Synthesis of Pentatetraene by Thermal Decomposition of a Vinylallene

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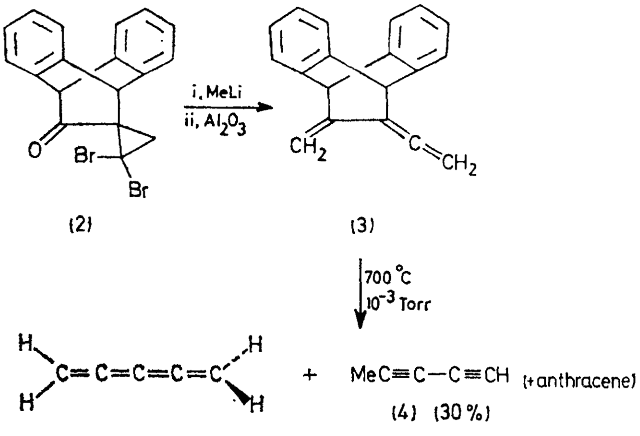
Summary Retro-Diels–Alder decomposition of vinylallene (**3**) under flash-thermolysis conditions mainly gives pentatetraene (**1**), which is surprisingly stable; it can be purified by g.l.c. and its spectra have been recorded.

For many years, pentatetraenes have been of considerable theoretical interest; charge densities, bond lengths, heats of formation, and rotational barriers have been calculated, especially for the unsubstituted pentatetraene (**1**).[1]



(2) (3)

(1) (70%) (4) (30%)

Since some tetrasubstituted pentatetraenes are known[2a] it is surprising that, with the exception of the Hoffman degradation of a quaternary ammonium salt,[3] no attempted synthesis of (**1**) has been reported, although HMO calculations predicted that (**1**) should be only slightly less stable than butatriene.[2b]

The retrodiene reaction, under flash thermolytic conditions, has proved to be extremely useful for the preparation of reactive unsaturated compounds;[4] we now report the synthesis of (**1**) by this method.

The reaction of MeLi with the bromoketone (**2**),[4] followed by dehydration over neutral alumina of the α-allenic tertiary alcohol formed, leads in fair yield to the vinylallene (**3**). Flash thermolysis of (**3**)[5] leads, *via* retro-Diels–Alder decomposition, to a 70:30 mixture of pentatetraene (**1**) and pentadiyne (**4**)[6] in 85% total yield.

Compound (**1**) appears to be more stable than butatriene [half-life in dilute $CHCl_3$ solution *ca.* 20 min at +40 °C; in the liquid phase at room temperature (1) rapidly gives an insoluble white polymer; no isomerisation is observed] and can be easily separated from the diyne (**4**) by g.l.c. at 25 °C. Structure (**1**) was unambiguously assigned according to its mass (M^+, m/e 64), n.m.r. (singlet at δ 5·22 in $CDCl_3$), i.r. [stretching vibrations in the gas phase at 2085 and 1660 cm^{-1} (expected[2c] at *ca.* 2100 and 1600 cm^{-1})], and u.v. spectra [λ_{max} (hexane) 201 (ϵ 100,000) and 242 nm (ϵ 17,000), in agreement with the spectra previously reported for substituted cumulenes.[2d]]

(*Received, 2nd February* 1976; *Com.* 101.)

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[1] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 590; M. J. S. Dewar and M. C. Kohn, *ibid.*, 1972, **94**, 2699; J. P. C. M. Van Dongen, M. J. A. de Bie, and R. Steur, *Tetrahedron Letters*, 1973, 1371, and references cited therein.

[2] H. Fischer, 'The Chemistry of Alkenes,' vol. I, ed. S. Patai, London, 1964, (a) p. 1025; (b) p. 1137; (c) p. 1129; (d) p. 1146.

[3] D. D. Coffman, *J. Amer. Chem. Soc.*, 1935, **57**, 1978.

[4] For preceding paper in this series see: J. L. Ripoll, *Tetrahedron*, 1976, **32**, in the press.

[5] For a description of the apparatus and technique, see: J. L. Ripoll, *Bull. Soc. chim. France*, 1974, 2567.

[6] J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 1993.