REACTIONS OF OLEFIN OXIDES AND THIIRANES WITH DIALKYLISOTHIOCYANATOARSINES

A. V. Fokin, A. F. Kolomiets,
and G. S. Levskaya

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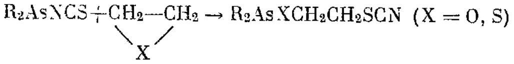
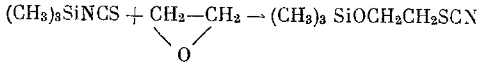
As was established previously [1, 2], the isothiocyanates of secondary arsines react with ethylene oxide (EO) and ethylene sulfide (ES) to give the 2-thiocyanatoethyl esters of arsinous and thioarsinous acids.

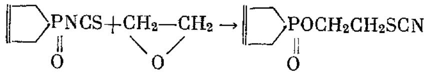


$$R_2AsNCS + CH_2{-}CH_2(X) \rightarrow R_2AsXCH_2CH_2SCN \quad (X = O, S)$$

Similar transformations were also observed in the reaction of EO with organylisothiocyanatosilanes [3, 4] and the isothiocyanates of phosphorus acids [5].



$$(CH_3)_3SiNCS + CH_2{-}CH_2(O) \rightarrow (CH_3)_3\,SiOCH_2CH_2SCN$$



In the process of forming the condensation products the isothiocyanato group of the starting compounds is isomerized to the thiocyanato group in all of the enumerated cases, which from the standpoint of structural chemistry seems anomalous and can be explained only by the peculiarities in the behavior of the isothiocyanato group, attached to a nonmetal atom, and (or) the specifics of the catalysis mechanism. In an attempt to ascertain the reasons for such unusual transformations we made a more detailed study of the reactions of the isothiocyanates of secondary arsines with olefin oxides and thiiranes.

It proved that the dialkylisothiocyanatoarsines and the chromatographically pure olefin oxides (or thiiranes) do not react with each other if the reaction mass is carefully protected from atmospheric moisture. A necessary condition for reaction is the presence of even trace amounts of either hydroxyl-containing or thiol compounds. Dimethylisothiocyanatoarsine condenses with EO at 40-50°C, and with ES at 20-25°, with slight heat evolution, in the presence of 1 mole % of water, alcohol, or n-butylmercaptan. Diphenylisothiocyanatoarsine reacts with somewhat greater difficulty. However, in the presence of catalysts the processes are completed at 60-80° in the case of both EO and ES.

The most efficient catalyst of the discussed reactions is pyridine thiocyanate hydrate, which can be replaced by a mixture of alcohol and pyridine, and by pyridine alone if traces of moisture are present. In the presence of 1 mole % of pyridine thiocyanate hydrate, dimethylisothiocyanatoarsine reacts smoothly with EO even at ~20°, while with ES the reaction must be run under cooling in order to avoid isomerization of the latter. When catalyzed by pyridine thiocyanate hydrate, propylene sulfide and propylene oxide react just as easily as EO and ES. Here the end products are formed in at least 80% yield.

The obtained data make it possible to assume that in the discussed reactions the three-membered ring of the olefin oxides (or thiiranes) is not opened by the dialkylisothiocyanatoarsine molecule, but rather by the thiocyanic acid that is formed in the presence of the hydroxyl-containing or thiol compound. The subsequent exchange reaction of the alkanol thiocyanate or alkanethiol thiocyanate with the dialkylisothiocyanatoarsine gives the end product and HSCN, which enters into the subsequent transformations.

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TABLE 1. 2-Thiocyanatoalkyl Dialkylarsinites and Thioarsinites $R_2AsXCHR'CH_2SCN$

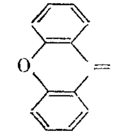
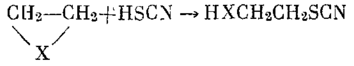
Compound	R	R′	X	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	found, %		Empirical formula	Calculated, %	
								As	S		As	S
(I)	CH_3	H	O	89,6	86 (3)	1,3738	1,5345	36,05	15,15	$C_5H_{10}AsNOS$	36,25	15,46
(II)	CH_3	CH_3	O	88,8	78—80 (2)	1,3044	1,5192	33,90	14,15	$C_6H_{11}AsNOS$	34,0	14,50
(III)	C_4H_9	H	O	82,5	125—127 (3)	1,1312	1,5172	25,59	10,86	$C_{11}H_{22}AsNOS$	25,78	11,01
(IV)	C_6H_5	H	O	97,2	—	1,2667	1,6325	22,47	9,40	$C_{15}H_{14}AsNOS$	22,65	9,67
(V)	CH_3	H	S	92,8	104—105 (1)	1,5298	1,5990	33,80	28,60	$C_5H_{10}AsNS_2$	33,60	28,72
(VI)	CH_3	CH_3	S	76,6	99—101 (3)	1,3981	1,5914	30,91	27,27	$C_6H_{12}AsNS_2$	31,65	27,03
(VII)	C_2H_5	H	S	92,5	119—120 (2)	1,3143	1,5773	30,1	24,9	$C_7H_{14}AsNS_2$	29,88	25,49
(VIII)	C_6H_5	H	S	95,2	—	1,3837	1,6670	20,9	18,4	$C_{15}H_{14}AsNS_2$	21,61	18,44
(IX)	 = R_2	H	S	99,0	mp 114	—	—	21,2	17,5	$C_{14}H_{12}AsNOS_2$	21,46	18,33

TABLE 2. 2-Thiocyanatoalkyl Esters of Carboxylic Acids $RC(O)OCHR'CH_2SCN$

Compound	R	R′	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found, %			Empirical formula	Calculated, %		
							Cl	N	S		Cl	N	S
(X)	CH_3	H	78,3	86—88 (2)	1,1894	1,4770	—	9,85	22,21	$C_5H_7NO_2S$	—	9,66	22,07
(XI)	$ClCH_2$	H	70,4	130—131 (2)	1,3861	1,5128	19,51	8,10	17,91	$C_5H_6ClNO_2S$	19,77	7,79	17,83
(XII)	C_2H_5O	H	60,8	114—115 (3)	1,2102	1,4761	—	8,12	18;39	$C_6H_9NO_3S$	—	7,99	18,28
(XIII)	2,4-$Cl_2C_6H_3OCH_2$	H	94,0	mp 36—37	—	—	23,42	4,64	10,77	$C_{11}H_9Cl_2NO_3S$	23,20	4,58	10,45
(XIV)	CH_3	CH_3	91,7	86—87 (1)	1,1386	1,4708	—	8,74	20,17	$C_6H_9NO_2S$	—	8,81	20,12
(XV)	$ClCH_2$	CH_3	72,4	120—121 (1)	1,2994	1,4970	—	7,17	16,72	$C_6H_8ClNO_2S$	—	7,24	16,56
(XVI)	2,4-$Cl_2C_6H_3OCH_2$	CH_3	87,5	—	1,3620	1,5505	22,14	4,41	10,15	$C_{12}H_{11}Cl_2NO_3S$	22,20	4,37	10,0

$$R_2AsNCS + R'XH \rightleftarrows R_2AsXR' + HSCN$$



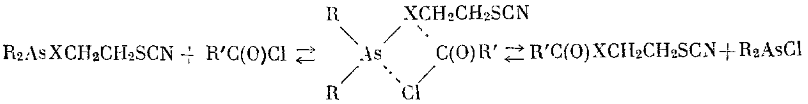
$$R_2AsNCS + HXCH_2CH_2SCN \rightarrow R_2AsXCH_2CH_2SCN + HSCN$$
$$(X = O, S)$$

As a result, the anomalous transformations in the discussed systems are caused by the catalytic nature of the progressing processes. The formation of thiocyanate-containing compounds from isothiocyanatoarsines is the result of two consecutive nucleophilic substitution reactions: that of the NCS^- anion with the C atom of the oxirane or thiirane ring, and then of the alkoxide or mercaptide anion with the arsenic atom.

It is interesting to mention the higher reactivity of the thiiranes when compared with their oxygen analogs in the reactions with dialkylisothiocyanatoarsines. This fact can be explained only by the difference in the energies of forming the transition states that involve the arsenic atom. In this case, the same as in the other reactions of tricoordination arsenic compounds with thiol compounds, there is a substantial energy gain if conditions exist for additional $3\,p_\pi - 4\,d_\pi$ interaction in the reaction complex.

The 2-thiocyanatoalkyl esters of the arsinous and thioarsinous acids formed in the discussed reactions are heat stable compounds. They are converted to secondary haloarsines when treated with acyl halides and phosphoryl halides. The second products of these exchange reactions are the thiocyanatoalkyl esters of carboxylic (or thiocarboxylic) acids or phosphorus acids. The IR spectra of the latter have absorption bands with a maximum at 2185 cm^{-1} ($\nu_{C \equiv N}$), which confirms the thiocyanate structure of these compounds and of the starting thiocyanatoalkyl esters of the arsinous (thioarsinous) acids.

While studying the exchange reactions of the 2-thiocyanatoalkyl esters of the arsinous and thioarsinous acids with acyl halides and phosphoryl halides it was shown that they belong among the typical equilibrium processes, and in many respects resemble the analogous reactions of 2-thiocyanatoethoxytrimethylsilane [4].



Formation of the end products is determined mainly by the polarity of the acyl halide bonds. ^+M Substituents on the carbonyl or phosphoryl group exert a negative effect on the course of the process. In the general case the equilibrium is shifted to the right when reaction is with acyl chlorides under moderate heating, while in the case of ethyl chloroformate and phosphoryl(phosphonyl) chlorides only if the dialkylchloroarsines are removed from the reaction sphere. The esters and amides of chlorophosphates do not react with the 2-thiocyanatoethyl esters of arsinous acids.

It should be mentioned that the esters of arsinous acids are completely inert toward acyl fluorides, with which the 2-thiocyanatoethoxysilanes react most easily [4]. The esters of thioarsinous acids enter into exchange reactions with substantially greater difficulty than their oxygen analogs, and acceptable yields of the end compounds can be obtained only by the efficient removal of the haloarsines from the reaction sphere. The above enumerated characteristics of the studied reactions reflect the general regularity in the course of the exchange reactions of a nonmetal atom, which is manifested in a maximum reaction effect if the condition exists for $(n-1)p_\pi - nd_\pi$ conjugation between the nonmetal atom and the heteroatom in the transition complex.

EXPERIMENTAL METHOD

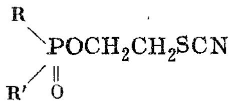
2-Thiocyanatoalkyl Esters of Dialkylarsinous Acids (typical experiment). With stirring, to a mixture of 0.05 mole of the dialkylisothiocyanatoarsine and 0.01 g of pyridine thiocyanate hydrate (or 0.1 ml of alcohol and 0.1 ml of pyridine) was added 0.05 mole of the olefin oxide. The reaction mass was kept at 20° for 12-15 h, heated at 40-50° for 1-2 h, and then fractionally distilled. The 2-thiocyanatoalkyl esters of the dialkylarsinous acids (I)-(IV) were obtained in 82-95% yields.

2-Thiocyanatoalkyl Esters of Dialkylthioarsinous Acids. The indicated compounds were obtained in a similar manner from 0.05 mole of the dialkylisothiocyanatoarsine, 0.1 g of pyridine thiocyanate hydrate, and 0.05 mole of the thiirane, with the only difference that the reactants were stirred under cooling, maintaining the temperature of the reaction mass below −5°. The yields and some of the properties of the obtained compounds (V)-(IX) are given in Table 1.

TABLE 3. 2-Thiocyanatoalkylthiol Esters of Carboxylic Acids $RC(O)SCHR'CH_2SCN$

R	R′	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found, %		Empirical formula	Calculated, %	
						N	S		N	S
CH_3	H	78,0	118—119 (4)	1,2360	1,5436	8,92	39,78	$C_5H_7NOS_2$	8,69	39,78
$ClCH_2$	H	69,1	136—137 (2)	1,3933	1,5670	7,41	32,64	$C_5H_6ClNOS_2$	7,17	32,72
CH_3	CH_3	68,6	107—109 (2)	1,1854	1,5302	7,93	36,69	$C_6H_9NOS_2$	8,00	36,58
2,4-$Cl_2C_6H_3OCH_2$	H	98,8	mp 99	—	—	4,43	20,01	$C_{11}H_9Cl_2NO_2S_2$	4,35	19,89
2-$CH_3OC_6H_4OCH_2$	H	98,5	210—212 (2)	1,3405	1,5900	4,87	22,57	$C_{12}H_{13}NO_3S_2$	4,92	22,62
3,5-$(CH_3)_2$-4-$ClC_6H_2OCH_2$	H	98,0	mp 85	—	—	5,51	20,30	$C_{13}H_{14}ClNO_2S_2$	4,94	20,32

TABLE 4. 2-Thiocyanatoalkyl Esters of Phosphorus Acids



$$\begin{matrix}R\\ & \diagdown\\ & & P(O)OCH_2CH_2SCN\\ & \diagup\\ R'\end{matrix}$$

R	R′	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found, %		Empirical formula	Calculated, %	
						P	S		P	S
C_2H_5O	C_2H_5O	72,3	96—98 (0,1)	1,1905	1,4515	12,4	13,2	$C_7H_{14}NO_4PS$	12,9	13,4
CH_3	-C_4H_9O	78,9	104—105 (0,1)	1,1430	1,4668	12,5	13,5	$C_8H_{16}NO_3PS$	13,1	13,5
n-C_4H_9O	n-C_4H_9O	97,3	—	1,1320	1,4610	9,9	10,5	$C_{11}H_{22}NO_4PS$	10,05	10,8

2-Thiocyanatoalkyl (Alkylthiol) Esters of Carboxylic Acids. a) A mixture of 0.05 mole of the 2-thiocyanatoalkyl ester of dimethylarsinous (or dimethylthioarsinous) acid and 0.075-0.1 mole of the carboxylic acid chloride was heated at 60-80° for 1-3 h, the unreacted acyl chloride and formed dimethylchloroarsine were removed in the vacuum of a water-jet pump, and the residue was fractionally distilled at 1-3 mm of Hg. The yields and properties of the obtained compounds (X), (XI), (XIV), and (XV) are given in Table 2.

b) A mixture of 0.05 mole of the carboxylic acid chloride and 0.05 mole of the 2-thiocyanatoalkyl ester of dimethylarsinous or dimethylthioarsinous acid was heated at 40-60° and a residual pressure of 50-60 mm Hg of until the calculated amount of dimethylchloroarsine was evolved. The residue was fractionally distilled in vacuo at 1-3 mm or else it was recrystallized to give the product in 60-95% yield. The compounds obtained by this method are given in Tables 2 [(XII), (XIII), (XVI)] and 3.

The 2-Thiocyanatoethyl Esters of the Phosphorus Acids were obtained under the same conditions from 0.05 mole of the chlorophosphate (or chlorophosphonate) and 0.05 mole of 2-thiocyanatoethoxydimethylarsine. The obtained results are given in Table 4.

CONCLUSIONS

1. A study was made of the reactions of dialkylisothiocyanatoarsines with α-oxides and thiiranes. A mechanism was proposed for the formation of the 2-thiocyanatoalkyl esters of arsinous (thioarsinous) acids.

2. Some characteristics of the exchange reactions of the 2-thiocyanatoalkyl esters of arsinous and thioarsinous acids with acyl halides and phosphoryl halides were established.

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