

Flash Vacuum Pyrolysis of Cyclopropene–Anthracene Adducts

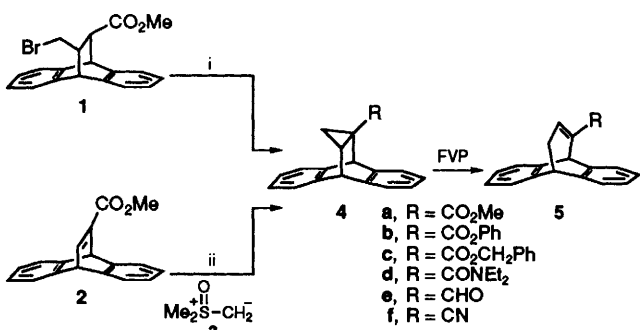
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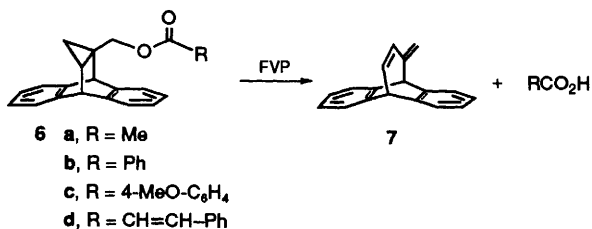
Flash vacuum pyrolysis of cyclopropene–anthracene adducts **4**, **6** and **8** results in ring opening of the cyclopropane moiety to yield **5**, **7** and **5a**, respectively.

The retro Diels–Alder reaction of anthracene adducts, induced by flash vacuum pyrolysis (FVP), has been extensively employed as the key step in numerous syntheses of important natural products,¹ particularly those possessing reactive double bonds.² Meanwhile, the behaviour of cyclopropane derivatives under thermal conditions, *i.e.* thermally induced epimerization *via* cyclopropane ring opening–ring closure reactions, has been the subject of much theoretical interest.³ We now report that upon FVP, the cyclopropane moiety in the cyclopropene–anthracene adduct, *e.g.* **4**, ring opens to give products that vary according to the nature of substituent R, but without any product from a retro Diels–Alder reaction being observed.

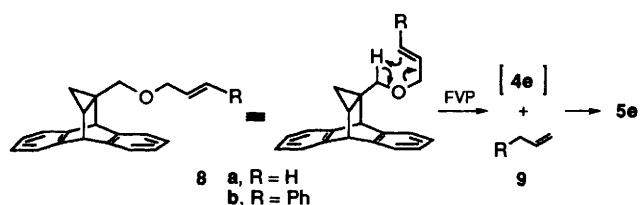
FVP (400–450 °C, 0.05 mm) of ester **4a**, prepared either by base treatment of the anthracene–methyl bromocrotonate adduct **1** or by reaction of the anthracene–methyl propiolate adduct **2** with sulfonium ylide **3**, gives dibenzohomobarrellene **5a** (78%).[†] Esters **4b** and **c**, amide **4d**, aldehyde **4e** and nitrile **4f** (all prepared from **4a**) also undergo similar ring opening to give the corresponding ring-expanded products **5b–f** in 87, 79, 81, 73 and 71% isolated yields, respectively, (Scheme 1). NMR analysis of the crude products of **4a–f** reveals the presence of trace amounts of anthracene, which could mean



Scheme 1 Reagents and conditions: i, LDA, THF–HMPA, room temp., 12 h, 95%; ii, **3**, Me₂SO, room temp., 2 h then 50 °C, 1 h, 93%



Scheme 2



Scheme 3

that the retro Diels–Alder reaction is competing under the pyrolysis conditions but is overwhelmed by the ring-expansion reaction.

When substituent R in adduct **4** is methoxycarbonyl, as in the series **6a–d** (prepared from **4a** in a straightforward manner), consecutive cyclopropane ring opening–elimination reaction takes place upon pyrolysis to yield the labile unsaturated hydrocarbon **7** (mp 109–111 °C from methanol in 38, 43, 39 and 42% purified yields from **6a–d**, respectively). The carboxylic acids eliminated from the reactions of **6b–d** have also been isolated (Scheme 2).

In the case of allylic ethers **8a** and **b** FVP results in extensive decomposition, as evident from the NMR and TLC analyses of the crude products. Interestingly, silica gel chromatography of both crude mixtures, using 5% ethyl acetate in hexane as eluent, provides the same unsaturated aldehyde **5e** (34 and 25% from **8a** and **b**, respectively), with, additionally, 3-phenylpropene **9** in the case of **8b** (6% yield). Again, none of the cyclopropene derivative expected from a retro Diels–Alder reaction of **8** could be detected (Scheme 3).

Mechanistically, the formation of **5** from **4** (and also **7** from **6**) can be interpreted as involving the well established cyclopropane ring opening *via* a biradical intermediate³ followed by hydrogen radical migration as the key steps. For **8**, it is most likely that a retro-ene reaction initially takes place to give **4e**, which readily ring opens to yield the observed aldehyde **5e** as shown in Scheme 3.

It should be noted that 1-cyanocyclopropene and, very recently, 1-methylcyclopropene carboxylate have been prepared and isolated in the forms of their Diels–Alder adducts.^{4,5} Our work here shows that the cyclopropenes cannot be regenerated from **4a** or **4f** by a FVP reverse Diels–Alder reaction as the latter fails to compete with ring opening reaction, the thermolysis yielding cleanly **5a** and **5f**, respectively. The reactions described here provide a convenient entry into dibenzohomobarrellene derivatives.

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Footnote

[†] Yields shown are isolated yields and all compounds described are fully characterized. Elemental analyses were performed by the Scientific and Technological Research Equipment Centre, Chulalongkorn University, Bangkok and by the Elemental Analysis Unit, Department of Chemistry, Faculty of Science, Silpakorn University, Nakorn Pathom.

References

- M.-C. Lasne and J.-L. Ripoll, *Synthesis*, 1985, 121.
- C. Mahidol, C. Thebtaranonth, Y. Thebtaranonth and C. Yenjai, *Tetrahedron Lett.*, 1989, **30**, 3857.
- D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, 1964, **86**, 564; J. E. Baldwin and C. B. Selden, *J. Am. Chem. Soc.*, 1993, **115**, 2239.