

Multiple pathways to ring-contracted aromatic hydrocarbons

Roger F.C. Brown and Frank W. Eastwood

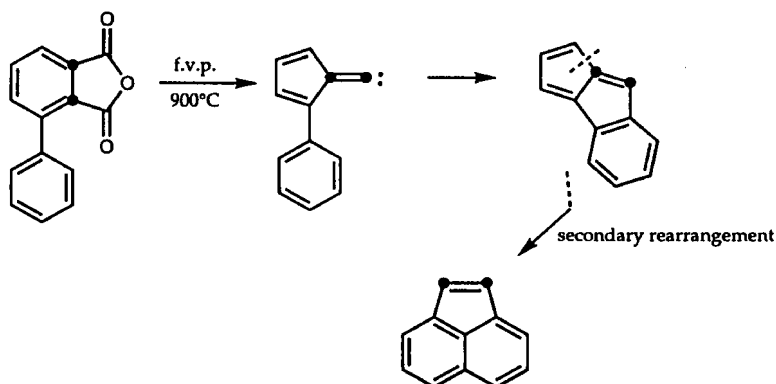
Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia

Abstract: The conversion of 3-phenylphthalic anhydride into cyclopent[*a*]indene (benzopentalene) by flash vacuum pyrolysis (FVP) is not unique; eighteen biphenyl-based anhydrides, allyl esters and bis-allyl esters can form benzopentalene. Similarly, triphenylene derivatives with 1,2-, 1,3-, 1,4- and 2,3- anhydride or bis-allyl ester functions form cyclopent[*h,i*]acephenanthrylene on FVP.

Introduction

Flash vacuum pyrolysis (FVP) of 3-phenylphthalic anhydride at 900°C forms cyclopent[*a*]indene (benzopentalene) accompanied by acenaphthylene and a little benzene (ref. 1). Benzopentalene dimerizes at room temperature and n.m.r. spectra of pyrolysates containing it must be run at -70°C. Proton n.m.r. spectra are valuable for detecting and estimating benzopentalene because the whole of the spectrum lies between δ 5.4 and 6.7, a region which is usually blank in the spectra of polycyclic aromatic hydrocarbons. The proposed mechanism of benzopentalene formation (ref. 1) has now been confirmed by a C-13 labelling experiment (Scheme 1).

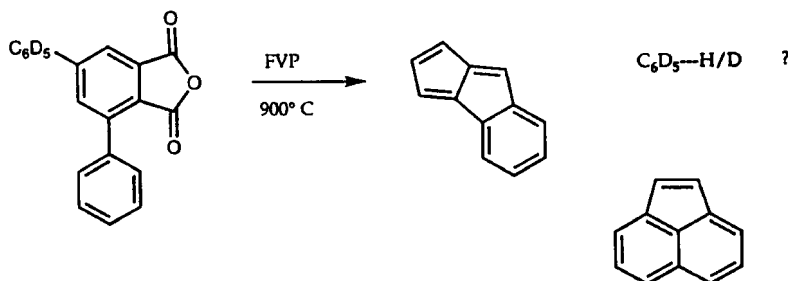
Scheme 1



This experiment confirmed our belief that acenaphthylene is a product of secondary rearrangement, but the origin of the small amount of benzene observed is still obscure.

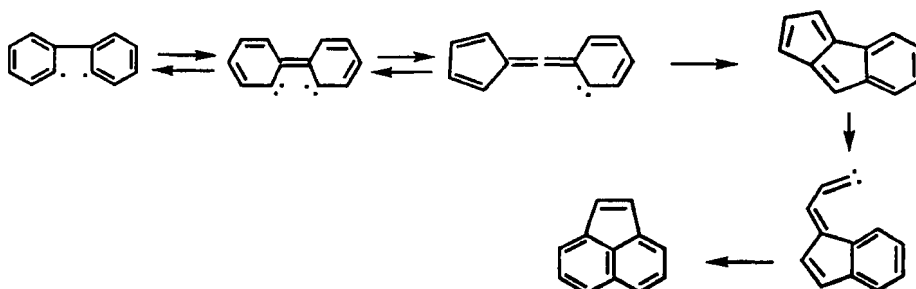
An even more obscure problem is that of the loss of one phenyl group on FVP of 3,5-diphenylphthalic anhydride; the products are benzopentalene, acenaphthylene and benzene, rather than the expected 2-phenylbenzopentalene. We are investigating the FVP of the D₅-phenyl derivative shown in Scheme 2, and preliminary results show that the benzopentalene contains little or no deuterium, but the benzene contains a range of deuterated species in which C₆H₀₋₂D₆₋₄ are prominent (GC - MS). We are still unable to propose a mechanism for this extraordinary loss of the 5-phenyl group. Loss of phenyl is not quite complete however; some less volatile material which deposits in the tube exit has the expected composition C₁₈H₁₂ (MS). These results are all the more extraordinary because our first experiment in this area, the FVP of tetraphenylphthalic anhydride, gave 1,2,3-triphenylbenzopentalene in 74% isolated yield (ref. 2) and we have searched in vain for loss of phenyl groups in this system.

Scheme 2



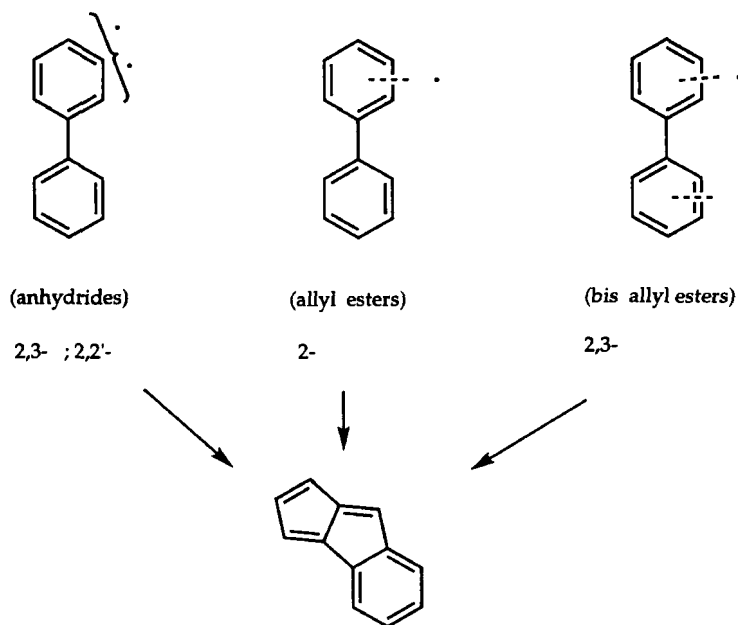
In other respects the pathway leading to benzopentalene seemed to be unique and well-defined, until the discovery of Wiersum and Jenneskens (ref.3) that FVP of both biphenylene and diphenic anhydride at 850 - 900°C gave benzopentalene (isolated as dimer; see ref. 4) and acenaphthylene. Both precursors were considered to be generating the biphenyl-2,2'-diradical which could then undergo the ring contraction and carbene insertion reactions necessary for benzopentalene formation (Scheme 3).

Scheme 3



This result led us to undertake a survey of the FVP behaviour of all the possible cyclic anhydrides, bis-allyl esters and allyl esters based on biphenyl - 18 compounds in all. At 1050 - 1100°C all of the compounds gave some benzopentalene, although only in a few cases was the yield substantial (> 20%); these cases are noted below the names in Scheme 4, and of course they include the original 3-phenylphthalic anhydride. Anhydrides and bis-allyl esters are assumed to generate arynes or diradicals, and allyl esters of monocarboxylic acids to generate aryl radicals. The problem then is to understand how so many related but different reactive intermediates can lead to the same product, benzopentalene (Scheme 4).

Scheme 4



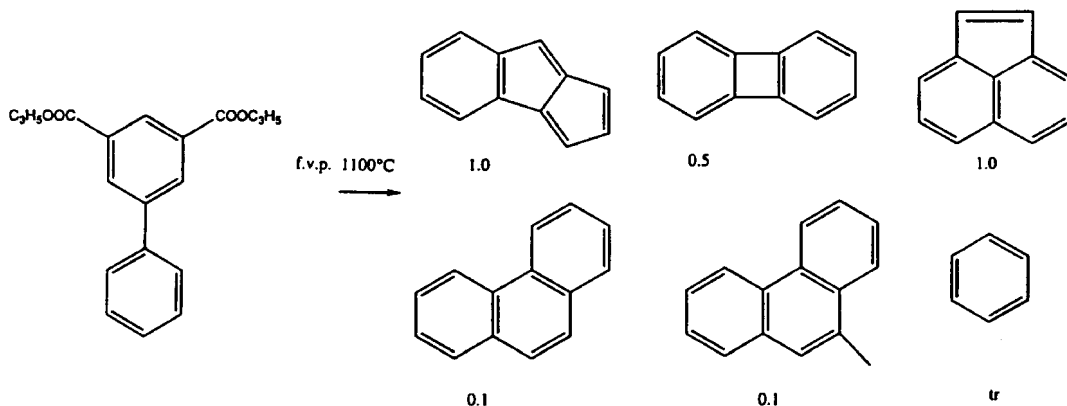
.....but ALL 18 compounds give some benzopentalene

There are numerous logical possibilities, amongst which are the following:

- Hydrogen atoms are so mobile at these temperatures that the location of initial substituents is irrelevant. Hydrogen atoms exchange between 2- and 2' positions.
- All species can rearrange, or rearrange and lose H, to give biphenyl-2,3-yne which then undergoes the usual ring contraction and insertion to form benzopentalene.
- Arynes not suitably placed for trapping by adjacent phenyl can ring-contrast and cyclise by a different mechanism.
- Aryl radicals can undergo ring contraction; the ring-contracted species can undergo cyclisation by a different mechanism.

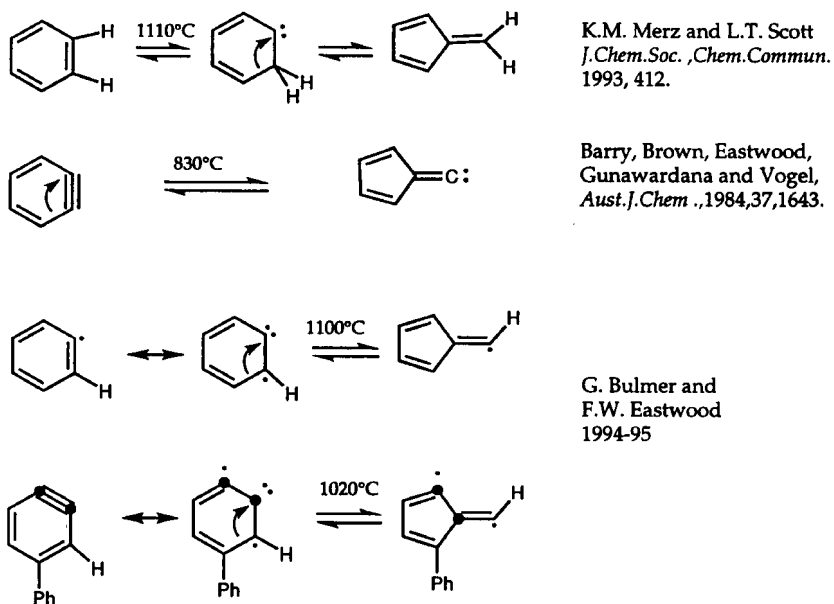
All of these pyrolytic reactions form mixtures of hydrocarbon products which are usually complex. The product distribution from one diester, diallyl biphenyl-3,5-dicarboxylate, is shown in Scheme 5. In addition to the expected $C_{12}H_8$ isomers this mixture contains phenanthrenes which we consider to incorporate carbon atoms from the allyl radicals formed at the same time.

Scheme 5



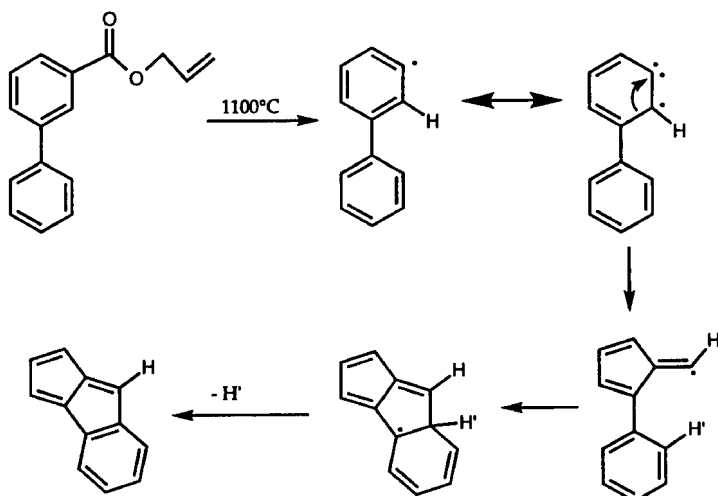
These results in the biphenyl series have led us to consider mechanisms of ring contraction beyond those established for benzene by Merz and Scott (ref.5) and proposed by our group for benzyne (ref. 6). The new mechanisms require direct ring contraction of an aryl radical, and an alternative mode of ring contraction of an aryne where the group which can trap a reactive intermediate is not adjacent to the aryne. The two familiar mechanisms and the two new proposals are shown in Scheme 6.

Scheme 6



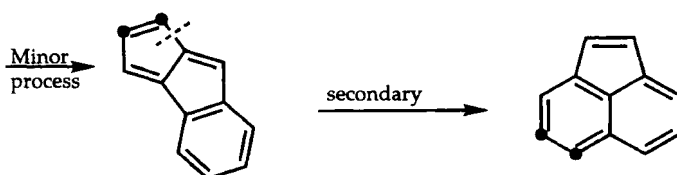
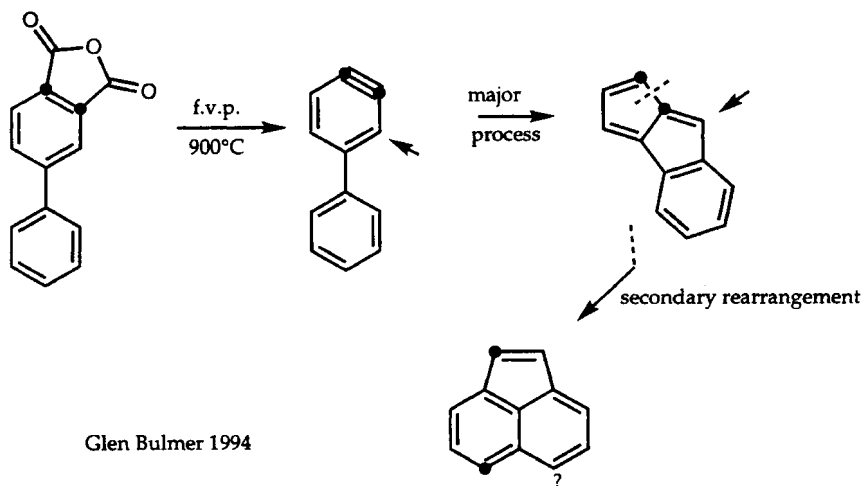
The idea of ring contraction of an aryl radical can be illustrated by the example of benzopentalene formation from allyl biphenyl-3-carboxylate (Scheme 7) although at this stage there are no labelling studies to support this hypothesis. In the case of 4-phenylphthalic anhydride there is ^{13}C labelling

Scheme 7



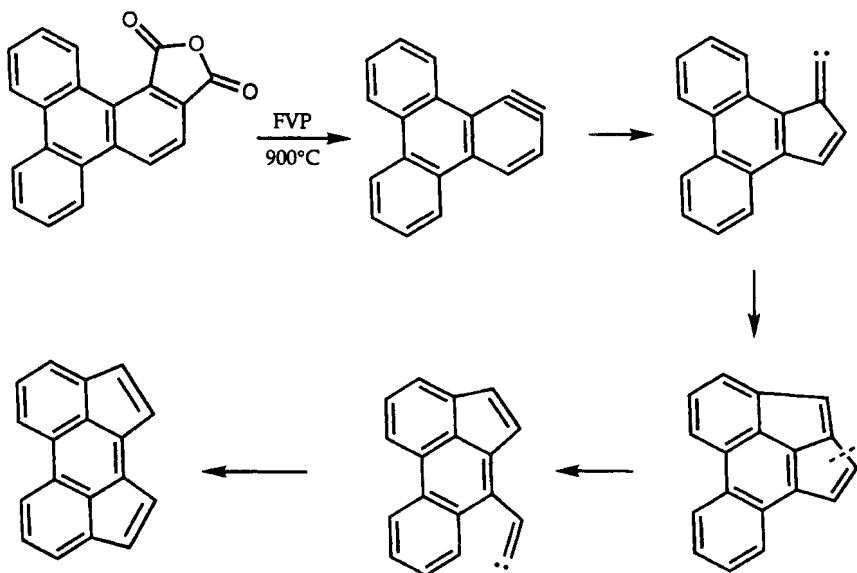
evidence for the occurrence of an unexpected mode of ring contraction; Scheme 8 shows the distribution of ^{13}C in benzopentalene formed by FVP of 1,2- $^{13}\text{C}_2$ -4-phenylphthalic anhydride. The key observations are that the labels are never separated, C3 appears to become the carbon arrowed in the product, and that there is a second minor process which presumably involves initial hydrogen migration.

Scheme 8



Similar multiple pathways to rearranged products containing five-membered rings have been found in the triphenylene series. The starting point for this work was the observation by Neilen and Wiersum (ref. 7) that triphenylene lost two hydrogen atoms on FVP at 1000°C and gave some cyclopent[*h,i*]acephenanthrylene. The mechanism proposed involved initial loss of hydrogen atoms to give the 1,2-aryne. We have checked that this mechanism is possible by generation of the 1,2-aryne, and indeed cyclopent[*h,i*]acephenanthrylene (CPAP) is formed in good yield by the pathway proposed by Neilen and Wiersum (Scheme 9).

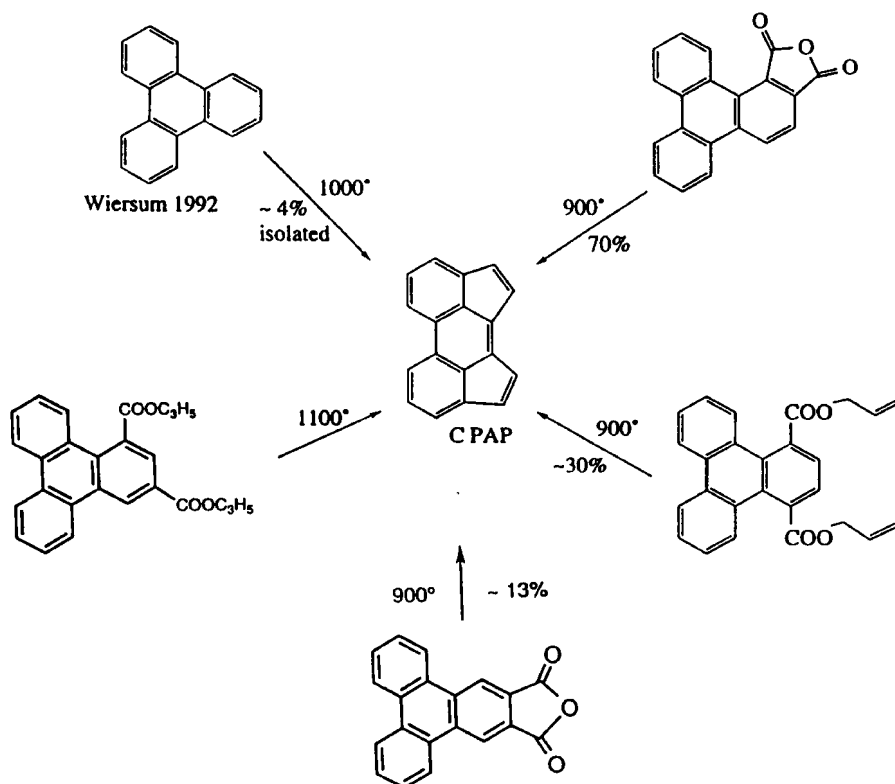
Scheme 9



Cyclopent[*h,i*]acephenanthrylene
'CPAP'; 70%.

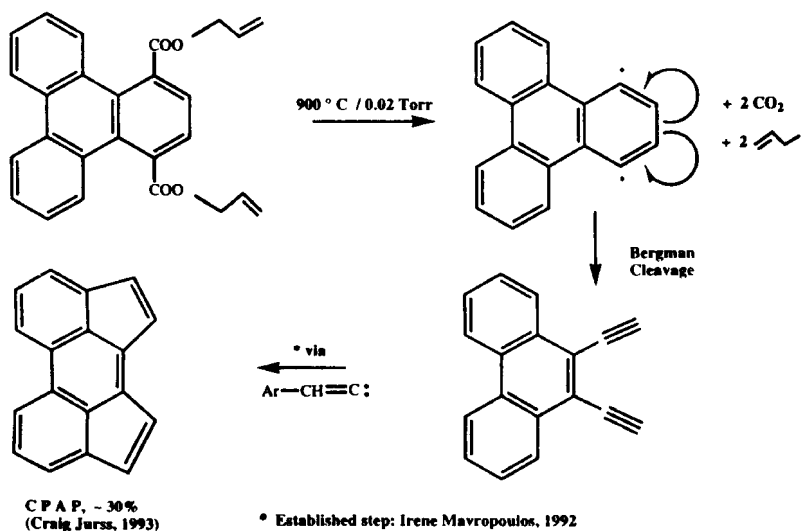
Guided by our experience in the biphenyl series, we then examined the FVP of four triphenylene derivatives substituted in the same ring, and once again we found that all four aryne or diradical intermediates led to formation of the rearranged hydrocarbon CPAP. Scheme 10 shows the pyrolytic behaviour of triphenylene and the four chosen pyrolytic starting materials.

Scheme 10



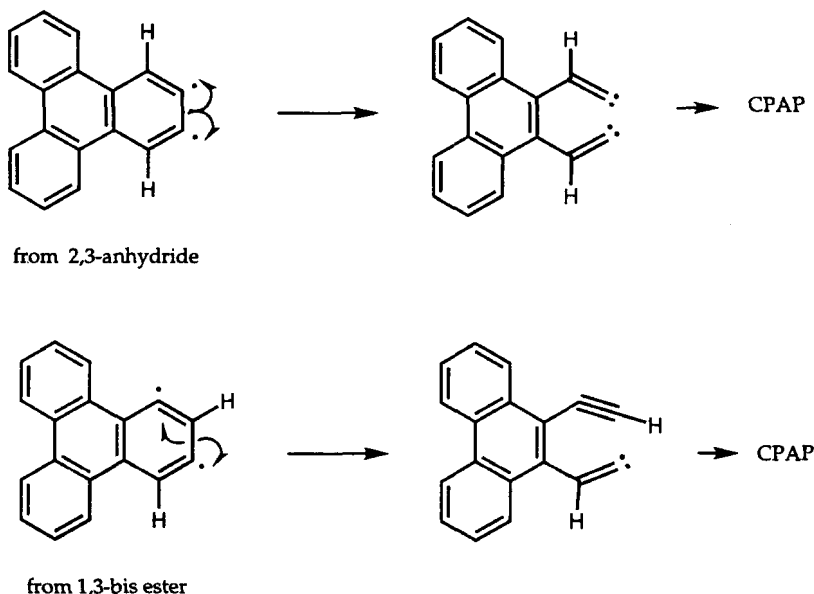
It is not quite so difficult to propose mechanisms for these rearrangements in the triphenylene series. In particular we consider that the 1,4-diallyl diester leads by radical fission and decarboxylation to the triphenylene 1,4-diradical which in turn undergoes Bergman fission to give 9,10-bisethynylphenanthrene. Independent experiments had established that 9,10-bisethynylphenanthrene can isomerise to CPAP under the same conditions (Scheme 11).

Scheme 11



In the case of the 2,3-diradical, fission of the 2,3-bond as shown in Scheme 12 would form a phenanthrene bearing two methylenecarbene functions at positions 9 and 10. This intermediate could cyclise by double insertion into the *peri* C-H bonds to form CPAP, and would probably also equilibrate with 9,10-bisethynylphenanthrene.

Scheme 12



The behaviour of the 1,3 diradical can be explained in a similar manner (Scheme 12); radical fission of the 2,3-bond would lead to one ethynyl group and one methylenecarbene group at C9 and C10 of phenanthrene, and these functions could lead to CPAP formation with only a minor perturbation of the previous pathway.

Acknowledgement

We thank the Australian Research Council for generous support of this work.

References

1. R.F.C. Brown, N. Choi, and F.W. Eastwood, *Aust.J.Chem.*, **48**, 185 (1995).
2. R.F.C. Brown, K.J. Coulston, F.W. Eastwood and T. Korakis, *Tetrahedron Lett.*, **29**, 6791 (1988).
3. U.E. Wiersum and L.W. Jenneskens, *Tetrahedron Lett.*, **34**, 6615 (1993).
4. R.F.C. Brown, N. Choi, K.J. Coulston, F.W. Eastwood, U.E. Wiersum and L.W. Jenneskens, *Tetrahedron Lett.*, **35**, 4405 (1994).
5. K.M. Merz and L.T. Scott, *J.Chem.Soc., Chem. Commun.*, 412 (1993).
6. M. Barry, R.F.C. Brown, F.W. Eastwood, D. Gunawardana and C. Vogel, *Aust.J.Chem.*, **37**, 1643 (1984).
7. U.E. Wiersum, *Janssen Chim.Acta*, **10**, 3 (1992)