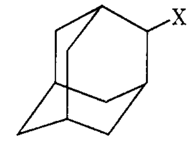
Stereochemical Inhibition of Intramolecular 1,2 Shifts. The Intermolecular Nature of Hydride Shifts in the Adamantane Series[1]

Sir:

Many rearrangements are known involving the interconversion of adamantane derivatives.[2] Reactions in concentrated sulfuric acid are illustrative.[3-6] At 28°, 2-adamantanol (Ia) is converted to an equilibrium mixture containing >98% 1-adamantanol (IIa).[3b,4] This isomerization forms one of the mechanistic bases for the preparation of adamantanone by the reaction of adamantane with sulfuric acid at 77°.[3a,b] 2-Methyl-2-adamantanol (IIIa) undergoes extensive isomerization in concentrated H_2SO_4.[3c,5] At room temperature or below, 2-methyl-1-adamantanol (IVa) and the syn and anti isomers of 4-methyl-1-adamantanol (Va) are the major products. Under these conditions IVa and the Va isomers equilibrate rapidly. At higher temperatures IIIa gives other products such as 3-methyl-1-adamantanol and 5-methyl-2-adamantanone, in which both alkyl and oxygen functions have shifted. Rearrangements are also observed[6] during Koch-Haaf reactions,[7] carried out in sulfuric acid. Thus, Koch-Haaf reaction of IIIa gives the kind of rearranged (IVb, Vb) and unrearranged products (IIIb)[8] as are found (IIIa-Va) from isomerization.



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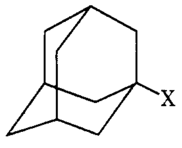

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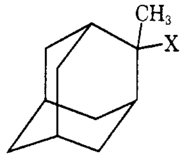

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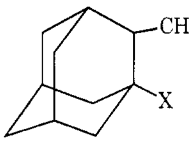

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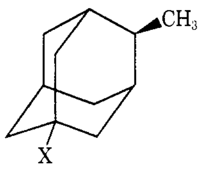
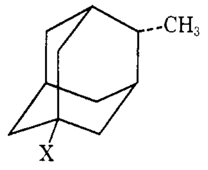


syn-V

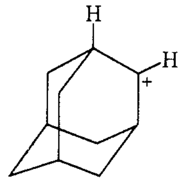


anti-V

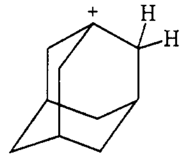
series a, X = OH; series b, X = CO_2H

These rearrangements have appeared to involve simple intramolecular 1,2-hydride shifts (VI → VII). We now wish to show that these hydride shifts are, in fact, intermolecular since they can be prevented by the use of sufficiently dilute reaction conditions. Intramolecular rearrangements are first order in substrate, and should be concentration independent. Intermolecular hydride shifts are second order, and should be highly concentration dependent.

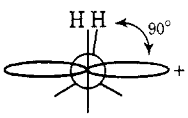
Intramolecular 1,2 shifts should be strongly inhibited on the adamantane nucleus.[1,8a] Carbonium ion rearrangements should be most facile when the vacant orbital and the C–R bond (where R is the migrating group) are coplanar, *i.e.*, a 0° dihedral angle exists. In VI this angle is 90°, the worst possible angle; in VII the angle of 60° is almost as bad. The twisted transition state connecting VI and VII should be highly unfavorable. For these reasons, the preferred mechanism for interconverting various bridgehead and bridge adamantyl cations is intermolecular, not intramolecular. There is already considerable evidence (*e.g.*, in the formation of disproportionation products) that such intermolecular hydride shifts occur readily in the adamantane series.[3,5,9]

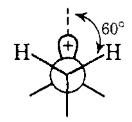


VI



VII





In 1967 Landa, Burkhard, and Vais reported that the Koch–Haaf reaction on 2-adamantanol (Ia) gave the unrearranged 2-adamantane carboxylic acid (Ib).[6a] We had already studied this reaction, but in our hands the product was the *rearranged* acid IIb. Exchange of correspondence and further experiments revealed that the cause of this discrepancy was not the SO_3 content of the sulfuric acid employed,[10] but rather the total amount of acid relative to the reactants.[6b] In other words, *the dilution was the key reaction variable.* Our results, combined with Landa's,[6b] revealed the following dilution dependence. When 1 g of 2-adamantanol (Ia) was treated with HCOOH, the fraction of 1-acid (IIb) depended on the volume of 96% H_2SO_4 used: 30 ml gave *ca.* 100% IIb; 52 ml, 35%; 300 ml, 14%; and 1000 ml, 0.5%. The isomerization reaction of Ia and IIa is similarly concentration dependent. At a concentration of 0.8 *M*, a solution of either Ia or IIa in 96% sulfuric acid is converted to the equilibrium mixture (1.2–1.4% Ia and 98.6–98.8% IIa) within several minutes. Using a concentration of 0.004 *M* no rearrangement of IIa to Ia was found, and only a partial conversion (66%) of Ia to IIa took place. When the concentration was further reduced to 0.0004 *M*, no conversion of Ia to IIa was observed.

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(1) Presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970, Abstracts, No. PETR 040, 051, and 052. Also see P. v. R. Schleyer, *Angew. Chem.*, **81**, 539 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 529 (1969).

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

(3) (a) H. W. Geluk and J. L. M. A. Schlatmann, *Chem. Commun.*, 426 (1967); (b) *Tetrahedron*, **24**, 5361 (1968); (c) *Recl. Trav. Chim. Pays-Bas*, **88**, 13 (1969).

(4) *Cf.* Sun Oil Co., Netherlands Patent Application 6,511,851; *Chem. Abstr.*, **65**, 3768*b* (1966).

(5) M. A. McKervey, J. R. Alford, J. F. McGarrity, and E. J. F. Rea, *Tetrahedron Lett.*, 5165 (1968).

(6) (a) S. Landa, J. Burkhard, and J. Vais, *Z. Chem.*, **7**, 388 (1967); (b) J. Burkhard, J. Vais, and S. Landa, *ibid.*, **9**, 29 (1969); (c) J. Vais, J. Burkhard, and S. Landa, *ibid.*, **9**, 268 (1969).

(7) H. Koch and W. Haaf, *Org. Syn.*, **44**, 1 (1964).

(8) Landa, *et al.*,[6c] did not detect IIIb among the Koch–Haaf products of IIIa. Their chemical method of analysis converted IIIb to 2-ethylideneadamantane by rearrangement, rather than to 2,2-dimethyladamantane, which they expected. We have identified IIIb as a normal component of the mixture of acids from IIIa.

(8a) NOTE ADDED IN PROOF. This conclusion has also been reached independently by D. M. Brouwer and H. Hogeveen (*Recl. Trav. Chim. Pays-Bas*, **89**, 211 (1970)), based on the lack of line broadening in the nmr spectrum of the stable 1-adamantyl cation. Similar nmr observations have been made by G. A. Olah and by M. Saunders, private communications.

(9) (a) H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5369 (1968); (b) H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968); (c) unpublished observations.

(10) *Cf.* R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 6332 (1959); P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *ibid.*, **87**, 2590 (1965).

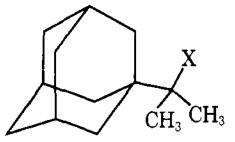
Table I. Effect of Dilution on Koch–Haaf Reaction Products

Starting material	Prod dist from higher concn (%)	Prod dist from dilute condn (%)
2-Adamantanol (Ia)	IIb[a]	Ib[a]
2-Methyl-2-adamantanol (IIIa)	IIb (6) IVb (56) Vb (38)	IIIb (>97)
2-Methyl-1-adamantanol (IVa)	IIIb (8) IVb (60) Vb (32)[b]	IVb (>97)
4-Methyl-1-adamantanol (Va)	IIIb (7) IVb (29) Vb (64)	Vb (>97)[b]
Dimethyl-(1-adamantyl)carbinol (VIIIa)	IXb only	VIIIb (87) IXb (13)

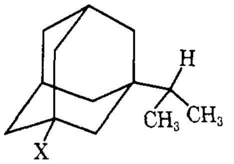
[a] Relative amounts of 1- and 2-acids depend on concentration. See text and ref 6b. [b] The syn:anti ratio was 1:1 in each case.

By the use of high dilution conditions, the rearrangements summarized in Table I could be prevented. It was often necessary to use a very large relative amount of sulfuric acid to accomplish this end. It was also sometimes necessary (and frequently more convenient) to use an immiscible cosolvent such as CCl_4 in order to obtain the necessary high dilutions for these Koch–Haaf reactions. In this modification, the substrate (and HCOOH) in CCl_4 are added slowly to a well-stirred mixture of H_2SO_4 and CCl_4; slow diffusion of the organic material from CCl_4 to H_2SO_4 helps to accomplish the desired result.

It is possible to avoid the mixture of acids (IIIb–Vb) obtained from IIIa;[6c,8] high dilution conditions give IIIb. Similarly, the isomeric alcohols IVa and Va can quite cleanly be transformed to the corresponding acids IVb and Vb without rearrangement. Other rearrangements can also be prevented, for example the Koch–Haaf conversion of VIIIa to IXb.[11] By the use of the CCl_4 procedure, a product containing a 7:1 ratio of VIIIb:IXb is obtained.



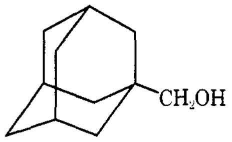
VIII



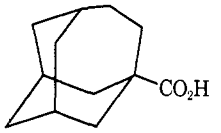
IX

a, X = OH
b, X = CO_2H

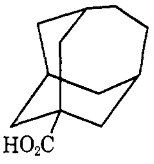
The product from 1-adamantylcarbinol (X) under ordinary Koch–Haaf conditions is not just 3-homoadamantanecarboxylic acid (XI) as believed earlier,[12] but is rather a mixture of the 3-acid (XI) and what appears to be the 1-acid (XII).[13]



X



XI



XII

Although we have other evidence (*e.g.*, disproportionation products) to support our claim that the mechanisms summarized in Table I involve intermolecular hydride transfers, the effect of dilution alone would seem to establish the point. It is possible that at least some of the many rearrangements involving apparent hydride shifts, reported over the years, may not have been intramolecular as supposed.[14] Dilution studies afford a convenient method for determining the molecularity of such processes.

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[11] (a) R. C. Fort, Jr., Ph.D. Thesis, Princeton University, 1964; see R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966); (b) J. Weber, Dissertation, Aachen, 1966.

[12] H. Stetter and P. Goebel, *Chem. Ber.*, **96**, 550 (1963); H. Stetter, M. Schwarz, and A. Hirschhorn, *ibid.*, **92**, 1629 (1959).

[13] According to a recent report (F. N. Stepanov and S. S. Gutz, *Zh. Org. Khim.*, **4**, 1933 (1968); *Chem. Abstr.*, **70**, 28456 (1969)) the Koch–Haaf product could be converted electrolytically to 1-methoxyhomoadamantane. Although these authors believed that this product arose by rearrangement during the electrolysis, it seems more likely on the basis of the present work that the rearrangement (*via* intermolecular hydride shifts) occurred during the Koch–Haaf reaction of X. The presence of XII in the Koch–Haaf product would be expected to yield the observed 1-methoxyhomoadamantane without rearrangement.

[14] *Cf.*, *e.g.*, H. Van Bekkum, B. Van De Graaf, G. Van Minnen-Pathuis, J. A. Peters, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **89**, 521 (1970).

[15] National Institutes of Health Postdoctoral Fellows (a) 1968–1970; (b) 1967–1969.

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Bicyclo[2.1.0]pent-2-ene. ${}^6J_{HH}$ Spin–Spin Coupling in the Cyclopentadiene Diels–Alder Adduct[1]

Sir:

Bicyclo[2.1.0]pent-2-ene, first prepared in 1966 by Brauman, Ellis, and van Tamelen,[2] may now be secured in quantities sufficient for synthetic utilization.[3] During our initial studies with this strained olefin, we encountered and characterized the major cycloadduct it forms with cyclopentadiene.

Solutions of bicyclopentene and cyclopentadiene at 0° for 24 hr, after concentration, vacuum distillation, and purification by glpc, afford a $C_{10}H_{12}$ product (C, 90.81; H, 9.08; m/e 132, base peak m/e 66) showing nmr absorptions centered at δ 6.19 (2), 2.81 (2), 2.09 (2), 1.59 (1), 1.13 (3), and 0.81 (2) ppm. The adduct

[1] Supported in part by National Science Foundation Grant No. GP-9259, Cities Service Oil Co., and the Petroleum Research Fund of the American Chemical Society.

[2] J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, **88**, 846 (1966).

[3] A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., submitted for publication. Synthetic chemistry based on bicyclo[2.1.0]pent-2-ene has up to now been limited to conversions to bicyclopentane and bicyclopentane-2,3-d_2: P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **90**, 4746 (1968); **91**, 1684 (1969).