Solvolysis of 1-Adamantylcarbinyl and 3-Homoadamantyl Derivatives. Mechanism of the Neopentyl Cation Rearrangement[1]

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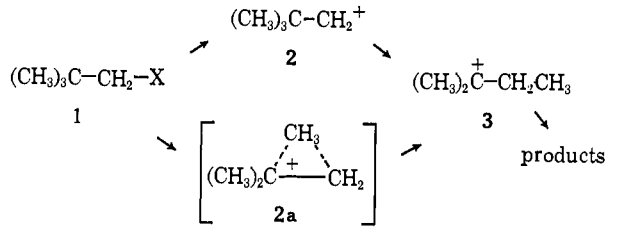
Abstract: The solvolyses of 1-adamantylcarbinyl arenesulfonates in various solvents have been studied as a model for interpretation of the corresponding reactions of neopentyl derivatives. Whereas the later yield products derived entirely from the *t*-amyl cation, it has not been clear whether the ionization and rearrangement processes are concerted or sequential. Since the primary 1-adamantylcarbinyl cation contains a strain-free ring structure while the tertiary 3-homoadamantyl cation possesses a highly strained ring structure, a diminished driving force for Wagner–Meerwein rearrangement would be anticipated in this system. This is evidenced in the formation of both primary (6%) and tertiary (94%) acetates in the acetolysis of 1-adamantylcarbinyl tosylate under conditions of kinetic control at 120°. The same acetate mixture is also obtained from 3-homoadamantyl bromide under these conditions, together with 1-adamantylcarbinyl bromide, which does not react further. From 1-adamantylcarbinyl tosylate under other kinetically controlled conditions (alkaline aqueous diglyme) only tertiary product can be detected, while primary products are exclusively formed under thermodynamic control (unbuffered acetic acid or buffered formic acid). Despite the steric bias against rearrangement of 1-adamantylcarbinyl relative to neopentyl derivatives, the solvolysis rates of 1-adamantylcarbinyl arenesulfonates in various media are slightly faster, not slower, than those of neopentyl arenesulfonates under the same conditions. This indicates that the ionization–rearrangement steps in both systems are not concerted, and stepwise mechanisms involving primary carbonium ions or ion pairs pertain.

When a primary carbonium ion is generated at at position adjacent to a fully substituted carbon atom, a considerable propensity for rearrangement to a more stable tertiary cation exists. The neopentyl system is the structurally simplest example of this type. Reactions of neopentyl derivatives **1** under carbonium ion conditions proceed with rearrangement to yield substitution and elimination products derived from the *t*-amyl cation (**3**).[3]



Substituted neopentyl-type compounds, whether of the acyclic (**4**), monocyclic (**5–8**), or polycyclic series (**9–14**) (Chart I), undergo similar rearrangements virtually exclusively. For **10** alone among the nonheterocyclic examples in Chart I has any unrearranged product (2%) been observed.[4] Compound **13**, a special case, solvolyzes without rearrangement in dilute hydrochloric acid at a very slow rate as a consequence of the positively charged nitrogen atom.[5b] All other compounds in Chart I share with neopentyl a steric resistance to SN2 reactions and are ideal substrates for examining the carbonium ion reactions of primary systems. Chart I summarizes literature references and solvolysis rate data relative to neopentyl.

Recently Skell[6] and Karabatsos[7] and their coworkers have established by isotopic labeling that the parent neopentyl rearrangement proceeds entirely by a simple 1,2-methyl shift, under a variety of conditions of carbonium ion generation. Thus, the mechanism is not complicated by such subtle possibilities as 1,3-hydride shifts,[8] or protonated cyclopropane intermediates.[8a,9]

(1) Presented in preliminary form at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 26P.

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(3) For representative examples, see F. C. Whitmore and H. S. Rothrock, *J. Am. Chem. Soc.*, **54**, 3431 (1932); F. C. Whitmore, E. L. Wittle, and A. H. Popkin, *ibid.*, **61**, 1586 (1939); I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157, 161, 164, 166, 169, 171 (1946); I. Dostrovsky, E. D. Hughes, and C. K. Ingold, *ibid.*, 173 (1946); F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *J. Am. Chem. Soc.*, **69**, 2108 (1947); F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955); M. L. Bender and H. Robbins, *ibid.*, **78**, 1699 (1956); W. Gerrard and M. A. Wheelans, *J. Chem. Soc.*, 4296 (1956); A. Streitwieser, Jr., D. P. Stevenson, and W. D. Schaeffer, *J. Am. Chem. Soc.*, **81**, 1110 (1959); P. A. Naro and J. A. Dixon, *ibid.*, **81**, 1681 (1959); F. Cramer and H. J. Baldauf, *Ber.*, **92**, 370 (1959); A. Maccoll and D. S. Swinbourne, *Proc. Chem. Soc.*, 409 (1960); E. S. Lewis and W. C. Herndon, *J. Am. Chem. Soc.*, **83**, 1961 (1961); P. A. Naro and J. A. Dixon, *J. Org. Chem.*, **26**, 1021 (1961); C. N. Pillai and H. Pines, *J. Am. Chem. Soc.*, **83**, 3274 (1961); M. S. Silver, *ibid.*, **83**, 3482 (1961); I. Necsoiu, L. Barladeanu, and C. Nenitzescu, *Chem. Ind.* (London), 1753 (1961); A. P. Krapcho and M. Benson, *J. Am. Chem. Soc.*, **84**, 1036 (1962).

(4) K. B. Wiberg and B. R. Lowry, *ibid.*, **85**, 3188 (1963).

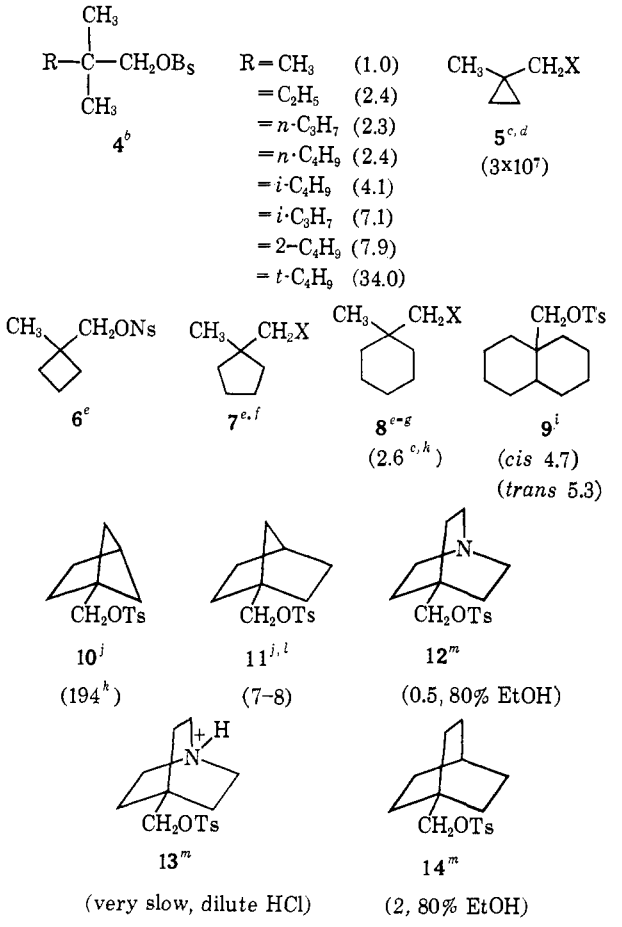
(5) (a) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958); (b) C. A. Grob, R. M. Hoegerle, and M. Ohta, *ibid.*, **45**, 1823 (1962).

(6) P. S. Skell, I. Starer, and A. P. Krapcho, *J. Am. Chem. Soc.*, **82**, 5257 (1960).

(7) (a) G. J. Karabatsos and J. D. Graham, *ibid.*, **82**, 5250 (1960); (b) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **86**, 1994 (1964).

(8) (a) G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2838 (1962); (b) O. A. Reutov and T. N. Shatkina, *Tetrahedron*, **18**, 237 (1962); *Bull. Acad. Sci. USSR*, **1**, 180 (1963); (c) P. S. Skell and R. J. Maxwell, *J. Am. Chem. Soc.*, **84**, 3963 (1962); (d) A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964); (e) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965); (f) C. C. Lee,

Chart I. Neopentyl Systems. Literature References and Relative Acetolysis Rates[a]



[a] Acetolysis rate in parentheses; neopentyl = 1. [b] E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, **25**, 2195 (1960). [c] S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952). [d] (a) D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964); (b) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961). [e] Additional work on this problem will be published shortly by P. von R. Schleyer, E. K. Kline, III, C. W. Woodworth, and J. E. Nordlander. [f] G. LeNy, Thesis, University of Paris, France, 1964. [g] R. S. Bly, Jr., and H. S. Dryden, Jr., *Chem. Ind.* (London), 1287 (1959). [h] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962). [i] W. G. Dauben and J. B. Rogan, *J. Am. Chem. Soc.*, **79**, 5002 (1957). [j] See ref 4. [k] Total rate: solvolysis + internal return. [l] R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958). [m] See ref 5.

The neopentyl rearrangement is then a simple alkyl migration, but the timing of the steps is of considerable interest. There has been ongoing controversy over whether or not the neopentyl cation (**2**) actually exists as a discrete intermediate. In the conversion of neopentyl derivatives (**1**) to products, do the ionization and rearrangement steps take place separately (**1** → **2** → **3**) or are they concerted? If the latter is true, to what extent does methyl migration (transition state **2a**) assist in the ionization? These questions have been considered in several reviews[10] without agreement having been reached; the available evidence for participation seems permissive rather than demanding. It is the purpose of the present paper to contribute to the solution of this problem.[11]

Evidence for Participation. The solvolytic behavior of ethyl derivatives provides a frame of reference for the interpretation of corresponding neopentyl reactions. Even in the weakly nucleophilic solvent, formic acid, ethyl tosylate reacts without rearrangement.[12] This result precludes the possibility of hydrogen participation under these conditions. In the neopentyl series, on the other hand, rearrangements are the rule,[3] but this in itself does not provide positive evidence in favor of participation. In unsymmetrical systems of this type rearrangement is a necessary but not a sufficient condition for participation. Alkyl migration could follow ionization in a separate step, provided only that the rearrangement occurs much faster than other possible reactions of the first-formed primary carbonium ion.

Several types of kinetic evidence have been interpreted in terms of the participation mechanism, **1** → **2a** → **3**. Winstein and Marshall[13,14] observed that in many solvents, especially the more nucleophilic ones, ethyl tosylate reacted faster than neopentyl tosylate.[10a] In formic acid, however, the rates were virtually identical. It was argued that even in formic acid the ionization of ethyl tosylate must reasonably be aided to a significant extent by nucleophilic solvent participation, an interaction sterically denied neopentyl tosylate. Thus some other rate-enhancing factor must be present in the neopentyl solvolysis. Winstein and Marshall argued against the operation of other important steric or inductive effects, and concluded that methyl participation most likely was the rate-enhancing factor involved.

Other authors have endorsed this interpretation that β-alkyl migration is significantly developed in the ionization transition state.[15–17] McElrath and coworkers[15] observed that acetolysis rates for a series of primary 2,2-dimethylalkyl *p*-bromobenzenesulfonates (**4**) increased moderately as the bulk of R increased (Chart I). This was attributed to carbon participation with relief of B strain. Several groups have measured solvolysis rates of cyclic and bicyclic primary neopentyl-type arenesulfonates. As presented in Chart I, most of these substrates solvolyze faster than neopentyl tosylate, but only slightly so.[18] The exception, **10**,[21] a highly strained substance, gives a combined acetolysis and isomerization rate almost 200 times greater than neopentyl. The rationalizations offered[16,22] for

J. E. Kruger, and E. W. C. Wong, *J. Am. Chem. Soc.*, **87**, 3985 (1965); C. C. Lee and J. E. Kruger, *ibid.*, **87**, 3986 (1965); (g) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **87**, 4349 (1965).

(9) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964).

(10) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 122 ff; (b) Y. Pocker in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 6 ff; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 584 ff; (d) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 513.

(11) See footnote *e*, Chart I.

(12) C. C. Lee and M. K. Frost, *Can. J. Chem.*, **43**, 526 (1965).

(13) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, 74, 1120 (1952).

(14) Similar observations had been made earlier for the bromides by I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 171 (1946).

(15) See footnote *b*, Chart I.

(16) See footnote *l*, Chart I.

(17) (a) W. H. Saunders, Jr., and R. H. Paine, *J. Am. Chem. Soc.*, **83**, 882 (1961); (b) P. Warrick, Jr., and W. H. Saunders Jr., *ibid.*, **84**, 4095 (1962).

(18) The vastly accelerated rate of the cyclopropylcarbinyl derivative **5**[19] is due to the unique electronic properties of the cyclopropyl ring,[20] and is not directly comparable to the other compounds.

(19) See footnote *d*, Chart I.

(20) For references, see P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

(21) See footnote *h*, Chart I.

(22) See footnote *i*, Chart I.

these rate enhancements have been based on steric promotion of anchimeric assistance.

Stereochemical evidence favoring the concerted mechanism has been provided by Sanderson and Mosher,[23] who observed that optically active neopentanol-1-*d* undergoes deoxideation[24] to give, among other products, optically active 2-methyl-1-butene-3-*d*. The same authors also reported, however, that the 2-methyl-2-butanol-3-*d* produced in the silver ion assisted hydrolysis of optically active neopentyl-1-*d* iodide was optically inactive, a result inconsistent with a concerted ionization–rearrangement.

Finally, it should be noted that in carbonium ion reactions of neopentyl derivatives, neopentyl products have been detected at most in trace amounts[5,16,25] (see above) and may in these cases be attributed to direct displacements. Failure to trap a possible neopentyl cation cannot, of course, rule out its existence but does nevertheless render it suspect.

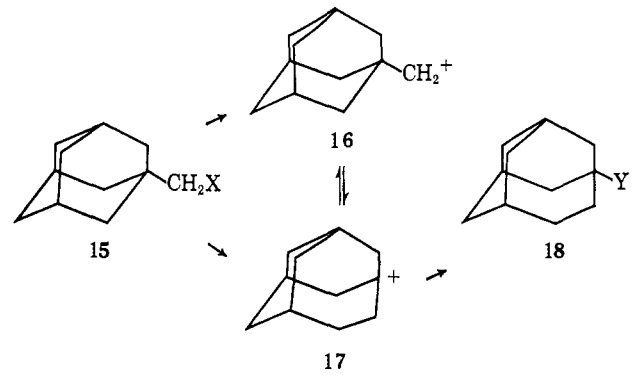
Arguments against Participation. Tertiary carbonium ions are well known to be appreciably more stable than primary.[10a] It has been estimated that each additional methyl group in the series ethyl, isopropyl, *t*-butyl is capable of producing a solvolysis rate enhancement of 10^6 with a suitable leaving group under limiting conditions.[20a,26] Differences approaching this value, which corresponds to an activation free-energy difference of 8.2 kcal at 25°, have been observed in favorable cases.[26] The neopentyl rearrangement, **2** → **3**, must have considerable driving force, approaching 16 kcal or 10^{12} in rate. Evidence for "rate enhancement" in neopentyl solvolyses is only inferential. At most, the observed rates are only equal to, not greater than, those of corresponding ethyl derivatives. At best it would appear that the rate-enhancing factor for neopentyl, whatever the cause, can only be a small number. Compared with the available **1** → **3** driving force, the observed rate enhancements seem trivial. It is doubtful, even if participation occurs, that the methyl group in the transition state is very far along the rearrangement coordinate.

A good case can be made that the "rate-enhancing factor" in neopentyl solvolyses is inductive in origin. Winstein and Marshall[13] argued in 1952 that "ionization rates may be expected to be insensitive to β-methyl substitution (in the absence of important steric effects)." Subsequent chemical experience has refuted this contention. Streitwieser[10a] has shown that the solvolysis rates of primary, secondary, and tertiary systems correlate well against Taft's[27] σ^* constants. Further work has confirmed this finding. For acetolysis of secondary acyclic tosylates, $\rho^* = -2.6$;[28,29] for formolysis the value is higher, $\rho^* = -3.5$.[29] A ρ^* value of -2.2 was estimated for solvolysis of tertiary *p*-nitrobenzoates in 60% aqueous acetone.[30] If, for illustrative purposes, one assumes $\rho^* = -4.0$ for a limiting ionization mechanism in the primary series,[31] it is readily calculated ($\sigma^*_{CH_3} = 0.00$, $\sigma^*_{i\text{-}C_4H_9} = -0.30$)[27] that ethyl tosylate should solvolyze some 16-fold more slowly than neopentyl. At least some of the smaller rate enhancements recorded in Chart I, namely **8**, **9**, and **14**, can also be explained on a purely inductive basis, for these compounds differ in the degree of substitution at the β carbon.

In addition, it is possible that part of the enhanced acetolysis rates of 1-bicyclo[2.1.1]hexylcarbinyl tosylate (**10**)[4] and 1-bicyclo[2.2.1]heptylcarbinyl tosylate (**11**)[16] may be the result of freer access of solvent to the ionization sites than in the parent neopentyl system. In these species the $C_\alpha C_\beta C_\gamma$ bond angles are constrained to values considerably larger than tetrahedral, and both compounds, especially **10**, are greatly more reactive in direct displacement reactions than neopentyl tosylate.[4,10a,16]

Thus, it seems clear that the small rate differences recorded in Chart I cannot be considered strong evidence in favor of the participation mechanism.

Design of Present Experimental Approach. Ideally, one would like to have a neopentyl-type system which would react by an ionic mechanism and still not rearrange, perhaps because of some adverse stereochemical feature. In such a compound there would be no question of participation, and its solvolysis rate could be compared with that of neopentyl. In practice, because of the great driving force for conversion of a primary to a tertiary carbonium ion, a nonrearranging neopentyl system would be hard to achieve. However, a molecule with considerable steric bias against rearrangement is readily available, 1-adamantylcarbinyl arenesulfonate **15**. This substrate incorporates a



neopentyl part structure whose rearrangement to a tertiary homoadamantyl cation **17** would be much less favorable than the similar transformation **2** → **3** in the parent neopentyl system. The formation of **17** would sacrifice the uniquely strain-free quality of the adaman-

(23) W. A. Sanderson and H. S. Mosher, *J. Am. Chem. Soc.*, **83**, 5033 (1961); see also W. A. Sanderson and H. S. Mosher, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstract S-123.

(24) Presumably a carbonium ion reaction; see P. S. Skell and I. Starer, *ibid.*, **81**, 4117 (1959); **82**, 2971 (1960).

(25) (a) D. Y. Curtin and S. M. Gerber, *ibid.*, 74, 4052 (1952); (b) *cf.* N. Rabjohn and C. A. Drake, *ibid.*, **88**, 3154 (1966).

(26) F. R. Jensen and R. J. Oeullette, *ibid.*, **83**, 4478 (1961); **85**, 363 (1963).

(27) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(28) W. Pritzkow and K. H. Schöppler, *Ber.*, **95**, 834 (1962).

(29) P. E. Peterson, R. E. Kelley, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965); J. J. Harper, unpublished work, Princeton University.

(30) C. F. Wilcox, Jr., and M. E. Mesirov, *ibid.*, **84**, 2757 (1962).

(31) The value of ρ^* for a limiting solvolysis should grow more negative from tertiary to secondary to primary. This is the order in which the carbonium ion becomes less stable and thus makes a greater electron demand upon substituents, and is likewise the order in which the transition state should increasingly resemble the cationic intermediate. Streitwieser[10a] found $\rho^* = -0.74$ for the ethanolysis of a series of unbranched primary benzenesulfonates and tosylates, but here the mechanism is doubtless far from limiting.

tane skeleton.[32] Ion **17** has been estimated to have a total of about 10-kcal strain from conformational considerations.[32] Interestingly, **18** and **17** seem to be strained over-all to comparable extents,[30] for the rate of solvolysis of **18** (X = Br) has been reported to be very nearly the same as that of *t*-butyl bromide.[33] Models show that the cation center in **17** can be planar or nearly so. The source of strain in **17** lies in the distorted ring structure.

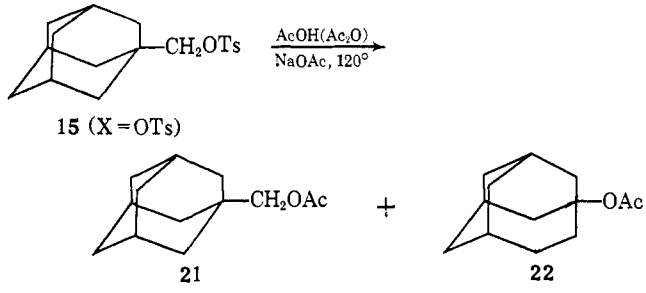
It was postulated, therefore, that the solvolysis of neopentyl tosylate **1** and 1-adamantylcarbinyl tosylate **15** (X = OTs) should have closely similar rates if the slow steps involve simple ionization (to **2** and **16**, respectively), but that the neopentyl system should solvolyze faster if the rate-determining step comprises both ionization and significant rearrangement.

In **15** strain effects would oppose rearrangement. The converse situation also interested us: molecules whose rearrangement would be facilitated by the relief of strain.[11] Such compounds should solvolyze at appreciably faster rates than neopentyl, provided the concerted mechanism can be operative. Of the compounds listed in Chart I, **10** alone appears clearly to be in this category,[34] but the interpretation of the rate

19 **20**

reported[16] is complicated by the extreme instability of the 1-norbornyl cation, the presumed intermediate in the process. Our results with **6**, **7**, and **8** will be presented separately.[11]

Product Studies. The acetolysis of 1-adamantylcarbinyl tosylate **15** (X = OTs, 0.04 *M*) in the presence of 0.08 *M* sodium acetate and 1% acetic anhydride, at 120° (reflux) for 72 hr, yielded virtually quantitatively a mixture of 6.8% 1-adamantylcarbinyl acetate **21** and 93.2% 3-homoadamantyl acetate **22**, by gas



15 (X = OTs) **21** **22**

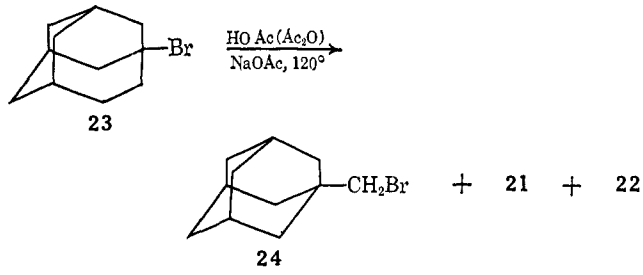
chromatographic analysis. Control experiments established that neither product was rearranged under the reaction conditions. As the unrearranged acetate **21** could arise from either an SN1 or SN2 process, an attempt was made to distinguish between these possibilities by increasing the nucleophilicity of the medium. The acetolysis was repeated with 5 and 10 equiv of sodium acetate present, and the product composition was found to be unaltered, as shown in Table I. The

Table I. Acetolysis Products of 1-Adamantylcarbinyl Tosylate **15** (X = OTs)

Concn of **15** (X = OTs), *M*	Concn of NaOAc, *M*	Products % **21**	Products % **22**
0.04	0.08	6.8	93.2
0.04	0.20	5.6	94.4
0.04	0.40	6.3	93.7

invariance of the proportion of primary acetate formed while varying the sodium acetate concentration over a considerable range suggests that the primary product is derived from the corresponding carbonium ion. If so, these results would indicate simple ionization of **15** to 1-adamantylcarbinyl cation (**16**) followed by partial or complete equilibration of the latter with 3-homoadamantyl cation (**17**), and capture of the carbonium ions by acetic acid or acetate ion to form the observed products.

Evidence confirming this hypothesis was furnished by a study of the acetolysis products of 3-homoadamantyl bromide[33] (**23**) in the same medium. After 10 hr, a virtually quantitative mixture of the isomeric acetates **21** and **22** along with 1-adamantylcarbinyl bromide (**24**)



23 **24**

was isolated. The yields are summarized in Table II.

Table II. Acetolysis Products of 3-Homoadamantyl Bromide (**23**)

Concn of **23**, *M*	Concn of NaOAc, *M*	Products % **24**	Products % **21**	Products % **22**
0.04	0.08	59.4	2.8 (6.9)[a]	37.8 (93.1)[a]
0.04	0.20	18.9	4.6 (5.7)[a]	76.5 (94.3)[a]
0.04	0.40	10.5	5.0 (5.6)[a]	84.5 (94.4)[a]

[a] Percentages of acetate products only.

As the concentration of acetate ion was increased, the proportion of primary bromide product **24** decreased, indicating the latter to be formed by external rather than (or as well as) internal return.[10a,36,37] The relative

(32) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(33) H. Stetter and P. Goebel, *Ber.*, **96**, 550 (1963). The rate constants reported here for **18** (X = Br) in 80% ethanol have been duplicated to within 10%: W. Washburn,[2c] unpublished observation.

(34) Unpublished examples are also known to us: (a) W. G. Dauben (Conférence, July 15, 1964, Paris, France, Abstracts; *Bull. Soc. Chim. France*, **11b**, 3 (1964)) reported that **19** and **20** acetolyzed with rates 180 and 1500 times faster than neopentyl tosylate to give ring-enlarged products. (b) The results of LeNy[35] with **7** and **8** will be discussed in a forthcoming paper.[11]

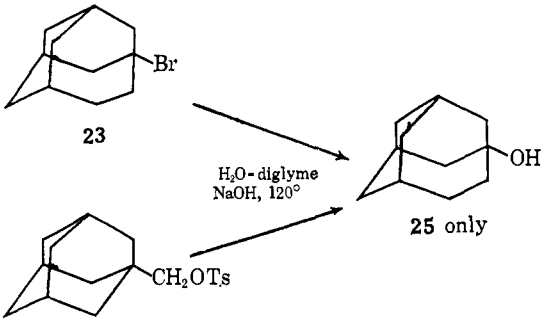
(35) See footnote *f*, Chart I.

(36) S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanisms," Special Publication No. 19, The Chemical Society, London, 1965, p 109 ff.

(37) External return can also be demonstrated during the solvolysis of 1-adamantylcarbinyl *p*-nitrobenzenesulfonate (**15**, X = ONs) in the presence of sodium tosylate. The rate constant drifts downward, and 1-adamantylcarbinyl tosylate (**15**, X = OTs) can be isolated at partial reaction times (J. J. Harper, unpublished observation).

proportions of acetates **21** and **22**, however, were constant and the same as from the primary tosylate, **15** (X = OTs). Primary bromide **24** was found separately to be inert under the reaction condtions, and thus the acetate products are derived entirely from the tertiary bromide **23**. These results demonstrate, therefore, that the primary–tertiary carbonium ion equilibration **16** → **17** is complete before product formation, when approached from either side under these conditions. From the acetate product composition it may be calculated that the transition-state free energies for product formation from the two carbonium ions **16** and **17** differ by 2.2 kcal/mole. This value becomes the free-energy difference between the cations on the assumption that both form acetate products **21** and **22** with the same rate constant. Actually the primary cation **16** should be the more reactive; if by a factor of 10, then the energy difference between the carbonium ions would be 4.0 kcal/mole.

Comparative solvolyses of primary tosylate **15** (X = OTs) and tertiary bromide **23** were also carried out in 80% aqueous diglyme containing 4, 8, and 16 equiv of sodium hydroxide at 120°, and in 80% aqueous ethanol in the presence of 2 equiv of sodium carbonate at 82°. The hydrolyses of either **15** (X = OTs) or **23** in aqueous diglyme produced virtually quantitatively 3-homoadamantanol **25** as the only detectable product. Thus, the carbonium ion equilibrium is evidently more lopsided in this medium than in boiling acetic acid. Stetter and Goebel[33] have reported that nitrous acid deamination of **15** (X = NH_2) gave a 93% yield of **25**.



In aqueous ethanolysis the tertiary bromide **23** again produced only tertiary products: the alcohol **25** and the corresponding ether **26**. The primary tosylate **15** (X = OTs), however, yielded, in addition to predominant amounts of the same products, small amounts of the primary alcohol **15** (X = OH) and ether **15** (X = OC_2H_5). The results are shown in Table III. Evidently

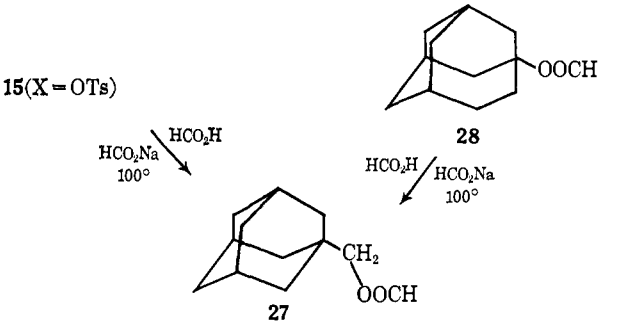
Table III. Solvolysis Products of **15** (X = OTs) and **23** in 80% Aqueous Ethanol (Plus Sodium Carbonate) at 82°

	% products			
Substrate	1-Ad-CH_2OH **15** (X = OH)	1-AdCH_2-OEt **15** (X = OEt)	3-Homo-AdOH **25**	3-Homo-AdOEt **18** (Y = OEt)
15 (X = OTs)	2.4	1.7	56.2	39.7
23	...	...	62.5	37.5

in this highly nucleophilic medium the primary cation **16** from **15** reacts with the solvent at a rate not much slower than that at which it rearranges to tertiary cation **17**.

Very different solvolytic results were obtained if the base was not present to neutralize the strong acid formed. The acetolysis of **15** (X = OTs) in the absence of sodium acetate at 120° yielded virtually quantitatively only 1-adamantylcarbinyl acetate (**21**). Consistently, 3-homoadamantyl acetate **22** when heated under reflux in acetic acid containing 1 equiv of *p*-toluenesulfonic acid was found after 72 hr to be completely isomerized to **21**. Thus, whereas the relative carbonium ion stabilities are tertiary (**17**) > primary (**16**), the order is inverted for the corresponding acetates, primary (**21**) > tertiary (**22**).[38]

Formolysis of **15** (X = OTs, 0.04 *M*) at 100° for 72 hr, even in the presence of 2 equiv of sodium formate, produced only primary formate **27**. However, 3-homoadamantyl formate **28**, synthesized independently, was found to isomerize completely to **27** in 30 min in the same medium. Thus, thermodynamic control prevails even in boiling buffered formic acid.[39] Doubtless,



from the preceding results, the tertiary formate **28** was first formed but rearranged to the observed product.

Rate Studies. Solvolysis rate data for neopentyl (**1**) and for 1-adamantylcarbinyl (**15**) tosylates and *p*-nitrobenzenesulfonates (nosylates) in acetic acid and formic acid, and for the nosylates in ethanol, are given in Table IV. Table V summarizes the relative rates of these compounds. In all cases 1-adamantylcarbinyl derivatives (**15**) solvolyze slightly faster than their neopentyl counterparts.

Support for the postulated primary ionization of these compounds is found in their "*m*" values.[10a,40] For neopentyl tosylate, *m* = 0.64 at 75° for two solvents, acetic and formic acids;[13] at 25°, using extrapolated data from Table IV, *m* = 0.74. For 1-adamantylcarbinyl tosylate (**15**, X = OTs) *m* = 0.71 at 75° and 0.63 at 25°. The nosylates in these solvents give similar values: neopentyl, *m* = 0.57 at 75°, 0.67 at 25°; 1-adamantylcarbinyl, *m* = 0.71 at 75°, 0.77 at 25°. These values are considerably higher than those usually found for primary arenesulfonates subject to SN2 attack, and they are, in fact, comparable in magnitude to secondary arenesulfonates whose solvolyses are considered to be limiting.[10a,13,40]

(38) An earlier related example of this balance has been furnished by Stetter and Goebel.[33]

(39) Other examples of rearrangements under these conditions have been reported; see, for example, J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954), and ref 17.

(40) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948), and subsequent papers.

Table IV. Solvolysis Rates of Neopentyl and Related Arenesulfonates

Compound	Solvent	Temp, °C	k_1, sec^{-1}	ΔH^*, kcal	ΔS^*, eu
$(CH_3)_3CCH_2OTs$	HOAc	100.0[a]	1.74×10^{-8}[b]		
			$(2.03 \pm 0.04) \times 10^{-8}$[c]		
		75.0[a]	8.32×10^{-8}[b]	30.7	−3.1
		50.0[a]	2.48×10^{-9}[b]	31.5[h]	−1.0[h]
		25.0[a]	4.11×10^{-11}[b]		
	HCOOH	75.0	1.89×10^{-5}[i]		
		50.0[a]	8.51×10^{-7}	27.0[i]	−2.8[i]
		25.0	2.28×10^{-8}[i]		
$(CH_3)_3CCH_2ONs$	HOAc	110.95	$(8.32 \pm 0.33) \times 10^{-5}$[d]		
		100.0	$(2.92 \pm 0.042) \times 10^{-5}$[c]		
		92.25	$(1.28 \pm 0.01) \times 10^{-5}$[d]		
		75.0	$(1.48 \pm 0.16) \times 10^{-8}$[c]	29.4	−1.1
		50.0[a]	5.28×10^{-8}		
		25.0[a]	1.05×10^{-9}		
	HCOOH	75.0	$(1.91 \pm 0.04) \times 10^{-4}$[c]	25.7	−1.8
		50.0	$(9.93 \pm 0.40) \times 10^{-8}$[e]		
		25.0[a]	3.16×10^{-7}		
	EtOH	100.0	$(9.53 \pm 0.23) \times 10^{-6}$[e]		
		75.0	$(5.71 \pm 0.19) \times 10^{-7}$[e]	28.3	−6.0
		50.0[a]	2.23×10^{-8}		
		25.0[a]	5.07×10^{-10}		
1-Adamantyl-CH_2OTs	HOAc	118.8	$(1.27 \pm 0.08) \times 10^{-5}$[e]		
		100.0	$(2.18 \pm 0.36) \times 10^{-6}$[f]		
			$(2.14 \pm 0.10) \times 10^{-6}$[e]	(27.8)[f]	(−10.4)[f]
			$(2.18 \pm 0.02) \times 10^{-6}$[c]	(26.8)[e]	(−13.2)[e]
		75.0	$(1.38 \pm 0.38) \times 10^{-7}$[f]	27.3	−11.8
		50.0[a]	6.12×10^{-9}		
		25.0[a]	1.60×10^{-10}		
	HCOOH	75.0	$(5.76 \pm 0.65) \times 10^{-5}$[c]	(30.1)[g]	(+8.1)[g]
		60.0	$(7.78 \pm 0.72) \times 10^{-6}$[c]		
		50.0[a]	1.85×10^{-6}		
		25.0[a]	3.36×10^{-8}		
1-Adamantyl-CH_2ONs	AcOH	118.8	$(1.59 \pm 0.09) \times 10^{-4}$[e]	(23.4)[e]	(−16.6)[e]
		100.0	$(3.18 \pm 0.18) \times 10^{-5}$[c]	(28.9)[e]	(−2.0)[e]
			$(3.55 \pm 0.11) \times 10^{-5}$[e]		
		75.0	$(1.80 \pm 0.08) \times 10^{-6}$[c]	27.6	−5.6
		50.0[a]	7.97×10^{-8}		
		25.0[a]	1.99×10^{-9}		
	HCOOH	75.0	$(7.34 \pm 0.19) \times 10^{-4}$[c]	25.1	−1.2
		50.0	$(4.13 \pm 0.09) \times 10^{-5}$[c]		
		25.0[a]	1.44×10^{-6}		
	EtOH	100.0	$(1.66 \pm 0.03) \times 10^{-5}$[e]		
		75.0	$(9.45 \pm 0.33) \times 10^{-7}$[e]	28.9	−3.5
		50.0[a]	3.47×10^{-8}		
		25.0[a]	7.38×10^{-10}		

[a] Rate constants and activation parameters machine (IBM-7094) calculated from available data using a program written by Dr. Gerald J. Gleicher. [b] Calculated from an average of the literature data: 8.01×10^{-8} sec^{-1} at 74.71°[41]; 1.66×10^{-7} sec^{-1} at 99.58°.[13] The literature estimates are 8.35×10^{-8} sec^{-1} at 75°;[13] 2.17×10^{-9} sec^{-1} at 49.60°;[41] and 3.41×10^{-11} sec^{-1} at 25.0°.[13] [c] Determined by J. J. H. [d] Determined by E. K. Kline, A.B. Thesis, Princeton University, 1963. [e] Determined by R. C. F.[2e] [f] Determined by R. D. N.[2f] [g] Rather large error in the rate constants make these values especially uncertain. [h] Reference 41. [i] Reference 13.

Table V. Rates of 1-Adamantylcarbinyl Arenesulfonates Relative to Neopentyl under the Same Conditions

Compound	Solvent	Relative rates 50°	75°	100°
1-Adamantylcarbinyl tosylate (**15**, X = OTs)	HOAc	2.5	1.7	1.2
	HCOOH	2.2	3.1	...
	HOAc	1.5	1.2	1.1[a]
1-Adamantylcarbinyl nosylate (**15**, X = ONs)	HCOOH	4.2	3.8	...
	EtOH	1.6	1.7	1.7

[a] A special salt effect[36] was observed with this compound.[37] In the presence of added $LiClO_4$, $k_{ext}^0/k_t^0 = 1.8$ at 100°. If the k_{ext}^0 value is used, the rate relative to neopentyl is 2.0. The neopentyl arenesulfonates solvolyze normally. This work[37] will be described separately.

Discussion

We believe our results strongly support a stepwise mechanistic pathway involving simple ionization of **1** and **15** to primary cations **2** and **16** (as their ion pairs), followed by rearrangement. That these reactions are ionic (SN1 rather than SN2) seems established from the observtions cited. The question at issue is whether or not ionization–rearrangement in neopentyl systems is concerted.

Winstein[41] recognized early that participation in neopentyl systems might be enhanced if strain were relieved thereby; *i.e.*, relief of strain might provide part of the driving force for neighboring carbon participation. Compounds **6** (X = ONs) (4000 × neopentyl, HOAc, 75°),[11] **7** (X = ONs) (114 × neopentyl),[11] **10**, **19**, **20**, and possibly **11** provide examples of this kind of rate enhancement. However, relative to the total driving forces due to relief of strain, these enhancements are relatively small.[11] For example, **6**, with

(41) See footnote *c*, Chart I.

about 26 kcal of ground-state strain,[42] on acetolysis gives exclusively cyclopentane products with about 6-kcal strain.[42] A potential 20 kcal of strain relief, corresponding to a rate difference at 75° of $10^{12.5}$, is present in this system, but the observed rate enhancement is only $10^{3.6}$.[11]

The converse to strain relief, strain increase, should also affect reaction rates, *providing participation is present in the parent neopentyl system.* There are two possibilities.

(1) Neopentyl arenesulfonate solvolyses are anchimerically assisted by methyl participation. The observed rate constants must then reflect this participation and be enhanced thereby. Neopentyl-type systems where strain relief during rearrangement is possible should exhibit further rate enhancements. Neopentyl-type systems where strain *increases* during rearrangement (*e.g.*, **15** → **17**) should exhibit decreased solvolysis rates relative to neopentyl.

(2) Neopentyl arenesulfonate solvolyses proceed through discrete primary cation ion-pair intermediates and are not anchimerically assisted. The rate constants are then "normal," but may be influenced by inductive effects, solvation effects, etc., to a small extent. Neopentyl-type systems in which substantial relief of strain by rearrangement is possible would give enhanced rates due to a change in mechanism from the unassisted to the assisted type. Neopentyl-type systems where strain would increase on ionization (*e.g.*, **15** → **17**) should *not* exhibit rate retardation, for ionization and rearrangement are not concerted.

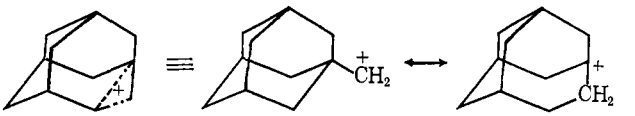
Our results (Table V) clearly favor the second possibility. 1-Adamantylcarbinyl arenesulfonates (**15**) solvolyze slightly faster, not slower, than their neopentyl counterparts, despite the formation of some unrearranged product under kinetic conditions. The small difference in rate is probably due to a difference in inductive effect, for the adamantyl and the *t*-butyl group differ in the degree of substitution β to the reaction center. Nicholas[2f] has found that the pK_a of 1-adamantanecarboxylic acid is 0.25 unit greater than the pK_a of pivalic acid in 50% ethanol,[16] in agreement with this idea. Many of the other small rate enhancements listed in Chart I (*e.g.*, **4**, **8**, **9**, and **14**) probably stem from this cause.

The present conclusion of stepwise ionization–rearrangement in the neopentyl system can easily be reconciled with the evidence cited above favoring the concerted mechanism. This evidence was suggestive, but none was of a nature to exclude the two-step process. The apparent rate-enhancing factor present in neopentyl solvolyses relative to ethyl[13,14] very likely is inductive rather than participative in origin. Likewise minor variations in rate in neopentyl-type systems may be explained on this basis, or these may be due to differences in access of the solvent to the reaction site or to differences in the degree of relief of steric strain between the leaving group and the adjacent substituents. In fact, steric congestion in the neopentyl ground state could be responsible for an augmented rate of simple ionization, compensating for a greater nucleophilic solvent involvement in the ethyl case.[13]

(42) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 193.

The preservation of optical activity in 2-methyl-1-butene-3-*d* from deoxideation of neopentyl-1-*d* alcohol[23] can be accommodated by stepwise ionization–rearrangement, providing the methyl migration occurs at a rate comparable to or greater than that for conformational isomerization of the carbonium ion by rotation around the C_1–C_2 bond.[43] There is evidence,[24] however, that the deoxideation process (like the deamination of primary amines) may produce carbonium ions of properties quite different from those resulting from simple halide or arenesulfonate ionizations, and caution in generalizing such results is indicated.

There remains, finally, one possibility still to be considered: formation of a nonclassical carbonium ion intermediate **29** in place of the equilibrating primary and tertiary cations **16** and **17**. The latter would thus become contributing resonance structures rather than discrete species. In view of the compression in energy between



29 16 17

cations **16** and **17** relative to their open-chain counterparts **2** and **3**, structure **29** is not an implausible one, and could, of course, account for the products formed. As with all saturated systems where the question of a nonclassical carbonium ion arises,[44] an experimental distinction between the alternatives is very difficult to establish. The occurrence of cation **29** cannot be rigorously excluded by the present results, and indeed evidence has been obtained, to be reported shortly,[45] which will make essential a thorough discussion of the possible role of this species. For the present, however, it should be emphasized that the intermediacy of **29** requires that it be formed from adamantylcarbinyl tosylate (**15**, X = OTs) at virtually the same rate as neopentyl tosylate **1** yields neopentyl cation **2**, or conceivably in this context *t*-amyl cation **3**. Such a coincidence can at this point be viewed only as unlikely; there is little reason to suspect that processes from substrates so similar in structure to intermediates so dissimilar should take place isokinetically.

Experimental Section

General Comments. Melting points (capillary) are corrected. Boiling points are uncorrected. Gas chromatography was done with a Barber-Colman Model 5340 gas chromatograph. Two stationary phases (in 15 ft × 1/4 in. o.d. copper columns) gave good separations of the reactants and products in this work: diethylene glycol polyadipate LAC-446 10% on 60–80 mesh Diatoport S, and silicone oil 710 10% on 60–80 mesh Chromosorb P (both from F and M Scientific Corp.). Thin layer chromatography (tlc) was carried out on silica gel, using chloroform or chloroform–acetone mixtures as the developing solvent and sulfuric acid spraying followed by 100° heating as the visualization method. Elemental analyses were performed by Galbraith Laboratories, Inc., and by Mr. George Robertson. Infrared spectra were obtained with a Perkin-Elmer Model 137 spectrophotometer, using *ca.* 1% solu-

(43) (a) It has been argued, however, that this rotational barrier should be very small: H. S. Mosher, private communication. (b) For a related reaction in which such rotational isomerization is crucial, see B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957).

(44) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

(45) See ref 37 and Table V, footnote *a*.

tions in carbon tetrachloride. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer, using 5–10% solutions in carbon tetrachloride.

1-Adamantylcarbinol (15, X = OH). 1-Adamantanecarboxylic acid was reduced directly with lithium aluminum hydride in ether in the usual manner,[48] producing the carbinol in 86% yield (0.10-mole scale), with mp 115–116° after recrystallization from methanol–water (lit.[47] mp 115°). The acid was obtained by direct carboxylation of adamantane, according to Koch and Haaf,[48] and had mp 180–181° (lit.[48] mp 181°). Alternatively, the acid was prepared by carbonation of the Grignard reagent from 2.15 g (0.010 mole) of 1-bromoadamantane and 0.24 g (0.010 g-atom) of magnesium turnings in 25 ml of ether, using the method of Putnambeker and Zoellner;[49] the product (0.72 g, 0.0040 mole, 40%) had mp 178–180° after recrystallization from ethanol–water.[50] The acid from both sources was homogeneous by tlc. The carbinol was homogeneous by tlc and by gas chromatography on the polyester column.

1-Adamantylcarbinyl Tosylate (15, X = OTs). The procedure of Stetter, *et al.*,[47] was followed, yielding products of mp 76.5–78 and 77.4–78.4° (lit. mp 76–78°). The former sample showed only one spot on tlc.

1-Adamantylcarbinyl *p*-Nitrobenzenesulfonate (15, X = ONs). This ester was prepared just as the tosylate **15**, mp 125.8–127.0°. *Anal.* Calcd for $C_{17}H_{21}NSO_5$: C, 58.20; H, 6.04; N, 3.99. Found: C, 58.16; H, 6.07; N, 3.92.

1-Adamantylcarbinyl Acetate (21). 1-Adamantylcarbinol (**15**, X = OH) (1.66 g, 0.010 mole) and 4.1 g (0.040 mole) of acetic anhydride were allowed to react in 25 ml of dry pyridine for 1.0 hr at 100°. The cooled reaction mixture was added to excess 10% sulfuric acid and extracted with ether. The ether solution was washed with water, dried over anhydrous magnesium sulfate, and distilled, yielding 1.66 g (0.0080 mole, 80%) of the acetate, bp 110–113° (2.5 mm). The product was purified (solvent impurities only) by gas chromatography. Its nmr spectrum was typical of 1-substituted adamantanes.[51] *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.04; H, 9.43.

1-Adamantylcarbinyl Bromide (23). A mixture of 1.66 g (0.010 mole) of 1-adamantylcarbinol (**15**, X = OH), 43 g of concentrated hydrobromic acid, and 56 g (0.025 mole) of zinc bromide (Lucas reagent[52]) was heated under reflux for 10 hr. A white crystalline material collected at the bottom of the condenser. The contents of the flask and condenser were added to 400 ml of water and extracted with 500 ml of ether. The ether solution was washed with 100 ml of 5% sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The ether was removed by flash distillation, and the residue was sublimed under vacuum (70–75°, 2.5 mm), yielding 2.22 g (0.0097 mole, 97%) of 1-adamantylcarbinyl bromide (**23**), mp 41–43° (lit.[33] mp 42–43°). Its nmr spectrum showed the typical[51] 1-adamantyl ring absorption pattern, at τ 7.92, 8.24, and 8.36, plus a sharp singlet for the exocyclic methylene group at τ 6.80.

1-Adamantylcarbinyl Ethyl Ether (15, X = OEt). A magnetically stirred mixture of 0.83 g (0.0050 mole) of 1-adamantylcarbinol, 50 ml of freshly purified[53] diglyme, and 1.95 g (0.050 mole) of sodium amide was heated at 100° under a dry nitrogen atmosphere for 2.5 hr, at the end of which time nitrogen evolution had ceased. To the cooled mixture was added a solution of 7.8 g (0.050 mole) of ethyl iodide in 25 ml of freshly purified[53] dimethylformamide. Heating at 100° and stirring were maintained for 24 hr. The cooled product mixture was poured cautiously onto 500 g of ice in a separatory funnel, and the resulting mixture was warmed to room temperature and extracted with 200 ml of ether. The ether solution was washed with water and dried over anhydrous calcium chloride, and the ether was distilled off. The residual crude product (0.45 g, 0.0023 mole, 46%) was purified by vpc on the polyester column. Its nmr spectrum had the typical[51] 1-adamantyl pattern at τ 8.08, 8.30, and 8.49, a singlet at τ 7.12 for the methylene group attached to the ring, and the ethyl group quartet and triplet at τ 6.63 and 8.87, respectively. *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.23; H, 11.41.

1-Adamantylcarbinyl Formate (27). A solution of 1.66 g (0.010 mole) of 1-adamantylcarbinol (**15**, X = OH), 100 ml of pentane, and 25.0 g (0.16 mole) of crude formic benzoic anhydride[54] was stirred magnetically at room temperature for 24 hr and was then poured into 500 ml of water, containing 0.5 ml of pyridine, in a separatory funnel. The resulting mixture was extracted with 200 ml of ether, and the ether solution was washed with 5% sodium bicarbonate solution, 10% sulfuric acid, and 5% sodium bicarbonate solution again, and was dried over anhydrous magnesium sulfate. The ether was distilled off, leaving 1.53 g (0.0080 mole, 80%) of residual crude 1-adamantylcarbinyl formate. The product was purified by vpc (solvent being the only volatile impurity). Its nmr spectrum had the absorption pattern typical of 1-substituted adamantanes[51] plus sharp singlets at τ 6.26 for the exocyclic methylene group and at τ 2.01 for the formyl proton. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.99; H, 9.50.

3-Homoadamantanol (25). A mixture of 150 ml of 65% (v/v) aqueous diglyme, 3.20 g (0.010 mole) of 1-adamantylcarbinyl tosylate (**15**, X = OTs), and 2.12 g (0.020 mole) of anhydrous sodium carbonate was heated under reflux for 72 hr. The cooled reaction mixture was poured into 500 ml of water and extracted with 500 ml of ether. The ether layer was washed with water and dried over anhydrous magnesium sulfate. The ether was distilled off and the residue was sublimed under vacuum (130–135°, 1 mm), yielding 1.59 g (0.0096 mole, 96%) of 3-homoadamantanol (**25**), mp 274–276° (lit.[33] mp 274–275.5°). The product was homogeneous by tlc and also by vpc on the silicone oil column, where a control run showed that 1% of 1-adamantylcarbinol (**15**, X = OH), if present, could readily have been detected. The nmr spectrum of the product consisted of broad peaks at τ 7.90, 8.13, and 8.41 (relative intensities roughly 1:3:1) plus a sharp singlet at τ 8.60 for the hydroxyl proton.

3-Homoadamantyl Bromide (23). 3-Homoadamantanol (**25**, X = OH) was treated with phosphorus tribromide by the procedure of Stetter and Goebel.[33] The crude product was sublimed under vacuum (95°, 1 mm), yielding 80% (0.0080-mole scale) of 3-homoadamantyl bromide (**23**), mp 125–126° (lit.[33] mp 124.5–125.5°). The vapor-phase chromatogram of the product on the polyester column showed just one peak; a control chromatogram established that 1% of 1-adamantylcarbinyl bromide (**24**) could have been readily detected if present. The product was also homogeneous by tlc. Its nmr spectrum consisted of a highly irregular pattern of nine principle peaks between τ 7.1 and 8.7.

3-Homoadamantyl Acetate (22). 3-Homoadamantanol (**25**) and acetic anhydride were allowed to react in pyridine, as described for 1-adamantylcarbinyl acetate **21**, above. The product, bp 108–110° (1.5 mm), was obtained in 80% yield (0.0080-mole scale). It was homogeneous according to vpc on the polyester column. Its nmr spectrum consisted of an irregular pattern of three main peaks for the ring protons, at τ 7.94 (most intense), 8.20 (least intense), and 8.44, with considerable fine structure, plus a strong narrow singlet at τ 8.14 for the acetate protons. *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.73; H, 9.50.

3-Homoadamantyl Ethyl Ether (18, X = OEt). This compound was prepared from 3-homoadamantanol (**25**), sodium amide, and ethyl iodide, as described above for 1-adamantylcarbinyl ethyl ether (**15**, X = OEt). It was obtained in 46% yield (0.0023-mole scale) and had bp 85–87° (2.5 mm). It was further purified by vpc. Its nmr spectrum resembled that of 3-homoadamantanol, consisting of broad singlets at τ 8.01, 8.22, and 8.47 (relative intensities approximately 1:3:1) for the ring protons plus a triplet at τ 8.95 and a quartet at τ 6.66 for the ethyl group. *Anal.* Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.11; H, 11.38.

3-Homoadamantyl Formate (28). 3-Homoadamantanol (**25**) and formic benzoic anhydride were allowed to react in pentane, as described above for 1-adamantylcarbinyl formate (**27**). The product was obtained in 45% yield (0.010-mole scale) and had bp 105–107° (2.5 mm). It was further purified (solvent impurities only) by vpc. Its nmr spectrum consisted of broad peaks for the ring protons at τ 7.86, 8.20, and 8.47 (of decreasing intensities in

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the order written), plus a singlet for the formyl proton at τ 2.14. *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.46.

Preparative Acetolysis of 1-Adamantylcarbinyl Tosylate (15, X = OTs) in the Presence of Sodium Acetate. A mixture of 125 ml of glacial acetic acid, 1.2 ml of acetic anhydride, 1.60 g (0.005 mole, molarity = 0.040) of **15** (X = OTs), and 0.82 g (0.010 mole) of anhydrous sodium acetate was heated under reflux for 72 hr. After cooling to room temperature, the reaction mixture was poured into 300 ml of water and extracted with 200 ml of ether. The ether solution was washed with 200-ml portions of water, 5% sodium bicarbonate (washings basic to indicator paper), and water, and was dried over anhydrous potassium carbonate. The solvent was removed by flash distillation. The residual liquid, 1.15 g, was subjected to vapor-phase chromatography on the diethylene glycol polyadipate column and showed two peaks of relative areas 6.8 and 93.2%, with the minor component eluted first. The eluents were collected separately. The minor product was identified as 1-adamantylcarbinyl acetate (**21**); its vpc retention time, infrared spectrum, and nmr spectrum matched perfectly those of the synthetically prepared material (see above). The major product was identified as 3-homoadamantyl acetate (**22**) by the same criteria. The liquid product was distilled under vacuum without fractionation, yielding 0.885 g (0.0042 mole, 84% of theoretical) of the clear, colorless acetate mixture. The residue was 0.16 g (0.00050 mole, 10% recovery) of the starting tosylate (**15**, X = OTs), identified by its infrared spectrum.

The acetolysis was also performed twice more as described above, but using 2.05 g (0.025 mole) of sodium acetate in one run and 4.10 g (0.050 mole) of sodium acetate in another run. The product composition, reported in Table II, was found to be invariant, within experimental error, with the amount of sodium acetate present in the reaction mixture. Control experiments were run which established that both of the product acetates **21** and **22** were stable under the reaction conditions.

Preparative Acetolysis of 1-Adamantylcarbinyl Tosylate (15, X = OTs) in the Absence of Sodium Acetate. The acetolysis of **15** (X = OTs) was carried out as above, except that the sodium acetate was omitted. Under these conditions the product, in 88% yield, was exclusively 1-adamantylcarbinyl acetate (**21**). In addition, 5.5% of the unchanged starting material was recovered and identified by its infrared spectrum. In a control experiment, a solution of 0.180 g (0.00086 mole) of 3-homoadamantyl acetate (**22**) in 50 ml of acetic acid containing 1.0 ml of acetic anhydride and 0.164 g (0.00086 mole) of *p*-toluenesulfonic acid monohydrate was heated under reflux for 72 hr and worked up as described above. The product was entirely 1-adamantylcarbinyl acetate (**21**), identified by its vpc retention time and infrared spectrum.

Preparative Solvolysis of 1-Adamantylcarbinyl Tosylate (15, X = OTs) in Aqueous Diglyme in the Presence of Sodium Hydroxide. A mixture of 125 ml of 20% water–80% purified diglyme (v/v), 1.60 g (0.0050 mole, molarity = 0.040) of **15** (X = OTs), and 0.80 g (0.20 mole) of sodium hydroxide was heated under reflux for 72 hr. The product was extracted with ether and washed as described above under acetolysis of **15** (X = OTs). After distillation of most of the ether, the concentrated product solution was subjected to vpc on the silicone oil column and showed just one peak (in addition to that of the solvent), of retention time corresponding to 3-homoadamantanol **25**. The rest of the ether was distilled, and the residual solid was sublimed under vacuum (130–135°, 1 mm), yielding 0.75 g (0.0045 mole, 90%) of colorless, crystalline solid, identified as 3-homoadamantanol **20** by its vpc retention time, infrared spectrum, melting point, and mixture melting point. (A control vapor-phase chromatogram showed that 1% of 1-adamantylcarbinol (**15**, X = OH) could have been readily detected if present.) Its thin layer chromatogram likewise showed only one spot. The residue from sublimation was 0.08 g (0.00025 mole, 5% recovery) of 1-adamantylcarbinyl *p*-toluenesulfonate (**15**, X = OTs) identified by its infrared spectrum.

The solvolysis was also performed twice more, as described above, but using 1.60 g (0.040 mole) of sodium hydroxide in one run and 3.20 g (0.080 mole) of sodium hydroxide in another run. The product was exclusively 3-homoadamantanol **25** in each case.

Preparative Solvolysis of 1-Adamantylcarbinyl Tosylate (15, X = OTs) in Aqueous Ethanol in the Presence of Sodium Carbonate. A mixture of 125 ml of 20% water–80% ethanol (v/v), 1.60 g (0.0050 mole, molarity = 0.04) of **15** (X = OTs), and 1.06 g (0.01 mole) of anhydrous sodium carbonate was heated under reflux for 170 hr. The product was extracted with ether and washed as described above under acetolysis of **15** (X = OTs). After distillation of most of the solvent, the vapor-phase chromatogram of the concentrated product solution on the silicone oil column showed four peaks (in addition to that of the solvent), of relative areas 1.7, 2.4, 56.2, and 39.7%, in the order of increasing retention times. The four peaks were identified as 1-adamantylcarbinyl ether ether (**15**, X = OEt), 1-adamantylcarbinol (**15**, X = OT), 3-homoadamantanol (**25**), and 3-homoadamantyl ethyl ether (**18**, X = OEt), respectively, by their identity in retention times with those of the synthetically prepared materials. After removal of the rest of the solvent on a rotary evaporator, the residue was 0.90 g (101% of theoretical, based on the above product composition and assuming complete solvolysis of the tosylate **15** (X = OTs)).

Preparative Formolysis of 1-Adamantylcarbinyl Tosylate (15, X = OTs) in the Presence of Sodium Formate. A mixture of 125 ml of anhydrous formic acid, 1.60 g (0.0050 mole, molarity = 0.040) of **15** (X = OTs), and 0.68 g (0.010 mole) of anhydrous sodium formate was heated under reflux for 72 hr. The product was extracted with ether, washed, and dried as described above under acetolysis of **15** (X = OTs). After distillation of the solvent, the product was distilled under vacuum (0.85 g, 0.0045 mole, 90%), bp 108–110° (2.5 mm). It was identified as 1-adamantylcarbinyl formate (**27**) by its vpc retention time, infrared spectrum, and nmr spectrum. The vapor-phase chromatogram also indicated the presence of a small amount of 3-homoadamantanol (**25**), which probably resulted from autodecomposition of formic acid to water and carbon monoxide.

Preparative Formolysis of 3-Homoadamantyl Formate (28) in the Presence of Sodium Formate. A mixture of 25 ml of anhydrous formic acid, 0.194 g (0.0010 mole, molarity = 0.040) of 3-homoadamantyl formate (**28**), and 0.136 g (0.0020 mole) of anhydrous sodium formate was heated under reflux for 30 min. The reaction was worked up as described above for the formolysis of **15** (X = OTs). Vpc of the product showed two peaks, of relative areas 2 and 98%, with the minor component eluted first. The eluents were collected separately and were identified as 3-homoadamantanol (**25**) and 1-adamantylcarbinyl formate (**27**), respectively, by their vpc retention times, infrared spectra, and nmr spectra.

Preparative Acetolysis of 3-Homoadamantyl Bromide (23) in the Presence of Sodium Acetate. A mixture of 65 ml of glacial acetic acid, 1.00 ml of acetic anhydride, 0.57 g (0.0025 mole, molarity = 0.04) of 3-homoadamantyl bromide (**23**), and 0.41 g (0.0050 mole) of anhydrous sodium acetate were heated under reflux for 10 hr. The product mixture was worked up as described above for acetolysis of 1-adamantylcarbinyl tosylate **15** (X = OTs). The crude product, 0.50 g (0.0024 mole, 99% of theoretical), was subjected to vpc on the diethylene glycol polyadipate column and showed three peaks, of relative areas 59.4, 2.8, and 37.8%, in the order of increasing retention times. The peaks were identified as those of 1-adamantylcarbinyl bromide (**24**), 1-adamantylcarbinyl acetate (**21**), and 3-homoadamantyl acetate (**22**), respectively, by the identity of their retention times with those of the synthetically prepared materials. The acetolysis was also performed twice more as described above, but using 1.025 g (0.0125 mole) of sodium acetate in one run and 2.05 g (0.025 mole) of sodium acetate in another run. The ratio of the acetates **21** and **22** was found to be essentially invariant with the amount of sodium acetate present in the reaction mixture. However, the amount of 1-adamantylcarbinyl bromide (**23**) sharply decreased with increasing acetate ion concentration (Table II). 1-Adamantylcarbinyl bromide (**24**) was found in a control experiment to be inert under these conditions, being recovered quantitatively.

Preparative Solvolysis of 3-Homoadamantyl Bromide (23) in Aqueous Diglyme in the Presence of Sodium Hydroxide. A mixture of 65 ml of 20% water–80% purified diglyme (v/v), 0.57 g (0.0025 mole, molarity = 0.04) of 3-homoadamantyl bromide (**23**), and 0.40 g (0.010 mole) of sodium hydroxide was heated under reflux for 10 hr, and then worked up as described above for the solvolysis of 1-adamantylcarbinyl tosylate (**15**, X = OTs) under similar conditions. The crude solid product, 0.46 g, was subjected to vpc on the silicone oil column and showed just one solute peak. The crude product was sublimed under vacuum (130–135°, 1 mm), yielding 0.40 g (0.0024 mole, 96%) of colorless, crystalline material, which was identified as 3-homoadamantanol (**25**), by its vpc retention time, infrared spectrum, and melting point. A control vapor-phase chromatogram showed that 1% of 1-adamantylcarbinol (**15**, X = OH) could have been readily detected if present. Its thin-layer chromatogram likewise showed only one spot. The solvolysis was also performed twice more as described above, but using 0.80 g (0.020 mole) of sodium hydroxide in one run and 1.60

g (0.040 mole) of sodium hydroxide in another run. The product was exclusively 3-homoadamantanol (**25**) in each case.

Preparative Solvolysis of 3-Homoadamantyl Bromide (23) in Aqueous Ethanol in the Presence of Sodium Carbonate. A mixture of 65 ml of 20% water–80% ethanol (v/v), 0.57 g (0.0025 mole, molarity = 0.04) of 3-homoadamantyl bromide (**23**), and 0.53 g (0.0050 mole) of anhydrous sodium carbonate was heated under reflux for 10 hr, and was then worked up as described for the similar solvolysis of 3-adamantylcarbinyl tosylate (**15**, X = OTs). The crude semisolid product, 0.49 g, was subjected to vpc on the silicone oil column and showed two peaks, of relative areas 37.5 and 62.5%, with the major component eluted first. The major product was identified as 3-homoadamantanol (**25**) and the minor product as 3-homoadamantyl ethyl ether (**18**, X = OEt) by their vpc retention times. Control vpc experiments were run which showed that 1% of primary alcohol **15** (X = OH) or primary ether **15** (X = OEt) could have been detected if present.

Neopentyl *p*-Nitrobenzenesulfonate. Commercially available neopentyl alcohol was converted to its nosylate by the standard procedure, mp 111.8–112.0°. *Anal.* Calcd: C, 48.35; H, 5.23. Found: C, 48.53; H, 5.55.

Kinetic Procedures. Standard titrimetric ampoule procedures were employed.[4,5,11,13,15,16,19,21,22,35,51,55] The solvents were carefully dried and fractionally distilled. Two separate runs to about three half-lives were made by each investigator at each temperature; agreement between runs was generally good. Table IV provides examples of the kind of agreement found between different investigators. Three separate studies, years apart, of the acetolysis of 1-adamantylcarbinyl tosylate (**15**, X = OTs) gave excellent agreement of the rate constants at a common temperature, 100°, and of the activation parameters. On the other hand, two studies on the corresponding nosylate, while giving moderately good agreement at 100° (11%), gave widely different activation parameters. This illustrates just one of the possible pitfalls of overenthusiastic interpretation of small differences in enthalpies and entropies of activation.[56]

(55) See footnote g, Chart I.

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Substituent Effects in Unimolecular Ion Decompositions. III. Elucidation of Competing Alternative Pathways for the Formation of a Particular Ion[1]

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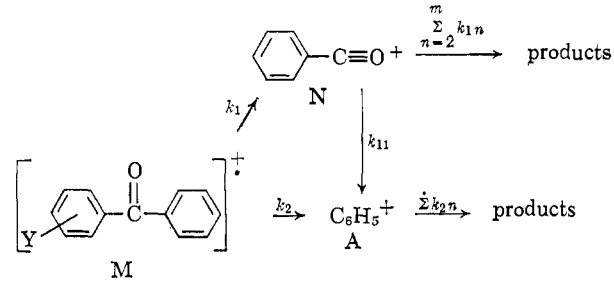
Abstract: Substituent effects may be used to indicate the existence of two pathways for the formation of an ion in mass spectra. For example, the $C_6H_5^+$ ion in the mass spectra of substituted benzophenones is indicated to be formed by two pathways: directly from the molecular ion, and also through the intermediacy of the benzoyl ion. This mechanism is confirmed by elimination of the first process at low voltages. Similar data are found for the $C_3H_7^+$ ion in the spectra of substituted butyrophenones. Further use of the low-voltage technique is demonstrated in the determination of the origin of the $C_2H_3O^+$ ion in *m*- and *p*-*t*-butylacetophenone.

Substituent effects offer promise in the unraveling of structural detail of ions formed in the mass spectrometer and of the kinetic processes relating them. A significant correlation with Hammett σ constants[2] obtained in solution indicates similarity in the structure and behavior of the gas phase ion to that of species found in solution chemistry, both for ion abundance data[3] and for appearance potentials.[4–7]

In the previous paper of this series,[3] ion-abundance data were demonstrated to yield useful information about the structures of ions and transition states in the formation of acyl ions (N) from substituted acylbenzenes (M), M → N in Scheme I. This simple case was ideal for study, since there are no alternative pathways for the formation of the acyl ion, nor is there a substituent effect on further decomposition of this ion. The present paper extends this technique to the more complex system in which a particular product ion can be formed from a particular precursor ion by competing reaction paths. To our knowledge no techniques for the study of such a situation have been discussed previously; isotopic labeling will not distinguish these

Scheme I



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