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A RING-OPENING REACTION OF AND SOME CYCLISATIONS TO THE ADAMANTANE SYSTEM. A QUASI-FAVORSKY REACTION OF A β-BROMOKETONE.

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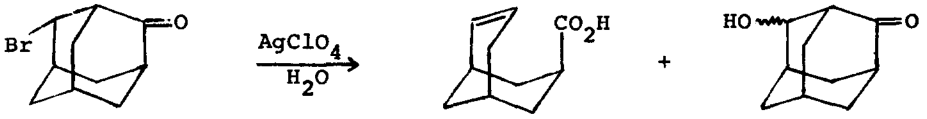
Some ring-opening reactions of 1,3-disubstituted adamantanes resulting in 3,7-disubstituted bicyclo[3,3,1]nonanes (1,2,3) have been described. The latter can be reconverted into 1,3-disubstituted adamantanes by acid catalysed cyclisations (4,5).

We wish to report a novel fragmentation reaction of a 2,4-disubstituted adamantane (I) to a bicyclo[3,3,1]nonane derivative (II) and the first two examples of the formation of 2-monosubstituted adamantanes by acid catalysed cyclisation of the bicyclo[3,3,1]nonane systems VI and VII.

Reaction of 4e-bromoadamantanone (I) (6) with silver perchlorate in a mixture of water and acetone (1:2) gave only minor amounts (3%) of the expected 4-hydroxyadamantanone (III) (mixture of 4a- and 4e isomers), the major product (71%) being bicyclo[3,3,1]nonene-2-carboxylic acid-7 (II).



I II III

The structural assignment of II (mp 195-198°) was based on its analytical[*] and spectral[*] data.

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[*] All new compounds (collected in Table I) gave satisfactory elemental analyses and the expected molecular weights (from the mass spectra) and infrared spectra.

TABLE I

Compound	Yield %	mp	NMR spectrum (τ)[1]
II	71	195-198°	($CDCl_3$) 4.37 (c) (2 H); 7.1-8.5 (c) (11 H); -1.3 (s, broad) (1 H)
IV	94[2], 81[3]	288-290°	(CCl_4) 5.60 (q) J = 3.0 Hz (1 H); 7.04 (q) J = 3.5 Hz (1 H); 7.7-8.4 (c) (12 H)
VI	86	oil[6]	($CDCl_3$) 4.0-4.5 (c) (2 H); 6.43 (d) J = 6.0 Hz (2 H); 7.5-8.7 (c)
VII	60	167.5-168°	($CDCl_3$ + $(CD_3)_2SO$) 6.17 (c) (1 H); 6.68 (c) (2 H); 7.8-8.6 (c)
X	26[4]	163-165°	(CCl_4) 6.52 (c) (2 H); 7.7-8.6 (c)[7] (28 H)
XI	11[5]	268-269°	(CCl_4) 5.90 (c) (1 H); 6.92 (d, broad) J = 2.5 Hz (2 H); 7.8-8.6 (13 H)

1) TMS: τ = 10.00, s = singlet, d = doublet, q = quintuplet, c = complex signal(s)
2) From II; 3) From V; 4,5) From VII; 6) bp 100°/12 mm;
7) Characteristic pattern for 2-substituted adamantanes (11).

Structural confirmation of II was obtained by allowing it to react with concentrated sulfuric acid at roomtemperature furnishing the expected lactone IV (mp 288-290°), identical in all respects with the Baeyer-Villiger oxidation product (monoperphthalic acid in ether) of adamantanone (V) (Scheme I). Base-catalysed fragmentation reactions of β-haloketones have been reported (7). The fragmentation of the β-bromoketone (I) bears some relationship with the known quasi-Favorsky reaction of certain α-bromoketones, which is assumed to proceed by a "push-pull" mechanism (8,9). Accordingly the mechanism of the ring-opening of I (in its hydrated form) may be presented as follows (Fig. 1). The reaction presumably is stereochemically favoured by the rigid coplanar arrangement of the reaction centra.

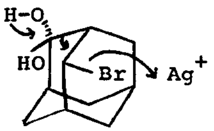
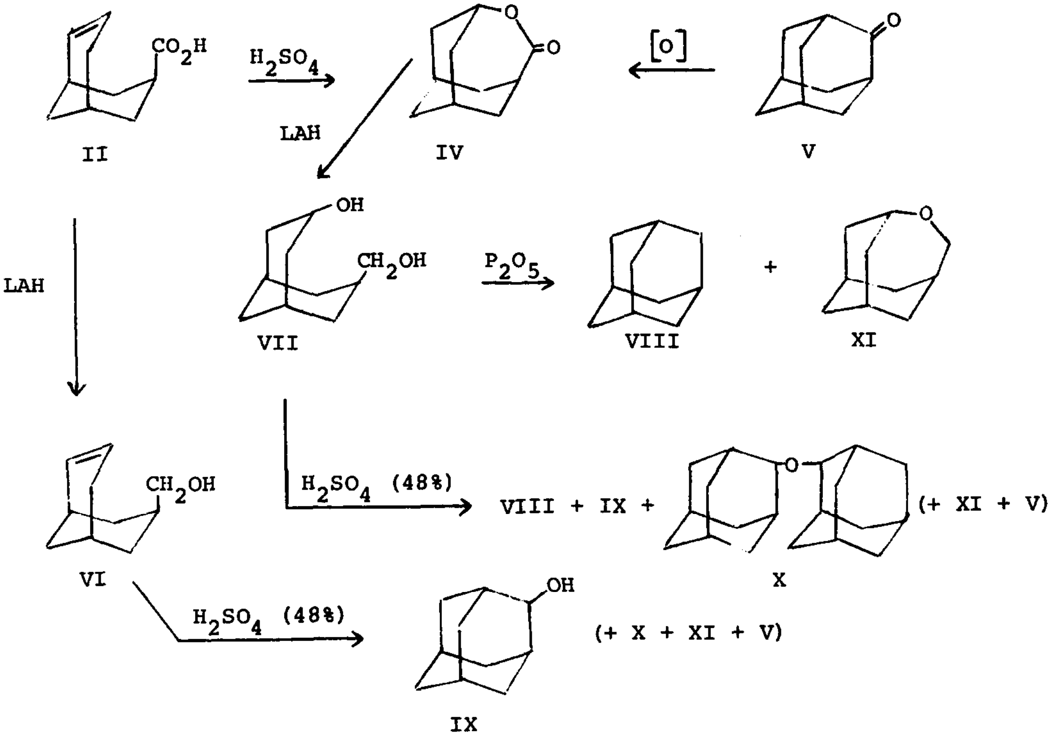


FIG. 1

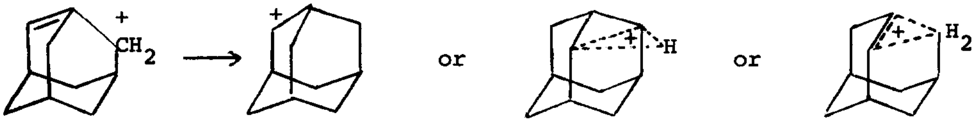
Reduction of the unsaturated acid II with lithium aluminium hydride (LAH) afforded the alcohol VI, whil reduction of the lactone IV gave the diol VII. (Scheme I).

SCHEME I



Unlike known cyclisations of 3,7-disubstituted bicyclo[3,3,1]nonanes in acid medium, which result in 1,3-disubstituted adamantanes, compounds VI and VII on treatment with 48% sulfuric acid in dioxan gave 2-monosubstituted adamantanes. From VI the known 2-hydroxyadamantane (IX) (10) was obtained in 80% yield, along with trace amounts of di(2-adamantyl)ether (X), 2-oxa-tricyclo$[4,3,1,1^{4,8}]$undecane (XI) and adamantanone (V) (12) (detected by analytical glc). The cyclisation of VII gave adamantane (VIII) (17%), 2-hydroxyadamantane (IX) (39%) and di(2-adamantyl)ether (X) (26%), while very small amounts of XI and V were also formed. Larger amounts of XI could be obtained by reaction of VII with phosphorous pentoxide, giving a mixture of adamantane (VIII) (10%) and 2-oxa-tricyclo $[4,3,1,1^{4,8}]$undecane (XI) (11%) along with non identified material. No trace of V, IX or X could be detected.

The cyclisation of VI and VII may proceed through the secondary adamantyl carboniumion (XII) or the cations XIII or XIV.



XII XIII XIV

The appreciable amounts of adamantane obtained from the cyclisations of VII must have been formed by a hydride abstraction of XII from for instance 2-hydroxy-adamantane. Analogous reactions have been reported (12,13). No attempt has yet been made to isolate and identify the corresponding oxidation product.

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