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

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

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

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

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

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

azide incorporation than %RN$_3$) is independent of sodium azide concentration. Here k_N and k_W are the second-order rate constants for attack by azide ion and water, respectively, on the appropriate substrate or intermediate.

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

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

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

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

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

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

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

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

(13) National Institutes of Health Postdoctoral Fellows: (a) 1969–1970; (b) 1968–1970; (c) A. B. Thesis, Princeton University, 1970.

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

Sir:

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

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

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

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

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

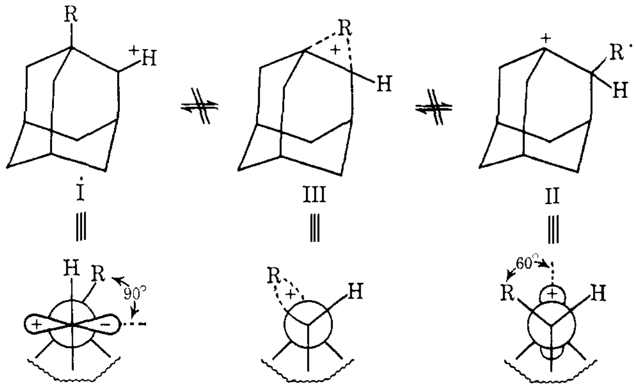
(4) (a) H. Hogeveen and D. M. Brouwer, *Recl. Trav. Chim. Pays-Bas*, in press. We are indebted to Dr. Hogeveen and to Dr. Brouwer for exchanges of information. (b) G. A. Olah, private communication. (c) M. Saunders, private communication.

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

(6) P. v. R. Schleyer, D. J. Raber, L. K. Lam, S. H. Liggero, M. A. McKervey, and J. L. M. A. Schlatmann, *J. Amer. Chem. Soc.*, in press, and references therein cited.

(7) *E.g.*, (a) R. D. Nicholas, Ph.D. Thesis, Princeton University, 1960; (b) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (c) A. Schneider, R. W. Warren, and E. J. Janoski, *J. Org. Chem.*, **31**, 1617 (1966), and unpublished work; (d) P. v. R. Schleyer, G. J. Gleicher, and C. A. Cupas, *ibid.*, **31**, 2014 (1966); (e) K. R. Blanchard, Ph.D. Thesis, Princeton University, 1966; (f) M. A. McKervey, J. R. Alford, J. F. McGarrity, and E. J. F. Rea, *Tetrahedron Lett.*, 5165 (1968); (g) H. W. Geluk and J. L. M. A. Schlatmann, *Recl. Trav. Chim. Pays-Bas*, **88**, 13 (1969).

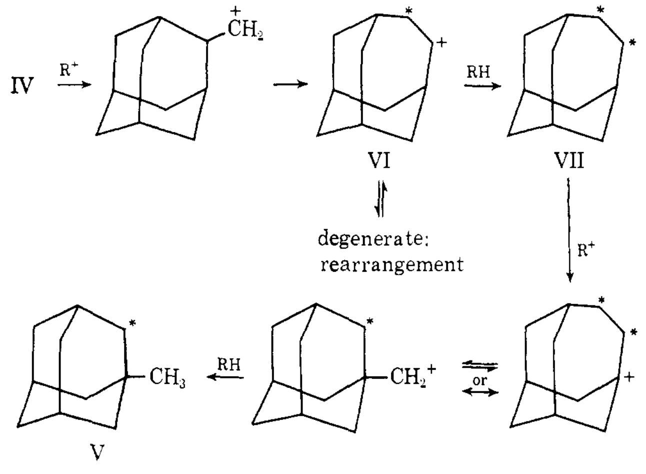
Chart I



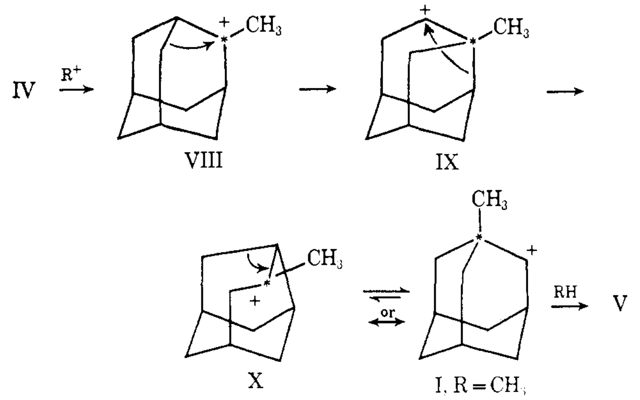
are now known to proceed intermolecularly,[6] but the alkyl shifts pose an unresolved problem. The simplest example is the interconversion of 2-methyl- (IV) and 1-methyladamantane (V),[7a] the thermodynamics of which have been studied in detail.[7e] Equilibrium, established by aluminum halide catalysis, strongly favors the 1-methyl isomer (V) (98% at 25°).[7b,e] An intermolecular methyl-shift mechanism is ruled out because the disproportionation products (*e.g.*, adamantane and 1,3-dimethyladamantane) expected on this basis are not, in fact, observed.[8]

We have now studied the mechanism of the isomerization of 2-methyladamantane (IV) to 1-methyladamantane (V) by means of isotopic labeling in order to distinguish among three types of intramolecular processes: (1) direct 1,2-methyl shift (*via* the sequence IV → II → III → I → V; R = CH_3); (2) ring expansion (*via* VI) to homoadamantane[9a] (VII) followed by ring contraction[9b,c] (Scheme I); (3) skeletal isomerization (a likely route involves rearrangement of VIII to the 4-protoadamantyl cation (IX[10]), a degenerate-type 4-protoadamantyl isomerization (IX → X)),[11] and lastly rearrangement back to the adamantane skeleton, *via* I (R = CH_3)[12] (Scheme II).

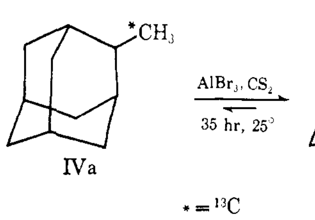
Scheme I



Scheme II



Mechanism 2 would involve scrambling of methyl and ring carbons. This possibility was eliminated by demonstrating that 2-*methyl*-^{13}C-adamantane (IVa)[13] rearranges to 1-*methyl*-^{13}C-adamantane (Va) with no detectable gain of label in the adamantane nucleus.[16]



The direct 1,2-methyl shift process (mechanism 1) was ruled out by ^{14}C ring-labeling results. When 2-methyladamantane-2-^{14}C (IVb)[19] was rearranged, the product was shown to be 1-methyladamantane-1-^{14}C (Vb) *with at least 90 + 3% of the starting activity at the 1 position and none in the methyl group.*[20,24]

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(8) Ethyladamantanes do disproportionate by a mechanism different from those being considered here: A. Schneider and R. W. Warren, *Amer. Chem. Soc., Div. Petrol. Chem. Preprints*, **15** (2), B56 (1970); 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, Abstracts, No. PETR 54.

(9) (a) S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4571 (1969), and references cited therein. (b) Homoadamantane rearranges to the methyladamantanes under the reaction conditions.[7e] (c) The 4-homoadamantyl cation (VI) is known to undergo extensive degenerate rearrangement which would lead to further label scrambling: J. E. Nordlander, F. Wu, S. P. Jindal, and J. B. Hamilton, *J. Amer. Chem. Soc.*, **91**, 3962 (1969); P. v. R. Schleyer, E. Funke, and S. H. Liggero, *ibid.*, **91**, 3965 (1969).

(10) *Cf.* M. L. Sinnott, H. J. Storesund, and M. C. Whiting, *Chem. Commun.*, 1000 (1969); R. E. Hall, A. B. Thesis, Princeton University, 1970.

(11) Demonstrated independently in the methyl-free system; D. Lenoir, to be published.[1]

(12) Ions X and I are in mobile equilibrium or constitute a bridged ion; D. Lenoir, to be published.[1]

(13) Prepared by the Pd–C catalyzed hydrogenation of 2-(*methylene*-^{13}C)adamantane. This olefin was obtained in a yield of 63% by a modified[14] Wittig reaction[15] from adamantanone and triphenyl(*methyl*-^{13}C)phosphine iodide (70% ^{13}C in the starting $^{13}CH_3I$).

(14) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962); R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(15) G. Wittig and U. Schöllkopf, *Org. Syn.*, **40**, 66 (1960).

(16) Analysis by mass spectroscopy. The main fragmentation of 1-methyladamantane (V) involves cleavage of the C–CH_3 bond (*m/e*135 for $M^+ - 15$).[17] The *m/e* 136/(135 + 136) ratio was found to be 0.107 ± 0.002 for unlabeled 1-methyladamantane (V); labeled material (Va), obtained by rearrangement of IVa at room temperature until equilibrium had been reached, gave the same ratio: 0.105 ± 0.002. 1-Methyladamantane-*methyl*-^{13}C, prepared conventionally,[18] also gave the same result.

(17) Z. Dolejšek, S. Hála, V. Hanuš, and S. Landa, *Collect. Czech. Chem. Commun.*, **31**, 435 (1966).

(18) E. Ōsawa, Z. Majerski, and P. v. R. Schleyer, *J. Org. Chem.*, in press.

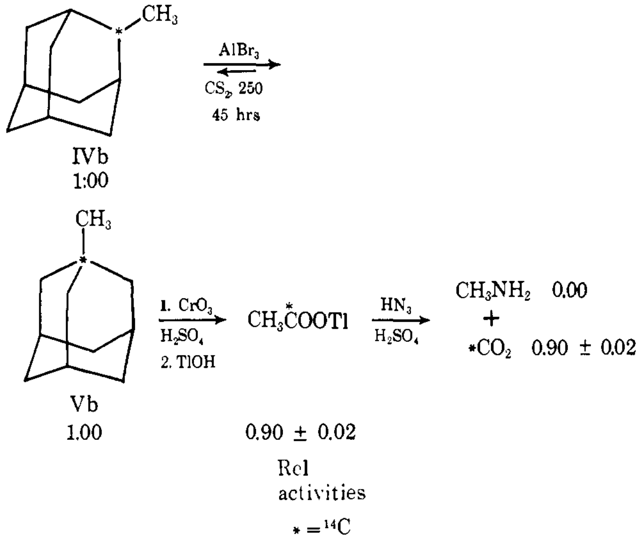
(19) Z. Majerski, A. P. Wolf, and P. v. R. Schleyer, *J. Label. Compounds*, in press.

(20) Analysis by the Kuhn–Roth degradation.[19,21] The yield of acetic acid, isolated as the thallous salt,[22] was 30–40%. Modified Schmidt degradation[19,22] showed the activity to reside exclusively in the carboxyl group.

(21) R. Kuhn and H. Roth, *Ber.*, **66**, 1274 (1933); W. Kirsten and E. Stenhagen, *Acta Chem. Scand.*, **6**, 682 (1952); 2 *M* CrO_3, 3.75 *M* H_2SO_4 at 152° were the conditions used.

(22) Mp 127–127.5°; lit. mp 126.5–127.5°.[23]

(23) A. P. Wolf, C. S. Redvanly, and R. C. Anderson, *J. Amer. Chem. Soc.*, **79**, 3717 (1957).



These results demonstrate that *the methyl group remains attached predominantly to the same carbon atom during the rearrangement of 2-methyladamantane (IV) to 1-methyladamantane (V).* Direct 1,2-methyl shifts (mechanism 3) do not take place to a significant extent. Mechanism 3 involving skeletal rearrangement, however, is perfectly consistent with the labeling patterns observed.[24] It seems probable that this type of mechanism is a general one for many adamantane rearrangements[7] and for those involving molecules not possessing favorable geometry for direct 1,2 shifts.

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[24] Control experiments[25] have shown that not more than 1–3% of label scrambling occurs in the adamantane nucleus during the $AlBr_3$ treatment and the Kuhn–Roth degradation of 1-methyladamantane-*1* (or *2*)-^{14}C.

[25] S. H. Liggero, Z. Majerski, P. v. R. Schleyer, A. P. Wolf, C. S. Redvanly, H. Wynberg, J. A. Boerma, and J. Strating, *J. Label. Compounds*, in press; Z. Majerski, S. H. Liggero, P. v. R. Schleyer, and A. P. Wolf, submitted for publication, and unpublished results.

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Charge-Transfer Photochemistry of Rhodium(III)[1]

Sir:

Although there have been many studies of the photochemistry of cobalt(III) complexes, studies of the rhodium(III) and iridium(III) analogs are rare.[2] Of the existing reports only Moggi's study[3] of $Rh(NH_3)_5Cl^{2+}$ can be regarded as definitive. Much of this previous work has involved irradiation of metal-centered absorption bands and the net photochemical reactions have involved the exchange of coordinated ligands with solvent species.[2–4] To the present there have been no reports of photoredox behavior in rhodium(III) or iridium(III) complexes. In fact there have been some attempts to compare the photochemistry of rhodium(III) and iridium(III) to that of chromium(III), even to the extent of suggesting that rules for predicting photochemical reactions of chromium[2a,5] are also applicable to complexes of these heavier metals.[4] A consideration which heretofore has been neglected is that photoreduction of either rhodium(III) or iridium(III) complexes would produce a pair of *bulk* radicals, the corresponding divalent metallo complex, and an oxidized ligand, which ought to recombine. Thus net product yields are expected to show only ligand exchange and that only to the extent that the divalent complexes may equilibrate during their short lifetimes. No *net* photoreduction should be observed.

We report here our preliminary observations in the first study of the charge-transfer photochemistry of rhodium(III). We have chosen $Rh(NH_3)_5I^{2+}$ for this study because the $I^- \rightarrow Rh(III)$ bands occur at relatively low energy,[6] but also because the primary oxidized product, I, forms a well-characterized easily detected complex ion, I_2^-.[7]

The continuous 254-nm irradiation of $Rh(NH_3)_5I^{2+}$ in the absence of free I^- produces high yields of NH_3[8] and aquated iodoammine complexes of rhodium(III)[9] as well as a small yield of *trans*-$Rh(NH_3)_4I_2^+$ (Table I). In the presence of small amounts of I^- the yields of *trans*-$Rh(NH_3)_4I_2^+$, ϕ_t, and NH_3, ϕ_{NH_3}, are identical within the limits of experimental error. It is very significant that these same products are obtained under conditions where irradiation of I^- produces $e^-(aq)$,[10–12] which can react with nonabsorbing amounts of Rh-

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[1] (a) Support of this research by the National Science Foundation (Grant No. GP 17082) is gratefully acknowledged; (b) presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970.

[2] For recent reviews see (a) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968); (b) D. Valentine, Jr., *Advan. Photochem.*, **6**, 123 (1968); (c) V. Balzani, L. Moggi, F. Scandola, and V. Carassitti, *Inorg. Chem. Acta Rev.*, **1**, 7 (1967); (d) E. L. Wehry, *Quart. Rev., Chem. Soc.*, **21**, 213 (1967).

[3] L. Moggi, *Gazz. Chim. Ital.*, **97**, 1089 (1967).

[4] (a) R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, **90**, 2437 (1968); (b) *Inorg. Chem.*, **8**, 2231 (1969).

[5] A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

[6] C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962.

[7] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957).

[8] W. Bollster, C. Bushman, and P. Tiduell, *Anal. Chem.*, **33**, 592 (1961).

[9] This complex elutes from a cation-exchange resin (Dowex 50 W-2X H^+ form, 200–400 mesh) as a 2+ ion slightly ahead of $Rh(NH_3)_5I^{2+}$. Elemental analysis of the eluted material shows Rh:N:I = 1:3.6:1, indicating a mixture of aquoammine complexes. The spectral maxima of the eluted material are red shifted from those of $Rh(NH_3)_5I^{2+}$.

[10] G. Stein, *Advan. Chem. Ser.*, No. **50**, 230 (1965).

[11] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, **67**, 2613 (1963).

[12] For the conditions of concentration employed in the continuous photolysis of $I^-,Rh(NH_3)_5OH_2^{3+}$ (Table I) one would anticipate some ion-pair formation and probably some ion-pair photolysis. In such case the reactions listed under photoreduction (b) below may be regarded as short circuited; *i.e.*, the photoelectron would not be expected to have a significant lifetime in the bulk solvent. The spectral properties of these systems suggest that I^- is the predominant absorbing species. In the complementary flash-photolysis work $[I^-]$ is necessarily small enough that ion-pair formation is unlikely.