

### 3-Methylenebicyclo[3.2.2]nona-6,8-diene

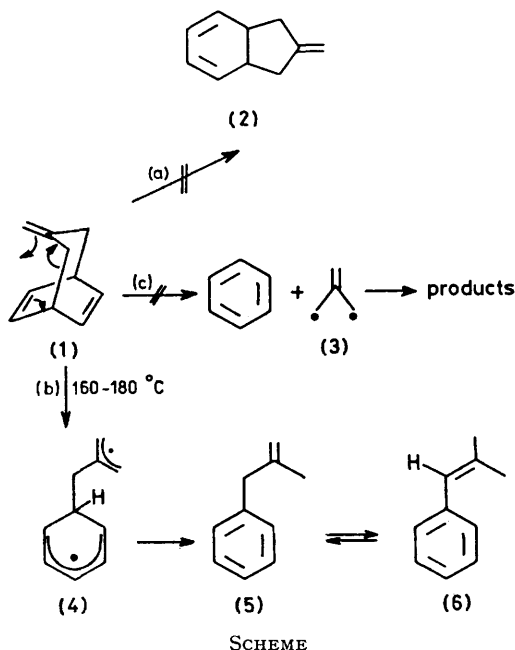
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*Summary* The synthesis of a novel C<sub>10</sub>-hydrocarbon, the formal addition product of trimethylenemethane to benzene, and its thermal rearrangement are reported.

IN the last decade the chemistry of trimethylenemethane (**3**) has been investigated extensively.<sup>1</sup> The title compound (**1**) constitutes a novel C<sub>10</sub>-hydrocarbon, the formal addition product of (**3**) to benzene. Compound (**1**) could conceivably

undergo several alternative thermal rearrangements: (a) Cope rearrangement to 8-methylenebicyclo[4.3.0]nona-2,4-diene (**2**); (b) one-bond cleavage leading to the diradical (**4**) and products thereof; (c) possibly also formation of two highly resonance stabilised species [(**3**): delocalisation energy (DE) =  $1.46\beta$  and benzene: DE =  $2.0\beta$ ] thus providing an alternative route to (**3**) (Scheme).



It therefore seemed interesting to synthesise (**1**) and investigate its thermo- and photo-chemistry. There are only few synthetic entries into this bicyclo[3.2.2]nona-6,8-diene system,<sup>2,3</sup> and we used the following one stage synthesis. Reaction of 2-methoxyallyl bromide† (from bromination of 2-methoxypropene with *N*-bromosuccinimide<sup>4</sup>) with benzene in the presence of silver trifluoroacetate and sodium carbonate produces, after work-up and spinning

band distillation, a mixture (70:30) of phenylacetone and bicyclo[3.2.2]nona-6,8-dien-3-one in *ca.* 10% yield. The mixture of ketones was added to methylenetriphenylphosphorane<sup>5</sup> in Me<sub>2</sub>SO-pentane at 0 °C over 5 min. Stirring at room temperature for 1 h, quenching in brine, extraction with *n*-pentane, and removal of solvent produced a mixture (70:30) of 2-methylenephénylpropane (**5**) and (**1**) in 75% yield, from which pure (**1**) [Fourier transform n.m.r.:  $\delta$  (CDCl<sub>3</sub>; Me<sub>4</sub>Si; 90 MHz) 2.24 (dt, 4H), 3.07 (septet, 2H), 4.59 (quintet, 2H), and 6.28 (sextet, 4H)] was isolated by preparative v.p.c. (10% OV 17, Chromosorb W, T = 100 °C).‡

Gas phase thermolysis of (**1**) (breakseal technique)<sup>6</sup> at 180 °C ( $k = 8.0 \times 10^{-5} \text{ s}^{-1}$ ) produces cleanly a mixture of 13% (**5**) and 87% 2,2-dimethylstyrene (**6**). A detailed study under low conversion conditions revealed, however, that (**6**) is not a primary reaction product in the thermolysis of (**1**), but is, in fact, derived from (**5**). When pure samples of (**5**) or (**6**) are thermolysed under the same conditions as (**1**), they rapidly interconvert, leading to an identical equilibrium mixture of 13% (**5**) and 87% (**6**), starting from either isomer.

No evidence was found for the formation of either (**2**) (which would be stable under the reaction conditions<sup>7</sup>) or (**3**), or products thereof. From the results it seems clear that (**1**) isomerises under relatively mild conditions and *via* a one-bond cleavage first to the highly stabilised diradical (**4**) which is stabilised by the delocalisation energy of an allylic radical (*ca.* 11 kcal mol<sup>-1</sup>) and a pentadienyl radical (*ca.* 15 kcal mol<sup>-1</sup>), both contributing towards a lowering of the activation enthalpy. The diradical (**4**) can, after a formal 1,4-H-shift (or consecutive 1,3- and 1,2-H-shifts), close to produce (**5**), which then isomerises under the reaction conditions to give the mixture of (**5**) and (**6**).

Direct and sensitised photolysis of (**1**) does not produce the expected quadricyclane but leads, even under high dilution conditions, to the formation of polymers.

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† In modification of the published procedure (refs. 2 and 4) the 2-methoxyallyl bromide was not isolated and the crude reaction mixture in CCl<sub>4</sub> was used.

‡ Compound (**1**) is a liquid, b.p. *ca.* 110 °C. All analytical and spectroscopic data were in agreement with the structure of (**1**).

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<sup>4</sup> G. Greenwood and H. M. R. Hoffmann, *J. Org. Chem.*, 1972, **37**, 611.

<sup>5</sup> R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, 1963, **28**, 1128.

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<sup>7</sup> J. A. Berson, Yale University, personal communication.