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Thiylation of Functionalized Electrophiles with Sulfur in Basic Reductive Systems

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Abstract—Functionalized electrophiles, specifically acetyl chloride, benzoyl chloride, chloroacetylchloride, benzenesulfonyl chloride, and *N*,*N*,4-trichlorobenzenesulfonamide, were brought into reaction with sulfur in the systems hydrazine hydrate–NaOH and sodium sulfide–water–ethanol. The efficiencies of these systems were compared. The reaction of chloroacetyl chloride with sulfur in the system hydrazine hydrate–base afforded new types of polymeric compounds, poly[(diacylhydrazine)polysulfides]. The reaction mechanisms were discussed.

In continuation of our studies on reactions of sulfur with mono- and difunctional electrophiles in the system hydrazine hydrate–alkali [1–3], we extended the series of electrophilic reagents by including such compounds as acetyl chloride, benzoyl chloride, chloroacetyl chloride, benzenesulfonyl chloride, and *N*,*N*,4-trichlorobenzenesulfonamide. The same substrates were also involved in reaction with sodium disulfide generated from sulfur and sodium sulfide in aqueous alcohol in the absence of hydrazine hydrate with a view to elucidate the effect of the latter on the reaction direction.

Sodium disulfide was generated in two ways: (1) from sulfur in the system hydrazine hydrate–aqueous NaOH and (2) from sodium sulfide and sulfur in aqueous alcohol. In both cases, the reactions of sodium disulfide with the above electrophiles were carried out at room temperature, and the reactions were accompanied by heat evolution. The reaction conditions and the yields and properties of the products are summarized in Tables 1 and 2. Among the examined electrophiles, only acetyl chloride failed to react with sodium disulfide, regardless of the method of its generation; as a result, acetyl chloride was reduced to acetic acid. The reaction of benzoyl chloride with sodium disulfide generated from sulfur in the system hydrazine hydrate–NaOH gave a mixture of dibenzoyl polysulfides [scheme (1)], the major components of which were tri- and tetrasulfides **I**. Sodium disulfide obtained from sodium sulfide and sulfur in aqueous alcohol reacted with benzoyl chloride according to scheme (2) to afford dibenzoyl disulfide (**II**).

$$S_8 + 8NaOH + 2NH_2NH_2 \cdot H_2O$$
$$\longrightarrow 4Na_2S_2 + 2N_2 + 10H_2O,$$
$$Na_2S_n + 2C_6H_5COCl$$
$$\longrightarrow \underset{\mathbf{I}}{C_6H_5COS_{3(4)}COC_6H_5} + 2NaCl, \quad (1)$$

$$Na_2S + S \xrightarrow{H_2O,\ C_2H_5OH} Na_2S_2$$
$$\xrightarrow{2C_6H_5COCl} \underset{\mathbf{II}}{C_6H_5COS_2COC_6H_5}. \quad (2)$$

The nature of the polysulfide anions formed upon dissolution of sulfur in hydrazine hydrate–aqueous alkali depends on the ratio MOH : S : N_2H_4 and conditions. Presumably, reaction (1) gives rise to an equilibrium between polysulfide ions [scheme (3)] [4].

$$S^{2-} \rightleftarrows S_2^{2-} \rightleftarrows S_3^{2-} \rightleftarrows S_n^{2-}. \quad (3)$$

In all cases, the ratio MOH : S was 1 : 1 which should favor predominant formation of disulfides M_2S_2. However, in the presence of a strictly stoichiometric amount of hydrazine hydrate, tri- and tetrasulfide ions were mainly generated. We succeeded in obtaining disulide ions only when used a 4–5-fold excess of hydrazine hydrate. In the presence of excess hydrazine hydrate, benzoyl chloride reacted only with hydrazine to give *N*,*N*'-dibenzoylhydrazine (**III**) according to scheme (4). Likewise, the same product was formed at a high rate in the reactions of benzoyl chloride with pure hydrazine hydrate or the system hydrazine hydrate–alkali.

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Table 1. Reactions of functionalized electrophiles with sulfur in the system hydrazine hydrate–NaOH–water (NaOH, 0.1 mol; S, 0.1 mol, hydrazine hydrate, 5 ml; water, 30 ml)

Reagent			Temperature, °C	Product			mp, °C
formula	g	mol		no.	yield, g (%)	appearance	
C_6H_5COCl	14[a]	0.1[a]	54	**I**	7.5 (45.5)	White powder	112–117
C_6H_5COCl	14[b]	0.1[b]	70	**III**	8 (66.2)	White prisms	205–206
$ClCH_2COCl$	6.8	0.06	60	**VI**	3.4 (56.6)	Yellow powder	105–135
$ClCH_2COCl$	6.8[b]	0.06[b]	65	**VII**	4.2 (45.8)	Yellowish–green	95
$C_6H_5SO_2Cl$	17.7	0.1	84	**IX**	7.2 (38.1)	——	125
$4\text{-}ClC_6H_4SO_2NCl_2$	2.6	0.01	50	**X**	1.5 (78.9)	White powder	135–138

Found, %						Formula	Calculated, %					
C	H	Cl	N	O	S		C	H	Cl	N	O	S
49.52	3.40	–	–	9.74	37.12	$C_{14}H_8O_2S_{3.8}$	50.97	2.42	–	–	9.70	36.89
68.47	5.37	–	11.0	14.45	–	$C_{14}H_{14}N_2O_2$	69.4	5.78	–	11.57	13.22	–
23.52	3.39	4.38	12.41	15.84	40.46	$C_4H_6Cl_{0.25}N_2O_2S_{2.5}$	23.65	2.96	4.37	13.80	15.77	39.43
23.24	3.22	3.14	14.64	19.79	35.97	$C_4H_6Cl_{0.17}N_2O_2S_2$	24.39	3.04	3.15	14.20	16.26	32.50
38.32	2.65	–	–	18.00	41.40	$C_{12}H_{10}O_4S_5$	38.69	2.65	–	–	16.93	42.33
37.55	3.51	19.65	7.36	14.39	17.54	$C_6H_6NClO_2S$	37.5	3.13	18.25	7.29	17.16	16.67

[a] Amount of hydrazine hydrate 1.2 ml. [b] Amount of hydrazine hydrate 10 ml.

Table 2. Reactions of functionalized electrophiles with sulfur in the system $Na_2S\cdot H_2O$–S–water–ethanol (0.05 mol : 0.05 mol : 2.5 ml : 1 ml)

Reagent			Temperature, °C	Product			mp, °C
formula	g	mol		no.	yield, g (%)	appearance	
C_6H_5COCl	14	0.1	60	**II**	4.5 (33)	White plates	131–132
$ClCH_2COCl$	11.3[a]	0.1[a]	82	**VIII**	2.9 (47.5)	Brown rubber	115–120
$C_6H_5SO_2Cl$	17.7	0.1	70	**IXa**	4.6 (23.4)	White prisms	180–183

Found, %				Formula	Calculated, %			
C	H	O	S		C	H	O	S
61.18	3.05	12.27	23.35	$C_{14}H_8O_2S_2$	61.31	3.05	11.68	23.36
19.40	2.70	12.47	65.11	$C_2H_2OS_{2.5}$	19.67	1.64	13.11	65.57
36.69	2.65	16.42	44.47	$C_{12}H_{10}O_4S_{5.5}$	36.65	2.54	16.26	44.57

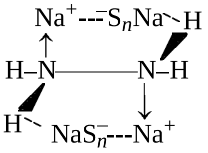
[a] Found Cl, %: 0.58.

$$S_8 + 8NaOH + 2NH_2NH_2\cdot H_2O \longrightarrow 4Na_2S_2 + 2N_2 + 10H_2O,$$

$$2C_6H_5COCl + NH_2NH_2 \longrightarrow \underset{\mathbf{III}}{C_6H_5CONH\text{–}NHCOC_6H_5} + 2NaCl. \tag{4}$$

Presumably, excess hydrazine solvates disulfide ions formed in the system. Disulfide ions are strongly activated via complex **IV** formation.

Complex **IV** is known to effectively react with aldehydes, yielding the corresponding aldehyde azines [5]. It was assumed that aldehydes are initially con-



IV

verted into thioaldehydes which then react with hydrazine at a high rate. Probably, in our case benzoyl chloride initially reacts with complex **IV** to give sodium benzothioate which quickly reacts with hydrazine according to scheme (5). It is also possible that hydrazine is a stronger nucleophile than polysulfide ions with respect to benzoyl chloride.

$$C_6H_5COCl + Na_2S_2 \longrightarrow C_6H_5COSNa + NaCl,$$

$$2C_6H_5COSNa + NH_2NH_2$$

$$\longrightarrow C_6H_5CONH–NHCOC_6H_5 + 2NaSH. \qquad (5)$$

III

The reaction of chloroacetyl chloride with sulfur in the system hydrazine hydrate–NaOH in water led to formation of mixed S,N,O-containing polymers. The sulfur concentration in the product decreases as the fraction of hydrazine hydrate in the system increases. The data of elemental analysis and IR spectroscopy suggest that chloracetyl chloride initially reacts with hydrazine to give *N,N'*-bis(chloroacetyl)hydrazine (**V**) which then undergoes polycondensation with sodium polysulfides according to scheme (6).

$$S_8 + 8NaOH + 2NH_2NH_2 \cdot H_2O \rightarrow 4Na_2S_2 + 2N_2 + 10H_2O,$$

$$NH_2NH_2 + 2ClCH_2COCl$$

$$\xrightarrow[-2HCl]{} ClCH_2CONH–NHCOCH_2Cl, \qquad (6)$$

V

$$nClCH_2CONH–NHCOCH_2Cl + nNa_2S_m$$

$$\rightarrow Cl\text{-}\!\!\left[CH_2CONH–NHCOCH_2S_m \right]_n + 2nNaCl,$$

VI, VII

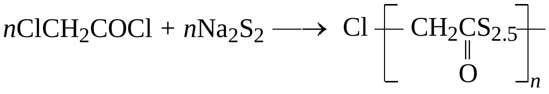
VI, $m = 2.5$, $n = 4$; **VII**, $m = 2$, $n = 6$.

Probably, initial thiylation of chloroacetyl chloride with complex **IV** gives sodium chloro(thioacetate) which then quickly reacts with hydrazine following scheme (5). This assumption is supported by the fact that in the absence of sulfur chloroacetyl chloride reacts with hydrazine very difficultly, presumably because of its decomposition to the corresponding ketene.

Polymer **VI** is formed when the system contains 5 ml of hydrazine hydrate; molecules **VI** include alternating di- and trisulfide bridges. Presumably, under these conditions sulfide ions disproportionate according to scheme (3), and the equilibrium therein is displaced to the right. Excess hydrazine hydrate stabilizes disulfide ions and favors formation of polymer **VII** having only disulfide bridges (compound **VII** was obtained in the presence of 10 ml of hydrazine hydrate). The molecular weight of **VII** is higher than that of **VI** (1131 and 810 au, respectively; calculated from the concentration of terminal chlorine atoms). Polymers **VI** and **VII** were isolated as yellow and yellowish–green powders, respectively.

The reaction of chloroacetyl chloride with sodium disulfide generated from sodium sulfide and sulfur in aqueous–alcoholic medium gave thiocol-like polysulfide polymer **VIII** according to scheme (7).

$$Na_2S + S \xrightarrow{H_2O,\ C_2H_5OH} Na_2S_2,$$



$$nClCH_2COCl + nNa_2S_2 \longrightarrow Cl\!\left[CH_2\underset{\displaystyle \overset{\|}{O}}{C}S_{2.5} \right]_n \qquad (7)$$

VIII

Polymer **VIII** is a typical rubber-like thiocol which melts over a wide temperature range (115–126°C). Judging by its elemental composition, its structure involves alternating di- and trisulfide units (Table 2). The molecular weight of **VIII** (calculated from the residual chlorine concentration) is 6120 au, i.e., it is considerably higher that the molecular weights of polymers **VI** and **VII**. Polymers **VI**, **VII** and **VIII** are characterized by different IR spectra. The IR spectra of **VI** and **VII** are consistent with the assumed structure, cm^{-1}: 3219 [ν(NHN)]; 2991, 2930, 2855 [ν(CH_2)]; 1702 [ν(NHCO)]; 1490, 1403 [ν(CH_2)]; 1291, 1202, 1127, 880 [ν(CN)]; 763, 639 [ν(CS)]; 544, 453, 427 [ν(SS)]. In the IR spectrum of **VIII** we observed absorption bands typical of poly(methylenepolysulfide) polymers, cm^{-1}: 2963, 2919 [ν(CH_2)]; 1685 [ν(CO)]; 1374, 1299, 1267, 1164 [ν(CH_2)]; 1067, 998 [ν(CC)]; 786, 754, 734, 652 [ν(CS)]; 587, 467 [ν(SS)] [6].

Thus, by the reaction of chloroacetyl chloride with sulfur in the system hydrazine hydrate–alkali we obtained polymeric products of new types, namely poly[(diacylhydrazine) polysulfides].

The reaction of benzenesulfonyl chloride with sulfur in the system hydrazine hydrate–NaOH, as well as with the system sodium sulfide–sulfur, aforded bis(phenylsulfonyl) polysulfides **IX** and **IXa** [scheme (8)].

$$S_8 + 8NaOH + 2NH_2NH_2 \cdot H_2O \longrightarrow 4Na_2S_2 + 2N_2 + 10H_2O,$$

$$Na_2S + S \xrightarrow{H_2O,\ C_2H_5OH} Na_2S_2, \qquad (8)$$

$$C_6H_5SO_2Cl + Na_2S_n \longrightarrow \underset{\textbf{IX, IXa}}{C_6H_5SO_2S_nSO_2C_6H_5},$$

$$\textbf{IX},\ n = 5;\ \textbf{IXa},\ n = 5.5.$$

Despite the fact that the amount of sulfur was sufficient to generate only sodium disulfide, polysulfides **IX** and **IXa** fromed by reaction (8) contained both tri- and tetrasulfide bridges. This means that sulfide ions disproportionate in basic reducing medium according to scheme (3). Presumably, sodium sulfide is partially oxidized to sodium sulfite or sulfate. Therefore, the remaining sodium sulfide reacts with sulfur to give sodium tri- and tetrasulfides. The IR spectra of products **IX** and **IXa** are consistent with the proposed structures, cm^{-1}: 3190 [ν(CH–Ar)]; 1930, 1685 [ν(C=C)]; 1411, 1400, 1160, 1130 [$\nu(SO_2)$]; 1060 [ν(S=O)]; 765, 720, 670 [ν(CS)]; 580, 520, 510 [ν(SS)].

N,*N*,4-Trichlorobenzenesulfonamide reacted with sulfur in the system hydrazine hydrate–alkali to afford 4-chlorobenzenesulfonamide (**X**) [scheme (9)]. Presumably, the reaction also involves intermediate thiylation of the dichloro amide.

$$S_8 + 8NaOH + 3NH_2NH_2\#f\cdot{}_{H_2O} + 4ClC_6H_4SO_2NCl_2 \longrightarrow 4Na_2S_2 + 3N_2 + 11H_2O + \underset{\textbf{X}}{4ClC_6H_4SO_2NH_2} + 2HCl. \qquad (9)$$

On the whole, the yields of sulfur-containing products in the system hydrazine hydrate–alkali are higher than in the system sodium sulfide–sulfur (Tables 1, 2).

EXPERIMENTAL

The IR spectra were recorded on a Sample Scant: 250 IFS-25 spectrometer from samples prepared as KBr pellets or thin films. The mass spectra were obtained on an LKB-2091 GC–MS system; energy of ionizing electrons 57 eV, 25-m SB-5 capillary column.

Reactions of electrophilic reagents with sulfur in the system hydrazine hydrate–NaOH. Required amount of sulfur was added in portions to a solution containing required amounts of alkali, hydrazine hydrate, and water, heated to 40–50°C. The mixture was heated for 1–2 h at 85–90°C and cooled to room temperature, and the corresponding electrophile was added. All reactions were accompanied by heat evolution and precipitation of products. The reaction conditions and the yields and properties of the products are given in Table 1.

Reactions of electrophilic reagents with the system $Na_2S \cdot H_2O$–S–water–ethanol. A mixture of $Na_2S \cdot H_2O$, water, and ethanol was heated to 45°C until it became homogeneous. Required amount of sulfur was added in portions, the mixture was heated for 1–2 h at 85–90°C and cooled to 25°C, and the corresponding electrophile was added at 25°C. All reactions were accompanied by heat evolution and precipitation of products. The reaction conditions and the yields and properties of the products are given in Table 2.

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