CONDENSED PYRIDINES.

2.* SYNTHESIS AND REACTIONS OF 4,6-DISUBSTITUTED 3-CYANO-PYRIDINE-2[1H]THIONE AND 3-CYANOPYRIDINE-2[1H]SELENONE

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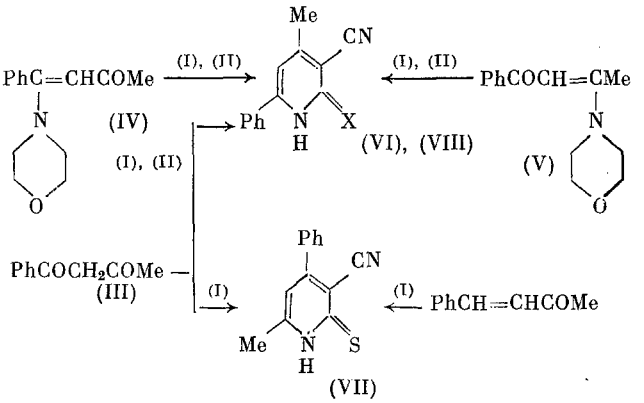
3-Cyanopyridine-2[1H]thiones are important as intermediates in the synthesis of physiologically active compounds, dyes, etc. Different methods have been proposed for their preparation: reaction of substituted 2-halopyridines with alkali metal sulfides or with thiourea [2-5], condensation of 1,3-dicarbonyl compounds or α,β-unsaturated ketones with cyanothioacetamide (I) [5, 6], recyclization of 2,2-dialkyl-4-aminocyano-1,3-dithia-4-cyclohexenes [7], reaction of gem-dithiols with arylidenemalononitriles [7], thiolation of 1,5-ketonitriles [5, 7]. The selenium analogs of 3-cyanopyridine-2[1H]-thiones are unknown.

To synthesize the 3-cyanopyridine-2[1H]selenenones and to study their reactivity in comparison with the properties of analogous thiones, we developed a method for preparing cyanoselenoacetamide (II), based on the reaction of malonodinitrile with H_2Se in the presence of catalytic amounts of Et_3N. Selenoamide (II) was found to be a convenient reagent in the synthesis of 3-cyanopyridine-2[1H]selenones: Condensation of (II) with acetylacetone or dibenzoylmethane leads to 4,6-dimethyl- or 4,6-diphenyl-3-cyanopyridine-2[1H]selenone in a yield of 86 and 62%, respectively [1].

In the present work, we studied the condensation of (I) and (II) with benzoylacetone (III) and enamines: 1-(1-morpholino)-1-phenyl-1-buten-3-one (IV) and 2-(1-morpholino)-4-phenyl-2-buten-4-one (V). Our aim was to study not only the synthesis of the new substituted 3-cyanopyridine-2[1H]thiones and 3-cyanopyridine-2[1H]selenones, but also the structure of products of reaction of amides (I) or (II) with asymmetric 1,3-diketones and enamines, since in this case the formation of isomeric 4,6-disubstituted pyridinethiones and pyridineselenones is possible.

In fact, in the reaction of (I) with (III) in the presence of Et_3N in ethanol, a product is formed in a 66% yield, melting at 224-226°C, consisting of a mixture of two isomers: 4-methyl-6-phenyl-3-cyanopyridine-2[1H]thione (VI) and 4-phenyl-6-methyl-3-cyanopyridine-2[1H]thione (VII) in a ratio of 2:1. After chromatography on silica gel, thione (VI), mp 235-236°C, and thione (VII), mp 274-276°C, were isolated. Their structure was confirmed by the



X = S (VI), Se (VIII).

*For Communication 1, see [1].

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TABLE 1. 4,6-Disubstituted 3-Cyano-2-Y-methylthio(seleno)-pyridines (IX)-(XI) and 3-Amino-2-Y-thieno(selenopheno)[2,3-b]pyridines (XII)-(XIV) (Y = COOH, COOMe, COOEt, $CONH_2$, CN, and COPh)

Compound	Yield, %	mp, °C*	Empirical formula	Found/Calculated			
				C	H	N	S(Se)
(IXa)	84	234–235	$C_{15}H_{12}N_2O_2S$	63,14 63,36	4,02 4,26	9,80 9,85	10,97 11,28
(IXb)	69	164–165	$C_{16}H_{14}N_2O_2S$	64,39 64,41	4,59 4,73	9,22 9,39	10,54 10,75
(IXc)	90	159–160	$C_{17}H_{16}N_2O_2S$	65,20 65,36	4,93 5,16	9,04 8,97	9,97 10,26
(IXd)	74	240–241	$C_{15}H_{13}N_3OS$	63,54 63,60	4,66 4,59	14,60 14,83	11,07 11,32
(IXe)	77	222–223	$C_{15}H_{11}N_3S$	67,81 67,90	4,07 4,18	15,77 15,84	11,80 11,08
(IXf)	85	165–166	$C_{21}H_{16}N_2OS$	73,17 73,23	4,44 4,68	8,01 8,13	9,07 9,31
(Xa)	79	141–142	$C_{15}H_{12}N_2O_2S$	63,29 63,36	4,04 4,26	9,70 9,85	11,02 11,28
(Xb)	85	113–114	$C_{16}H_{14}N_2O_2S$	64,49 64,41	4,60 4,73	9,42 9,39	10,52 10,75
(Xc)	77	93–94	$C_{17}H_{16}N_2O_2S$	63,19 65,36	4,95 5,16	8,88 8,97	10,20 10,26
(Xd)	74	196–197	$C_{15}H_{13}N_3OS$	63,69 63,60	4,40 4,59	14,90 14,83	11,00 11,32
(Xe)	79	144–145	$C_{15}H_{11}N_3S$	67,82 67,90	4,11 4,18	15,80 15,84	11,84 12,08
(Xf)	72	142–143	$C_{21}H_{16}N_2OS$	73,27 73,23	4,49 4,68	8,15 8,13	9,20 9,31
(XIc)	66	134–135	$C_{17}H_{16}N_2O_2Se$	56,96 56,82	4,55 4,49	7,63 7,80	21,71 22,00
(XIe)	96	207–208	$C_{15}H_{11}N_3Se$	57,42 57,69	3,30 3,55	13,29 13,46	24,96 25,30
(XIf)	95	143–144	$C_{21}H_{16}N_2OSe$	64,51 64,45	3,95 4,12	7,11 7,16	19,88 20,19
(XIIb)	65	168–169	$C_{16}H_{14}N_2O_2S$	64,52 64,41	4,70 4,73	9,41 9,39	10,59 10,75
(XIIc)	82	130–131	$C_{17}H_{16}N_2O_2S$	65,21 65,36	5,12 5,16	8,93 8,97	10,05 10,26
(XIId)	73	226–227	$C_{15}H_{13}N_3OS$	63,67 63,60	4,48 4,59	14,70 14,83	11,27 11,32
(XIIe)	59	193–194	$C_{15}H_{11}N_3S$	67,73 67,90	3,90 4,18	15,88 15,84	11,95 12,08
(XIIf)	70	171–172	$C_{21}H_{16}N_2OS$	73,05 73,23	4,57 4,68	8,04 8,13	9,19 9,31
(XIIIb)	76	174–175,5	$C_{16}H_{14}N_2O_2S$	64,45 64,41	4,62 4,73	9,33 9,39	10,67 10,75
(XIIIc)	79	162–163	$C_{17}H_{16}N_2O_2S$	65,21 65,36	4,89 5,16	8,80 8,97	10,06 10,26
(XIIId)	89	209–210	$C_{15}H_{13}N_3OS$	63,62 63,60	4,36 4,59	14,71 14,83	11,18 11,32
(XIIIe)	74	175–176	$C_{15}H_{11}N_3S$	67,74 67,90	4,02 4,18	15,67 15,84	11,88 12,08
(XIIIf)	87	162–163	$C_{21}H_{16}N_2OS$	73,09 73,23	4,55 4,68	8,02 8,13	9,14 9,31
(XIVc)	84	131–133	$C_{17}H_{16}N_2O_2Se$	56,67 56,82	4,34 4,49	7,59 7,80	21,80 22,00
(XIVe)	88	206	$C_{15}H_{11}N_3Se$	57,46 57,69	3,49 3,55	13,30 13,46	25,07 25,30
(XIVf)	81	197–198	$C_{21}H_{16}N_2OSe$	64,28 64,45	3,96 4,12	7,00 7,16	20,04 20,19

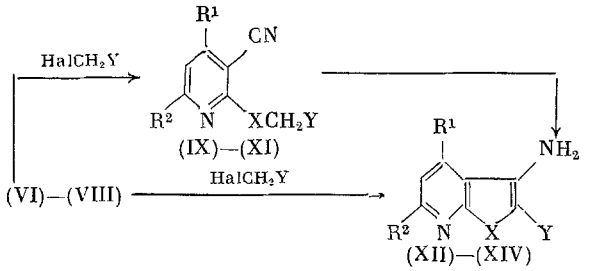
*Solvents for recrystallization: (IXa-e), (Xd), (XIIId) — ethyl acetate; (IXf), (XIc, f), (XIIf), (XIVc, e, f) — ethanol; (Xb, c) — hexane; (Xe, f), (XIId), (XIIIc, e) — 1-butanol; (Xa) — water; (XIIc, e, f) — 2-propanol; (XIIIb) — nitromethane; (XIe) — reprecipitated by hexane from acetone.

data of IR and PMR spectra, and also by synthesizing (VI) from enamines (IV) and (V) (see below), and thione (VII) by condensing (I) with benzylideneacetone by the method in [5].

By condensing (I) with (III) under similar conditions, a product with mp 223°C had already been obtained in [6]. Structure (VI) was attributed to it. The data obtained indicate that this product is a mixture of two isomers.

It is interesting to note that the condensation of (II) with (III) in the presence of Et_3N proceeds with the formation of one isomer — 4-methyl-6-phenyl-3-cyanopyridine-2[1H]-selenone (VIII): The TLC and PMR data of the reaction product indicate the absence of a second isomer. Additional studies are required to explain the formation of only one isomer in the reaction of cyanoselenoacetamide (II) with diketone (III), in contrast to the reaction of two isomers.

We studied the alkylation reaction of thiones (VI), (VII), and selenone (VIII), and found that these compounds are readily alkylated at the S or Se atom to form substituted cyanopyridines (IX), (X), or (XI). The yields and the physical constants of the compounds obtained are listed in Table 1.



R^1 = Me, R^2 = Ph; X = S (IX), (XII); R^1 = Me, R^2 = Ph; X = Se (XI), (XIV); R^1 = = Ph, R^2 = Me; X = S (X), (XIII); Y = COOH (a), COOMe (b), COOEt (c), $CONH_2$ (d), CN (e), COPh (f).

According to Thorp and Ziegler, cyclization of compounds (IX)-(XI) leads to 3-aminothieno[2,3-b]pyridines (XII), (XIII), or 3-aminoselenopheno[2,3-b]pyridines (XIV). 3-Aminothieno(selenopheno)pyridines (XII)-(XIV) can also be obtained directly from thiones (VI), (VII) and selenone (VIII) without the intermediate isolation of S- or Se-substituted cyanopyridines.

The structure of the compounds obtained was confirmed by the data of IR and PMR spectroscopy. In the IR spectra of compounds (IX)-(XI) there is an adsorption band of a conjugated nitrile group, while in the spectra of the cyclization products several bands appear belonging to the stretching and deformational vibrations of the amino group. Compared with the S- and Se-substituted cyanopyridines (IXe)-(XIe), for compounds (XIIe)-(XIVe) the absorption band of the nitrile group is considerably shifted to the region of lower frequencies because of conjugation with the heterocyclic system (to 2198 cm^{-1} for (XIIe) and (XIIIe) and to 2187 cm^{-1} for (XIVe)), with simultaneous increase in the intensity. In the PMR spectra of the cyclization products (XII)-(XIV), instead of the proton signals of the methylene group of the S- and Se-substituted cyanopyridines (IX)-(XI) there appear signals of the amino group protons. Characteristic changes are also observed in the position of signals of protons of the same type for the corresponding compounds (IX)-(XIV) (Table 2).

When the relative disposition of the 4,6-substituents in 3-aminothieno[2,3-b]pyridines (XII), (XIII) is changed, characteristic changes are observed in the PMR spectra. On transition from 4-methyl-6-phenyl-(XII) to 6-methyl-4-phenyl-3-aminothieno[2,3-b]pyridine (XIII), there is a shift of the proton signals of the pyridine ring, the methyl group, and the amino group, on average of 0.65, 0.26, and 0.82 ppm, respectively, to the region of stronger fields. Similar regularities are also observed when the PMR spectra of S-substituted cyanopyridines (IX) and (X) are compared. According to the PMR spectral and experimental data for compounds (IX)-(XI), these compounds can be arranged into the following series: Y = Ph—CO > CN > COOR > COOH > $CONH_2$, according to ease of cyclization.

EXPERIMENTAL

The UV spectra were run on the "Hitachi MPS-50" spectrophotometer in ethanol. The IR spectra were recorded on the "Perkin-Elmer 457" spectrometer in KBr tablets. The PMR spectra were run on the "Varian FT-80A" (80 MHz) and "Bruker HX-90E" (90 MHz) spectrometers in DMSO-d_6,

TABLE 2. IR and PMR Spectra of 4,6-Disubstituted 3-Cyano-2-Y-methylthio(seleno)pyridines (IX)-(XI) and 3-Amino-2-Y-thieno-(selenopheno)[2,3-b]pyridines (XII)-(XIV)

Compound	IR spectrum (ν, cm^{-1})				PMR spectrum (δ, ppm)					
	CH_3, CH_2	CN	NH_2	Y	Ph (m)	Py (c)	CH_3 (c)	CH_2 (c)	NH_2 (c)	Y
(IXa)	2930, 2980	2218		1708	7,3–8,2	7,78	2,28	4,10		
(IXb)	2930, 2944, 2990	2217		1734	7,4–8,2	7,80	2,29	4,19		3,63 s
(IXc)	2930, 2982	2216		1735	7,4–8,1	7,75	2,48	4,17		4,07 q 1,14 t
(IXd)	2918, 2960	2218		1625, 3160, 3485	7,4–8,3	7,83	2,49	4,04		3,67 s
(IXe)	2935, 2980	2217		2242	7,4–8,3	7,90	2,51	4,42		
(IXf)	2905, 2980	2215		1684	7,1–8,1	7,70	2,29	4,95		
(Xa)	2930, 2990	2219		1740	7,57	7,26	2,52	4,03		
(Xb)	2220, 2258	2216		1745	7,56	7,25	2,50	4,12		3,67 s
(Xc)	2930, 2978, 2990	2218		1738	7,56	7,26	2,51	4,11		4,15 q 1,21 t
(Xd)	2920, 2960	2220		1670, 3270, 3495	7,58	7,26	2,54	3,99		7,15 s
(Xe)	2920, 2978	2218		2243	7,56	7,38	2,62	4,38		
(Xf)	2930, 2990	2210		1672	7,4–8,2	7,22	2,23	4,85		
(XIc)	2910, 2945, 2992	2224		1732	7,4–8,1	7,82	2,30	4,11		4,03 q 1,12 t
(XIe)	2930, 2955	2224		2247	7,4–8,2	7,90	2,51	4,21		
(XIf)	2961, 2980	2220		1680	7,3–8,1	7,78	2,46	4,91		
(XIIb)			3340, 3400, 3462	1670	7,4–8,1	7,74	2,80		6,75	3,78 s
(XIIc)			3355, 3410, 3480	1667	7,4–8,2	7,74	2,81		6,75	4,26 q 1,29 t
(XIId)			3108, 3300, 3448, 3480	1640	7,4–8,2	7,73	2,85		6,87	7,24 s
(XIIe)			3230, 3330, 3462	2198	7,3–8,2	7,78	2,81		6,50	
(XIIf)			3260, 3440	1580	7,4–8,2	7,80	2,87		7,55	
(XIIIb)			3337, 3480	1672	7,54	7,12	2,60		5,75	3,77 s
(XIIIc)			3358, 3472	1665	7,48	7,09	2,56		5,71	4,20 q 1,25 t
(XIIId)			3150, 3258, 3320, 3440, 3480	1640	7,51	7,07	2,58		5,80	7,16 s
(XIIIe)			3210, 3330, 3463	2198	7,54	7,17	2,60		5,56	
(XIIIf)			3380, 3470	1597	7,5–7,8	7,15	2,60		6,85	
(XIVc)			3350, 3490	1668	7,4–8,2	7,74	2,82		6,85	4,22 q 1,27 t
(XIVe)			3240, 3342, 3465	2187	7,4–8,2	7,76	2,80		6,36	
(XIVf)			3260, 3420	1593	7,4–8,2	7,78	2,83		7,90	

with TMS as internal standard. The course of the reaction and the individuality of the compounds were determined by the TLC method in a 3:1 benzene–acetone system.

4-Methyl-6-phenyl-3-cyanopyridine-2[1H]thione (VI). a) A mixture of 2.3 g (10 mmoles) of 1-(1-morpholino)-1-phenyl-1-buten-3-one (IV), 1 g (10 mmoles) of cyanothioacetamide (I), and 0.6 ml of glacial AcOH in 30 ml of ethanol was boiled for 5 min, and then was held for 2 h at 20°C. The precipitate was washed with alcohol and hexane. Yield, 1.8 g (79%) of (VI), mp 235-236°C (from AcOH).

b) A mixture of 0.46 g (2 mmoles) of 2-(1-morpholino)-4-phenyl-2-buten-4-one (V), 0.2 g of (I), and 0.2 ml of glacial AcOH was boiled for 5 min, and then was allowed to stand overnight. The precipitate was washed with alcohol and hexane. Yield, 0.2 g (44%) of (VI), mp 234-235°C. IR spectrum (KBr, ν, cm^{-1}): 2200 (CN). PMR spectrum (δ, ppm): 2.42 s (CH_3), 7.04 s (CH), 7.58 m (C_6H_5).

Reaction of Benzoylacetone (III) with Cyanothioacetamide (I). A mixture of 1.6 g (10 mmoles) of diketone (III), 1 g (10 mmoles) of (I), and 0.2 ml of Et_3N in 20 ml of ethanol was stirred for 3 h at 20°C. The precipitate was washed with alcohol and hexane. Yield, 1.5 g (66%) of a product melting at 224-226°C. A 0.2-g portion of this product was chromatographed on silica gel "Silperal" in a 3:1 benzene–acetone mixture to give 0.13 g (66%) of (VI), mp 235-236°C, R_f 0.47 and 0.07 g (34%) of (VII), mp 274-276°C, R_f 0.32.

4-Methyl-6-phenyl-3-cyanopyridine-2[1H]selenone (VIII). A mixture of 1.6 g (10 mmoles) of diketone (III), 1.5 g (10 mmoles) of selenoamide (II), and 0.2 ml of Et_3N in 20 ml of ethanol was heated to boiling in an argon atmosphere, and then cooled. Yield, 2.0 g (73%) of (VIII), mp 195-198°C (dec.). UV spectrum (ethanol, λ_{max}, nm, log ε): 217 (4.14), 280 (4.07), 342 (3.99), 440 (3.22). IR spectrum (KBr, ν, cm^{-1}): 2224 (CN). PMR spectrum (δ, ppm): 2.44 s (CH_3), 7.00 s (CH), 7.3-7.9 m (C_6H_5), 14.47 s (NH). Selenone (VIII) was obtained from (II) and enamines (IV) or (V) in yields of 70 and 56%, respectively.

4,6-Disubstituted 3-Cyano-2-Y-methylthiopyridines (IX), (X) and 3-Cyano-2-Y-methylselenopyridine (XI). General Procedure. An equivalent amount of a 10% aqueous solution of KOH (5.6 ml) was added to a solution of 10 mmoles of (VI), (VII), or (VIII) in 20-25 ml of DMFA. Then, 10 mmoles of the halide ($HalCH_2Y$) were added at 20°C, the mixture was held at 20°C for 10-15 min, and was diluted with 5-10 ml of water. The precipitate was washed with alcohol and recrystallized from the corresponding solvent (see Table 1).

4,6-Disubstituted 3-Amino-2-Y-thieno[2,3-b]pyridines (XII), (XIII), and 3-Amino-3-Y-selenopheno[2,3-b]pyridine (XIV). a) A 5.6-ml portion of 10% KOH and then 10 mmoles of halide ($HalCH_2Y$) were added to a solution of 10 mmoles of (VI), (VII), or (VIII) in 20-25 ml of DMFA, and then the mixture was stirred for 10-20 min, was diluted with another 2-5 ml of 10% KOH, and was allowed to stand for 3-5 h at 20°C. The mixture was diluted with a twofold volume of water, and the precipitate was recrystallized. The physical constants of compound (XII)-(XIV) are listed in Table 1.

b) A mixture of 10 mmoles of S- or Se-substituted cyanopyridines (IX)-(XI), 20-25 ml of DMFA and 2-5 ml of 10% KOH was stirred at 0°C for 3-5 h, diluted with a twofold volume of water, and the precipitate was separated.

CONCLUSIONS

1. Methods for synthesizing 4-methyl-6-phenyl-3-cyanopyridine-2[1H]thione were developed, based on the reaction of enamines with cyanothioacetamide, and 4-methyl-6-phenyl-3-cyanopyridine-2[1H]selenone, based on the reaction of enamines or benzoylacetone with cyanoselenoacetamide.

2. The reaction of benzoylacetone with cyanothioacetamide leads to the formation of a mixture of 4-methyl-6-phenyl- and 6-methyl-4-phenyl-3-cyanopyridine-2[1H]thiones in a ratio of 2:1.

3. Alkylation of 3-cyanopyridine-2[1H]thiones and 3-cyanopyridine-2[1H]selenones, proceeding through the intermediate formation of 3-cyano-2-alkylthio(seleno)pyridines, leads to derivatives of 3-aminothieno-[2,3-b]- and 3-aminoselenopheno[2,3-b]pyridines.

LITERATURE CITED

1. V. P. Litvinov, V. Yu. Mortikov, Yu. A. Sharanin, and A. M. Shestopalov, Synthesis, 731 (1984).

2. F. Guerrera, M. A. Siracusa, and B. Tornetta, Farm. Ed. Sci., 31, 21 (1976).
3. C. O. Okafor, J. Org. Chem., 47, 592 (1982).
4. B. Harry and L. Yale, Pyridine and Its Derivatives, Part IV, E. Klinsberg, Editor, Academic Press, New York–London (1964), p. 345.
5. A. A. Krauze, Z. A. Bomika, A. M. Shestopalov, L. A. Rodinovskaya, Yu. É. Pelcher, G. Ya. Dubur, Yu. A. Sharanin, and V. K. Promonenkov, Khim. Geterotsikl. Soedin., 377 (1981).
6. U. Schmidt and H. Kubitzek, Chem. Ber., 93, 1559 (1960).
7. Yu. A. Sharanin, V. K. Promenenkov, and A. M. Shestopalov, Zh. Org. Khim., 18, 630, 1782, 2003 (1982).

REACTION OF $NaGaH_4$ WITH ALCOHOLS

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The interaction of gallohydrides of alkali metals with alcohols up until now has not been investigated. The study of $NaAlH_4$ alcoholysis in THF by the method of ^{27}Al NMR with sucessive action of 1, 2, 3, and 4 moles of alcohols (CH_3OH, C_2H_5OH, i-C_3H_7OH, and t-C_4H_9OH) showed that the intermediate products of alcoholysis disproportionate yielding $NaAlH_4$ and stable $NaAlH(OR)_3$ (CH_3OH and t-C_4H_9OH) or $NaAl(OR)_4$ (C_2H_5OH and i-C_3H_7OH) [1].

To compare the reactivity of $NaGaH_4$ and $NaAlH_4$, we investigated the reaction of $NaGaH_4$ with methyl, ethyl, isopropyl, and tert-butyl alcohols in a solution of THF containing 1, 2, 3, and 4 moles of the corresponding alcohol.

The alcoholysis of $NaGaH_4$ proceeds more slowly that the reaction of $NaAlH_4$. The first mole of CH_3OH or C_2H_5OH reacts with the $NaGaH_4$ at 20°C after 30-40 min, the scond mole of CH_3OH after 60-80 min, while the substitution of the second hydride hydrogen on the ethoxy group proceeds more slowly and is complete after 1.5 h at 65°C. Investigation of the structure of products by ^{71}Ga NMR, with a ratio of $NaGaH_4$:ROH = 1:1 and 1:2, where R = CH_3 and C_2H_5, revealed that the initial $NaGaH_4$ is found in solution, with δ = 92 ppm and J_{Ga-H} = 585 Hz. The signal of $NaGaH_4$ in the ^{71}Ga NMR spectra disappears upon addition of the third mole of CH_3OH or C_2H_5OH and from the reaction mixture the stable monohydride products $NaGaH(OCH_3)_3$ and $NaGaH(OC_2H_5)_3$ precipitate.

This enables one to assume that the products of the alcoholysis with CH_3OH and C_2H_5OH with a 1:1 and 1:2 ratio of reagents [$NaGaH(OCH_3)_3$ and $NaGaH(OC_2H_5)_3$] are subject to disproportionation of $NaGaH_4$ but are stable in THF solution in accordance with the scheme

$$NaGaH_4 + ROH \rightarrow NaGaH_3OR + H_2$$
$$3NaGaH_3OR \rightarrow 2NaGaH_4 + NaGaH(OR)_3$$
$$R = CH_3;\ C_2H_5$$

The methoxy compounds disproportionate faster than the ethoxy compounds.

The complexes of $NaGa(OCH_3)_4$ and $NaGa(OC_2H_5)_4$ were obtained by heating $NaGaH_4$ with excess alcohol in an autoclave at 110°C. The reaction of $NaGaH_4$ with isopropyl alcohol with a 1:1 ratio of reagents at 20°C also proceeds rapidly; however, the products of disproportionation in the reaction mixture were not detected. The ^{71}Ga NMR spectrum of the reaction solution shows the absence of $NaGaH_4$ and $NaGaH_3$(O–i-C_3H_7) precipitated from the solution. With a 1:2 ratio of $NaGaH_4$:i-C_3H_7 the reaction terminates in the formation of $NaGaH_2$(O–i-$C_3H_7)_2$ at 20°C for 20 h and at 65°C for 3 h. The reaction of the third and fourth moles of isopropyl alcohol with $NaGaH_4$ proceeds only in an autoclave at 110°C, while for the formation of NaGa(O–i-$C_3H_7)_4$ an excess of alcohol is required. The precipitation of individual products during the alcoholysis of $NaGaH_4$ by isopropyl alcohol with all ratios of reagents and the absence of a product of disproportionation in the reaction solution enable one to assume that the reaction proceeds stepwise by the scheme

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