

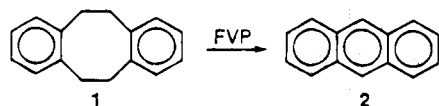
Regiospecific Formation of Anthracenes in the Flash Vacuum Pyrolysis of Dibenzosuberones¹

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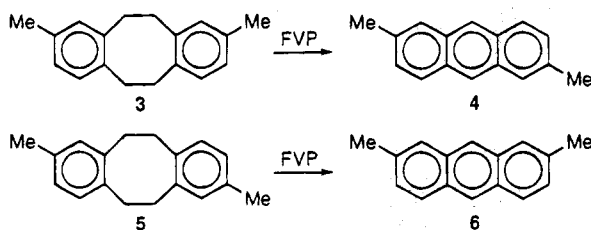
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The flash vacuum pyrolysis (FVP) of the [4 + 4] dimer of *o*-xylylene (**1**) gives anthracene (**2**) as the major product.² This remarkable transformation is highly regio-

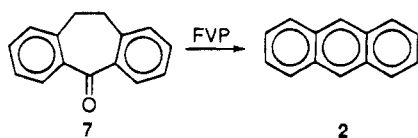


specific: compound **3**, the "cisoid" dimethyl derivative of **1**, gives 2,6-dimethylantracene (**4**) whereas **5**, the "transoid" dimethyl derivative of **1**, gives 2,7-dimethylantracene (**6**). This high regiospecificity indicates that the



rearrangement is unimolecular as reversion to either *o*-xylylene or benzocyclobutene would give a mixture of the two possible dimethylantracenes.

The mechanism proposed for this conversion, presented in Scheme 1 ($-Z- = -CH_2CH_2-$), involves the loss of ethylene from a diradical intermediate. If the general mechanism presented in Scheme 1 is correct, many analogs of **1** which could lose small molecules other than ethylene should give anthracene under FVP conditions. Indeed, Wiersum has reported that the FVP of dibenzosuberone (**7**) gives **2** quantitatively,³ and this conver-



sion fits into our general mechanistic scheme ($-Z- = -C(O)-$). Our proposed mechanism indicates that the reaction should be highly regiospecific and involve a 180° ring flip.

We have studied the FVP of three substituted dibenzosuberones, the 2,9-dimethyl- (**8**), 2,9-dichloro- (**9**), and 2,9-diamino- (**10**) dibenzosuberones, and have found that they give very good yields of the expected disubstituted

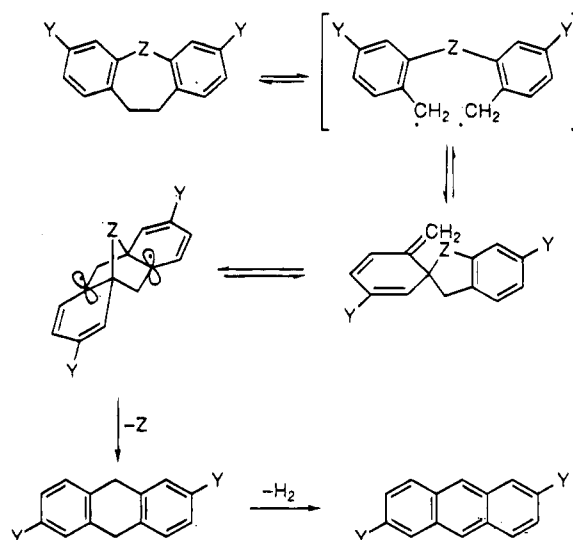
[†] Ames Laboratory Summer Student Trainee.

(1) Based on work by J.L.T. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

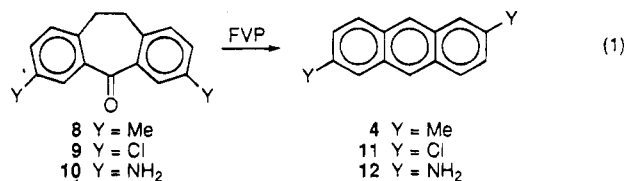
(2) Trahanovsky, W. S.; Surber, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4995.

(3) Wiersum, U. E. *Rec. Trav. Chim. Pays-Bas.* **1982**, *101*, 317.

Scheme 1

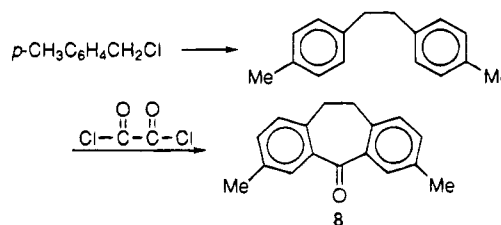


anthracenes **4**, **11**, and **12**, respectively. The results of this study are presented herein.



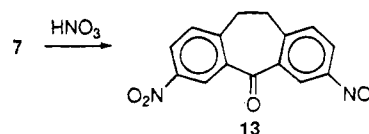
Results

Synthesis of **8** was accomplished by a two-step route: coupling of *p*-methylbenzyl chloride⁴ followed by the addition of the carbonyl group through bis-acylation



utilizing oxalyl chloride at high dilution. The expected "cisoid" structure is confirmed by the ¹H and ¹³C NMR spectra of **8**.

The first step of the synthesis of **9** was nitration of dibenzosuberone (**7**) with fuming nitric acid to give **13**, which is analogous to a reaction reported for fluorenone.⁵

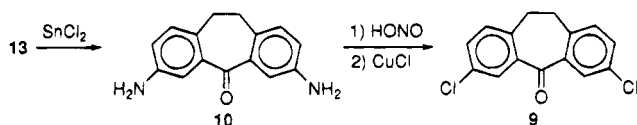


The nitro groups were reduced with SnCl₂ to give the diamino compound **10** which was converted to dichloride

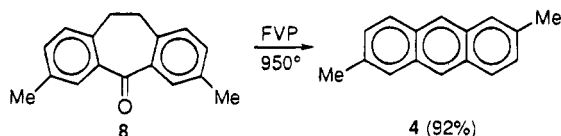
(4) Trahanovsky, W. S.; Brixius, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6778.

(5) Kaneda, T.; Ishikawa, S.; Daimon, H.; Katsura, T.; Ueda, M.; Oda, K.; Horio, M. *Macromol. Chem.* **1982**, *183*, 417.

9 by the Sandmeyer reaction. The ^1H and ^{13}C NMR spectra of **13**, **10**, and **9** confirm the expected "cisoid" structures.



The FVP of **8** gave **4** as the sole product. Under the best conditions for this reaction (950 °C, 0.002 torr) 92% of **4** and 7% of unchanged **8** (determined by ^1H NMR analysis using an internal standard) were obtained. Higher pyrolysis temperatures led to the formation of decomposition products and lower yields of **4**.



The "transoid" structure of **4** is confirmed by both its ^1H NMR spectrum (**4** has one signal for the equivalent 9,10 protons at δ 8.26 whereas the "cisoid" isomer **6** shows two signals at δ 8.34 and 8.20²) and ^{13}C NMR spectrum (**4** has eight signals whereas as the "cisoid" isomer **6** shows nine signals²). Because of the differences of the 9,10-protons of the two isomers, the regioselectivity could be determined by ^1H NMR analysis and was found to be >98%.

The FVP of the dichloro ketone **9** at 950 °C, 0.002 torr, gave 96% of the dichloroanthracene **11** and 3% of unchanged **9**. The "transoid" structure of **11** is confirmed by its ^1H and ^{13}C NMR spectra.

The FVP of the diamino ketone **10** at 940 °C, 0.0001 torr, produced a bright yellow solid that condensed in the pyrolysis tube directly above the cold trap. This bright yellow material, which was only slightly soluble, was scraped out, and its ^1H and ^{13}C NMR and high resolution mass spectra are consistent with those expected for anthracene **12**. The bright yellow color of **12** is similar to the reported⁶ color of related compounds such as 1,5-diaminonaphthalene (yellow), 9,10-diaminophenanthrene (pale yellow), and the three amino anthracenes:⁷ 1-amino (yellow, $\lambda_{\text{max}} = 402$ nm, $\epsilon = 3.4 \times 10^3$), 2-amino (yellow, $\lambda_{\text{max}} = 413$, $\epsilon = 3.4 \times 10^3$), and 9-amino (golden, $\lambda_{\text{max}} = 417$, $\epsilon = 5.2 \times 10^3$). The UV-visible spectrum of **12** in EtOH showed a strong absorbance at 275 nm ($\epsilon = 3.07 \times 10^4$) and a broad absorbance at 425 nm ($\epsilon = 2 \times 10^3$). Acidification of this solution with HCl gave a colorless solution with the strongest absorbance at 245 nm and no significant absorbance greater than 380 nm. The spectrum is similar to that of anthracene which has its λ_{max} at 251 nm.⁶ The protonated amino groups of **12** do not have free pairs of electrons which can interact with the π electrons of the anthracene unit, and thus the UV-visible spectrum of diprotonated **12** should be similar to that of anthracene. The yield of **12** was 57%. Diamine **12** decomposes rapidly in solution but appears to be stable if stored under nitrogen in its crystalline state.

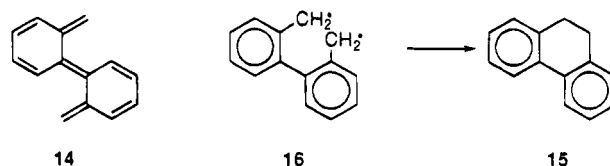
Discussion

The FVP of dibenzosuberones produces anthracenes in moderate to high yield and with high regioselectivity

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involving a 180° ring flip (see eq 1). The high yield of the reaction rules out mechanisms involving fragmentation followed by recombination. A unimolecular mechanism for this conversion has been proposed,³ but on the basis of this mechanism one would expect to obtain dihydrophenanthrenes and phenanthrenes as products also and these are not observed. This reported mechanism involves intermediate **14** which would be expected to produce 9,10-dihydrophenanthrene (**15**) via diradical **16**.³ It has been shown that **15** loses hydrogen to form



phenanthrene (**17**) more slowly than 9,10-dihydroanthracene (**18**) loses hydrogen to form anthracene (**2**).³ One could argue that **14** forms both **15** and **18** reversibly but irreversible conversion of **18** to **2** results in production of **2** only. However, if this were the case, pyrolysis of **15** should give some **2** but only phenanthrene (**17**) is obtained when **15** is pyrolyzed at higher temperatures.³ The mechanism presented in Scheme 1 nicely accounts for the conversion of dibenzosuberones to anthracenes.

Experimental Section

Methods and Materials. Some general methods have been described previously.⁹ ^1H and ^{13}C NMR spectra were recorded on a Nicolet NT-300 spectrometer. IR spectra were obtained on either a Beckman Acculab II or an IBM FTIR Model 98. GCMS were performed on a Finnegan 4000 mass spectrometer. HRMS were performed at the University of Nebraska, Lincoln, NE. All materials were commercially available and used as received except where indicated.

2,9-Dimethyldibenzosuberone (8). 4,4'-Dimethylbibenzyl was prepared by the method of Trahanovsky and Brixius,⁴ mp 79–81 °C (lit.⁴ 80–81 °C). To a rapidly stirred (mechanically) suspension of 1.25 g (9.37 mmol) of AlCl_3 in 200 mL of dry CS_2 at 0 °C was added over a 2.5 h period a solution of 4,4'-dimethylbibenzyl (1.79 g, 8.52 mmol) and oxalyl chloride (1.2 g, 9.4 mmol) in 50 mL of dry CS_2 . The reaction mixture was heated to reflux for 2 h and then allowed to cool to room temperature. The reaction mixture was poured into a beaker containing cracked ice and 10% HCl, leaving the sludge in the reaction flask. The reaction flask was then rinsed with portions of CCl_4 , and the washings were added to the beaker. The organic layer was separated, washed with water and then 10% NaOH, dried (MgSO_4), and concentrated. Column chromatography (alumina, Et_2O -hexane 1:20) gave a colorless oil which solidified upon standing. Recrystallization from MeOH gave 0.16 g (0.68 mmol, 8.0%) of **8** as colorless plates: mp 70–71 °C; ^1H NMR (CDCl_3) δ 7.80 (s, 2 H), 7.31–7.20 (m, 2 H), 7.10–7.05 (m, 2 H), 3.17 (s, 4 H), 2.35 (s, 6 H); ^{13}C NMR (CDCl_3) δ 195.97 (s), 139.08 (s), 138.50 (s), 136.08 (s), 133.05 (d, $J = 10.9$ Hz), 130.74 (d, $J = 19.6$ Hz), 129.28 (d, $J = 9.8$ Hz), 34.64 (m), 20.83 (q, $J = 16.4$ Hz); IR (CCl_4) 3100, 3000, 2960, 1650, 1600, 1305, 1286 cm^{-1} ; ms (70 eV) 236 (100), 235 (28), 222 (12), 221 (76), 208 (31), 207 (21), 193 (69), 192 (37), 191 (32), 189 (19), 179 (13), 178 (60), 165 (20), 117 (13), 115 (22), 104 (11), 103 (33), 102 (17), 96 (15), 94 (15), 91 (19), 89 (34), 82 (15), 78 (22), 77 (34), 76 (15), 65 (16), 63 (20), 51 (26). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}$: C, 86.40; H, 6.85. Found: C, 86.54; H, 6.98.

2,9-Diaminodibenzosuberone (10). To 26.74 g (0.128 mmol) of dibenzosuberone (**7**) in a round-bottom flask at 0 °C

(8) *UV Atlas of Organic Compounds*; Plenum Press: New York, 1967; Vol. III.

(9) (a) Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6691. (b) Chou, C.-H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 4138.

was added dropwise over a 30 min period 500 mL of chilled fuming nitric acid (90%). After a reflux condenser was attached to the flask, the reaction mixture was heated slowly to 100 °C for 2 h. The oil bath was removed, and the reaction was allowed to cool to room temperature. The reaction solution was carefully poured into 3 L of water and the product was collected by filtration. The crude material was stirred in 100 mL of boiling EtOH, and the insoluble product was removed by filtration of the hot mixture. The treatment was repeated and then the product was recrystallized from CH₃NO₂ to give 25.6 g (85.8 mmol, 67%) of 2,9-dinitrodibenzosuberone (**13**):¹⁰ ¹H NMR (acetone-*d*₆/DMSO-*d*₆) δ 8.78 (d, *J* = 2.39 Hz, 2 H), 8.41 (dd, *J* = 2.39, 8.32 Hz, 2 H), 7.75 (d, *J* = 8.32 Hz, 2 H), 3.46 (s, 4 H); ¹³C NMR (acetone-*d*₆/DMSO-*d*₆) δ 190.18, 148.92, 146.76, 137.90, 131.38, 126.70, 125.50, 33.78; IR (KBr) 3078, 1651, 1610, 1520, 1418, 1344, 1265, 1236, 1094, 931, 922, 899, 856, 845, 796, 781, 750 (s), 717, 679, 617 (s) cm⁻¹; MS (70 eV) 299 (16), 298 (P, 100), 281 (22), 270 (37), 252 (11), 251 (27), 223 (11), 206 (13), 20 (20), 178 (51), 177 (42), 176 (57), 166 (12), 165 (13), 152 (22), 151 (27), 150 (14), 89 (21), 88 (20), 77 (11), 76 (33), 75 (16), 63 (38), 51 (15).

To 2.0 g (9 mmol) of SnCl₂·2H₂O in a 25 mL round-bottom flask were added sequentially 1.6 mL of concd HCl and 2.9 mL of glacial acetic acid. Cautiously, 0.32 g (1.07 mmol) of **13** was added with stirring. The reaction mixture was heated to reflux for 1 h. After the reaction mixture was allowed to cool, it was diluted with 15 mL of water. The solution was gravity filtered through paper. The reaction flask was rinsed with concd HCl which was used to wash the precipitate. The precipitate was then washed with water. The filtrate was cooled to 0 °C and made basic to litmus using 10% NaOH. The yellow colloidal precipitate was collected by suction filtration, and the product was washed well with water. After drying, the product was recrystallized from EtOH to give 0.23 g (0.96 mmol, 90%) of **10** as flocculent yellow needles: mp 171–171.5 °C; ¹H NMR (CD₂Cl₂) δ 7.23 (d, *J* = 2.57 Hz, 2 H), 7.01 (d, *J* = 8.08 Hz, 2 H), 6.77 (dd, *J* = 2.57, 8.08 Hz, 2 H), 3.72 (br s, 4 H), 3.02 (s, 4 H); ¹³C NMR (CD₂Cl₂/DMSO-*d*₆) 195.56, 146.21, 138.95, 130.57, 129.93, 118.59, 115.03, 34.23; IR (KBr) 3848 (br), 3697 (br), 1597, 1574, 1312, 1217, 895, 830, 816, 789, 710, 673 cm⁻¹; ms (70 eV) 239 (16), 238 (P, 100), 237 (23), 223 (17), 222 (10), 221 (16), 210 (14), 209 (58), 208 (15), 195 (12), 194 (16), 193 (22), 180 (10), 165 (12), 119 (10), 104 (62), 90 (12), 51 (11); high resolution MS Calcd for C₁₅H₁₄N₂O 238.1109, found 238.1110.

2,9-Dichlorodibenzosuberone (9). To 0.540 g (2.27 mmol) of diamine **10** was added 15 mL of concd HCl, and the flask was heated gently until diamine **10** dissolved. The reaction mixture was cooled to 0 °C. To the heterogeneous reaction mixture was added an aqueous solution of NaNO₂ (0.41 g in 4 mL of H₂O). After stirring the solution for 5 min, an additional 125 mL of concd HCl cooled to 0 °C was added. The resulting solution was stirred at 0 °C for 20 min. A quantity of CuCl 0.50 g (5.0 mmol) in 100 mL of H₂O cooled to 0 °C was added in one portion. After stirring the mixture for 5 min, the ice bath was removed and the reaction mixture was allowed to warm to room temperature. After the reaction solution was stirred at room temperature for 3 h, it was heated slowly to 55–60 °C and kept at that temperature for 4 h. Upon cooling, the product was collected by filtration and washed well with water. Column chromatography (silica gel, Et₂O–hexane 1:10) gave 0.26 g (1.0 mmol, 44%) of **9** as colorless needles: mp 119–121 °C (lit.¹¹ 78–79 °C); ¹H NMR (CDCl₃) δ 7.98 (d, *J* = 2.5 Hz, 2 H), 7.43 (dd, *J* = 2.5, 8.1 Hz, 2 H), 7.15 (d, *J* = 8.1 Hz, 2 H), 3.17 (s, 4 H); ¹³C NMR (CDCl₃) δ 192.38, 140.26, 139.18, 132.95, 132.49, 130.97, 130.57, 34.29; MS (70 eV) 280 (9), 279 (12), 278 (56), 277 (36), 276 (88), 275 (40), 248 (16), 243 (27), 242 (16), 241 (79), 240 (13), 215 (12), 214 (16), 213 (36), 212 (37), 206 (21), 179 (15), 178 (100), 177 (27), 176 (50), 151 (14), 120 (12), 106 (17), 103 (30), 102 (30), 93 (14), 89 (56), 88 (68), 87 (15), 76 (18), 75 (29), 63 (24), 51 (11);

IR (KBr) 2951, 2862, 1637, 1583, 1477, 1296, 1261, 1231, 1042, 835, 785, 625 cm⁻¹ (lit.¹¹ (nujol mull) 1650, 1595, 1295, 1270, 845, 785 cm⁻¹).

Flash Vacuum Pyrolysis (FVP) was performed as previously described.^{12,13}

FVP of 2,9-Dimethyldibenzosuberone (8). A quantity of **8** (5–20 mg) was pyrolyzed with an oven temperature of 900–1000 °C and pressure between 0.001 to 0.004 torr. The sample head temperature was kept between 60 to 80 °C. The average time for a pyrolysis was ca. 2 h. The pyrolysis was worked-up as follows. The pyrolysis trap was rinsed with four portions of CH₂Cl₂. The rinsings were combined and concentrated. The pyrolyzate was taken up in hot CD₂Cl₂, and CDCl₃ was added. The internal standard, *s*-CHCl₂CHCl₂, which was purified immediately before use by passing it through a short column of alumina, was added by syringe. The amount added was obtained by weighing the syringe before and after the transfer.

Several runs were combined and the product was purified by recrystallization from CHCl₃. For 2,6-dimethylanthracene (**4**): mp 239–243 °C (lit.¹⁴ 248 °C); ¹H NMR (CDCl₃) δ 8.26 (s, 2 H), 7.88 (d, *J* = 8.56 Hz, 2 H), 7.73 (d, *J* = 1.33 Hz, 2 H), 7.29 (dd, *J* = 1.33, 8.56 Hz, 2 H), 2.53 (s, 6 H); ¹³C NMR (CDCl₃/CD₂Cl₂) δ 134.40, 131.38, 130.32, 127.95, 127.52, 126.02, 124.58, 21.48; IR (KBr) 2907, 1471, 1375, 1301, 925, 903 (s), 872, 791 cm⁻¹ (lit.¹⁵ (KBr) 1474, 1460, 1449, 1378, 1305, 1273, 1171, 1139, 1041, 963, 942, 905 (s), 873, 793 cm⁻¹).

FVP of 2,9-Dichlorodibenzosuberone (9). Compound **9** was pyrolyzed under the same conditions used for **7**. For 2,6-dichloroanthracene (**11**): mp 263–266 °C (lit.¹⁶ 273–274 °C); ¹H NMR (CDCl₃) δ 8.31 (s, 2 H), 7.97 (d, *J* = 1.9 Hz, 2 H), 7.93 (d, *J* = 9.0 Hz, 2 H), 7.42 (dd, *J* = 1.9, 9.0 Hz, 2 H); ¹³C NMR (CDCl₃) δ 131.92, 131.56, 130.30, 129.81, 127.36, 126.47, 125.71; MS (70 eV) 250 (9), 249 (9), 248 (65), 247 (15), 246 (100), 176 (43), 175 (13), 174 (11), 124 (18), 123 (27), 105 (13), 88 (44), 87 (26), 75 (13); IR (KBr) 926, 901 (s), 800 cm⁻¹ (lit.¹³ (nujol mull) 901, 799 cm⁻¹).

FVP of 2,9-Diaminodibenzosuberone (10). Diamine **10** (48 mg, 20.1 mmol) was pyrolyzed at an oven temperature of 950 °C and a pressure between 0.001 to 0.004 torr. The sample head temperature was kept between 100 and 120 °C. The brilliant yellow product was scraped out with a spatula to give 24 mg (11.5 mmol, 57%) of **12**:¹⁷ mp > 300 °C dec; ¹H NMR (acetone-*d*₆/DMSO-*d*₆) δ 7.86 (s, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.01 (dd, *J* = 1.32, 8.9 Hz, 2H), 6.92 (d, *J* = 1.32 Hz, 2H), 4.94 (br s, 4H); ¹³C NMR δ (DMSO-*d*₆) 143.9, 130.5, 127.9, 127.1, 121.3, 120.4, 103.7 [Chromium(III) acetylacetonate was added to shorten relaxation times];¹⁸ IR (KBr) 3323 (br), 1637, 1477, 1018, 891, 800 cm⁻¹; UV-vis (EtOH) λ_{max} 275 nm (ε = 3.07 × 10⁴ L/mol cm), λ_{max} = 425 nm (ε = 2 × 10³ L/mol cm); high resolution MS calcd for C₁₄H₁₂N₂ 208.1002, found 208.1002.

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