

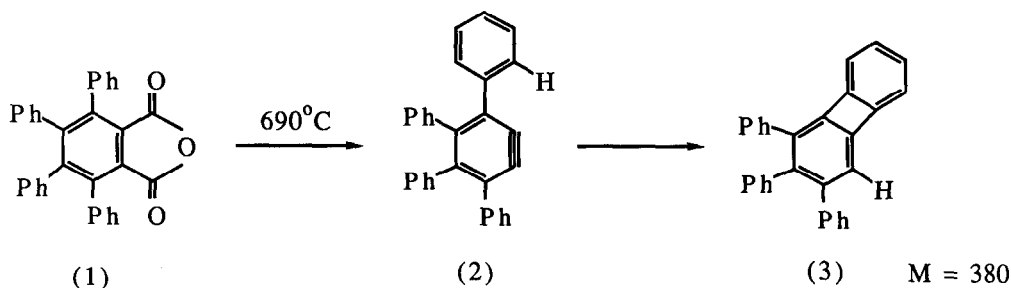
THE PYROLYSIS OF TETRAPHENYLPHTHALIC ANHYDRIDE: FORMATION OF 1,2,3-TRIPHENYLBENZOPENTALENE

Roger F.C. Brown*, Karen J. Coulston, Frank W. Eastwood* and Terry Korakis

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

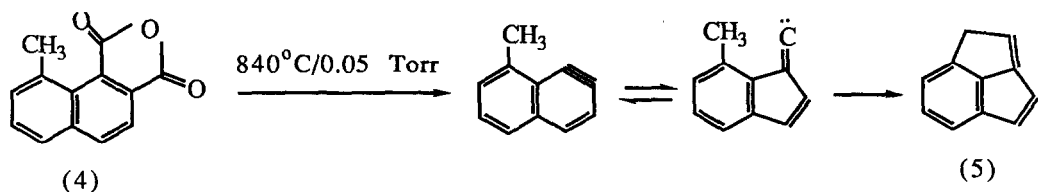
Abstract: The primary product of flash vacuum pyrolysis of tetraphenylphthalic anhydride at 860°C/0.04 Torr is 1,2,3-triphenylbenzopentalene (74%) and not 1,2,3-triphenylbiphenylene, as suggested by Fields and Meyerson (1968) for the product of pyrolysis at 690°C with long contact time (15-20 sec.).

In the course of their pioneering work on the reactions of arynes, generated by the pyrolysis of aromatic anhydrides, with aromatic and heteroaromatic compounds, Fields and Meyerson¹ noted that tetraphenylphthalic anhydride (1) was unique amongst those examined in that it showed little interaction with the added aromatic compounds. They pyrolysed this anhydride (0.01 mole) with the aromatic compound (0.1 mole) at 690°C for 15-20 sec. and showed by low voltage mass spectrometry that products of molecular weight 382, 380, 378, 306, 304 and 302 were formed. In most experiments the compound of mass 380 was the major product, and its formation was rationalised through the following proposed intramolecular reaction of the aryne (2) to give 1,2,3-triphenylbiphenylene (3).

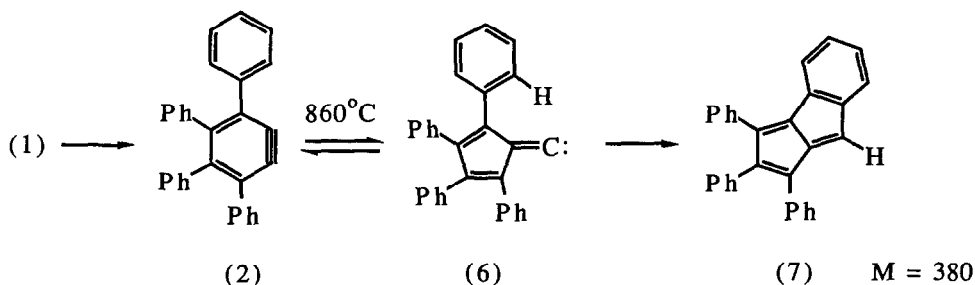


The other compounds appeared to be secondary products formed by loss of H_2 or C_6H_4 from the compound of mass 380.

Our recent work on the scrambling of the label in benzyne derived from $[1,6\text{-}^{13}\text{C}_2]$ phthalic anhydride,² and on the pyrolysis of 8-methylnaphthalene-1,2-dicarboxylic anhydride(4)^{3,4} to give 1*H*-cyclopent[*cd*]indene (5), suggested that the primary benzyne intermediate (2) must equilibrate with the cyclopentadienyliidene (6), and that this is unlikely to yield the speculative structure (3) on intramolecular trapping.



Flash vacuum pyrolysis of (1) at $860^\circ\text{C}/0.04$ Torr produced a dark green pyrolysate which on chromatography over silica gave 1,2,3-triphenylbenzopentalene (7) (74%) which was recrystallized from light petroleum as green crystals, m.p. $186\text{--}188^\circ\text{C}$ (lit.⁵, $186\text{--}187^\circ\text{C}$). Its spectroscopic properties⁶ were in agreement with those reported by Le Goff.⁵ The yield estimated by spectrometry of the pyrolysate at 585 nm was 80%; small amounts of (1) and of other products were also present (t.l.c.).



We propose that the primary intramolecular reaction involves insertion of the carbene centre in (6) into a C-H bond of an adjacent phenyl group, so leading directly to (7). A search for further examples of this behaviour is in progress.

Acknowledgements

We thank the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Australian Research Grants Scheme for support of this research programme.

References and Notes

1. E.K. Fields and S. Meyerson, *Advances in Physical Organic Chemistry*, Vol. 6, p.1. Academic Press, New York, 1968.
2. M. Barry, R.F.C. Brown, F.W. Eastwood, D.A. Gunawardana and C. Vogel, *Aust. J. Chem.*, 1984, **37**, 1643.
3. R.F.C. Brown, K.J. Coulston, F.W. Eastwood and S. Saminathan, *Aust. J. Chem.*, 1987, **40**, 107.
4. R.F.C. Brown, K.J. Coulston, B.J. Dobney, F.W. Eastwood and G.D. Fallon, *Aust. J. Chem.*, 1987, **40**, 1687.
5. E. Le Goff, *J. Am. Chem. Soc.*, 1962, **84**, 1505.
6. Spectra of (7) obtained from (1) : Mass spectrum: m/z 381(32%) 380(M,100), 379(8), 378(11), 377(9), 376(11); 303(8), 302(16). λ_{max} (cyclohexane) nm, $\log \epsilon$ (lit.⁵ $\log \epsilon$):272,4.48 (4.47); 293, 4.49, (4.48); 409,3.88(3.89); 425sh, 3.83(3.85); 585,2.41(2.39). ^1H n.m.r. (200 MHz, CDCl_3) δ 6.33,s,1H ; 6.69,m,3H; 6.85,m,3H ; 7.0 - 7.3,m, 13H.

(Received in UK 26 September 1988)