Pergamon

Tetrahedron Letters, Vol. 37, No. 37, pp. 6819-6820, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01488-8

Formation of Biphenylene by Elimination of C_2 from 9,10-Didehydrophenanthrene at 1100°C

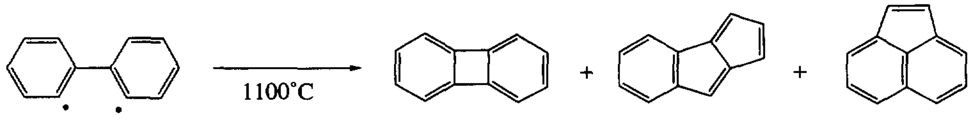
Roger F.C. Brown, Karen J. Coulston and Frank W. Eastwood

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

Abstract: Flash vacuum pyrolysis of phenanthrene-9,10-dicarboxylic anhydride **5** and of 2,2-dimethyl-5-(9'-fluorenylidene)-1,3-dioxan-4,6-dione **8** at 1100°C/0.03-0.04 mm Hg gave pyrolysates which were analysed by ^{1}H NMR spectroscopy and shown to contain phenanthrene **9** as a major constituent and biphenylene **2** as a minor one. Copyright © 1996 Elsevier Science Ltd

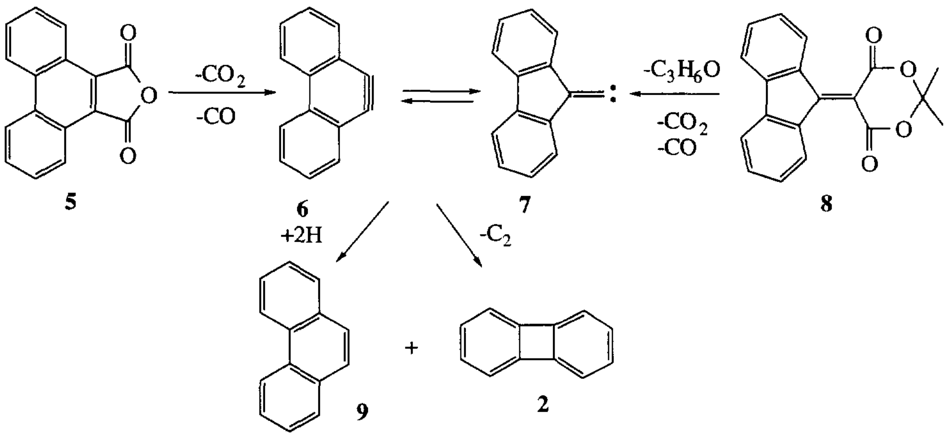
It was reported by L.T. Scott[1] and U.E. Wiersum[2] at separate meetings that pyrolysis at 1100°C of chrysene ($C_{18}H_{12}$) yields cyclopent[*cd*]fluoranthene ($C_{18}H_{10}$). The latter author reported also that indeno[2,1-*a*]indene ($C_{16}H_{10}$) and fluoranthene ($C_{16}H_{10}$) were present with cyclopent[*cd*]fluoranthene in the pyrolysate of chrysene and proposed a mechanism for the formation of these compounds which involved sequential loss of two hydrogen atoms and a C_2 fragment. In addition, Scott[1] described the pyrolysis of benzo[*ghi*]perylene ($C_{22}H_{12}$) at 1100°C and its conversion into dicyclopenta[*cd,fg*]pyrene ($C_{20}H_{10}$) and speculated that this conversion might be initiated by loss of acetylene. As a contribution to understanding the processes involved in these reactions, we describe our findings on the behaviour of 9,10-didehydrophenanthrene (**6** $\rightleftharpoons$ **7**) when formed in the gas phase at 1100°C.

We sought to determine if C_2 could be lost from 9,10-didehydrophenanthrene **6** or 9-fluorenylidenecarbene **7**, which are assumed to be interconvertible, since this might result in the formation of 2,2'-didehydrobiphenyl **1** which is known to be converted at 1100°C into biphenylene **2**, cyclopent[*a*]indene **3** and acenaphthylene **4**.[3]



1 **2** **3** **4**

9,10-Phenanthrenedicarboxylic anhydride[4] **5** (9 mg) was pyrolysed at 1100°/0.03 mm Hg and the cold pyrolysate was dissolved in $CDCl_3$ under nitrogen, stored at -76°C and the ^{1}H NMR spectrum measured at -60°C (recovered pyrolysate 1.5 mg). The spectrum showed the major product to be phenanthrene **9**. The spectrum of biphenylene **2** was clearly recognisable but the spectra of cyclopent[*a*]indene **3** and acenaphthylene **4** were not observed. From the integrated signals the ratio of **9**:**2** was 92:8. 2,2-Dimethyl-5-(9'-fluorenylidene)-1,3-dioxan-4,6-dione[8] **8** (30 mg) was pyrolysed at 1100°/0.04 mm Hg and the ^{1}H NMR spectrum of the pyrolysate determined as described above (recovered pyrolysate 1.6 mg). The spectrum showed the presence of acetone, phenanthrene and biphenylene. Again, the spectra of cyclopent[*a*]indene and acenapthylene were not observed. The ratio of **9**:**2** was 94:6. When phenanthrene was pyrolysed at 1100° under the same conditions it was recovered unchanged.[9]



In our apparatus under the pyrolytic conditions described, biphenylene would be converted to only a small extent into cyclopent[*a*]indene and acenapththylene. We suggest that biphenylene is formed directly from 9,10-didehydrophenanthrene rather than through 2,2'-didehydrobiphenyl.

REFERENCES AND NOTES

1. Scott, L.T. "Fragments of fullerenes: Novel syntheses, structures and reactions", *Pure & Appl. Chem.*, **1996**, *68*, 291-300. Presented at Eighth International Symposium on Novel Aromatic Compounds, Braunschweig, Germany, July 1995.
2. Wiersum, U.E. "Carbene intermediates in high temperature interconversions of polyaromatics", International Chemical Congress of Pacific Basin Societies, Honolulu, USA, December 1995.
3. Brown, R.F.C.; Choi, N.; Coulston, K.J.; Eastwood, F.W.; Wiersum, U.E.; Jenneskens, L.W. *Tetrahedron Lett.*, **1994**, *35*, 4405-4408.
4. Reduction of 9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene[5] with SnCl$_2$ in acetic/hydrochloric acids[6] gave 9,9-dimethyl-10-phenanthrone and 9,10-dimethylphenanthrene. Oxidation of the hydrocarbon (340 mg) with aqueous sodium dichromate[7] gave a neutral fraction (100 mg), consisting of 9,9-dimethyl-10-phenanthrone and 9,10-dimethylphenanthrene (ca. 10%), and phenanthrene-9,10-dicarboxylic acid (14 mg). The acid was dehydrated with acetic anhydride to give anhydride **5**, subl. > 260°C, ν_{max} 1842, 1771 cm^{-1}, m/z 248.
5. Zincke, Th.; Tropp, W. *Liebigs Ann.*, **1908**, *362*, 242-259.
6. Rimmer, R.W.; Christiansen, R.G.; Brown, R.K.; Sandin, R.B. *J. Am. Chem. Soc.*, **1950**, *72*, 2298-2299.
7. Bavin, P.M.G. *Can. J. Chem.*, **1960**, *38*, 911-916.
8. Baxter, G.J.; Brown, R.F.C. *Aust. J. Chem.*, **1975**, *28*, 1551-1557.
9. Phenanthrene when pyrolysed at 1100°C under different conditions yields a small amount of pyracyclene (cyclopent[*fg*]acenaphthylene).[1]

(*Received in UK* 15 *July* 1996; *accepted* 26 *July* 1996)