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Application of Flash Vacuum Pyrolysis to the Synthesis of Sulfur-containing Heteroaromatic Systems

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Abstract: The FVP method of ethynyl and chlorovinyl materials is applied to the ready formation of sulfur-containing fused heteroaromatic systems. The pyrolysis of the chlorovinyl materials is assumed to involve a mechanism different from that of the ethynyl materials. © 1999 Elsevier Science Ltd. All rights reserved.

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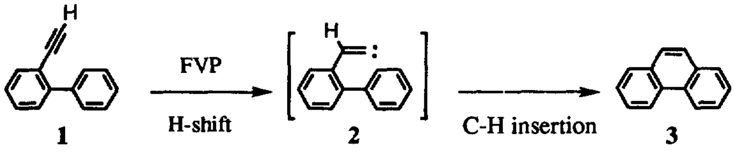
In 1974, Brown and coworkers reported an important flash vacuum pyrolysis of biphenyl-2-ylacetylene **1** that generated the vinylcarbene **2**, subsequently leading to the formation of phenanthrene **3** (Scheme 1).[1] The great synthetic potential of this reaction was first demonstrated by Scott et al. in the elegant synthesis of corannulene.[2] Since then, a variety of unique related compounds have been prepared by this FVP method.[3] The application of the method, however, has been limited mostly to polycyclic aromatic hydrocarbon systems.[4] Sulfur-containing fused heteroaromatic systems have attracted current attention as advanced materials, such as organic conductors[5] and FET,[6] so the development of their ready synthesis becomes increasingly important. We now would like to report an application of the FVP method to the synthesis of such sulfur-containing heteroaromatic systems.



Scheme 1

First of all, we studied simple pyrolyses of the mono-ethynyl derivatives of phenylthiophenes, which are summarized in Table 1.[7] The FVP reactions of the derivatives **4a**, **6a**, and **8a** with an ethynyl group on the thiophene part smoothly occurred under the conditions of 1000 °C and 0.1 Torr to give the corresponding naphthothiophenes **5**, **7**, and **9** in 76-86 % yields (Runs 1, 3, and 5).[8] Alternative pyrolysis of the chlorovinyl derivatives **4b**, **6b**, and **8b** as the ethynyl precursors also gave the respective compounds in high yields (Runs 2, 4, and 6). However, this was not the case with the pyrolysis of the compound **10a** with an ethynyl group on the benzene part, which gave the expected product **9** in only 14-18% yield, and instead acenaphthylene **11** was

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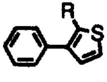
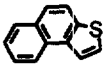
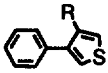
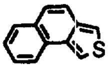
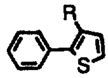
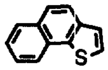
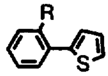
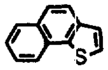
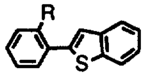
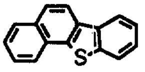
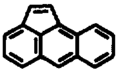
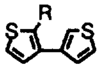
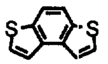
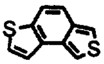
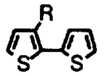
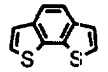
Table 1. Flash vacuum pyrolyses of mono-ethynyl and chlorovinyl-substituted phenylthiophenes and bithiophenes[a]

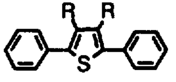
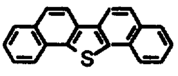
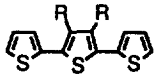
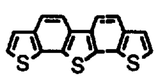
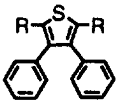
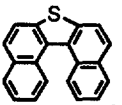
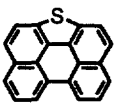
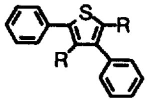
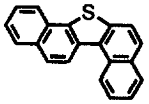
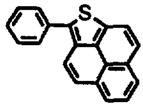
Run	Material	Product (yield)	
			
1	**4a** R: $C\equiv CH$	**5** (76%)	
2	**4b** R: $CCl{=}CH_2$	(73%)	
			
3	**6a** R: $C\equiv CH$	**7** (85%)	
4	**6b** R: $CCl{=}CH_2$	(84%)	
			
5	**8a** R: $C\equiv CH$	**9** (86%)	
6	**8b** R: $CCl{=}CH_2$	(73%)	
			
7	**10a** R: $C\equiv CH$	**9** (18%, 14%[b])	**11** (41%, 25%[b])
8	**10b** R: $CCl{=}CH_2$	(64%, 81%[b])	(10%, 2%[b])
			
9	**12a** R: $C\equiv CH$	**13** (9%[b])	**14** (24%[b])
10	**12b** R: $CCl{=}CH_2$	(92%[b])	(not formed)
			
11	**15a** R: $C\equiv CH$	**16** (98%)	**17** (not formed)
12	**15b** R: $CCl{=}CH_2$	(87%)	
			
13	**18a** R: $C\equiv CH$	**19** (63%)	
14	**18b** R: $CCl{=}CH_2$	(69%)	

[a] Optimum pyrolysis was carried out at 1000 °C under 0.1 Torr, unless otherwise stated.
[b] Pyrolytic conditions: 800 °C, 0.1 Torr.

obtained in 25-41% yield (Run 7). In contrast, pyrolysis of the chlorovinyl compound **10b** formed the desired **9** in 64-81% yield together with a small amount of **11** (2-10%) (Run 8). Similar different results were also observed for the pyrolyses of the benzothiophene derivatives **12a** and **12b** (Runs 9 and 10). These results suggest involvement of different reaction paths for the pyrolyses of the two kinds of materials (*vide infra*). Pyrolysis of the bithiophene derivatives **15** and **18**, irrespective of the material used, successfully occurred to produce the expected benzodithiophenes **16** and **19**, respectively, in high yields (Runs 11-14). In the reaction of **15**, there is a possibility of forming another structural isomer **17**, which was, however, not detected at all. This is ascribable to thermodynamical instability of **17** as compared to **16**.

The pyrolysis of the bis-functional systems offers a ready access to complicated polycyclic sulfur-containing aromatics that are less accessible by conventional methods. In this case, the optimum conditions require a higher vacuum 0.01 Torr because of the lower volatility of the pyrolyzed materials. Unlike the above mono-functional case, use of bis-chlorovinyl materials is more advantageous than that of bis-ethynyl materials, as shown in Table 2. The pyrolysis of **24a** and **24b** afforded not only the desired compound **25** but also the additionally fused compound **26**. A separate pyrolytic experiment of **25** confirmed that **26** was derived from **25**. The pyrolysate of **27a** and **27b** comprised a mixture of two cyclization products **28** and **29**, of which the relative product ratios were appreciably different depending on the materials used.

Table 2. Flash vacuum pyrolyses of bis-ethynyl and chlorovinyl-substituted materials[a]

Run	Material	Product (yield)	
			
1	**20a** R: $C\equiv CH$	**21** (63%)	
2	**20b** R: $CCl=CH_2$	(89%)	
			
3	**22a** R: $C\equiv CH$	**23** (trace)	
4	**22b** R: $CCl=CH_2$	(52%)	
			
5	**24a** R: $C\equiv CH$	**25** (50%[b])	**26** (11%[b])
6	**24b** R: $CCl=CH_2$	(33%, 68%[b])	(47%, 7%[b])
			
7	**27a** R: $C\equiv CH$	**28** (7%)	**29** (6%)
8	**27b** R: $CCl=CH_2$	(43%)	(9%)

[a] Optimum pyrolysis was carried out at 1000 °C under 0.01 Torr, unless otherwise stated.

[b] Pyrolytic conditions: 800°C, 0.01 Torr.

It has been generally accepted that pyrolysis of the chlorovinyl substance proceeds through the same path as that of the ethynyl substance, except that the former initially undergoes an elimination reaction to the latter. However, the different pyrolytic behaviors of both kinds of materials of **10** and **12** call for consideration of different reaction mechanisms. Scheme 2 illustrates a speculative mechanism for the pyrolytic reactions of **10a** and **10b**, which is considered on the basis of a calculation of the thermodynamic energies of the possible intermediates using MOPAC PM3.[9] Pyrolysis of **10a** first generates the vinyl carbene species **30**, then leading to naphthothiophene **9** or competitively to acenaphthylene **11**.[10] On the other hand, pyrolysis of **10b** is speculated to have dual reaction paths: one is simple HCl elimination from **10b** to **10a**, then following the same reaction path. The other possibly starts with Cl• elimination from **10b**, and the resultant radical species **35** attacks the β-site of the thiophene moiety to give **37**, which then rearranges to **9**.

In summary, the FVP method has turned out to be very effective for the ready formation of the fused sulfur-containing heteroaromatic systems. In addition, it has been revealed that the pyrolytic mechanisms of the ethynyl and chlorovinyl materials are not necessarily the same, which is contrary to the conventionally accepted understanding.

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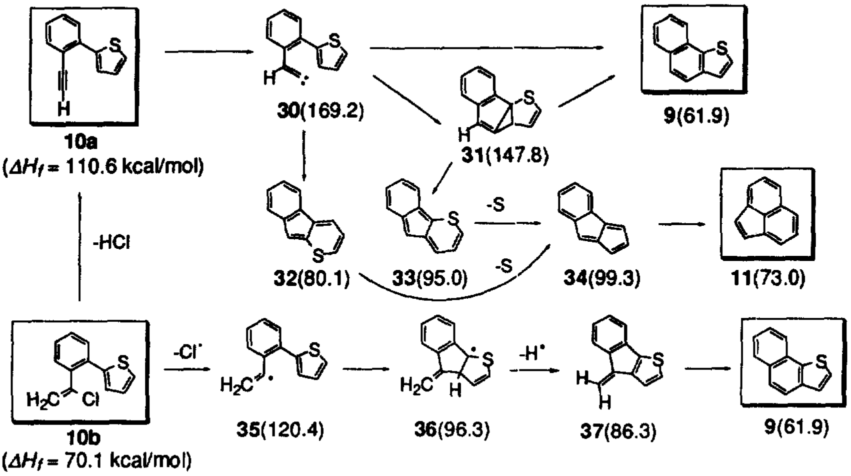

Scheme 2. A speculative mechanism for the pyrolyses of **10a** and **10b**. Values in parentheses indicate the calculated heat of formation.

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[7] All the ethynyl materials for pyrolysis were prepared by Sonogashira coupling reactions of the corresponding bromo aromatics with trimethylsilylacetylene followed by alkaline detrimethylsilylation. The chlorovinyl materials were obtained by hydrochlorination of the trimethylsilylethynyl intermediates: Scott, L.T.; Necula, A. *Tetrahedron Lett.* **1997**, *38*, 1877-1880.

[8] All the pyrolytic products were isolated and characterized by their spectroscopic analyses. The yields do not take into account recovery of the precursors. A typical pyrolytic experiment is as follows: the pyrolysis apparatus consists of a quartz tube, 45 cm in length and 28 mm in diameter, equipped with a nitrogen flow valve at one end and with a trap cooled in a liquid nitrogen Dewer flask at the other end, which is further connected with a vacuum pump. The tube was set in an electric furnace with a length of 35 cm in such a way that the middle part of the tube can be heated. 2-Ethynyl-3-phenylthiophene (**4a**) (25 mg, 0.14 mmol) was placed at the first end of the tube and gradually sublimed at 40 °C under 0.1 Torr under a slow nitrogen stream to fly across the hot zone, which was heated at 1000 °C. The pyrolysis was completed in 3 h, and the pyrolysate collected in the cold trap was taken up with dichloromethane and purified by column chromatography on silica gel with dichloromethane followed by recrystallization from methanol to give colorless plates of naphtho[2,1-*b*]thiophene (**5**) with mp 114-115 °C (19 mg, 76% yield).

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