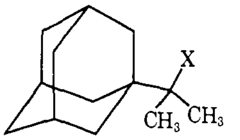
Table I. Effect of Dilution on Koch–Haaf Reaction Products

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)

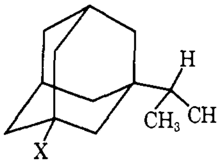
[a] Relative amounts of 1- and 2-acids depend on concentration. See text and ref 6b. [b] The syn : anti ratio was 1 : 1 in each case.

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.



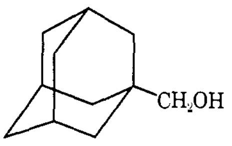
VIII



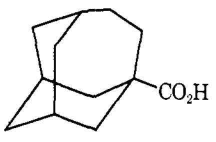
IX

a, X = OH
b, X = CO_2H

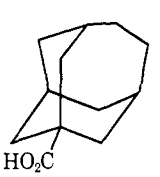
The product from 1-adamantylcarbinol (X) under ordinary Koch–Haaf conditions is not just 3-homoadamantanecarboxylic acid (XI) as believed earlier,[12] but is rather a mixture of the 3-acid (XI) and what appears to be the 1-acid (XII).[13]



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

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[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).

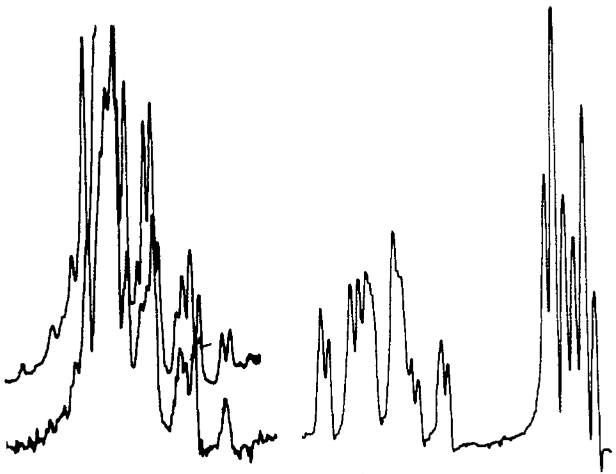
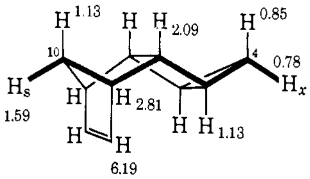
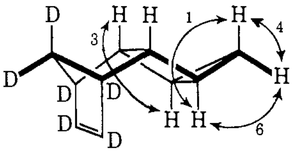


Figure 1. Nmr spectra at 100 MHz of the C(4)-H proton absorptions in tetracyclodecene 1 (left, above), tetracyclodecene-d_6 2 (left, below), and tetracyclodecane 3 (right).

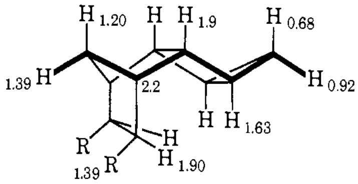
from bicyclopentene and cyclopentadiene-d_6[4] has peaks at δ 2.09 (2), 1.13 (2), and 0.81 (2). Analysis of these spectra, and consideration of the nmr characteristics of bicyclopentane,[5] norbornene,[6] and substituted norbornenes,[7] lead unambiguously to the stereochemical, chemical-shift, and coupling-constant assignments shown (**1**, **2**). The striking +0.5-ppm chemical-shift change of the cyclopropyl methine protons on going to the dihydro or dideuterio analogs **3** or **4** further supports the stereochemical assignment of the Diels–Alder adduct as the *endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]-dec-8-ene **1**.



1



2

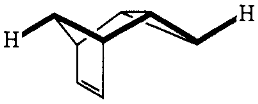


3, R = H
4, R = D

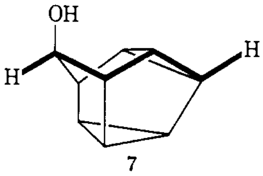
Differences in the nmr spectra of adducts **1** and **2** (Figure 1, left), even at 100 MHz,[8] contain unmistakable evidence for an apparently unprecedented proton–proton spin–spin coupling of 1 Hz over six saturated bonds between C(4)–H_x and one of the two unique protons in the cyclopentadiene-derived half of **1**. Spin-tickling experiments suggested that C(10)–H_s was responsible for the coupling. The derivatives **3** and **4** showed the same long-range coupling. Detailed analysis of both C(10)-H resonance patterns in **3** and **4** made possible a conclusive assignment: C(10)–H_s coupled to C(4)–H_x, ^6J = 1 Hz. In Figure 1 (right), the nmr pattern for the cyclopropyl methylene protons in **3** makes clear the stereochemical specificity of the long-range coupling. The upfield proton, C(4)–H_n, appears as a doublet of triplets thanks to coupling interactions with C(4)–H_x and the C(3,5) protons. The downfield cyclopropyl methylene proton in **3** shows the same pattern but with each line further split into a doublet.

The stereochemical trend set by significant spin–spin couplings over four saturated bonds involving protons in an ╱╲╱╲ or ╲╱╲╱ arrangement, as in bicyclobutane (**5**),[9,10] and over five saturated bonds in a ╲╱╲╱╲ geometry, as in structures **6**[11] and **7**,[12] may be extrapolated one step further along the zigzag path to reach the ╲╱╲╱╲╱ relationship present in structures **1**, **3**, and **4** which show the 1-Hz ^6J coupling.

5



6



7

The ^6J examples here reported, and the association of long-range spin–spin interactions with multiple coupling paths[11,13] through ring-strained rigid moieties[14] fixing protons at the ends of zigzag coplanar arrays of saturated bonds, are fully consistent. The examples contrast with expectations based on "through space" coupling mechanisms[15] and the proposition that ^6J couplings will generally be small.[16]

Other systems we expect to show ^6J and still longer range spin–spin nmr interactions, and other aspects of the chemistry of bicyclopentene, are being investigated.[17]

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(4) Obtained following the procedure suggested by C. A. Stewart, Jr.

(5) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, 702, 1 (1967).

(6) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, 90, 3721 (1968); A. P. Marchand and J. E. Rose, *ibid.*, 90, 3724 (1968).

(7) H. E. Simmons, *ibid.*, **83**, 1657 (1961); J. C. Davis, Jr., and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

(8) Nmr spectra of these adducts at 220 MHz, recorded at the National Science Foundation Grant No. GP-8540 supported regional HR-220 facility at the California Institute of Technology, Pasadena, Calif., confirmed chemical-shift and coupling-constant assignments based on 100-MHz data.

(9) K. B. Wiberg, G. M. Lampman, R. P. Cuila, D. S. Conner, P. Schertler, and J. Laranish, *Tetrahedron*, **21**, 2749 (1965).

(10) S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969).

(11) K. Tori and M. Ohtsuro, *Chem. Commun.*, 886 (1966).

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(17) See also J. E. Baldwin, R. K. Pinschmidt, Jr., and H. A. Andrist, *ibid.*, **92**, 5249 (1970); S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *ibid.*, **92**, 5260 (1970).

(18) National Institutes of Health Predoctoral Fellow, 1968–1970.

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