

THERMAL DECOMPOSITION OF 2H-[1,2,4]OXADIAZOLO[2,3-a]PYRIDINE-2-THIONE AND 2H-[1,2,4]OXADIAZOLO[2,3-b]PYRIDAZINE-2-THIONE

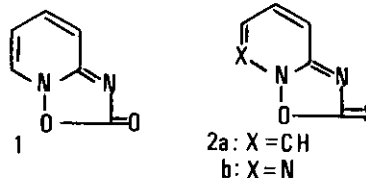
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Abstract--Pyrolysis of 2H-[1,2,4]oxadiazolo[2,3-a]pyridine-2-thione gave 3-(2-pyridyl)-2H-pyrido[1,2-a]-s-triazine-2,4(3H)-dione. 2-Isocyanatopyridine which is considered to be the intermediate in the reaction was utilized to the synthesis of N,N'-substituted ureas. Similar investigation was carried out on 2H-[1,2,4]oxadiazolo[2,3-b]pyridazine-2-thione.

Although the character of 2H-[1,2,4]oxadiazolo[2,3-a]pyridin-2-one (1) under pyrolysis has been reported in earlier paper¹ and the synthesis of its 2-thione analogue, *i.e.*, 2H-[1,2,4]oxadiazolo[2,3-a]pyridine-2-thione (2a) was reported recently,² the detailed study on the behavior of the latter compound under the pyrolytic conditions has not been performed.

In this connection, Taurins *et al.*² described the explosive character of 2a upon heating but the products formed during the explosion were not revealed.



We wish to show the results of the thermal decomposition of 2a and b, and also, wish to suggest the reaction mechanism and to describe the synthetic utilization of the reaction in this paper.

When solid 2a was heated under reduced pressure (0.1 mmHg), the explosive decomposition took place at ca. 140°C and sublimation of products was observed. The products were collected and separated into hexane-soluble and hexane-insoluble parts. The former consisted of elemental sulfur (yield 80%). The latter was further separated into benzene-soluble and -insoluble parts. The soluble part consisted of N,N'-(2,2-dipyridyl)urea (3a, yield 5%). The last product was very insoluble in various solvents although it could be recrystallized from CHCl₃-DMSO (9:1) without change of the constitution to give white needles (yield 80%).

The compound was identical with 3-(2-pyridyl)-2H-pyrido[1,2-a]-s-triazine-2,4(3H)-dione (4a) which had been reported by Gizycki *et al.*³

No other characteristic compounds were detected from the mixture of the

products (by TLC and NMR spectrum of the mixture).

Similar decomposition proceeded under the conditions in which decaline, DMSO,⁴ or *p*-xylene-PPh₃ coexisted. It was found that the behaviour of 2 towards pyrolysis was quite different from that of 1.^{1,5} The results are shown in Table I.

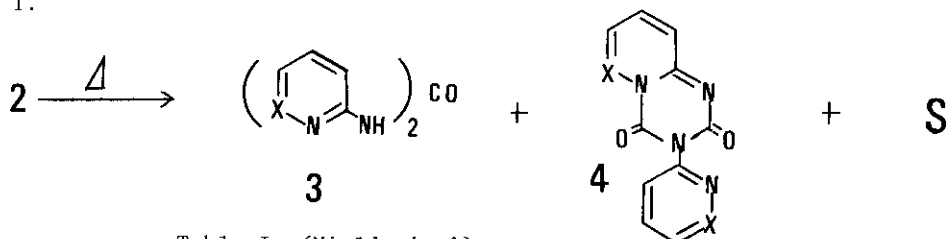


Table I. (Yields in %)

2	Conditions	3	4	sulfur
2a	without solvent, 0.1 mmHg, 140°C	5 (3a, mp 174°C ^a)	80 (4a, mp 242°C ^b)	80
	in DMSO, 80°C for 1hr	21	68	80
	in decalin(suspension), 80°C for 2hr	14	82	95
	with PPh ₃ , in xylene, 80°C for 1hr	5	85	90(Ph ₃ P-S)
2b	in DMSO, 80°C for 1hr	20 (3b, mp 298°C dec.)	78 (4b, mp 254°C dec.)	85
	in PhH(suspension), reflux for 1hr	trace	80	91

a) Lit. mp 175°C, R.Camps, *Arch.Pharm.*, 240,351(1902).

b) Lit. mp 245°C, see footnote 3.

These results readily led us to a conclusion that aza-heteroaromatic Δ -isocyanates (5a and b) might be present as the intermediates of 4 although the attempts to detect 5a and b have been unsuccessful.⁶ It has been reported that ordinary aza-heteroaromatic Δ -isocyanates readily undergo the cyclo-dimerization and are too unstable to be isolated.³ It is also acceptable that 3 was formed from 5 by the action of moisture.

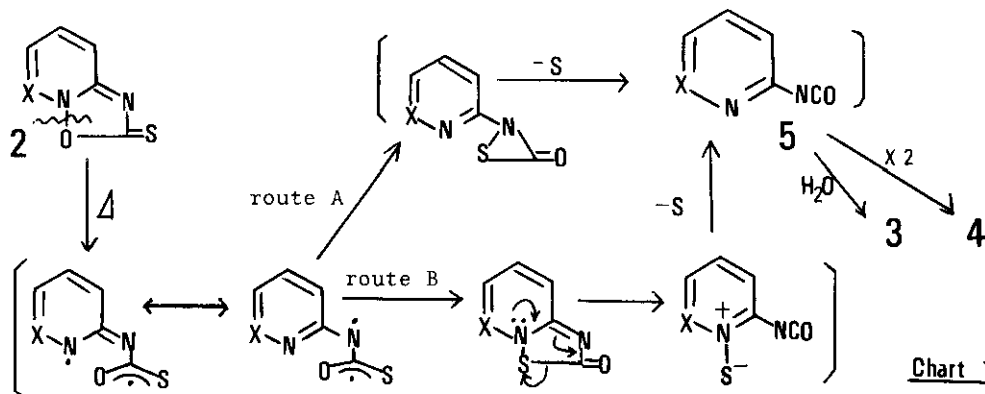


Chart 1

Thus, the routes A and B shown in Chart 1 would be worth due consideration as for the mechanism of the formation of the products, although to distinguish the plausible route is rather difficult.

Further, the aza-heteroaromatic α -isocyanates (5) generated in the reaction were employed for the synthesis of N,N'-substituted ureas as shown in Table II.

Compounds 2 were heated with amines at 80-90°C (principally in PhH or DMSO) for 1-2 hr.

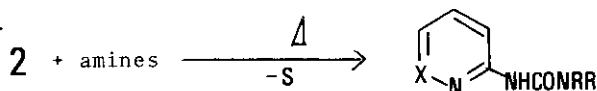

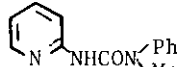
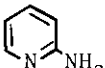

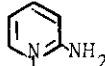


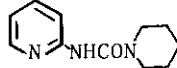
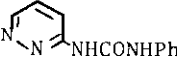
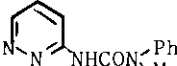
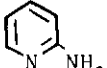

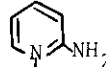

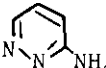


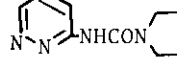


Table II.

2	Amines	Ureas (mp °C)	Yields (%)
2a	PhNH ₂	 (184 [*])	83
	PhNHMe	 (79)	87
		 (174)	92
		 (219)	41
		 (85)	40
2b	PhNH ₂	 (240)	41
	PhNHMe	 (96)	54
		 (263)	69
		 (230 dec.)	20
		 (298 dec.)	82
	 (104)	59	

* Lit. mp 180°C, D.G.Crosby and C.Niemann, *J.Amer.Chem.Soc.*, 76,4458(1954)

Some of those ureas are difficult to obtain by the alternative route, *i.e.*, the reaction between amines and isocyanates, because the described heteroaromatic α -isocyanates are unavailable by means of their instability as mentioned before.

Thus, **2** is usable as the precursor of those isocyanates in the synthesis of unsymmetrically substituted ureas.

FOOTNOTES

- 1) R. F. C. Brown and R. J. Smith, Aust. J. Chem., 25, 607 (1972).
- 2) D. Rousseau and A. Taurins, Can. J. Chem., 55, 3736 (1977).
- 3) U. v. Gizycki and G. Oertel, Angew. Chem., 80, 363 (1968).
- 4) Although Taurins *et al.*² directed the recrystallization of **2a** from DMSO, it quickly decomposed at elevated temperature in DMSO.
- 5) A. R. Katritzky, J. Chem. Soc., 2063 (1956).
- 6) An emulsion of **2a** with Nujor was heated at ca. 200°C in a KBr cell, and the immediate measurement of the infrared spectrum did not show -N=C=O stretching while the complete decomposition of **2a** into **4a** was observed.

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