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PREPARATION OF 1-AMINOMETHYLENEMERCAPTO DERIVATIVES OF 2,4,6,8-TETRATHIAADAMANTANE AND ADAMANTANE

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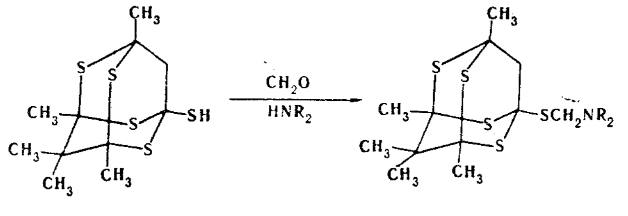
UDC 547.597'547.842:542.953.2

1-Aminomethylenemercapto derivatives of 3,5,7,9,9-pentamethyl-2,4,6,8-tetrathiaadamantane and adamantane were obtained by aminomethylation of 3,5,7,9,9-pentamethyl-2,4,6,8-tetrathiaadamantane-1-thiol and adamantane-1-thiol.

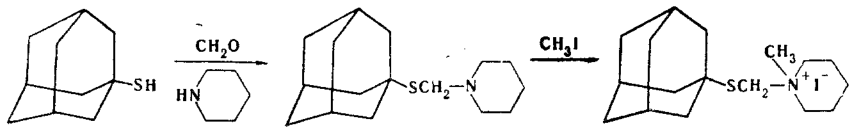
Amino derivatives of adamantane display physiological activity, including antivirus action [1]. In this connection, the amino derivatives of hetero-analogs of adamantane seem of interest.

In the present paper we describe a number of 1-aminomethylenemercapto derivatives obtained by aminomethylation of 3,5,7,9,9-pentamethyl-2,4,6,8-tetrathiaadamantane-1-thiol (I) and adamantane-1-thiol (II). The hydrogen atom in the SH group of these thiols was found to be sufficiently labile to undergo the Mannich reaction with formaldehyde and secondary amines (dimethylamine, diethylamine, piperidine, hexamethyleneimine, morpholine, and piperazine). 1-Aminomethylenemercapto derivatives of 2,4,6,8-tetrathiaadamantane (III-VII) and of adamantane (IX-XII) are formed in good yields, and good yields of bis-(adamantylmethylenemercapto) derivatives of piperazine (VIII and XIII) are also obtained in reaction with piperazine (Table 1).



I

III, IV



II

XII

XII a

III $R = CH_3$; IV $R = C_2H_5$

The PMR spectra of 2,4,6,8-tetrathiaadamantane derivatives III-VIII contain a singlet at 4.0-4.55 ppm, which is characteristic for the SCH_2N grouping; signals of protons of CH_3 groups were observed at 1.27-1.49 ppm, and the singlet at 1.97-2.24 ppm corresponded to the

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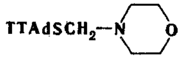
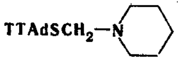
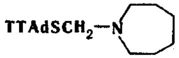
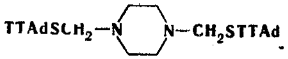
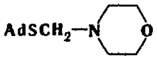
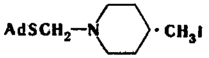
TABLE 1. Characteristics of the Synthesized Compounds

	Compound[a]	mp, °C	Empirical formula	Found, %					Calc. %					Yield, %
				C	H	I	N	S	C	H	I	N	S	
III	$TTAdSCH_2N(CH_3)_2$	104—105	$C_{14}H_{25}NS_5$	45,5	6,7	—	3,9	44,5	45,7	6,8	—	3,8	43,7	93
IV	$TTAdSCH_2N(C_2H_5)_2$	46—47[b]	$C_{16}H_{29}NS_5$	48,2	7,3	—	3,0	40,6	48,6	7,4	—	3,5	40,5	96
V		99—101	$C_{16}H_{27}NOS_5$	46,8	6,6	—	3,0	40,1	46,9	6,6	—	3,4	39,1	56
VI		150—151	$C_{17}H_{29}NS_5$	50,4	7,4	—	3,2	39,4	50,1	7,1	—	3,4	39,3	93
VII		90—93	$C_{18}H_{35}NS_5$	51,2	7,6	—	3,2	37,9	51,3	7,4	—	3,3	38,0	35
VIII		196—200	$C_{28}H_{46}N_2S_{10}$	46,3	6,3	—	3,7	43,5	46,0	6,3	—	3,8	43,8	83
IXa	$AdSCH_2N(CH_3)_2 \cdot CH_3I$	215—217	$C_{13}H_{23}NS \cdot CH_3I$	45,7	7,1	34,3	3,5	8,5	45,8	7,1	34,6	3,8	8,7	62[c]
Xa	$AdSCH_2N(C_2H_5)_2 \cdot CH_3I$	135—138	$C_{15}H_{27}NS \cdot CH_3I$	47,5	7,6	31,4	3,3	8,1	48,6	7,6	32,1	3,5	8,1	98[c]
XI		42—44	$C_{15}H_{25}NOS$	67,6	9,6	—	5,1	11,6	67,7	0,4	—	5,2	12,0	98
XIIa		145—149	$C_{16}H_{27}NS \cdot CH_3I$	50,0	7,4	30,6	3,2	12,1	50,1	7.4	31,2	3,4	12,0	98[c]
XIII		186—188	$C_{26}H_{42}N_2S_2$	69,4	9,4	—	6,1	15,0	70,0	9,5	—	6,5	14,4	28

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[a] Symbols: Ad = 1-adamantyl and TTAd = 1-(3,5,7,9,9-pentamethyl-2,4,6,8-tetrathiaadamantyl).
[b] Without purification because of decomposition during recrystallization.
[c] Presented for IX, X, and XII, respectively.

methyl bridge in the ring. The singlet of the SCH_2N protons appeared in the spectra of adamantane derivatives IX-XIII at 3.6-3.9 ppm, and the signals of the protons of the adamantane ring were found at 1.25-1.95 ppm. In addition, the spectra contained the corresponding signals of the protons of the amine component. The band at 2520 cm^{-1} (2580 cm^{-1} for adamantane derivatives) that is characteristic for the SH group of the starting thiols was absent in the IR spectra of the 2,4,6,8-tetrathiaadamantane and adamantane derivatives.

Compounds IX, X, and XII, which are viscous liquids, were characterized in the form of their methiodides.

EXPERIMENTAL

The PMR spectra of CCl_4 solutions of the compounds ($CHCl_3$ solutions of VII and XIII) were obtained with a Varian -A-56-60A spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer.

3,5,7,9,9-Pentamethyl-2,4,6,8-tetrathiaadamantane-1-thiol (I). This compound, with mp 160-161°, was obtained in 30% yield by condensation of 3,3-dimethylpentane-2,4-dione [2] with CH_3COSH in the presence of $ZnCl_2$ by the method in [3].

Adamantane-1-thiol (II). This compound, with mp 110-112°, was obtained in 58% from bromoadamantane through the isothiuronium salt by the method in [4].

N-[(3,5,7,9,9-Pentamethyl-2,4,6,8-tetrathia-1-adamantylmercapto)methyl]dimethylamine (III). A 0.3-ml sample of dimethylamine was added dropwise with stirring to 0.62 g of thiol I in 10 ml of alcohol, after which 0.3 ml of 37% CH_2O was added dropwise. The mixture was refluxed for 3 h, after which the alcohol was evaporated, and the product was purified by recrystallization from alcohol.

Compounds IV-VII were similarly obtained by condensation of thiol I with $(C_2H_5)_2NH$, morpholine, piperidine, and hexamethyleneimine, respectively.

N,N'-Bis[(3,5,7,9,9-pentamethyl-2,4,6,8-tetrathiaadamantylmercapto)methyl]piperazine (VIII). A 0.11-g sample of piperazine hydrate was added with stirring to 0.31 g of thiol I in 10 ml of alcohol, after which 0.15 ml of 37% CH_2O was added dropwise. The mixture was refluxed for 3 h, after which the alcohol was evaporated, and the VIII was purified by recrystallization from benzene.

N-(1-Adamantylmercaptomethyl)dimethylamine Methiodide (IXa). A 0.3-ml sample of dimethylamine was added dropwise with stirring to 0.34 g of thiol II in 10 ml of alcohol, after which 0.3 ml of 37% CH_2O was added dropwise. The mixture was refluxed for 3 h, after which the alcohol was evaporated. The liquid IX was heated gently with excess CH_3I, after which the solvent was evaporated to give IXa, which was purified by recrystallization from alcohol.

Compound XI was obtained by condensation of II with CH_2O and morpholine, as in the preparation of IX, whereas Xa and XIIa were obtained by condensation with dimethylamine and piperidine, respectively. The methiodides were obtained in quantitative yields.

N,N'-Bis(1-adamantylmercaptomethyl)piperazine (XIII). This compound was obtained from 0.34 g of thiol II, 0.21 g of piperazine hydrate, and 0.3 ml of CH_2O, as in the preparation of VIII.

The yields and properties of the compounds obtained in this study are presented in Table 1.

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