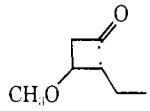
chemistry. Especially interesting is the stereospecificity in the formation of **3** since published work indicates that in the vapor, cyclobutanones lose CO *via* a triplet mechanism.[13]

The lack of total stereospecificity in the products from irradiation of ketones **1c** and **1t** can be accounted for entirely as the result of contamination of solutions of **1c** with **1t** and *vice versa*. The most satisfactory separation of ketones **1c** and **1t** (by gas–liquid chromatography) leads to a few per cent of cis–trans isomerization under our conditions.

The photoreactions of cyclobutanones cannot be quenched by 1,3-dienes, a result which argues for the intermediacy of either an excited singlet or very rapidly decomposing (unquenchable) triplet.[14] The lack of scrambling of stereochemistry in the photoreactions reported in Tables I and II rules out any intermediate capable of surviving long enough to undergo bond rotations. Since the triplet states of **1c** and **1t** are not expected to undergo concerted rearrangements,[15] any triplet intermediate would be expected to suffer substantial loss of stereochemistry.[16] We conclude, therefore, that the excited singlet ketone is probably a precursor of the photoproducts.[17]

One can envision either (1) a set of competing concerted reactions occurring from the excited singlets of **1c** and **1t**, or (2) a set of competing reactions from a singlet biradical **7** generated from the excited singlet states of **1c** and **1t** (or some combination of these two). Although these possibilities are quite similar conceptually we feel that the singlet biradical hypothesis is more attractive because it readily (a) explains the stereoselectivity of formation of **2** and **4**, (b) allows rationalization of the three kinds of reactions observed



7

from **1** on the basis of one intermediate, and (c) allows rationalization of the reaction inefficiency on the basis of cyclization of **7** to **1**. The latter piece of evidence is quite convincing, since the net inefficiency of the reactions is unlikely to be attributable to an intersystem crossing from S_1 to produce an unreactive triplet.[18] Finally, the trapping by butadiene, of an intermediate whose structure probably resembles **7**, adds further support to the singlet biradical hypothesis.[17]

Recent evidence has been put forth supporting the proposition that singlet 1,4 biradicals can undergo stereospecific cyclization and hydrogen reversion.[18b] The data reported here indicate that stereospecificity, *per se*, may not be a firm diagnostic test for the concertedness of cycloeliminations and (invoking microscopic reversibility) cycloadditions.

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Solvent Assistance in the Solvolysis of Secondary Substrates. The Use of Added Azide Ion as a Mechanistic Probe

Sir:

Recent work has revealed a striking difference in the solvolytic behavior between simple secondary (*e.g.*, isopropyl) and 2-adamantyl tosylates.[1] This behavior has been interpreted to indicate that considerable nucleophilic solvent assistance to ionization, ordinarily present in simple secondary substrates, is absent or is sharply reduced in the solvolysis of 2-adamantyl tosylate. The lessened role of solvent assistance in 2-adamantyl solvolysis is attributed to steric hindrance which would be present in a pentacovalent transition state. In order to test this conclusion further we have studied the solvolysis of 2-adamantyl tosylate in the presence of azide ion, a strong nucleophile.

The classic studies of Hughes and Ingold[2] introduced the technique of adding strong nucleophiles (lyate ion, azide ion) to a solvolysis medium in order to determine the susceptibility of a given substrate to direct displacement (SN2) reactions. When such a strong nucleophile produces a marked rate enhancement and a quantitatively corresponding alteration in the product composition (when this can be determined), a bimolecular substitution process is implicated.

Added azide ion has been used in another way: to trap carbonium ions.[3] For solvolyses proceeding *via* a carbonium-ion (k_c)[4] pathway, the degree of azide incorporation increases with the stability of the carbonium ion, as measured by the solvolysis rate.[5] As is often found, the selectivity of an intermediate increases with its stability.[6]

(13) (a) N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969). (b) NOTE ADDED IN PROOF. Recent results reported by N. E. Lee, H. A. J. Carless, and E. K. C. Lee (*J. Amer. Chem. Soc.*, **92**, 4482 (1970)) demonstrated that loss of CO from 2,3-dimethylcyclobutanone is not stereospecific, but that cycloelimination is moderately stereospecific (vapor photolysis).
(14) A singlet-state decomposition has been previously suggested for cyclobutanones: N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, 2, 39 (1970); H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968).
(15) Because the singlet excited state of ketene is energetically below that of cyclobutanone 1, it is possible that ketene produced from cycloelimination is in an electronically excited state.
(16) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).
(17) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **92**, 5724 (1970).
(18) (a) For example, singlet biradicals, believed to be produced by type II abstraction,[18b] do not possess a lifetime sufficient to allow racemization, whereas the related triplet biradicals are significantly racemized during its lifetime. (b) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, 91, 7751 (1969).

(1) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (c) P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); (d) M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969); (e) J. A. Bone and M. C. Whiting, *ibid.*, 115 (1970): (f) D. Lendir and P. v. R. Schleyer, *ibid.*, 941 (1970).
(2) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969; (b) L. C. Batemen, K. A. Cooper, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 925 (1940).
(3) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, pp 37–38.
(4) For definition and discussion of these terms see ref 1a.
(5) R. A. Sneen, J. V. Carter, and P. S. Kay, *J. Amer. Chem. Soc.*, **88**, 2594 (1966).
(6) (a) Z. Majerski, S. Borčić, and D. E. Sunko, *Tetrahedron*, **25**, 301 (1969); (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 22; (c) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 155.

Table I. Solvolysis of Alkyl Derivatives in 75% Aqueous Dioxane in the Presence of Sodium Azide

Substrate,[a] temp, °C	$[NaN_3]$, M	$k_t \times 10^5$, sec^{-1}	—RN_3, %— Obsd[b]	Calcd[d]
1-Adamantyl bromide, 100	0.00		0	
	0.06		8	
	0.10		6	
2-Adamantyl tosylate, 75	0.00	6.77 ± 0.10	0	0
	0.06	8.55 ± 0.32	12	21
	0.10	9.12 ± 0.80	10	26
2-Propyl tosylate, 50	0.00	1.30 ± 0.04	0	0
	0.06	7.48 ± 0.06	83	83
	0.10	8.34 ± 0.50	87	85
2-Octyl brosylate, 65[c]	0.00	2.38	0	0
	0.06	10.6	76	78
	0.10	16.0	84	85

[a] 0.02 M in all cases. [b] Determined titrimetrically. [c] Reference 7c; the values for 0.06 and 0.10 M NaN_3 were interpolated from the data in this reference. [d] Calculated by eq 2.

We wished to test the behavior of 2-adamantyl tosylate toward solvolysis in the presence of added azide. In addition, two model compounds were also examined. The bridgehead substrate, 1-adamantyl bromide, cannot be attacked at the rear; it must solvolyze by a k_c mechanism.[1] Isopropyl tosylate was chosen as a simple, open secondary substrate. The initial studies were carried out with 75% aqueous dioxane in order to allow comparison with Sneen's[7a] data on the 2-octyl system, but experimental difficulties encountered with this solvent system led us to use 80% aqueous ethanol for more precise and extensive studies. The latter solvent offers the additional advantage that attack by ethanol leads to a definite product (an ethyl ether), rather than to an oxonium ion (as in the case of dioxane or acetone), which is then partitioned between azide ion and water.[7a]

Table II. Solvolysis of Alkyl Derivatives in 80% Aqueous Ethanol in the Presence of Sodium Azide

Substrate,[a] temp, °C	$[NaN_3]$, M	$k_t \times 10^5$, sec^{-1}	—RN_3, %— Obsd	Calcd[d]	ROH, %	ROC_2H_5, %
1-Adamantyl bromide, 75[b]	0.00	12.6 ± 0.1	0.0	0	49	51
	0.02	13.0 ± 1.3	0.4	3	41	58
	0.04	13.2 ± 0.1	0.4	5	45	54
	0.06	14.2 ± 0.7	0.6	12	43	56
2-Adamantyl tosylate, 75[b]	0.00	1.94 ± 0.05	0.0	0	71	29
	0.02	2.10 ± 0.01	0.1	8	68	31
	0.04	2.17 ± 0.01	0.4	11	66	33
	0.06	2.26 ± 0.01	0.7	16	65	34
2-Propyl tosylate, 50[c]	0.00	5.75 ± 0.06	0	0	100	
	0.02	8.27 ± 0.29	31	30	69	
	0.04	12.5 ± 0.40	54	54	46	
	0.06	16.9 ± 0.20	65	66	35	

[a] 0.01 M in all cases. [b] Products determined by gas chromatography. [c] Products determined titrimetrically. [d] Calculated by eq 2.

On this basis, the large azide incorporation found in the solvolysis of simple secondary substrates (*e.g.*, 2-octyl brosylate[7a]) is not consistent with a carbonium-ion (k_c) pathway, and some other mechanism must be operating.[1,5] Simple secondary carbonium ions are not very stable, and should not be very selective. In 75% aqueous dioxane the solvolysis of 2-octyl brosylate in the presence of azide ion[7] exhibits S_N2 kinetics (eq 1).

$$k_t = k_s[\text{solvent}] + k_N[N_3^-] \quad (1)$$

The rate enhancements observed due to added azide are quite large. The same is true of the amounts of azide product formed, which amounts are, in fact, in quantitative agreement with the rate enhancements produced by added azide (Table I).[8]

There are two situations, then, in which a large proportion of azide product should be formed when azide ion is added to a solvolysis medium: (1) if highly stable carbonium-ion intermediates are present, or (2) if bimolecular displacement mechanisms (perhaps *via* ion pairs)[7,8] are involved.

The kinetic results and product data for 75% dioxane are presented in Table I, and the data for 80% ethanol are given in Table II. The amount of product resulting from azide attack is readily obtained from the difference between theoretical and experimental infinity titers;[6a,7a] thus both rate and product data can be obtained from titration alone. The distribution of all three products (alkyl azide, alcohol, and ether) in the aqueous ethanol solvolyses could be analyzed by gas chromatography; the azide incorporations so determined were in good agreement with those measured titrimetrically. Appropriate control experiments indicated that all products were stable to the reaction conditions.

Examination of the data in Tables I and II shows the striking similarity of the behavior of the secondary 2-adamantyl tosylate and the tertiary 1-adamantyl bromide. On the other hand, the simple secondary substrates, 2-propyl and 2-octyl arenesulfonates, provide a direct contrast. The latter compounds alone show a marked rate enhancement due to added azide and a major diversion of product to azide. In fact, the rate enhancement (the ratio of rates in the presence and absence of added azide) and the amount of alkyl azide formed are *quantitatively* related by eq 2.[9]

2-Adamantyl tosylate and 1-adamantyl bromide show very little rate enhancement due to added azide and only minor amounts of alkyl azide formation, especially

(7) (a) H. Weiner and R. A. Sneen, *J. Amer. Chem. Soc.*, **87**, 287, 292 (1965); (b) R. A. Sneen and J. W. Larsen, *ibid.*, **88**, 2593 (1966); (c) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969).

(8) Sneen[7] has pointed out that in 75% dioxane 2-octyl brosylate "exhibits the defining characteristics of an S_N2 reaction, bimolecular kinetics and inversion of configuration," [7c] but he interprets the mechanism as involving "a reversibly formed ion pair, attack on which by nucleophile is rate determining." It is not necessary in the present paper to discuss merits of the classical S_N2 *vs.* the ion-pair mechanism. What we wish to demonstrate is that 2-adamantyl tosylate behaves entirely differently than 2-octyl brosylate or 2-propyl tosylate under S_N2 conditions.

(9) For an analogous situation, see P. v. R. Schleyer and C. J. Lancelot, *J. Amer. Chem. Soc.*, **91**, 4297 (1969).

in 80% ethanol (Table II). Furthermore, eq 2 does *not* relate rate and product data.

$$1 - (1/\text{rate enhancement}) = \%RN_3/100 \quad (2)$$

The effect of sodium azide on the observed rate constants is brought out clearly when the data are treated by eq 3,[10] where k is the observed rate con-

$$k = k^0(1 + \beta[N_3^-]) \quad (3)$$

stant and k^0 is the rate constant in the absence of azide ion. The value of β (equal to the slope of the straight line resulting from a plot of k/k^0 *vs.* the concentration of sodium azide) indicates the magnitude of the rate enhancement produced when solvolysis is carried out in the presence of azide ion. Similarly, the ratio k_N/k_W (eq 4)[5] (a more meaningful measure of

$$k_N/k_W = (\%RN_3)[H_2O]/\%(ROH)[N_3^-] \quad (4)$$

azide incorporation than $\%RN_3$) is independent of sodium azide concentration. Here k_N and k_W are the second-order rate constants for attack by azide ion and water, respectively, on the appropriate substrate or intermediate.

The values of β and k_N/k_W (Table III) show the remarkable contrast between the 2- and 1-adamantyl derivatives, on one hand, and the acyclic secondary arenesulfonates, on the other. For bridgehead 1-adamantyl bromide (which must solvolyze *via* a k_c process) and 2-adamantyl tosylate the values of β are very small and presumably reflect normal salt effects; the k_N/k_W ratios are also very low and approach the limiting value of unity which would be anticipated for a relatively unstable (nondiscriminating) carbonium ion. In contrast the high values of both β and k_N/k_W for 2-propyl tosylate and 2-octyl brosylate are those expected for solvolytic pathways involving back-side displacements by nucleophile

Table III. Derived Parameters for Solvolysis of Alkyl Derivatives in the Presence of Sodium Azide

Substrate	75% dioxane		80% ethanol	
	β	k_N/k_W	β	k_N/k_W
1-Adamantyl bromide		12	2	2.5
2-Adamantyl tosylate	3.5	16	3	1.7
2-Propyl tosylate	62	1050	57	740[b]
2-Octyl brosylate[a]	59	770		

[a] Data from ref 7c. [b] Equal amounts of ether and alcohol products were assumed; any reasonable deviation from this would not affect significantly the magnitude of the k_N/k_W ratio.

In this work we have used the behavior of added azide ion as a model for nucleophilic attack by solvent. Azide ion is a better nucleophile than typical solvolysis solvents.[12] Hence, if azide is found not to participate nucleophilically with a given substrate, it follows that solvent will not do so either. Tables I–III afford further evidence for our interpretation of the role of solvent in secondary solvolyses: nucleophilic solvent assistance is relatively unimportant in the solvolysis of 2-adamantyl tosylate but integrally involved in the solvolysis of ordinary secondary derivatives.[1a-c,9]

(10) Equation 3 has the same form as Winstein's[11] equation for salt effects; we have used β rather than b since the rate increases we have observed for the simple secondary systems do not appear to be the result of ordinary salt effects.

(11) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2780 (1956).

(12) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

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Stereochemical Inhibition of Intramolecular 1,2 Shifts. Mechanistic Evidence for Skeletal Rearrangement during Apparent 1,2-Methyl Shifts of Adamantane[1]

Sir:

Evidence is accumulating that intramolecular 1,2 shifts on the adamantane nucleus (I⇌II) are strongly inhibited.[1-6] The nmr spectrum of the 1-adamantyl cation in strong acid solution[3] does not show line broadening at even high temperatures; thus, 1,2-hydride shifts occur very slowly, if at all.[2,4] Methyl-substituted adamantyl cations (*e.g.*, the 2-methyl-2-adamantyl and the 3-methyl-1-adamantyl cations) are stable in strong acid solution and show no tendency to interconvert.[5] The inhibition of intramolecular 1,2 shifts is due to the unfavorable stereochemical relationship between the migrating group, R, and the vacant orbital at the adjacent carbonium center.[1,4c,6] The transition state for such an intramolecular 1,2 shift (III) is badly twisted and must be very unfavorable energetically (Chart I).

Many adamantane rearrangements involving apparent 1,2 shifts are known.[1,5-7] The hydride shifts

(1) Presented at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstracts, No. PETR 40. *Cf.* also P. v. R. Schleyer, *Angew. Chem.*, **81**, 539 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 529 (1969).

(2) Apparent 1,2-hydride shifts in sulfuric acid solution have been shown to take place intermolecularly, rather than intramolecularly.[1,6]

(3) P. v. R. Schleyer, R. C. Fort, W. E. Watts, M. B. Comisarow, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 4195 (1964); G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *ibid.*, **87**, 2997 (1965); G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968).

(4) (a) H. Hogeveen and D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, in press. We are indebted to Dr. Hogeveen and to Dr. Brouwer for exchanges of information. (b) G. A. Olah, private communication. (c) M. Saunders, private communication.

(5) H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968). A more extensive study has been carried out by G. D. Mateescu and G. A. Olah, private communication.

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