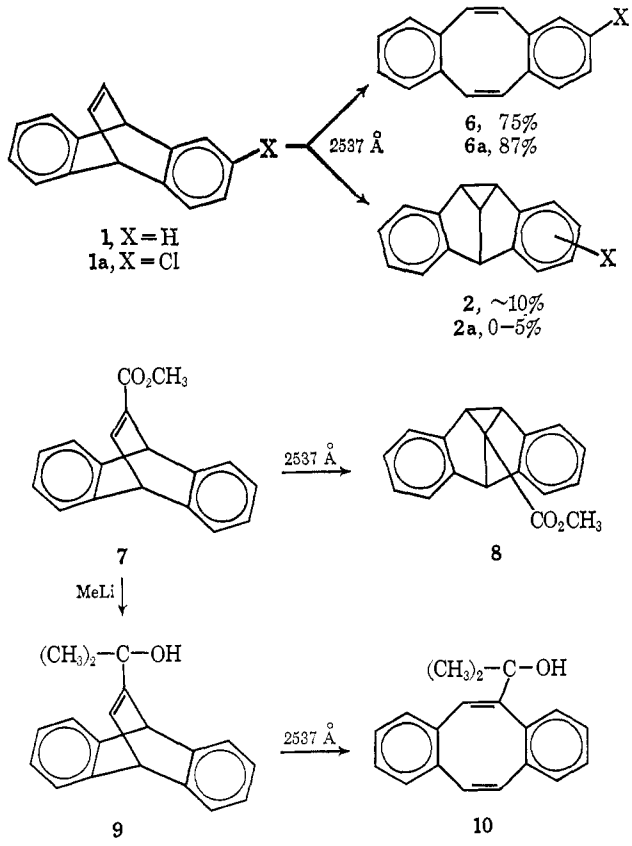

lows then that the conjugated double bond is the active chromophore.

These results support the mechanism proposed by Brewer and Heaney,[2] wherein rearrangement to cyclooctatetraenes occurs from the excited singlet, and semibullvalenes from the excited triplet.

Thus, in view of the ready accessibility of benzo-[5] and dibenzobarrelenes,[9] direct irradiation (2537 Å) appears to be the most convenient synthetic route to benzo- and dibenzocyclooctatetraenes. Elucidation of the mechanistic details and the efficiency (Φ) of the direct and sensitized irradiation of **1** and **3** are presently being investigated.

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The Fate of the Isobutyldiazonium Ion[1]

Sir:

There is lack of agreement on the mechanisms and processes involved in product formation from thermal decomposition of N-alkyl-N-nitrosoacetamides[2] and diazotization of alkylamines[3,4] since product compositions vary widely with changes in reaction conditions.[2-4] In this investigation, the isobutyl system was studied since from product analysis coupled with suitable labeling experiments the product-forming processes can be unravelled.

With the exception of isobutylene all products can be related to a unique structural precursor. For example, 1-butene, *cis*- and *trans*-2-butenes, and the *sec*-butyl substitution products result from the *sec*-butyl cation. However, isobutylene can arise either from the isobutyldiazonium ion (**1d**$^+$) by concerted loss of nitrogen and protium or from the *t*-butyl cation which is formed from **1d**$^+$ by hydride shift. Thus, by means of appropriate labeling experiments[5] it is determined that from either protic or aprotic reactions approximately 70% of the isobutylene is formed *via* the *t*-butyl cation (Table I).[5] With this information it is now possible to ascertain the amounts of isobutyl, *sec*-butyl, and *t*-butyl product-forming precursors. The various reaction pathways are outlined in Scheme I and tabulated in Table II. Thus in the poorly solvating medium, chloroform, hydrocarbon and substitution products

Table I. Extent of Hydride Shift in Isobutylene Produced from Isobutyldiazonium Ion

	Isobutylene			
	Deuterium content % mole[a,b]		% hydride shift	
Amine precursor	d_{n-1}	d_n	Uncor[c]	Cor[d]
$(CH_3)_2CHCD_2NH_2$ (d_2)	13.5	86.5	61	73[e]
$(CH_3)_2CDCH_2NH_2$ (d_1)	46	54	63	60[e]
$(CD_3)_2CDCH_2NH_2$ (d_7)	76	24	108	61

[a] Low-voltage mass spectrometry, corrected for isotopic content of amine precursor. [b] Values are from typical runs in protic and aprotic media. [c] Calculated using statistical factors. [d] Calculated using a k_H/k_D value (multiplicative) of 1.12–1.13/D atom; *i.e.*, this value gives the best fit; *cf.* ref 5. [e] Estimated primary k_H/k_D for hydride shift is 1.2.

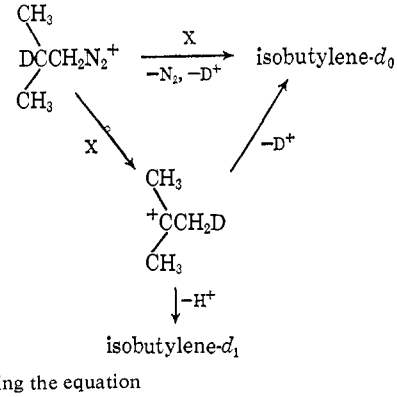
(1) Financial support (Grant No. GP-3976) from the National Science Foundation is gratefully acknowledged.

(2) Previously observed from thermal decomposition of N-isobutyl-N-nitroso amides in various aprotic media. It was suggested that the reaction proceeds predominantly *via* concerted cyclic processes of the covalent diazo ester intermediate and that isomerization is controlled by steric factors: E. H. White, *J. Am. Chem. Soc.*, 77, 6014 (1955).

(3) (a) J. H. Bayless, F. D. Mendicino, and L. Friedman, *ibid.*, 87, 8790 (1965), reported that diazotization of isobutylamine in chloroform gives substitution products consisting of 5% *t*-butyl, 9% *sec*-butyl, and 86% isobutyl derivatives. This is not compatible[3] with "proposed" carbonium ion reactions of isobutyl precursors in *protic* media where large amounts of rearrangement occur leading predominately to *t*-butyl substitution products.[4]

(4) L. G. Cannell and R. W. Taft, *ibid.*, 78, 5812 (1956).

(5) For 2-deuterioisobutylamine the followihg scheme outlines the routes to isobutylene-d_0 and -d_1. *X*, the extent of hydride shift, was

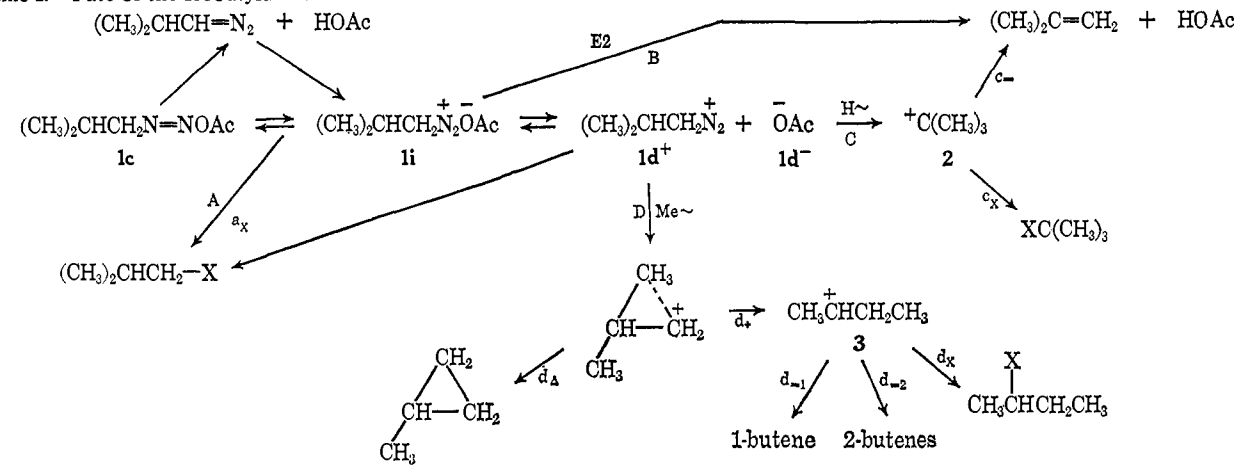


calculated using the equation

$$X = d_n\left[\frac{n}{m(k_H/k_D)^n} + 1\right]$$

where *m* and *n* are the number of H atoms and D atoms in the amine and d_n is the mole fraction of isobutylene that did not lose deuterium. The (k_H/k_D) is an unresolved combination of primary and secondary deuterium isotope effects.

Scheme I. Fate of the Isobutyldiazonium Ion



arise from ~60% isobutyl (A + B), ~23% *t*-butyl (C), and ~16% *sec*-butyl (D) precursors, while in water the *t*-butyl cation is the predominate product precursor.[6]

crease as routes C and D increase); (2) the olefin:substitution product ratio from the *t*-butyl cation (**2**) decreases (route $c_{=}$:route c_X); (3) cyclopropane formation

Table II. Product-Forming Routes from Diazotization[a] of Isobutylamine

Solvent[b]	A[c]	B[d]	C	$c_{=}/c_X$	D	d_Δ	d_+	$d_{=2}/d_{=1}$	d_x[e]	C/D[f]	C + D
Chloroform[g]	53	7.4	23	6.4	16	5.7	11	0.85	5.6	1.4	39
Benzene[g]	51	8.2	25	3.3	16	4.6	11	0.84	5.9	1.6	41
Benzene (N)[h]	56	7.6	21	5.5	15	4.9	11	0.92	5.9	1.4	36
Acetic acid	18	5.3	46	0.31	31	1.3	29	1.7	20	1.5	77
50% aqueous acetic acid	11	2.6	52	0.13	34	0.5	33	1.8	24	1.5	86
Water ($HClO_4$)	7.2	1.6	52	0.08	39	0.3	39	2.7	25	1.3	91

[a] Normalized product yields calculated from data in ref 2; total from routes A + B + C + D = 100%. [b] Refluxing solvent or 90–95° whichever is lower. [c] Total from route A = $a_X = a_{OAc} + a_{OH}$. [d] 30% of the isobutylene arises *via* this route. [e] Total from route $d_x = d_{OAc} + d_{OH}$. [f] Hydride shift/methyl shift. [g] Results are representative of highly reproducible product composition. [h] Decomposition of N-isobutyl-N-nitrosoacetamide.

An attractive postulate to explain these results is that diazonium acetate ion pair (**1i**) [and/or covalent diazo ester (**1c**)] is the last common intermediate in the diazotization process.[8] In poorly solvating media this would be expected to exist predominantly as a tight ion pair,[9] while with increasing solvation solvent-separated ions **1i′** and dissociated ions $\mathbf{1d^+}$,$\mathbf{1d^-}$ achieve greater importance.[10] It is proposed that rearrangement can occur from **1i′** and $\mathbf{1d^+}$ but not from **1c** and **1i**. Thus, as the solvating power of the medium increases (Table II): (1) rearrangement increases (routes A and B decreases (d_Δ); (4) the ratio of 2-butenes ($d_{=2}$) to 1-butene ($d_{=1}$) increases [olefins formed from the *sec*-butyl cation (**3**)]; and (5) the ratio of hydride to methyl shift (route C:route D) remains essentially constant.[11] Hence, there is no need to invoke the intermediacy of the high-energy isobutyl (a primary) cation (route e in the Streitwieser scheme)[8] to account for the reaction products.

The extent of solvation of both the cation and its counterion adequately account for most of the observations. Increased rearrangement (1) at the expense of direct product formation *via* SN1, SN2, E1,[12] and E2 processes is expected as the solvating power of the medium increases. Decrease in the olefin:substitution ratio (2)[13] from **2**, the reduced amount of cyclopropane formation (3), and the preference of 2-butene (4) from **3** are consistent with the decrease in basicity and reactivity of the counterion[14] in the more highly solvating media. Thus, as the medium becomes more solvating a greater proportion of the cationic intermediates rearrange to more thermodynamically stable species.

(6) These values were determined from normalized product yields of the hydrocarbons and substitution products. Methylcyclopropane is included as a *sec*-butyl-derived product since it is formed by proton abstraction by the counterion during a methyl shift, *i.e.*, from a bridged methyl cation or nonequilibrating protonated cyclopropane:[7] A. T. Jurewicz and L. Friedman, *J. Am. Chem. Soc.*, **89**, 149 (1967).

(7) See also the formation of 1,1-dimethylcyclopropane from neopentyl tosylate: G. M. Fraser and H. M. R. Hoffmann, *Chem. Commun.*, 561 (1967).

(8) (a) This is an extension of the Streitwieser proposal which postulates that the diazonium ion, rather than a carbonium ion, is the last common intermediate from diazotization: A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957). (b) Striking evidence for the intermediacy of the diazonium ion is the fact that diazotization of optically active *n*-butylamine in acetic acid gives *n*-butyl acetate with ~76% net inversion of configuration [A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem, Soc.*, **79**, 2888 (1957)] and the stereospecific rearrangement of optically active 1-deuterioneopentylamine to 3-deuterio-2-methyl-1-butene and *t*-amyl alcohol [W. D. Guthrie, *ibid.*, **89**, 6718 (1967)].

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

(10) Ionization and dissociation of **1c** and **1i** is analogous to the scheme proposed for solvolysis reactions: S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

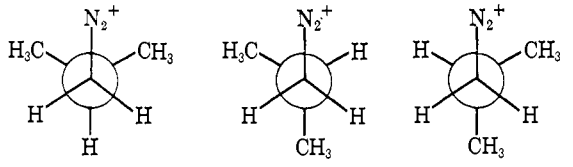
(11) Slight variations can be attributed to differences in reaction temperature inasmuch as methyl shift is favored at higher temperatures.[4] Thus, for example, the ratio route C:route D at 30° is ~2.5–3.0, whereas at 100° it is ~1.3–1.6.

(12) D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963).

(13) *Cf.* M. Cocivera and S. Winstein, *ibid.*, **85**, 1702 (1963).

(14) (a) D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, **88**, 2345 (1966), and references contained therein. (b) For the importance of the nucleophilicity of the counterion see W. Kirmse and K. Horn, *Tetrahedron Letters*, 1827 (1967).

The fact that the route C:route D ratio is constant and is solvent (but not temperature)[11] independent suggests that the rearranging precursor ions, either **1i′** or **1d**$^+$, are the "same" in all media (*i.e.*, they are in the same states of solvation) and that the ratio of hydride to methyl shift reflects the ratio of their respective precursor conformers: **4** and **5** (a and b) (of **1i′** and **1d**$^+$). The sum of these species, however, *increases* with *increasing solvating* power of the medium.



4 **5a** **5b**

From these and related experiments with other *primary* aliphatic amines[8b,15] it can be concluded that carbonium ions are not formed by unimolecular fission of the corresponding diazonium ion. In these systems carbonium ions are apparently only formed by concerted rearrangement processes.

(15) Similar results are obtained from *n*-butylamine and neopentylamine.

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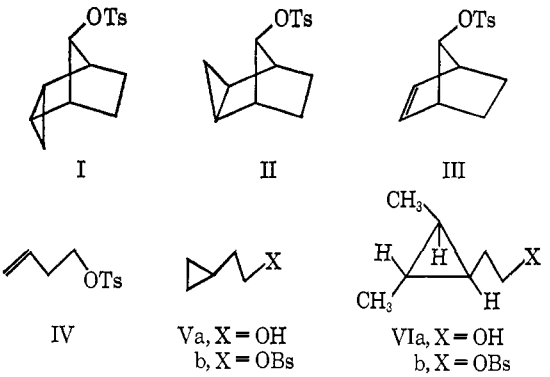
Rates of Solvolysis of 2-Cyclopropylethyl Brosylates[1]

Sir:

The ability of the cyclopropyl group to interact with a positive center separated from it by one carbon atom has been the subject of much recent discussion,[2] and some striking examples have been reported; for example, I solvolyzes[2a] 10^{14} times faster than isomeric II and 10^3 times faster than the analogous norbornenyl derivative III in which the cyclopropane ring in I is replaced by a double bond. Therefore, although little anchimeric assistance is observed in the open-chain homoallylic system IV[3] ($k_{IV}/k_{n\text{-butyl}} = 3.7$, for formolysis), the possibility exists that the solvolysis of esters of 2-cyclopropylethanol (V) might be significantly assisted.

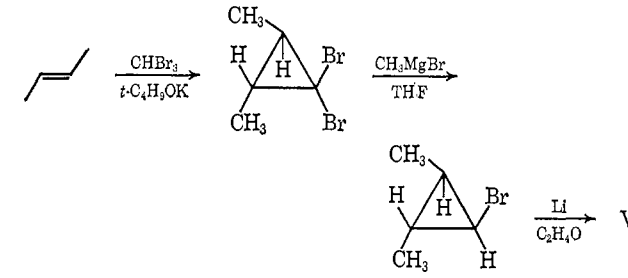
Sauers and Ubersax[2b] have examined the formolysis of the brosylate of V-α,α-d_2 and claim that their results can be explained "without recourse to intermediates other than classical ones. If such intermediates are involved they cannot be the sole intermediates." In



I II III

IV Va, X = OH; b, X = OBs VIa, X = OH; b, X = OBs

view of their uncertainty (their experiments could not demonstrate the presence or absence of participation) further work is clearly needed; we have accordingly measured the rates of formolysis of the brosylate of V and its dimethyl derivative VI, and compared them with the corresponding rate for ethyl brosylate. Vb was prepared from the alcohol;[4] Va by the method of Tipson.[5,6] VIb was likewise prepared from VIa, which in turn was obtained by the following route.[7,8]



Solvolysis of Vb in anhydrous formic acid containing sodium formate[9] at 85°, followed by treatment with lithium aluminum hydride, gave the alcohols VII, VIII, IX, and Va, in agreement with previous work.[2b,10] The rates of formolysis were measured spectrophotometrically in anhydrous formic acid containing sodium formate (5% excess over ester) at 75°; the results are shown in Table I. The rates were unaffected by addition of larger excesses of sodium formate.

Table I. First-Order Rate Constants (k_1) for the Solvolysis of Brosylates in Anhydrous Formic Acid at 75°

Compound	$k_1 \times 10^5$, sec^{-1}	Relative rate
EtOBs	4.26	1.00
Vb	3.94	0.93
VIb	13.30	3.12

The fact that VIb solvolyzes about three times faster than Vb must be attributed to participation by the cyclopropyl group, for introduction of methyl substituents into the β position of simple alkyl tosylates

(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (b) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, **31**, 495 (1966); (c) G. E. Cartier and S. E. Bunce, *J. Am. Chem. Soc.*, **85**, 932 (1963); (d) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (e) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (f) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); (g) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); (h) P. K. Freeman and D. M. Balls, *Tetrahedron Letters*, 437 (1967); (i) C. F. Wilcox, Jr., and R. G. Jesaitis, *ibid.*, 2567 (1967); (j) M. Hanack and H. M. Ensslin, *ibid.*, 4445 (1965); (k) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Am. Chem. Soc.*, **86**, 1867 (1964).

(3) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965).

(4) H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959).

(5) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(6) All new compounds gave satisfactory analyses, etc.

(7) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

(8) D. Seyferth and B. Prokai, *J. Org. Chem.*, **31**, 1702 (1966).

(9) In the absence of base (sodium formate), Vb reacted rapidly in formic acid by opening of the cyclopropane ring; this was established by the rapid disappearance of the nmr signals corresponding to cyclopropane protons.

(10) Sauers and Ubersax[2b] give the following ratios for alcohols VII, VIII, IX, and Va: 36:12:17:35.