

Preparative Flash Vacuum Thermolysis. Formation of 3-Noradamantylacetylene *via* Adamantylidenecarbene

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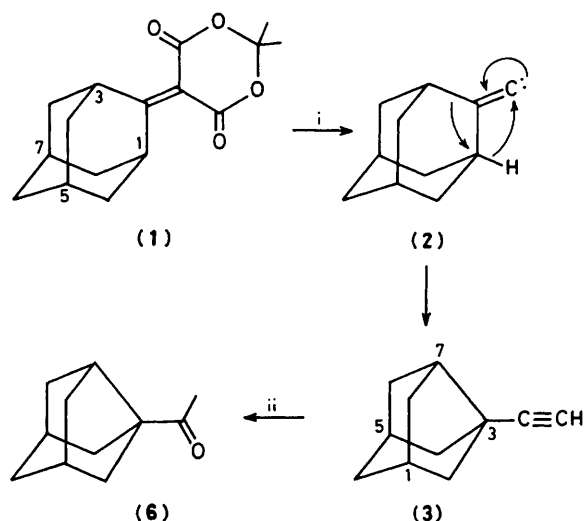
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3-Ethynyltricyclo[3.3.1.0^{3,7}]nonane is conveniently prepared from adamantanone, *via* an anomalous alkylidenecarbene rearrangement, by flash vacuum thermolysis of 5-adamantylidene-2,2-dimethyl-1,3-dioxane-4,6-dione.

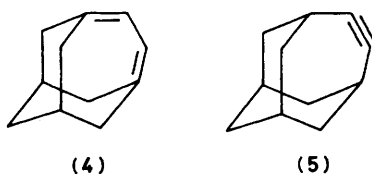
The readily accessible 5-alkylidene derivatives of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) are of interest for the preparation by flash vacuum thermolysis (F.V.T.)^{1,2} of naphthols³ or pyrrolizin-3-one³ *via* intermediate alkylidene-ketenes.⁴ When not intramolecularly trapped, the alkylidene-ketenes can be isolated² or can undergo sequential de-

carbonylation to alkylidenecarbenes,⁵ which rearrange to acetylenes.⁶ When cycloalkylidenecarbenes are generated from their Meldrum's acid precursors, ring enlargement occurs, *e.g.*, cycloheptylidenecarbene yields cyclo-octyne and cyclohexylidenecarbene ultimately gives cyclohepta-1,3-diene.⁶

We now report that F.V.T. at 600 °C of 5-adamantylidene-



Scheme 1. i, 600 °C, 0.05 mmHg, $-\text{Me}_2\text{CO}$, $-\text{CO}_2$, $-\text{CO}$; ii, H^+ , HgSO_4 .



2,2-dimethyl-1,3-dioxane-4,6-dione, (1), is an excellent method for preparation⁷ of 3-ethynyltricyclo[3.3.1.0^{3,7}]nonane (3-noradamantylacetylene), (3)[†] (Scheme 1).

Formation of (3) must proceed *via* ring contraction of the adamantylidene carbene (2) which cannot undergo ring expansion to either the anti-Bredt olefin (4) or the homo-adamantyne (5).⁸ Although the conversion (2) \rightarrow (3) can be rationalized as indicated, ¹³C labelling studies have shown that carbon scrambling is a common process in high temperature carbene rearrangements,⁹ and for example occurs with 1-adamantylacetylene.¹⁰

[†] The reaction was run in apparatus described in ref. 1, Figure 1. (1) (0.01 mol) was sublimed into the quartz tube at a rate of 0.3–0.5 g h⁻¹. From the pyrolysate, collected in the cold trap (1.6 g after evaporation of carbon dioxide and acetone), 1.3 g of (3) was isolated by preparative g.c. (yield, 81%).

Compound (1) [m.p. 211–212 °C; ¹H n.m.r. (CDCl_3 , 270 MHz) δ 1.74 (s, 6H, CH_3), 1.86–2.02 (m, 10H, CH_2), 2.02–2.12 (m, 2H, 5-CH + 7-CH), and 4.02 (s, 2H, 1-CH + 3-CH)] crystallizes when equivalent amounts of adamantanone and Meldrum's acid are dissolved in pyridine. The structure of (3), a colourless oil, [¹H n.m.r. (CDCl_3 , 270 MHz), δ 1.50–1.64 (m, 6H, 6- CH_2 + 8- CH_2 + 9- CH_2), 1.86 (s, 4H, 2- CH_2 + 4- CH_2), 2.12 (s, 1H, $-\text{C}\equiv\text{CH}$), 2.20 (s, 2H, 1-CH + 5-CH), and 2.52 (t, 1H, 7-CH, J 7.0 Hz); i.r. (NaCl) 2110 and 2310 cm^{-1} ($-\text{C}\equiv\text{CH}$)] is confirmed by hydration to the known¹¹ 3-noradamantyl methyl ketone (6) and its oxime,¹¹ m.p. 152–153 °C, and 2,4-dinitrophenylhydrazone, m.p. 160–161 °C.

The reaction signifies a one-step transformation of the adamantane skeleton to the 3-substituted noradamantane series.^{11,12}

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