TABLE I

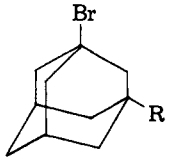
SOLVOLYSIS OF 1-ADAMANTYL BROMIDES IN 80% ETHANOL, 70°

Compounds	$10^5 k_1$, sec.$^{-1}$	Rel. rate	ΔH^*, kcal.	ΔS^*, e.u.
1-Bromoadamantane (I)	8.76	1.00	23.1	−10.1
1-Bromo-3-methyladamantane (VIa)	6.05	0.69	23.6	−9.6
1-Bromo-3,5-dimethyladamantane (VII)	4.12	0.47	24.5	−7.4
1-Bromo-3,5,7-trimethyladamantane (VIII)		0.31[a]		
1-Bromo-3-ethyladamantane (VIb)	8.42	0.96	23.3	−9.4
1-Bromo-3-isopropyladamantane (VIc)	11.9	1.36	24.5	−5.4

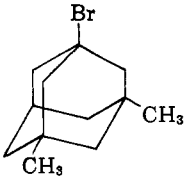
[a] At 75°.[10]

to carbonium ion reactivities.[2a,8,9] It appeared to us and to Grob, Schwarz, and Fischer[10] that the adamantane system would be ideal for testing the effect of C–C hyperconjugative variations on reaction rate.[10] Previous systems which have been examined in this respect (as III) suffer from the disadvantage that added substituents γ to the reaction site might have introduced steric and conformational effects and not just electronic ones.[4,8] Progressive substitution of methyl groups at the remaining three bridgehead positions of 1-bromoadamantane (I) is free from this objection. The added methyl groups in VIa, VII, and VIII should be strain free[2a]; they should cause no appreciable distortion of the rigid molecule; and they are too far from the reaction site to interfere sterically. However, the methyl groups might stabilize the 1-adamantyl cation (IV), since contributing secondary hyperconjugative species are transformed to tertiary by such substitution (compare IVa, b, c, and d).

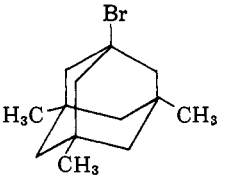
Were the C–C hyperconjugation explanation for the 10^3 solvolysis rate difference between 1-adamantyl bromide (I) and 1-bicyclo[2.2.2]octyl bromide (II) sound, a significant rate enhancement for each methyl substituent in going from 1-adamantyl bromide (I) to its 3-methyl (VIa), 3,5-dimethyl (VII), and 3,5,7-trimethyl (VIII) homologs would be expected. In actual fact (Table I) the addition of methyl groups *retards* the solvolysis rate. This rate-depressing effect is cumulative; each successive methyl substituent decreases the rate of the preceding compound by a factor of two-thirds (Table I). Other alkyl substituents also have but a small effect on the solvolysis rate; that of the ethyl derivative VIb is practically the same as for 1-adamantyl bromide (I), while a 3-isopropyl group (VIc) gives a slight rate enhancement (1.4 times).



VIa, R = CH_3
b, R = C_2H_5
c, R = i-C_3H_7



VII



VIII

These results establish the unimportance of C–C hyperconjugation effects in determining solvolysis rates.[2,7,8,10] The reactivity difference between 1-adamantyl bromide (I) and 1-bicyclo[2.2.2]octyl bromide (II) cannot be attributed to this cause. We have suggested that the rate of II is slowed relative to I because serious nonbonded repulsion between C-1 and C-4 in the bicyclo[2.2.2]octyl bridgehead ion (Va) resists flattening.[2a] This factor is not present in the 1-adamantyl cation (IVa), where the bridgehead position can become more nearly planar during ionization without encountering any serious 1,4-C–C nonbonded interactions.[2,5] It is also possible that a "cage effect" may differentially stabilize IVa.[2]

The rate-retarding influence of methyl groups (Table I) is surprising in view of the widely evident electron-releasing effects of methyl substituents. It is certainly true that methyl groups are electron donors when attached to carbons sp or sp^2 hybridized, but the same need not be true for CH_3–C (sp^3) situations.[2a] Kwart and Miller[11] have argued that methyl groups in saturated molecules can be electron withdrawing and we feel that the present results provide excellent support for this contention. The exact hybridization of carbon in a saturated molecule[12] would be expected to change with structural variations, so that methyl need not be electron withdrawing in every situation.

A differential solvation effect might also be responsible for the rate-retarding influence of the methyl groups (Table I).[13] However, changes of solvent produced no significant change in relative solvolysis rates. For example, in 50% ethanol the rates of I, VIa, and VII are 1.00, 0.75, and 0.46, respectively.[14] Furthermore, bulk effects seem to be excluded by the contrary influence of ethyl (VIb) and isopropyl (VIc) substitution from the effect of two (VII) and three (VIII) methyl groups. We believe inherent electrical effects of substituents are being observed in these saturated systems, and we plan to extend these investigations.

Acknowledgment.—We wish to thank the Petroleum Research Foundation for support of this research and Professor C. A. Grob for informing us of his results prior to their publication.[10]

(8) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961); P. von R. Schleyer, *ibid.*, **86**, 1854 (1964).

(9) H. Fischer, C. A. Grob, and W. Schwarz, *Tetrahedron Letters*, **No. 1**, 25 (1962).

(10) C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, **47**, in press.

(11) H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961).

(12) As measured, for example, by the $J_{C^{13}-H}$ constant. See K. Mislow, *Tetrahedron Letters*, **No. 22**, 1415 (1964), and references therein cited.

(13) *Cf.* R. A. Clement, J. N. Naghizadeh, and M. R. Rice, *J. Am. Chem. Soc.*, **82**, 2449 (1960); E. M. Arnett, P. M. Duggleby, and J. J. Burke, *ibid.*, **85**, 1350 (1963); J. B. Hyne and R. Wills, *ibid.*, **85**, 3650 (1963).

(14) Professor E. M. Arnett and Dr. W. G. Bentrude have kindly measured the heats of solution of I, VIa, and VII in alcoholic solvents of different water content. They conclude that there is no apparent difference in the way the heats of solution of the different compounds respond to solvent change (private communication).

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Stable Carbonium Ions. VIII. The 1-Adamantyl Cation[1,2]

Sir:

Solution of 1-adamantyl fluoride or chloride (I) in SbF_5 or SbF_5–liquid SO_2 solution[3] produces a new

(1) Part VII: G. A. Olah, E. B. Baker, and M. B. Comisarow, *J. Am. Chem. Soc.*, **86**, 1265 (1964).

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

(3) For experimental procedures see G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

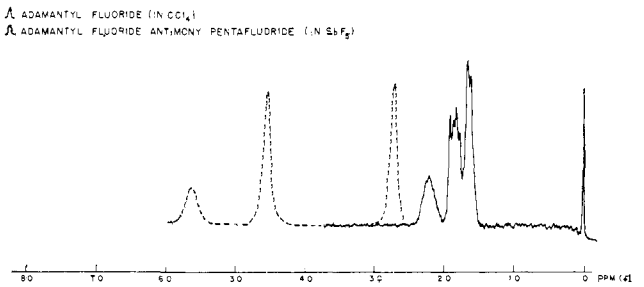
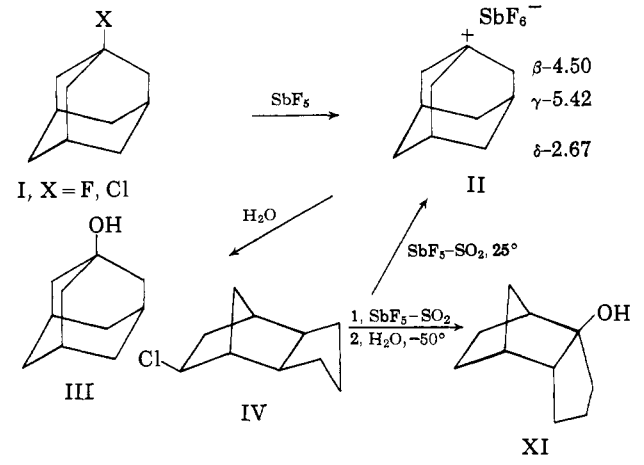
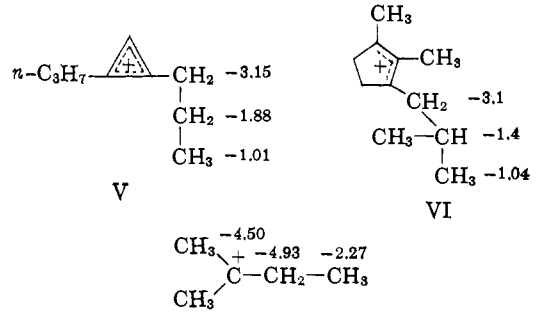


Fig. 1.—The n.m.r. spectra of 1-adamantyl fluoride (I, X = F) and the 1-adamantyl cation (II).

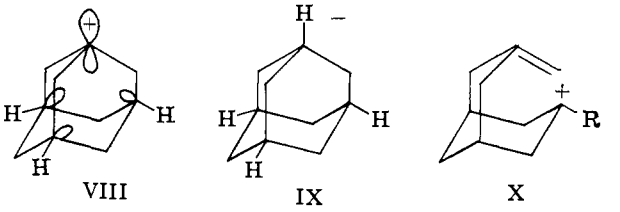
species with a distinctly different n.m.r. spectrum from its covalent precursors (Fig. 1). We believe this new species to be the 1-adamantyl cation (II), stabilized as the SbF_6^- salt.[3] That skeletal integrity is preserved in the ion is revealed by hydrolysis.[3] Pure 1-adamantanol (III), identified by gas chromatographic retention times and mixture melting point and spectrographic comparisons, is produced in high yield. The three n.m.r. peaks of the 1-adamantyl cation (II) can easily be assigned from their areas and chemical shifts: the six protons β to the charge are at -4.50 p.p.m. (in SbF_5 solution, relative to external tetramethylsilane), the three γ-protons are at -5.42 p.p.m., and the six remaining δ-protons resonate at -2.67 p.p.m. (II). These chemical shifts are somewhat solvent and concentration sensitive,[3] but internal shifts are reasonably constant.



That the γ- and not the β-protons are the most deshielded in II is truly exceptional. The effect of charge on chemical shift would be expected to diminish with increase in distance, as is found generally (*e.g.*, V,[4] VI,[5] and VII[3,6,7]). We have considered several possible explanations for the pronounced deshielding of the γ-protons. A rapid intermolecular hydride exchange specifically involving the bridgehead hydrogens might distribute positive charge on time average. This possibility is unlikely since the n.m.r. spectrum of the 1-adamantyl ion (II) undergoes no significant change over a temperature change from -90 to $+40°$. Furthermore, the n.m.r. spectra of the 3-methyl- and 3,5-dimethyl-substituted 1-adamantyl cations[8] have about the same chemical shifts as II for the remaining γ-bridgehead protons, despite their smaller number. If charge were being distributed over these bridgehead hydrogens by exchange, the number of such hydrogens should influence the observed chemical shifts.



It appears that some intramolecular process is operative in the transferal of positive charge to the bridgehead positions. In the 1-adamantyl cation one lobe of the empty p-orbital extends into the adamantane "cage" where overlap with the backsides of the three sp^3 bridgehead C–H orbitals is possible (VIII).[2,7] Such overlap would distribute charge selectively to the bridgehead positions, and this may account for their downfield position in the n.m.r. spectrum.



Support for this backside orbital interaction hypothesis stems from a different source. The e.s.r. spectrum of the adamantane radical anion (IX)[9] suggests that the added electron resides in the central molecular cavity and spin couples with the four bridgehead hydrogens. Results supporting this conclusion have been observed with hexamethylenetetramine and with several adamantane derivatives.[9]

An alternative explanation based upon important contributions from C–C hyperconjugation (*e.g.*, resonance between II and X, R = H) appears to be less likely.[2,10] The solvolysis of 1-adamantyl bromide (I, X = Br) in aqueous ethanol solution is *retarded* slightly —not enhanced—by substitution of methyl groups for hydrogens at the remaining bridgeheads.[2,10] It would be expected that X (R = CH_3) would contribute more effectively to the resonance hybrid involving a 1-cation than would X (R = H) because of the greater ability of methyl to stabilize a positive charge. Were C–C hyperconjugation an effective method for charge delocalization, a rate effect of methyl substitution opposite to that actually observed would have been expected.

In SbF_5–SO_2 solution, 2-*exo*-chloro-*exo*-trimethylenenorbornane (IV) is also a precursor of the 1-adamantyl cation (II). When IV is dissolved in SbF_5–liquid SO_2 at $-70°$, a species is formed whose n.m.r. spectrum is

(4) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

(5) N. C. Deno and J. J. Houser, *ibid.*, **86**, 1741 (1964); also see ref. 7.

(6) D. M. Brouwer and E. L. Mackor, *Proc. Chem. Soc.* (London), 147 (1964).

(7) See N. C. Deno in "Progress in Physical Organic Chemistry," S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Vol. II, Interscience Publishers, New York, N. Y., 1964, pp. 129–193.

(8) To be reported subsequently.

(9) K. W. Bowers, G. J. Nolfi, Jr., and F. D. Greene, *J. Am. Chem. Soc.*, **85**, 3707, (1963); private communications.

(10) R. C. Fort, Jr., and P. von R. Schleyer, *ibid.*, **86**, 4194 (1964); C. A. Grob, W. Schwarz, and H. P. Fischer, *Helv. Chim. Acta*, in press.

quite different from that of II. At −35°, there is no significant change in the spectrum, but at higher temperatures the characteristic spectrum of II appears. These changes can also be monitored by hydrolysis experiments. A solution of IV in SbF_5–SO_2 kept below −50° gave upon hydrolysis a single alcoholic product, identified as *endo*-trimethylene-5-*exo*-norbornanol (XI).[8,11] Hydrolysis of a solution of IV in SbF_5–SO_2 which had been allowed to warm to −10° analyzed for 45% 1-adamantanol (III), 35% XI, and four minor products by gas chromatography. When a solution of IV in SbF_5–SO_2 had warmed to room temperature, hydrolysis gave 96% 1-adamantanol (III) and 4% of a single second component. Sublimation of the hydrolysate gave essentially pure 1-adamantanol (III), identical in all respects with authentic material.

The rearrangement of 2-*exo*-chloro-*exo*-trimethylenenorbornane (IV) to the 1-adamantyl cation (II) is particularly noteworthy. Heretofore, rearrangements of tricyclic precursors to adamantane and its homologs[2,12] have been confined to hydrocarbons and catalyzed by strong Lewis acids. It has been argued that such systems should be uniquely effective in permitting extremely complex and drastic rearrangements, since carbonium ions can be generated intermolecularly, reversibly, and repeatedly at numerous sites on a molecular framework.[2,12] With compounds such as IV, the site of carbonium ion formation is predetermined, and rearrangements must necessarily proceed by a sequential, intramolecular process which ordinarily limits the rearrangement potential of a given system. The unusual stabilizing effect of SbF_5 on carbonium ions[3] overcomes this difficulty, and rearrangements as complex as any observed under the most favorable of chemical circumstances are possible. In SbF_5, carbonium ions with the greatest over-all stability tend to form, *i.e.*, the most stable carbonium ion *per se*, in a structure with the most stable carbon skeleton. The bridgehead 1-adamantyl cation (II) is not the most stable tricyclic $C_{10}H_{15}$ cation *per se*, but it is present in an extremely stable ring system, and the over-all strain or instability of II is at a minimum.

Unlike sulfuric acid systems, which seem to favor ring opening with formation of stable, allylic cations,[5,7] SbF_5 preserves the number of rings in the precursor, and side reactions are unimportant.[3] The present results imply that preparative conditions may be found for the conversion of IV or similar compounds into adamantane derivatives in high yields.

Acknowledgments.—We wish to thank the Alfred P. Sloan Foundation and the Petroleum Research Foundation for support of this research at Princeton University.

(11) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); D. L. Heywood, B. Phillips, and H. A. Stansbury, Jr., *J. Org. Chem.*, **26**, 281 (1961).

(12) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. von R. Schleyer and R. D. Nicholas, *Tetrahedron Letters*, **No. 9**, 305 (1961).

(13) Alfred P. Sloan Research Fellow, 1962–1966.

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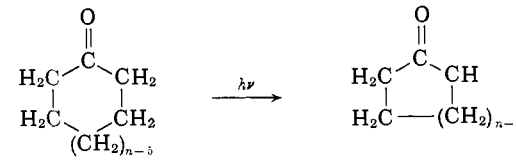
A Novel Photoisomerization Reaction of Cyclic Ketones

Sir:

The photochemistry of the cyclic ketones in the liquid phase has not been systematically studied.[1] For two reasons it can be expected that such a study would prove interesting: (i) the reactions of the cyclic ketones in the gas phase (mainly decarbonylation) are subject to pressure quenching[2] so that in the condensed phase these reactions may be superseded by other processes; (ii) the study of light emission from cyclopentanone[3] in the condensed phase shows the presence of a triplet state which is not observed in the gas-phase photochemistry.

In the course of a systematic study of the photolysis of 5-, 6-, 7-, and 8-membered cyclic ketones as pure liquids, a new photoisomerization reaction has been discovered which is interesting both in its complexity and the nature of the excited state from which it originates. The reaction which can be represented by the general equation (1) has been observed when n = 6, 7,



(1)

and 8 and in 3-methylcyclohexanone. In cyclooctanone, a variant of this reaction gives 2-propylcyclopentanone as well. 3-Methylcyclohexanone gives mostly, if not entirely, 2,4-dimethylcyclopentanone. In all cases the chief product is a condensed material, while isomeric aldehydes are formed in about the same yield as the ring contracted product.

In cyclohexanone reaction 1, which gives rise to 2-methylcyclopentanone, accounts for 6% of the ketone that is photolyzed. In Fig. 1 the yields of 5-hexenal

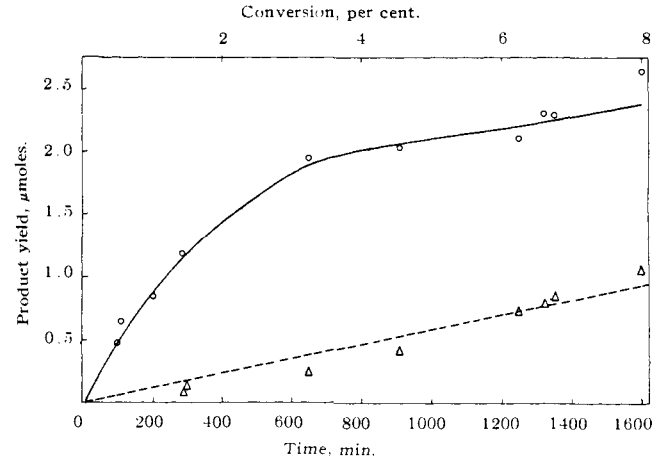


Fig. 1.—Product yields in photolysis of cyclohexanone at 3130 Å. as a pure liquid: open circles, 5-hexenal; open triangles, 2-methylcyclopentanone. Conversion refers to cyclohexanone that had been photolyzed.

and 2-methylcyclopentanone have been plotted as functions of time and per cent conversion. The leveling off in the yield of 5-hexenal may be due to a quenching action by this product on excited cyclohexanone. If

(1) R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(2) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4344, 4348 (1961).

(3) S. R. La Paglia and B. C. Roquitte, *Can. J. Chem.*, **41**, 287 (1963); *J. Phys. Chem.*, **66**, 1739 (1962).