A Novel Flash Vacuum Pyrolysis Route to Acridine[1]

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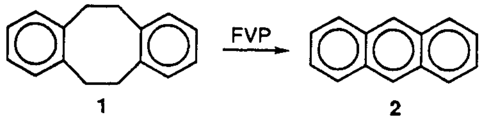
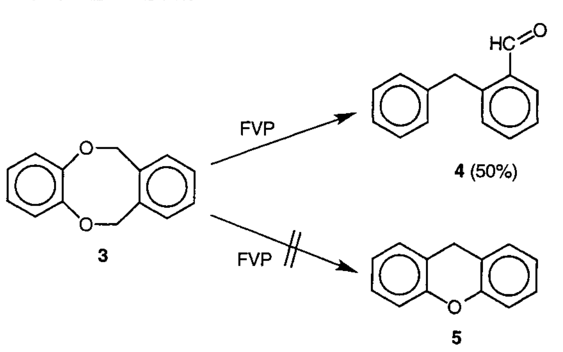
The flash vacuum pyrolysis (FVP) of 5,6,11,12-tetrahydrodibenzo[*b,f*]azocine (**6**) gives a good yield (75 %) of acridine (**7**). A mechanism for this novel reaction is presented.

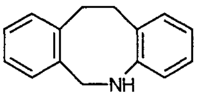


The flash vacuum pyrolysis (FVP) of the [4 + 4] dimer of *o*-xylylene (**1**) gives anthracene (**2**) as the major product.[2] We have proposed a general mechanism for this remarkable transformation, presented in Scheme 1 ($-Z- = -CH_2CH_2-$), which overall involves the splitting of one bridge of the starting material and loss 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.

The FVP of cyclic diether **3** was also studied[5] but rearrangement to **4** was observed instead of formation of **5**, the product expected on the basis of the general mechanism shown in Scheme 1.



In an effort to further explore the scope of these reactions we studied the FVP of the aza analog **6**, 5,6,11,12-tetrahydrodibenzo[*b,f*]azocine. On the basis of the mechanism presented in Scheme 1, we expected to obtain acridine (**7**) and/or anthracene (**2**) as the major product or products.



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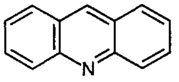

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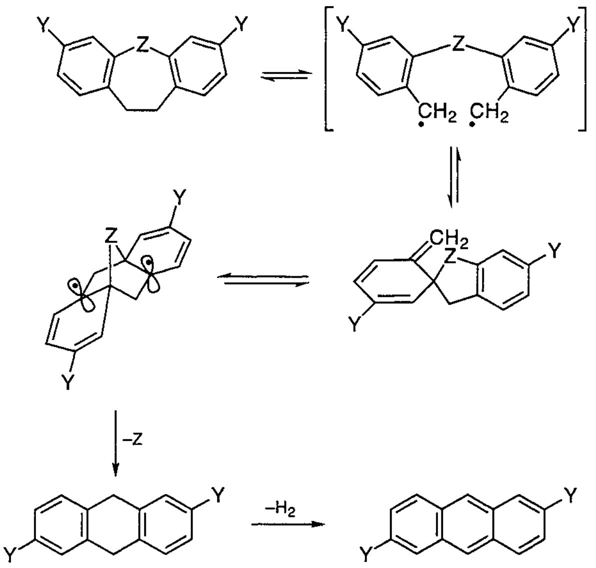
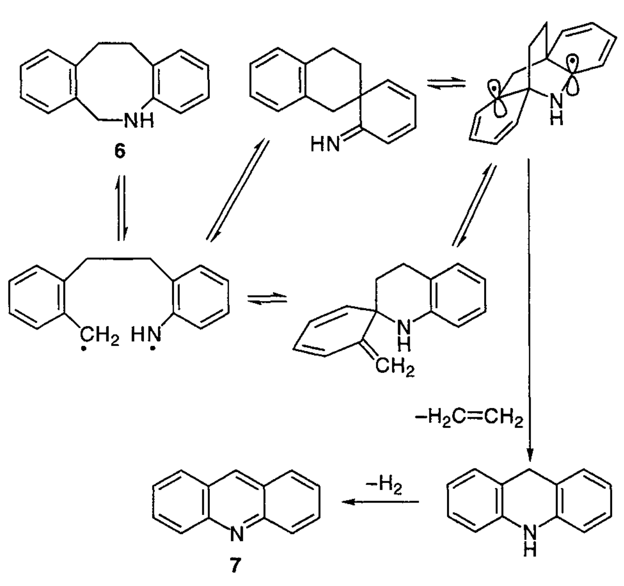
The FVP of **6** at 750 °C and 10^{-4} Torr gave a 75 % yield of acridine (**7**), an 8 % yield of stilbene (**8**), and a small amount of another product with MW 168. GC/MS analysis of the crude pyrolysis products indicated that no anthracene (**2**) was formed in the pyrolysis.

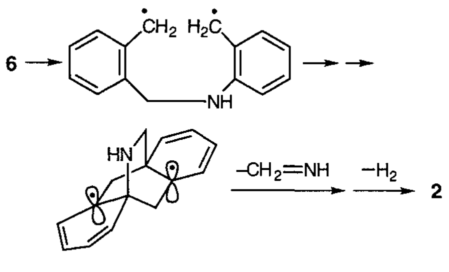


Scheme 1



Scheme 2

The formation of acridine (**7**) is accounted for by the mechanism presented in Scheme 2. The corresponding mechanism for the formation of anthracene (**2**) would require initial cleavage of the C–C bridge of **6** and loss of $CH_2=NH$ from the bridged diradical **9**. In general, C–N bonds are weaker than the analogous C–C bonds and thus it is reasonable that acridine (**7**) is formed in preference to anthracene (**2**).[6] We do not have a good explanation for the formation of the minor product stilbene (**8**).



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The FVP of substituted 5,6,11,12-tetrahydrodibenzo-[*b,f*]azocines should be a good preparative route to gram quantities of substituted acridines if the substituents can survive the FVP conditions. It should be possible to predict the position of the substituents on the basis of the mechanism presented in Scheme 2.

Some general methods have been described previously.[7] ^{1}H NMR spectra were recorded on a Nicolet NT-300 spectrometer. GCMS were performed on a Finnigan 4000 mass spectrometer. All materials were commercially available and used as received.

5,6,11,12-Tetrahydrodibenzo[*b,f*]azocine (6):

Prepared by washing 5,6,11,12-tetrahydrodibenzo[*b,f*]acozine hydrochloride with 10% NaOH soln.

^{1}H NMR (CDCl$_3$): δ = 7.15–6.65 (m, 7H), 6.49 (d, 1H, J = 7.8 Hz), 4.43 (s, 2H), 3.30 (t, 2H, J = 6.5 Hz), 3.20 (t, 2H, J = 6.6 Hz); [Lit.[8] ^{1}H NMR (CDCl$_3$): δ = 7.10 (s, 4H), 6.97–6.42 (m, 4H), 4.34 (s, 2H), 3.41 (br s, 1H), 3.25 (t, 4H, $|J|$ = 3.0 Hz)].

FVP of 5,6,11,12-Tetrahydrodibenzo[*b,f*]azocine (6):[9,10]

A quantity of **6** (200 mg, 0.96 mmol) was pyrolyzed at 750 °C in the normal manner (see refs 9, 10). GC and ^{1}H NMR spectral analyses of the crude product mixture indicated acridine (**7**) was formed as a major product (75%) along with stilbene (**8**) and another minor product (MW 168).

7:

^{1}H NMR (CDCl$_3$): δ = 8.80 (s, 1H), 8.25 (br d, 2H, J = 10 Hz), 8.03 (br d, 2H, J = 10 Hz), 7.85–7.74 (m, 2H), 7.60–7.50 (m, 2H); [Lit.[11] ^{1}H NMR (CDCl$_3$): δ = 8.74 (s, 1H), 8.24 (br d, 2H, J = 9 Hz), 7.98 (br d, 2H, J = 8.4 Hz), 7.82–7.72 (m, 2H), 7.56–7.46 (m, 2H)].

GC/MS (70 eV) m/z (%) = 181 (0.9), 180 (13.80), 179 (100), 178 (21), 152 (11), 151 (13), 90 (17), 89 (41), 76 (18), 75 (14), 63 (12); [Lit.[12] MS (70 eV): *m/z* (%) = 179 (100), 178 (20), 152 (11), 151 (11), 126 (4), 90 (4), 89 (11), 76 (8), 75 (7), 63 (9)].

8:

GC/MS (70 eV): *m/z* (%) = 182 (1.12), 181 (14.04), 180 (100), 179 (74), 178 (46), 176 (14), 165 (35), 152 (14), 90 (19), 89 (60), 88 (23), 83 (13), 76 (45), 75 (11), 63 (11).

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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.
(3) Trahanovsky, W. S.; Tunkel, J. L.; Thoen, J. C.; Wang, Y. *J. Org. Chem.* **1995**, *60*, 8407.
(4) Wiersum, U. E. *Rec. Trav. Chim. Pays-Bas.* **1982**, *101*, 317.
(5) Trahanovsky, W. S.; Lee, S.-K.; Fennell, J. W. *J. Org. Chem.* **1995**, *60*, 8410.
(6) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemsitry*, 3rd ed.; Harper and Row: New York, 1987; pp 161–162.
(7) Trahanovsky, W. S.; Cassady, T. J.; Woods, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6691.
(8) Paquette, L. A.; Anderson, L. B.; Hansen, J. F.; Lang, S. A., Jr., Berk, J. *J. Am. Chem. Soc.* **1972**, *94*, 4907.
(9) Trahanovsky, W. S.; Ong, C. C.; Pataky, J. G.; Weitl, F. L.; Mullen, P. W.; Clardy, J. C.; Hansen, R. S. *J. Org. Chem.* **1971**, *36*, 3575.
(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.
(11) Ramaprasad, S.; Nauman, M.; Morden, K. Y. *Spectroscopy Lett.* **1988**, *21*, 383.
(12) Acheson, R. M.; Aplin, R. T.; Bolton, R. G. *Org. Mass Spectrom.* **1974**, *8*, 95.