adenosine were condensed according to the general procedure. The deacylation was carried out in 15 *M* methanolic ammonia for 20 hr. and the desired product was obtained in 65% yield using an extinction of 27,100 at 252 mμ (pH 6).

Guanylyl-(3′→5′)-cytidine.—Pyridinium $N^2,O^{2'},O^{5'}$-triacetylguanosine 3′-phosphate and $N,O^{2'},O^{3'}$-tribenzoylcytidine were treated under the standard conditions. After giving the methanolic ammonia treatment for 20 hr. the dinucleoside phosphate was obtained in 26% yield using an extinction of 16,900 at 271 mμ (pH 6).

Guanylyl-(3′→5′)-guanosine.—Pyridinium $N^2,O^{2'},O^{5'}$-triacetylguanosine 3′-phosphate and $N^2,O^{2'},O^{3'}$-triacetylguanosine were condensed by the dicyclohexylcarbodiimide procedure. The deacetylation was carried out in aqueous 7.5 *N* ammonium hydroxide (25 ml.) for 50 hr. at room temperature. The yield was 31%, assuming no hypochromicity for the product.

Guanylyl-(3′→5′)-uridine.—Pyridinium $N^2,O^{2'},O^{5'}$-triacetylguanosine 3′-phosphate and $O^{2'},O^{3'}$-dibenzoyluridine were condensed under the standard conditions. The deacylation was performed with a mixture of aqueous concentrated ammonium hydroxide–pyridine (1:1; 25 ml.) for 35 hr. The desired product was obtained in 78% yield using an extinction of 20,800 at 262 mμ (pH 7). Degradation by the *Lactobacillus acidophilus* R-26 phosphodiesterase[19] was carried out using 10.7 optical density units (at 252 mμ, pH 7) of the dinucleoside phosphate. Paper chromatography of the total incubation mixture in solvent C showed that the starting material was completely degraded to uridine and guanosine 3′-phosphate.

Degradations with the Snake Venom Phosphodiesterase.—Cytidylyl-(3′→5′)-cytidine (0.5 μmole), cytidylyl-(3′→5′)-uridine (0.6 μmole), cytidylyl-(3′→5′)-adenosine (0.3 μmole), and cytidylyl-(3′→5′)-guanosine (0.6 μmole) were each incubated with the purified venom phosphodiesterase preparation[29] using amounts previously standardized.[24] Degradation to the expected nucleosides and nucleoside 5′-phosphates was complete as followed by paper chromatography in the solvent 2-propanol–0.1 *M* boric acid–concentrated ammonia (7:2:1, v./v.). The identity of the nucleoside 5′-phosphates was further confirmed by elution of their spots and subsequent paper electrophoresis at pH 7.1.

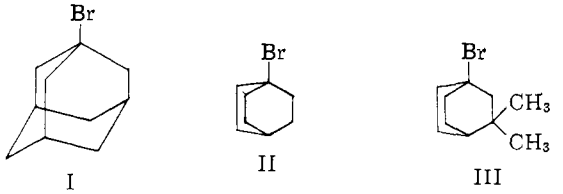
(29) W. E. Razzell and H. G. Khorana, *J. Biol. Chem.*, **235**, 2105 (1959).

COMMUNICATIONS TO THE EDITOR

Bridgehead Adamantane Carbonium Ion Reactivities[1,2]

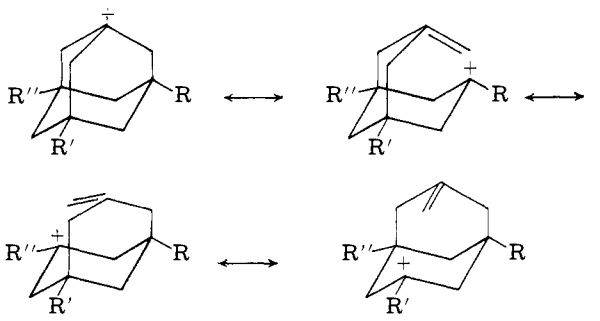
Sir:

Previous investigations have established the unusual bridgehead positions of bridged ring systems toward carbonium ion processes.[2-6] The considerable variation—10^{13}—in solvolysis rates between bridgehead derivatives in different ring systems[2-6] has been attributed to changes in conformational strain factors in proceeding from the ground state to the transition state.[2a,5] Estimates of angle strain provide a satisfactory quantitative explanation for the 10^3 reactivity difference between *t*-butyl bromide and 1-adamantyl bromide (I), but do not account for the further 10^3 difference between I and 1-bicyclo[2.2.2]octyl bromide (II).[5] The geometry around the reaction sites of both I and II is the same, and both would be expected to have nearly the same solvolytic reactivity, on the basis of angle strain considerations.[2-5]

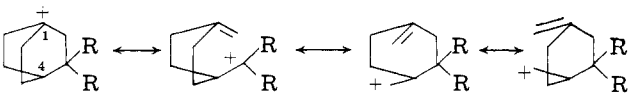


I II III

A possible explanation for the rate spread between I and II is based on electronic differences in the corresponding bridgehead carbonium ions IV and V. The geometry of ions IV and V is ideal for C–C hyperconjugation,[7] which, conceivably, might be of greater importance for IVa (all second degree contributing hyperconjugative forms) than for Va (all first degree contributing hyperconjugative forms). Such hyperconjugation might thus account for the greater reactivity of I over II. Doering and co-workers[4] found that solvolysis of 1-bromo-3,3-dimethylbicyclo[2.2.2]octane (III) was about two times more rapid than that of II; C–C hyperconjugation (compare Va and Vb) might be responsible for the accelerative effect of methyl substituents, since in Vb one of the contributing forms is tertiary.



IVa, R = R′ = R″ = H
b, R = CH_3, R′ = R″ = H
c, R = R′ = CH_3, R″ = H
d, R = R′ = R″ = CH_3



Va, R = H
b, R = CH_3

It has been argued earlier that hyperconjugative differences of this type do not contribute significantly

(1) Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964, Abstracts, p. 22N.

(2) For background details, see (a) R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (b) P. von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 4195 (1964).

(3) Reviews: D. E. Applequist and J. D. Roberts, *Chem. Rev.*, **54**, 1065 (1954); U. Schöllkopf, *Angew. Chem.*, **72**, 147 (1960).

(4) W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher, and W. P. Whelan, Jr., *J. Am. Chem. Soc.*, **75**, 1008 (1953); see M. Finkelstein, Ph.D. Thesis, Yale University, 1955, and ref. 10.

(5) P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961).

(6) H. Stetter, J. Mayer, M. Schwarz, and K. Wulff, *Ber.*, **93**, 226 (1960); H. Stetter and P. Goebel, *ibid.*, **96**, 550 (1963).

(7) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

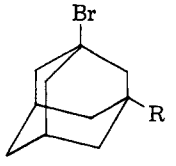
TABLE I
SOLVOLYSIS OF 1-ADAMANTYL BROMIDES IN 80% ETHANOL, 70°

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

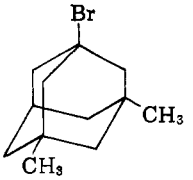
[a] At 75°.[10]

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).

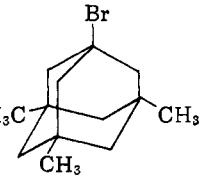
Were the C–C hyperconjugation explanation for the 10^3 solvolysis rate difference between 1-adamantyl bromide (I) and 1-bicyclo[2.2.2]octyl bromide (II) sound, a significant rate enhancement for each methyl substituent in going from 1-adamantyl bromide (I) to its 3-methyl (VIa), 3,5-dimethyl (VII), and 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).

(15) National Science Foundation Predoctoral Fellow, 1963–1964.

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

FRICK CHEMICAL LABORATORY RAYMOND C. FORT, JR.[15]
PRINCETON UNIVERSITY PAUL VON RAGUÉ SCHLEYER[16]
PRINCETON, NEW JERSEY 08540

RECEIVED JULY 23, 1964

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).