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Flash Vacuum Thermolysis of Biphenylene and Diphenic Anhydride. Formation of 6*b*,7,10,10*a*-Tetrahydro-*as*-indaceno[1,8-*jkl*]fluoranthene. Evidence for the Intermediacy of *as*-Indacene on the $C_{12}H_8$ Potential Energy Surface.

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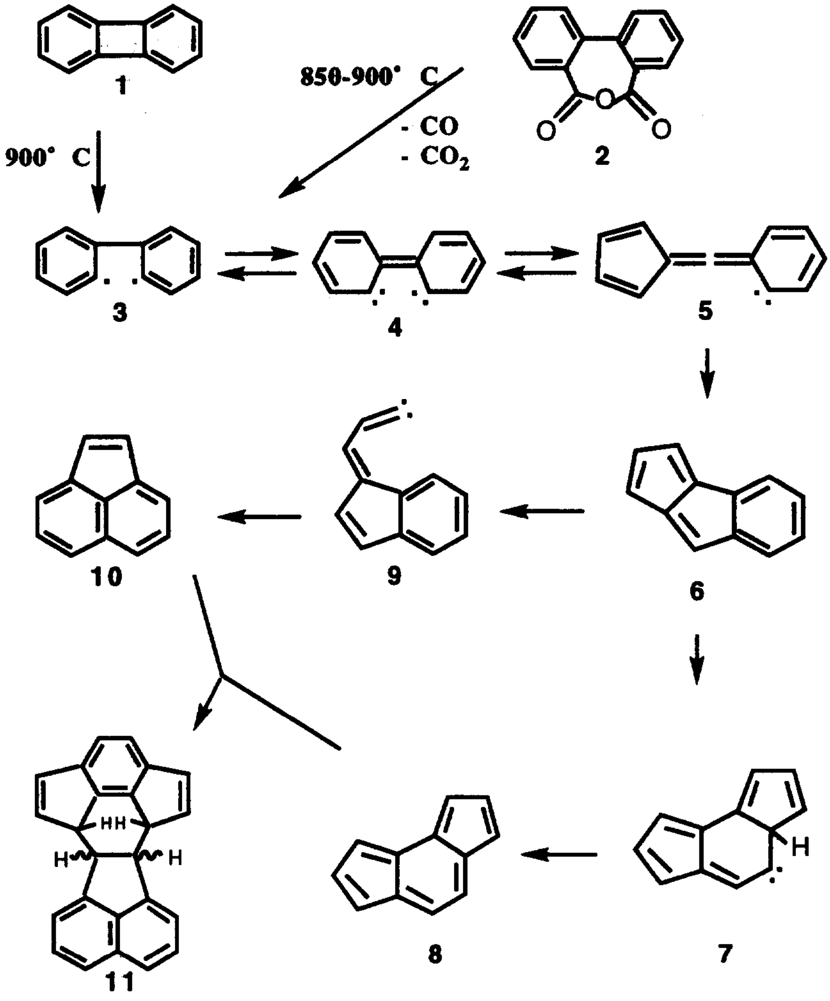
Abstract: Flash Vacuum Thermolysis (FVT) of biphenylene (**1**) and of diphenic anhydride (**2**) at 900 °C gave acenaphtylene (**10**), *exo-* and *endo*-6*b*,7,10,10*a*-tetrahydro-*as*-indaceno[1,8-*jkl*]fluoranthene (**11**) in high yield. The isolation of compound **11** provides evidence for the occurrence of the anti-aromatic *as*-indacene (**8**) on the $C_{12}H_8$ potential energy surface

It is well established that Flash Vacuum Thermolysis (FVT) of phthalic anhydride, benzocyclobutenedione and 5-[7-(2-norbornenylidene)] Meldrum's acid, respectively, gives access to *o*-benzyne.[1-3] These precursors have been used to gain insight in the spectroscopic properties of benzyne[2] and its equilibration[1,3,4] with cyclopentadienylidene carbene. However, *o*-benzyne undergoes consecutive dimerisation reactions to biphenylene (1) and biphenyl. In addition, extensive carbonization occurs upon FVT with gram quantities of phthalic anhydride.[5] In this context, we questioned ourselves whether biphenylene (1) would undergo *retro*-cleavage to *o*-benzyne.[6] As a consequence, we now report some unforseen results that stress the conclusion that the primary intermediate, *i.e.* diradical **3**, does *not* decompose to *o*-benzyne. Instead it equilibrates intramolecularly on the $C_{12}H_8$ potential energy surface under FVT conditions. The isolation of *exo-* and *endo*-6*b*,7,10,10*a*-tetrahydro-*as*-indaceno[1,8-*jkl*]fluoranthene (**11**) makes it reasonable to believe that the hitherto elusive *as*-indacene (**8**)[7] is generated as a discrete $C_{12}H_8$ species in the FVT of **1** and **2**. As a highly reactive diene **8** is eventually trapped by the simultaneously generated isomer acenaphthylene (**10**).

In our preparative FVT apparatus[3,8] biphenylene (1) started to decompose above 850 °C. Upon sublimation into the quartz tube at 900 °C (rate 0.3-0.4 g. in 30 min.) yellow crystalline acenaphthylene (**10**) collected in the cold trap (N_2(l); mass recovery 45%) and a yellow-brown solid material deposited in the bend of the quartz tube (mass recovery 55%); no carbonization was observed.[1,3,5] Extraction of the latter with *n*-hexane gave a soluble fraction that contained acenaphthylene (**10**) and a trace amount of starting material **1**;

Scheme

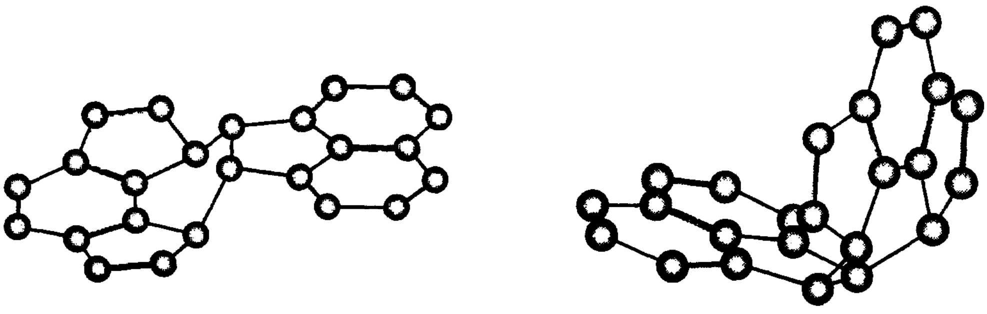


the residual part of the deposit dissolved in chloroform. ^{1}H-, ^{13}C NMR, IR and MS analysis of the chloroform fraction revealed that it was a mixture of *exo*- and *endo*-6*b*,7,10,10*a*-tetrahydro-*as*-indaceno[1,8-*jkl*]fluoranthene (**11**; ratio *exo* and *endo* 0.85:0.15,).[9] Compound **11**, a formal *o*-benzyne tetramer *cq.* a $C_{12}H_8$ dimer, is readily recognized as the Diels-Alder adduct of acenaphthylene (**10**) and the unknown *as*-indacene (7)![10] Additional support for this course of reaction was obtained with diphenic anhydride (**2**); FVT at 850-900 °C gave compounds **10**, **11** and a minor amount of biphenylene (**1**) (mass recovery 85-90% with respect to 2).[11] These results corroborate that diradical **3** must indeed be considered as the primary intermediate in FVT of compounds **1** and **2**, respectively. To gain insight in the conformations of the *exo*- and *endo* forms of **11** MMX[12] and AM1[13] calculations were done; two minima were located (Figure).[14]

Our observations can be rationalized by invoking that the residual bond between the two phenyl radicals in diradical **3** is not a *genuine* single bond,[15] so that it persistently stays in the $C_{12}H_8$ energy surface. Although numerous $C_{12}H_8$ intermediates can be formulated, a tentative mechanism is proposed based on literature precedents (Scheme). We propose that **3** rearranges to the bicarbenoid **4** that undergoes a Wolff-type ring-contraction to **5**.[1,16,17] The latter can give carbene-insertion to form cyclopent[*a*]indene (**6**). From compound **6** the elusive, anti aromatic[7] *as*-indacene (**8**) can be rationalized[16] by a ring-contraction ring-expansion mechanism to carbene **7** followed by a 1,2-H migration. Cyclopent[*a*]indene (**6**) was recently identified at temperatures below -70 °C and was found to be highly reactive[17] in line with its predicted[7] resonance energy per π-electron, which is close to zero. The identification of acenaphthylene (**10**) in the generation of **6**[17] suggests that the latter also escapes via homolytic cleavage of a carbon-carbon bond of the annulated cyclopentadiene-ring and a sequential 1,5-H shift to the carbenoid species **9** as a precursor for **10**.[18]

Since calculations[19] predict that *as*-indacene (**8**) possesses an *o*-xylylene substructure, it will act as a highly reactive diene in the Diels-Alder reaction with dienophile **10**, thus furnishing *exo*- and *endo*-6*b*,7,10,10*a*-tetrahydro-*as*-indaceno[1,8-*jkl*]fluoranthene (**11**). In summary, the isolation of the stereomers **11** from biphenylene (**1**) and diphenic anhydride (**2**) under FVT conditions, provides good evidence for the *in situ* generation of *as*-indacene (**8**) via a sequence of $C_{12}H_8$ interconversions starting with the primary formed diradical **3**. Despite the predicted high reactivity[7,10] at ambient temperature, **8** appears to survive in the high temperature dilute gasphase.[20]

Figure. *Exo*- and *endo* conformers of compound **11** calculated with AM1; hydrogen atoms are omitted for clarity.[12-14]



Exo - **11** (ΔH_f^0 149.51 kcal/mole) *Endo* - **11** (ΔH_f^0 155.03 kcal/mole)

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9. Compound **11**: DSC; 200 ^{o}C (dec.); ^{1}H NMR (CDCl$_3$) δ 7.67 (d, ^{3}J(HH)= 8.0 Hz, 2H), 7.30 (m, 4H), 7.14 (m, ^{3}J(HH)= 8.0 Hz, 2H), 6.89 (m, 2H), 6.59 (bs, 2H), 3.80 (m, ^{3}J(HH)= 4.0 Hz, 2Hz) and 3.23 (m, ^{3}J(HH)= 4.0 Hz, 2H) ppm; ^{13}C NMR (CDCl$_3$) δ 155.2, 152.8, 151.0, 132.8, 129.8, 128.2, 123.5, 122.2, 120.8, 116.5, 58.0, 41.0 ppm.; MS/EI (%, fragment), 304 (40, $M^{+\cdot}$), 152 (100, $C_{12}H_8^{+}$); Exact mass: calculated for $C_{24}H_{16}$ 304.1252, found 304.1254. Besides the *methine* and *five-membered ring* proton multiplets, additional low intensity multiplets at δ 3.34, 3.66, 6.43 and 6.99 ppm., respectively, were observed in the ^{1}H NMR spectrum, which indicates the presence of a second minor conformer. The integral ratio between the multiplets of both conformers is 0.85:0.15. Based on the discernable coupling constants, hey are tentatively assigned to the *exo*-**11** and *endo*-**11** conformers.
10. Despite subtle synthetic strategies, *as*-indacene (**8**) has never been prepared ; Prinzbach, H.; Knothe, L. *Pure & Appl. Chem.*, **1986**, *58*, 25 and references cited.
11. FVT at 750 ^{o}C of diphenic anhydride (**2**) quantitatively yields fluorenone as the only product. The latter is stable up to 1000 ^{o}C; further increase of the temperature leads to extensive carbonization.^{5} Note that FVT of dibenzothiophene sulfone gives dibenzofuran in high yield; Fields, E.K.; Meyerson, S. *J. Am. Chem. Soc.*, **1966**, *88*, 2836. We found that FVT of 2-hydroxy-biphenyl-2'-carboxylic acid lactone also gave dibenzofuran: cf. also Wiersum, U.E. *Rec. Trav. Chim., Pays Bas*, **1982**, *101*, 365.
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17. Brown, R.F.C.; Choi, N.; Eastwood, F.W. *Abstracts of the 7th. International Symposium on Novel Aromatic Compounds*, Victoria, Canada, July 1992 (*ISNA7, poster 18*); FVT of 3-phenylphthalic anhydride at 900 ^{o}C gave cyclopent[*a*]indene (**6**) and acenaphthylene (**10**). The generation of $C_{12}H_8$ intermediates from another precursor may explain differences in the product composition; Brown, R.F.C. *personal communication.*
18. Brown, R.F.C.; Eastwood, F.W.; Wong, N.R. *Tetrahedron Lett.*, **1993**, *34*, 1223.
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