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Flash vacuum pyrolysis of 3-aroylcinnolines: interesting routes toward polynuclear aromatic compounds

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Abstract—Flash vacuum pyrolysis of 3-aroylcinnolines 3 at 900°C and 0.02 Torr yielded phenanthrene and arylacetylene derivatives as the major products beside anthracene and diarylacetylene derivatives as minor products. Also, FVP of 3-(2-thienoyl)-cinnoline gave three isomeric naphthothiophenes, phenyl-2-thienylacetylene and phenylacetylene. On the other hand, 3-(2-furoyl)-cinoline gave dibenzofuran as a major product besides naphtho[1,2-*b*]furan and phenylacetylene.

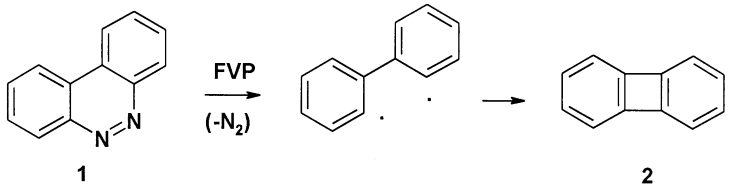
1. Introduction

Flash vacuum pyrolysis (FVP) of benzo[*c*]cinnoline **1** at around 850–900°C offers a good synthetic procedure for the generation of biphenylene **2**.[1,2] The synthetic potential of FVP of other condensed cinnolines and fused pyridazines was further investigated and shown to offer easy direct access to the corresponding polycyclic and aza analogs of **2** which are otherwise difficult to prepare.[1–10] Moreover, pyrolysis of 1,10-dialkylbenzo[*c*]cinnolines have also been studied and the products were correlated with the mass fragmentation pattern of the starting compounds.[11,12] These pyrolytic conversions take place via initial N_2 elimination and formation of a diradical intermediate (Scheme 1).

2. Results and discussion

In the present work and as an extension of the utility of FVP of cinnolines in organic synthesis, we describe our results on the application of this technique to 3-aroylcinnolines **3**. We have recently described an efficient synthesis of compound **3** from the readily available appropriate aryl methyl ketones.[13] Thus, FVP of compound **3a** at 900°C and 0.02 Torr gave good yields of phenanthrene **4a** and phenylacetylene **6** as the major products beside anthracene **5a** and diphenylacetylene **7** (Scheme 2, Table 1). Similarly, FVP of 3-*p*-chlorobenzoylcinnoline **3b** under the same conditions gave phenanthrene **4a**, 3-chlorophenanthrene **4b**, anthracene **5a**, 2-chloroanthracene **5b**, and phenylacetylene **6**. On the other hand, FVP of *p*-methoxy—**3c** and *p*-nitro—**3d** cinnoline derivatives gave mainly, phenanthrene **4a**, anthracene **5a**, phenylacetylene **6** in addition to minor percentages of benzene and anisole (from **3c**) and benzene only (from **3d**).

The mechanistic pathways for the conversion of **3** into the corresponding products **4**–**7** are illustrated in Scheme 3. The first step involves N_2 elimination to give the diradical **8**, which can lose CO to give the diradical **9**. The latter cyclizes to phenanthrenes **4**, isomerizes to diarylacetylenenes **7**, or cyclizes to the highly unstable benzobutene **10**. The latter converts into intermediates **11** and **12** via a number of valence bond isomerizations and hydrogen shifts to give finally the anthracene derivatives **5**. Alternatively, anthracenes **5** may be formed as a result of isomerization of



1 2

Scheme 1.

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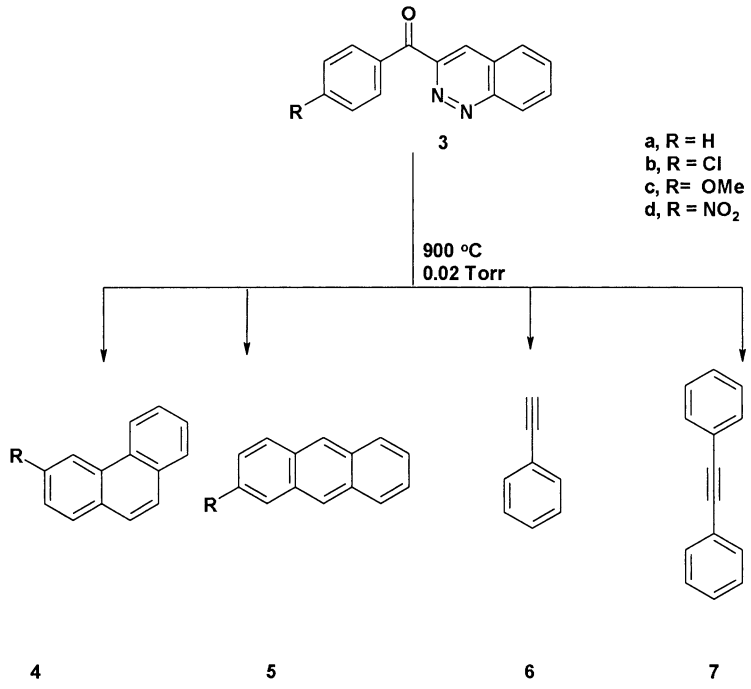
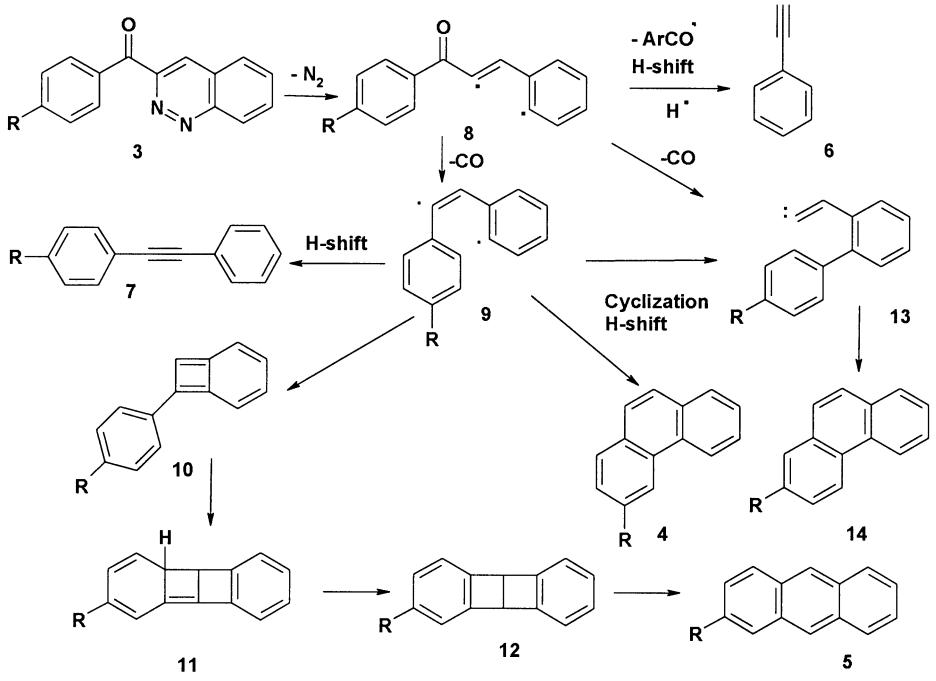


Scheme 2.

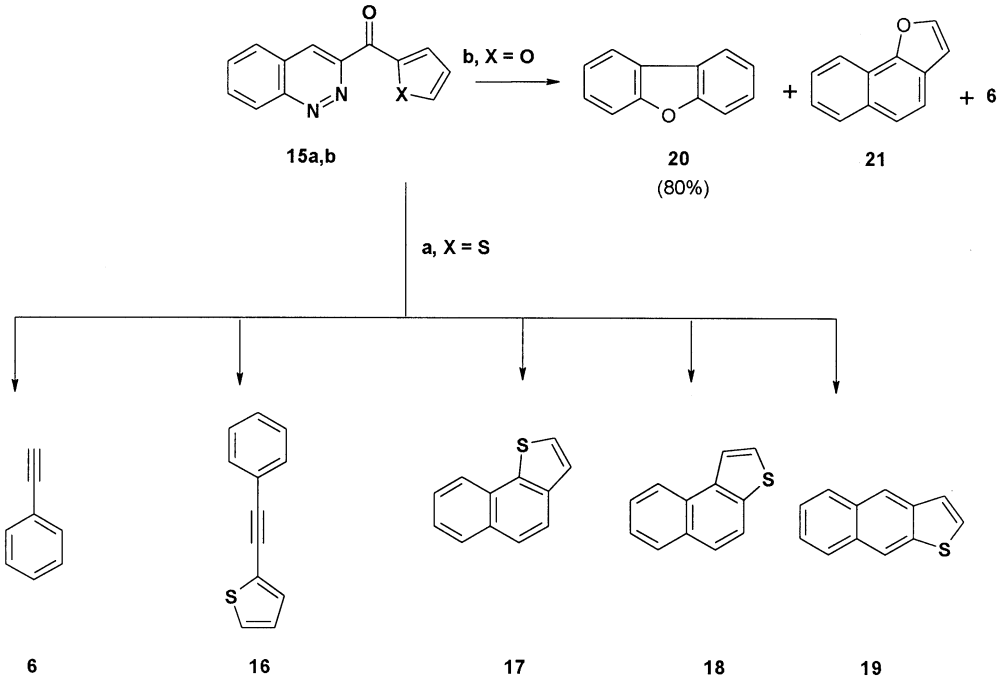
Table 1. Yields and references of FVP products of **3a–c**, **15a**,**b**

Substrate	Products (yield %)[references]
3a	**4a** (30)[18], **5a** (7.5)[19], **6** (36)[20], **7** (6)[21]
3b	**4a** (30)[18], **4b** (15)[22], **5a** (13)[19], **5b** (2)[23], **6** (30)[18]
3c	**4a** (15)[18], **5a** (3)[19], **6** (10)[18]
3d	**4a** (46)[18], **5a** (15)[19], **6** (36)[20]
15a	**6** (5)[18], **16** (20)[24], **17** (15)[25], **18** (25)[25], **19** (16)[26]
15b	**20** (80)[27], **21** (5)[25], **6** (6)[18]

phenanthrenes, where such conversion was reported at 850°C over SiO_2.[14] The possibility of the formation of methylenecarbene **13** from the diradical **9** cannot be excluded and was reported to give phenanthrene under similar conditions in the FVP of biphenyl-2-ylacetylene.[15] The isolation of 3-chlorophenanthrene **4b** from FVP of **3b** supports the pathway **9**–**4**. The other isomeric chlorophenanthrenes and 1-chloroanthracene were not detected in the spectral data of the pyrolysates of **3b** when compared with reference spectra available in literature. The formation



Scheme 3.



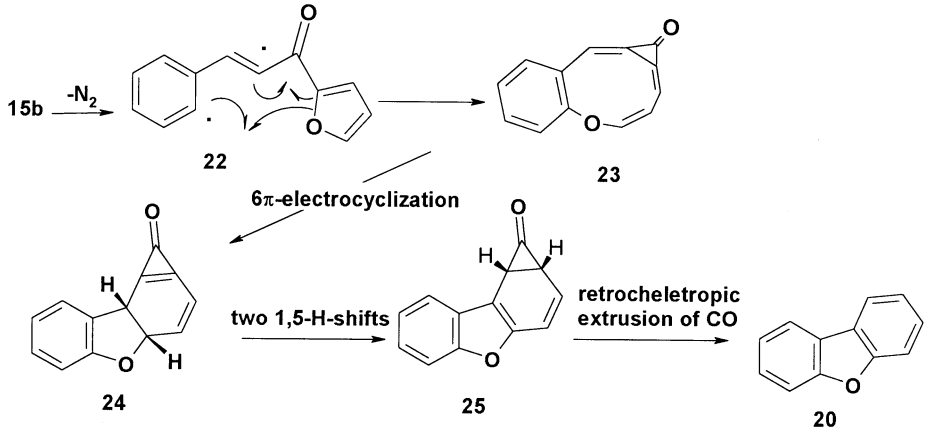
Scheme 4.

of acetylene and benzene derivatives comes from the fragmentation of the diradical **8** into aroyl radicals and phenylacetylene radical. The latter converts into phenylacetylene **6** upon gaining of H-radical. In all cases, R group may be lost as a radical and substituted by gaining H-radical (examples of similar behaviors were reported).[1]

Moreover, the ease and potential wide applicability of the preparation of the starting aroylcinnolines **3**[13] predicts the possible extension of the present approach for the synthesis of angular heteroarenes. We thus, investigated the FVP of 3-(2-thienoyl)cinnoline **15a** under the same conditions. The products from this latter reaction were identified as phenylacetylene **6**, phenyl-2-thienylacetylene **16**, naphtho[1,2-*b*]-thiophene **17**, naphtho[2,1-*b*]thiophene **18** and naphtho-[2,3-*b*]thiophene **19**. The formation of both isomeric **17**, **18** supports the involvement of both intermediates **9**, **13** as precursors. On the other hand, FVP of 3-(2-furoyl)-cinnoline **15b** gave unexpectedly high yield of dibenzofuran **20** beside naphtho[1,2-*b*]furan **21** and phenylacetylene **6** (Scheme 4).

The formation of dibenzofuran **20** must involve a number of rearrangements for which we suggest the pathways shown in Scheme 5, which starts with the diradical **22**. The latter rearranges into [1]benzononatetraene **23** which then undergoes electrocyclization into **24**. Conversion of **24** into **20** goes through two successive 1,5-H-shifts to give **25** followed by carbon monoxide extrusion. In support of the formation of **23** by furan ring rearrangement is the reported mechanism for the sensitized photo-rearrangement of furylidenetetralones.[16]

Further mechanistic studies and applications of this method for the synthesis of other polynuclear linear and angular arenes and heteroarenes are under investigation.



Scheme 5.

3. Spectral data of products

4a, MS: *m*/*z*=178 (M^+); IR (KBr): 3060, 1498, 1450, 1038, 866, 815, 736; ^{1}H NMR ($CDCl_3$): δ 8.75 (d, *J*=8.1 Hz, 2H), 7.96 (dd, *J*=7.8, 1.3 Hz, 2H), 7.81 (s, 2H), 7.71 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 132.0, 130.2, 128.5, 126.8, 126.4, 122.6.

4b, MS: *m*/*z*=212, 214 (M^+, M+2); ^{1}H NMR ($CDCl_3$): δ 8.64 (s, 1H), 8.59 (d, *J*=8.9 Hz, 1H), 7.89–7.54 (m, 7H).

5a, MS: *m*/*z*=178 (M^+); IR (KBr): 3060, 1952, 1538, 1152, 952, 867, 720; ^{1}H NMR ($CDCl_3$): δ 8.41 (s, 2H), 7.98 (m, 4H), 7.45 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 131.6, 128.1, 126.1, 125.3.

5b, MS: *m*/*z*=212, 214 (M^+, M+2); ^{1}H NMR ($CDCl_3$): δ 8.35 (s, 1H), 8.31 (s, 1H), 7.90 (m 4H), 7.50 (m, 2H), 7.37 (d, *J*=8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 132.2, 131.8, 131.7, 131.0, 129.8, 129.7, 128.2, 128.0, 126.5, 126.3, 126.0, 125.7, 125.4, 122.2.

6, MS: *m*/*z*=102 (M^+); IR (KBr): 3292, 3060, 2100, 1498, 758, 691; ^{1}H NMR ($CDCl_3$): δ 7.49 (dd, *J*=1.8, 7.9 Hz, 2H), 7.29 (m, 3H), 3.10 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 132.1, 128.7, 128.2, 122.1, 83.6, 77.1.

7, MS: *m*/*z*=178 (M^+); IR (KBr): 3070, 1601, 1499, 1450, 1306, 1026, 755, 690; ^{1}H NMR ($CDCl_3$): δ 7.52 (dd, *J*=1.9, 7.9 Hz, 4H), 7.30 (m, 6H); ^{13}C NMR ($CDCl_3$): δ 131.5, 128.3, 128.1, 123.2, 89.4.

16, MS: *m*/*z*=184 (M^+); IR (KBr): 2210; ^{1}H NMR ($CDCl_3$): δ 7.40–7.10 (m, 7H), 6.90 (m, 1H).

17, MS: *m*/*z*=184 (M^+); IR (KBr): 3051, 1323, 1259, 810; ^{1}H NMR ($CDCl_3$): δ 8.17 (d, *J*=8.1 Hz, 1H), 7.95 (d, *J*=8.1 Hz, 1H), 7.84 (d, *J*=8.6 Hz, 1H), 7.75 (d, *J*=8.6 Hz, 1H), 7.53–7.62 (m, 2H), 7.52 (d, *J*=5.3 Hz, 1H), 7.48 (d, *J*=5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 137.3, 130.7, 129.0, 128.8, 126.6, 125.6, 125.5, 125.2, 125.0, 123.6, 122.0.

18, MS: *m*/*z*=184 (M^+); IR (KBr): 3067, 1263, 1113, 806; ^{1}H NMR ($CDCl_3$): δ 8.33 (d, *J*=8.4 Hz, 1H), 7.99 (d, *J*=5.3 Hz, 1H), 7.94 (d, *J*=8.4 Hz, 1H), 7.88 (d, *J*=8.7 Hz, 1H), 7.74 (d, *J*=8.7 Hz, 1H), 7.60 (m, 2H), 7.52 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 137.3, 135.9, 130.9, 129.3, 128.5, 126.4, 125.8, 125.2, 125.0, 123.6, 122.0, 120.6.

19, MS: *m*/*z*=184 (M^+); ^{1}H NMR ($CDCl_3$): δ 8.37 (s, 1H), 8.33 (s, 1H), 8.00–7.90 (m, 2H), 7.55 (d, *J*=5.6 Hz, 1H), 7.50–7.45 (m, 2H), 7.41 (d, *J*=5.6 Hz, 1H).

20, MS: *m*/*z*=168 (M^+); IR (KBr): 3070, 1590, 1490, 1312, 1195, 1195, 1100, 840, 750, 720; ^{1}H NMR ($CDCl_3$): δ 7.95 (d, *J*=7.6 Hz, 2H), 7.53 (d, *J*=8.3 Hz, 2H), 7.41 (t, *J*=8.3 Hz, 2H), 7.31 (t, *J*=7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 156, 127.0, 124.1, 122.6, 120.6, 111.6.

21, MS: *m*/*z*=168 (M^+); IR (KBr): 3050, 1510, 1392, 810; ^{1}H NMR ($CDCl_3$): δ 8.31 (d, *J*=8.2 Hz, 1H), 7.93 (d, *J*=8.2 Hz, 1H), 7.76 (d, *J*=2.0 Hz, 1H), 7.65–7.50 (m, 4H), 6.90 (d, *J*=2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 150.5, 144.1, 131.4, 128.3, 126.3, 125.0, 123.4, 122.9, 121.5, 120.0, 119.7, 107.6.

4. Experimental

IR: (KBr) Shimadzu IR-740 spectrometer. ^{1}H and ^{13}C NMR: Bruker Avance 400 spectrometer. Ms: Gc/Ms INCOS XL Finnigan MAT.

4.1. Flash vacuum pyrolysis of 3a–d, 15a,b

The apparatus used was similar to the one which has been described recently.[17] The sample was volatilized from a tube in a Büchi Kugelrohr oven through a 30×2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 900°C, the temperature being monitored by a Pt/Pt-13%Rh thermocouple situated at the center of the furnace. The products were collected in a U-shaped trap, cooled in liquid nitrogen. The whole system was maintained at a pressure of 10^{-2} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions, the contact time in the hot zone was estimated to be ≅10 ms. The different zones of the products collected in the U-shaped trap were analyzed by ^{1}H, ^{13}C NMR, IR and GC–MS. Relative and percent yields were determined from ^{1}H NMR. Compounds obtained were identified by comparison of their ^{1}H, ^{13}C NMR, IR with reported data (cf. Table 1).

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