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Pyrolysis and Photolysis Processes of Pyran and Thiopyran Derivatives

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Summary. Pyrolysis and photolysis of 2-amino-3,5-dicyano-6-phenyl-4*H*-pyran (**1**) afford HNCO, acrylonitrile, cinnamonitrile, and 2-hydroxy-3,5-dicyano-6-phenylpyridine. Pyrolysis of 2-carboxyimino-3,5-dicyano-6-phenyl-4*H*-pyran (**2**) gives HCN, acrylonitrile, cinnamonitrile and 2-hydroxy-3,5-dicyano-6-phenylpyridine. Furthermore, both pyrolysis and photolysis of 2,6-diamino-3,5-dicyanothiopyran (**3a**) gives rise to HNCS, acrylonitrile and 6-amino-3,5-dicyano-6-mercaptopyridin. Moreover, comparative studies of pyrolysis and photolysis of 2,6-dicyano-4-arylthiopyran derivatives **3b–d** revealed similar results. The similarity of products obtained from pyrolysis and photolysis and the mechanistic implications of these data are discussed.

Keywords. Pyran; Thiopyran; Pyrolysis; Photolysis.

Pyrolyse- und Photolyseprozesse von Pyran- und Thiopyranderivaten

Zusammenfassung. Pyrolyse und Photolyse von 2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran (**1**) ergeben HNCO, Acrylnitril, Zimtsäurenitril und 2-Hydroxy-3,5-dicyano-6-phenyl pyridin. Durch Pyrolyse von 2-Carboximino-3,5-dicyano-6-phenyl-4*H*-pyran (**2**) entstehen HCN, Acrylnitril, Zimtsäurenitril und 2-Hydroxy-3,5-dicyano-6-phenylpyridin. Weiters resultieren sowohl Photolyse als auch Pyrolyse von 2,6-Diamino-3,5-dicyanithiopyran (**3a**) in der Bildung von HNCS, Acrylnitril und 6-Amino-3,5-dicyano-6-mercaptopyridin. Vergleichende Untersuchungen zur Pyrolyse und Photolyse von 2,6-Dicyano-4-arylthiopyranderivaten (**3b-d**) lieferten vergleichbare Ergebnisse. Die Ähnlichkeit der Resultate von Pyrolyse und Photolyse sowie die sich daraus ergebenden mechanistischen Implikationen werden diskutiert.

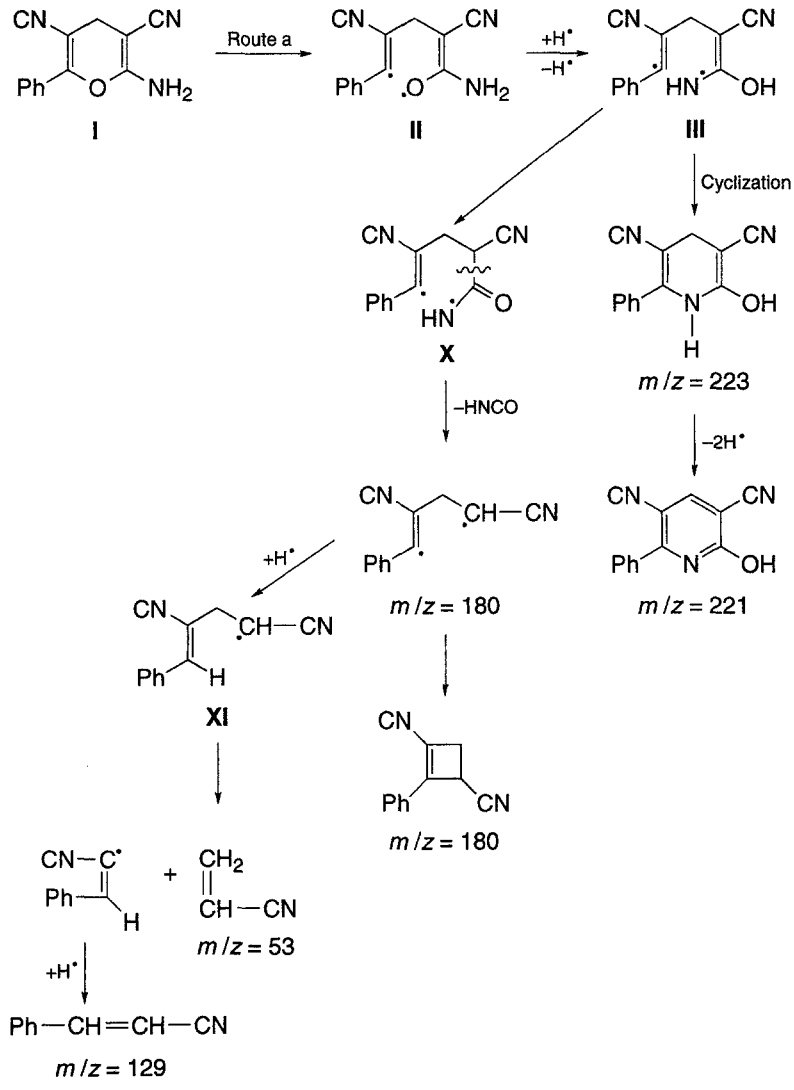
Introduction

Literature contains a number of reports describing pyrolysis of nonaromatic pyran and thiopyran derivatives [1,2]. Thus, heating 2*H*-thiopyran at 240–260 °C affords thiophene [3], photolysis of 4,4-diphenyl-4*H*-pyran in *tert*-butyl alcohol gives rise to a mixture of aldehydes [4,5].

Results and Discussion

Pyrolysis and photolysis of 2-amino-3,5-dicyano-6-phenyl-4*H*-pyran (**1**) give rise to HNCO, acrylonitrile, cinnamonitrile, and 2-hydroxy-3,5-dicyano-6-phenylpyridine

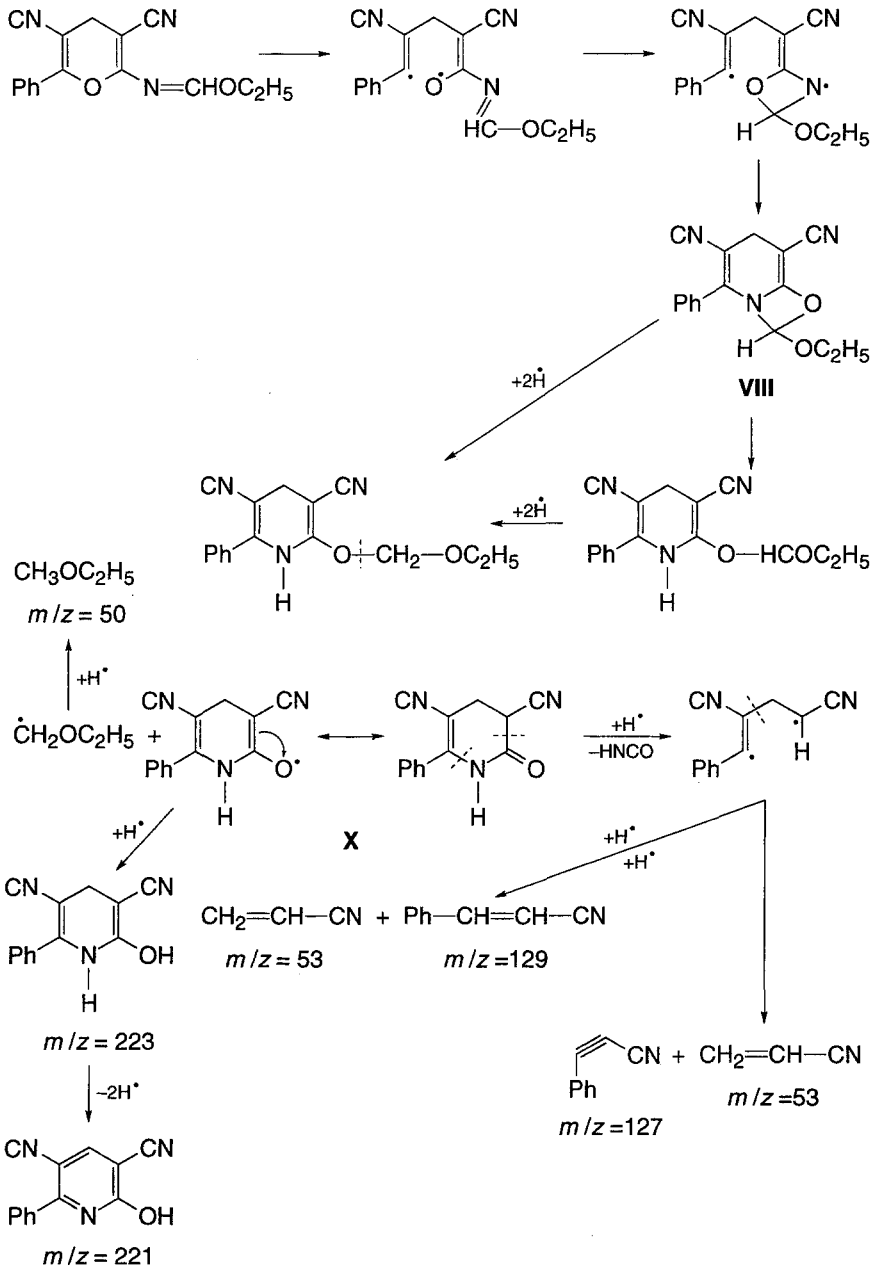
as shown in Scheme 1.



Scheme 1

The process may imply homolysis of the -O-C- bond (Scheme 1, Route a) to give biradical **II** which ultimately isomerizes [6] to biradical **III** [7] which in turn may undergo cyclization to afford 1,4-dihydropyridine ($m/z = 223$), ultimately suffering aromatization to the characterized product 2-hydroxy-3,5-dicyano-6-phenylpyrid ine ($m/z = 221$). Photoisomerization of some 2,4,4,6-tetrasubstituted 4*H*-thiopyrans to isomeric 2*H*-thiopyrans in almost quantitative yield has been reported [8], and the majority of phototranspositions are best rationalized by a sequence of C-S and CO bond fission into biradical intermediates as in the photolysis of furans and thiophenes [9,10].

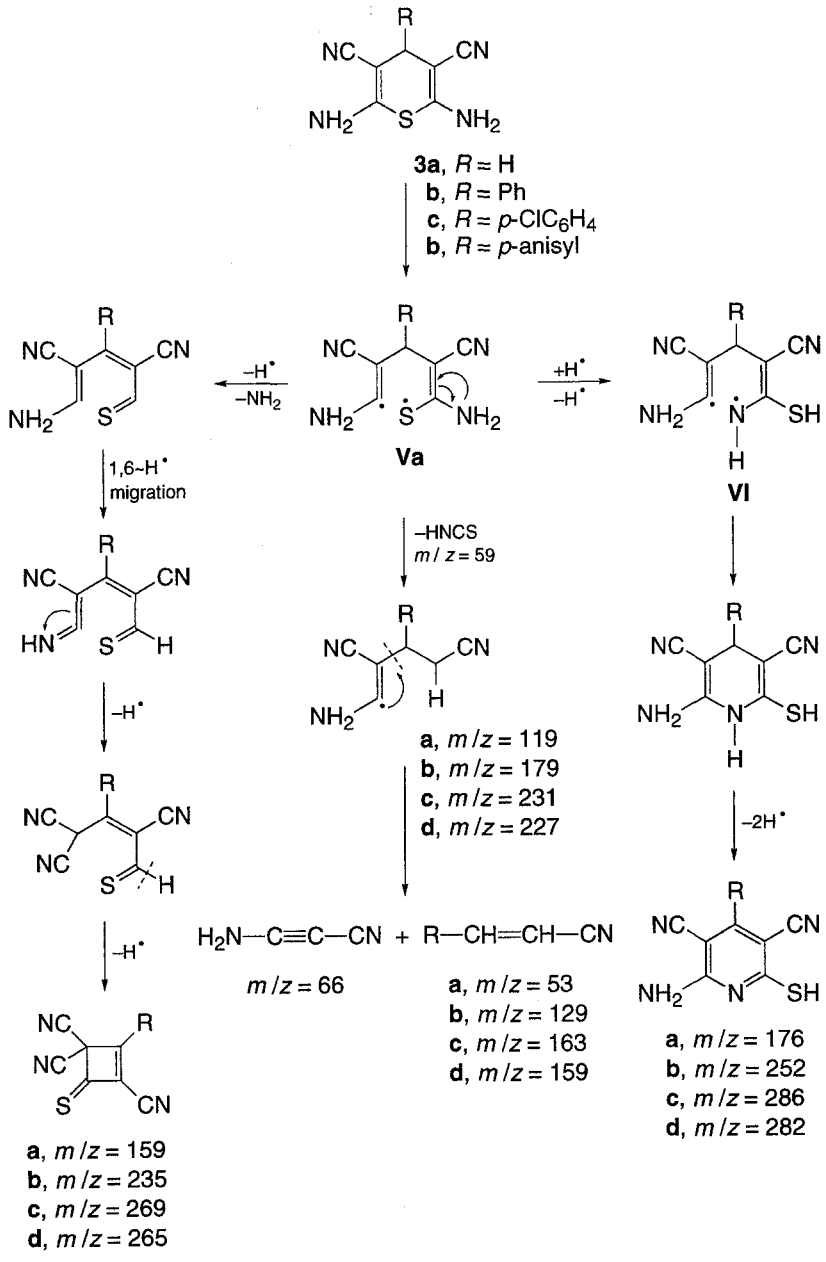
Biradical **III** may isomerize to species **X** which loses HNCO and undergoes hydrogen abstraction to afford radical **XI** which is the precursor for both identified



Scheme 2

products, acrylonitrile ($m/z = 53$) and cinnamonitrile ($m/z = 129$). Furthermore, formation of 2-hydroxy-3,5-dicyano-6-phenylpyridine may be attributed to the rearrangement of the aromatic heterocycles which involves the interchange of two hetero atoms, which are singly bonded to a common ring carbon atom [10–13].

Pyrolysis and photolysis of 2-carboxyimino-3,5-dicyano-6-phenyl-4*H*-pyran (**2**) gives acrylonitrile ($m/z = 53$), cinnamonitrile ($m/z = 129$), and 1,2-dihydro-2-hydroxy-3,5-dicyano-6-phenylpyridine ($m/z = 223$) as shown in Scheme 2.



Scheme 3

Compound **2** may undergo O-C bond fission followed by several steps involving a rearrangement [9–12] to give species **VIII** which suffers N-C bond homolysis according to the bond energy values [14], followed by hydrogen abstraction to afford the ether derivative **IX**. Moreover, **IX** ultimately may decompose to the pyridone radical **X** [14] which is the precursor of acrylonitrile and cinnamonitrile as shown in Scheme 2.

Pyrolysis and photolysis of 2,6-diamino-3,5-dicyanothiopyran (**3a**) afford acrylonitrile ($m/z = 53$) and 2-amino-3,5-dicyanopyridinethione ($m/z = 176$). The process

suggests homolysis of the C-S bond [15] to afford biradical **V** which isomerizes to biradical **VI**, suffers dehydrogenative cyclization to 2-amino-3,5- dicyano-6-mercaptopyridine ($m/z = 176$), whereas biradical **V** loses HNCS to afford acrylonitrile ($m/z = 53$) and aminocyano-acetylene ($m/z = 66$) which has not been identified (cf. Scheme 3 and Tables 1 and 2).

Experimental

Melting points were measured with a Gallenkamp apparatus and are uncorrected. HNCS was detected by acidified ferric nitrate solution [13]. TLC was carried out on glass plates covered with silica gel (20–40 mesh), eluting with ethylacetate-benzene (2:8 v/v).

Gas liquid chromatography was carried out on Perkin-Elmer Sigma 3B instrument. Columns used were 4 ft × 4 mm, packed with 30% SE 30 on Chromosorb W (35–80 mesh) or 10% SE on Celite (60–80 mesh); nitrogen was used as carrier gas. Molecular weights were determined by a mass spectrophotometer model A.E.I.M.S. 902.

Starting materials

2-Amino-3,5-dicyano-6-phenyl-4*H*-pyran (**1**): m.p.: 205 °C (Ref. [17]: m.p.: 205 °C); 2-carboxyimino-3,5-dicyano-6-phenyl-4*H*-pyran (**2**): m.p.: 135 °C (Ref. [17]: m.p.: 135 °C); 2,6-diamino-3,5dicyano-thiopyran (**3a**): m.p.: 215 °C Ref. [17]: m.p.: 215 °C); 2,6-diamino-3,5-dicyano-4-phenylthiopyran (**3b**): m.p.: 184 °C (Ref. [18]: m.p.: 184 °C); 2,6-diamino-3,5-dicyano-4-p-chlorophenyl-thiopyran (**3c**): m.p.: 250–252 °C (Ref. [18]: m.p.: 250–252 °C); 2,6-diamino-3-5-dicyano-4-p-methoxyphenylthiopyran (**3d**) m.p.: 300 °C (Ref. [18]: m.p.: 300 °C).

Table 1.

	Photolysis			**Pyrolysis**		
	1	**2**	**3a**	**1**	**1**	**3a**
HNCS	–	–	Evolve	–	–	evolved
Acrylonitrile[a]	0.03 (10)	0.015 (5)	0.03 (10)	traces	traces	traces
HNCO	evolved	evolved	–	evolved	–	–
Cinnamonitrile[b]	0.03 (10)	0.05 (16.6)	–	0.1 (2)	0.07 (1.4)	–
2-Hydroxy-3,5-dicyano-6-phenylpyridine[c]	0.18 (60)	0.19 (63.3)	–	1.9 (38.1)	1.5 (30)	–
2-Amino-3,5-dicyano-6-mercaptopyridine[d]	–	–	0.20 (66.6)	–	–	2.4 (48)
Residue	0.03 (10)	0.03 (10)	0.01 (3.3)	0.9 (18)	1.5 (30)	0.2 (4)

Pyrolysis and photolysis products of pyran and thiopyran derivatives **1**–**3a**; amounts are given in g (%); [a]b.p.: 77 °C, D_n^{20} 1.3910, identified by ^{1}H NMR and IR, consistent with authentic samples (Ref. [19]); [b]m.p.: 18–20 °C, b.p.: 254–255 °C, D_n^{20} 1.6010, identified by ^{1}H NMR and IR, consistent with authentic samples (Ref. [20]).

Table 2.

	Photolysis			Pyrolysis		
	3b	**3c**	**3d**	**3b**	**3c**	**3d**
HNCS	evolved	evolved	evolved	evolved	evolved	evolved
Cinnamonitrile[a]	0.06 (20)	–	–	0.2 (4)	–	–
p-Chlorocinnamonitrile[b]	–	0.08 (26.6)	–	–	1.8 (36)	–
p-Methoxycinnamonitrile	–	–	0.126 (42)	–	–	1.5 (30)
2-Amino-3,5-dicyano-4-phenyl-6-mercaptopyridine[d]	0.12 (40)	–	–	2.5 (60)	–	–
2-Amino-2,5-dicyano-4-*p*-chlorophenyl-4-mercaptopyridine[e]	–	0.12 (40)	–	–	2.4 (48)	–
2-Amino-3,5-dicyano-4-*p*-methoxyphenyl-6-mercaptopyridine[f]	–	–	0.15 (50)	–	–	2.6 (52)
Residue	0.03 (10)	0.03 (10)	0.02 (6.6)	1.0 (20)	0.6 (12)	0.75 (15)

Pyrolysis and photolysis products of 4-arylthiopyran derivatives **3b–d**; amounts are given in g (%); [a]m.p.: 20–21 °C, b.p.: 134 °C/12 mm, D_n^{20} 1.6010, identified by IR, coincident with authentic samples (Ref. [20]); [b]m.p.: 45 °C, crystallized from pet. ether, identified by IR, coincident with authentic samples (Ref. [21]); [c]m.p.: 64 °C, crystallized from ethanol [22], identified by IR and ^{1} HNMR, coincident with authentic samples (Ref. [22]); [d]m.p.: 180 °C, IR: 3400-3300 cm^{-1} NH_2 3300–3200 cm^{-1} (NH), 2200 cm^{-1} (CN), ^{1}H NMR: $\delta = 6.5$ (s, 2H, NH_2), 7.2–7.8 (m, 5H, Ar-H), 11.0 (s, 1H, NH) ppm, calcd. for $C_{13}H_8N_4S$: C, 61.9, H, 3.2, N, 22.2, S, 12.7, found: C, 62.0, H, 3.4, N, 22.2, S, 12.9; [e]m.p.: 125 °C, IR: 3420-3300 cm^{-1} (NH_2), 3300-3250 cm^{-1} (NH), 2220 cm^{-1} (CN), ^{1}H NMR: $\delta = 7.0$ (s, 2H, NH_2), 7.1–7.6 (m, 4H, Ar-H), 11.5 (s, 1H, NH) ppm, calcd. for $C_{13}H_7N_4SCl$: C, 54.5, H, 2.4, N, 19.6, S, 11.2, found: C, 54.7, H, 2.6, N, 19.6, S, 11.4; [f]m.p.: 112 °C, IR: 3400-3330 cm^{-1} (NH_2), 3330-3200 cm^{-1} (NH), 2210 cm^{-1} (CN), ^{1}H NMR: $\delta = 3.4$ (s, 3H, OCH_3), 6.9 (s, 2H NH_2), 7.0–7.5 (m, 4H, Ar-H), 10.7 (s, 1H, NH), calcd. for $C_{14}H_{10}N_4OS$: C, 59.6, H, 3.5, N, 19.9, S, 11.3, found: C, 59.8, H, 3.4, N, 20.0, S, 22.5.

*Pyrolysis of pyran and thiopyran derivatives (***1, 2, 3a–d***); general procedure*

5 g of pyran or thiopyran derivatives were pyrolyzed in a sealed tube in a nitrogen atmosphere at 180–200 °C for 3 h. The gases evolved were detected by standard chemical means.

The pyrolysate was subjected to vacuum distillation, and the remaining oil was separated into its constituents by means of column chromatography over silica gel using a gradient elution technique.

The separated products were identified by their physical constants, TLC, GLC, IR and MS as compared with authentic samples. The results are listed in Tables 1–4 cf. Schemes 1–3).

*Photolysis of pyran and thiopyran derivatives (***1,2, 3a–d***); general procedure*

A solution of pyran or thiopyran derivatives **1–3** (300 mg) in methanol (400 ml) was irradiated with a Hanovia high-pressure quartz mercury-vapor lamp (700 W) which had been lowered into a water-

cooled quartz immersion well. Purified dry nitrogen was passed through the solution for 0.5 h prior to irradiation, and a low stream of nitrogen was continued during photolysis. After 5 h the solvent was removed by distillation *in vacuo* below 30 °C, leaving a dark yellow mixture of solid and liquid. The residual solid was chromatographed on a silica gel column ethylacetate-benzene 1:9. The results are given in Table 1.

Synthesis of 2-mercaptopyridine derivatives

A solution of compounds **3a–d** (0.01 mol in ethanol) was treated with a little amount of triethylamine and refluxed for 5 h. The solid product formed was collected by filtration and recrystallized from the proper solvent.

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