$\frac{1-(1-\text{Benzoylvinyl})-2-(1-\text{benzoylvinylthio})-4,5-\text{diphenylimidazole (Xa).} \text{ This was obtained in a similar manner to that for (IXa) from 0.12 g (0.5 mmole) 4,5-diphenylimidazol-2-thione (VIII) and 0.13 g (1 mmole) ketone (IIa) by boiling for 2-3 h. 0.15 g of the N,S-diadduct (Xa) was separated. IR spectrum (v, cm⁻¹): 1670 (C=0), 1640 (NC=C), 1596 (SC=C).$

CONCLUSIONS

1. By interacting benzimidazol-2-one with benzoyl- and thenoylacetylenes in acetonitrile in the presence of triethylamine, the N,N-diadducts are obtained. Under similar conditions 4,5-diphenylimidazol-2-one forms both the N-mono- and N,N-diadducts.

2. The sulfur analogs of the imidazolones react with a twofold excess of benzoylacetylene to form the N,S-diadducts.

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HETARYLADAMANTANES COMMUNICATION 4.*

SYNTHESIS, STRUCTURE, AND PROPERTIES OF 6-(1-

ADAMANTYL)-3-CYANOPYRIDINE-2(1H)-THIONE

V. P. Litvinov, E. É. Apënova,Yu. A. Sharanin, V. N. Nesterov,V. E. Shklover, and Yu. T. Struchkov

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Substituted 3-cyanopyridine-2(1H)-thiones have attracted the attention of investigators in view of their broad biological activity and the possibility of their use as intermediates in the synthesis of a wide range of condensed heterocyclic systems [2]. Adamantanes are also known to display biological activity [3].

In order to combine these entities into a single molecule, and to establish their influence on the structure and properties of the resulting hetaryladamantanes, we have developed a synthetic method for the novel 6-(1-adamantyl)-3-cyanopyridine-2(1H)-thiones (III), as follows:



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 145-153, January, 1986. Original article submitted August 2, 1984.

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Fig. 1. Structure of the molecule of (IV).

Reaction of 1-adamantyl methyl ketone (I) with ethyl formate in the presence of 1 equivalent of sodium and a catalytic amount of ethanol in ether at 15-20°C gives 82% of the sodium salt of 3-(1-adamantyl)-1-hydroxyprop-1-en-3-one (II), a labile compound which decomposes on standing in air. Successive treatment of the salt (II) in alcohol with acetic acid and cyanothioacetamide affords 62% of the yellow pyridinethione (III), which is stable in the crystalline state but unstable in solution, undergoing oxidation on slow crystallization to bis[6-(1-adamanty1)-3-cyanopyrid-2-y1] disulfide (IV).

The structures of the pyridinethione (III) and the disulfide (IV) were established by UV, IR, and PMR spectroscopy (see the Experimental section), and by mass spectrometry (see the following Communication). It was, however, not possible to establish the position of the adamantyl substituent in the pyridine ring (4 or 6) from these results. The molecular and crystal structure of the disulfide (IV) was therefore examined by x-ray structural analysis

The molecule of (IV) is composed of two 6-(1-adamanty1)-3-cyanopyridine groups linked by a disulfide bridge (Fig. 1). Table 1 shows the principal molecular parameters for the aromatic disulfides (IV)-(IX). The most important geometric property of these molecules, the torsion angle relative to the disulfide bond CSSC (δ), is 80.8(5)° in (IV), which approaches the lower limit of the range of angles δ (90 ± 10)° found in organic disulfides [4].

Organic disulfides may be divided into two groups, depending on their torsion angles CSSC (τ) [9]. The first group contains compounds in which the S-S bond is approximately coplanar with the ring ($\tau \simeq 0^{\circ}$). The second groups consists of compounds in which the S-S bond is approximately perpendicular to the ring ($\tau \simeq 90^{\circ}$). The values of the angles in (IV) [-31.3(5)° and 16.8(5)°] enable (IV) to be assigned to the first group, although they also indicate some twisting along the C-S bonds. The dihedral angle formed by the planes of the pyridine rings* is 91.3°.

The length of the S-S bond in (IV) [2.022(3) Å] is the same as that in diphenyl disulfide (VII) [2.023(1) Å], and is slightly greater than that in bis-2-pyridyl disulfide (V) [2.016(2) Å]. The S-S distance in most organic disulfides lies in the range 2.03 \pm 0.02 Å [10], although the length of the ordinary S-S σ bond is 2.10 Å [11]. The slight shortening of this bond is usually attributed to conjugation between the aromatic rings and the sulfur atoms [4] (if the angle τ is small). However, shortening of the S-S distance is also seen in organic disulfides in which the sulfur atoms are bonded to saturated carbon atoms, for instance in dibenzyl disulfide [2.015(3) Å] [12]. On the other hand, a relationship has been suggested between the length of the S-S bond and the torsion angle δ [11]. If the value of δ is close to 0°, repulsion between the unshared electron pairs (UEP) of the atoms is at a maximum, resulting in lengthening of the S-S bond. The conditions are most favorable for

^{*}Atoms N¹, C², C³, C⁴, C⁵, and C⁶ stand out from the plane passing through them (-0.773z-0.631y-0.064z + 6.083 = 0) by 0.03, 0.001, -0.005, 0.002, 0.004, and 0.006 Å, respectively. Atoms S¹, C⁷, C¹⁷, and N¹⁶ stand, out from this plane by -0.02, 0, 0.02, and 0.07 Å, respectively. Atoms N¹, C², C³, C⁴, C⁵, and C⁶ stand out from the plane passing through them (0.146x-0.041y-0.988z + 5.602 = 0) by 0.004, 0.005, -0.007, 0, 0.01 and -0.01 Å, respectively. Atoms S¹, C⁷, C¹⁷, and N¹⁶ stand out from this plane by 0.08, -0.03, -0.03, and -0.04 Å, respectively.

TABLE 1. Principal Geometric Parameters of the Molecules of Aromatic Disulfides (IV)-(IX)

Compound	S-S bond length, A	C—S bond length, A	CSS valence angle, deg	CSSC torsion angle ô, deg	CCSS torsion angle T, deg*	Lit. cita- tion
Bis{6-adamanty1-1)-3- cyanopyrid-2-y1] disulfide (IV)	2,022(3)	1,772(6), 1,787(6)	101,1(2), 105,3(2)	80,8(5)	-31,3(5), 16,8(5)	This communi- cation
Bis-2-pyridyl disulfide (V)	2,016(2)	1,785(2)	105,7(1)	87,1	7	[4]
Bis-2-pyrimidinyl disul- fide dihydrate (VI)	2,016(1)	1,781(2)	104,7(1)	82,5	4	[5]
Diphenyl disulfide (VII) 2,2'-Dicarboxydiphenyl disulfide (VIII)	2,023(1) 2,047(3)	1,788(3) 1,790(7)	105,9(1) 106,3(2)	~90 86,7	~0 15	[6] [7]
2,2'-Diaminodiphenyl di- sulfide (IX)	2,060(3)	1,76(1)	103,3(3)	90,5	~90	[8]

*For (IV), the NCSS angle is given.

 π interactions when δ approximates to 90°, since in such a case repulsion of the UEP of the sulfur atoms is at a minimum, which should result in shortening of the S-S bond. From the results given in Table 1, however, and from those reported in [9], there is no such relationship. The lengths of the C²-S¹ [1.772(6) Å] and C²'-S¹ [1.787(6) Å] bonds in (IV) are close to the values given in Table 1, and are somewhat shorter than the standard value for the C-S single bond [1.817(5) Å] [13].

Noteworthy are the short nonvalence contacts $S^1...N^1$ [3.111(5) Å] and $S^1'...N^1$ [3.023(5) Å] (the sum of the van der Waals radii of the S and N atoms is 3.35 Å [14]) and $C^{17}...S^1$ [3.040(8) Å] and $C^{17}...S^1$ [2.977(2) Å] the sum of the van der Waals radii of the C and S atoms is 3.50 Å [14]), contacts $S^1...N^1$ and $S^1'...N^1$ probably influencing the unfolding of the pyridine rings relative to the corresponding CSS planes. Similar nonvalence contacts are seen in (V). In accordance with the values of the nonvalence S...N contacts, the valence angle $C^2S^1S^1$, 101.1(2)°, is slightly less than the angle $C^2S^1S^1$, 105.3(2)°. These values for the valence angles are similar to the corresponding values observed in organic disulfides [4, 11].

The mean distances C-N [1.324(19) Å] and C-C [1.389(13) Å] in the heterocycles, C-C [1.496(12) Å] between the pyridine and adamantyl rings, C-C(N) [1.434(14) Å] and C=N [1.130(6) Å] are close to the literature values [1.340(5), 1.394(5), 1.510(5), 1.426(5) Å [13], 1.148(5) Å [15].

Examination of molecular packing in the crystal of (IV) (Fig. 2) shows that there are several intermolecular contacts between the cyanopyridine group attached to S¹ in the original molecule and the same grouping in the (IV) molecule derived from the initial transformation (2-x; y; 1-z), which are only slightly greater than twice the van der Waals radius of carbon, 3.40 Å [14]: C³...C³ 3.466(9) Å, C³...C¹⁷ 3.519(9) Å, C⁴...C¹⁷ 3.532(10) Å.

We have investigated the properties of the pyridinethione (III), and in particular we have found that it is readily alkylated by compounds of the type XCH_2R at the sulfur atom at $\sim 20^{\circ}C$, in alcohol in the presence of base, to give the substituted pyridines (Xa-f) in 41-78% yield. On treatment with an excess of alkali, (Xb-f) undergo Thorpe cyclization to give the thieno[2,3-b]pyridines (XIb-f). The latter are, however, more readily obtained without the intermediate isolation of the alkylated pyridinethiones (Xb-f) by treatment of the pyridinethione (III) with the alkylating agent XCH_2R in the presence of excess alkali in DMF. In the preparation of the thienopyridine (XIf), the reaction is carried out in alcohol rather than DMF, since in the latter case considerable resinification of the reaction mix-ture occurs.



X = Cl; Br; R = H(a), CN(b), COOMe(c), COOEt(d), CONH₂(e), COPh(f).



Fig. 2. Molecular packing in the crystal of (II), projected along the *ac* boundary. The original molecule is isolated.

The IR spectra of the pyridines (Xa-f) show strong absorption for the stretching vibrations of the conjugated nitrile group at 2220 cm⁻¹, and in the case of (Xb) there is also weak absorption for the unconjugated nitrile group. In addition, the IR spectra of (Xc-f) show absorption for the carbonyl (1690-1680 cm⁻¹) and ester (1745-1740 cm⁻¹) groups. Following cyclization of (XB-f), the IR spectra of the resulting compounds (XIb-f) no longer contain absorption for the nitrile group, but several bands appear for the stretching (3490-3222 cm⁻¹) and deformational (1610-1580 cm⁻¹) vibrations of the amino group.

The PMR spectra of the pyridines (Xa-f) and the thienopyridines (XIb-f) display signals characteristic of the pyridine protons, $J_H^4 H^5 = 9$ Hz. In addition, the PMR spectra of (Xb-f) show a singlet for the methylene protons at 3.93-4.93 ppm which disappears in the cyclization products (XIb-f), with the appearance of a broadened signal for the amino-group protons.

EXPERIMENTAL

IR spectra were obtained on a UR-20 in KBr disks, and UV spectra on a Specord UV-VIS spectrophotometer, in ethanol. The PMR spectra were recorded on Tesla BS-467 (60 MHz) and Bruker WM-250 (250 MHz) instruments, in DMSO-d₆ relative to TMS. Mass spectra were obtained on a Varian MAT-CH-6, with direct introduction of the sample into the ion source, ionizing-electron energy 70 eV; the masses of the molecular ions in the mass spectra are given for the principal isotope ³²S. TLC was carried out on Silufol UV-254 plates, in the system acetone-hexane, 3:5.

1-Adamanty1 methy1 ketone was obtained as described in [1], mp 54-56°C.

Sodium Salt of 3-(1-Adamanty1)-1-hydroxyprop-1-en-3-one (II). To a mixture of 1.1 g (48 mmoles) of finely divided sodium in 50 ml of dry ether was added slowly with stirring $\sim 20^{\circ}$ C 1-2 ml of a solution of 8.6 g (48 mmoles) of (I) and 4.67 ml (58 mmoles) of ethyl

<pre>t) and Thieno[2,3-b]-</pre>	Coloulated %
captopyridines ()	
6-(1-Adamanty1)-3-cyano-2-merc	Found - %
ercapto-Substituted	-
2. 2-Me ines (XI)	
BLE rid	

				Found,	%	and construction was done as con-			Calcula	ted, %	
Compound	Yield,%	mp, °C (solvent)	σ	Н	7.	s	Eurpirical formula	σ	H	z	ß
(Xa)	78	161-162,5 (abs.EtOH)	74,55	7,10	9,69	11,13	$\mathrm{C}_{17}\mathrm{H}_{20}\mathrm{N}_{2}\mathrm{S}$	71,79	60'2.	9,85	11.27
(X b)	58	164-165 (abs. EtOH)	69,62	6,33	13,52	10,20	C ₁₈ H ₁₉ N ₃ S	69,89	6,19	13,58	10.36
(Xc)	61)	134-135 (abs. EtOH)	66,67	6,64	8,30	9,24	$C_{19}H_{22}N_2O_2S$	66, 64	6.47	8,18	9,36
(Yq)	64	93-93,5 (fr AcOH)	67,48	6.90	7,59	8,92	$C_{20}H_{24}N_2O_2S$	67,38	6,78	7,85	8,99
(Xe)	41	169-170 (fr. AcOH)	66,03	6,72	12,81	9,59	C ₁₈ H ₂₁ N ₃ OS	66.03	6,46	12,83	9,79
(Xf)	75	145,5-147 (abs.EtOH)	74,27	6,43	7,20	8,08	$C_{24}H_{24}N_2OS$	74,19	6,23	7,21	8,25
(X] b)	54	255–256,5 (fr. AcOH)	69,85	.6,14	13,73	10,31	C ₁₈ H ₁₉ N ₃ S	69,89	6,19	13,58	10,36
(XIc)	85	211-212 (fr.AcOH)	66,56	6,44	8,29	9,16	$C_{19}H_{22}N_2O_2S$	66,64	6,47	8,18	9,36
(XI¢)	66	176-177 (fr. AcOH)	67,34	6,82	7,86	8,87	$C_{20}H_{24}N_{2}O_{2}S$	67,38	6,78	7,85	8,99
(XIC)	78	306-307,5 (fr. AcOH)	65,66	6,64	12.51	9,60	C ₁₈ H ₂₁ N ₃ OS	66,03	6,46	12,83	9,79
(XIF)	47	176-176,5 (119. EtOH)	73,27	6,57	6,94	8,09	C24H24N2OS	74,19	6,23	7,21	8,25

						₂ CH ₃),	3,93 s(CH2)	(2)			H_2), 1,27 t		h)
	J, Hz (DMSO-d ₆)	other protons	2,60 s (CH ₃)	4,36 s (CH ₂)	4,13 s (CH2), 3,64 s (CH3)	4,14 s(CH ₃ CO), 4,09 q (CH	$7,60.s(NH_2), 7,17 s(NH_2), 3$	7,53-8, 1 7 m (Ph), 4,93 s (CH	$7,26 \ s \ (NH_2)$	$7,27 \text{ s}(\text{NH}_2), 3,76 \text{ s}(\text{CH}_3)$	4,26 q (CH ₂), 3,64 br.s,(N	$7,12 \text{ s}(\text{NH}_2), 7,07 \text{ s}(\text{NH}_2)$	8,41 s (NH2), 7,48-7,85 m (F
	, ppm,	6:H-Ad (S)	1,70	1.74	1,71	1,62	1,73	1.50, 1, 29 $J_{AB} =$	=12 1,73	1,74	1,73	1,76	1,75
	ctrum, S	6H-Ad (S)	1,93	1,97	1,86	1,86	1,93	1,59	1,95	1,97	1,95	1,97	1,97
	IR spec	hH-Ad (S)	2,04	2,07	2,06	2,04	2,06	1,73	2,07	2,06	2,05	2,06	2,07
Spectral Properties of (X) and (XI)	MA	JH4, H⁵	8,5	9,0	9,0	9,0	9,0	9,0	9,0	9,0	9,0	9,0	9,0
		H ⁵ (d)	7,26	7,38	7,22	7,27	7,20	7,14	7,53	7,46	7,46	7,44	7,40
		H, (q)	8,12	8,23	8,15	8,15	8,12	8,12	8,44	8,45	8,48	8.34	8,59
	un, v cm ⁻¹	CO			1740	1745	1680	1690		1680	1670	1640	
		CN	2220	2225	2220	2225	2220	2220	2195				
	IR spectru (KBr)	$\rm NH_2$					3440-3420		3450-3220,	1630 3430-3310,	1620 3480-3370,	3380-3180,	1590 3490-3380, 1610
	UV spectrum,λ _{max} , nm (log ε) (EtOH)		221 (4,36), 267 (4,15),	315(3,75) 218(4,41), 261 (4,12),	$\begin{bmatrix} 304(3,89)\\ 220(4,50), 264(4,23), \end{bmatrix}$	310(3,91) 220(4,35), 273(3,60),	309(3,77) 222(4,40), 265(4,17),	310(3,83) 202(4,57), 222(4,41), 261(4,28), 312(3,80)	202(4,38), 228(4,16)	279(4,50), $355(3,71)202(4,34)$, $236(4,04)$	283(4,60), $368(3,73)203(4,37)$, $237(4,00)$,	285(4,49), 368(3,74) 204(4,32), 233(4,03)	285(4,50), 365(3,70) 281(4,31), 314(4,34)
TABLE 3.		Compound	(Xa)	(qX)	(X c)	(pX)	(X,e)	(X£)	(qIX)	(XIc)	(XIđ)	(XIe)	(XIF)

formate in 50 ml of dry ether, followed by 0.1 ml of ethanol. The rest of the ether solution of (I) and ethyl formate was then added dropwise to the mixture. After 12 h, the solid was filtered off, washed with 10 ml of dry ether, and dried, to give 9 g (82%) of (II), dec. 225-240°C.

<u>6-(1-Adamanty1)-3-cyanopyridine-2(1H)-thione (III)</u>. To a suspension of 5.03 g (22 mmoles) of (II) in 30 ml of ethanol was added with stirring 1.14 ml (20 mmoles) of acetic acid followed by 2.2 g (22 mmoles) of cyanothioacetamide, and the mixture heated to the boil (whereupon a solid separated). After cooling, the mixture was acidified with dil. HCl (1:1) to $\text{PH} \leq 6$, and the solid filtered off and washed with ethanol to give 3.7 g (62%) of (III), mp 222-225°C (decomp., from abs. ethanol). UV spectrum [EtOH, λ_{max} , nm (log ϵ)]: 244 (3.66, 309 (4.03), 408 (3.52). IR spectrum (KBr, ν , cm⁻¹): 2220 (CN). PMR spectrum (CDCl₃, δ , ppm): 1.80 s (6H, δ -H-Ad), 1.90 s (6H, β -H-Ad), 2.19 s (3H, γ -H-Ad), 6.58 d (1H, H⁵), 7.71 d (1H, H⁴), J_H4_H5 = 8 Hz, 10.73 br. s. (1H, NH). m/z M⁺ 270. Found: C 70.97; H 6.84; N 10.41; S 11.64%. C₁₆H₁₈N₂S. Calculated: C 71.07, H 6.71; N 10.36; S 11.85%.

Bis[6-(1-Adamanty1)-3-cyanopyrid-2-y1] Disulfide (IV). To a suspension of 0.135 g (0.5 mmole) of (III) in 5 ml of ethanol were added successively 0.28 ml (0.5 mmole) of 10% KOH and 2 ml of 5% alcoholic iodine, and the mixture stirred for 30 min at 20°C. The solid which separated was filtered off, washed with water and ethanol, and recrystallized to give 0.08 g (60%) of (IV), mp 247-249°C (chloroform-hexane). UV spectrum [EtOH, λ_{max} , nm (log ε)]: 218 (4.56), 257 (4.28), 298 (4.05). IR spectrum (KBr, ν , cm⁻¹): 2230 (CN). PMR spectrum (CDCl₈, δ , ppm): 1.57-1.70 m (12H, β -, δ -H-Ad), 1.95 s (3H, γ -H-Ad), 7.05 d (1H, H⁵), 7.80 d (1H, H⁴), J_H4_H5 = 8 Hz, m/z M⁺538. Found: C71.13; H 6.56; N 10.30; S 11.99%. C₃₂H₃₄N₄S₂. Calculated: C 71.34; H 6.36; N 10.39; S 11.90%.

<u>Substituted 6-(1-Adamantyl)-3-cyano-2-mercaptopyridines (Xa-f)</u>. To a suspension of 0.135 g (0.5 mmole) of (III) in 5 ml of ethanol was added 0.28 ml (0.5 mmole) of a 10% KOH solution. followed by 0.7 mmole of the alkylating agent XCH₂R. After 5 min, the mixture was diluted with water, and the solid filtered off and recrystallized. Data for (Xa-f) are given in Tables 2 and 3.

<u>Substituted 6-(1-Adamantyl)-3-aminothieno[2,3-b]pyridines (XIb-f)</u>. a) To a suspension of 0.135 g (0.5 mmole) of (III) in 5 ml of DMF was added 0.39 ml (0.7 mmole) of 10% KOH solution. The mixture was stirred until the solid had dissolved, then 0.6 mmole of XCH₂R was added. After 30 min, the solid was filtered off, washed with ethanol, and recrystal-lized.

b) To a suspension of 0.2 g (0.5 mmole) of (Xf) in 5 ml of ethanol was added with stirring 0.28 ml (0.5 mmole) of 10% KOH solution. After 30 min, the solid which had separated was filtered off, washed with aqueous ethanol, and recrystallized from ethanol to give 0.135 g (69%) of (XIf). Data for (XIb-f) are given in Tables 2 and 3.

 $\frac{X-\text{Ray Structural Examination of Bis[6-(1-adamanty1)-3-cyanopyrid-2-y1 Disulfide (IV).}{\text{The crystals of (IV) are monoclinic, and at 20°C <math>\alpha = 10.7767(9)$, b = 12.9868(7), c = 20.226(1), $\beta = 98.758(6)$ °, V = 2797.7(3) Å³, $d_{calc} = 1.28 \text{ g/m}^3$, Z = 4, $C_{32}H_{34}N_4S_2$, space group P2₁/c. The intensities of 2785 independent reflections were measured on a Hilger-Watts automatic four-circle diffractometer ($\lambda Mo K_{\alpha}$, graphite monochromator, $\theta/2\theta$ scanning, $\theta_{max} = 25^\circ$).

Anomalous scattering of the sulfur atoms was taken into account. The structure was calculated by the direct method using the MULTAN program, all the nonhydrogen atoms being visualized, and refined by the full-matrix least-squares method in anisotropic approximation for the nonhydrogen atoms from 1705 independent reflections with $I > 2\sigma$. In the final refinement, the calculations included all the hydrogen atoms in the geometrically calculated positions with fixed coordinates and isotropic temperature factors $B_{\rm ISO} = 6$ Å². The final R value was 0.069 ($R_W = 0.055$). All calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [16]. The atom coordinates are given in Table 4. Tables of the temperature factors may be obtained from the authors.

CONCLUSIONS

1. 6-(1-Adamanty1)-3-cyanopyridine-2(1H)-thione, a convenient synthon for the preparation of adamanty1-substituted thieno[2,3-b]pyridines, has been obtained for the first time.

2. Alkylation of the pyridinethione has given 2-mercapto-substituted 6-(1-adamanty1)-3-cyanopyridines, which cyclize in the presence of bases to 2-substituted-6-(1-adamanty1)-3aminothieno[2,3-b]pyridines.

Atom	X	Y	Z	Atom	x	Y	Z
Atom S^1 N^{18} C^2 C^3 C^4 C^5 C^6 C^7 C^8 C^9 C^{10} C^{13}	x 78849(24) 7130(4) 9848(6) 7833(6) 8556(6) 8495(6) 7759(7) 7088(6) 6249(6) 6602(7) 5709(7) 4413(7) 4038(7) 4430(8)	Y -857(14) 793(4) -2074(5) 55(5) -611(5) -467(5) 306(5) 936(5) 936(5) 1802(4) 2785(5) 3653(5) 3377(6) 2455(6) 2622(7) 2045(6)	$\begin{array}{c} z\\ 35964(10)\\ 4658(2)\\ 4502(4)\\ 4463(3)\\ 4925(4)\\ 5599(3)\\ 5794(3)\\ 5316(3)\\ 5468(3)\\ 5468(3)\\ 5118(3)\\ 5236(4)\\ 4959(4)\\ 5314(5)\\ 6050(5)\\ 694(2)\\ \end{array}$	Atom S ¹⁷ N ¹⁴ C ²⁷ C ³⁷ C ⁴⁷ C ⁵⁷ C ⁶⁷ C ⁶⁷ C ⁹⁷ C ¹⁰⁷ C ¹²⁷ C ¹²⁷ C ¹³⁷	X 61431 (21) 7308 (5) 2986 (6) 6220 (6) 5077 (6) 5133 (6) 6291 (6) 7382 (6) 8736 (8) 10079 (9) 10129 (8) 10245 (9) 14062 (8)	Y 3913(15) 2225(4) 1346(6) 1766(5) 2296(5) 3828(5) 3241(5) 3733(5) 4606(8) 5129(7) 5544(7) 4823(7) 3932(8) 3504(6)	2 32010(10) 3279(2) 2990(4) 3206(3) 3110(3) 3082(3) 3154(4) 3266(3) 3359(3) 3359(3) 3359(3) 33995(4) 3346(5) 2824(4) 29880(5) 2824(4)
C ¹⁴ C ¹⁵ C ¹⁶ C ¹⁷	6348(8) 4903(7) 5836(7) 9298(7)	2044(6) 1530(5) 3880(5) -1424(5)	6216(3) 5186(4) 5976(4) 4695(4)	C ¹⁴ ' C ¹⁵ ' C ¹⁶ ' C ¹⁷ '	9662(8) 10972(7) 8936(8) 3908(7)	3024(7) 4290(8) 4123(9) 1767(6)	3647(7) 4181(4) 2714(4) 3044(4)

TABLE 4. Atom Coordinates for (IV) (×10⁵ for S Atoms; ×10⁴ for N and C Atoms)

3. The structure of bis[6-(1-adamantyl)-3-cyanopyrid-2-yl] disulfide has been confirmed by an x-ray structural examination.

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CONDENSED PYRIDINES. COMMUNICATION 4.* THE MICHAEL REACTION IN THE SYNTHESIS OF SUB-STITUTED 3-CYANOPYRIDINE -2(1H) -THIONES

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Yu. A. Sharanin, A. M. Shestopalov, V. Yu. Mortikov, S. N. Melenchuk, V. K. Promonenkov, B. M. Zolotarev. and V. P. Litvinov

The only report of the use of the Michael reaction in the synthesis of substituted 3cyanopyridine-2(1H)-thiones is in the preparation of 4,6-diary1-3-cyanopyridine-2(1H)-thiones [2, 3]. These were obtained by reacting chalcones with cyanothioacetamide (I), to give, depending on the reaction conditions and the catalyst used, either substituted 3-cyanopyridine-2(1H)-thiones [2], or their hydrogenated analogs [3].

We here describe an examination of the reaction of arylidenemalononitriles (II) with (I), or arylidenecyanoacetamides (III) with malononitrile (IV), and ethyl cyanoacetate (V), and of arylidene derivatives of ethyl cyanoacetate (VI) with (I). Some new reactions of the Michael adducts formed have been observed. For example, in the reaction of (I) with (II) in the presence of an organic base, the previously unknown thioamides of 3-aryl-2,4,4-tricyano-2-butenoic acid (VII) were obtained via the Michael adduct (VIII). The formation of (VIII) was confirmed by the fact that the reaction between (III) and (IV) also gave the thioamide (VII).

We have shown that the thioamides (VII) react with ketones (IX) containing a methyl or methylene group in the α position to give pyridinethiones (X). The reaction appears to proceed via the formation of the Michael adducts followed by elimination of malononitrile (IV) and intramolecular cyclization of the intermediate (XI).

*For communication 3, see [1].

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