

\$0040-4039(96)00320-6

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

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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 2biphenylketimine derivates are able to cyclize and to form substituted phenanthridines¹ (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 reactor⁵ 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 benzene⁸ 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]	600	800	1000
main products [wt%]			
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 scission⁹ (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

$$\begin{array}{c} R' \\ R'' \end{array} = N - N H - Ph \qquad \stackrel{"1,3-H"}{\longleftarrow} \qquad \begin{array}{c} R' \\ R'' \end{array} \xrightarrow{} H \\ R'' \\ R'' \\ N = N - Ph \end{array} \xrightarrow{} \begin{array}{c} -N_2 \\ -N_2 \\ R'' \\ R'' \\ R'' \\ \end{array} \xrightarrow{} H \\ + \bullet Ph$$

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.



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



Acknowledgement. The authors thank the Fonds der Chemischen Industrie for financial support of this research.

References and Notes

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- 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.
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- GC: HP 5890 Series II (25 m FSOT column, SE 54, H₂); 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, N₂) / HP 5965 B.
- phenanthridine (8a): IR(FTIR): ṽ = 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); ¹³C-NMR (Varian UNITY 400; 100 MHz;
 [CDCl₃): 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[Imn]phenanthridine (8b): IR(FTIR): ṽ = 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); ¹³C-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.
- The molar yields of benzene correspond roughly with those of fluorene (from 1a) and methanophenanthrene (from 1b), respectively.
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- 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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(Received in Germany 14 November 1995; accepted 13 February 1996)