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New Synthesis of Alkyl Polysulfides by Treatment of Thiols, Disulfides and Thionitrites with Anhydrous Copper(II) Chloride

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Synopsis. Reaction of several divalent organic sulfur compounds with copper(II) chloride in acetonitrile gave the corresponding disulfides or other polysulfides in good yields under mild conditions.

In the course of our studies on the synthetic applications of thionitrites, the initial intermediates in the oxidation of either thiols or disulfides, we found that *t*-alkyl thionitrites were readily converted to the trisulfides upon treatment with anhydrous copper(II) chloride. Various other divalent organic sulfur compounds such as *t*-BuSH and di-*t*-butyl disulfide have now been found to react similarly with anhydrous copper(II) chloride under mild conditions to give either the corresponding disulfides or other polysulfides in good yields, as shown in Table 1. This paper deals with these reactions.

A few dialkyl trisulfides or tetrasulfides have been prepared either by the reaction of the corresponding disulfides[1] or thiols[2] with sulfur, by treatment of alkanesulfenyl chlorides with hydrogen sulfide,[3] or by the reaction of sulfur monochloride with alkanethiols.[4] Our new method which involves only mixing anhydrous copper(II) chloride with divalent organic sulfur compounds is simple and especially useful to prepare di-*t*-alkyl trisulfides or di-*t*-alkyl tetrasulfides. This method is also quite useful to prepare various disulfides from corresponding thiols upon slight modifications.

Di-*t*-butyl disulfide was added to a stirred mixture of acetonitrile and anhydrous copper(II) chloride at room temperature. After 5 h under nitrogen, the starting material disappeared completely and di-*t*-butyl trisulfide and di-*t*-butyl tetrasulfide were obtained (Run 1). The trisulfide and the tetrasulfide were separated by distillation, and then identified by elemental analysis. The main product was the tetrasulfide (63%).

Meanwhile, treatment of anhydrous copper(II) chloride with *t*-BuSH or *t*-BuSNO in acetonitrile was found to afford di-*t*-butyl trisulfide as the main product (Runs 2 and 5).

When di-*t*-butyl disulfide was treated with anhydrous iron(III) chloride in ether, the corresponding tri- and tetrasulfides were also obtained, though the reaction was slow and a small amount of the starting material always remained even after a prolonged reaction time (Run 8).

Treatment of *s*-BuSH with anhydrous copper(II) chloride at room temperature afforded di-*s*-butyl disulfide in a good yield without forming any di-*s*-butyl trisulfide or di-*s*-butyl tetrasulfide (Run 11). However, the same treatment of *s*-BuSH or di-*s*-butyl disulfide at a high reaction temperature (under reflux) gave di-*s*-butyl trisulfide in 66—79% yields (Runs 12 and 13).

Primary and aromatic divalent sulfur compounds did not give the corresponding trisulfides and tetrasulfides even after a prolonged reaction time, but gave the corresponding disulfides selectively only in several

TABLE 1. SYNTHESIS OF POLYSULFIDES FROM SEVERAL ORGANIC SULFUR COMPOUNDS WITH METAL HALIDES IN ACETONITRILE

Run	Substrate	Halide	[Halide][a] / [Substrate]	Temp °C	Time min	Yield/%[b] R_2S_2[c]	R_2S_3	R_2S_4
1	$(t\text{-Bu})_2S_2$	$CuCl_2$	2	25	300	0	25[e]	63[e]
2	*t*-BuSH	$CuCl_2$	4	25	90	trace	51[e]	43[e]
3	$t\text{-}C_5H_{11}SH$	$CuCl_2$	4	25	180	trace	49[e]	47[e]
4	$t\text{-}C_9H_{19}SH$	$CuCl_2$	4	25	150	trace	37[e]	55[e]
5	*t*-BuSNO	$CuCl_2$	1	25	20	trace	81[e]	3[e]
6	$t\text{-}C_5H_{11}SNO$	$CuCl_2$	1.5	25	10	9[e]	59[e]	8[e]
7	$t\text{-}C_9H_{19}SNO$	$CuCl_2$	1	25	20	trace	77[e]	4[e]
8	$(t\text{-Bu})_2S_2$	$FeCl_3$[g]	2	25[g]	840	10[e]	49[e]	41[e]
9	*t*-BuSH	CuCl	4	25[h]	20	quant.[e]	0	0
10	$t\text{-}C_5H_{11}SH$	CuCl	1	25[h]	40	88[e]	0	0
11	*s*-BuSH	$CuCl_2$	4	25	15	84[d]	0	0
12	*s*-BuSH	$CuCl_2$	6	82[f]	240	23[e]	66[e]	trace
13	$(s\text{-Bu})_2S_2$	$CuCl_2$	3	82[f]	360	20[e]	79[e]	trace
14	*s*-BuSNO	$CuCl_2$	1	25	5	91[e]	0	0
15	*n*-BuSH	$CuCl_2$	3	25	10	84[d]	0	0
16	$(n\text{-Bu})_2S_2$	$CuCl_2$	2	82[f]	720	quant.[d]	0	0
17	$n\text{-}C_8H_{17}SH$	$CuCl_2$	3	25	10	85[d]	0	0
18	$C_6H_5CH_2SH$	$CuCl_2$	3	25	10	quant.[d]	0	0
19	$C_6H_5CHMeSH$	$CuCl_2$	3	25	10	quant.[d]	0	0
20	*p*-TolSH	$CuCl_2$	3	25	10	quant.[d]	0	0

a) Molar ratio. b) Yield of 100% is achieved when 2/3 mol of the trisulfide or 1/2 mol of the tetrasulfide is obtained from 1 mol of the disulfide, or when 1/2 mol of the disulfide or 1/3 mol of the trisulfide or 1/4 mol of the tetrasulfide is afforded from 1 mol of the thiol or the thionitrite. c) Spectroscopic data of all the disulfides were identical with those of the authentic samples. d) Yield isolated. e) Yield determined by GLC. f) Refluxed in acetonitrile. g) Ethyl ether was used as the solvent. h) Air was bubbled into the solution.

TABLE 2. SPECTRAL DATA OF POLYSULFIDES

Compound	IR (neat, cm^{-1})	NMR (CCl_4, δ)	MS (70 eV, *m/e*, M^+)
$(t\text{-Bu})_2S_3$	1450, 1360, 1260	1.36(s) (lit,[7] 1.34)	210
$(t\text{-Bu})_2S_4$	1450, 1360, 1159	1.37(s) (lit,[7] 1.37)	242
$(t\text{-}C_5H_{11})_2S_3$	1450, 1378, 1150	0.95(t, 6H), 1.30(s, 12H), 1.68(q, 4H)	238
$(t\text{-}C_5H_{11})_2S_4$	1455, 1380, 1153	0.97(t, 6H), 1.35(s, 12H), 1.70(q, 4H)	270
$(t\text{-}C_9H_{19})_2S_3$	1452, 1373, 1135	0.6—2.1(m)	350
$(t\text{-}C_9H_{19})_2S_4$	1459, 1380, 1135	0.6—2.1(m)	382
$(s\text{-Bu})_2S_3$	1462, 1373, 1217	0.99(t, 6H), 1.37 (d, J=7 Hz, 6H) 1.50—1.92(m, 4H), 2.69—3.18 (m, 2H)	210

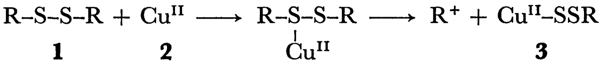
Table 3. Boiling points, and analytical data of polysulfides

Compound	Bp/°C(Torr) (bath temp)	Found(%)			Calcd(%)		
		C	H	S	C	H	S
$(t\text{-Bu})_2S_3$	65—75/2	45.75	8.69	45.82	45.66	8.62	45.71
$(t\text{-}C_5H_{11})_2S_3$	85—90/2	50.30	9.32	—	50.36	9.29	—
$(t\text{-}C_5H_{11})_2S_4$	95—100/2	44.02	7.81	—	44.39	8.19	—
$(t\text{-}C_9H_{19})_2S_3$	120—125/2	61.93	11.30	—	61.65	10.92	—
$(t\text{-}C_9H_{19})_2S_4$	130—135/2	56.14	9.85	—	56.48	10.00	—

minutes (Runs 15, 16, 17, 18, and 20). It is interesting to note that the treatment of *t*-BuSH with anhydrous copper(I) chloride in the presence of air at the room temperature also gave selectively di-*t*-butyl disulfide, no formation of the trisulfide or the tetrasulfide being confirmed (Run 9). Oxidation of thiols with CuCl was found to require atomospheric oxygen, while oxidation with $CuCl_2$ proceeded under nitrogen. Thus, the reaction is quite useful to prepare symmetrical polysulfides.

These experimental observations seem to suggest that the C–S bond in *t*-alkyl compounds is readily cleaved to form the relatively stable *t*-alkyl cation upon treatment with copper(II) ion.

Thus the following mechanism may be conceivable for the reaction with di-*t*-alkyl disulfide. Other *t*-alkyl sulfur compounds would behave similarly. Copper(II) chloride would be reduced to Cu^0 or copper(I) chloride.



$$\underset{\mathbf{1}}{R\text{-}S\text{-}S\text{-}R} + \underset{\mathbf{2}}{Cu^{II}} \longrightarrow \underset{\displaystyle Cu^{II}}{R\text{-}S\text{-}S\text{-}R} \longrightarrow R^+ + \underset{\mathbf{3}}{Cu^{II}\text{-}SSR}$$

$$\mathbf{3} + \mathbf{1} \longrightarrow \underset{\mathbf{4}}{R\text{-}S\text{-}S\text{-}S\text{-}R} + \underset{\mathbf{5}}{RS\text{-}Cu^{II}}$$

$$\mathbf{5} + \mathbf{1} \longrightarrow R^+ + \mathbf{4} + \underset{\mathbf{6}}{[Cu^0]} \xrightarrow{Cu^{II}} \underset{\mathbf{7}}{[Cu^I]}$$

$$\mathbf{5} + \mathbf{4} \longrightarrow R^+ + R\text{-}S\text{-}S\text{-}S\text{-}S\text{-}R + \mathbf{6} \xrightarrow{Cu^{II}} \mathbf{7}$$

The gas evolved during the reaction of di-*t*-butyl disulfide with anhydrous copper(II) chloride was analyzed through mass spectroscopy which gave a strong peak of 56 (C_4H_8). Thus *t*-butyl cation was found to be converted to the olefin. Meanwhile, the lack of C–S bond cleavage in primary and aromatic sulfur compounds and the low reactivities of the secondary sulfur compounds are also in keeping with the relative stabilities of the respective carbonium ions.

Experimental

All the melting points and boiling points were uncorrected. Elemental analysis of sulfur was carried out by Sagami Chemical Research Center and the analyses of other elements were carried out by the analytical labolatory in our university. Analytical determinations by GLC were performed on a Hitachi 163 gas chromatograph fitted with the following column (3 mm o.d. ×3 m): 10% SE-30 on Chromosorb W. ^{1}H-NMR spectra were taken at 60 MHz on a Hitachi R-24 A apparatus. IR spectra were recorded with a Hitachi 215 spectrometer. Mass spectra were recorded with a Hitachi RMU-6M spectrometer. Thionitrites were prepared from corresponding thiols by the method reported by us.[5] The followings are typical runs.

Reaction of Di-t-butyl Disulfide and Anhydrous Copper(II) Chloride. Di-*t*-butyl disulfide 3.56 g (20 mmol) was added to a stirred mixture of anhydrous copper(II) chloride 5.38 g (40 mmol) in 50 ml of anhydrous acetonitrile. The mixture was stirred at room temperature for 5 h. A saturated NaCl aq solution was added to the dark brown mixture and extracted with ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled, giving pure trisulfide and tetrasulfide. The amounts of the products were estimated by GLC: Di-*t*-butyl trisulfide 0.69 g (25%), di-*t*-butyl tetrasulfide 1.52 g (63%). Di-*t*-butyl trisulfide; mp 14—15 °C (lit,[6] 16.63 °C). Di-*t*-butyl tetrasulfide; bp (bath temperature), 80—90 °C/2 mmHg (lit,[6] 70 °C/2 mmHg).

t-Butyl thionitrite and *t*-BuSH were found to react similarly, and the results are shown in Table 1 while the physico-chemical properties are listed in Tables 2 and 3.

Reaction of Di-s-butyl Disulfide with Anhydrous Copper(II) Chloride. Di-*s*-butyl disulfide 1.16 g (6.5 mmol) and anhydrous copper(II) chloride 2.62 g (19.5 mmol) was refluxed in anhydrous acetonitrile for 6 h under nitrogen. The saturated NaCl aq solution was added into the mixture which was extracted with ether. The amount of di-*s*-butyl trisulfide was calibrated by GLC: 0.694 g (79%). The ethereal extract was dried ($MgSO_4$), concentrated and distilled giving 0.623 g of trisulfide: bp (bath temperature) 100—110 °C/2 mmHg (lit,[2] bp 79—80 °C/0.4 mmHg).

Primary and secondary thiols were found to react similarly and the results, physical properties and analytical data on the resulted products are listed in Tables 1, 2, and 3 respectively.

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