3. W. J. Middleton and C. G. Krespan, J. Org. Chem., 30, 1398 (1965).
4. I. L. Knunyants, B. L. Dyatkin, and E. M. Mochalina, Izv. Akad. Nauk SSSR, Ser. Khim., 1091, (1965).
5. D. P. Del'tsova and N. P. Gambaryan, Izv. Akad. Nauk SSSR, Ser. Khim., 1481, (1971).
6. A. Waterfeld, W. Bludssus, R. Mews, and O. Glemser, Z. Anorg. Allg. Chem., 464, 268 (1980).
7. M. E. Garst and D. Lukton, Synth. Commun., 10, 155 (1980).
8. B. L. Dyatkin, L. G. Zhuravkova, B. I. Martynov, S. R. Sterlin, and I. L. Knunyants, Chem. Commun., 618, (1972).
9. E. M. Rokhlin, E. G. Abduganiev, and U. Utebaev, Usp. Khim., 45, 1177 (1976).
10. Yu. V. Zeifman, L. T. Lantseva, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2640, (1978).
11. M. Khalifa, J. Chem. Soc., 1854, (1960).
12. Yu. Lyakhovetskii (Lyakhovetsky), M. Kalinkin, Z. Parnes, F. Latypova, and D. Kursanov, Chem. Commun., 766, (1980).
13. Yu. V. Zeifman, V. V. Tyuleneva, A. P. Pleshkova, R. G. Kostyanovskii, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 2732, (1975).
14. I. L. Knunyants, M. B. Bargamova, and S. I. Pletnev, Inventor's Certificate No. 869262 (USSR), Byull. Izobret., No. 14, 322, (1982).
15. I. L. Knunyants and É. G. Bykhovskaya, Dokl. Akad. Nauk SSSR, 131, 1338 (1960).
16. G. G. Krespan, J. Org. Chem., 34, 1278 (1969).

HETERYLADAMANTANES. COMMUNICATION 5. SYNTHESIS OF 6-(1-ADAMANTYL)-3-CYANOPYRIDIN-2(1H)-SELENONE AND RELATED SELENOPHENOPYRIDINES

E. É. Apenova, Yu. A. Sharanin, B. M. Zolotarev, and V. P. Litvinov

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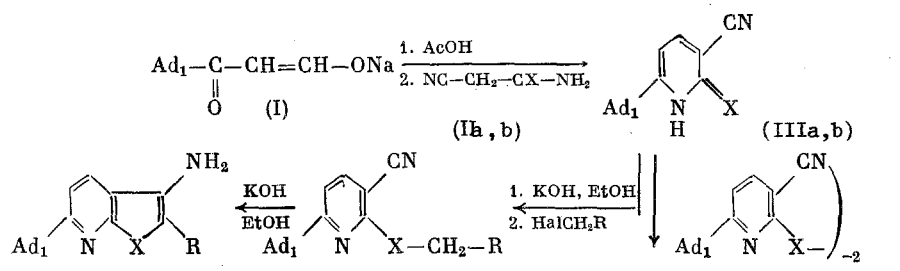
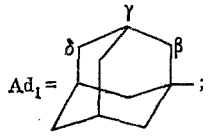
In a previous report [1] we have described the synthesis of 6-(1-adamantyl)-3-cyanopyridin-2(1H)-thione from the sodium salt of 3-(1-adamantyl)-1-hydroxyprop-1-en-3-one (I) and cyanothioacetamide (IIa). Continuing our investigation of heteryladamantanes we have studied the reaction of I with cyanoselenoacetamide (IIb) [2]. Under the previously described conditions in alcohol (with excess acetic acid) reacts with IIb to give a 52% yield of 6-(1-adamantyl)-3-cyanopyridin-2(1H)-selenone (IIIb) (compare [3] before).



where Hal = Cl, Br; X = S (a), X = Se (b); R = H (V), COOMe (VI), (XI); COOEt (VII), (XII); CN (VIII), (XIII); $CONH_2$ (IX), (XIV); COPh (X), (XV).



N. D. Zelenskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow.
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The structure of III was confirmed by elemental analytical data and by PMR and IR spectroscopy. Thus the PMR spectrum shows two characteristic doublets for the pyridine ring protons at 6.85 ppm (1H, H^5) and 7.75 ppm (1H, H^4) with J_{45} = 8 Hz as well as a broad singlet for the NH proton at 8.88 ppm. The IR spectrum includes an intense nitrile absorption at 2230 cm^{-1}.

Compound IIIb is less stable than the corresponding pyridine thione IIIa [1] and on standing is oxidized to bis[6-(1-adamantyl)-3-cyano-2-pyridyl]diselenide (IVb) the structure of which is confirmed by the M^+ 634 molecular ion in the mass spectrum and the absence of an NH signal in the PMR spectrum.

Analogously to the corresponding pyridine thione, the selenone (IIIb) is readily alkylated at the Se atom using an alkyl halide (RCH_2Hal) and an equivalent amount of base (10% KOH solution) to form the 2-seleno substituted 6-(1-adamantyl)-3-cyanopyridines (Vb-VIIb, IXb, Xb) in 45-78% yields. With the use of two equivalents of 10% KOH solution compounds VIb, VIIb, IXb, and Xb underwent Thrope cyclization to give the 2-substituted 6-(1-adamantyl)-3-aminoselenopheno[2,3-b]pyridines (XIb, XIIb, XIVb, XVb) in 50-90% yields. The PMR spectra of the alkylated products (VIb-Xb) show both signals for the protons of the pyridine ring together with a methylene proton singlet in the region 4.00-4.81 ppm with a characteristic splitting to ^{77}Se. In the spectra of XIb-XVb a broad singlet is observed for the amino group proton between 4.85 and 7.22 ppm.

Work up of IIIb with RCH_2Hal in the presence of an excess of base leads to an oily reaction product. The only exception is the reaction of IIIb with $ClCH_2CN$ which gives 6-(1-adamantyl)-3-aminoselenopheno[2,3-b]pyridine XIIIb in 70% yield. We were not able to isolate the intermediate 6-(1-adamantyl)-3-amino-2-cyanomethylselenopyridine VIIIb. Treatment of the same IIIb with an equivalent of 10% KOH followed by $ClCH_2CN$ gave a mixture of alkylated (VIIIb) and cyclic (XIIIb) products. This was indicated by the presence in the IR spectrum of the reaction mixture of two nitrile absorption bands at 2225 and 2190 cm^{-1} (for VIIIb) and a group of bands at 3440-3230 cm^{-1} and 1610-1580 cm^{-1} for the stretching and deformation absorption of the amino group in XIIIb. The ratio of VIIIb to XIIIb was 3:1 according to PMR spectroscopic data.

With the aim of studying the stability of IIIb-VIIb and IXb-XVb we have examined their behavior under electron impact when compared with the corresponding sulfur analogs (IIIa-XVa). The stability towards electron impact W_m is quite high amounting to 4-31% for substituted 6-(1-adamantyl)-3-cyano-2-mercapto (Va-Xa) and 6-(1-adamantyl)-3-cyano-2-selenopyridines (Vb-VIIb, IXb, Xb) and to 20-50% for thieno- and selenophenopyridines. As might be expected, the values of W_m for XIa,b-XVa,b exceed those for Va,b-Xa,b by at least 1.5 times. The first fragmentation process for the alkylated mercapto- and selenopyridines is separation of R (or RH) from $M^{+\cdot}$ to form a stable, cyclic, rearranged ion with m/z 283 or 284 for Va-Xa and with m/z 331 or 332 for Vb-VIIb, IXb, and Xb.

(IXa) m/z 327 m/z 284

For substituted thieno (XIa-XVa) or selenophenopyridines (XIb-XVb) the basic fragmentation step is the loss of m/z 57 or 55 ions from $M^{+\cdot}$. This mass corresponds to the empirical formula C_4H_9 and C_4H_7, elimination of which occurs from the adamantyl fragment of the molecule and which is also observed under electron impact dissociation of adamantane [4] and its derivatives [5]. For Va,b and Xa,b a similar process is only found to a small degree and appears only after elimination of R or R–H. For the disulfide (IVa) and diselenide (IVb) the characteristic process is breaking of the S–S or Se–Se bond with subsequent or simultaneous intramolecular rearrangement (and H atom migration) to form the sulfide or selenide cations with m/z 270 and 318, respectively. The difference between IVa and IVb is in the absence of S or S_2 loss in IVa and the presence of Se or Se_2 elimination ion peaks in IVb.

Peaks corresponding to breaking of the C–C bond between the adamantyl and pyridyl units were not observed in the sulfur compounds. At the same time peaks with m/z 135 (adamantyl cation) and m/z 43, 55, 57, 69, 71, etc. (elimination of selenopyridines from the adamantyl fragment) were characteristic of the selenium analogs.

TABLE 1. Substituted 6-(1-Adamantyl)-3-cyano-2-selenopyridines (Vb-VIIb, IXb-XVb) and 6-(1-Adamantyl)-3-aminoselenopheno[2,3-b]pyridines (XIb-XVb)

Compound	Yield, %	mp, °C (solvent)	Found, %				Empirical formula	Yield, %			
			C	H	N	Se		C	H	N	Se
(Vb)	67	117–117.5 (Absolute EtOH)	61,74	6,19	8,59	23,80	$C_{17}H_{20}N_2Se$	61,62	6,08	8,45	23,84
(VIb)	78	95–96 (Absolute EtOH)	59,03	5,76	7,17	19,73	$C_{19}H_{22}N_2O_2Se$	58,61	5,69	7,19	20,29
(VIIb)	48	65–66 (Aqueous EtOH)	59,39	6,50	6,67	19,36	$C_{20}H_{24}N_2O_2Se$	59,55	6,00	6,94	19,58
(IXb)	45	179–180 (Absolute EtOH)	58,14	5,97	10,88	21,23	$C_{18}H_{21}N_3OSe$	57,75	5,65	11,22	21,10
(Xb)	56	135–136 (Absolute EtOH)	66,38	5,73	6,45	18,14	$C_{24}H_{24}N_2OSe$	66,20	6,47	6,43	18,14
(XIb)	71	221—222 (MeOH)	59,08	6,35	6,68	20,01	$C_{19}H_{22}N_2O_2Se$	58,61	5,69	7,19	20,29
(XIIb)	50	223–224 (Absolute EtOH)	60,12	6,46	6,61	19,92	$C_{20}H_{24}N_2O_2Se$	59,55	6,00	6,94	19,58
(XIIIb)	70	272–273 (Absolute EtOH)	60,94	5,70	11,58	20,87	$C_{18}H_{19}N_3Se$	60,66	5,37	11,79	–
(XIVb)	90	292–297 (Glacial AcOH)	58,09	6,09	10,84	19,84	$C_{18}H_{21}N_3OSe$	57,75	5,65	11,22	–
(XVb)	86	147,5–148,5 (Aqueous EtOH)	65,34	5,99	6,12	16,77	$C_{24}H_{24}N_2OSe$	66,20	6,47	6,43	–

TABLE 2. Spectral Characteristics for Vb-XVb

Compound	UV Spectrum, EtOH, λ_{max}, nm (log ε)	IR spectrum (KBr, ν, cm^{-1})			PMR spectrum ($CDCl_3$, δ, ppm; J, Hz)						
		NH_2	CN	CO	H^4 d	H^5 d	JH^4, H^5	γH-Ad	βH-Ad	δH-Ad	other protons
(Vb)	226(4,29), 280(4,06), 323(3,57)		2225		7,83	7,03	8,0	2,10	2,00	1,76	2,56s (CH_3)
(VIb) *	225(4,47), 275(4,18), 315(3,82)		2225	1740	8,13	7,30	8,0	2,06	1,90	1,73	4,13s (CH_2) 3,66s (CH_3)
(VIIb)	226(4,29), 275(4,00), 314(3,66)		2225	1750	7,74	7,10	8,0	2,13	1,97	1,80	4,20 q (CH_2CH_3) 4,08s (CH_2CO) 1,25t (CH_3CH_2)
(VIIIb)			2225, 2190		7,74	7,12	8,0	2,03	1,95	1,80	4,00s (CH_2)
(IXb)	227(3,94), 275(3,62), 313(3,27)	3440–3420	2225	1680	7,78	7,17	8,0	2,14	1,97	1,80	6,66s (NH_2) 5,51s (NH_2) 3,90m (CH_2)
(Xb)	227(4,22), 240(4,19) 275(3,99), 366(3,55)		2215	1690	7,73	7,10	8,0	2,01	1,90	1,74 1,60 J_{AB}=12,5	7,45–8,13 m (Ph) 4,81s (CH_2)
(XIb)	206(4,31), 236(3,96), 291(4,46), 380(3,71)	3420–3180, 1615		1670	8,42	7,41	8,5	2,08	1,98	1,76	7,36 br s (NH_2) 3,76s (CH_3)
(XIIb)	235(4,04), 293(4,50), 377(3,76)	3500–3370, 1610		1680	7,76	7,33	8,5	2,14	2,05	1,80	6,00br s (NH_2) 4,33 q (CH_2CH_3) 1,40 t(CH_3)
(XIIIb)	204(4,25), 227(4,20), 284(4,26), 365(3,48)	3440–3230, 1630	2190		7,80	7,39	8,5	2,15	2,04	1,80	4,84 br s(NH_2)
(XIVb)	207(4,51), 234(4,27), 291(4,64), 375(3,90)	3440–3170, 1600		1650	8,29	7,46	8,5	2,06	1,98	1,76	7,22s (NH_2) 7,13s (NH_2)
(XVb)	319(4,51), 424(4,35)	3500–3200, 1600		1580	7,90	7,36	8,5	2,15	2,05	1,80	7,5–7,85 m (Ph) 7,22 br s (NH_2)

*PMR Spectra of VIb and XIVb in DMSO-d_6.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument for KBr tablets and UV spectra on a Specord UV-VIS instrument using ethanol solvent. PMR spectra were obtained on a Bruker WM-250 (250 MHz) in $CDCl_3$ and referred to TMS. Mass spectra were measured on Varian MAT CH-6 and MAT-311A (Germany) mass spectrometers with direct introduction of the sample into the ion source. The ion chamber temperature was 180°C, ionization intensity 70 eV and emission current 100 microamps. The temperature for sample heating varied with its volatility in the range 80-280°C. For clarity in the text nominal ion masses are given based on the ^{32}S and ^{80}Se isotopes. Ions with intensities less than 5% are excluded (with the exception of molecular and related ions and those mentioned in the discussion). TLC was carried out on Silufol UV-254 plates using acetone–hexane in the ratio 3:5.

Compounds IIIa-XVa were obtained by method [1].

6-(1-Adamantyl)-3-cyanopyridin-2(1H)-selenone (IIIb). Acetic acid (0.68 ml, 12 mmole) was added with stirring over 5 min at ~20°C under argon to a suspension of I (0.92 g, 4 mmole) in EtOH (10 ml) followed by addition of IIb (0.59 g, 4 mmole). After 45 min the precipitate was filtered off and washed with EtOH to give 0.66 g (52%) of IIIb with mp 185-190°C. UV spectrum (ethanol, λ_{max}, nm (log ε)): 222 (4.11), 335 (3.75), 438 (3.08). IR spectrum (KBr, ν, cm^{-1}): 2230 (CN). PMR spectrum ($CDCl_3$, δ, ppm): 1.80 s (6H, δH-Ad), 1.98 s (6H, βH-Ad), 2.13 s (CH, γH-Ad), 6.85 d (1H, H^5), 7.75 d (1H, H^4), $J_{H^4H^5}$= 8 Hz, 8.88 br s (1H, NH). M^+ 318. Found, %: N 8.41. $C_{16}H_{18}N_2Se$. Calculated, %: N 8.83.

Bis [6-(1-Adamantyl)-3-cyano-2-pyridyl]diselenide (IVb). To a suspension of IIIb (0.318 g, 1 mmole) in EtOH (5 ml) was added 10% KOH solution (1.12 ml, 2 mmole) and $K_3Fe(CN)_6$ (0.658 g, 2 mmole) in water (10 ml). The mixture was stirred for 30 min and the precipitated solid filtered off, washed with EtOH, water, dissolved in chloroform, and diluted with hexane. IVb (0.25 g, 80%) has mp 249-255°C (decomp.). UV spectrum (ethanol, λ_{max} nm (log ε)): 224 (4.34), 266 (4.08), 303 (3.77). IR spectrum (KBr, ν, cm^{-1}): 2225 (CN). PMR spectrum ($CDCl_3$, δ, ppm): 1.80 s (6H, δH-Ad), 1.98 s (6H, βH-Ad), 2.13 s (3H, γH-Ad), 6.83 d (1H, H^5), 7.76 d (1H, H^4), $J_{H^4H^5}$ = 8 Hz, M^+ 634. Found, %: C 60.59; H 5.80; N 8.53; Se 24.06. $C_{32}H_{34}N_4Se_2$. Calculated, %: C 60.75; H 5.41; N 8.85; Se 24.97%.

2-Seleno Substituted 6-(1-Adamantyl)-3-cyano-2-selenopyridines (Vb-Xb). To a suspension of IIIb (0.64 g, 2 mmole) in EtOH (10 ml) under argon was added 10% KOH solution (1.12 ml, 2 mmole). The obtained solution of the potassium salt of IIIb was filtered off in a stream of argon and the filtrate added to RCH_2Hal (3 mmole). A small volume of water was added dropwise, the precipitate filtered off, washed with aqueous EtOH, and recrystallized. The data for Vb-Xb is given in Tables 1 and 2.

2-Substituted 6-(1-Adamantyl)-3-aminoselenopheno[2,3-b]pyridines XIb, XIIb, XIVb, XVb. 10% KOH solution (1.68 ml, 3 mmole) was added at 20°C to a suspension of 1 mmole of VIb, VIIb, IXb, or Xb in EtOH (5 ml). After 30 min the precipitate was filtered off, washed with aqueous EtOH, and recrystallized. Data for XIb, XIIb, XIVb and XVb are given in Tables 1 and 2.

6-(1-Adamantyl)-3-aminoselenopheno[2,3-b]pyridine (XIIIb). A 10% solution of KOH (2.24 ml, 4 mmole) was added under argon to a suspension of IIIb (0.64 g, 2 mmole) in EtOH (10 ml). The mixture was filtered in an argon stream and the filtrate added to $ClCH_2CN$ (0.19 ml, 3 mmole). After dilution of the reaction product into water the precipitate was filtered off, washed with aqueous EtOH and recrystallized. Data for XIIIb is given in Tables 1 and 2.

The mass spectra of IIIa,b-VIIa,b, VIIIa, IXa,b-XIa,b, XIIa,b, and XVa,b may be obtained from the authors.

CONCLUSIONS

1. Reaction of the sodium salt of 3-(1-adamantyl)-1-hydroxyprop-1-en-3-one with cyanoselenoacetamide led to the first synthesis of 6-(1-adamantyl)-3-cyanopyridine-2(1H)-selenone.

2. 2-Seleno substituted 6-(1-adamantyl)-3-cyanopyridines have been obtained by alkylation of pyridineselenone with RCH_2HAl. Cyclization in the presence of base gives 2-substituted 6-(1-adamantyl)-3-aminoselenopheno[2,3-b]pyridines.

3. Under electron impact conditions 2-mercapto and 2-seleno substituted 6-(1-adamantyl)-3-cyanopyridines undergo cyclization to the corresponding substituted thieno- and selenopheno-pyridines. The sulfur-containing compounds do not show an ion peak corresponding to separa-

tion of the adamantyl and pyridyl rings, whereas such a process does occur in the case of the selenium analogs.

LITERATURE CITED

1. V. P. Litvinov, E. É. Apenova, Yu. A. Sharanin, V. N. Nesterov, V. E. Shklover, and Yu. T. Struchkov, Izv. Akad. Nauk SSSR, Ser. Khim., 145 (1968).
2. V. P. Litvinov, V. Yu. Mortikov, Yu. A. Sharanin, and A. M. Shestopalov, Synthesis, No. 1, 98 (1985).
3. V. P. Litvinov, E. É. Apenova, Yu. A. Sharanin, and A. M. Shestopalov, Zh. Org. Khim., No. 3, 669 (1985).
4. Z. Dolegsek, S. Hala, V. Hanus, and S. Landa, Collect. Czech. Chem. Commun., 31, 435 (1966).
5. J. Burkhard, J. Janku, V. Kubelka, J. Mitera, and S. Landa, Collect. Czech. Chem. Commun., 31, 1083 (1974).

REACTIONS OF DIAZAPHOSPHOLES WITH PHENYLDIAZOMETHANE

B. A. Arbuzov, É. N. Dianova, R. T. Galiaskarova, and P. P. Chernov

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Diphenyldiazomethane undergoes quantitative addition to the P=C bond of diazaphospholes with the formation of stable phosphirane-containing bicyclic compounds [1-3]. The reaction of 2-phenyl-5-methyl-1,2,3-diazaphosphole with diazomethane proceeds with the separation of nitrogen and the formation of a trimetric adduct of 1:1 composition [4].

In the present communication, the results of the investigation of the reaction of diazaphospholes with phenyldiazomethane are presented; analogies both with Ph_2CN_2 and with CH_2N_2 can be anticipated from this. According to the reactivity, 2-acetyl-5-methyl-1,2,3-diazaphosphole (AMDAP) proved to be far more active than the analogous 2-phenyl-substituted diazaphosphole (PMDAP). While $PhCHN_2$ reacts with the acetyldiazaphosphole at a temperature as low as −15°C, the reaction with the phenyldiazaphosphole proceeds sluggishly at 20°C. This is indicated by the intensive signal of $\delta^{31}P$ at 226 ppm for the initial diazaphosphole in the $\delta^{31}P$ NMR spectrum of the reaction mixture. The weak signals of $\delta^{31}P$ at 65 and −102.47 ppm can indicate the complex course of the reaction. The course of the reaction of AMDAP with $PhCHN_2$ is strongly influenced by the temperature, the order of the mixing, and the proportion of the reagents. A colorless precipitate is formed on the addition of AMDAP to a solution of $PhCHN_2$ in hexane with a 1:1 ratio of the reagents at −15°C. The precipitate is rapidly converted to a sticky mass from which a crystalline product with mp 160-161°C was obtained by treatment with ether and then recrystallization from CCl_4. According to the data of the mass spectrum and the elemental analysis, it is the 1:1 adduct of addition. The formation of the products of the two orientations (I) or (I') is possible in the reaction scheme.

The absence of the νNH band from the IR spectrum of the product and the appearance of a strong band at 3300 cm^{-1} in the spectrum of the crystals with mp 160-161°C can indicate that the Δ'-phosphapyrazoline derivative (I) or (I') formed in the first stage, isomerizes to the Δ^2-phosphapyrazoline derivative (II) or (II'). The PMR spectrum of the crystals with mp 160-161°C has the signals ($CDCl_3$, δ, ppm, J. Hz) $\delta H^1 = 5.05$, $^1J_{PH} = 42.7$; $\delta H^2 = 2.18$, $^4J_{N^1H^2} = 0.7$; $\delta H^3 = 2.32$, $^4J_{PH^3} = 0.9$. In the ^{31}P NMR spectrum, there is one signal, $\delta^{31}P$ = 30 ppm (CH_2Cl_2). The PMR and ^{31}P NMR spectral data indicate that one isomer (II) or (II'), and not two as was the case for diazoacetic ester [5], is formed in the reaction of AMDAP with $PhCHN_2$. The choice in favor of the structure (II) was made by us on the basis of the analogy between the ^{13}C NMR spectra of AMDAP, PMDAP, the chloro- and methoxydiazaphospholines (IV) and (V), and the bicyclic compound (IV) were obtained for the correct assignment of the signals. The spectral parameters are presented in Table 1.

A. M. Butlerov Chemical Institute, Kazan State University.

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