UNUSUAL THERMAL SOLID-PHASE REARRANGEMENT OF 2-ALLYLTHIO- AND 2-ALLYLSELENODIHYDROPYRIDINES

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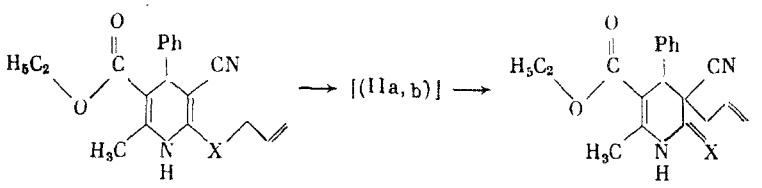
A previously unreported thermal solid-phase migration of the allyl group was found for 2-allylthio- and 2-allylselenodihydropyridines, leading to 3-allyl-3-cyano-3,4-dihydropyridine-2(1H)-thiones and -selenones. Analysis of the crystal structures did not indicate whether the solid-phase reaction, which is probably general in nature, is intra- or intermolecular.

A previously unreported solid-phase migration of the allyl group [1] occurs upon heating monocrystals of 2-allylthiohydropyridine (Ia) to give 3-allyl-3-cyano-3,4-dihydropyridine-2(1H)-thione (IIIa).



An x-ray diffraction structural analysis was carried out for (Ia) and (IIIa). However, the sample of (IIIa) was obtained not in the solid phase but rather upon heating an ethanolic solution of (Ia) since the monocrystal decomposes in the solid-phase conversion of (Ia) to (IIIa). The unit cell parameters were also determined for the intermediate phase (IIa)* obtained by heating a monocrystal of (Ia) at 64°C for 10-20 h.

The solid-phase conversion of (Ia) to (IIIa) was monitored by measuring the melting point (mp (Ia) 86-88°C, (IIIa) 178-180°C). The identical nature of the crystals of (IIIa) to the final product of heating monocrystals of (Ia) was demonstrated by IR and PMR spectroscopy in solution and the solid phase [2]. The results of the x-ray diffraction structural analysis are given in Table 1.

Going from (Ib) to (IIb) and then to (IIIb) proceeds so readily that crystals of (IIb), which are isostructural to the intermediate phase of thio analog (IIIa), separate out upon the crystallization of (Ib) from ethanolic solution.

Crystals of (IIIb) were obtained by heating a solution of (Ib) at 40°C. Such crystals may also be obtained by the slow crystallization of (Ib) from ethanol at 20°C. Molecules of (Ia) with boat conformation and (IIIa) with distorted boat conformation differ in the conformation of the heterocycle and orientation of the ethoxycarbonyl groups (Fig. 1).

Analysis of the crystal structures of (I) and (III) does not indicate whether the solid-phase transformation of (I) to (III), which is apparently general in nature, is intra-

*The crystal structure of (IIa) has not yet been determined due to crystal imperfection.

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TABLE 1. X-Ray Diffraction Analysis Data

Compound	a	b	c	β, deg	V, Å³	Z	Space group	R	Number of reflections
	Å								
(Ia)	17,071(4)	7,277(2)	29,065(6)	104,96(2)	3488(2)	8	$C2/c$	0,059	2201
(IIa)	17,255(7)	7,328(3)	30,085(9)	108,66(3)	3604(2)	8	–	–	–
(IIIa)	11,797(1)	12,274(4)	13,068(3)	104,07(1)	1835(6)	4	$P2_1/c$	0,036	1707
(IIb)	17,167(3)	7,340(2)	30,40(7)	93,3(8) (angle α)	3806(2)	8	–	–	–
(IIIb)	11,777(3)	12,345(3)	13,194(5)	104,44(3)	1853(1)	4	$P2_1/c$	–	–

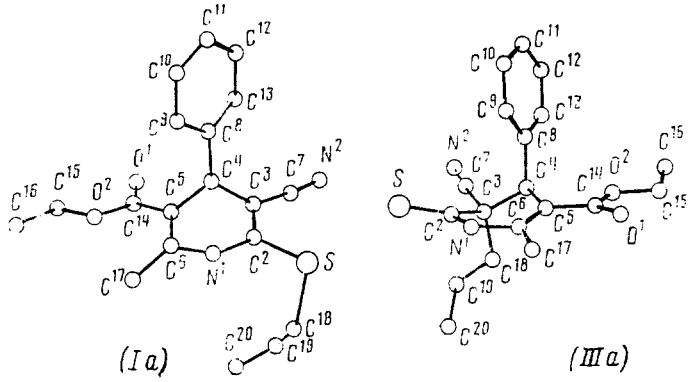

Fig. 1. Molecular structures of (Ia) and (IIIa)

or intermolecular. This question will be solved upon determination of the crystal structure of (IIa) or (IIb), which we propose to undertake in the near future.

LITERATURE CITED

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2. M. P. Goncharenko, V. K. Promonenkov, Yu. A. Sharanin, et al., Abstracts of the Conference on the Chemistry and Applications of Pyridine Pesticides [in Russian], Chernogolovka (1988), p. 124.