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Reactions of Diorganyl Disulfides with Dihaloalkanes in Basic Reductive Media. Synthesis of Bis(organylthio)alkanes

O. V. Alekminskaya, N. V. Russavskaya, N. A. Korchevin, and E. N. Deryagina

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

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Abstract—A convenient preparative synthesis of bis(organylthio)alkanes was developed. It is based on alkylation with dihaloalkanes of solutions of diorganyl disulfides in the basic reductive system hydrazine hydrate–alkali. The generation of organylthiolate anions from disulfides and the subsequent reaction of the anions with dihaloalkanes are performed in one reaction vessel without isolation of intermediate alkali metal thiolates. At the same time, the reactions of diphenyl or dithienyl disulfides with dihaloalkanes result in substitution with the thiolate anions of only one halogen atom to give the corresponding unsymmetrical sulfides. In certain cases in the presence of excess alkali the latter sulfides are dehalogenated to form alkyl vinyl sulfides.

Bis(organylthio)alkanes of the general formula $RS(CH_2)_nSR$ (**I**), which comprise two sulfide sulfur atoms, can serve as complex-forming and flotation agents, as well as metal corrosion inhibitors. By varying *n* in these compounds, thus varying the distance between the ligand centers, one can attain geometric characteristics ideal for coordination or adsorption. Quite recently Smith *et al.* [1, 2] showed that compounds **I** effectively catalyze selective chlorination of certain aromatic compounds [1, 2].

The known methods of synthesis of compounds **I** are based either on the reaction of thiols with formaldehyde (only for $n = 1$) or on the reaction of thiols or dithiols with organyl halides [3]. The potential of these methods is much restricted by the use of thiols and dithiols as starting materials, since they are hardly accessible and, moreover, highly volatile and unpleasantly odored compounds. Thiols and dithiols are readily oxidized to disulfides, and the latter are inactive in the above reactions.

However, thiols or the corresponding thiolates are easy to generate *in situ* by reductive cleavage of the S–S bond in disulfides [4]. Diorganyl disulfides are less volatile than thiols and more stable in handling and use. Moreover, they are fairly accessible reagents. They are synthesized by alkylation of sulfur in basic reductive media [5].

We found that bis(organylthio)alkanes (**I**) are formed by alkylation with dihaloalkanes of solutions of diorganyl disulfides in the basic reductive system hydrazine hydrate–alkali. Therewith, the S–S bond is reduced to give organylthiolate anions which then react with dielectrophiles (previously we used this approach to synthesize unsymmetrical sulfides from disulfides [4]).

$$2R_2S_2 + N_2H_4 \cdot H_2O + 4MOH \longrightarrow 4RSM + N_2 + 5H_2O,$$

$$2RSM + X(CH_2)_nX \longrightarrow \underset{\textbf{Ia–Ik}}{RS(CH_2)_nSR}, \qquad (1)$$

For R, M, X, Y, and *n*, see Table 1.

The generation from disulfides of organylthiolate anions and their subsequent reaction with dihaloalkanes by scheme (1) are accomplished in one reaction vessel without isolation of intermediate alkali metal thiolates. The conditions of synthesis and the yields of bis-sulfides **I** are listed in Table 1. As seen from the table, to improve the yields of compounds **I** requires that the basic reductive activity of the medium be sufficiently high (large excesses of alkali and hydrazine hydrate).

The example of the reaction of 1,2-dichloroethane with diethyl disulfide was used to show that even with a tenfold excess of dichloride the reaction involves no substitution of one of the chlorine atoms by the thiolate anion to give an unsymmetrical sulfide (1-ethylthio-2-chloroethane). The GC–MS data rule out formation of unsymmetrical sulfides in reactions (1) with dialkyl disulfides (R = Me, Et, Pr).

At the same time, unsymmetrical sulfides **II** are readily formed on the reactions of diphenyl or dithienyl disulfides with dihaloalkanes by scheme (2):

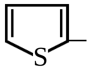
Table 1. Conditions of synthesis and yields of bis(organylthio)alkanes **I**

Comp. no.	R	M	*n*	X, Y	$R_2S_2:MOH:N_2H_4\cdot H_2O:X(CH_2)_nY$ molar ratio	Yield, %
Ia	Et	Na	1	Cl	0.05 : 0.2 : 0.7 : 0.05	77
Ib	Pr	Na	1	Cl	0.05 : 0.12 : 0.4 : 0.05	58
Ic	Me	Na	2	Cl	0.05 : 0.2 : 0.5 : 0.1	85
Ic	Me	Na	2	Cl	0.05 : 0.6 : 0.5 : 0.1	70[a]
Ic	Me	Na	2	Cl	0.05 : 0.1 : 0.5 : 0.1	38
Ic	Me	K	2	Cl	0.05 : 0.15 : 0.5 : 0.1	82
Id	Et	Na	2	Cl	0.05 : 0.22 : 0.8 : 0.05	74
Id	Et	Na	2	Cl	0.05 : 0.22 : 0.4 : 0.05	52[b]
Id	Et	Na	2	Cl	0.05 : 0.1 : 0.5 : 0.05	40
Id	Et	K	2	Cl	0.05 : 0.1 : 0.5 : 0.05	52
Id	Et	Na	2	Cl	0.05 : 0.2 : 0.8 : 0.5	78
Ie	Pr	Na	2	Cl	0.1 : 0.22 : 0.8 : 0.1	70
If	Ph	Na	2	Cl	0.009 : 0.018 : 0.1 : 0.009	66
If	Ph	Na	2	Br	0.009 : 0.018 : 0.1 : 0.009	73
If	Ph	Na	2	Cl	0.014 : 0.028 : 0.2 : 0.018	25[c]
Ig	C_4H_3S	Na	2	Cl	0.006 : 0.012 : 0.2 : 0.006	6[d]
Ih	8-Quinolyl	K	2	Cl	0.01 : 0.022 : 0.3 : 0.01	20[e]
Ii	Et	Na	3	Cl, Br	0.05 : 0.22 : 0.5 : 0.05	84
Ii	Et	Na	3	Cl, Br	0.05 : 1.0 : 0.8 : 0.1	80
Ii	Et	Na	3	Cl, Br	0.05 : 0.1 : 0.5 : 0.05	41
Ij	Et	Na	4	Br	0.05 : 0.22 : 0.7 : 0.1	76
Ij	Et	Na	4	Br	0.05 : 0.22 : 0.3 : 0.1	48[b]
Ik	Et	Na	5	Br	0.05 : 0.23 : 0.8 : 0.1	68

[a] Simultaneously $CH_3SCH=CH_2$ (**IIIa**) is formed (yield 8%). [b] Hydrazine hydrate was diluted with water (1 : 1 by volume). [c] β-Chloroethyl phenyl sulfide (**IIa**) is formed (yield 68%). [d] The major reaction product is β-chloroethyl 2-thienyl sulfide (**IIb**) (yield 85%). [e] 8-Quinolyl vinyl sulfide (**IIIb**) is formed (yield 31%). With sodium 8-quinolylthiolate, the yields of compounds **Ih** and **IIIb** are 32 and 18%.

$$2R_2S_2 + N_2H_4\cdot H_2O + 4MOH \longrightarrow 4RSM + N_2 + 5H_2O,$$

$$RSM + ClCH_2CH_2Cl \xrightarrow[-MCl]{} \underset{\textbf{IIa, IIb}}{RSCH_2CH_2Cl}, \qquad (2)$$

R = Ph (**a**),  (**b**).

Diphenyl disulfide already with a double excess of dichloroethane gives primarily sulfide **IIa**. With dithienyl disulfide even at equimolar reagent amounts, the major product of reaction (2) is unsymmetrical sulfide **IIb**. The different reactivities of dialkyl and diaryl(hetaryl) disulfides in their reactions with dihaloalkanes by schemes (1) and (2) are apparently explained by different solubilities of sulfides **II** in the aqueous system hydrazine hydrate–alkali. Sulfides like **II** formed from dialkyl disulfides in the first stage of reaction (1) are readily soluble in the aqueous system, and, therefore, they convert into bis-sulfides **I** without passing into the organic phase.

$$\textbf{II} + RSM \xrightarrow[-MX]{} \textbf{I}.$$

Sulfides **IIa** and **IIb** are worse soluble in water, and, therefore, they quickly pass into the organic phase. It is not also excluded that the reason for the different reactivities of dialkyl and diaryl(hetaryl) disulfides in reactions (1) and (2) may lie in the reduced nucleophilicity of aryl- and thienylthiolate anions.

Reactions (1) and (2) with excess alkali sometimes involve dehalogenation of sulfides **II** to form unsaturated sulfides **III** by scheme (3).

$$RS(CH_2)_nCl \xrightarrow[-HCl]{} \underset{\textbf{IIIa, IIIb}}{RSCH=CH_2}, \qquad (3)$$

n = 2, R = Me (**a**), 8-quinolyl (**b**).

Sulfides **III** are formed with a sixfold or greater excess of alkali, as shown with the reaction with dimethyl disulfide by scheme (1) as example. At the same time, reaction (1) with di(8-quinolyl) disulfide

Table 2. Physicochemical characteristics of compounds **I–III**

Comp. no.	bp, °C (*p*, mm) (mp, °C)	^{1}H NMR spectrum, δ, ppm	Reference
Ia	95 (40)	1.25 t (CH_3), 2.65 q (CCH_2S), 3.81 s (SCH_2S)	[6]
Ib	132 (54)	0.98 t (CH_3), 1.61 m (CCH_2C), 2.61 t (CCH_2S), 3.64 s (SCH_2S)	[7]
Ic	77 (20)	2.08 s (CH_3), 2.65 s (CH_2)	[8]
Id	134 (45)	1.25 t (CH_3), 2.52 q (CH_3CH_2S), 2.72 s (SCH_2CH_2S)	[9]
Ie	102 (40)	0.97 t (CH_3), 1.61 m (CCH_2C), 2.52 t ($CCCH_2S$), 3.70 s (SCH_2CH_2S)	[10]
If	(65–66)	3.06 s (CH_2S), 7.26 (H_{Ar})	[11]
Ig	[a]	2.92 s (CH_2S), 6.90–7.38 m (thienyl H)	–
Ih	[b]	3.45 s (CH_2S), 7.10–8.94 m (quinolyl H)	–
Ii	125 (35)	1.25 t (CH_3), 2.59 m (CH_2S), 1.88 m (CCH_2C)	[12]
Ij	125 (35)	1.24 t (CH_3), 2.51 m (CH_2S), 1.68 m (CCH_2C)	[12]
Ik	106 (2)	1.24 t (CH_3), 2.51 m (CH_2S), 1.53 m (CCH_2C)	[12]
IIa	180 (5)	3.20 s (CH_2S), 3.57 t (CCH_2Cl), 7.26 m (H_{Ar})	[13]
IIb[c]	110 (5)	3.01 s (CH_2S), 3.61 t (CH_2Cl), 6.90–7.38 m (thienyl H)	
IIIb	(35–39)	5.57 d (*trans*-C=CH), 5.71 d (*cis*-C=CH), 6.75 d. d (SCH=) (J_{cis} 9, J_{trans} 17 Hz), 6.92–8.78 m (quinolyl H)	[14]

[a] Identified by the ^{1}H NMR spectrum in mixture with sulfide **IIb** (not isolated individual). [b] Identified by the ^{1}H NMR spectrum in mixture with vinyl sulfide **IIIb** (not isolated individual). [c] Found, %: Cl 19.76; S 35.92. $C_6H_7ClS_2$. Calculated, %: Cl 19.89, S 35.83.

even at an equimolar amount of alkali results in exclusive formation of sulfide **IIIb** in a moderate yield. Such reaction result can be explained by the effect of the quinoline nitrogen which acts as a basic center located in the immediate vicinity of the leaving group. Actually, the diquinolyl disulfide is fairly difficultly reduced by the hydrazine hydrate–alkali system. As a result, for preparing an equimolar mixture we used sodium 8-mercaptoquinolinate.

Thus, we proposed a convenient preparative synthetic procedure for bis(organylthio)alkanes **I**. They are formed by alkylation with dihaloalkanes of solutions of diorganyl disulfides in the basic reductive system hydrazine hydrate–alkali. The generation of organylthiolate anions from disulfides and the subsequent reaction of the anions with dihaloalkanes are accomplished in one reaction vessel without isolation of intermediate alkali metal thiolates. At the same time, the reactions of diphenyl or dithienyl disulfides with dihaloalkanes involve substitution by the thiolate anions of only one halogen atom, yielding unsymmetrical sulfides **II**. When excess alkali is used, some sulfides **II** undergo dehalogenation to give alkyl vinyl sulfides **III**.

EXPERIMENTAL

The IR spectra were obtained on an IFS-25 instrument in thin films or KBr pellets. The NMR spectra were measured on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$ solutions, internal reference HMDS.

The reaction progress was followed and the purity of the reaction products was determined by GLC on an LKhM-80MD chromatograph (column 2000 × 3 mm, packing 5% XE-60 on Chromaton N-AW-HMDS), carrier gas helium, linear temperature programming at a rate of 12 deg/min.

Gas chromatography–mass spectrometry was performed on an AHP 5972 GC–MS system (capillary column 50 000 × 0.2 mm × 0.5 μm, liquid phase PONA, carrier gas helium, linear temperature programming at a rate of 12 deg/min).

The physicochemical characteristics of the synthesized compounds are listed in Table 2.

Synthesis of bis(organylthio)alkanes I. A four-neck flask equipped with a stirrer, a reflux condenser, a thermometer, and a charging device was charged with required amouns of alkali, hydrazine hydrate, and diorganyl disulfide (Table 1). The mixture was vigorously stirred with heating (90°C) until homogeneous (2–3 h), cooled to room temperature, and, after addition of dihalide, heated at 50°C for 2 h and cooled. The organic layer was separated and dried over $CaCl_2$. The yields of the reaction products, calculated from GLC data, are listed in Table 1. The target products were isolated by vacuum distillation of the reaction mixtures. Compound **If** was recrystallized from ethanol after distillation. The IR spectra of compounds **I** all showed strong bands due to stretching (2850–2970 cm^{-1}) and deformation (1410–1350 cm^{-1}) vibrations characteristic of methylene and methyl C–H bonds.

Organyl chloromethyl sulfides **II** were obtained in a similar way under the conditions given in Table 1 and isolated by vacuum distillation of the reaction mixtures.

8-Quinolyl vinyl sulfide (**IIIb**) was isolated by recrystallization from ethanol.

Methyl vinyl sulfide (**IIIa**) was identified by GC–MS. Mass spectrum, m/z (I_{rel}, %): 74 (10) (M^+), 72 (100) $(M - H_2)^+$, 59 (8) $(M - CH_3)^+$, 57 (97) $(HC{\equiv}CS)^+$, 46 (10) $(CH_2S)^+$, 39 (75) $(M - H_2S - H)^+$.

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