spect to the sulfur atom) side. After the formation of a carbonium ion, one should observe attack by the nucleophile from the side opposite to the polarized molecule or cation, but the sulfur atom with an unshared pair of electrons directed toward the double bond is located there in a favorable position. The sulfur atom acts as a nucleophile and closes the ring to give a sulfonium ion with the positive charge delocalized over the molecule. In this case the double bond and the sulfur atom draw close together; this is possible owing to the flexibility of the macroring.

In conclusion, we thank G. A. Tolstikov and N. N. Novitskaya for providing us with samples for this research and N. S. Zefirov for his discussion of the results.

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SYNTHESIS OF HALO DERIVATIVES OF 2-SELENAADAMANTANE*

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The corresponding halo derivatives of 2-selenaadamantane were obtained by reaction of bicyclonona-3,7-diene with selenium tetrahalides. The structures of the reaction products were confirmed by the results of analysis and PMR and IR spectral data.

One of the most widely used methods for the synthesis of heteroadamantanes is cyclization of bicyclo[3.3.1]nona-2,6-diene (I) and its derivatives [2]. Tetrachlorothiaselenaadamantane, one of the few polycyclic compounds that contain selenium in the ring, was obtained [3] via this general scheme from 2,6-dichlorothiabicyclo[3.3.1]nona-3,7-diene.

Considering the high tendency of selenium tetrahalides to undergo addition to multiple bonds [4], we decided to use this type of reaction for the synthesis of selenaadamantanes. By varying the reaction conditions and the ratio and order of addition of the reagents we found conditions under which primarily tetrabromoselenaadamantane (IIa) is formed from selenium tetrabromide and diolefin I. The composition and structure of the product were confirmed by the results of elementary analysis and the spectral characteristics. The reaction of selenium tetrachloride with diene I under the same mild conditions leads to the formation of 2,2,4,8-tetrachloro-2-selenaadamantane (IIb). The most likely process in the formation of the selenaadamantanes is transannular addition of selenium tetrahalide to the double bonds of diolefin I. The choice of adamantane structure II from the other possible structures was made on the basis of the following considerations. First, one should immediately exclude from consideration the products of intermolecular addition, one of which — bis(3-chlorobicyclo[3.3.1]non-6-en-2-yl)selenium dichloride — we obtained especially for comparison. In contrast to selenaadamantanes IIa and IIb, IV contains multiple bonds that are readily detected in the PMR spectrum. Second, alternative structure V is also excluded, since the

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TABLE 1. Constants, Spectral Characteristics, and Yields of Selenaadamantanes IIa,b–IIIa,b

Compound	X	mp, °C	R_f	Found, %			Empirical formula	Calc., %			PMR spectrum,[a] δ					ν_{C-Se}, cm⁻¹	Yield, %
				C	H	Hal		C	H	Hal	9-H,10-H (4H)	6-H (2H)	5-H,7-H (2H)	1-H,3-H 2H	4-H,8-H (2H)		
IIa	Br	169—170[b]	0,63[c]	20,7	2,3	61,4	$C_9H_{12}Br_4Se$	20,8	2,3	61,6	2,38	2,70	3,03	3,23	5,36	720	49
IIb	Cl	133—134[d]	0,37[e]	31,9	3,9	41,9	$C_9H_{12}Cl_4Se$	31,7	3,6	41,6	2,21	2,53	2,93	3,08	5,05	755	33
IIIa	Br	135[f]	0,78[g]	28,3	3,4	44,3	$C_9H_{12}Br_2Se$	28,3	3,4	44,6	2,35	2.67	3,03	3,23	5,30	730	75
IIIb	Cl	154[f]	0,28[e]	39,9	4,3	26,4	$C_9H_{12}Cl_2Se$	40,0	4,5	26,3	2,26	2,54	2,90	3,08	5,05	750	55

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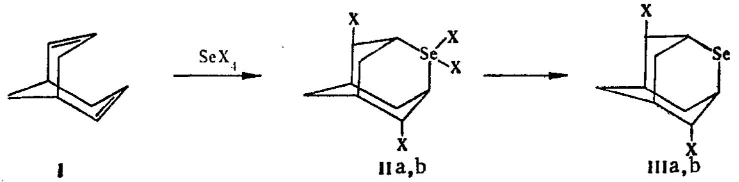
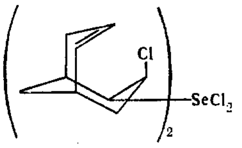
a) The chemical shifts of the centers of the multiplets are presented. b) Purified by sublimation in vacuo at 130°C (2 mm). c) In an acetonitrile–benzene system (2:1). d) From acetonitrile. e) In an ether–benzene system (2:1). f) From acetone. g) In a hexane–benzene system (2:1).

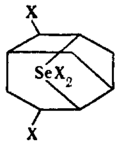
protons in the α position relative to the selenium atom in it are nonequivalent, which could have been readily observed in the PMR spectrum; in fact, these protons (1-H and 3-H) are equivalent (see Table 1) and their position (δ 3.23 ppm) is in good agreement with the data in [3].



I IIa,b IIIa,b



IV



V

II, III a X=Br; b X=Cl

In regard to the orientation of the halogen atoms, by virtue of the trans stereospecificity of electrophilic addition [3, 5] to diene I derivatives it can be assumed that in IIa,b they are di-exo-oriented with respect to the selenium atom.

The halogen atoms in the 2 position of IIa,b are readily eliminated in the absence of a base (see [1, 6] for comparison) by refluxing in acetone. The resulting dihaloselenaadamantanes IIIa,b have IR and PMR spectra that are practically identical to the spectra of IIa,b; this serves as a convincing confirmation of their structures.

EXPERIMENTAL

The course of the reactions and the individuality of the substances were monitored by thin-layer chromatography (TLC) on activity II aluminum oxide. The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer. The PMR spectra of carbon tetrachloride solutions of the compounds were recorded with a Tesla BS-487A spectrometer (80 MHz) with tetramethylsilane as the internal standard.

2,2,4,8-Tetrahalo-2-selenaadamantanes (IIa,b). A 0.01-mole sample of selenium tetrahalide was added with stirring and cooling to a solution of 0.01 mole of bicyclo[3.3.1]nona-2,6-diene in 100 ml of ether (the selenium tetrahalide was prepared from selenium dioxide and the hydrohalic acid). The resulting precipitate was removed by filtration and dried in a vacuum desiccator.

4,8-Dihalo-2-selenaadamantanes (IIIa,b). A solution of 0.002 mole of IIa or IIb in 15 ml of acetone was refluxed for 30 min, after which the solvent was removed by vacuum evaporation, and the crystals were removed by filtration, dried in a vacuum desiccator, and purified by recrystallization.

Bis(3-chlorobicyclo[3.3.1]non-6-en-2-yl)selenium Dichloride (IV). A 1.1-g (0.005 mole) sample of tetrachloroselenium was added with stirring to a solution of 1.2 g (0.01 mole) of bicyclo[3.3.1]nona-2,6-diene in 50 ml of ether, after which the ether layer was separated and dried over anhydrous calcium chloride. The solvent was removed in vacuo to give 1.1 g (47.8%) of IV with mp 106° (from acetonitrile). PMR spectrum: 1.30 (4H, t, J = 3 Hz, 9-H, 9'-H), 1.57 (4H, m, 4-H, 4'-H), 2.28 (4H, m, 8-H, 8'-H), 2.44 (2H, m, 5-H, 5'-H), 2.60 (2H, m, 1-H, 1'-H), 3.02 (2H, t, J = 2 Hz, 2-H, 2'-H), 3.17 (2H, m, 7-H, 7'-H), 3.78 (2H, q, J = 3.5 Hz, 6-H, 6'-H), 5.12 (2H, m, 7-H, 7'-H). Found, %: C 46.6; H 5.2. $C_{18}H_{24}Cl_4Se$. Calculated, %: C 46.8; H 5.2.

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FREE-RADICAL ADDITION OF ALKANETHIOLS TO 1-VINYLPYRROLES

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In the presence of 2,2'-azobisisobutyronitrile or in the absence of an initiator alkanethiols add to 1-vinylpyrroles exclusively counter to Markovnikov's rule to give 1-(2'-alkylthioethyl)pyrroles (in yields up to 94%).

A new reaction of acetylene with ketoximes, which made it possible in one step to synthesize 1-vinylpyrroles with a variety of substituents in the 4 and 5 positions, was recently discovered [1, 2]. In the present research we investigated the addition of alkanethiols to these 1-vinylpyrroles in the presence and absence of free-radical initiators. The literature contains rather contradictory data on the order of addition of hydrogen sulfide and mercaptans to N-vinyl compounds. It is known that cyclic enamines [3, 4] add mercaptans in accordance with Markovnikov's rule (the thiiyl radical is directed to the α-carbon atom of the vinyl group) under the influence of radical initiators and under noncatalytic conditions. There are data [5] that indicate that hydrogen sulfide and thiols add to N-vinyl compounds of the pyrrole series counter to Markovnikov's rule. Thus β-addition products were obtained [6, 7] when hydrogen sulfide was passed through a heated alcoholic alkali solution of N-vinylcarbazole and also when heated N-vinylindole containing potassium metal was treated with hydrogen sulfide. Refluxing N-vinylcarbazole with thiocresol and 2-mercaptoanthraquinone without a catalyst led to β-addition products [6, 7]. The free-radical addition of thiols to N-vinylindole and N-vinylimidazole under the influence of 2,2'-azobisisobutyronitrile (AIBN) proceeds with the formation of a mixture containing α- and β-addition products [8]. According to the data in [8], thiols do not add to N-vinylindole in the absence of initiators.

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