8410 *J. Org. Chem.* **1995**, *60*, 8410–8411

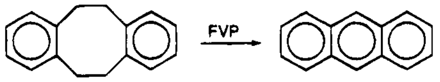
Formation of 2-(2′-Hydroxybenzyl)benzaldehyde by the Flash Vacuum Pyrolysis of 6*H*,11*H*-Dibenzo[*b*,*f*][1,4]dioxocin[1]

Walter S. Trahanovsky,* Suk-Kyu Lee, and
Jared W. Fennell

*Department of Chemistry, Iowa State University and
Ames Laboratory, Ames, Iowa 50011*

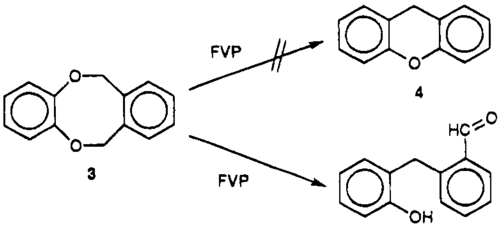
Received April 12, 1993

The flash vacuum pyrolysis (FVP) of the [4 + 4] dimer of *o*-xylylene (**1**) gives anthracene (**2**) as the major product.[2] We have proposed a general mechanism for this remarkable transformation, presented in Scheme 1, which overall involves the loss of one bridge of the starting material and splitting of the other bridge and flipping of the two remaining moieties by 180°.[3] The FVP of dibenzosuberone, –Z– = –C(O)–, also fits this scheme, giving a high yield of anthracene,[4] and we have shown by studying substituted compounds that both this reaction[3] and the FVP of *o*-xylylene [4 + 4] dimers[2] involve a 180° ring flip.



1 2

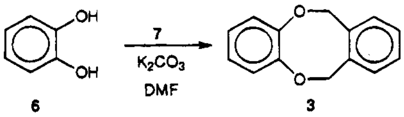
Thus we expected on the basis of this general mechanism that the FVP of cyclic diether **3** would give **4**, but instead we obtained a good yield of **5**. The results of this study are reported in this Note.



3 4 5

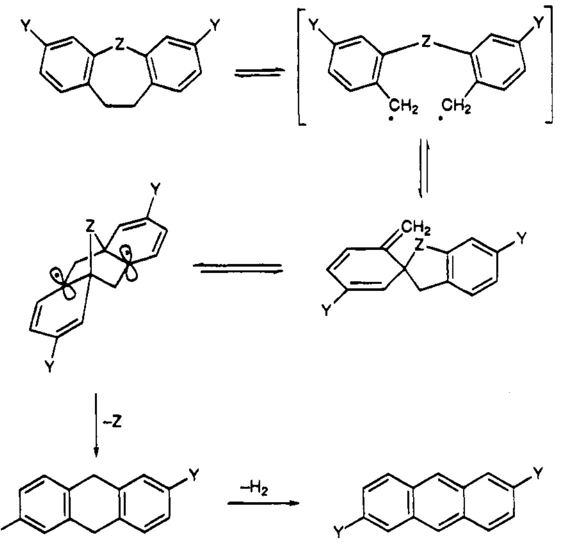
Results

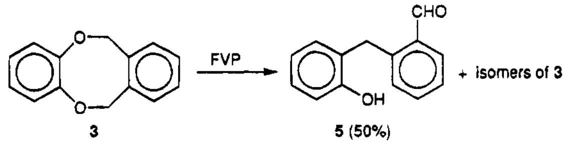
Compound **3** was prepared from catechol (**6**) and α,α′-dichloro-*o*-xylene (**7**) in excellent yield. The FVP of **3** at 580 °C and at 10^{-4} torr gave a 50% yield of **5** as the major product along with other isomers of **3** (25%) and recovered **3**. The structure of **5** was determined by its spectral properties: its ^{1}H NMR spectrum includes a singlet at δ 10.17 for the aldehydic proton, a multiplet at δ 7.9–6.75 for the benzene protons, a singlet at δ 6.50 for the phenol proton, and a singlet at δ 4.37 for the methylene proton; the IR spectrum of **5** shows strong absorptions at 3300–2800 cm^{-1} for the phenol group and at 1660 cm^{-1} for the aldehyde group; the high resolution mass spectral data for **5** is consistent with the molecular formula $C_{14}H_{12}O_2$.



6 3

Scheme 1





3 5 (50%)

Discussion

A pathway which accounts for the formation of **5** by the FVP of **3** is presented in Scheme 2. Homolytic cleavage of the weakest bond of **3** to form diradical **8** is a reasonable first step. Diradical **8** could close to form spiro compound **9** or spiro compound **10**. Calculated[5] heats of formation, ΔH_f's, of **9** and **10** indicate that **9** with its carbonyl group is *ca.* 20 kcal/mol more stable than **10** which means that the formation of **9** should dominate. Spiro compound **9** could undergo homolytic cleavage to give diradical **11** which could produce **5** by an intramolecular hydrogen-atom transfer. Alternatively, **9** could undergo a concerted rearrangement to **5**. In principle, spiro compound **9**, as well as spiro compound **10** if it is formed, could rearrange to diradical **12** which could give **4** by loss of formaldehyde, but these routes must be less important than the conversion of **9** to **5** since no **4** was observed and **5** is the major product. Calculated[5] ΔH_f's for **9** and **5** show that **5** is *ca.* 5 kcal/mol more stable than **9**, and this may be an important factor favoring the conversion of **9** to **5**. Also, the calculated ΔH_f for **3** shows that it is *ca.* 10 kcal/mol less stable than **5**, and thus the overall rearrangement of **3** to **5** is thermodynamically reasonable. The fact that the FVP of cyclic diether **3** does

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[1] Based on work by S.-K.L. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

[2] Trahanovsky, W. S.; Surber, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4995.

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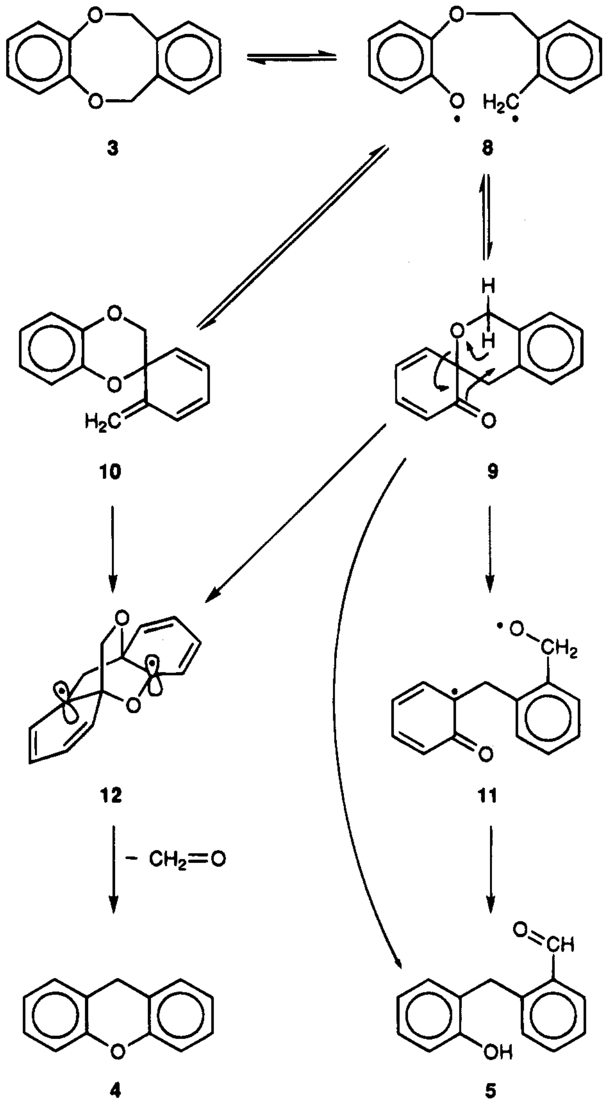
0022-3263/95/1960-8410$09.00/0

Scheme 2



not fit the general scheme which gives anthracene (**2**) (Scheme 1) may be because the alternative pathway that it takes, rearrangement to **5**, involves formation of an intermediate and product each of which is unusually stable because it has a carbonyl group.

The thermal rearrangement represented by the conversion of **3** to **5** should be somewhat general and may provide a useful preparative route to 2-(2′-hydroxybenzyl)benzaldehydes. However, substituents must be able to survive the FVP conditions, and unsymmetrical cyclic ethers may lead to mixtures of products.

Experimental Section

Methods and Materials. Some general methods have been described previously.[6] ^{1}H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 spectrometer. IR spectra were obtained on either a Beckman Acculab II or a Beckman 4250 spectrometer. GCMS were performed on a Finnegan 4000 mass spectrometer. HRMS were measured with either an Associated Electronics Industries MS-902 instrument or an MS 50 mass spectrometer. All materials were commercially available and used as received except where indicated.

6*H*,11*H*-Dibenzo[*b*,*f*][1,4]dioxocin (3). A solution of 1.75 g (10 mmol) of α,α′-dichloro-*o*-xylene (**7**) in 35 mL of DMF was added dropwise over 1.0 h to a stirred solution of 1.20 g (10.9 mmol) of catechol (**6**) and 2.80 g (20.6 mmol) of anhydrous potassium carbonate in 50 mL of DMF at 90 °C. After the reaction mixture was stirred at 90 °C for 12 h, it was cooled to room temperature and diluted with 300 mL of cold water. The resulting solution was extracted with ether (3 × 40 mL). The ether layers were combined and washed successively with 10% NaOH (3 × 30 mL) and saturated NaCl (3 × 30 mL). The organic layer was dried (MgSO$_4$) and concentrated to give 1.90 g (9.0 mmol, 90%) of **3** an oil: (lit.[7] mp 28 °C); ^{1}H NMR (CDCl$_3$) δ 7.4−6.8 (m, 8 H), 5.40 (s, 4 H) (lit.[8] (CD$_2$Cl$_2$) δ 7.3−6.9 (m, 8 H) and 5.41 (s, 4 H)); IR (neat, NaCl) 1490, 1240, 1100, 1000, 910, 740 cm^{-1} (lit.[7] (CHCl$_3$) 1575, 1480, 1230, 970, 740 cm^{-1}); GC/MS (70 eV) *m/e* (% base peak) 214 (0.23), 213 (2.46), 212 (17.65), 105 (9), 104 (100), 103 (20), 78 (23), 77 (10), 52 (11); high resolution mass spectrum calculated for $C_{14}H_{12}O_2$ 212.08373, measured 212.08365.

FVP was performed as previously described.[9,10]

FVP of 6*H*,11*H*-Dibenzo[*b*,*f*][1,4]dioxocin (3). A 500 mg (2.36 mmol) quantity of **3** was pyrolyzed at 580 °C in the normal manner. The pyrolysate in the liquid nitrogen trap was dissolved in CDCl$_3$ (to permit analysis by NMR). The pyrolysate which had deposited in the quartz tube after the hot zone was also dissolved in CDCl$_3$. The organic layers were combined, dried (MgSO$_4$), and concentrated, and the crude product was purified by thin layer chromatography on silica gel (50% ether in hexanes) to give 250 mg (1.18 mmol; 50%) of 2-(2′-hydroxybenzyl)benzaldehyde (**5**): mp 138−139 °C; ^{1}H NMR (CDCl$_3$) δ 10.17 (s, 1 H), 7.90−6.75 (m, 8 H), 6.50 (s, 1 H), 4.37 (s, 2 H); IR (KBr) 3300-2800, 1660, 1580, 1450, 1250, 1210, 740 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 194.77, 153.89, 142.35, 134.12, 133.57, 133.36, 131.71, 130.63, 127.98, 126.88, 126.15, 120.60, 116.14, 32.18; GC/MS (70 eV) *m/e* (% base peak) 214 (1.95), 213 (10.05), 212 (75.62), 211 (24), 196 (12), 195 (86), 194 (61), 184 (25), 183 (18), 181 (18), 177 (11), 169 (13), 167 (23), 166 (25), 165 (73), 155 (14), 153 (23), 152 (36), 151 (10), 141 (25), 139 (14), 129 (12), 128 (28), 127 (18), 119 (11), 118 (100), 115 (38), 105 (14), 97 (28), 91 (45), 90 (97), 89 (35), 82 (26), 82 (41), 78 (30), 77 (76), 76 (39), 75 (16), 65 (27), 64 (19), 63 (45), 55 (23), 53 (15), 52 (13), 51 (53), 50 (18); high resolution mass spectrum calculated for $C_{14}H_{12}O_2$ 212.08373, measured 212.08382.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-ENG-82.

JO930547E

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[10] Commercial apparatus is available from Kontes Scientific Glassware, Vineland, NJ 08360. For review, see Brown, R. C. F. *Pyrolysis Methods in Organic Chemistry*; Academic: New York, 1980; Chapter 2.