Generation and Fate of 1-Adamantyl-vinyl Cations

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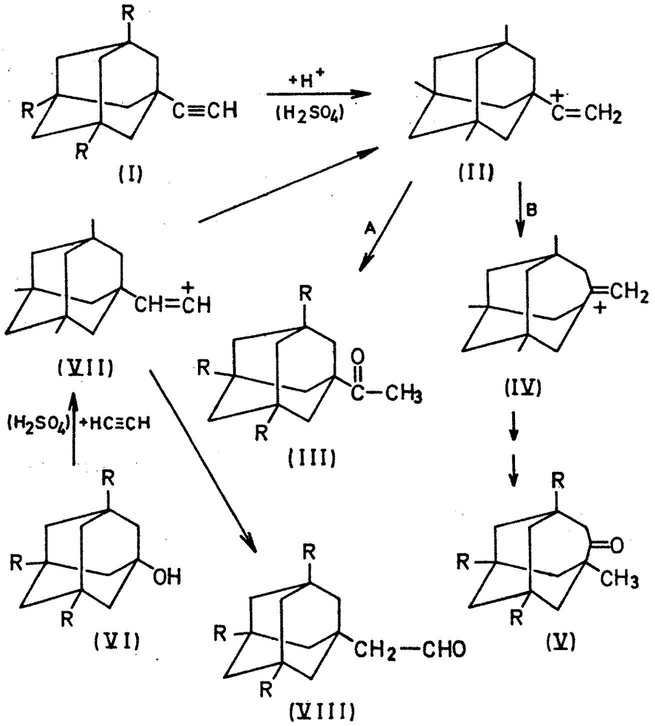
Summary The 1-(1-adamantyl)vinyl cations (II), generated in sulphuric acid either by addition of 1-adamantyl carbonium ions to acetylene or by protonation of 1-adamantylacetylenes (I), are transformed into mixtures of 1-adamantyl methyl ketones (III) and homoadamantan-4-ones (V).

VERY little attention has been paid to the behaviour of vinyl carbonium ions in strong acidic media with respect to skeletal rearrangements and hydride migrations. The present investigation complements earlier results[1] by revealing another means of stabilizing the 1-(1-adamantyl)-vinyl cation (II) and a more convenient source of (II).

By means of protonation of the two 1-adamantylacetylenes (Ia) and (Ib) in sulphuric acid, we were able to isolate the 1-adamantyl methyl ketones (III) and the homoadamantan-4-ones (V). As described in a previous communication,[1] the ketones (V) result from a sequence of carbonium ion rearrangements, which are initiated by a ring expansion of the 1-(1-adamantyl)vinyl cations (II) to the tertiary homoadamantyl carbonium ions (IV).

A second process for the generation of (II) in sulphuric acid involves the addition of 1-adamantyl carbonium ions to acetylene. In this case the key intermediate (VII) suffers partial hydride migration, while the main reaction furnishes the 1-adamantylacetaldehydes (VIII).[1] The ketones (III) and (V) were shown to be stable under the conditions of their formation.



In both synthetic routes the ratio of the products (III) : (V), reflecting the rate difference between pathways A and B, markedly increases when three methyl substituents are introduced into the bridgehead positions of the starting adamantanes (Ia) and (VIa), respectively (see Table). Another point which appears to be of mechanistic significance is the fact that the extent of ring expansion (step B) depends on the origin of (II). Apparently, the 1-(1-adamantyl)vinyl cations (II) can react more easily with sulphuric acid (or a corresponding species), when they are formed *via* proton addition to the 1-adamantylacetylenes (I). Our findings are consistent with the classical nature of vinyl cations. It should also be mentioned that the usual "hydrolysis" of (Ia) in nucleophilic solvents, carried out with mercury salts as catalyst, leads exclusively to the 1-adamantyl methyl ketone (IIIa).[2]

Relative yields of 1-*adamantyl methyl ketones* (III) *and homoadamantan*-4-*ones* (V) *generated in* 90% *sulphuric acid*

	Products (%)[a]	
Starting material	(III)	(V)
(Ia)	31·4	68·6
(Ib)	48·4	51·6
(VIa) + acetylene ..	10·6	89·4
(VIb) + acetylene ..	28·8	71·2

[a] Determined by g.l.c. analysis.

When (Ib) (34·6 mmoles) in n-hexane (200 ml.) is stirred with 90% sulphuric acid (300 ml.) at 5° for 1·5 hr., subsequent hydrolysis affords a mixture of (IIIb) and (Vb), b.p. 81—83°/0·3 mm, in 94% overall yield. This product (15·3 mmoles) was heated under reflux for 2 hr. with semicarbazide hydrochloride (7·6 mmoles) and sodium acetate in methanol (40 ml.), followed by evaporation at 20°, and the unchanged (Vb) (46%, m.p. 37—39°) was extracted from the residue with n-pentane. The semicarbazone of (IIIb) (42%) was freed from the inorganic salts by washing with water. After recrystallization (ethanol) the pure semicarbazone had m.p. 228—229°. It displays sharp singlets for all sorts of C–H protons in the n.m.r. ($CDCl_3$): τ 8·22 (3H), 8·70 (6H), 8·90 (6H), and 9·13 (9H).

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[1] K. Bott, *Tetrahedron Letters*, 1969, 1747.

[2] H. Stetter and P. Goebel, *Chem. Ber.*, 1962, **95**, 1039.