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CATIONIC REARRANGEMENTS OF SPIRO[ADAMANTANE-2,4'-HOMOADAMANTAN-5'-OL]

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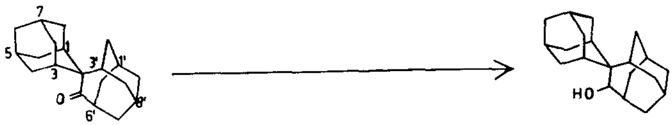
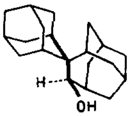
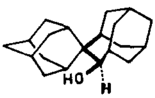
In a recent paper[1] we reported the synthesis of the first representative of a spirally connected adamantane-homoadamantane molecule (I). Subsequently Gill and Hands[2] also described this compound. We wish to record now some cationic rearrangements of spiro[adamantane-2,4'-homoadamantan-5'-ol] (II), (m.p. 189-192°, litt.[2] 191-193°), which could be obtained[3] in almost quantitative yield by reduction of I with $LiAlH_4$. Alcohol II has two possible extreme conformations (IIa and IIb) so that we might expect the formation of adamantylidene adamantane (III) and the annelated bis-homoadamantene (IV) in an anchimerically assisted ionisation-rearrangement sequence as well as products formed by degenerate rearrangements[4] of the homoadamantyl system.



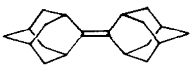
(I) (II)



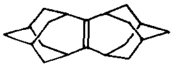
(IIa)



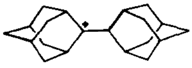
(IIb)



(III)



(IV)

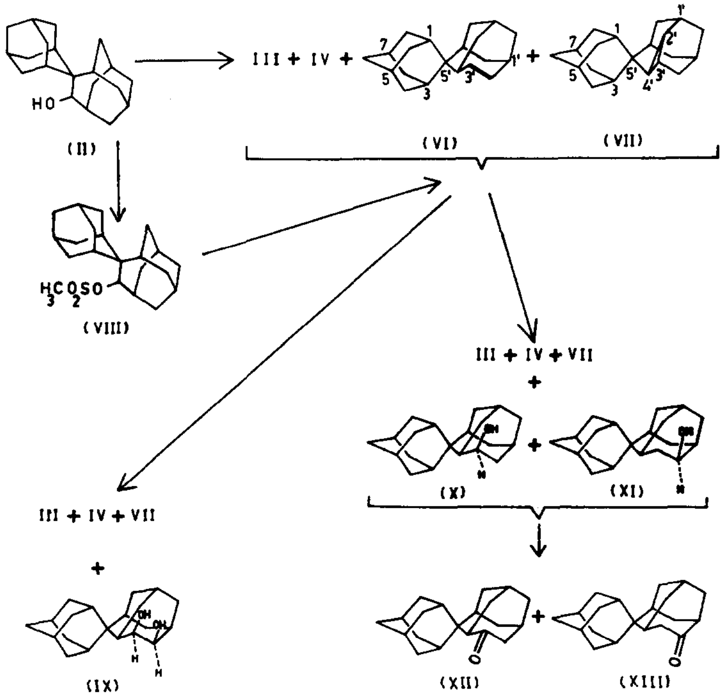


(V)

Compounds III and IV (m.p. 199-201°, litt.[2] 202-204°) were indeed formed as the only hydrocarbon constituents in almost all reactions performed[5] except in two cases.

(i) The reaction with concentrated H_2SO_4 gave besides III also 2,2'-biadamantane. Both products undoubtedly arise from the same intermediate carbonium ion V, the former by proton extrusion, the latter by an intermolecular hydride abstraction[6] by this cation from a tertiary position of another molecule. The expected mixture of tertiary alcohols is also formed.

(ii) Treatment of II with $SOCl_2$ in pyridine gave in 75% yield a mixture of two major and two minor $C_{20}H_{28}$ hydrocarbons. The major products were identified as spiro[adamantane-2,5'-homoadamantan-2'-ene] (VI) and spiro[adamantane-2,5'-(2',4'-dehydrohomoadamantane)] (VII) and the two minor components as III and IV.



This same mixture of hydrocarbons was obtained (100% yield) when mesylate VIII[7] was treated with $LiAlH_4$[8] in ether, or on adding acetone to VIII, or on treatment of II with tosylchloride/pyridine (46%, 41% recovered starting material). The formation of the hydrocarbon mixture in the latter case is in contrast with the results of Gill and Hands[2], who report for this reaction only the formation of III and IV.

The structure of VI was supported by olefinic absorptions[9] at τ = 3.7-4.4 (m) in the n.m.r. spectrum of the hydrocarbon mixture and also by conversion to other compounds whose structures could easily be established. Reaction of an ethereal solution of the hydrocarbon mixture with OsO_4/pyridine yielded besides a mixture of III, IV and VII the vicinal diol IX (m.p. 206-208°). Examination of models suggests a preference for OsO_4 approach from one side of the double bond leading to the stereochemistry depicted in IX. Treatment of the hydrocarbon mixture with B_2H_6 in THF solution, followed by oxidation with basic hydrogen peroxide gave besides III, IV and VII a mixture of the isomeric alcohols X and XI (m.p. 167-175°). Glpc analysis of the TMSE and acetate derivatives of this alcohol mixture indicates that almost certainly B_2H_6 also approaches the double bond in VI only from the less hindered side. Oxidation of the alcohol mixture with Cornforth[10] reagent gave in 84% yield a mixture of the isomeric spiroketones XII and XIII (m.p. 151-160°).

Hydrocarbon VII (m.p. 164-166°) could be isolated either by ozonolysis (CH_2Cl_2, -30°) of the original hydrocarbon mixture or by repeated crystallisation of the mixture of III, IV and VII obtained from the reaction of the original mixture with OsO_4 or B_2H_6.

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2. G.B. Gill and D. Hands, Tetrahedron Letters, 1971, 181.
3. All new compounds gave satisfactory elemental analyses and spectral data.

4. R.E. Leone and P. von R. Schleyer, Angew. Chem., **82**, 889 (1970).

5. As reagents were used: $ZnCl_2$ (5 min., 200°); BF_3 etherate (24 hrs., 20°); PBr_3 (24 hrs., 20°); $SOCl_2$ (24 hrs., 20°); H_3PO_4 (2 hrs., 140°); P.P.A. (1.5 hrs., 130°).

6. P. von R. Schleyer, L.K.M. Lam, D.J. Raber, J.L. Fry, M.A. McKervey, J.R. Alford, B.D. Cuddy, V.G. Keizer, H.W. Geluk and J.L.M.A. Schlatmann, J. Amer. Chem. Soc., **92**, 5246 (1970).

7. Mesylate VIII (dec. at 80°) was obtained in a yield of 70% by reaction of II with mesylchloride/pyridine.

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9. The olefinic protons of 4-homoadamantene have been reported to absorb at $\delta = 6.10$ in the n.m.r. spectrum. P. von R. Schleyer, E. Funke and S.H. Liggero, J. Amer. Chem. Soc., **91**, 3965 (1969).

10. R.H. Cornforth, J.W. Cornforth and G. Popják, Tetrahedron, **18**, 1351 (1962).