Gas phase pyrolysis of heterocyclic compounds, part 3.§ flow pyrolysis and annulation reactions of some nitrogen heterocycles. a product oriented study

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Abstract

Continuous flow pyrolysis (CFP) and annulation reactions of pyrrole (**1**), its benzo-annulated derivatives indole (**2**) and carbazole (**3**), pyridine (**4**), quinoline (**5**), and isoquinoline (**6**) have been investigated at 900 °C. While for **1**, **2**, **4-6** between 15 and 24 products were identified by GC-MS, **3** is rather stable under the reaction conditions and naphthalene (**18**) was found as the only substantial product. Except for **3**, about 10 compounds were always present in the pyrolysate, benzonitrile (**14**) (6-24%) and naphthalene (**18**) (2-21%) being the most prominent products. Compounds **4-6** have even 16 common pyrolysis products. Among the major products are nitrogen heterocycles like quinoline (**5**) (4-13%), isoquinoline (**6**) (0-8%), and indole (**2**) (0.5-3%), cyano-substituted aromatic hydrocarbons like **14**, 1-cyanonaphthalene (**17**) (0-16%), and 9-cycanoanthracene (**19**) (0-6%), as well as the corresponding unsubstituted parent compounds like **18**, phenanthrene (**31**) (2-10%), pyrene (**38**) (1-5%), and fluoranthene (**22**) (2-8%). In addition to the volatile products, several heavy compounds were identified by direct inlet MS. Possible routes of product formation are outlined. The relative amounts of unreacted starting material clearly indicate that benzo-annulation of pyrrole and pyridine causes considerable increase of thermal stability.

Keywords: Flow pyrolysis, benzo annulated heterocycles, pyridine, indole, quinoline, isoquinoline.

Introduction

Pyrolytic methods can be used for different purposes.[2] While by flash vacuum pyrolysis (FVP) small and often highly reactive species are obtained from suitable precursors, continuous flow pyrolysis (CFP) is employed in order to generate larger molecules. It has been shown that by the latter technique large aromatic molecules and even fullerenes can be generated from simple hydrocarbons.[3,4] This is achieved by reaction conditions that allow decomposition and composition reactions to proceed simultaneously. In a systematic investigation, we have studied the reactions of simple hetarenes like pyrrole, furan, and thiophene as well as their benzo- and dibenzo-annulated derivatives under CFP conditions.[5] One aspect of this study was to find out whether heterofullerens might be synthesized directly in this way. However, the main point of interest was to elucidate the influence of the heteroatom and the effect of benzo annulation on the formation of larger annulation products.

We have directed special emphasis to such reactions by which larger products are formed, thus analysing the annulation behaviour of educt molecules. We want to understand by "annulation behaviour" the tendency to form larger, polycyclic products under pyrolytic conditions. Such reactions will be initiated by fragmentation of the starting material, and in subsequent bimolecular reactions larger molecules are generated. Condensation is a special case in which the skeleton of the educt is retained when only hydrogen is ejected. In such a way, likewise larger polycyclic aromatic hydrocarbons (PAHs) and polycyclic hetarenes (PHAs) can be formed if arenes or hetarenes are used as starting material. In order to understand the annulation reactions which are secondary reactions occurring under CFP conditions, also the primary thermolysis reactions of the starting material in which the fragments used as "building blocks" in the annulation reactions are generated should be known. Direct information on the primary reactions is usually obtained in FVP or shock-wave studies. Since there is often a close resemblance between pyrolytic cleavage and fragmentation under electron impact, the mode of thermal decomposition of a compound may be estimated from its mass spectrum when direct evidence is lacking.[2,6]

Previously, we have reported our results obtained for thiophene,[7] benzo[*b*]thiophene, and dibenzothiophene.[1] In this communication the results for some nitrogen heterocycles, namely pyrrole (**1**), indole (**2**), carbazole (**3**), pyridine (**4**), quinoline (**5**), and isoquinoline (**6**) are presented. Compounds **1-5** were included in a gas-phase pyrolysis investigation of coal-related aromatic compounds by Bruisma et al.[8] in order to obtain kinetic data on their thermal stability. The relative stability order at temperatures between 1000 and 1220 K was found to be **5** > **4** > **1** > **2** > **3**. However, in this study no appropriate attempts to identify products were exerted. E.g., for **2** only benzene and toluene are mentioned as products.

This study is primarily product oriented and no mechanistic investigation. Reaction schemes and reaction pathways are to be understood as purely illustrative.

Results and Discusion

The compounds were pyrolysed in an argon stream at atmospheric pressure at 900 °C. In addition, quinoline (**5**) was pyrolysed at 1100 °C. The pyrolysate was analysed by GC-MS. The results are summarized in Tables 1-5. Non-volatile products were analysed by direct inlet (heated probe) MS.

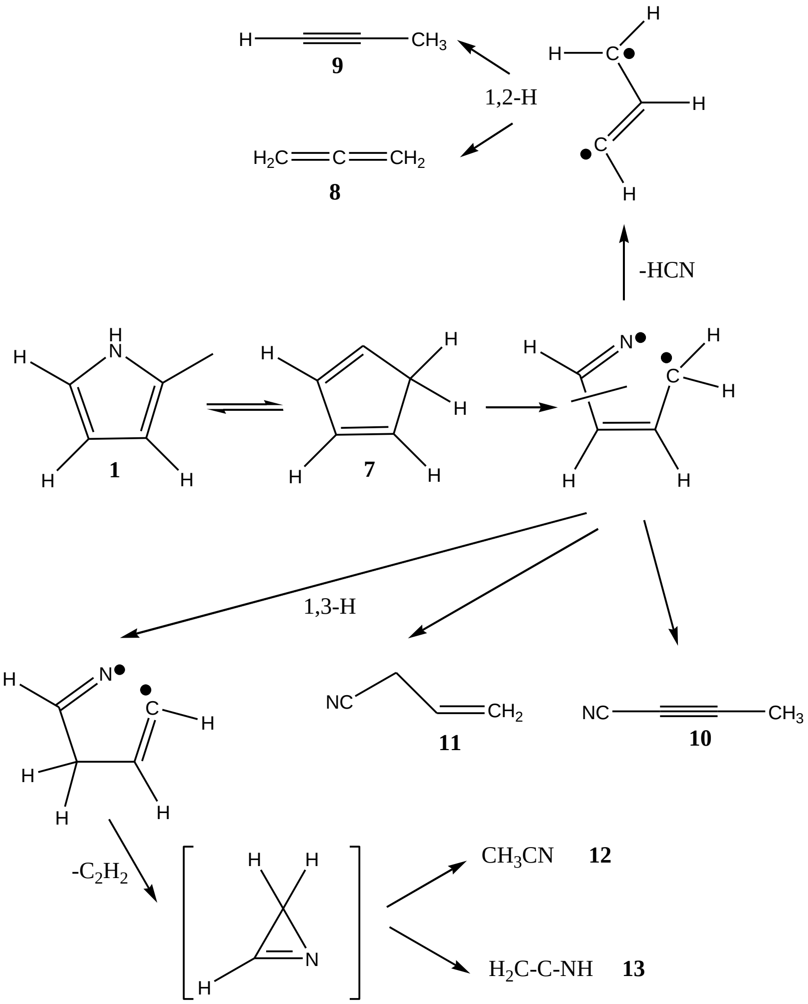
Pyrrole (1)

The thermal fragmentation of pyrrole (**1**) has been investigated meticulously. Patterson et al.[9] have pyrolysed **1** under continuous flow (CFP) conditions at 850 °C and identified about 40 products. Axworthy et al.[10] confirmed these results. Cullis and Norris[11] analyzed only some of the gaseous products. Lifshitz et al.[12] have studied the thermal fragmentation reactions of **1** by shock-wave experiments over the temperature range 1050-1450 K, and Mackie et al.[13] a little later by the same technique at temperatures from 1200 bis 1700 K. In both studies, *cis*-crotonitrile (**10**), allylcyanide (**11**), hydrogen cyanide, and propyne (**9**) were found as main products. Further products are acetylene, ketene imine (**13**), and allene (**8**).

Fragmentation of **1** is initiated by 1,2-hydrogen shift affording 2*H*-pyrrole (**7**)[13,14] which is followed by cleavage of the N1–C2 bond (Scheme 1). This reactive intermediate opens four reaction channels: a) 1,4-hydrogen shift affording *cis*-crotonitrile (**10**); b) 1,2-hydrogen shift affording allylcyanide (**11**); c) 1,3-hydrogen shift affording an intermediate that cleaves into acetylene and ketene imine (**13**); d) cleavage into hydrogen cyanide and a fragment C_3H_4 that isomerizes mainly to propyne (**9**) and to a lesser extent to allene (**8**). At higher pyrolysis temperatures also *trans*-crotonitrile was found.

Table 1. Composition of the pyrolysate of pyrrole (**1**) at 900 °C (GC-MS analysis)

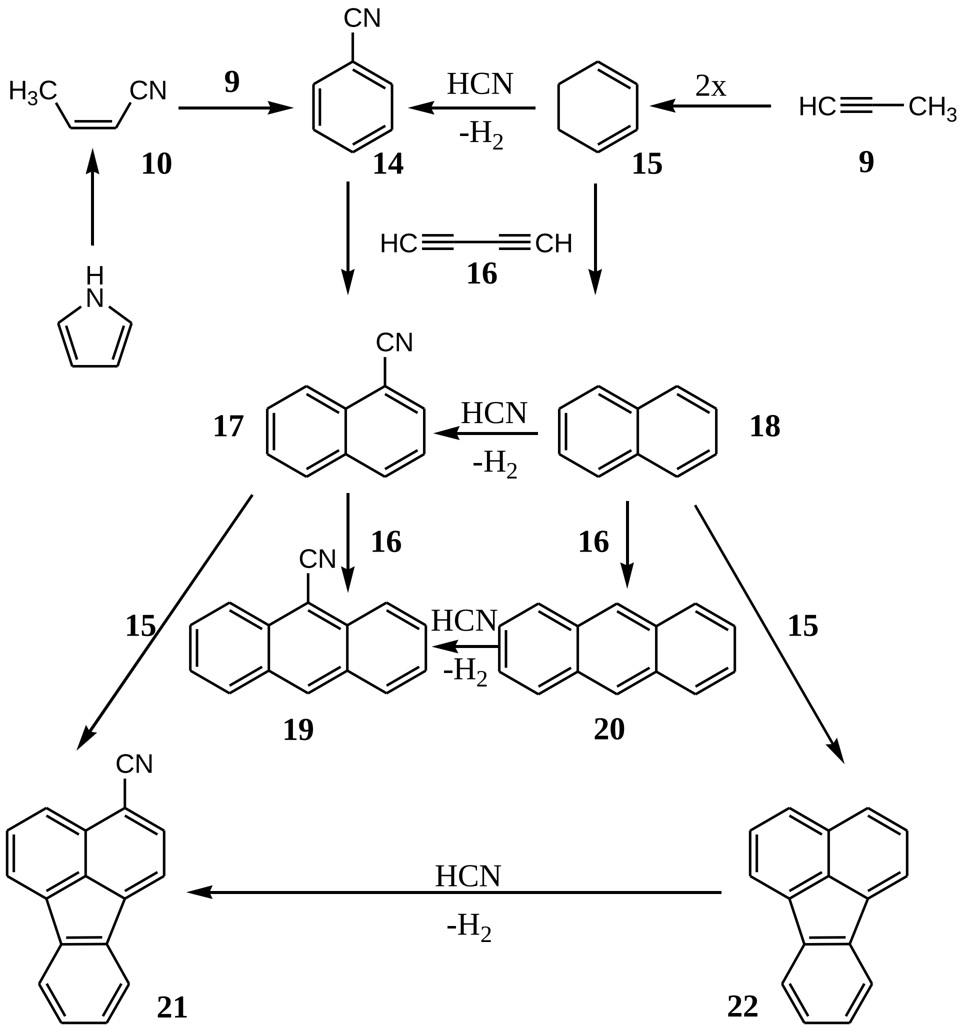
Product	%	Product	%
Benzonitrile (**14**)	24.1	Acenaphthylene (**39**)	3.6
Naphthalene (**18**)	20.6	Indole (**2**)	3.4
1-Cyanonaphthalene (**17**)[a]	15.8	9-Cyanoanthracene (**19**)[a]	< 0.1
Pyrrole (**1**)	11.6	3-Cyanofluoranthene (**21**)[a]	< 0.1
Quinoline (**5**)	5.9	Acridine (**23**)	< 0.1
Phenanthrene (**31**)	5.8	Pyridine (**4**)	< 0.1
Pyrene (**38**)	5.4	Carbazole (**3**)	< 0.1
Fluoranthene (**22**)	3.9	Isoquinoline (**6**)	< 0.1



Scheme 1. Thermal fragmentation of pyrrole (1).[13]

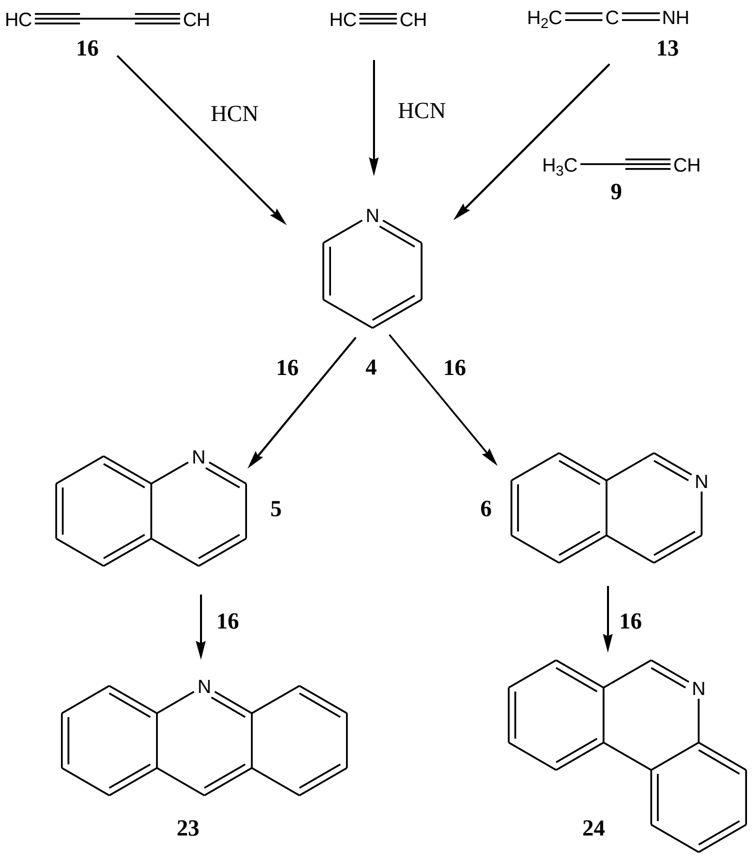
We have performed CFP of pyrrole (**1**) mainly in order to compare the generated products with those of CFP of indole (**2**) and carbazole (**3**). The products detected by GC-MS are summarized in Table 1. Apart from small amounts of quinoline (**5**) and indole (**2**), only traces of pyridine (**4**), isoquinoline (**6**), acridine (**23**) and carbazole (**3**) were found as nitrogen-containing heterocycles. Many more nitrogen compounds were found, in which the nitrogen atom is part of a cyanide substituent. Such products are benzonitrile (**14**), 1-cyanonaphthalene (**17**), 9-cyanoanthracene (**19**), 3-cyanofluorene (**21**) and their isomers. The latter cyano-substituted PAHs were found in traces.

Formation of these cyano compounds may either proceed *via* benzonitrile (**14**) to which various hydrocarbon fragments may annulate, or an already generated PAH skeleton will react with hydrogen cyanide and thus receive a nitrile group as a substituent. If also benzonitrile (**14**) is generated by the latter process from benzene (**15**) there is no principal difference between the two possibilities, only the sequence of the steps varies (Scheme 2).



Scheme 2. Generation of PAHs and their cyano derivatives in the flow pyrolysis of pyrrole (1).

Benzonitrile (**14**) may be formed also from propyne (**9**) with an isomerization product of **1**, namely *cis*-crotonitrile (**10**) or allylcyanide (**11**). Since we did not find benzene (**15**) in the pyrolysate, this reaction seems to be more likely than formation of **14** from the reaction of **15** with HCN. On the other hand, naphthalene (**18**) has been found in the pyrolysate, and this compound is most likely generated from **15** by the annulation reaction with 1,3-butadiyne (**16**) or similar C_4 species. Owing to this, both possibilities for the generation of cyano-substituted PAHs should be accepted. Pyridine (**4**) can either be generated from 1,3-butadiyne (**16**) and HCN or from ketene imine (**13**) and propyne (**9**) (Scheme 3). Annulation of **4** with **16** leads to quinoline (**5**) or isoquinoline (**6**).



Scheme 3. Generation of pyridine (4), quinoline (5), and isoquinoline (6) in the flow pyrolysis of pyrrole (1).

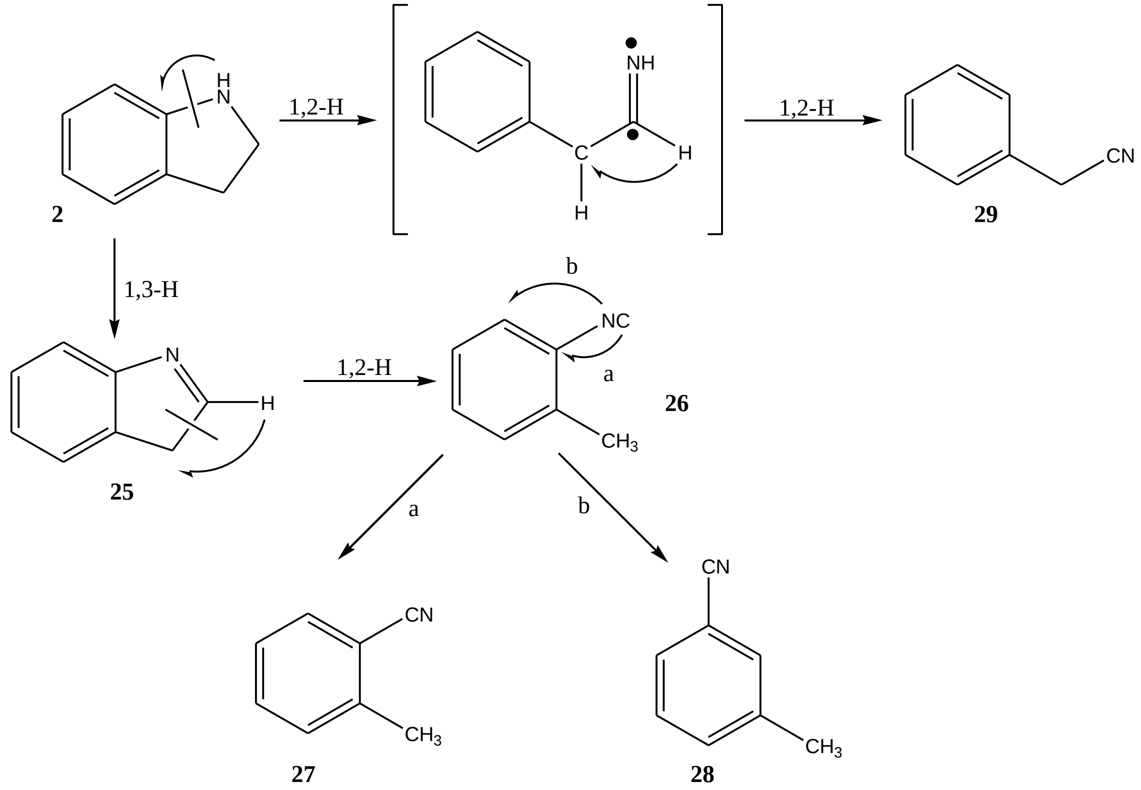
In a similar manner, annulation of pyrrole (**1**) with one or two molecules of **16** will generate indole (**2**) or carbazole (**3**), respectively. In these and similar annulation reactions 1,3-butadiyne (**16**) has been used as a reactant although it is not generated in the fragmentation of pyrrole (**1**) (Scheme 1). Therefore, it has to be assumed that **16** arises indirectly by combination of two acetylene molecules or equivalent radicalic species. Alternatively, the annulation reactions may be formulated with two acetylene molecules as reactants instead of one 1,3-butadiyne (**16**).

Table 2. Composition of the pyrolysate of indole (**2**) at 900 °C (GC-MS analysis)

Product	%	Product	%
Indole (**2**)	41.8	Naphthalene (**18**)	2.2
Benzonitrile (**14**)	13.1	Benzo[a]pyrene **41**)	1.9
Phenanthrene (**31**)	9.7	Fluoranthene (**22**)	1.7
Biphenyl (**46**)	6.7	Fluorene (**32**)	1.5
9-Cyanoanthracene (**19**)[a]	5.2	Isoquinoline (**6**)	1.0
Quinoline (**5**)	4.4	2-Cyanomethyl-enzonitrile(**42**)[a]	0.8
Anthracene (**20**)	3.5	Acridine (**23**)	0.6
2- or 3-Methylbenzonitril (**27**, **28**) or phenylacetonitrile (**29**)	2.8	3-Phenylindole[a]	0.6
Carbazole (**3**)	2.5		

[a] Including isomers.

In our CFP study we did not find other products than those Patterson et al.[9] have reported; however, the relative amounts of several products obtained are different. These authors found hydrogen cyanide (49%) as the main product, and pyridine (**4**) as well as benzene (**15**) as major products, whereas in our study **4** and **15** were found only as traces in the pyrolysate.



Scheme 4. Isomerization reactions of indole (2) in shock-wave experiments.[15]

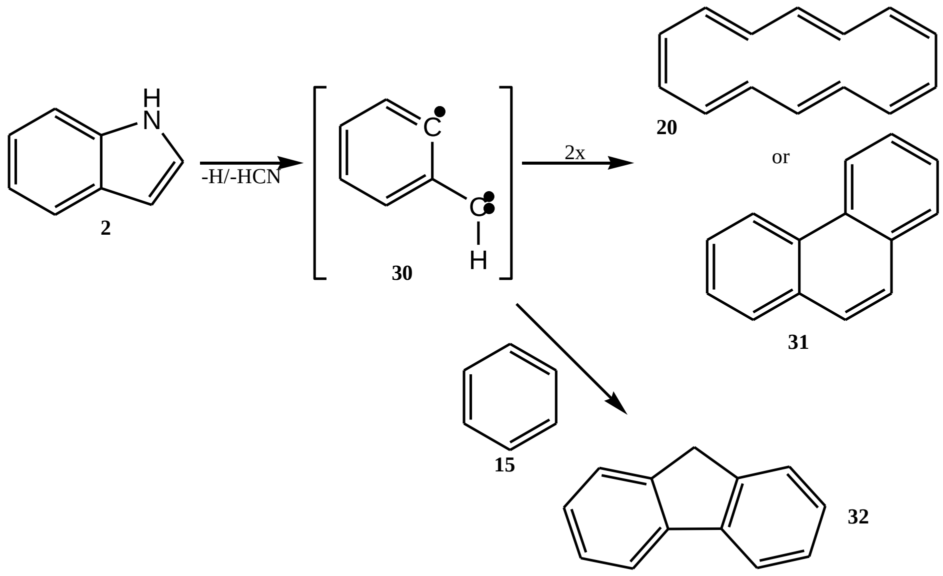
Indole (2)

Laskin and Lifshitz[15] have investigated the thermal fragmentation of indole (**2**) in the temperature range 800-1400 °C in shock-wave experiments. The main primary reactions are isomerizations. Three products were found as results of the opening of the pyrrole ring: phenylacetonitrile (**29**) and 2- and 3-methylbenzonitrile (**27**, **28**) (Scheme 4). The latter two compounds arise *via* indolenine (**25**) and 1-isocyano-2-methylbenzene (**26**).[15] The isomerization of **2** to **29** and **27** has been reported by Wentrup.[16,17] The main decomposition products were identified as acetylene, hydrogen cyanide, 1,3-butadiyne (**16**), benzonitrile (**14**), acetonitrile (**12**) and benzene (**15**). Among others, toluene was detected in low quantity. Decomposition commences by loss of a hydrogen atom affording indoyl radicals.

To our knowledge, no product-oriented CFP study of **2** has been published. We have investigated the product distribution in the CFP of **2** at 900 °C. The results are summarized in Table 2. By direct inlet MS only a few peaks could be assigned to additional products. The signal at *m/z* = 217 can be assigned to the M $^+$ peak of benzo[*b*]carbazole (**40**) ($C_{16}H_{11}N$) or an isomer. The peaks at *m/z* = 230 and 232 can be assigned to products with formulae $C_{16}H_{10}N_2$ or $C_{16}H_{12}N_2$, respectively, resulting from the condensation of two molecules of indole (**2**).

In the flow pyrolysis of **2**, only small amounts of nitrogen heterocycles like quinoline (**5**), isoquinoline (**6**), acridine (**23**), and carbazole (**3**) were generated. Compounds with the nitrogen atom being part of a cyano-substituent such as in benzonitrile (**14**) and 9-cyanoanthracene as well as their isomers were found in larger amounts. As in the shock-wave experiments,[15] the isomerization products **27-29** were found. The formation of **3**, **5**, **6**, and **23** can be explained as described for the pyrolysis of pyrrole (**1**) (Scheme 3). Benzo[*b*]carbazole (**40**) and its isomers are obtained from **3** by annulation with butadiyne (**16**).

The large amount of phenanthrene (**31**) and anthracene (**20**) compared with that of naphthalene (**18**) is remarkable. In the pyrolysis of pyrrole (**1**) it was much lower, and this indicates that different reaction paths are followed. From **2**, an intermediate **30** can be generated by loss of a hydrogen atom and HCN (Scheme 5). Dimerization of **30** affords phenanthrene (**31**) or anthracene (**20**), and reaction of **30** with benzene (**15**) produces fluorene (**32**). If **32** is generated alternatively by annulation of two butadiyne fragments to a cyclopentadiene, at least a small amount of indene (**46**) should be detected. Since this is not the case, this reaction path seems to be unlikely.



Scheme 5. Formation of phenanthrene (31), anthracene (20), and fluorene (32) in the flow pyrolysis of indole (2).

The amount of 9-cyanoanthracene (**19**) and its isomers, too, is considerably larger than found in the CFP of pyrrole (**1**) where it was not possible to decide whether **19** was generated from benzonitrile (**14**) by annulation with two butadiyne fragments or from benzene (**15**) by reaction with HCN and butadiyne annulation. Due to the fact that in the CFP of indole (**2**) both the relative amounts of **20**/**31** and that of their respective cyano-derivatives have increased, the reaction of HCN with the corresponding aromatic hydrocarbon is more probable. Also the formation of 2-cyanomethylbenzonitrile (**42**) and its isomers suggests a late introduction of the cyano group.

Carbazole (3)

In the literature, we did not find a CFP study of carbazole (**3**) in which the products were analyzed. We have studied the flow pyrolysis of **3** at 900 ^{o}C. In the GC-MS analysis of the pyrolysate, only naphthalene (**18**) (1.3%) was found beside recovered **3** (98.7%). The direct inlet MS indicates that traces of heavier compounds have been formed that can be described as "oligomers" of the starting material. Peaks at *m/z* = 330, 495, and 660 are assigned to a "dimer" $C_{24}H_{14}N_2$, a "trimer" $C_{36}H_{21}N_3$, and a "tetramer" $C_{48}H_{28}N_4$, respectively. These "oligomers" are generated by condensation reactions of **3** in which hydrogen molecules are split off. In addition, there are several signals in the direct inlet MS which could not be assigned.

Because the corresponding experimental studies remain to be performed, the thermal fragmentation of carbazole (**3**) has to be estimated from its mass spectrum[18] which shows the following stronger signals: *m/z* = 167 (100%, M $^{+}$); 166 (25%, M – H); 113 (5%, 166 – C_2H_2); 88 (5%); 76 (5%); 51 (4%); 39 (4%). The fragmentation pattern is only weakly pronounced, owing to the high stability of the radical cation M $^{+}$. M $^{+}$ mainly ejects the hydrogen atom from the N atom affording a carbazoyl cation followed by loss of a HCN molecule. An acetylene molecule is lost from the carbazolyl cation.

The main reaction in the CFP is loss of a hydrogen atom affording a carbazoyl radical, and the "oligomerization" products are generated by radicalic reactions. Naphthalene (**18**) arises *via* benzene (**15**).

Pyridine (4)

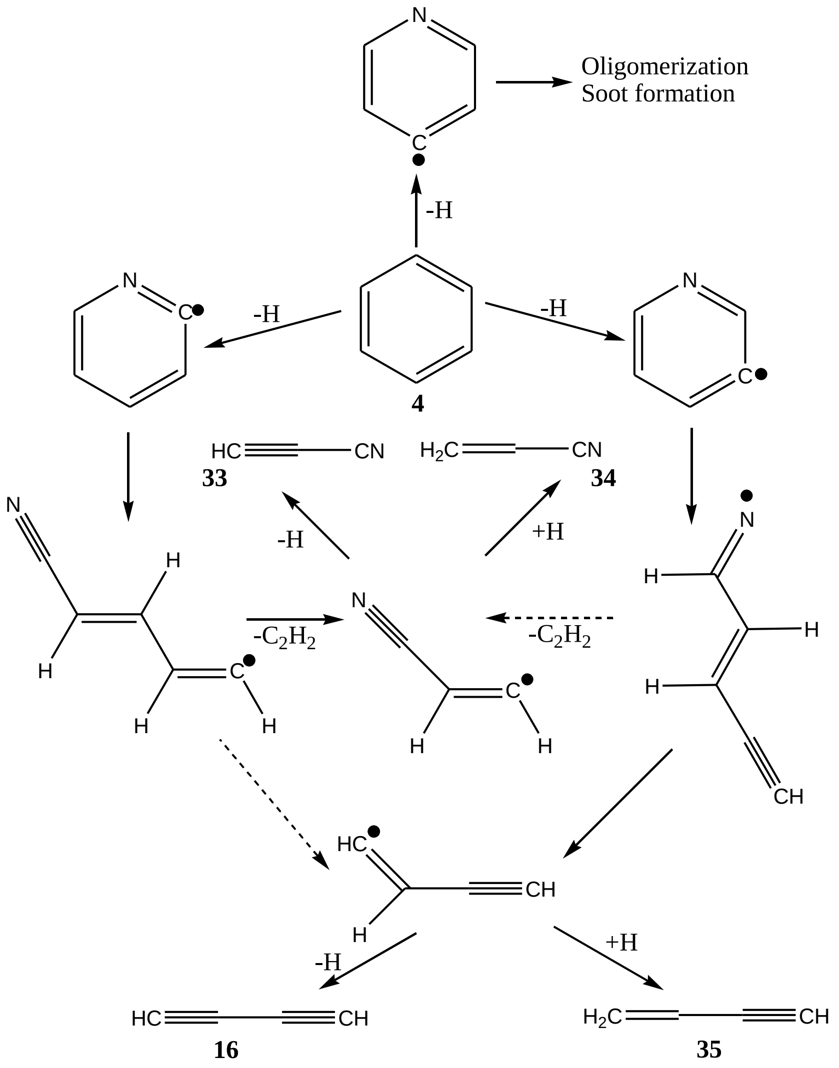
Hurd and Simon[19] have studied the CFP of pyridine (**4**) between 825 °C and 850 °C. Identified products were quinoline (**5**), benzonitrile (**14**), acetonitrile (**12**), acrylonitrile (**34**), and benzene (**15**); besides, a non-volatile residue was obtained but not analysed. Axworthy et al.[10] extended the temperature range to 850-1000 °C and confirmed these results. They found hydrogen cyanide as an additional product that appears generally in the pyrolysis of organic nitrogen compounds. The largest amount of nitrogen-containing products was found at 985 °C, and most nitrogen-free products were formed at 1025 °C. Houser et al.[20,21] showed that HCN formation is no primary process and requires several steps.

Hore and Russel[22] have analysed the mechanisms of thermal decomposition of **4** by IR laser pyrolysis. The reaction is initiated by formation of pyridyl radicals. While 2-pyridyl and 3-pyridyl radicals each lead to stable gaseous products, 4-pyridyl radicals produce solid deposits (Scheme 6). From 2-pyridyl radicals, acetylene, cyanoacetylene (**33**), and acrylonitrile (**34**) are generated, and from 3-pyridyl radicals, hydrogen cyanide, but-3-ene-1-yne (**35**), and 1,3-butadiyne (**16**) are formed.

Table 3. Composition of the pyrolysate of pyridine (**4**) at 900 °C (GC-MS analysis)

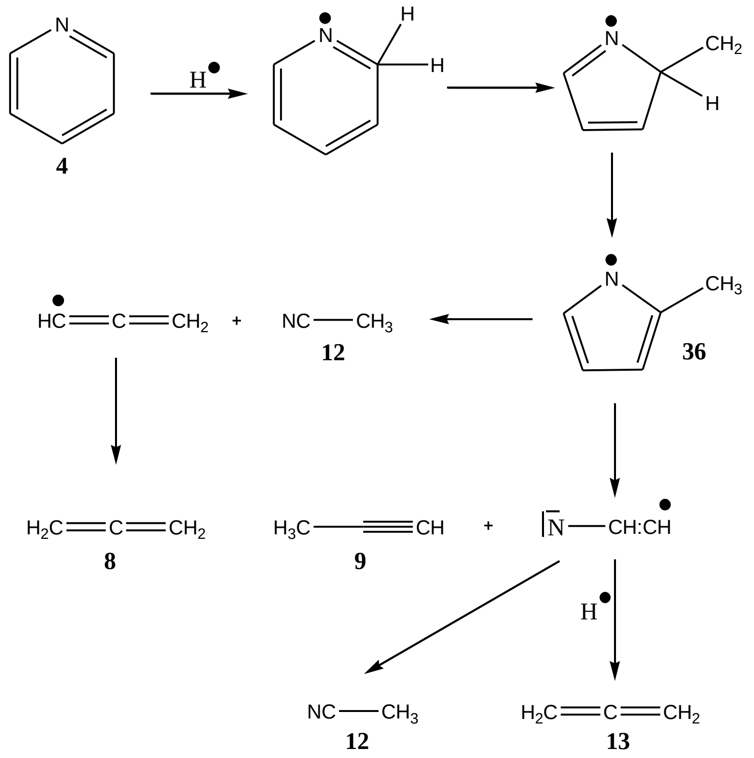
Product	%	Product	%
Naphthalene (**18**)	15.0	Acenaphthylene (**39**)	3.0
Quinoline (**5**)	11.8	Indole (**2**)	2.8
Benzonitrile (**14**)	8.8	Fluoranthene (**22**)	2.7
1-Cyanonaphthalene (**17**)[a]	8.1	Pyrene (**38**)	2.1
Phenanthridine (**24**)[a]	6.3	Carbazole (**3**)	1.5
9-Cyanoanthracene (**19**)[a]	6.2	Triphenylene (**47**) or chrysene (**45**)	1.4
Cyanopyridine	5.7	2-Phenylpyridine[a]	1.4
Pyridine (**4**)	5.3	Biphenyl (**46**)	0.8
Benzo[h]quinoline[a]	4.7	Benzo[*b*]acridine (**43**)[a]	0.6
Phenanthrene (**31**)	4.4	Fluorene (**32**)	0.5
Isoquinoline (**6**)	3.6	Phenylquinoline	0.5
Dipyridine	3.6	Phenylnaphthalene	0.4
Cyanoquinoline/-isoquinoline	3.4		

[a] Including isomers.



Scheme 6. Fragmentation of pyridine (4).[22]

Mackie et al.[23] suggested a reaction sequence for the formation of the by-products propyne (**9**), allene (**8**), acetonitrile (**12**), and ketene imine (**13**). In the first step a hydrogen atom is added to **4** (Scheme 7), a subsequent rearrangement affords the methylpyrrolyl radical **36** giving rise to the formation of compounds **8**, **9**, **12**, and **13**.

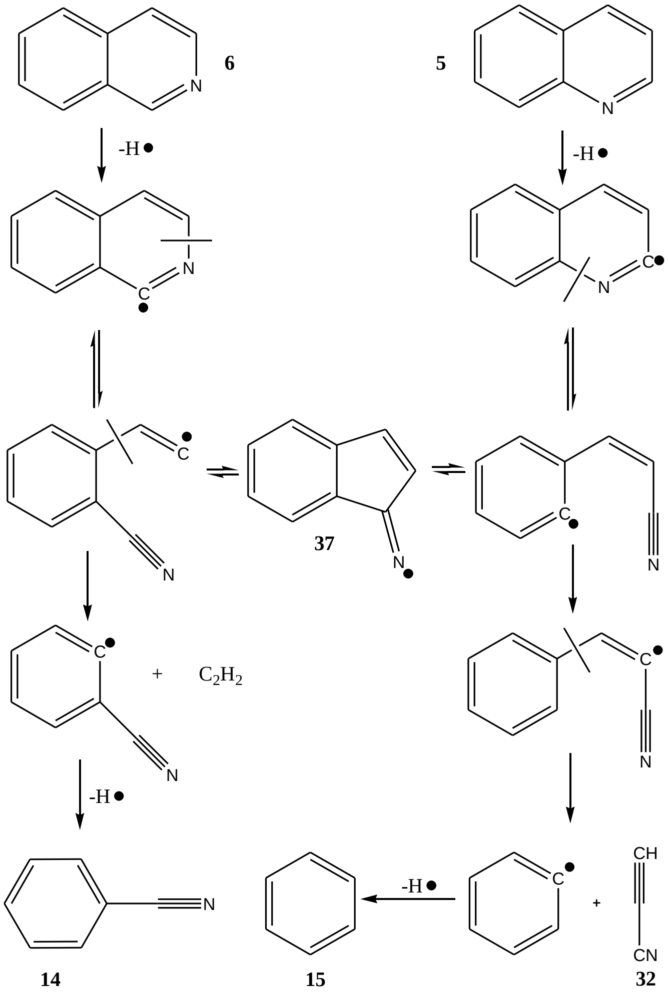


Scheme 7. Formation of propyne (9), allene (8), acetonitrile (12), and ketene imine (13) in the pyrolysis of pyridine (4).

The volatile products generated in our CFP study are collected in Table 3. In addition, heavy products as benzo[*b*]carbazole (**40**), benzo[*a*]pyrene (**41**) or their isomers were detected by direct inlet MS.

Bipyridines generated in CFP of pyridine (**4**) arise from recombination reactions of pyridyl radicals. Quinoline (**5**) and isoquinoline (**6**) are formed from **4** as shown in Scheme 3. The cyano derivatives of **5** and **6** arise from their reaction with HCN or from cyanopyridine by annulation with butadiyne (**16**). Annulation reactions of **5** and **6** may also afford benzoquinolines or phenanthridine (**24**) and benzo[*b*]acridine (**43**) or its isomers. Indole (**2**) was found in low amount and may arise from benzene (**14**) and ketene imine (**13**) or acetonitrile (**12**). Annulation of **2**with **16** leads to carbazole (**3**). It is plausible that only small amounts of **2** and **3** are generated because in the fragmentation of **4** only minor amounts of **13** and **12** were produced. Naphthalene (**18**) and other PAHs like anthracene (**20**), phenanthrene (**31**) and chrysene (**45**) arise from annulation reactions of benzene (**15**). Biphenyl (**46**) and triphenylene (**47**) are produced from **15** by condensation reactions.[24] Acenaphthylene (**39**) and fluoranthene (**22**) are probably formed from naphthalene (**18**) and acetylene (**13**) followed by annulation with **16**. However, **22** may also be generated from **18** and **15**.

Our investigation confirms earlier studies;[10,19,25] however, we could identify several additional products of higher molecular weight and low volatility.

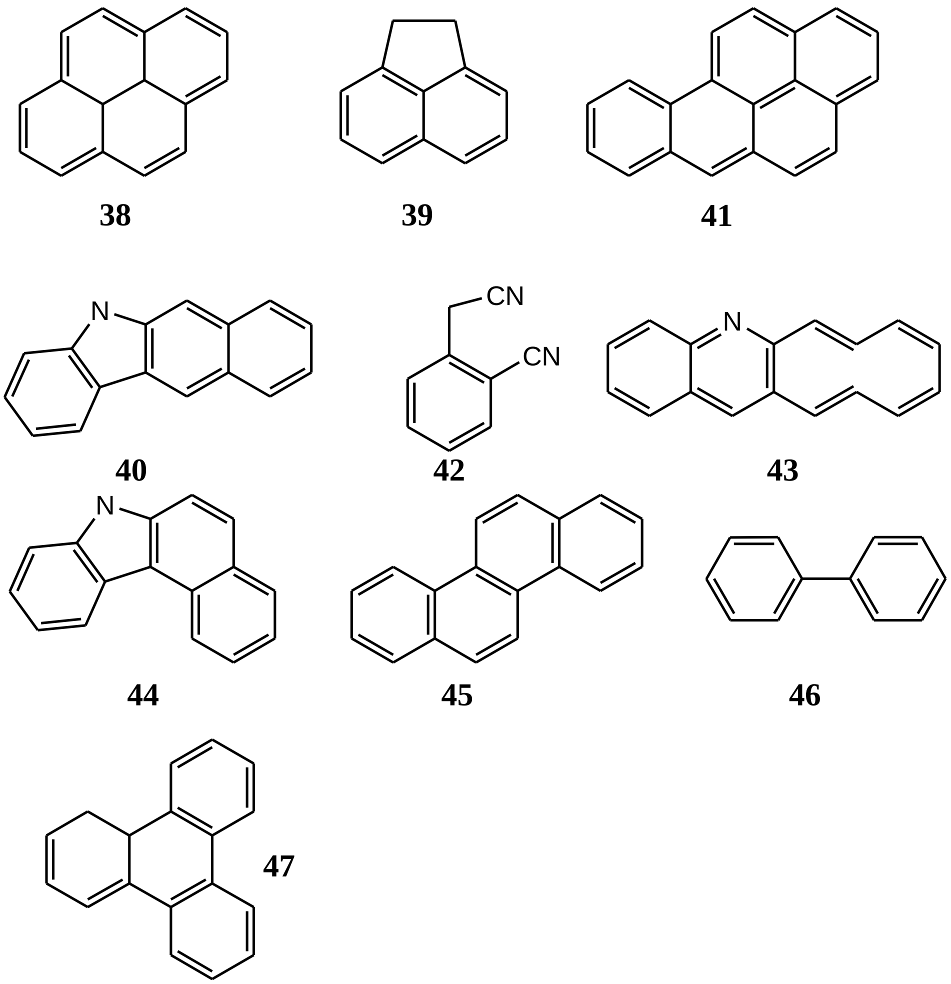


Scheme 8. Fragmentation of quinoline (5) and isoquinoline (6).[27]

Quinoline (5) and isoquinoline (6). Patterson et al.[26] have pyrolysed quinoline (**5**) and isoquinoline (**6**) under CFP conditions at 950 °C. Mutual isomerizations of **5** and **6** were observed. Several hydrocarbons like benzene (**15**), toluene, naphthalene (**18**), phenanthrene (**31**), and anthracene (**20**) were found in the pyrolysate. Beside indole (**2**) only nitriles were found as nitrogen-containing products such as benzonitrile (**14**), cyanostyrene, cyanonaphthalenes (**17**), and isomers. Axworthy et al.[10] could largely confirm the results of Patterson et al.[26] regarding the pyrolysis of **5**, but they did not confirm the isomerization of **5** to **6**.

Laskin and Lifshitz[27] have investigated the thermal decomposition of **5** and **6** in shock-wave experiments at temperatures between 1275 and 1700 K. The same decomposition products were found for both compounds: acetylene, benzonitrile (**14**), cyanoacetylene (**33**), benzene (**15**), hydrogen cyanide, phenylacetylene, and 1,3-butadiyne (**16**). In addition, trace quantities of C_6H_4, pyridine (**4**), and ethynylpyridine were found. The same product distribution of both isomers **5** and **6** is accounted for by assuming the 1-indene imine radical **37** as the common intermediate (Scheme 8). The quinolyl and the isoquinolyl radicals decompose in similar manners affording benzene (**15**) and cyanoacetylene (**33**), or benzonitrile (**14**) and acetylene, respectively. The other products are generated in an analogous way. Patterson et al.[26] considered cleavage of a C–N or C–C bond as the initial step in the fragmentation of **5** and **6**, while Laskin and Lifshitz[27] could show that hydrogen abstraction initiates the decomposition.

Hydrogen atoms can be ejected from both the pyridine and the benzene rings of **5** and **6**. Ejections from positions adjacent to the ring nitrogen atom are dominant. The preferred pathway for the decomposition of the pyridine ring involves a hydrogen atom ejection from the neighbouring ring carbon atom followed by β -scission resulting in the rupture of the C–N bond (Scheme 6). In quinoline (**5**) there is only one ortho site from which a hydrogen atom can be ejected. The preferred β -scission is the rupture of the C–N bond (Scheme 8). On the other hand, isoquinoline (**6**) has two ortho positions, and both are subjected to β -scission of the C–N bond, however, that one shown in Scheme 8 is preferred.[27]



Scheme 9

In our CFP study, **5** was pyrolysed at 900 and 1100 °C, **6** only at 900 °C. The products detected by GC-MS are collected in Tables 4 and 5. In the direct inlet mass spectra of the non-volatile residue of the soot extract, signals were found at *m/z*= 256, 383, and 510 which were assigned with high probability to "dimers" $C_{18}H_{12}N_2$, "trimers" $C_{27}H_{17}N_3$, and "tetramers" $C_{36}H_{22}N_4$ of the starting material. The latter two signals were only detected at the higher pyrolysis temperature, thus indicating that "oligomerization" increases with the temperature. The detection of "oligomers" of the starting molecules that arise from quinolyl and isoquinolyl radicals is in accord with the mechanism proposed by Laskin and Lifshitz.[27]

Comparison of the products generated from **5** and **6** at 900 °C indicates that largely the same main products in similar amounts are obtained. It is remarkable that the amount of **5.** obtained from the pyrolysis of **6** is larger than the amount of **6** produced in the pyrolysis of **5**. At 1100 °C no **6** was found in the pyrolysis of **5**. The tendency to generate PAHs like naphthalene (**18**), phenanthrene (**31**), anthracene (**20**), fluoranthene (**22**) or pyrene (**38**) was larger by about 5% when **6** was employed as starting material instead of **5**.

Table 4. Composition of the pyrolysate of quinoline (**5**) at 900 °C and 1100 °C (GC-MS analyses)

Product	900 °C %	1100 °C %	Product	900 °C %	1100 °C %
Quinoline (**5**)	35.7	32.3	Phenylquinoline	1.6	
Naphthalene (**18**)	10.3	13.6	Triphenylene (**47**) or chrysene (**45**)	1.5	
Phenanthrene (**31**)	9.2		Pyrene (**38**)	1.4	10.1
Isoquinoline (**6**)	7.5		Indole (**2**)	1.3	
Benzonitrile (**14**)	6.4	14.8	Acridine (**23**)	1.2	
9-Cyanoanthracene (**19**)[a]	4.6		Anthracene (**20**)	1.1	5.8
Benzene (**15**)	4.4		Acenaphthylene (**39**)	0.8	7.6
Benzo[*b*]acridine (**43**)[a]	3.6		Phenylnaphthalene	0.7	
Fluoranthene (**22**)	3.5	9.6	Benzo[c]carbazole (**44**)[a]	0.6	
Biphenyl (**46**)	2.7	3.0	Fluorene (**32**)	0.5	
1-Cyanonaphthalene (**17**)[a]	2.6	3.1	Indene (**46**)	0.3	
Cyanoquinoline/-isoquinoline	2.5		Benzo[a]pyrene (**41**)[a]	< 0.1	

[a] Including isomers.

Table 5. Composition of the pyrolysate of isoquinoline (**6**) at 900 °C (GC-MS analysis)

Product	%	Product	%
Naphthalene (**18**)	15.0	Pyrene (**38**)	2.1
Anthracene (**20**)	14.4	Phenanthridine (**24**) or acridine (**23**)	1.9
Quinoline (**5**)	13.2	Phenanthrene (**31**)	1.5
Isoquinoline (**6**)	11.1	Benzo[*b*]acridine (**43**)[a]	1.5
Benzonitrile (**14**)	8.8	Benzo[a]pyrene (**41**)[a]	1.4
Fluoranthene (**22**)	7.6	Acenaphthylene (**39**)	1.3
9-Cyanoanthracene (**19**)[a]	5.4	Phenylnaphthalene	1.3
Biphenyl (**46**)	5.0	Fluorene (**32**)	0.7
1-Cyanonaphthalene (**17**)[a]	4.3	Indole (**2**)	0.5
Triphenylene (**47**) or chrysene (**45**)	2.6	Phenylquinoline	0.4

[a] Including isomers.

Since the amount of benzene (**15**) decreases at the higher pyrolysis temperature and that of benzonitrile (**15**) increases, it is likely that **14** arises from **15** and HCN. The formation of other nitriles like **17** and **19** can be explained as for pyrrole (**1**) (Scheme 2). Also PAHs are generated in a similar way as described above (Scheme 2). It is also quite likely that **18**, **31**, **20** and biphenyl (**46**) arise from benzene (**15**) because the amount of **15** decreases while that of the PAHs increases with temperature. The amount of acenaphthylene (**39**) and fluoranthene (**22**) increases more clearly than that of naphthalene (**18**) indicating that **39** and **22** arise from **18** by reaction with acetylene and benzene (**15**), respectively.

PHAs like acridine (**23**) and benzo[*b*]acridine (**43**) as well as their isomers are generated from **5** or **6**, respectively, and one or two butadiyne fragments (**16**). Compounds like indole (**2**), carbazole (**3**), benzo[*b*]carbazole (**40**), and their isomers require formation of a five-membered heterocycle that can be formed in a reaction of propyne (**9**) with HCN. Since pyrrole (**1**) was not detected in the pyrolysate, it has to be assumed that instead of **1** a reactive intermediate is generated that subsequently reacts with **16**. Alternatively, it seems possible that indole (**2**) arises from benzene (**15**) and ketene imine (**13**).

Compared with earlier investigations,[10,26] several additional products were found. These are 9-cyanoanthracene (**20**) and its isomers, cyanoquinoline or cyanoisoquinoline, phenylquinoline, phenylnaphthalene, benzo[*b*]carbazole (**40**), acridine (**23**), benzo[*b*]acridine (**43**) and isomers.

Results and Discussion

The compounds investigated in this study are structurally too different for a uniform pyrolysis pattern. However, there are obviously common features in their CFP that allow some general conclusions. First of all, this relates to the annulation behaviour of **1**-**6**. While for **1**, **2**, **4**-**6** between 15 and 24 products were identified by GC-MS, **3** is rather stable under the reaction conditions, and naphthalene (**18**) was found as the only significant product. Except for **3**, about 10 compounds are always present in the pyrolysate, benzonitrile (**14**) (6-24%) and naphthalene (**18**) (2-21%) being the most prominent products. Compounds **4**-**6** have even 16 common pyrolysis products. Among the major products are N heterocycles like quinoline (**5**) (4-13%), isoquinoline (**6**) (0-8%), and indole (**2**) (0.5-3%), cyano-substituted aromatic hydrocarbons like **14**, 1-cyanonaphthalene (**17**) (0-16%), and 9-cycanoanthracene (**19**) (0-6%), as well as the corresponding unsubstituted parent compounds like naphthalene (**18**), phenanthrene (**31**) (2-10%), pyrene (**38**) (1-5%), and fluoranthene (**22**) (2-8%). From these results it may be concluded that similar reaction pathways with similar intermediates are followed in the CFP of **1**-**6**.

The distinct tendency to form PAHs and their cyano derivatives under CFP conditions at 900 ^{o}C can apparently be explained by a mechanism in which primarily the skeleton of a certain PAH is generated that can then react with HCN to afford its cyano derivative. Formation of nitrogen-containing five- and six-membered rings is of minor importance, because generally only low amounts of indole (**2**), carbazole (**3**), pyridine (**4**), quinoline (**5**), and isoquinoline (**6**) were detected in the pyrolysate. No compound with more than one ring-nitrogen atom has been found. The only products with more than one nitrogen atom are cyano derivatives of pyridine, quinoline and isoquinoline, and dinitriles like 2-(cyanomethyl)benzonitrile (**42**). HCN is thus the most important nitrogen-containing fragment that reacts with PAHs to afford cyano-derivatives.

With the exception of pyrrole (**1**), all compounds studied here give rise to the formation of "oligomers" by recombination reactions of radicals. For indole (**2**) and pyridine (**4**), "dimers" were detected, and "oligomers" up to "tetramers" of carbazole (**3**) and quinoline (**5**) were found. This indicates that decomposition of the starting material is initiated by loss of hydrogen atoms.

Carbazole (**3**) obviously behaves differently from the other compounds. At 900 ^{o}C, fragmentation occurs only to a little extent, and beside naphthalene (**18**) no product could be detected that arises from carbazole fragments. For the pyrolysis of **3**, these reaction conditions are not well suited. However, although the pyrolysate consisted mainly of unreacted **3**, this does not mean that no decomposition occurred. To the contrary, many more non-volatile and insoluble solid deposits ("soot") were formed as compared with the other compounds.

Since the CFP experiments for **1**-**6** were performed under largely the same conditions, the amounts of unreacted starting material can be considered as an indication of their relative thermal stability. The data in Tables 1-5 lead to the sequence pyridine (**4**) < isoquinoline (**6**) < pyrrole (**1**) < quinoline (**5**) < indole (**2**) < carbazole (**3**). For compounds **1**-**3** and **4**-**6** it is evident that benzo annulation considerably increases the thermal stability. In the pyridine series **4**-**6**, the large stability difference of the isomers **5** and **6** is remarkable. Even when the amounts of **5** and **6**, which seem to interconvert under CFP conditions, are added, the degree of decomposition is much higher for **6** than for **5**. With reference to Scheme 8, we have to conclude that either the formation of the isoquinolyl radical or its decomposition is much faster than that of the quinolyl radical.

Experimental Section

General Procedures. Commercial samples of pyrrole (**1**) (Fluka), indole (**2**) (Aldrich), carbazole (**3**) (Fluka), pyridine (**4**) (Fluka), quinoline (**5**) (Janssen), and isoquinoline (**6**) (Janssen) were used. The purity of the samples was checked by GC-MS analyses. Traces of 2,5-dimethylpyrrole and 1-ethenyl-1*H*-pyrrole were detected in **1**. No contaminants were found in **2** and **3**. The purity of **4** was 99.9%, and no impurities could be identified. **5** (95.7%) was contaminated with 2.2% isoquinoline (**6**), 1.6% methylnaphthalene, and 0.4% methyltetrahydroquinoline. As impurities of **6** (97.7%), 2-methylquinoline (1.4%), 6-methylquinoline (0.6%), and quinoline (**5**) (0.3%) were identified.

The CPF experiments were performed at atmospheric pressure in a continuous flow reactor consisting of a quartz tube of 110 cm length with an inner diameter of 22 mm that was heated by an oven (type 7/75) with a thermostat (RE 2.1) of Heraeus Instruments. The heated zone of the oven was 75 cm long. In flow direction the apparatus was inclined downward by 10°. The experiments were performed at constant oven temperature of 900 °C. Argon was used as carrier gas, flow rate 60 cm^3 min^{-1}. Residence times of molecules in the hot zone were about 20 s.

1. (27.2 g, 0.406 mol) was introduced into the apparatus by a dropping funnel within 90 min.
2. (26.1 g, 0.223 mol) was warmed to 60 °C and introduced into the apparatus by a dropping funnel within 90 min.
3. (3.2 g, 0.019 mol) was introduced into the apparatus by sublimation within 15 min. When larger quantities of **3** were employed, the pyrolysis tube was completely choked with soot.
4. (29.5 g, 0.373 mol) was introduced into the apparatus by a dropping funnel within 90 min.
5. (27.9 g, 0.216 mol) was introduced into the apparatus by a dropping funnel within 60 min.
6. (31.8 g, 0.247 mol) was introduced into the apparatus by a dropping funnel within 60 min.

The pyrolysis products were trapped in a cold trap cooled to 0 °C, and two washing flasks filled with toluene were kept at ambient temperature. After the apparatus had cooled to ambient temperature, the soot was washed off with toluene from the pyrolysis tube and the cold trap, crushed in an ultra sonic bath, and then transferred into a Soxhlet thimble. The soluble ingredients were extracted with the toluene solutions from the washing flasks in a Soxhlet apparatus. The extracts were concentrated to about 50 mL and analyzed by GC-MS and by direct inlet (solid probe) MS.

For the GC-MS analyses a Hewlett-Packard gas chromatograph (HP 5890 Series II) equipped with a cold injection system (Gerstel KAS 3) was used. An non-polar capillary column (SGE BPX5), length 50 m, inner diameter 0.15 mm, film thickness 0.4 μm, was used. The following temperature programs were applied.

Cold injection system: starting temperature 50 °C; heating rate 5 °C s^{-1}; intermediate temperature 150 °C held for 30 s; final temperature 250 °C held for 60 s; cooling to 50 °C.

Column oven: starting temperature 50 °C held for 10min; heating rate 5 °C min^{-1}; final temperature 300 °C.

Helium was used as carrier gas, flow rate 20cm^3 s^{-1}.

The gas chromatograph was connected to a Hewlett-Packard quadrupole mass spectrometer (HP5971A MSD). Electron impact ionization at 70 eV; measuring range 10-600 amu. The recorded mass spectra were compared electronically with spectra in the data base NBS49K (NIST).[18] For this purpose the program CHEMPC (Hewlett-Packard) was used.

Direct inlet mass spectra were recorded with a Fisons (now Micromass) instrument (VG Prospec 3000). Electron impact ionization at 70 eV; measuring range 10-1200 amu; ion source temperature 250 °C; source pressure 10^{-7} mbar. After background corrections for water (m/z = 18), air (28, 32, 40) and column bleeding at higher temperatures (207, 881) product composition was determined in area-% as measured for the intensities of the GC peaks (total ion current). The content of the solvent (toluene) is subtracted and discarded.

Gaseous products like ammonia and hydrogen cyanide were detected in all pyrolyses. Ammonia was identified with Nessler's reagent, and HCN as AgCN. No quantitative analyses were attempted.

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[§] Part 2, see ref.[1]

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