HETEROCYCLES, Vol 12, No 7, 1979

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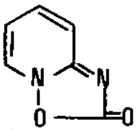
Abstract--Pyrolysis of 2H-[1,2,4]oxadiazolo[2,3-a]pyridine-2-thione gave 3-(2-pyridyl)-2H-pyrido[1,2-a]-s-triazine-2,4(3H)-dione. 2-Isocyanatopyridine which is considered to be the intermediate in the reaction was utilized to the synthesis of N,N'-substituted ureas. Similar investigation was carried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



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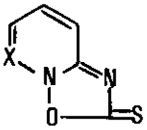


2a: X = CH
b: X = N

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 $CHCl_3$-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-PPh_3 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.

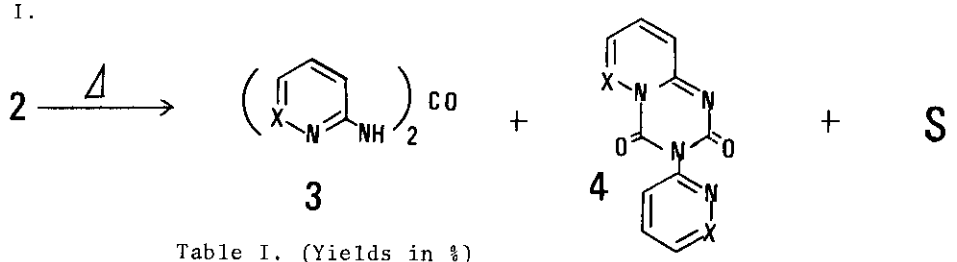


Table I. (Yields in %)

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_3P-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 α-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 have been reported that ordinary aza-heteroaromatic α-isocyanates readily undergo the cyclodimerization and are too unstable to be isolated.[3] It is also acceptable that **3** was formed from **5** by the action of moisture.

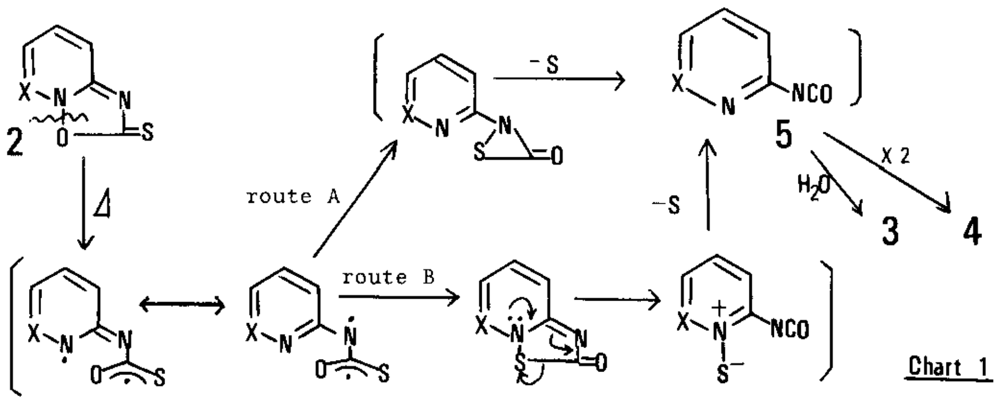


Chart 1

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.

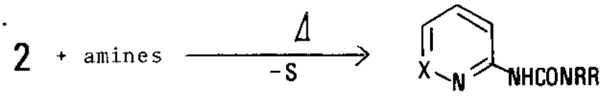
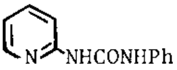
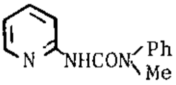
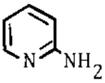
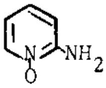
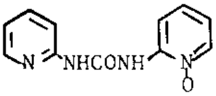
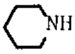
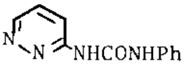
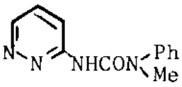
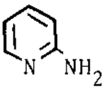
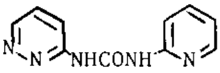
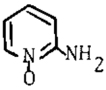
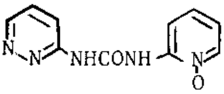
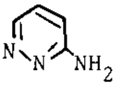
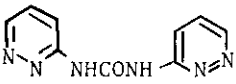
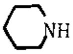


Table II.

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.

Received, 1st May, 1979