Addition of Adamantyl Carbonium Ion to Acetylene: Novel Vinyl Cation Rearrangement

By TADASHI SASAKI,* SHOJI EGUCHI, and TAKESHI TORU

(*Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan*)

IN recent years[1] studies on the vinyl cation intermediate, have included reports on its formation *via* addition of proton to alkynes[2] but not by the addition of carbonium ion to alkynes. We report its formation and rearrangement by addition of adamantyl carbonium ion to acetylene.

Acetylene was bubbled into a vigorously stirred mixture of 1-bromoadamantane, hexane, and concentrated sulphuric acid (1 : 10 v/v) at 5° for 5 hr., during which hydrogen bromide gas was evolved. The mixture was then poured onto ice-water and the worked-up product from the ether extracts gave a red precipitate on treatment with 2,4-dinitrophenylhydrazine. Purification of the crude hydrazone on a silica-gel column gave the known 2,4-dinitrophenylhydrazone of adamantyl methyl ketone[3] as orange needles (40%), m.p. 220–221° (lit.,[3] 219—220°).[†] The yield was less

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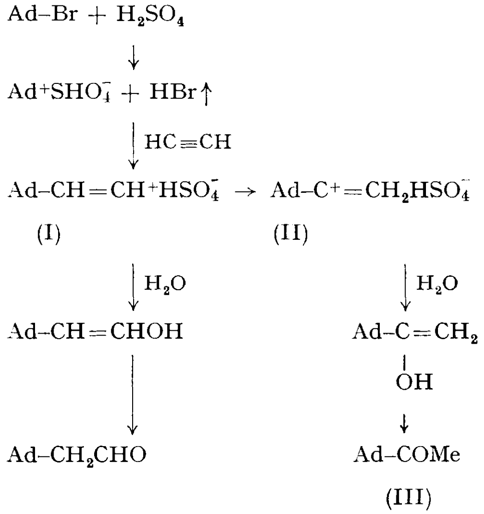
[†] The compound was satisfactorily identified by comparison of m.p., u.v., i.r., and n.m.r. data with those of an authentic sample and elemental analysis.



$$\begin{tikzcd}
\text{Ad–Br} + H_2SO_4 \arrow[d] & \\
\text{Ad}^+\text{SHO}_4^- + \text{HBr}\uparrow \arrow[d, "HC{\equiv}CH"] & \\
\underset{\text{(I)}}{\text{Ad–CH}{=}\text{CH}^+\text{HSO}_4^-} \arrow[r] \arrow[d, "H_2O"] & \underset{\text{(II)}}{\text{Ad–C}^+{=}\text{CH}_2\text{HSO}_4^-} \arrow[d, "H_2O"] \\
\text{Ad–CH}{=}\text{CHOH} \arrow[d] & \text{Ad–}\underset{\text{OH}}{\text{C}}{=}\text{CH}_2 \arrow[d] \\
\text{Ad–CH}_2\text{CHO} & \underset{\text{(III)}}{\text{Ad–COMe}}
\end{tikzcd}$$

with longer reaction times and higher temperatures (room temperature and 50°). No trace of the 2,4-dinitrophenylhydrazone of adamantylacetaldehyde could be isolated in several runs and only some formation of polymeric materials was observed.

Exclusive formation of adamantyl methyl ketone (III) may be explained by the formation of the vinyl cation (I) by addition of adamantyl carbonium ion to acetylene followed by complete rearrangement to the vinyl cation (II), presumably because of a large difference in stability between (I) and (II).

Addition of adamantyl carbonium ion to acetylene might offer a novel method for substitution at the bridgehead carbon, similar to the addition reactions of the bridgehead carbon with carbon monoxide,[4] nitriles,[1] and 1,1-dichloroethylene.[6]

(*Received, April* 16*th*, 1968; *Com.* 463.)

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[1] See *e.g.* W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 1960 and ref. 2.

[2] P. E. Peterson and J. E. Duddey, *J. Amer. Chem. Soc.*, 1966, **88**, 4990, and references therein.

[3] H. Stetter and E. Rauscher, *Chem. Ber.*, 1960, **93**, 2054.

[4] H. Stetter, M. Schwarz, and A. Hirschhorn, *Chem. Ber.*, 1959, **92**, 1629.

[5] H. Stetter, J. Mayer, M. Schwarz, and K. Wulff, *Chem. Ber.*, 1960, **93**, 226.

[6] K. Bott and H. Hellman, *Angew. Chem.*, 1966, **78**, 932.