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# Flash vacuum pyrolysis of azo and nitrosophenols: new routes towards hydroxyarylnitrenes and their reactions

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**Abstract**—Flash vacuum pyrolysis of phenylazonaphthols and nitrosonaphthols at 700°C and 0.02 Torr yielded quinoline, isoquinoline, indene and naphthols (and aniline only from the phenylazo derivatives). Similar FVP of *p*-nitroso and *p*-phenylazophenol gave pyridine. Also, FVP of phenanthraquinonemonophenylhydrazone and monooxime gave phenathridine and fluorenone. The formation of the heterocyclic system was assumed to involve nitrene and azatropone intermediates. © 2003 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

Considerable interest has been directed to the generation of arylnitrenes and their ring expansions to produce various azepine derivatives.[1–5] Studies on substituted arylnitrenes **2** support the formation of benzazirine **3** intermediates[3] in equilibrium with the corresponding nitrenes **2** which rearrange irreversibly to form didehydroazepines **4**. Useful synthetic approaches towards many functionalized azepines were investigated mainly by low temperature generation of arylnitrenes upon photolysis of arylazides **1** in suitable solvents. The latter subsequently add to the initially formed didehydroazepine derivatives **4** to give the corresponding functionalized azepines **5** (Scheme 1). As an example nitrene generated from 2-hydroxyethyl *o*-azidobenzoate led to the formation of diazepino-14-crown-4.[1b] Analogously pyridoazepines and thienoazepines have been prepared by the photolysis of the appropriate azidoquinolines and azidobenzothiophenes, respectively.[1b] In a recent study Dunkin et al. reported an interesting detailed study on the photochemical as well as thermal generation of 4-*H*-azepin-4-ones **10** from 4-azidophenols **6** upon photolysis or pyrolysis via the intermediate nitrenes **7** and possibly benzazirines **8**.[5] 4-*H*-Azepin-4-ones were only detected at low temperature by diffuse reflection IR spectroscopy (DRIFTS) which on attempted isolation at room temperature resulted only in polymeric products.[5] On the other hand, attempted extension of this methodology to naphthalene derivatives failed.[5] Substituted phenylnitrenes have also been shown to form aniline derivatives by hydrogen abstractions from the reaction medium.[4]

Recently, we have reported the static as well as the flash vacuum pyrolysis (FVP) of a number of α-oxoarylhydrazones **11** where the α-hydroxyazo tautomers **12** were proposed to contribute for the mechanistic pathways to account for the products of these pyrolytic reactions.[6] In extension of this work we have studied the FVP of the related *o*-arylazophenols. We discovered, in the present study, products that point to new methods of generating arylnitrenes from azo and nitrosophenolic compounds upon FVP (Scheme 2).

## 2. Results and discussion

FVP of 1-phenylazo-2-naphthol (**13**) at 700°C and 0.02 Torr gave a mixture of quinoline, isoquinoline, indene, 2-naphthol, aniline and benzene. On the other hand, FVP of the isomeric 2-phenylazo-1-naphthol (**14**) gave the same products though in lower yields with the exception of 1-naphthol instead of 2-naphthol (Scheme 3). These results led us to extend the work to study the FVP of the two isomeric nitroso derivatives **15** and **16**. Results from pyrolysis of these two isomeric nitroso derivatives were found to be identical with those obtained from compounds **13** and **14** only aniline and benzene were not detected in these latter reactions. Moreover, naphthols, the major products from the nitroso compounds are the minor products from the azo-compounds.

Scheme 3 illustrates the reaction products and their percent yields from each of the substrates **13**-**16**. Scheme 4 illustrates possible mechanistic routes leading to the formation of naphthols and indene. These start by homolytic

*Keywords*: phenylazophenol; nitrosophenol; phenylazonaphthols; nitrosonaphthols; phenanthraquinonemonophenylhydrazone; phenanthraquinonemonooxime; pyridine; quinoline; isoquinoline; indene; aniline; naphthols; phenanthridine; fluorenone.

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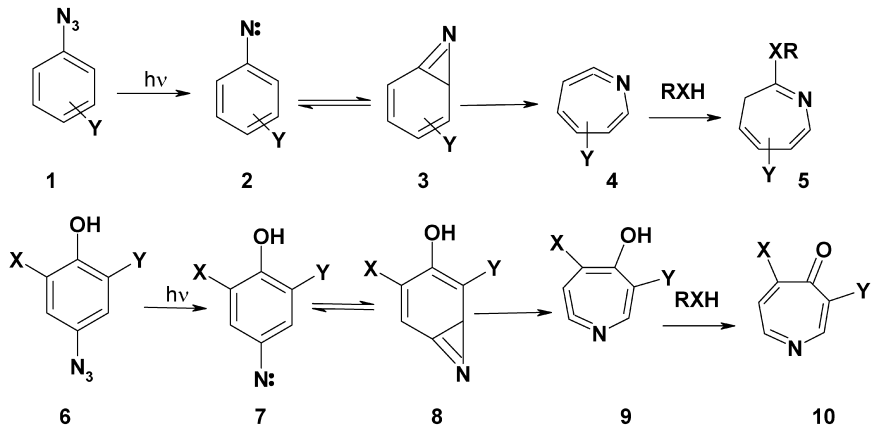
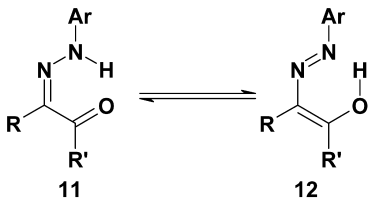


Scheme 1.



Scheme 2.

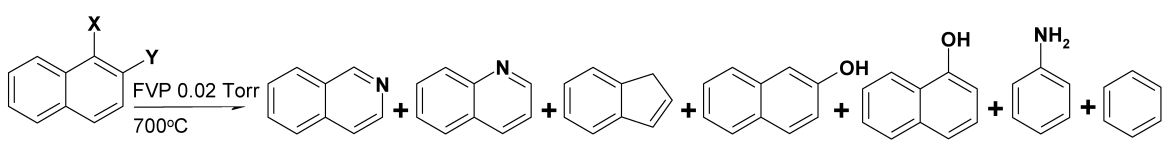
cleavage to form the phenyldiazonium radical which loses nitrogen to yield benzene and naphtholyl radical which either capture hydrogen to give naphthol or undergo hydrogen shift, isomerization, loss of CO and finally capture of hydrogen to give indene. The possible formation of the latter as a further pyrolysis product of the initially formed naphthols was excluded. This was evidenced by recovery of 1-naphthol and 2-naphthol as the only products upon FVP of each of them under similar conditions.

The formation of quinoline and isoquinoline can be explained through a mechanism including the intermediate formation of nitrenes. This can be accounted for as shown in Scheme 5. Thus, homolysis of the azo group of **13** (most probably via its tautomeric structure or resonance contributor) leads to the formation of phenylnitrene and 2-hydroxy-1-naphthylnitrene. The latter then undergo cycloaddition to the adjacent double bond to give the two isomeric naphthoazirenes. The latter then undergo electrocyclic 6-electron ring opening and hydrogen shift to give the corresponding benzoazatropones. The latter upon 6π-electrocyclization gave the corresponding cyclopropaquinolinone or cyclopropaisoquinolinone. Elimination of CO from the latter gave quinoline or isoquinoline, respectively.

Similar mechanism can be proposed for the isomeric 2-phenylazo-1-naphthol **14**. Similar ring contraction of uncondensed azepine derivatives has been reported to give pyridines.[4d] Other methods for generating arylnitrenes and their reactions, including ring expansions have been reviewed.[7] Interconversion of quinoline and isoquinoline at 850°C has been reported to occur at very small extent (0.7–2.3%),[8] however, this cannot account for the relative yields of these two isomeric compounds in our reaction mixtures. Similar mechanistic pathways can account for the products of the nitroso derivatives **15** and **16**. However, it seems that in the latter cases fragmentation as naphtholyl radicals and NO are the major pathway leading to increasing yields of the corresponding naphthols.

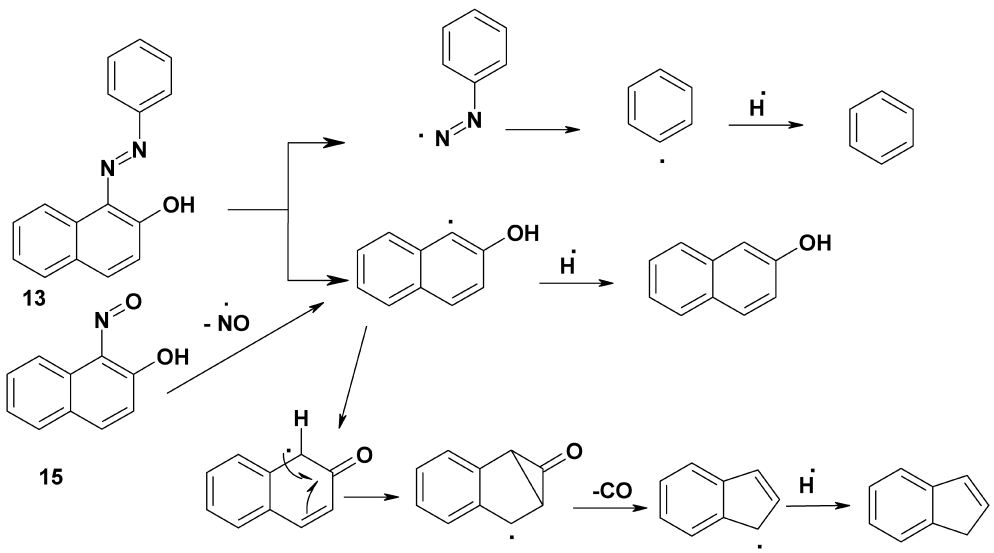
Evidence for an intermediate nitrenes was investigated by the products of FVP of 2-methoxy-1-phenylazonaphthalene **17** (Scheme 6). This gave naphtho[2,1-*d*][1,3]oxazole **18** identical with authentic sample[9] as a result of intramolecular nitrene CH insertion (on the $OCH_3$) followed by aromatization. 2-Naphthaldehyde **19** was also identified which could be produced from 2-methoxy-1-naphthyl radical rearrangement as reported.[10] These two products **18** and **19** establish the involvement of both the radical and nitrene as proposed in Schemes 4 and 5.

Extension of this work to *p*-phenylazophenol **20**, *p*-nitrosophenol **21**, 4-phenylazo-1-naphthol **22** and 4-nitroso-1-naphthol **23** gave similar products (Scheme 7). Thus, pyridine was obtained from **20** and **21** as expected. On the other hand, quinoline and isoquinoline were obtained from **22** and **23**, however, in lower yields than from **13**-**15**. We believe that this could be due to the more participation of

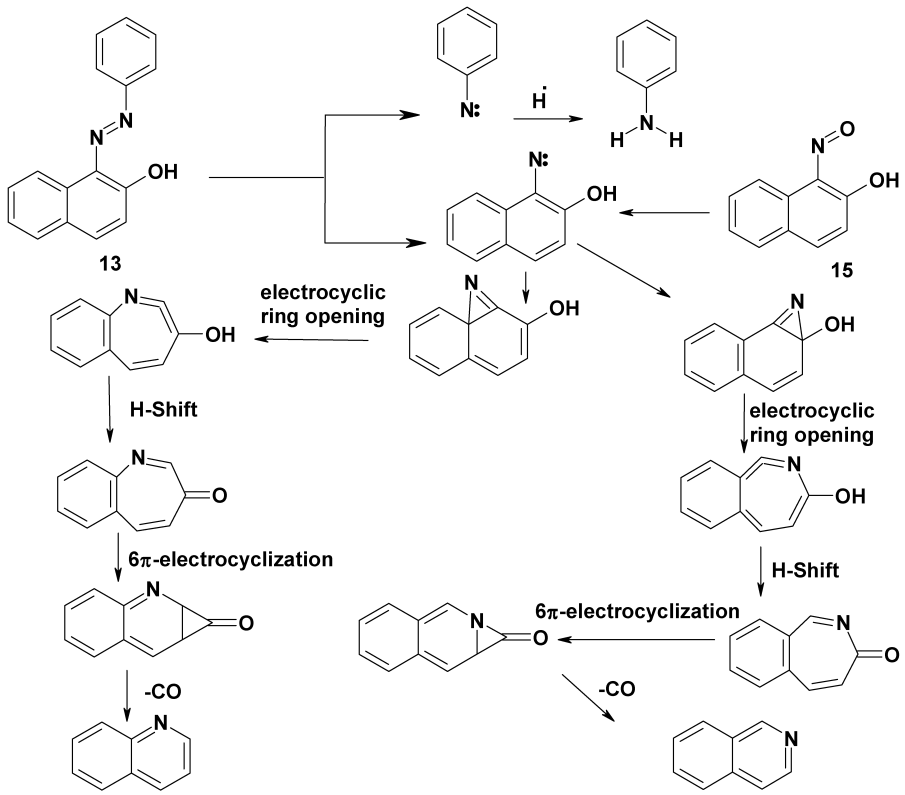


| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **13, X = $N_2$Ph, Y = OH** | 25% | 25% | 30% | 5% | 0% | 60% | 7% |
| **14, X = OH, Y = $N_2$Ph** | 10% | 22% | 15% | 0% | 10% | 70% | 10% |
| **15, X = NO, Y = OH** | 10% | 15% | 20% | 50% | 0% | 0% | 0% |
| **16, X = OH, Y = NO** | 5% | 8% | 12% | 0% | 70% | 0% | 0% |

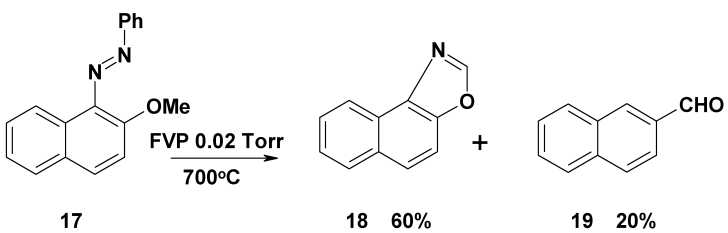
Scheme 3.



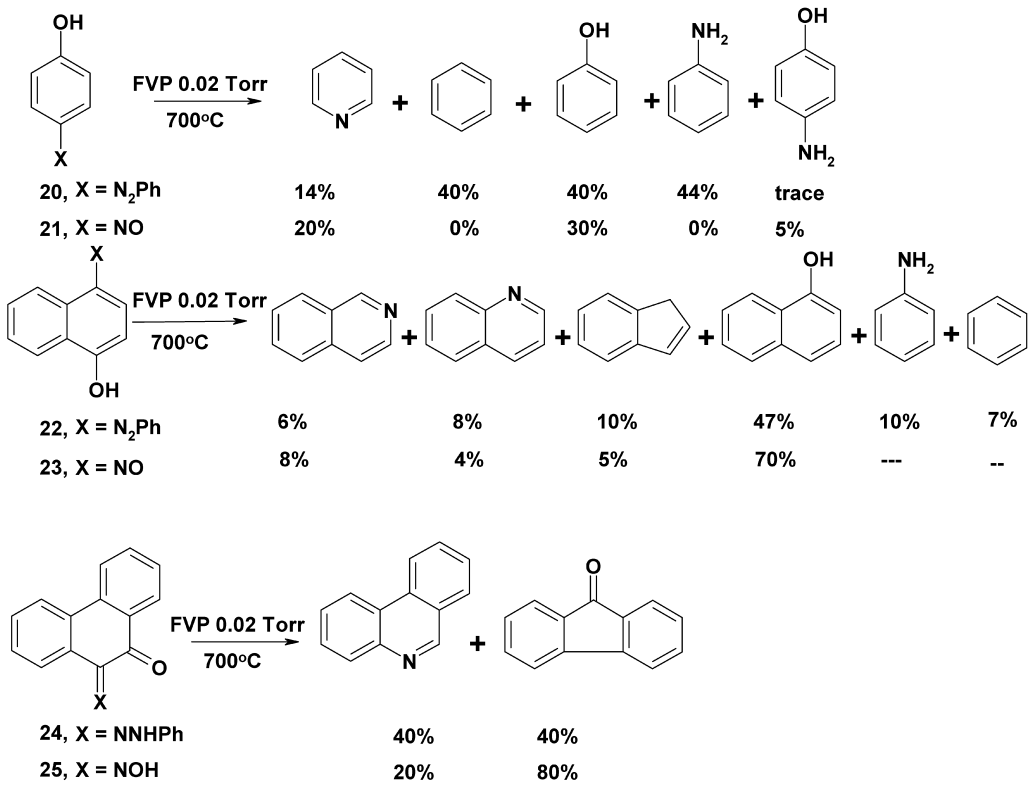

Scheme 4.




Scheme 5.




Scheme 6.




**Scheme 7.**

nitrene intermediates in the pyrolysis *o*-nitroso and *o*-arylazophenols than in case of *p*-nitroso and *p*-arylazophenols. In the latter cases the radical pathway seems to predominates over the nitrene pathway.

Finally, FVP of phenanthraquinone monophenylhydrazone **24** and phenanthraquinone monoxime **25** gave the expected phenanthridine but also fluorenone instead of the expected phenathren-9-ol (Scheme 7).

The present investigation offers an interesting approach to the conversion of some readily available aromatic compounds to their corresponding aza-aromatic compounds.

## 3. Experimental

IR: (KBr) Shimadzu IR-740 spectrometer. $^1$H and $^{13}$C NMR: Bruker Avance 400 spectrometer. Ms: GC/MS INCOS XL Finnigan MAT. Microanalysis: LECO CHNS-932. All FVP products were identified and analyzed by GC–MS, $^1$H, $^{13}$C NMR, and IR spectra. The starting compounds **13**,[12a] **14**,[13a] **15**,[12b] **16**,[13b] **17**,[13c] **20**,[12a] **21**,[13d] **22**,[13e] **23**,[13f] **24**,[13g] and **25**[13h] were prepared following reported procedures. Thus, compounds **13**, **15**, **20**, **21**, **22**, **23** were prepared either by coupling with benzenediazonium chloride or nitrosation of the appropriate phenolic compound following reported general experimental procedures.[12a,b] Also, compounds **14**, **16**, **24**, **25** were prepared by condensing *o*-naphthoquinone or phenanthraquinone with phenylhydrazine or hydroxylamine. Compounds **15**, **16**, **20**, **21** are also, readily available from Aldrich Chemical Company.

### 3.1. Flash vacuum pyrolysis of 1a–d, 11a,c, 18, 20

The apparatus used was similar to the one, which has been described in our recent publications.[6a,11] 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 700°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. Identity of compounds obtained were confirmed by comparison of their $^1$H, $^{13}$C NMR, IR with reported data. The spectral data of the FVP products were compared with their reference spectra available in FT-NMR Aldrich Catalog (quinoline,[14a] isoquinoline,[14b] indene,[14c] 2-naphthol,[14d] 1-naphthol,[14e] aniline,[14f] benzezene,[14g] 2-naphthaldehyde,[14h] pyridine,[14i] phenol,[14j] *p*-aminophenol,[14k] phenanthridine,[14l] and fluorenone[14m]).

### 3.2. Spectral data of products

**3.2.1. Quinoline.** MS: $m/z$=129 ($M^+$); $^1$H NMR ($CDCl_3$): $\delta$, 8.95 (dd, $J$=4.2, 1.5 Hz, 1H), 8.2 (d, $J$=8.4 Hz, 1H), 8.06 (d, $J$=8.2 Hz, 1H), 7.76 (d, $J$=8.1 Hz, 1H), 7.68 (dt, $J$=7.2, 1.4 Hz, 1H), 7.57 (dt, $J$=8.4, 1.1 Hz, 1H), 7.40 (dd, $J$=8.4,

4.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$): δ, 150.3, 148.3, 135.9, 129.4, 129.3, 128.2, 127.7, 126.4, 121.0.

**3.2.2. Isoquinoline.** MS: *m*/*z*=129 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 9.16 (s, 1H), 8.44 (d, *J*=5.7 Hz, 1H), 7.79 (d, *J*=5.6 Hz, 1H), 7.66 (d, *J*=8.1 Hz, 1H), 7.55 (dt, *J*=5.6, 1.1 Hz, 1H), 7.53 (d, *J*=6 Hz, 1H), 7.45 (dt, *J*=8.1, 1.1 Hz, 1H); $^{13}$C NMR ($CDCl_3$): δ, 152.4, 142.9, 135.6, 130.2, 128.6, 127.5, 127.1, 126.3, 120.3.

**3.2.3. Indene.** MS: *m*/*z*=116 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 7.45 (d, *J*=7.2 Hz, 1H), 7.34 (d, *J*=7.6 Hz), 7.25 (t, 1H, *J*=7.2 Hz), 7.15 (dt, 1H, *J*=0.6, 7.2 Hz), 6.85 (m, 1H), 6.50 (m, 1H), 3.35 (s, 2H); $^{13}$C NMR ($CDCl_3$): δ, 144.7, 143.5, 134.0, 132.0, 126.1, 124.4, 123.6, 120.9, 39.0.

**3.2.4. 2-Naphthol.** MS: *m*/*z*=144 ($M^+$); $^1$H NMR ($CDCl_3$+DMSO-$d_6$): δ, 9.5 (s, 1H), 7.68 (m, 3H), 7.33 (t, *J*=7.5 Hz, 1H), 7.20 (t, *J*=7.5 Hz, 1H), 7.11 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ, 155.3, 134.6, 129.0, 127.8, 127.4, 125.8 (2C), 122.4, 118.5, 108.7.

**3.2.5. 1-Naphthol.** MS: *m*/*z*=144 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 8.15 (m, 1H), 7.78 (m, 1H), 7.45 (m, 3H), 7.25 (t, *J*=8 Hz, 1H), 6.72 (d, *J*=7 Hz, 1H); $^{13}$C NMR ($CDCl_3$): δ, 151.2, 134.7, 127.6, 126.4, 125.8, 125.2, 124.3, 121.4, 120.7, 108.7.

**3.2.6. Aniline.** MS: *m*/*z*=93 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 3.67 (s, 2H), 6.75 (d, *J*=7.6 Hz, 2H), 6.86 (t, *J*=7.6 Hz, 1H), 7.25 (t, *J*=7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ, 146.4, 129.2, 118.4, 115.0.

**3.2.7. Benzene.** MS: *m*/*z*=78 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 7.31 (s); $^{13}$C NMR ($CDCl_3$): δ, 128.3.

**3.2.8. Naphtho[2,1-*d*][1,3]oxazole 18.** MS: *m*/*z*=169 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 8.51 (d, *J*=8 Hz, 1H), 8.19 (s, 1H), 7.92 (d, *J*=8.2 Hz, 1H), 7.77 (d, *J*=9 Hz, 1H), 7.65 (m, 2H), 7.52 (t, *J*=7 Hz, 1H); $^{13}$C NMR ($CDCl_3$): δ, 151.5, 147.4, 135.4, 131.1, 128.5, 127.2, 126.6, 126.5, 125.4, 122.0, 110.9.

**3.2.9. 2-Naphthaldehyde.** MS: *m*/*z*=156 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 10.19 (s, 1H), 8.27 (s, 1H), 7.98–7.81 (m, 4H), 7.65–7.65 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ, 192.0, 136.4, 134.3, 134.1, 132.6, 129.4, 129.0 (2C), 128.0, 127.0, 122.7.

**3.2.10. Pyridine.** MS: *m*/*z*=89 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 8.61 (m, 2H), 7.63 (m, 1H), 7.25 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ, 149.8, 135.8, 123.6.

**3.2.11. Phenol.** MS: *m*/*z*=94 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 7.22 (t, 2H), 6.91 (t, 1H), 6.81 (d, 2H), 5.7 (br, 1H); $^{13}$C NMR ($CDCl_3$): δ, 155.2, 129.7, 120.9, 115.4.

**3.2.12. *p*-Aminophenol.** MS: *m*/*z*=109 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 3.67 (s, 2H), 6.42 (d, *J*=7.6 Hz, 2H), 6.46 (d, *J*=7.6 Hz, 2H); $^{13}$C NMR ($CDCl_3$): δ, 148.1, 140.4, 115.4, 115.2.

**3.2.13. Phenanthridine.** MS: *m*/*z*=179 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 9.32 (s, 1H), 8.65 (d, *J*=8.3 Hz, 1H), 8.61 (dd, *J*=8.1, 1.2 Hz, 1H), 8.22 (d, *J*=8.2 Hz, 1H), 8.08 (d, *J*=8 Hz, 1H), 7.72 (m, 2H), 7.62 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ, 153.4, 144.3, 132.3, 130.8, 130.0, 128.5, 127.3, 126.9, 126.2, 123.9, 122.1, 121.7.

**3.2.14. Fluorenone.** MS: *m*/*z*=180 ($M^+$); $^1$H NMR ($CDCl_3$): δ, 7.63 (d, *J*=7.6 Hz, 2H), 7.43 (m, 4H), 7.25 (m, 2H); $^{13}$C NMR ($CDCl_3$): δ, 193.7, 144.3, 134.6, 134.0, 128.9, 124.1, 120.2.

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## References

1. (a) Smalley, R. K. *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 7, p 491, and references cited therein. (b) Le Count, D. J. *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 9, pp 37–39, and references cited therein.
2. Smith, P. A. S. In *Azides and Nitrenes*; Scriven, E. V., Ed.; Academic: New York, 1984; p 259.
3. Yunger, C. G.; Bell, R. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1359.
4. (a) Leyva, E.; Yung, M. J. T.; Platz, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 8307–8309, and references cited therein. (b) Abramovitch, R. A.; Chelland, S. R.; Scriven, E. F. V. *J. Org. Chem.* **1972**, *37*, 2705–2710. (c) Abramovitch, R. A.; Chelland, S. R.; Scriven, E. F. V. *J. Am. Chem. Soc.* **1972**, *94*, 1374–1376. (d) Sundberg, R. T.; Suter, S. R.; Brenner, M. *J. Am. Chem. Soc.* **1972**, *94*, 513–520.
5. Dunkin, I. R.; El Ayeb, A. A.; Gallivan, S. L.; Lynch, M. A. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1419–1427, and references cited therein.
6. (a) Ibrahim, Y. A.; Kaul, K.; Al-Awadi, N. A. *Tetrahedron* **2001**, *57*, 10171–10176. (b) Kumar, A.; Al-Awadi, N. A.; Elnagdi, M. H.; Ibrahim, Y. A.; Kaul, K. *Int. J. Chem. Kinet.* **2001**, *33*, 402–406.
7. (a) Moody, C. J. *Org. React. Mech.* **1985**, 223–243. (b) Aitken, R. A. *Org. React. Mech.* **1986**, 227–245. (c) Aitken, R. A. *Org. React. Mech.* **1987**, 247–269.
8. Patterson, J. M.; Issidorides, C. H.; Papadopoulos, E. P.; Smith, W. T. *Tetrahedron Lett.* **1970**, *11*, 1247–1250.
9. Katritzky, A. R.; Rachwal, B.; Rachwal, S. *J. Heterocycl. Chem.* **1993**, *30*, 135–139.
10. Aitken, R. A.; Drysdale, M. J.; Ferguson, G.; Lough, A. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 875–880.
11. Ibrahim, Y. A.; Al-Awadi, N. A.; Kaul, K. *Tetrahedron* **2001**, *57*, 7377–7381.
12. *Vogel Text Book of Practical Organic Chemistry*; 5th ed. Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Eds.; Wiley: New York, 1989; p 948 see also p 979.

13. (a) Zincke, Th. *Chem. Ber.* **1883**, *16*, 1563–1564. (b) Goldschmidt, H. *Chem. Ber.* **1884**, *17*, 213–217. (c) Hodges, G. R.; Smith, J. R. L.; Oakes, J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 617–627. (d) Yenes, S.; Messeguer, A. *Tetrahedron* **1999**, *55*, 14111–14122. (e) Zincke, Th.; Bindewald, H. *Chem. Ber.* **1884**, *17*, 3026–3033. (f) Woroshtzow, N. N.; Bogdanow, S. W. *Chem. Ber.* **1929**, *62B*, 68–80. (g) Mure, M.; Nii, K.; Inoue, T.; Itoh, S.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 2* **1990**, 315–320. (h) Auwers, K.; Meyer, V. *Chem. Ber.* **1889**, *22*, 1985–1995.

14. FT-NMR Aldrich Catalog 1; a, (3) 421A; b, (3) 456B; c, (2) 39C d, (2) 307C e, (2) 307B; f, (2) 451A; g, (2) 1A; h, (2) 977A; i, (3) 233A; j, (2) 243A; k, (2) 485B; l, (3) 463A; m, (2) 903B.