

A THERMAL RETRO [10+2] ROUTE TO BENZO[a]FULVENE

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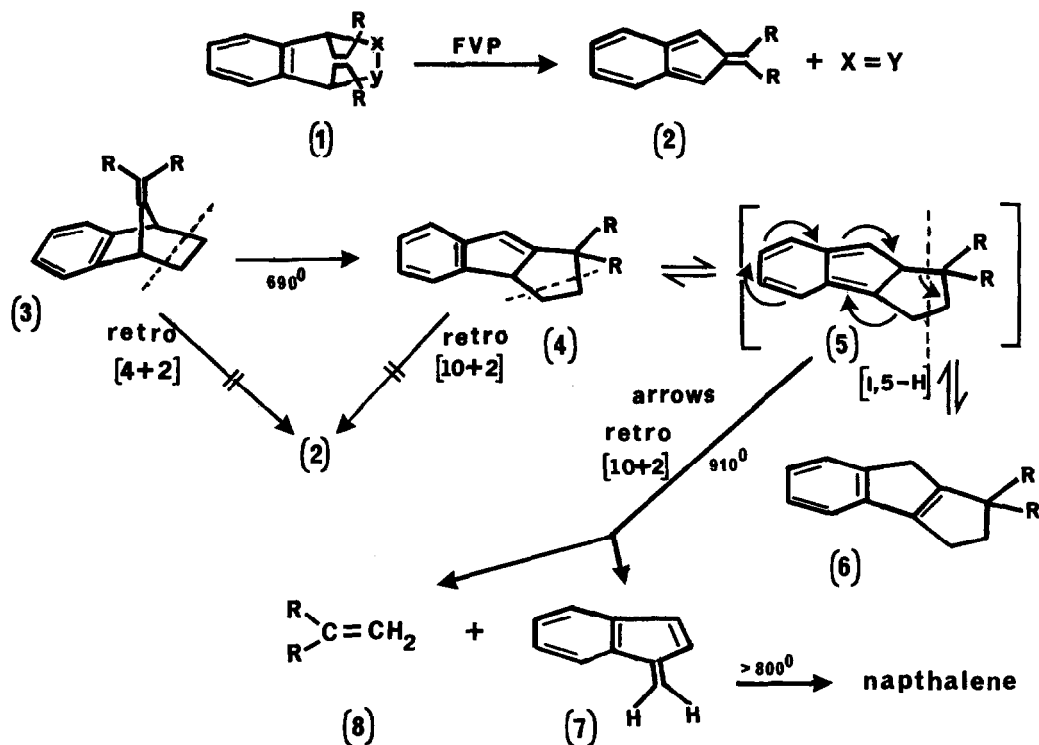
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As part of a systematic survey¹ of synthetic routes to isobenzofulvenes (benzo [c] fulvenes), (2), we investigated the flash vacuum pyrolysis (F.V.P.)² of compounds of type 1. In the event we uncovered a new route to benzo[a]fulvene (7). As the reaction proceeds in fair yield, in a single stage, from relatively accessible starting materials, it serves as a viable synthetic route to this compound.³

The starting material used was the 11-diphenylmethylene derivative (3, R=Ph), which was prepared from the benzyne adduct of 6,6-diphenylfulvene⁴ by selective hydrogenation (Pt/H₂) of the $\Delta^{5,6}$ -double bond [m.p. 115° pmr CDCl₃ δ 1.2-1.5 (m, C 5, 6-endo); 2.03-2.2(m, C 5,6-exo); 3.90 (t, C 1, 4); 7.10-7.45 (m, aromatic)].

Flash vacuum pyrolysis (F.V.P.)⁵ of this compound at 650°/0.04 mm Hg yielded a very clean pyrolysate (Fig. 1) consisting of 1,1-diphenylethylene and benzo[a]fulvene (7). In view of the work of Heaney *et al.*⁶ with 11-isopropylidenetricyclo[6,2,1,0^{2,7}]undeca-2,4,6-triene (3, R=Me), the first step in this reaction is presumed to be the 1,3-migration of the ethano-bridge to yield (4). Subsequent 1,5-H shift, characteristic of indenenes, would then yield the isoindene species (5). This compound is set up to undergo retro[10+2] cleavage to yield the two observed products (7) and (8). No evidence for the fragmentation of either (4) (retro[10+2]) or of (3) (retro[4+2]) to yield isobenzofulvenes (2) was observed. This latter result contrasts sharply with oxa or aza-bridged compounds which yield isobenzofurans^{7,8} or isoindoles⁹.

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Indeed this fragmentation is shown to be general¹⁰ for compounds derived from (3), since F.V.P. (690°/0.055 mm Hg) of the isopropylidene derivative (3, R=Me), in our hands, yielded not only the previously reported mixture of 2-isopropenylindene and the isomeric benzobicyclo [3,3,0] octenes (4 & 6, R=Me),⁶ but also significant amounts of benzo[a]fulvene (7). At even higher temperatures (910°/0.09 mm Hg) clean conversion to benzo[a]fulvene and naphthalene was observed. Separate injection of the fraction containing the 2:3-benzobicyclo[3,3,0] octenes (4 & 6) gave the same result and adds further support to the mechanistic sequence proposed above.

It is noteworthy that the overall conversion of (3) \rightarrow (4) involves the suprafacial 1,3-alkyl migration¹¹ of the ethano-bridge and that this reaction could, in principle, be concerted. Normally such concerted reactions are considered to be thermally disallowed according to Woodward and Hoffmann's orbital symmetry predictions.¹² However, Berson has recently presented cogent evidence for the concertedness of several 1,3-suprafacial migrations.¹³ The H-migration step to yield the more stable tricyclo[6,4,0,0^{2,6}] dodeca 2(6),8,10,12-tetraene (6) is obviously favoured in the methyl series and competes with thermal quenching at the tricyclo[6,4,0,0^{2,6}]dodeca-6,8,10,12-tetraene (4) stage. It appears reasonable that this isomerisation proceeds via the isoindene intermediate (5) in keeping with other known indene isomerisations.¹⁴⁻¹⁷ The allowed nature of these 1,5-suprafacial H-shifts accounts for the lower activation energy for this process compared with the fragmentation process. At higher temperature (910°) fragmentation does become the dominant reaction of the isoindene (5) which now proceeds to yield benzo[a]fulvene and the substituted ethylene. The significant yield of naphthalene in this process is most readily accounted for by the known thermal conversion of benzo[a]fulvene into naphthalene at temperatures above 800°.³

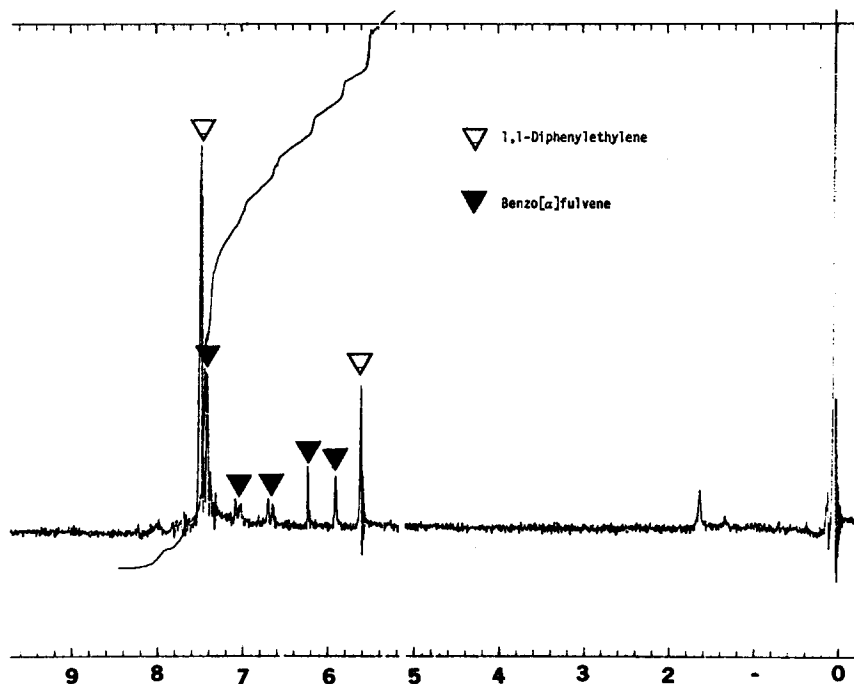


Fig. 1 PMR spectrum (100 MHz, CDCl_3) of pyrolysate from FVP of (3; R=Ph) at 650°.

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