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Cyclopent[*a*]indene (Benzopentalene): Generation by Flash Vacuum Pyrolysis and Subsequent Dimerisation.

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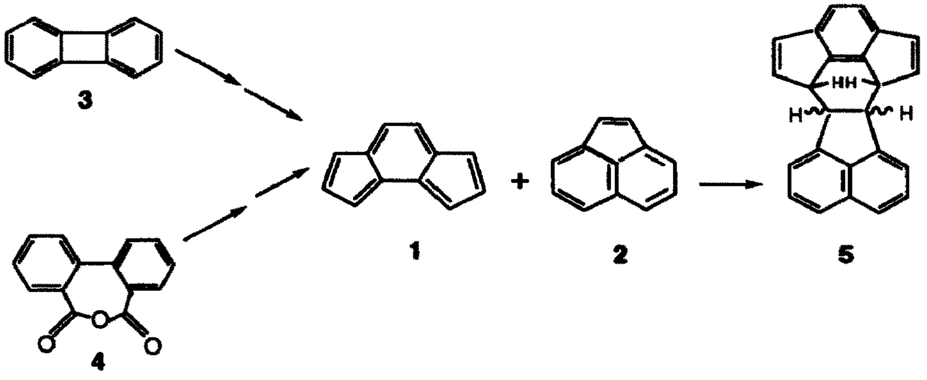
Abstract: Cyclopent[*a*]indene (benzopentalene, **7**) is generated by flash vacuum pyrolysis of 3-phenylphthalic anhydride (**6**), biphenylene (**3**) or diphenic anhydride (**4**). It dimerises readily and adds cyclopentadiene above -70 °C, but it does not equilibrate at 900 °C with *as*-indacene (**1**).

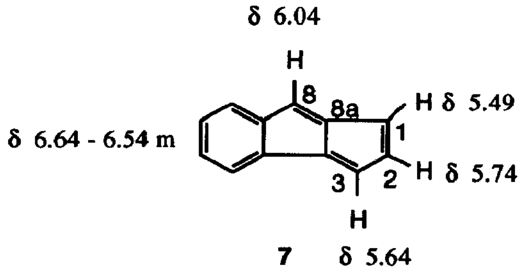
In a recent letter[1] from the Akzo/Utrecht authors, the trapping of the elusive $C_{12}H_8$ isomer *as*-indacene (**1**) by acenaphthylene (**2**) was postulated. A dimeric compound $C_{24}H_{16}$ was obtained from flash vacuum pyrolysis (FVP) of biphenylene (**3**) and of diphenic anhydride (**4**). The structure 6b,7,10,10a-tetrahydro-*as*-indaceno[1,8-*jkl*]fluoranthene (**5**) was proposed for this adduct (Scheme 1). In a series of Monash studies on FVP of aromatic anhydrides,[2] 3-phenylphthalic anhydride (**6**) was recently found to be a FVP precursor for the unstable $C_{12}H_8$ isomer cyclopent[a]indene (benzopentalene, **7**).[3] Although the Akzo/Utrecht group indicated **7** as the central

Scheme 1



intermediate in the formation of **1** and **2** as constituents of dimer **5**,[1] no evidence was found for the presence of **7** in the cold trap of their preparative apparatus.[4] Since anhydride **6** provides a good entrance to the $C_{12}H_8$ energy surface, its FVP and the chemistry of **7** were studied in more detail. Here we report the findings from FVP of **3**, **4** and **6**, under Monash conditions.[4]

FVP of tetraphenylphthalic anhydride was previously shown to produce 1,2,3-triphenylbenzopentalene[2] *via* C-H insertion in the benzyne-cyclopentadienylidene carbene equilibration mechanism.[5] Under similar conditions, 3-phenylphthalic anhydride (**6**) on FVP at 900 °C/0.02 Torr and washing the pyrolysate from the cold finger (-193 °C, CD_2Cl_2) for direct monitoring by ^1H NMR at -70 °C, gave cyclopent[*a*]indene (**7**), accompanied by acenaphthylene (**2**) and benzene (**8**) in approximate molar ratio of 10:1:1 (yield of **7** *ca.* 60%, Scheme 2). The 300 MHz ^1H NMR spectrum of cyclopent[*a*]indene (**7**) was well resolved from the other aromatic signals and the spectrum is assigned as shown below:



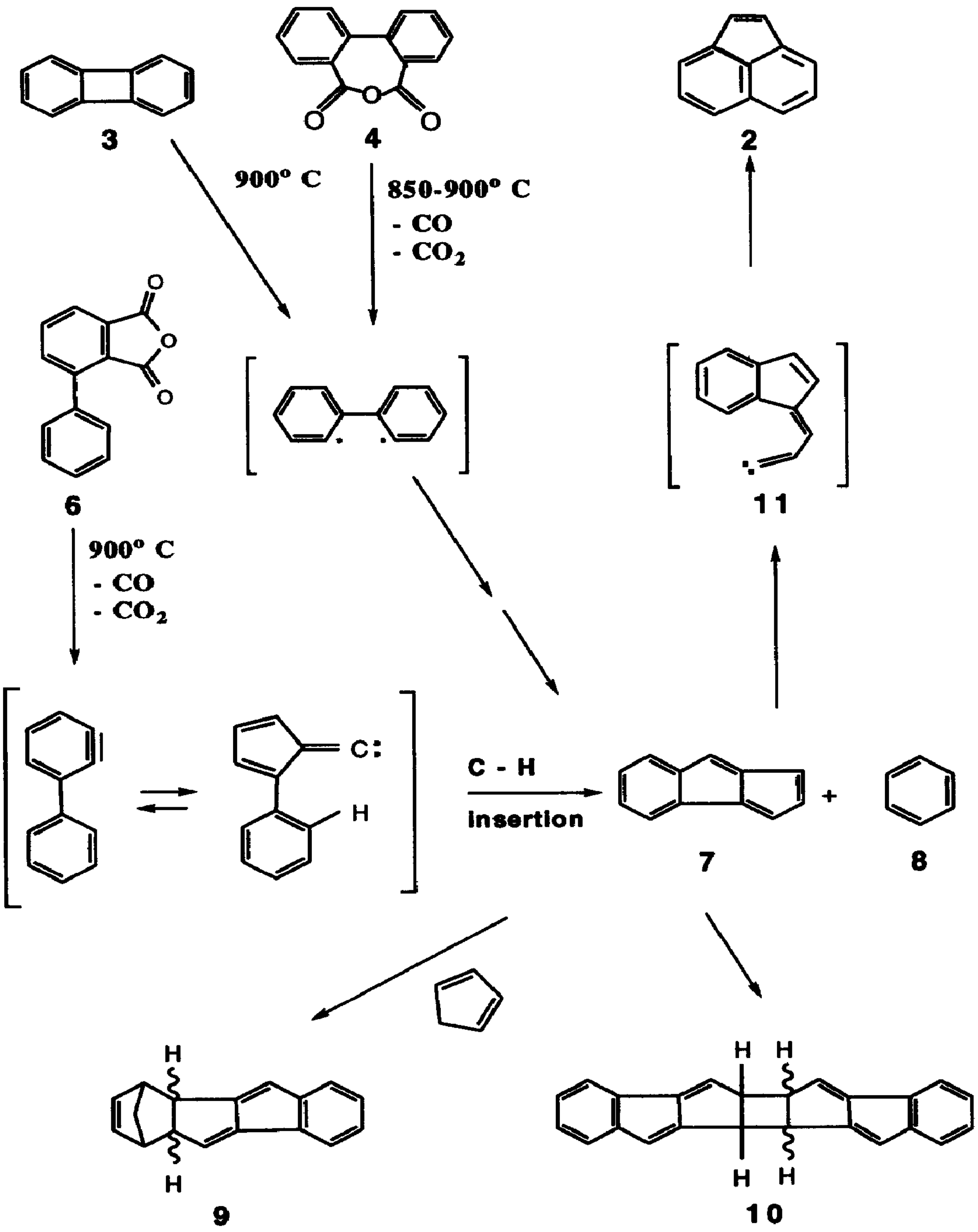
7

$J_{1,2} = 5.3$ Hz
$J_{2,3} = 1.9$ Hz
$J_{3,8} = 1.9$ Hz

Treatment at -78 °C of a CH_2Cl_2 solution of cyclopent[*a*]indene (**7**) from a similar pyrolysis of **6** (157 mg) with a large excess of cyclopentadiene, after raising to room temperature, gave on chromatography over silica a yellow liquid fraction **A** (119 mg) and a solid fraction **B** (42 mg). Further chromatography of **A** was necessary to remove acenaphthylene (**2**) and this then gave the cyclopentadiene adduct **9** as a yellow liquid (Scheme 2).[6] Purification of solid **B** by flash chromatography afforded a dimer $C_{24}H_{16}$ as a pale yellow solid (m.p. 150 °C, dec.). This compound showed ^1H and ^{13}C NMR spectra identical with those reported[1] for the hypothetical adduct **5**.[7] By analogy with the low temperature dimerisation of parent pentalene[8], the symmetrical structure **10**, was assigned to this dimer by the Monash group.[9] Closer consideration of the structure **5** reveals that the presence of four quaternary ^{13}C signals is more in line with the cyclopent[*a*]indene dimer structure **10**. Compound **5** would require five quaternary carbon signals.[10] Unequivocal proof for the dimer structure **10** was obtained from a comparison of its ^1H NMR pattern and UV/Vis spectrum[7] with those found for the cyclopentadiene adduct **9**.[6] The apparent difference in the decomposition temperature of the two samples (200 *vs.* 150 °C) may arise from instability. Dimer **10** decomposes over a few days, so that X-ray structure determination has not yet been possible.

The Monash group has examined the cold trap pyrolysates[4] from (**3**) and (**4**), using low temperature ^1H NMR ($CDCl_3$, -60 °C). In biphenylene pyrolysates the products were biphenylene (**3**), cyclopent[*a*]indene (**7**), acenaphthylene (**2**) and benzene (**8**) in approximate ratio 1:1.6:3.2:0.4. In diphenic anhydride (**4**) pyrolysates the products in addition to fluorenone[1], were biphenylene (**3**), cyclopent[*a*]indene (**7**) and acenaphthylene (**2**) in approximate ratio 1:4.5:0.9. After 24 h in $CDCl_3$ at 20 °C the spectrum of the dimer **10** replaced that of **7** in 75% yield based on integrals. The formation of acenaphthylene (**2**) in these pyrolyses is attributed[1] to a secondary cleavage of the C_1-C_{8a} bond in **7** to carbene **11**, followed by recyclisation to **2**.[11]

Scheme 2


3
4
2
900° C
850-900° C
- CO
- CO_2
6
11
900° C
- CO
- CO_2
C:
H
C - H
insertion
7
+
8
9
10
H
O

We conclude that the dimeric hydrocarbon $C_{24}H_{16}$ obtained after FVP of **3**, **4** and **6** possesses structure **10** and not the previously proposed structure **5**. Hence, *as*-Indacene is restored to its status as a synthetic challenge,[12] rather than as an established transient intermediate.

References and Notes:

1. Wiersum, U.E. and Jenneskens, L.W. *Tetrahedron Lett.*, **1993**, *34*, 6615.
2. Brown, R.F.C., Coulston, K.J., Eastwood, F.W. and Korakis, T. *Tetrahedron Lett.*, **1988**, *29*, 6791.
3. Choi, N. *Ph.D. Thesis, Monash University*, **1993**; Brown, R.F.C., Choi, N. and Eastwood, F.W. *Abstracts of the 7th, International Symposium on Novel Aromatic Compounds,* Victoria BC, Canada, July 19-14, 1992, Poster 18.
4. In the Monash equipment the distance from the hot zone to the cold surface in the trap is *ca.* 8 cm, while in the Akzo/Utrecht preparative set up with a bent quartz tube, this is 25-30 cm.
5. Brown, R.F.C. and Eastwood, F.W. *Synlett*, **1993**, 9.
6. Spectroscopic data of compound **9**; ^{1}H NMR δ ($CDCl_3$, 200 MHz) 7.67, d, *J* 7.0 Hz, H6; 7.22-7.00,m, H7-H9; 6.54, app. t., *J* 2.1 Hz, H5 ; 6.20, m, H10; 5.73,t, *J* 1.8 Hz, H2 and H3; 3.83, 3.39, 3.12, 2.95, 4 m, 4 xCH; 1.77, m, and 1.64, m, bridge CH_2. ^{13}C NMR δ ($CDCl_3$, 50.3 MHz) 154.8, 152.7, 150.5, 3 x $C_{quat.}$ signals; 135.7, 133.3, 132.5, 3 x CH signals; 129.6, $C_{quat.}$; 127.7, 123.1, 121.9, 120.3, 115.7, 5 x CH signals; 60.0, CH; 52.6, CH_2; 45.6, 44.4, 43.5, 3 x =CH signals. (Found: C, 93.6; H, 6.8. $C_{17}H_{14}$ requires C, 93.5; H, 6.5%.) Mass spectrum: *m/z* 218 ($M^{+\cdot}$, 6%), 202 (10), 152 (100), 89 (23), 83 (35). UV/Vis (C_6H_{12}; $\lambda_{max.}$ (log ε)) 232 (3.98); 267 (4.25); 297 (3.46); 307 (3.49); 319 (3.41); 336 (3.04); 366 (2.80).
7. Spectroscopic data of compound **10**; m.p. 130-150 °C (dec). ^{1}H NMR δ ($CDCl_3$, 200 MHz) 7.66, d, *J* 7.2 Hz, H4,7; 7.33-7.21, m, H2,3,8,9; 7.18-7.08, m, H1,10; 6.89, app. t, *J* 2.1 Hz, 2H; 6.49, s, 2H; 3.79, app. t, *J* 2.4 Hz, 2H; 3.22, d, *J* 4.2 Hz, 2H. ^{13}C NMR δ ($CDCl_3$, 50.3 MHz) 155.7, 151.9, 151.0, 129.8, $C_{quat.}$ signals; 134.1, 128.3, 123.6, 122.5, 120.8, 116.7, 58.0, 40.8, CH signals (Found, C, 94.4; H, 5.5. $C_{24}H_{16}$ requires C, 94.7; H, 5.3 %). Mass spectrum: *m/z* 304 ($M^{+\cdot}$, 6%), 152 (100). UV/Vis (C_6H_{12}; $\lambda_{max.}$ (log ε)) 234 (4.37); 246 (4.48); 255 (4.55); 262 (4.54); 309 (3.91); 323 (3.83); 341 (3.41); 376 (3.43).
8. Dönges, R., Hafner, K. and Lindner, H.J. *Tetrahedron Lett.*, **1976**, *17*, 1345.
9. The stereochemistry of **9** is not known and neither the regiochemistry nor the stereochemistry of dimer **10** has been established. The formation of a minor isomer[1] was also observed in the Monash experiments.
10. In the assigment for **5**,[1] based on quantitative ^{1}H-decoupled ^{13}C NMR, two quaternaries were thought to coincide.
11. FVP at 900 °C (Akzo/Utrecht apparatus) leaves **2** unchanged: at gradually higher temperatures carbonisation rather than (reversible) formation of **7**, *c.q.* dimer **10**, was observed.
12. Prinzbach, H. and Knothe, L., *Pure & Appl. Chem.*, **1986**, *58*, 25.

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