FRAGMENTATION AND RING CLOSURE IN THE DIAMANTANE SYSTEM.

PROTODIAMANTANF

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Protodiamantane (pentacyclo[7.3.1.1^{4,12}.0^{1,7}.0^{6,11}]tetradecane, I) is the most likely pen-

ultimate $C_{14}H_{20}$ isomer in the rearrangement sequence[1] leading from tetrahydro-Binor-S (II)[2]

to diamantane (III).[3] Our rational synthesis of I by a cleavage-recombination sequence involves

IV, a rare example of a diene prone to anti-Markovnikov addition under ionic conditions.

II[2]   I   III

1,6-Dibromodiamantane (V)[4] was reductively cleaved by activated powdered zinc[5,6] in dimethyl

formamide to give the intriguing fixed chair 1,5-diene, IV, m.p. 121-124°, in 83% yield. Polymeric

by-product was separated by column chromatography on silica gel; the volatile tetracyclo-

[7.3.1.1^{4,12}.0^{2,7}]tetradeca-6,11-diene (IV) eluted first with hexane: nmr (CDCl$_3$) δ 5.55 (d, 2

olefinic H's), δ 1.82 (br s), δ 2.05 (s), δ 2.22 (br mult), δ 2.5 (br); ir (nujol) 1662 cm^{-1}

(C = C stretch).

V   IV   VI   VII
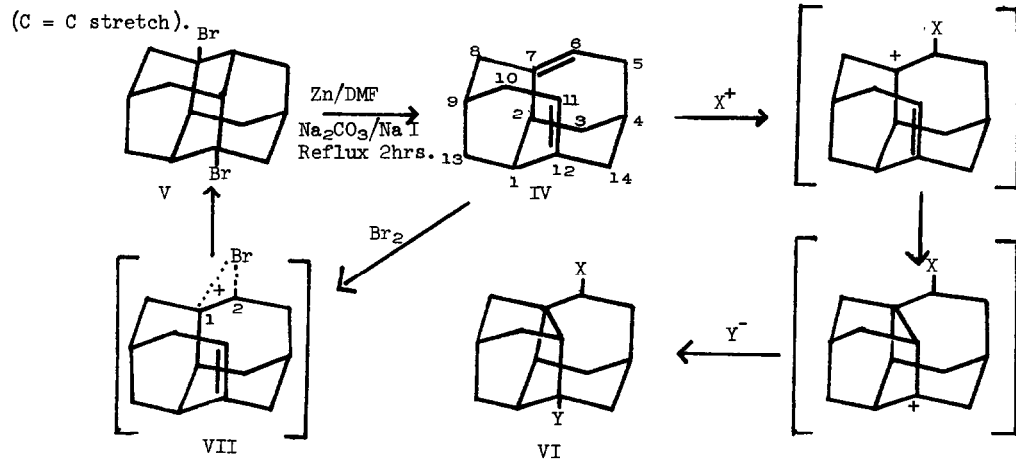
Markovnikov addition of X^+ Y^- to diene IV should generate the protodiamantane ring system,
VI. However, molecular mechanics calculations indicate that the isomerization of I to III should
be highly exothermic, ΔH isom = 19.3 kcal/mole (see below).[7] Thus, there is considerable thermo-
dynamic bias towards forming the diamantane (III) rather than the protodiamantane (I) ring system.
It should be recalled that tertiary carbocations are generally only 10-15 kcal/mole less stable
than secondary cations in solution.[8]

Hydride transfer in H_2SO_4 is a particularly convenient synthetic reaction in stable tertiary
carbonium ion chemistry.[9] Unexpectedly, IV was converted not to I, but quantitatively (glc) to III
with H_2SO_4/methylcyclohexane at 0°. I is not converted to III under these conditions but the
rearrangement does occur upon heating. Likewise, I rearranges readily and without the intervention
of a glc detectable intermediate or the formation of by-products to III in the presence of aluminum
bromide.

$$IV \quad \xrightarrow[0^\circ]{H_2SO_4/\text{methylcyclohexane}} \quad III \quad \xleftarrow[H_2SO_4/\text{methylcyclohexane}, \Delta]{AlBr_3 \text{ or}} \quad I$$
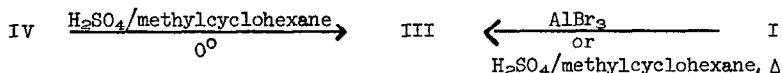
Bromine similarly regenerates the starting dibromide V from IV rather than giving VI
(X = Y = Br). This reaction and the hydride transfer at 0° involve at least formal examples of
anti-Markovnikov addition.

Perhaps the bromination involves bromonium ion VII, which, although unsymmetrically bridged,
attacks the <u>trans</u>-annular double bond preferentially by the less substituted carbon-2. Even if
VI (X = Y = Br) were to form, it should rearrange readily to V because of the exo-leaving group
at C-2. These rationalizations are less applicable to the hydride transfer reaction (IV → III)
because hydrogen obviously is a poor leaving group and has much less propensity towards bridging
than does bromine. However, carbocations have reasonably long lifetimes in sulfuric acid, and the
formation of the most stable cyclization reduction product III is understandable, if bothersome,
when one's objective is the synthesis of I.

Conditions for HBr addition can be varied to produce either the diamantane or the proto-
diamantane skeleton. Gaseous HBr addition to IV in hexane gives 1-bromodiamantane (VIII) plus
a tetracyclic dibromide, possibly IX, whereas aqueous HBr in HMPA or acetic acid-methylcyclohexane
gives only VIII and 1-diamantanol (X). The best conditions found for preparation of I involve
reaction with 48% aqueous HBr in hexane at 0°. Glc (5% carbowax 20M, 3m x 6mm glass column, 150°)
analysis of reaction progress indicated disappearance of diene (retention time 1.5 min) and
appearance of XI (55%) and VIII (45%) (retention times 8.2 and 11.2 min) and no other products.
The bromide mixture was refluxed with tri-n-butyl tin hydride[4] in benzene for four hours, and the

resulting protodiamantane (I) (55% of mixture) was separated by preparative gas chromatography (retention time 13 minutes, 20% carbowax 20M, 6m x 6mm, 150°, helium pressure 1.7 atm; the second component, diamantane (III), had a retention time of 16 min). Protodiamantane (I), m.p. 145-147°, has an MS-9 exact mass of 188.156701 (Calcd. 188.156493) and complex splitting in the δ 2.2-1.2 nmr region (CDCl$_3$) with an intense broad singlet at δ 1.58; the ir (KBr) spectrum shows a strong CH-band at 2900 cm^{-1} and weak bands at 1450, 1330, 1100, 1060 and 1010 cm^{-1}.
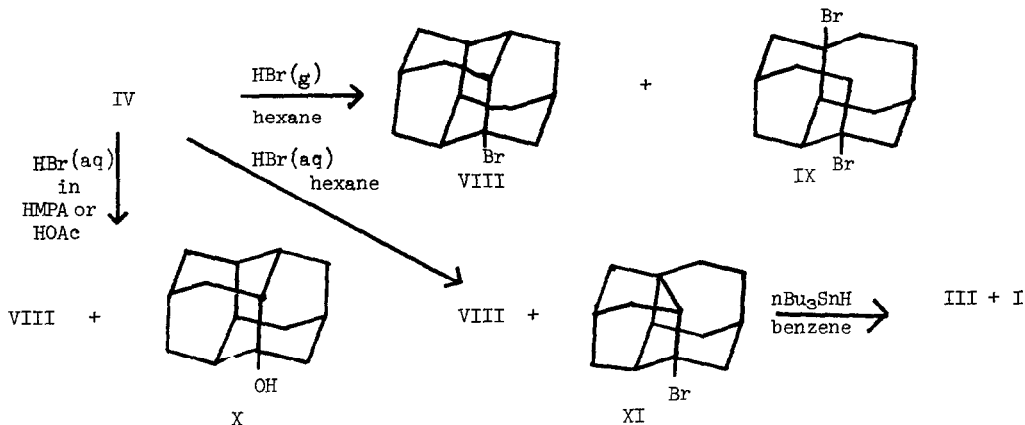
Only four C$_{14}$H$_{20}$ isomers lacking methyl groups (I, XII-XIV), can be generated from diamantane (III) by skeletal alterations involving movement of any of its C-C bonds to an adjacent carbon. Despite its quaternary carbon, our molecular mechanics calculations[7] indicate I to be only somewhat less stable than XII or XIII. However, the other quaternary isomer, XIV, is quite strained.

	III	I	XII	XIII	XIV
$\Delta H_f^°$(Calc.)[7] kcal/mole, 25°	-37.4	-18.1	-24.4	-22.4	+21.6
Strain	10.7	31.1	23.6	25.7	70.8

IV affords a rare opportunity of studying a degenerate Cope rearrangement in a rigidly-held chair 1,5-hexadiene system.[10] Although optically active IV was recovered from partial reaction with achiral (-) sym-tetraisopinocamphenyl diborane,[11] we have not yet been able to find conditions under which racemization of IV competes successfully with conversion to intractable material. IV not only has potential as an intermediate for the synthesis of 1,6-disubstituted diamantanes and 2,6-disubstituted protodiamantanes (VI), but also may provide a diagnostic tool to probe mechanistic details of olefin additions.

FOOTNOTES AND REFERENCES

1. We have analyzed this complicated process involving over 400 possible structures by computer programs to be described in full elsewhere. This is an elaboration of the approach used by H.W. Whitlock and H.W. Siefken, J. Amer. Chem. Soc., 90, 4929 (1968).

2. ^{13}C-nmr analysis (Prof. E. Wenkert, private communication) indicates this compound (see Ref. 3) to be either pentacyclo[8.4.0.0^{2,7}.0^{4,8}.0^{9,13}]tetradecane or pentacyclo[8.4.0.0^{2,6}.0^{3,8}.0^{9,13}]tetradecane.

3. (a) T.M. Gund, V.Z. Williams, Jr., E. Osawa, and P.v.R. Schleyer, Tetrahedron Lett., 3877 (1970); (b) D. Faulkner, R.A. Glendinning, D.E. Johnston, and M.A. McKervey, Tetrahedron Lett., 1671 (1971); (c) T. Courtney, D.E. Johnston, M.A. McKervey and J.J. Rooney, J. Chem. Soc., Perkin Trans. I, 2691 (1972).

4. T.M. Gund, P.v.R. Schleyer, C. Hoogzand, Tetrahedron Lett., 1583 (1971).

5. For similar fragmentation reactions see: (a) F.N. Stepanov and V.D. Sukhoverkhov, Angew. Chem., Internat. Ed., 6, 864 (1967); F.N. Stepanov, V.D. Sukhoverkhov, V.F. Baklam, and A.G. Yurchenko, J. Org. Chem. U.S.S.R., 6, 887 (1970).

6. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol.I, John Wiley and Sons, Inc., New York, 1967, p. 1276.

7. The force field employed is essentially that described by J.L. Fry, E.M. Engler and P.v.R. Schleyer, J. Amer. Chem. Soc., 94, 4628 (1972).

8. D.M. Brouwer and H. Hogeveen, Prog. Phys. Org. Chem., 9, 179 (1972); H. Hogeveen, Adv. Phys. Org. Chem., to be published; M. Saunders, P. Vogel, E.L. Hagen, and J. Rosenfeld, Accounts Chem. Res., 6, 53 (1973).

9. See W.D. Graham and P.v.R. Schleyer, Tetrahedron Lett., 1179 (1972); J.S. Wishnok, P.v.R. Schleyer, E. Funke, G.D. Pandit, R.O. Williams, and A. Nickon, J. Org. Chem., 38, 539 (1973); J.S. Wishnok, S.H. Liggero and W.D. Graham, unpublished observations.

10. Suggested by Prof. R. Hoffmann, private communication.

11. W.L. Waters, J. Org. Chem. 36, 1569 (1971).