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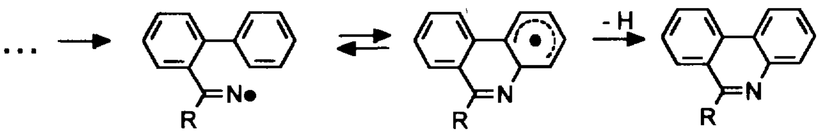
Thermal Ring Enlargement of Aromatic Cyclopentadienylidene Iminyl Radicals. Intramolecular Radical Addition to the N Atom of Nitriles Results in High Yields of Aza-Aromatics

Jörg Hofmann, Kathrin Schulz, Gerhard Zimmermann*
Department of High Temperature Reactions at the Institute of Chemical Technology,
University of Leipzig, Permoserstr. 15, D-04303 Leipzig, Germany

Abstract: It has been demonstrated that ketiminyl radicals, formed at high temperatures (1000 °C, 0.3 s) in oxygen-free nitrogen from phenylhydrazones of benz-anellated cyclopentadienones (fluorenone (**9a**), methanophenanthrenone (**9b**)), yield into phenanthridine (**8a**) and benzo[lmn]-phenanthridine (**8b**) in yields > 60%. The results point to a predominant addition of intermediately generated phenyl type radicals **5** to the N atom of the nitrile groups followed by bimolecular H-abstraction of the cyclic imidoyl radicals to **8** (scheme 3). Copyright © 1996 Elsevier Science Ltd

It is well known that iminyl radicals generated by persulfate oxidation or thermolysis (80 °C) from 2-biphenylketimine derivates are able to cyclize and to form substituted phenanthridines[1] (scheme 1). However, less is known about the consecutive reactions of cyclic aromatic ketiminyl radicals.[2]

Scheme 1



We report here on the formation of phenanthridines by thermal decomposition of easily synthesizable phenylhydrazones of fluorenone (**1a**) and methanophenanthrenone (**1b**)[3] in a previously described electrically heated tubular quartz reactor[5] at temperatures ≥ 600 °C in presence of oxygen-free nitrogen to lower the partial pressure of reactive species (reaction time 0.3 s). The pyrolyzates were collected in a cooled trap and analyzed by GC, GC-MS and GC-FTIR.[6] The main products were isolated by liquid chromatography and spectroscopically characterized.[7] The volatile products apart from aniline and benzene[8] as well as about 5 % of gaseous and non-volatile side products are listed in tables 1 and 2.

Table 1: Composition of the liquid pyrolyzates from the phenylhydrazone of fluorenone (**1a**)

reaction temperature [°C] main products [wt.-%]	600	800	1000
fluorene (**9a**)	27	26	23
fluoren-9-ylideneamine (**3a**)	30	28	3
2-nitrilo-biphenyl (**6a**)	2	4	7
phenanthridine (**8a**)	9	22	64
others*	32	20	3

* 4 products: M = 242 (2 x) - isomeric phenylfluorenes
M = 255 (2 x) - phenyl-9-aminofluorenylidenes

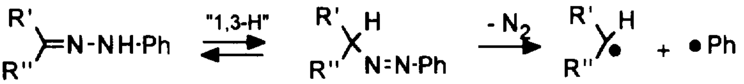
Table 2: Composition of the liquid pyrolyzates from the phenylhydrazone of methanophenanthrenone (**1b**)

reaction temperature [°C] main products [wt.-%]	600	800	1000
methanophenanthrene (**9b**)	28	20	18
cyclopenta[def]phenanthrene-4-ylideneamine (**3b**)	34	32	4
4-nitrilo-phenanthrene (**6b**)	2	3	3
benzo[lmn]phenanthridine (**8b**)	7	22	72
others**	29	23	3

** 4 products: M = 268 (2 x), M = 281 (2 x)

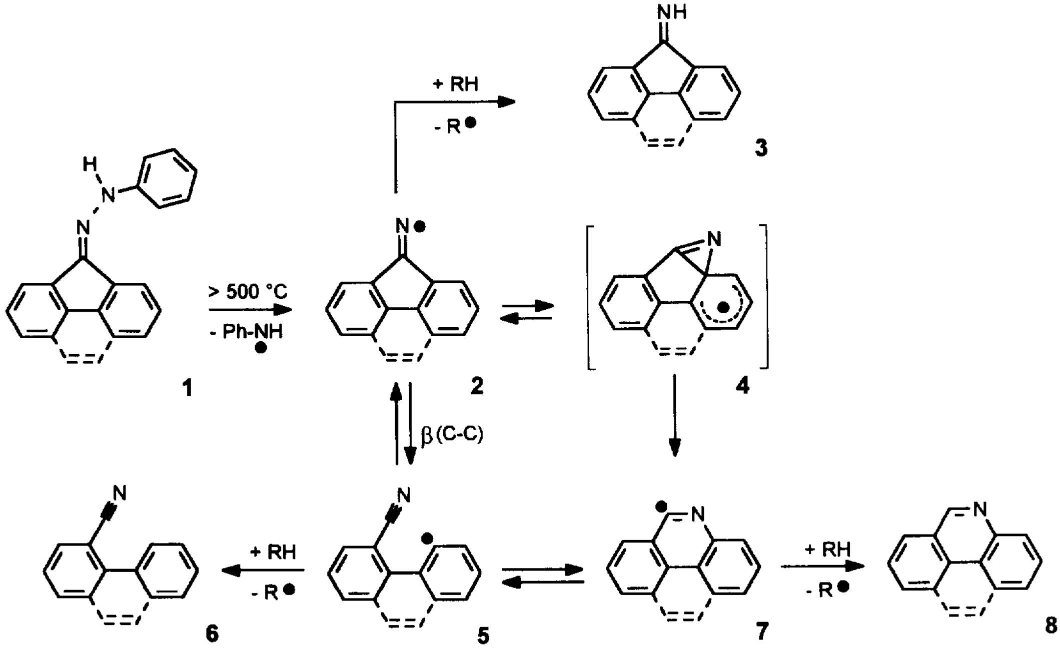
At 600 °C, the main reaction products are the ketimines **3** (40 %) besides fluorene (**9a**) and methanophenanthrene (**9b**), respectively, while at 800 °C, the formation of the phenanthridines **8** gains importance. However, at 1000 °C the phenanthridines and the aromatic hydrocarbons **9** represent the main products only.
The mechanistic interpretation of the experimental results is in line with competing radical pathways which are thought to be set off by (i) N-N-bond scission[9] (cf. scheme 3) and in parts by (ii) an assumed conversion of the phenylhydrazones **1** into the corresponding azo-compounds followed by their instant decomposition (cf. scheme 2).

Scheme 2



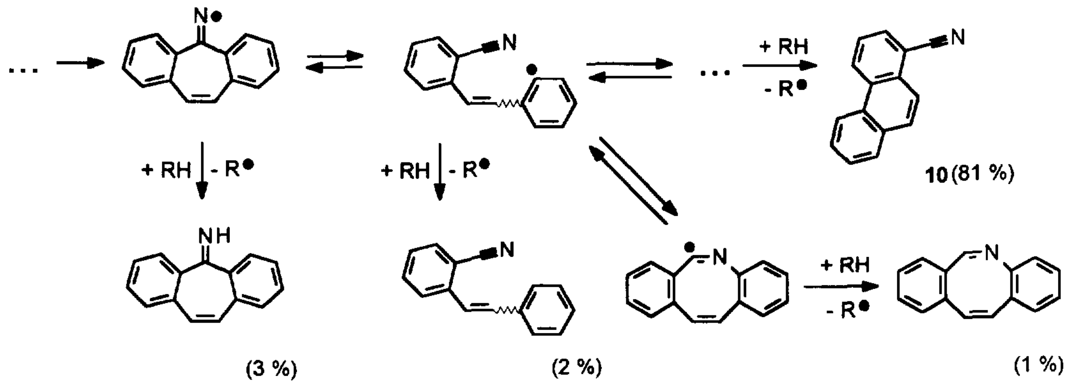
Since, at temperatures above 600 °C, fluorene (**9a**) and methanophenanthrene (**9b**) are formed in parallel to the N-containing compounds **3**, **6** and **8** in a ratio between 1 : 3 and 1 : 4 the pathway (ii) is considered to represent an important side reaction. The formation of the aromatic hydrocarbons **9** in question, the ketimines **2** and the nitrilo-aromatics **6** are the result of conventional bimolecular H-abstraction of the corresponding radicals (**2** and **5**) (scheme 3), but the one of **8a** and **8b** necessitates additional intermediates **4** but **7** at least. The "aza-cyclopropene" intermediate **4** (thought to be the result of the less likely aza-analogous neophyl rearrangement of **2**) might not be, however, an important intermediate, because we failed to detect benzylidene phenylamine and/or phenanthridine when the phenylhydrazone of benzophenone was thermally converted under comparable conditions.[10] Consequently, the endo-cyclization of the phenyltype radical **5** to **7** and its conversion to **8** by bimolecular H-abstraction must be the dominant pathway at high temperatures.

Scheme 3



Though there are a few papers in which the addition of C-centred radicals to the N atom of C≡N-bonds are mentioned to interpret results from experiments at low temperatures,[11] the addition to the C atom is strongly favoured[2,12] by reasons of differences in the electronegativity between carbon and nitrogen. Therefore, the formation of aza-aromatics by a preceded intramolecular radical addition to the N atom is obviously restricted to such intermediate radicals of type **5**, which are not able to form five- and/or six-membered carbon cycles by intramolecular radical addition. This is proved to be true by comparison of phenyltype radicals from six- and seven-membered cycloalkadienones. An example is demonstrated in scheme 4. As to be expected, high yields of 1-nitrilo-phenanthrene **10** from the pyrolysis of the phenylhydrazone of 5H-dibenzo[a,d]cyclohepten-5-one demonstrates impressively that the addition to the N atom of the corresponding nitriles has no chance to compete with addition reactions to C atoms of aromatic structures, if such a competition is to be assumed.

Scheme 4



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References and Notes

1. Forrester, A. R.; Gill, M.; Sadd, J. S.; Thomson, R. H. *J. Chem. Soc., Perkin Trans I* **1979**, 612 - 615.
2. See for example: Beckwith, A. L. J.; O'Shea, D. M.; Westwood, S. W. *J. Am. Chem. Soc.* **1988**, *110*, 2565 - 2575.
3. **1a** and **1b** were synthesized by analogy to ref.[4] The corresponding ketones, phenylhydrazone and trace amounts of acetic acid were dissolved in ethanol, distilled under reflux for 1 hour and recrystallized from ethanol.
4. *Organikum*, 15th ed., Deutscher Verlag der Wissenschaften, Berlin, **1977**, 485.
5. Zimmermann, G.; Nuechter, M.; Remmler, M.; Findeisen, M.; Hopf, H.; Ernst, L.; Mlynek, C. *Chem. Ber.* **1994**, *127*, 1747-1753.
6. GC: HP 5890 Series II (25 m FSOT column, SE 54, H_2); GC-MS: HP 5890 Series II (12 m FSOT column, SE 54, He) / HP 5971 A; GC-FTIR: HP 5890 Series II (25 m FSOT column, SE 54, N_2) / HP 5965 B.
7. phenanthridine (**8a**): IR(FTIR): $\tilde{\nu}$ = 3077 cm^{-1}, 3020, 1611, 1594, 1482, 1456, 1236, 1141, 1035, 956, 887; MS, *m/z*(%): 76 (10), 89 (5), 150 (7), 151 (13), 152 (10), 178 (20), 179 (100), 180 (15); ^{13}C-NMR (Varian UNITY 400; 100 MHz; [$CDCl_3$]): δ = 120.9 ppm, 121.8, 122.3, 124.4, 125.3, 127.0, 127.7, 127.9, 129.8, 129.9, 134.1, 147.2, 150.8; benzo[lmn]phenanthridine (**8b**): IR(FTIR): $\tilde{\nu}$ = 3055 cm^{-1}, 3010, 1586, 1481, 1426, 1248, 1175, 1085, 930, 896, 824; MS, *m/z*(%): 75 (5), 87 (9), 88 (15), 101 (15), 174 (5), 175 (8), 176 (7), 201 (10), 202 (21), 203 (100), 204 (16); ^{13}C-NMR: δ = 119.1 ppm, 120.4, 125.1, 125.2, 126.3, 126.4, 126.7, 127.7, 127.8, 128.5, 128.9, 130.1, 130.9, 142.9, 154.2.
8. The molar yields of benzene correspond roughly with those of fluorene (from **1a**) and methanophenanthrene (from **1b**), respectively.
9. McNab, H. *J. Chem. Soc., Perkin Trans I* **1984**, 371 - 376.
10. Phenanthridine is known to be formed in the pyrolysis of 1,2-diphenylmethylene imine (see for example: Pictet, A.; Aukersmit, H. J. *Ber. Dtsch. Chem. Ges.* **1889**, *22*, 3339 - 3344.
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