.*, this value gives the best fit. [e] Estimated primary $k_\mathrm{H}/k_\mathrm{D}$ for hydride shift is 1.2.

In all the systems investigated the deuterium content

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[14] Calculations based on either loss of hydrogen or deuterium gave identical results.

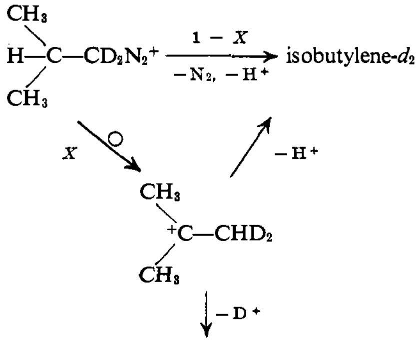
[15] This value was used since all the precursors gave similar amounts of rearrangement when it was employed.

[16] It is assumed that the $k_\mathrm{H}/k_\mathrm{D}$ should be taken to the *n*th power (multiplicative effect) since it is expected that the $k_\mathrm{H}/k_\mathrm{D}$ should be constant for the cases involved. If this is not done the $k_\mathrm{H}/k_\mathrm{D}$ for the entire system varies between 1.12 and 2.36 for **3** and **2**, respectively. The assumption is not unreasonable inasmuch as it has been found that acetolysis rates of cyclopentanol-1-d_1, *cis*- and *trans*-cyclopentanol-2-d_1, and cyclopentanol-2,2,5,5-d_4 tosylates (SN1 process) are retarded relative to the nondeuterio compound as a result of an isotope effect of about 1.15–1.2 *per deuterium atom* (*i.e.*, a multiplicative effect): A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958). Similarly, solvolysis of *t*-amyl chloride (deuterium substitution at the β-carbon atoms) in 80% aqueous ethanol requires a $k_\mathrm{H}/k_\mathrm{D}$ = 1.15 *per deuterium atom* in order to explain the rate data: V. J. Shiner, *ibid.*, **75**, 2925 (1953).

[17] It is now possible to calculate the absolute amount of hydrocarbon and substitution products arising directly from various species (isobutyldiazonium ion, *sec*-butyl cation, and *t*-butyl cation) involved in deamination of isobutylamine.[4b]

[18] These values (Table IV) and the equations used are corrected from that given in ref 2, p 70.

[19] The equation used for calculating *X* from **1** is $X = d_{n-1}\{n/[m \cdot (k_\mathrm{H}/k_\mathrm{D})^n] + 1\}$ and is different from that used for **2** and **3** since the routes for deuterium loss are exchanged.



of the isobutylene was found to be solvent independent (Tables III and IV). This was somewhat unexpected since a variation of deuterium content with a change in the amount of rearrangement was anticipated. However, analysis of the processes occurring predicts the observed results. Thus the ratio of isobutyl precursor going to isobutylene in aprotic (k_i^a) and protic (k_i^p) deamination is equal to a constant (K_i). A similar constant (K_t) can be obtained for *t*-butyl cation similarly going to isobutylene. In both cases the statistical

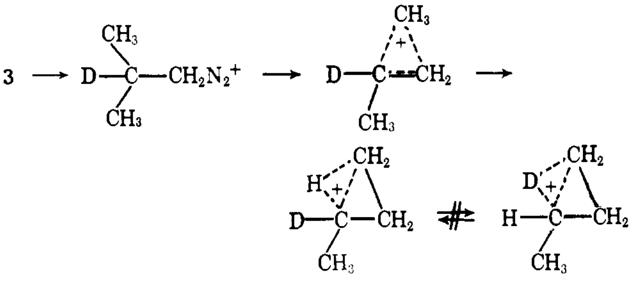
$$k_i^a/k_i^p = K_i$$

factors cancel. Since both K_t and K_i refer to the same

$$k_t^a/k_t^p = K_t$$

process,[20] loss of a proton to form isobutylene, they should be equal. Identical deuterium content of isobutylene from protic and aprotic solvents is a necessary corollary of this postulate, since the deuterium content is not dependent on the total amount of hydride shift occurring.

The deuterium contents of methylcyclopropane, 1-butene, and *trans*-2-butene obtained by diazotization of isobutyl-2-d_1-amine (Table III) were also consistent with the results obtained from other labeled isobutylamines in that formation of methylcyclopropane and 1-butene occurred with complete retention of deuterium. The deuterium retention in methylcyclopropane excludes the involvement of the methine hydrogen in an equilibrating protonated cyclopropane. However, limited equilibration between methyl hydrogens is possible.



The extent of hydride rearrangement of the *sec*-butyl cation formed by methyl migration can be estimated by the deuterium content of *trans*-2-butene. In aqueous acetic acid the calculated[10] amount of

$$(CH_3)_2CDCH_2N_2^+ \longrightarrow CH_3CD^+CH_2CH_3 \rightleftarrows CH_3CDHCH^+CH_3$$

hydride shift is 9%. This is in good agreement with the results calculated from 2-methyl-d_3-*n*-propyl-2,3,3,3-d_4-amine.

All previous investigations concerned with the possibility of an equilibrating protonated cyclopropane were on primary systems.[3,21] The possibility of such equilibrating species from *sec*-butyldiazonium ion was therefore investigated.

Aprotic as well as protic diazotization of *sec*-butyl-4,4,4-d_3-amine gave hydrocarbon mixtures (3% methylcyclopropane, 23.5% *trans*-2-butene, 15% *cis*-2-butene, and 58.5% 1-butene; 1% methylcyclopropane, 49% *trans*-2-butene, 22% *cis*-2-butene, and 28% 1-butene, respectively) that were essentially identical with the hydrocarbon products obtained by aprotic[7] and protic[7,22] diazotization of unlabeled amine.

The possible existence of an equilibrating protonated cyclopropane can be estimated from the degree of scrambling of deuterium in the methylcyclopropane. In both aprotic and protic diazotization the deuterium content (Table V) of methylcyclopropane (~98% d_2, 2% d_3) indicates at best a limited involvement of a partially equilibrating protonated methylcyclopropane.

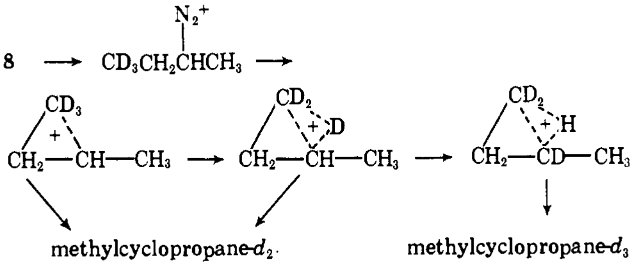
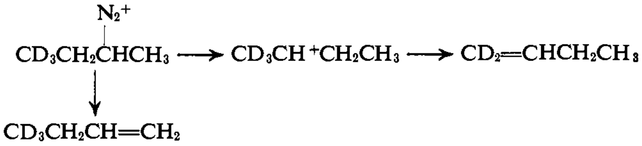


Table V. Diazotization of *sec*-Butyl-4,4,4-d_3-amine[a,b]

	Deuterium content,[c] mol %					
						
Acid–solvent	d_2	d_3	d_2[d]	d_3[d]	d_2	d_3
HOAc–HCCl₃	97.9	2.1	0	100	5	95
HOAc–H₂O[e]	98.1	1.9	0	100	6	94

[a] Amine (4.4% d_1, 95.6% d_2; 1 equiv), HOAc (1 equiv), and OcONO (1.1 equiv) and solvent at reflux. [b] Duplicate runs. [c] Low-voltage mass spectrometry. Deuterium content corrected for d_2 in the starting amine. [d] Identical results for *cis*-2-butene. [e] Sodium nitrite used; reaction effected at room temperature.

As expected, complete retention of deuterium was observed in the *cis*- and *trans*-2-butenes. However, the 1-butene lost deuterium. In aprotic diazotization the deuterium content was 5% d_2 and 95% d_3, while in protic diazotization it decreased slightly (6% d_2 and 94% d_3). The loss of deuterium results from 1,2-hydride shift, followed by deprotonation, yielding 2-butenes and 1-butene. An estimation of hydride shift could be determined if it is assumed that the 2-butyl cation is identical with that obtained from diazotization of isobutylamine followed by methyl migration. Applying this approximation the extent of hydride shift in aprotic and protic diazotization of *sec*-butyl-4,4,4-d_3-amine is calculated to be about 11 and 15%, respectively.



$$\begin{tikzcd} CD_3CH_2\overset{N_2^+}{C}HCH_3 \arrow[r] \arrow[d] & CD_3CH^+CH_2CH_3 \arrow[r] & CD_2{=}CHCH_2CH_3 \\ CD_3CH_2CH{=}CH_2 & & \end{tikzcd}$$

The results obtained in the hydrocarbon fraction are in good agreement with those from the gegenion frac-

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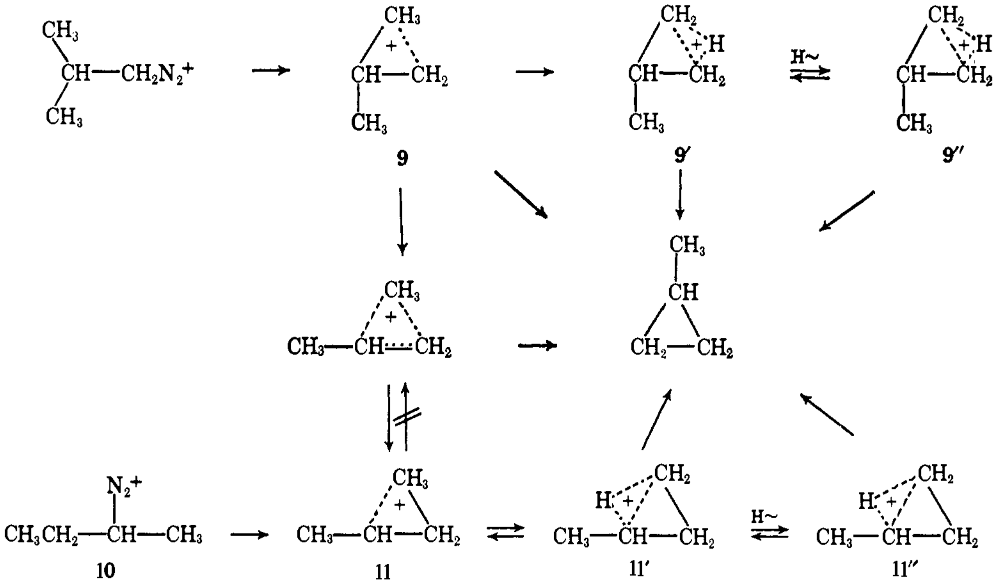
[20] From isobutyl precursor it is loss of the methine hydrogen and from *t*-butyl precursor it is loss of a methyl hydrogen.

[21] G. J. Karabatsos, C. E. Orzech, and S. Meyerson, *J. Am. Chem. Soc.*, 87, 4394 (1965); C. C. Lee, J. E. Kruger, and E. W. C. Wong, *ibid.*, 87, 3985 (1965); C. C. Lee and J. E. Kruger, *ibid.*, 87, 3986 (1965); A. A. Aboderin and R. L. Baird, *ibid.*, 86, 2300 (1964).

[22] W. B. Smith and W. H. Watson, Jr., *ibid.*, 84, 3174 (1962).

Scheme I



tion[3a] with some minor differences. The deuterium contents of the methylcyclopropane from **1**, **2**, and **8** all indicate that a minor amount of equilibration occurred. This is in contrast to the *n*-propyl system where extensive equilibration has been observed.[21] Scheme I accounts for these differences. In the isobutyl system limited equilibration occurs (**9′** to **9′′**);[23] however, if **11** is reached equilibration back to **9** does not take place. This is based on the absence of isobutylene or isobutyl and *t*-butyl substitution products from *sec*-butylamine. The minor amount of equilibration (**11′** to **11′′**) from **10**[24] is to be contrasted with the absence of participation of the tertiary hydrogen from **9**,[25] which could be expected to occur according to the proposed scheme. This may be the result of **9** or **9′** and **9′′** going to methylcyclopropane without going *via* **10** or if the amount that goes *via* **10** is less than 25% it could not be detected (*i.e.*, 25% × 2% = 0.5% which is the level of precision of the analysis) by low-voltage mass spectral analysis.

Experimental Section[26]

General Reaction Procedure. The procedure developed earlier[27] was employed in the diazotization reactions. A solution of the amine (0.01 mol), acetic acid (0.01 mol), and octyl nitrite (0.011 mol)[28] in chloroform (110 ml) was heated to reflux.[29] The olefins were trapped in heptane and glpc analyzed. Samples used for deuterium analysis were directly glpc trapped.

***n*-Butoxyethyl isobutyrate-2-d_1** was prepared from tetramethyl-1,3-cyclobutanedione, *n*-butoxyethyl alcohol-d_1,[30] and sodium methoxide according to the procedure[31] used to prepare *t*-butyl isobutyrate. The yield of *n*-butoxyethyl isobutyrate-2-d_1 (231 g, 1.22 mol), bp 105–106°, n^{20}_{D} 1.4155, was 61%. The infrared spectrum had a carbonyl stretch at 5.76 μ and no O–H absorption.

Isobutyl-2-d_1 Alcohol. Reduction[32] of *n*-butoxyethyl isobutyrate-2-d_1 (230 g, 1.2 mol) with lithium aluminum hydride (42. g, 1.1 mol) gave isobutyl-2-d_1 alcohol (71 g, 0.94 mol), bp 108° (lit.[33] bp 105–106.5°), in a 78% yield. Nmr integration gave the following deuterium content of the tertiary hydrogen: 15% d_0 and 85% d_1.

Isobutyl-2-d_1 *p*-toluenesulfonate was prepared in 85% yield according to the procedure used to prepare dodecyl *p*-toluenesulfonate.[34]

N-Isobutyl-2-d_1-phthalimide. Isobutyl-2-d_1 *p*-toluenesulfonate (98 g, 0.43 mol) and potassium phthalimide (89 g, 0.48 mol) in dimethylformamide (350 ml) gave[35] a 73% yield of crude N-isobutyl-2-d_1-phthalimide (67.5 g, 0.37 mol). A small portion of the crude phthalimide was recrystallized from ethanol, mp 90–91° (lit.[36] mp of d_0 compound 92–93°).

Isobutyl-2-d_1-amine Hydrochloride. N-Isobutyl-2-d_1-phthalimide was converted[35] in 68% yield to the isobutyl-2-d_1-amine hydrochloride (27.5 g, 0.25 mol). The crude amine hydrochloride was dissolved in water and treated with charcoal to give white amine hydrochloride, mp 177° (lit.[37] mp of d_0 compound 177–178°). The deuterium content, 13.4% d_0 and 86.6% d_1, was determined by low-voltage mass spectrometry. This is in accord with the nmr analysis on isobutyl-2-d_1 alcohol (15% d_0, 85% d_1).

Octadeuterioisopropyl Alcohol. A mixture of hexadeuterioacetone (95 g, 1.48 mol), sodium deuterioxide (2 ml of 1 *N* NaOD solution), and rhodium on carbon (0.4 g of 5% Rh on carbon) was treated with deuterium gas (53 l.) for 1 hr.[38] The mixture was filtered and the yield of distilled octadeuterioisopropyl alcohol was 71% (71 g, 1.05 mol), bp 80–83°, n^{25}_{D} 1.3727 (lit.[39] bp of d_0 compound 82°, n^{20}_{D} 1.37757). The infrared spectrum showed no carbon–hydrogen stretch, but a carbon–deuterium stretch at 4.48 μ.

Heptadeuterioisopropyl *p*-toluenesulfonate was prepared in a 76% (177 g, 0.8 mol) yield according to the procedure used to prepare dodecyl *p*-toluenesulfonate.[34]

Heptadeuterioisobutyronitrile was prepared from heptadeuterio-

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(23) Determined from the deuterium contents of methylcyclopropane obtained from 1 and 2.

(24) Determined from the deuterium content of methylcyclopropane obtained from 8.

(25) Determined from the deuterium content of methylcyclopropane obtained from 3.

(26) Boiling and melting points are uncorrected. Deuterium analyses obtained on a General Electric Analytical mass spectrometer.

(27) L. Friedman and J. H. Bayless, *J. Am. Chem. Soc.*, **91**, 1790 (1969).

(28) Sodium nitrite was used when the reactions were effected in glacial or aqueous acetic acid.

(29) Reactions in glacial and aqueous acetic acid were carried out at room temperature.

(30) Prepared from hydrolysis of the corresponding borate ester: L. Friedman, J. H. Bayless, and A. T. Jurewicz, *J. Org. Chem.*, in press.

(31) R. H. Hasek, D. Clark, E. U. Elam, and R. G. Nations, *ibid.*, 27, 3106 (1962).

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

(33) E. L. Eliel and T. J. Prosser, *J. Am. Chem. Soc.*, **78**, 4045 (1956).

(34) E. S. Marvel and V. C. Sekera, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 366.

(35) *Cf.* J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, 73, 2059 (1951).

(36) A. Neuman, *Chem. Ber.*, 23, 999 (1890).

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

(38) *Cf.* E. Breitner, E. Roginski, and P. N. Rylander, *J. Org. Chem.*, 24, 1855 (1959).

(39) *Cf.* ref 37, Vol. V, p 2783.

isopropyl *p*-toluenesulfonate (177 g, 0.8 mol) and sodium cyanide (53 g, 1.08 mol) in DMSO (250 ml) according to the procedure[40] used to convert alkyl halides into nitriles. The yield of heptadeuterioisobutyronitrile, bp 103–105°, $n^{24}\text{D}$ 1.3706 (lit.[41] bp of d_0 compound 103.5°, $n^{15}\text{D}$ 1.37563), was 28%.

2-Methyl-d_3-propyl-2,3,3,3-d_4-amine. Reduction[32] of heptadeuterioisobutyronitrile (7.5 g, 0.1 mol) with lithium aluminum hydride (7.6 g, 0.2 mol) yielded 81% of 2-methyl-d_3-propyl-2,3,3,3-d_4-amine (6.4 g, 0.08 mol), bp 67–69°, $n^{22}\text{D}$ 1.3963 (lit.[37] bp of d_0 compound 69°). The deuterium content of the amine was 7% d_6 and 94% d_7 as determined by low-voltage mass spectrometry. Nmr showed that most of the d_6 was a result of hydrogen on a methyl group.

Ethyl Methylmalonate. Decarbonylation of ethoxalyl propionate gave ethyl methylmalonate.[42] The yield of distilled material, bp 195–196°, $n^{28}\text{D}$ 1.4092 (lit.[42,43] bp 194–196°, $n^{16.5}\text{D}$ 1.4148), was 89%.

2-Methyl-4,4,4-d_3-butyric Acid. Alkylation of ethyl methylmalonate (174 g, 1 mol) with ethyl-2,2,2-d_3 *p*-toluenesulfonate (152.5 g, 0.75 mol), followed by ester hydrolysis and decarboxylation, according to the procedure used to prepare pelargonic acid,[44] gave 2-methyl-4,4,4-d_3-butyric acid (31.5 g, 0.31 mol), bp 173–177° (lit.[45] bp of d_0 compound 177°), in a 41% yield. The infrared spectrum was identical with that of known 2-methylbutyric acid except for a sharp absorption at 4.51 μ which is attributable to carbon–deuterium stretching vibrations.

***sec*-Butyl-4,4,4-d_3-amine.** Chilled concentrated sulfuric acid[46] (250 ml) was added dropwise at 0° to 2-methyl-4,4,4-d_3-butyric acid (31.5 g, 0.31 mol). The mixture was heated to 40° and sodium azide (22.8 g, 0.35 mol) was added at such a rate that the temperature in the reaction flask did not go above 50°. Upon the completion of the addition of sodium azide, the mixture was heated at 120° for 12 hr.[47] The solution was neutralized with concentrated potassium hydroxide and then extracted with three 100-ml portions of ether. The ether extract was dried over sodium sulfate and HCl gas was bubbled into the ether solution. A tan solid precipitated. The solid was dissolved in water and treated with charcoal. The water was stripped off leaving white *sec*-butyl-4,4,4-d_3 amine hydrochloride (24.4 g, 0.22 mol, 70%), mp 144–146° (mp of d_0 compound 147–148°). A weak nmr signal was observed for the C-4 methyl hydrogens and low-voltage mass spectrometry showed the deuterium content to be 4.4% d_2 and 95.6% d_3.

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[40] L. Friedman and H. Shechter, *J. Org. Chem.*, **25**, 877 (1960).

[41] *Cf.* ref 37, Vol. V, p 1902.

[42] R. F. B. Cox and S. M. McElvain, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 279.

[43] G. Wittig, M. Heintzeler, and M. H. Wetterling, *Ann.*, **557**, 204 (1947).

[44] E. Reid and J. R. Ruhoff, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 474.

[45] *Cf.* ref 37, Vol. IV, p 2150.

[46] T. Moritsugu, Ph.D. Thesis, Ohio State University, Columbus, Ohio, 1954.

[47] It was subsequently found that heating for 1 hr at 100° was adequate.

Alkylation of Arenes *via* Aprotic Diazotization of Alkylamines[1]

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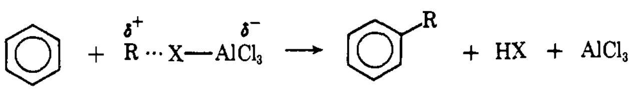
Abstract: Alkylation of arenes *via* aprotic diazotization of aliphatic amines gave low yields of substituted arenes. Its value as a preparative method is negated by the low yields (0.5–2.5%); however, the reaction was studied because of its theoretical interest. The minor amounts of rearrangement that occured in the alkylarene fraction suggests that the intermediate involved is short lived, and that π-complex formation predominates. The isomer composition of cymenes from diazotization of isopropylamine in toluene and the relative selectivity exhibited by isopropylation in toluene–benzene mixtures suggest that cationic intermediates are involved in aprotic diazotizations.

Cationic intermediates from various precursors have been shown to be involved in Friedel–Crafts alkylation. Formation of a carbonium ion was originally postulated;[3] however, subsequent studies[4] indicated that a displacement by the aromatic ring on the alkyl derivative–catalyst complex was also involved. Kinetic studies on methylation,[4c] ethylation,[4c] and benzylation[4a] with alkyl chlorides and aluminum chloride showed a first-order dependence on arene. Thus the displacement by the arene on the alkyl derivative–catalyst complex was postulated to be the rate-controlling step in the reaction. In cases where stabilization might occur (*i.e.*, *t*-butyl cation) a carbonium ion could be involved; however, it has been suggested[5] that even this is at best an ion pair rather than a free carbonium ion.



The exact mechanistic features of Friedel–Crafts reactions are dependent on the solvent system and the electrophile involved.[6] Either σ-complex[4a–d] or π-

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[1] (a) Financial support (Grant No. GP-3976) from the National Science Foundation in gratefully acknowledged. (b) A preliminary account of a portion of this work has been published: A. T. Jurewicz, J. H. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 5788 (1965). (c) For the preceding paper in this series, see L. Friedman and A. T. Jurewicz, *ibid.*, **91**, 1803 (1969).

[2] Based on the Ph.D. dissertation of A. T. Jurewicz, Case Institute of Technology, 1967.

[3] C. C. Price, *Org. Reactions*, **3**, 1 (1946); C. C. Price, *Chem. Rev.*, **29**, 37 (1941).

[4] (a) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); (b) H. C. Brown and H. Jungk, *ibid.*, **77**, 5584 (1955); (c) H. Jungk, C. R. Smoot, and H. C. Brown, *ibid.*, **78**, 2185 (1956); (d) C. R. Smoot and H. C. Brown, *ibid.*, **78**, 6249 (1956); (e) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).

[5] G. A. Olah, S. H. Flood, and M. E. Moffatt, *ibid.*, **86**, 1060 (1964).

[6] G. A. Olah, S. H. Flood, S. J. Kohn, M. E. Moffatt, and N. A. Overchuck, *ibid.*, **86**, 1046 (1964).