BRIEF COMMUNICATIONS

UDC 547.79/78 + 542.959

HETEROCYCLIC DERIVATIVES OF DIMETHYL SULFIDE

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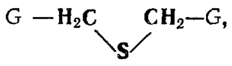
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 5, pp. 792-793, 1965

Bis(2-thiazolylmethyl)- and bis(5-tetrazolylmethyl)-sulfides are synthesized. With a view to studying their physiological action, it was of interest to prepare dimethylsulfides, with a hydrogen atom in each methyl group replaced by a heterocyclic group. The present communication describes the synthesis of compounds where the heterocyclic groups are thiazolyl (Ia, b) and tetrazolyl (Ic).

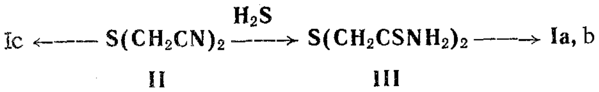


$$\mathrm{G{-}H_2C}\underset{\mathrm{S}}{\diagdown\diagup}\mathrm{CH_2{-}G},$$

where G is 2-[(4-methyl) thiazolyl](Ia), 2-[(4-phenyl) thiazolyl](Ib), or 5-tetrazolyl (Ic).

The starting materials for these syntheses were di(acetonitrile)-sulfide (II), and di(thioacetamido) sulfide (III) prepared from it. According to [1], an inconsiderable yield (~ 10%) of the latter compound can be prepared from chloroacetonitrile and hydrogen sulfide.

Reaction of thioamide III with chloroacetone and ω-bromoacetophenone gives respectively compounds Ia and Ib. Bis(5-tetrazolylmethyl) sulfide (Ic) is prepared by reacting bis(acetonitrile) sulfide (II) with sodium azide:



$$\mathrm{Ic} \longleftarrow \underset{\mathrm{II}}{\mathrm{S(CH_2CN)_2}} \xrightarrow{\mathrm{H_2S}} \underset{\mathrm{III}}{\mathrm{S(CH_2CSNH_2)_2}} \longrightarrow \mathrm{Ia, b}$$

Experimental

Bis(acetonitrile) sulfide (II). Prepared as described in [1]. Yield 23%, mp 43-44° (from methanol). The literature gives [1] 45.5-46.5°.

Bis(thioacetamido) sulfide (III). 1.12 g (0.01 mole) II was dissolved in 5 ml pyridine, 2 ml triethylamine added, and hydrogen sulfide passed in for 3-4 hr. The reaction products were left overnight, then poured into cold water. The oil which separated quickly crystallized, yield 1.25 g (70%), recrystallized from water, heated to 60-70° with the addition of activated charcoal (water added to the thioamide). Coarse pale yellow flat prisms, up to 3 cm long, mp 124-125° (the literature gives 124°).

Bis [2-(4-methyl) thiazolylmethyl] sulfide (Ia). 1 ml (0.01 mole) freshly-distilled chloroacetone was added to 0.9 g (0.005 mole) III, and the mixture carefully heated on a water bath until reaction began, with evolution of heat. After cooling, a precipitate of hydrochloride of Ia separated from the dark brown liquid, yield 1.35 g (80%). It was recrystallized by dissolving in absolute alcohol, and precipitating with dry ether. Rhombic prisms, mp 205-206° (decomp). Found: C 36.17; H 4.39; N 8.54; Cl 21.14%. Calculated for $C_{10}H_{12}N_2S_3 \cdot 2HCl$: C 36.47; H 4.28; N 8.51; Cl 21.53%.

Base Ia was obtained by making an aqueous solution of the hydrochloride alkaline with ammonia (pH 10-11). On cooling, the oil which separated out was recrystallized, yield 92%, mp 68-69° (from 1 : 1 aqueous alcohol). Sparingly soluble in water. Dissolved in alcohol, benzene, acetone, ether. Found: N 11.33%. Calculated for $C_{10}H_{12}N_2S_3$: N 10.92%. Picrate mp 121-122° (from alcohol). Mixed mp with picric acid 105-106°. Found: C 36.67; H 2.65; N 16.03; S 13.48%. Calculated for $C_{10}H_{12}N_2S_3 \cdot 2C_6H_3N_3O_7$: C 36.97; H 2.54; N 15.67; S 13.46%.

Bis [2-(4-phenyl) thiazolylmethyl] sulfide (Ib). A mixture of 1.8 g (0.01 mole) II and 3.98 g (0.02 mole) bromoacetophenone was heated on a water bath for 10-15 min. The reaction products were dissolved in alcohol, and made alkaline with ammonia (pH 8-9). Prisms were precipitated, yield 5.3 g (98%), mp 80-81° (from alcohol); Insoluble in water. Found: C 63.26; H 4.14; N 7.22; S 25.06%. Calculated for $C_{20}H_{16}N_2S_3$: C 63.13; H 4.24; N 7.36; S 25.27%.

Bis (5-tetrazolylmethyl) sulfide (Ic). A mixture of 1.7 g (0.015 mole) III, 1.95 g (0.03 mole) sodium azide, and 1.60 g ammonium chloride in 20 ml dimethylformamide was heated on a glycerine bath at 120° (7 hr). The sodium chloride which separated was filtered off, the solvent distilled off, and the resinous residue dissolved in acetone, with addition of active charcoal. Yield 1 g (33%), colorless rhombic plates mp 214-215° (from alcohol). Soluble on heating in water, insoluble in benzene, chloroform, dioxane. Found: C 24.90; H. 3.32; N 15.64; S 15.59%. Calculated for $C_4H_6N_8S$: C 24.24; H 3.05; N 15.56; S 16.17%.

In the IR spectrum (IKS-14, NaCl prism) a strong narrow absorption band at 1076 cm^{-1} was observed, corresponding to vibration of the tetrazole ring.

REFERENCES

1. N. Zweigbergk, Ber., 45, 3337, 1912.
2. J. Johnson, J. H. Thomas, and H. Schaffer, J. Am. Chem. Soc., 80, 699, 1955.

UDC 547.712.2

HETEROATOM DERIVATIVES OF AZIRIDINE.
II. Reaction of N, N'-Diaziridinylsulfide, -disulfide, -sulfoxide, and -sulfone with Methyl Iodide*

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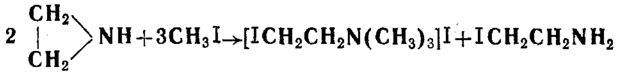
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 5, pp. 794-796, 1965

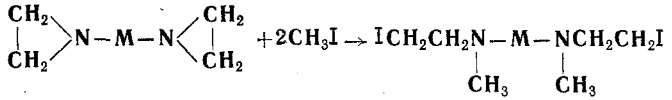
Reaction of N, N-diaziridinylsulfide, -disulfide, -sulfoxide, and -sulfone with methyl iodide, which takes place with opening of the ethyleneimine ring to give respectively N, N'-dimethylbis(β-iodoethylamino) sulfide, -disulfide, -sulfoxide, and sulfone, is investigated. The first three compounds are obtained in up to 70% yield, while the yields of the rest are inconsiderable. The properties of these substances are investigated, and their IR spectra determined. The higher alkyl iodides do not react similarly.

Ethyleneimine reacts very readily with methyl iodide, with opening of the aziridine ring, and formation of trimethyl-β-iodoethylammonium iodide [3]:



$$2\,(CH_2)_2NH + 3CH_3I \rightarrow [ICH_2CH_2N(CH_3)_3]I + ICH_2CH_2NH_2$$

The present investigation of the reaction of methyl iodide with the previously described [1, 4] N, N'-diaziridinylsulfide (I), -disulfide (II), -sulfoxide (III), and -sulfone (IV) showed that in all cases enlargement of the ethyleneimine ring occurred. However, unlike the case of ethyleneimine, only one molecule of CH_3I added to each aziridine ring of I-IV. Reaction leads to formation of the corresponding N, N'-dimethylbis (β-iodoethylamino) derivatives V-VIII [2]:



$$(CH_2)_2N{-}M{-}N(CH_2)_2 + 2CH_3I \rightarrow ICH_2CH_2N(CH_3){-}M{-}N(CH_3)CH_2CH_2I$$

I–IV V–VIII

$M = S(I,V);\ S_2(II,VI);\ SO(III,VII);\ SO_2(IV,VIII)$

The yields of addition products V-VII reach 70%, based on the starting ethyleneimine, and only VIII is formed in inconsiderable amount.

N, N'-dimethylbis (β-iodoethylamino) sulfide (V), -disulfide (VI), -sulfoxide (VII), and -sulfone (VIII) are rather stable, slightly yellow crystalline compounds, soluble in alcohol, acetone, and chloroform. Compounds VII and VIII are soluble in water.

The IR spectra of V-VIII (see Figure) support the structure put forward for them. The spectra show a new band characteristic of the C–I bond (490 cm^{-1}), and the characteristic bands of the ethyleneimine ring (1475, 3075 cm^{-1} and others) are absent. Insofar as, in consequence, a diaziridone structure for the products of addition of MeI to ethylene-

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* For Part I see [1] and [2]. Presented at the Conference on Heterocyclic Rings in Organic Synthesis, Kiev, 1964.