

## Homoadamantane Methyl Ketone, A Novel Re-arrangement Product from the Addition of 1-Adamantyl Cation to Prop-2-ynyl Alcohol

By JIBAN K. CHAKRABARTY\* and ALEC TODD

(Lilly Research Centre Limited, Erl Wood Manor, Windlesham, Surrey)

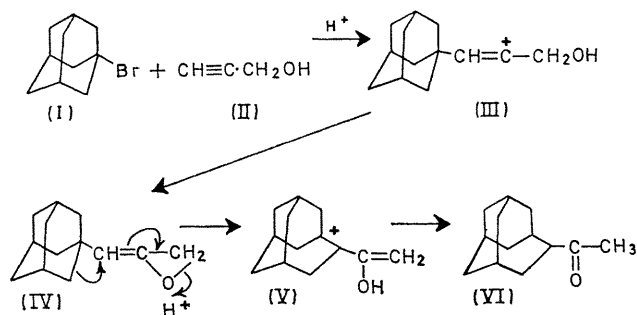
**Summary** The addition reaction of the 1-adamantyl cation with prop-2-ynyl alcohol in conc.  $H_2SO_4$  gives a rearranged product, homoadamantyl methyl ketone; evidence for its structure is presented.

THE reaction of the adamantyl cation with acetylene leading to the formation of 1-adamantylvinyl cation has been recently described.<sup>1-3</sup> T. Sasaki *et al.*<sup>1</sup> reported the exclusive formation of 1-adamantyl methyl ketone through the rearrangement of this vinyl cation, while Bott<sup>2b</sup> reported the formation of both 1-adamantyl methyl ketone and 1-methylhomoadamantan-2-one as a result of such rearrangement. He claimed<sup>2a</sup> that adamantane-1-acetaldehyde was the major reaction product. Kell and McQuillin,<sup>3</sup> however, reported that a sulphate intermediate is involved, and the formation of homoadamantane is favoured by the presence of water in the medium. They also extended the reaction to substituted acetylenes,  $RC\equiv CH$ , to give the ketones  $AdCH_2COR$ , where Ad = adamantyl and R is either Ph, Pr<sup>n</sup>, or  $n-C_8H_{13}$ .

In view of the above reports, we record our results on the reaction of the 1-adamantyl cation derived from 1-bromoadamantane, with prop-2-ynyl alcohol. When this reaction is carried out in concentrated  $H_2SO_4$ , homoadamantyl methyl ketone (VI) is formed. A reaction mechanism may be postulated as in the Scheme.

Cation (V) may be formed from the adduct (III) via a

rearrangement of the intermediate epoxide (IV). Compensation of this bridgehead cation by an intermolecular hydride shift<sup>4</sup> would then lead to the final product (VI).



SCHEME

Prop-2-ynyl alcohol (4-fold excess) in n-hexane was added dropwise to a stirred solution of 1-bromoadamantane in 98%  $H_2SO_4$  at 0–5°. The mixture was stirred for 4 h, poured on to ice-water, and extracted with ether. The ether extract on usual work-up afforded an oil, i.r. (neat); 1710s  $cm^{-1}$  (C=O). This on careful distillation produced only one fraction, b.p. 105° at 0.25 mmHg (*ca.* 15%).

Decomposition and/or polymerisation of the original crude oil seemed to have occurred during this distillation.

Structure (VI) for the distillate is suggested on the basis of the following physical and chemical evidence. I.r. (neat):  $1710\text{ cm}^{-1}$  (C=O); † n.m.r.:  $\delta$  ( $\text{CDCl}_3$ ) 2.8br [1H, t,  $J$  ca. 8 Hz ‡  $>\text{CHC}(\text{O})-$ ], 2.1 (ca. 3H, s, Ac), 2.5—1.5 p.p.m. (ca. 16H, m, other skeletal protons).

The semicarbazone had m.p.  $233\text{--}235^\circ$  (EtOH);  $m/e$  ( $M^+$ ) 249 and the 2,4-dinitrophenylhydrazone had m.p.

$167\text{--}168^\circ$  (EtOH). These derivatives had the expected i.r. and n.m.r. spectroscopic properties.

All new compounds gave satisfactory analyses. Spectra were measured with Perkin-Elmer 457 and Varian A60-A instruments.

We thank our colleagues in the Analytical Department for spectral data.

(Received, March 29th, 1971; Com. 443.)

† This is not consistent with the absorption of homoadamantanone which usually appears at a lower frequency.<sup>3,5</sup>

‡ The observed coupling constant is consistent with the theoretical values ( $\approx 8.8, < 2$  Hz) for the three neighbouring protons as predicted from a consideration of a molecular model.

<sup>1</sup> T. Sasaki, S. Eguchi, and T. Toru, *Chem. Comm.*, 1968, 780.

<sup>2</sup> (a) K. Bott, *Tetrahedron Letters*, 1969, 1747. (b) K. Bott, *Chem. Comm.*, 1969, 1349.

<sup>3</sup> D. R. Kell and F. J. McQuillin, *Chem. Comm.*, 1970, 599.

<sup>4</sup> (a) P. v. R. Schleyer, *Angew. Chem. Internat. Edn.*, 1969, 8, 529. Cf. Z. Majerski, P. v. R. Schleyer, and A. P. Wolf, *J. Amer. Chem. Soc.*, 1970, 92, 5731; (b) H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, 1968, 24, 5369; (c) K. Bott, *Chem. Ber.*, 1968, 101, 564.

<sup>5</sup> (a) R. M. Black and G. B. Gill, *J. Chem. Soc. (C)*, 1970, 671.; (b) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, 1970, 92, 6670; (c) P. v. R. Schleyer, E. Funke, and S. H. Liggero, *J. Amer. Chem. Soc.*, 1969, 91, 3965.