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Reactions of Highly Hindered Spiroadamantanes

G. B. Gill* and D. Hands

Department of Chemistry, The University, Nottingham NG7 2RD

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The recent interest in the reactions of hindered biadamantanes[1,2] prompts us to record some unusual features in the chemistry of these compounds. Reduction of adamantan-2-one (I) with 40% sodium amalgam in dry ether under nitrogen (3.5h), followed by work-up with dilute acetic acid, gave 2,2'-dihydroxy-2,2'-biadamantane (II; 90%),[2] m.p. 266-268°. When (II) was dissolved in warm glacial acetic acid the epoxide (III; 95%),[2] m.p. 183-184°, was formed. Surprisingly, however, small quantities of spiro[adamantane-2,4'-homoadamantan-5'-one] (IV)[2] were also isolated. The pinacolone (IV), m.p. 177-178.5°, was the major product (ca. 96% isolated yield) of the reaction of (II) with stronger acids (HCO_2H, CF_3CO_2H, or c. H_2SO_4), but in all cases the spiro-epoxide (III) was also formed. The ratios of (III):(IV) obtained under controlled conditions (e.g. $CHCl_2CO_2H$, 25°, 12h) starting separately with pure pinacol (II), or epoxide (III), or pure pinacolone (IV), were identical. Thus, (III) and (IV) are in equilibrium under conditions of acid catalysis (Scheme).

Scheme

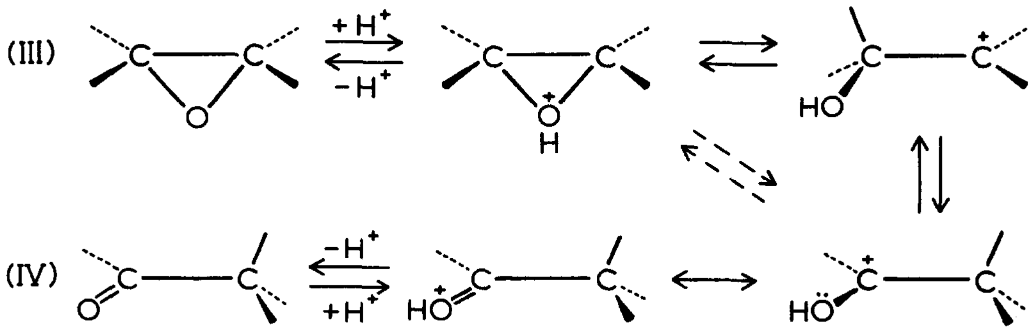


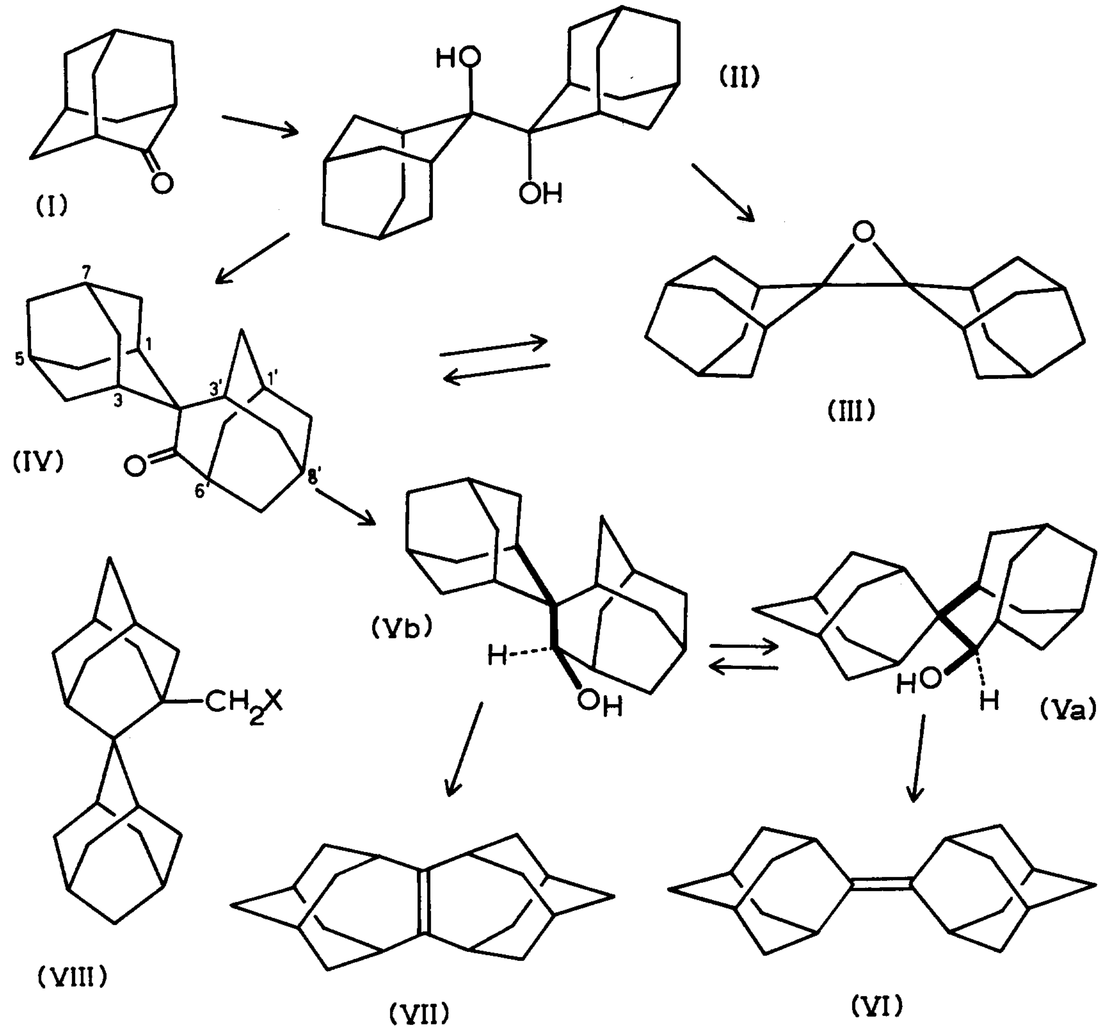
TABLE Ratios[a] of epoxide (III) and pinacolone (IV) formed on treatment of pinacol (II) with acids at 25°.

Acid[b]	CH_3CO_2H	HCO_2H	CF_3CO_2H	H_2SO_4[c]		$CHCl_2CO_2H$[d]		
Time (h)	12	12	12	12		12	12[e]	24
% (III)	97.0	0.5	2.0	9.0	9.5	1.0	1.0[e]	1.0
% (IV)	3.0	99.5	98.0	91.0	90.5	99.0	99.0[e]	99.0

[a] Determined by g.l.c; the results are quoted to the nearest 0.5%, the approx. experimental error. [b] Unpurified commercial grade reagents were used. [c] Determined at 0°. [d] Additional data, % (III): % (IV) [time, min]:- 93.5:6.5 [3], 91.5:8.5 [6], 88.5:11.5 [10], 84.5:15.5 [15], 80.5:19.5 [20] 74:26 [30], 59:41 [46], and 48.5:51.5 [60]; $k \sim 1.5 \times 10^{-4} sec^{-1}$. [e] Starting material was pure (IV).

The results presented in the Table indicate that not only is epoxide (III) equilibrated with (IV) in acidic media, but also that (III) is the significant intermediate in the pinacolic reaction (II) → (IV). This last observation follows from the results in dichloroacetic acid solution, and in the solvent the rate of formation of (III) appeared to depend simply upon the rate of solution of (II). To our knowledge these results are unique in the series of tetra-alkyl pinacols or epoxides. In the tetra-aryl series, however, Gebhart and Adams[3] have shown that in the acid-catalyzed rearrangement of benzopinacol about 80% of the pinacolone is formed indirectly (i.e.from the epoxide) which indicates a preference for the trans-arrangement of hydroxyl groups in benzopinacol. On this basis, pinacol (II) appears to have a 100% preference for the trans-conformation, and hence the description[2] of (II) as a ramshackle molecule is far from the truth. The isomerisation of $^{14}C=O$ labelled benzopinacolone in strongly acidic media also indicates the possible intermediacy of the conjugate acid of the epoxide.[4] Nevertheless, the conversion (IV) → (III) and the apparent thermodynamic stability of epoxide (III) are most unusual; the stability presumably results from less severe non-bonded interactions than are present in either (II) or (IV).

Molecular models indicate that in (IV) the conformation which has a molecular plane of symmetry is strongly preferred. The oxygen atom of the C=O function is nestled between the axial H atoms at C-4 and C-9 and the low reactivity of (IV) is therefore not surprising: it failed to yield to the Wolff-Kishner or Clemmensen reactions, or to react with hydroxylamine, semicarbazide, 2,4-dinitrophenylhydrazine, or methylmagnesium iodide under normal conditions. Reduction with $LiAlH_4$ gave the alcohol (V; 89%), m.p. 191-193°.



Attempts to convert (V) to the spiro adamantane-2,2'-adamantane system, as in (VIII), by carbonium ion rearrangement failed. With AcOH-HCl (160°, 18h) the product was adamantylidene adamantane (VI), [1]m.p. 184-185°; 60 MHz n.m.r. (CCl_4)τ7.12 (4H, multiplet; allylic H), and 8.23 (24H, complex m); m/e 268 (100%). However, reaction of (V) with hot phosphoric acid yielded a sublimate which contained (VI) and a second hydrocarbon in the ratio ca. 3:1. The minor component was identified as hexacyclo[11, 3, 1, $1^{3,7}$, $1^{5,9}$, $1^{11,15}$, $0^{2,10}$] eicos-2-ene (VII), m.p. 202-204°; raman spectrum (solid phase)[5] 1649 cm^{-1}; 60 MHz n.m.r. (CCl_4)τ7.96 (8H complex m; bridgehead H), 8.17-8.30 (20H, complex m); m/e 268 (100%).[6] Compounds (VI) and (VII) were also formed in the reaction of (V) with tosyl chloride in pyridine.

The separation of (VI) and (VII) was facilitated by the characteristic reaction of (VI) with bromine;[1] the interesting hydrocarbon (VII) was inert to Br_2-CCl_4 and indeed appears generally to lack normal olefinic reactivity. Models indicate an unusual situation-the π bond in (VII) is protected by four pairs of axial H atoms such that the attack by electrophilic reagents is likely to be difficult or impossible. Isomerisation of (VII) to (VI) was not detectable in trifluoroacetic acid in 4h at room temperature.

The alcohol (V) has two possible extreme conformations (Va) and (Vb) in which the hydroxyl group is respectively equatorial and axial to the seven-membered ring defined by C(1')--C(2')-C(3')-C(4')-C(5')-C(6')-C(10'). In each conformation there exists a perfect trans-coplanar arrangement (indicated by the thickened bonds) of O-C(5')-C(4')-migrating centre{i.e. C(3') or C(1)} such that (VI) and (VII) can be formed in anchimerically assisted ionisation-rearrangement sequences. It is interesting to note that in the least hindered conformation of (V){OH in the "bowsprit" position} the atoms O-C(5')-C(6')-C(7') are trans-coplanar. Hence there exists the further (as yet undetected) possibility of degenerate rearrangements of the homoadamantyl system, one product of which could be (VIII) among the two possible spirohomoadamantenes and various spirohomoadamantanes.

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5. We thank Dr. H.G.M. Edwards, Department of Structural Chemistry, University of Bradford, for determining the raman spectrum of (VII).
6. The mass spectra of (VI) and (VII) were essentially identical.

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