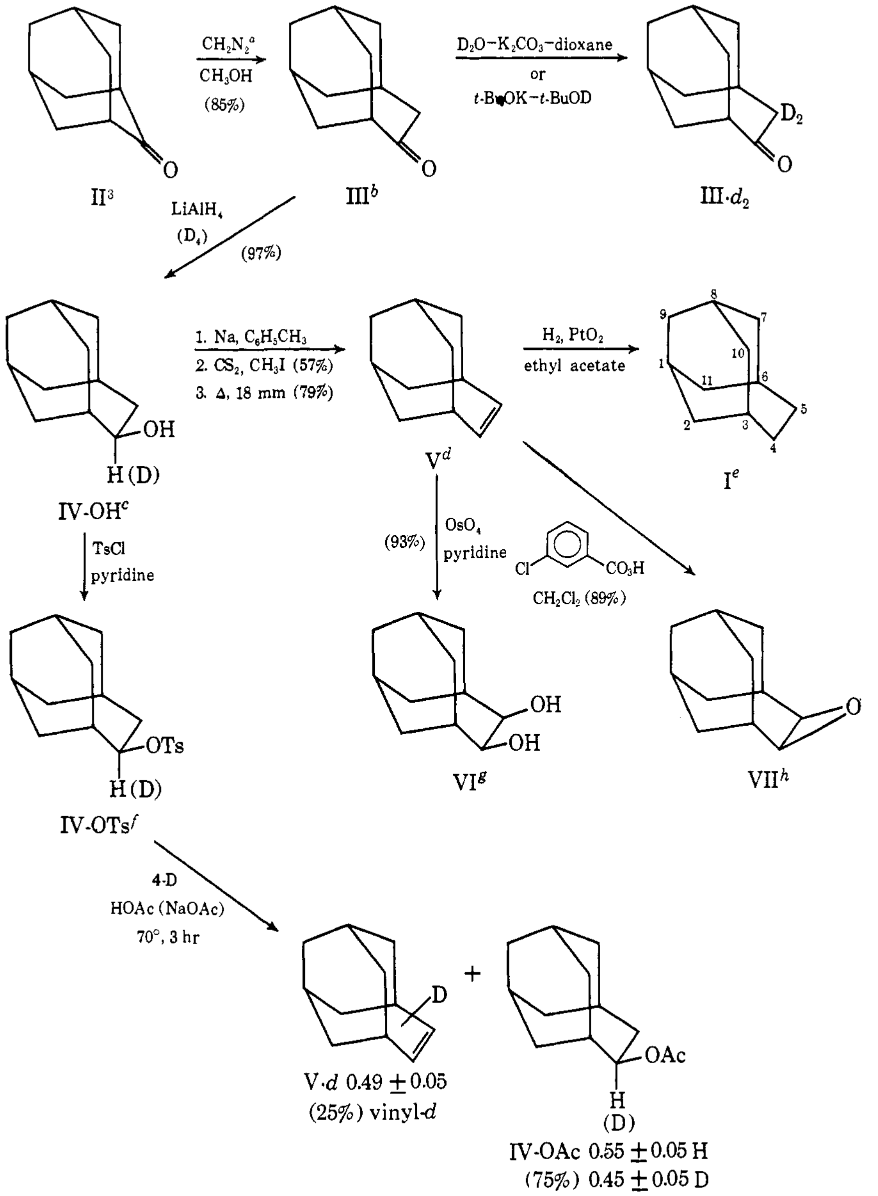
Homoadamantane. I. A New Synthesis. Conformational Evidence. The Degenerate 4-Homoadamantyl Cation

Sir:

Despite its close relationship to diamondoid molecules, homoadamantane (I)[1] has been little studied; bridgehead-substituted compounds are virtually the only derivatives which have been described.[1,2] We have found that simple diazomethane ring homologation of adamantanone (II)[3] gives an 85% yield of 4-homoadamantanone (III)[4] and provides an easy route to derivatives of homoadamantane substituted on the ethylene bridge and to homoadamantane (I) itself. An outline of the experiments we have performed is given in Chart I.

Chart I



[a] *In situ* generation from N-methyl-N-nitroso-*p*-toluenesulfonamide ("Diazald"); *cf.* T. J. deBoer and H. J. Backer, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 225. [b] ν_{CO} 1697 cm^{-1} (CCl_4); mp 270–271.5°; oxime mp 146.5–148°. [c] Mp 269.5–270.5°. [d] Mp 237–238°; ir (CCl_4) 1650, 715 cm^{-1}; nmr (CCl_4) δ 1.68 (10 H, m), 2.0–2.5 (4 H, m), 6.10 (2 H, d of d, $J = 6.1, 3.5$ Hz). [e] Identical with authentic sample.[1] [f] Mp 71–73°; acetolysis rate constants: 50.3°, 2.87×10^{-4} sec^{-1}; 76.6°, 4.28×10^{-3} sec^{-1}; $\Delta H^{\ddagger} = 22.4$ kcal/mole; $\Delta S^{\ddagger} = -5.6$ eu. [g] Mp 287–293°; ν_{OH} 3634, 3545 cm^{-1}. [h] Mp 300–301°; nmr (CCl_4) δ 1.5–2.0 (12 H, m), 2.2–2.6. (2 H, broad s), 2.92 (2 H, m).

A conformational problem exists in homoadamantane: is the ethylene bridge twisted or not?[2c,6]

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(1) H. Stetter and P. Goebel, *Chem. Ber.*, **96**, 550 (1963); H. Stetter and E. Rauscher, *ibid.*, **93**, 1161 (1960); H. Stetter, M. Schwarz, and A. Hirschhorn, *ibid.*, **92**, 1629 (1959).

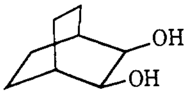
(2) Review: R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964). (In this review, homoadamantane (tricyclo[4.3.1.1^{3,8}]undecane) was misnumbered. The correct numbering is shown in I.) For references to more recent work see; (a) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, **88**, 4475 (1966); (b) K. R. Blanchard, Ph.D. Thesis, Princeton University, 1966; *Diss. Abstr.*, **28**, 1848B (1967); (c) G. J. Gleicher and P. von R. Schleyer, *ibid.*, **89**, 582 (1967); (d) F. N. Stepanov and S. S. Guts, *Zh. Org. Khim.*, **4**, 1933 (1968); (e) M. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (f) B. R. Vogt, *Tetrahedron Letters*, 1579 (1968).

(3) H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5361, 5369 (1968).

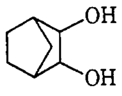
(4) We have been informed of similar[5a] and alternative syntheses[5b] of III.

(5) (a) M. J. T. Robinson, private communication; (b) J. E. Nordlander, F. Y.-H. Wu, and S. P. Jindal, *J. Am. Chem. Soc.*, **91**, 3962 (1969).

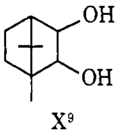
Dreiding models, which overemphasize angle strain, favor a twisted (C_2) conformation, while computer conformational analysis calculations indicate that the untwisted (C_{2v}) structure should be more stable.[2c] To gain information on this point, *cis*-4,5-homoadamantanediol (VI) was prepared from the interesting olefin, 4-homoadamantene (V). The large magnitude of the infrared intramolecular hydrogen bonding spectral shift ($\Delta\nu$ = 89 cm^{-1}; *cf.* model compounds VIII–X)[9] of this diol indicates a very low value for the dihedral angle; the preferred conformation in homoadamantane (I) is essentially untwisted.[6,9]



VIII[6,9]



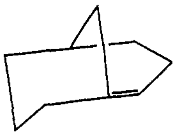
IX[9]



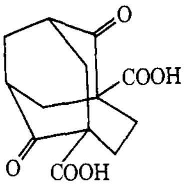
X[9]

	VIII[6,9]	IX[9]		X[9]
$\Delta\nu$, cm^{-1}	83	103	*exo,cis*	90, 91, 96
		102	*endo,cis*	95, 95

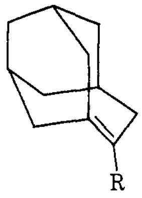
Recent successful preparations of the "anti-Bredt's rule" olefin, bicyclo[3.3.1]non-1-ene (XI),[10] and the successful bisdecarboxylation of the homoadamantanedionedicarboxylic acid XII[2f] prompted an attempt to find evidence for 3-homoadamantene (XIII, R = H) or more precisely the corresponding enol (XIII, R = O$^-$), which models indicate not to be impossibly strained.



XI



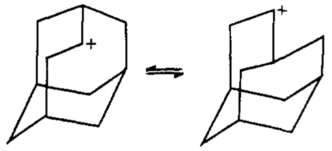
XII



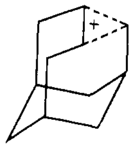
XIII

4-Homoadamantanone (III) readily underwent hydrogen–deuterium exchange at the methylene group adjacent to the carbonyl group (to give III-d_2) under mild conditions (K_2CO_3–D_2O–dioxane), but further exchange could not be effected even by use of KOC(CH_3)$_3$ in DOC(CH_3)$_3$. Nmr and mass spectral analysis confirmed that bridgehead deuteration had not taken place under these conditions. These results show that structures of type XIII, if accessible at all, will be highly strained species.[11]

Because of the possibility of degenerate Wagner–Meerwein (and hydride shift)[12] rearrangements, 4-homoadamantyl cation chemistry is especially intriguing. Degenerate classical cation interconversions (XIV) or bridged ion formation (XV) are possible.



XIV



XV

The preparative acetolysis of 4-homoadamantyl-4-*d* tosylate (IV-OTs-4*d*) was carried out at 70° for 3 hr in the presence of excess sodium acetate. The deuterium-labeling pattern in the products was determined by repetitive nmr integration. 4-Homoadamantyl acetate (IV-OAc), 75% of the product, displayed 0.55 ± 0.05 of a C*H*OAc signal, while homoadamantene (V-*d*) (25%) integrated for 1.51 ± 0.05 vinyl hydrogen atoms. Mass spectral analysis on both products showed that very little, if any, deuterium had been lost during solvolysis. These scrambling results, within experimental error, can be accommodated by formulations XIV or XV.[13]

From measured acetolysis rate constants (Chart I), a value of 1.38×10^{-5} sec^{-1} (unbuffered) for 4-homoadamantyl tosylate (IV-OTs) was calculated at 25°. By using the Foote–Schleyer relationship[14] (ν_{CO} 1697 cm^{-1} for 4-homoadamantanone (III); dihedral angles ϕ = 0 and 60°) it can be estimated that 4-homoadamantyl tosylate (IV-OTs) reacts some 20 times *slower* than expected, even when the nonbonded strain relief term is omitted. Any strain relief of IV-OTs on solvolysis would make the agreement between calculated and observed values even worse. Such negative deviations from the Foote–Schleyer relationship[14] are rare;[15] steric hindrance to ionization may be a cause,[16] but other factors may be involved.

Because canceling effects may be present, nonclassical ion (XV) formation cannot definitely be ruled out. However, the evidence currently available—deuterium scrambling and the apparent absence of rate enhancement—can satisfactorily be accommodated by the intermediacy of rapidly equilibrating ions XIV. We are obtaining additional data to help differentiate between these possibilities.

Acknowledgments. We are especially indebted to Professor J. E. Nordlander for advising us of his work[5b] and for graciously agreeing to simultaneous publication. Support of this research was through grants from

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[6] A similar conformational problem exists with bicyclo[2.2.2]octane, where twisted (D_3) and untwisted (D_{3h}) conformations are possible.[2c] The latest X-ray evidence on bridgehead bicyclooctyl derivatives indicates untwisted[7] or slightly twisted[8] forms to be favored

[7] O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968).

[8] A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc.*, *B*, 1249 (1968).

[9] Review: M. Tichyy in "Advances in Organic Chemistry: Methods and Results," Vol. 5, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., John Wiley & Sons, Inc., New York, N. Y., 1965, p 115. Also see L. P. Kuhn, P. von R. Schleyer, W. F. Baitinger, Jr., and L. Eberson, *J. Am. Chem. Soc.*, **86**, 650 (1964), and references therein cited.

[10] J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967); J. R. Wiseman, *ibid.*, 89, 5966 (1967); P. M. Lesko and R. B. Turner, *ibid.*, **90**, 6888 (1968).

[11] Bicyclo[3.3.1]nonan-2-one exchanges the bridgehead hydrogen for deuterium with 0.1 *M* NaOD in D_2O at 95° (J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965)).

[12] Nordlander[5b] has presented a thorough analysis of the consequences of these degenerate rearrangements.

[13] Our experimental results are generally in excellent agreement with those of Nordlander,[6b] but his group finds slightly more deuterium scrambling in the acetate product (IV-OAc) (61.0 ± 0.8%, at 40° *vs.* 55 ± 5%, at 70°), and hydride shifts are considered to occur.[12] After submission of this paper we have investigated this problem further, and additional results are in hand. Acetolysis of 4-homoadamantyl-5,5-d_2 tosylate and 4-homoadamantyl-4,5,5-d_3 tosylate provides supporting evidence for a minor reaction pathway involving hydride shifts in addition to the predominate Wagner–Meerwein path. These results will be reported in full later.

[14] C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

[15] *Cf.* P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964).

[16] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966); H. C. Brown and S. Ikegami, *J. Am. Chem. Soc.*, **90**, 7122 (1968); S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

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Free-Radical Intermediates in the Reactions of Organolithium Reagents with Alkyl Halides[1]

Sir:

It is recognized that the reaction of numerous organometallic reagents with alkyl halides can proceed by electron transfer (reaction 1).[2] Among the experi-

$$R^-M^+ + R'X \longrightarrow R\cdot + R\cdot' + MX \qquad (1)$$

mental observations supporting these conclusions are (a) the formation of 2,3-dimethyl-2,3-diphenylbutane in the presence of cumene,[3] (b) the formation of trityl radical from trityl chloride,[4] (c) nuclear polarization in the olefinic products[5] or in the alkyl halide,[6] and (d) the formation of the expected coupling and disproportionation products of R· and R·′.[3,7] Evidence for radical intermediates is particularly compelling for the reactions of organolithium reagents,[3-7] even though an analysis of the reaction products is complicated by the occurrence of metal–halogen interchange,[8] a process that may itself occur *via* radical intermediates.

We now present direct evidence for radical formation in the reaction between alkyl halides and alkyllithium reagents. We have found that free radicals are easily detected by esr spectroscopy in the reaction between organolithium reagents and bromine, iodine, alkyl bromides, or alkyl iodides in benzene solutions containing ether or tetramethylethylenediamine at a concentration approximately equal to that of the lithium reagent.[9] Detection of radicals was possible in a standard flow system approximately 0.03 sec after mixing solutions of the alkyl halide (0.2 *M*) and lithium reagent (0.1 *M*). The reaction of *n*-butyllithium with ethyl, *n*-propyl, *n*-butyl, *n*-octyl, isopropyl, or *t*-butyl iodide furnished the spectrum of the alkyl radical derived from the iodide (Figure 1). Free radicals are therefore detected before an appreciable amount of metal–halogen interconversion has occurred. In the reaction with bromine or iodine the *n*-butyl radical was detected from *n*-butyllithium only after the color of the halogen had been discharged, and the radical observed quite likely reflects the subsequent reaction between the organolithium reagent and the first-formed alkyl halide.

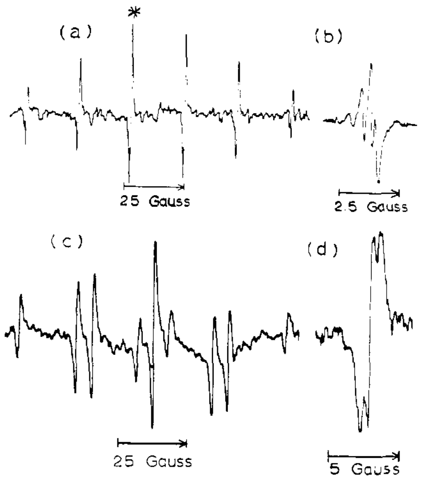

Figure 1. (a) *t*-Butyl radical prepared by the reaction of *n*-butyllithium with *t*-butyl iodide. Only the central six lines of a ten-line pattern are shown, $a^H = 22.8$ G; (b) second-order splitting of the starred peak in (a); relative intensities are roughly 1:8:27:48:42 (see R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962)); (c) *n*-butyl radical prepared by the reaction of *n*-butyllithium with *t*-butyl bromide, $a_{C-1}^H = 21.7$, $a_{C-2}^H = 27.6$ g; (d) central line of (c) under higher resolution, $a_{C-3}^H \approx 0.5$ G.

Isobutyl and *t*-butyl bromides, ethylene dibromide, or benzyl chloride reacted with *n*-butyllithium to give only the esr spectrum of the *n*-butyl radical (Figure 1); *sec*-butyllithium and ethyl bromide yielded a mixture of the two radicals.

The results obtained from our studies of the reaction of alkyl halides with organolithium reagents suggest a simple rationalization in terms of reactions 1–4.[10] We presume that the ether or amine is required to increase the rate of reaction 1 and therby increase the steady-

$$R\cdot + R'X \longrightarrow RX + R\cdot' \qquad (2)$$

$$R\cdot' + RLi \longrightarrow R'Li + R\cdot \qquad (3)$$

$$R\cdot + R\cdot' \longrightarrow \text{alkanes and alkenes} \qquad (4)$$

state concentration of radicals. The effect of the cosolvent may be to dissociate the polymeric organolithium reagent by functioning as a Lewis base. Alternately, the cosolvent may be more intimately involved in the electron-transfer reaction.[9] The nature of the radicals that we have observed seems to be correlated by the relative rates of the atom-transfer reactions 2 and 3. When X = iodine, R = *n*-butyl, and R′ = ethyl, propyl, butyl, etc., the relative rates of reactions 2 and 3 lead to $[R\cdot']/[R\cdot] > 20$. On the other hand, when X = bromine or chlorine, either R· or a mixture of R· and R·′ was observed. These results apparently reflect the fact that k_2 is much greater for alkyl iodides than for alkyl bromides or chlorides.[11] The factors controlling

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(1) Electron Transfer Processes. X. This work was supported by a grant from the National Science Foundation.

(2) See G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **86**, 1807 (1964), for pertinent references.

(3) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

(4) J. Schmidlin, *Chem. Ber.*, 43, 1137 (1910); F. S. D'yachkovskii, N. N. Bubnov, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **123**, 870 (1958).

(5) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

(6) A. R. Lepley, *Chem. Commun.*, 64 (1969); A. R. Lepley and R. L. Landau, *J. Amer. Chem. Soc.*, **91**, 748 (1969); H. R. Ward, R. G. Lawler, and R. A. Cooper, *ibid.*, **91**, 746 (1969).

(7) R. C. Fuson, *ibid.*, 48, 2681 (1926); C. S. Marvel, F. D. Hager, and D. D. Coffman, *ibid.*, **49**, 2323 (1927); F. S. D'yachkovskii and A. E. Shilov, *Russ. Chem. Rev.*, **35**, 300 (1966); D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963).

(8) R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

(9) See J. F. Eastham and G. W. Gibson, *J. Amer. Chem. Soc.*, **85**, 2171 (1963); C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965); **88**, 5668 (1966).

(10) Additional intermediates such as $RI\cdot^-$, $R_nLi_{n-1}\cdot$, RIR, can be imagined. Our results do not require these intermediates since the radicals we observe have hfsc similar to those reported for radicals formed by the radiolysis of alkanes: R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(11) For example, the methyl radical at 65° abstracts the halogen atom from methyl iodide 7000 times more readily than from methyl bromide: F. W. Evans and M. Szwarc, *Trans. Faraday Soc.*, **57**, 1905 (1961). The difference in energy of activation for attack on iodine or bromine is approximately one-half the difference in bond dissociation energies: M. Szwarc, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 91.