[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY UNIVERSITY OF ILLINOIS]

Thioethers from Halogen Compounds and Cuprous Mercaptides. II

BY ROGER ADAMS AND ALDO FERRETTI*

RECEIVED FEBRUARY 27, 1959

The reaction of aliphatic cuprous mercaptides with various halogen compounds has been further explored. Aliphatic and aromatic thioethers have been formed by condensation of cuprous mercaptides with 2-bromothiophene, 2-bromopyridine and 2-bromofuroic acid, the last with concomitant decarboxylation. β-Bromostyrene, 1-bromo-2-methyl-1-propene and 1-chloro- or 1-bromo-dodecane represent prototypes of other halogen compounds which undergo this reaction.

In a recent article from this Laboratory[1] the use of cuprous phenylmercaptide and cuprous *n*-butyl mercaptide for the preparation of thioethers from aryl halides was reported. The study of this method of synthesis of thioethers has now been extended, first, to the reaction of various halogen compounds with cuprous ethylmercaptide, and second, to the displacement of halogens in heterocyclic and aliphatic compounds with various cuprous mercaptides.

The previous observation has been confirmed that inactivated aryl chlorides react under the conditions used with cuprous aryl mercaptides, but not with alkyl mercaptides, to give thioethers. Aryl bromides and activated aryl chlorides such as *o*-chloronitrobenzene, however, react with both aliphatic and aromatic mercaptides.

The bromine atoms in 2-bromothiophene and 2-bromofuroic acid are readily replaced by ethylmercapto, *n*-butylmercapto or phenylmercapto groups, though bromofuroic acid undergoes concomitant decarboxylation. The bromine atom in 2-bromopyridine is replaced in low yields.

The character of the ring substituents of the aryl bromide has a marked influence on the time necessary for the displacement reaction of the halogen to reach completion. In general, the yields are good, but, for example, they were noticeably lower when 2,6-dibromo-4-nitrophenol and *p*-bromoaniline were treated with cuprous ethylmercaptide. Furthermore, no identifiable product resulted from the condensation of *p*-bromophenol with this same mercaptide.

Polyhalogenated aromatic compounds give in some cases anomalous results with cuprous ethyl- and *n*-butylmercaptides. 1,2- and 1,4-Dibromobenzene form the expected dithioethers with these mercaptides. 2,5-Dibromotoluene, 4,4′-Dibromophenyl, 4,4′-dibromobibenzyl, 1,3,5-tribromobenzene and 2,4,6-tribromomesitylene give the polythioethers with cuprous ethylmercaptide. However, the reactions failed when 1,2,4,5-tetrabromobenzene, hexabromobenzene, tetraiodophthalic anhydride and 2,4,6-tribromo-3-iodotoluene were condensed with cuprous ethylmercaptide. Small quantities of partial-substitution products resulted when the reactions proceeded a short time. After a normal heating period, however, only tars were obtained.

Experimental evidence on the mechanism was sought through a study of the reaction of cuprous *t*-butylmercaptide with these same halogen compounds. Unfortunately this mercaptide decomposes below the temperature at which reaction with the halogen compound normally takes place and tars result. By limiting the heating to a minimum 1,2,4-tribromo-5-*t*-butylmercaptobenzene was isolated in small amounts from the reaction with 1,2,4,5-tetrabromobenzene, and 1-bromo-4-*t*-butylmercaptobenzene from the reaction with *p*-dibromobenzene.

Vinyl bromides in general react with cuprous mercaptides both aliphatic and aromatic to give vinyl thioethers. β-Bromostyrene and 1-bromo-2-methyl-1-propene were used as prototypes in this study. This method of synthesis of vinyl thioethers appears to be superior to that using vinyl halides and sodium mercaptides,[2-7] or to any of the others reported.[8-20]

Methyl α-bromoacrylate and α-bromoacrylic acid and cuprous phenylmercaptide yield the corresponding thioethers contaminated with by-products which are very difficult to remove.

1,2-Dibromoethylene gives with cuprous phenylmercaptide a mixture of *cis* (18%) and *trans* (42%) 1,2-diphenylmercaptoethylene; both isomers, upon hydrogen peroxide oxidation, are converted to the *trans*-sulfone, 1,2-dibenzenesulfonylethylene. But with cuprous ethylmercaptide, hydrogen bromide is eliminated with the formation of ethylmercaptoacetylene which resisted attempts to purify completely; upon oxidation with hydrogen peroxide, ethylmercaptocarboxylic acid is formed.

$$BrHC{=}CHBr + CuSEt \longrightarrow HC{\equiv}CSEt \xrightarrow{H_2O_2} HO_2CSEt + CO_2$$

* On leave of absence Ente Nazionale Idrocarburi, San Donato Milanese (Italy).

(1) R. Adams, W. Reifschneider and M. D. Nair, *Croatica Chem. Acta*, 29 (1957).

(2) D. Strömholm, *Ber.*, **33**, 840 (1900).

(3) J. Loevenich, J. Losen and A. Dierichs, *ibid.*, **60**, 950 (1927).

(4) E. Fromm, H. Benzinger and F. Schäfer, *Ann.*, **394**, 325 (1912).

(5) N. W. Cusa and H. McCombie, *J. Chem. Soc.*, 767 (1937).

(6) E. Fromm and E. Siebert, *Ber.*, **55**, 1014 (1922).

(7) H. Baganz and K. E. Krüger, *ibid.*, **91**, 809 (1958).

(8) S. Ruhemann and H. E. Stapleton, *J. Chem. Soc.*, **77**, 1182 (1900).

(9) E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1316 (1935).

(10) W. Reppe and F. Nicolai, German Patent 617,543 (1935); *C. A.*, **30**, 7334 (1936).

(11) I. G. Farbenind, A.G., French Patent 777,427, Feb. 1935; *C. A.*, **29**, 4024⁸ (1935).

(12) L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3089 (1949).

(13) J. C. Whitner, Jr., and E. E. Reid, THIS JOURNAL, **43**, 637 (1921).

(14) T F. Doumani, U. S. Patent 2,402,878 (1946); *C. A.*, **40**, 6496⁷ (1946).

(15) W. J. Croxall, L. R. Freimiller and E. V. Shropeshire, THIS JOURNAL, **72**, 4275 (1950).

(16) W. J. Croxall and L. R. Freimiller, U. S. Patent 2,532,291, Dec. 1950; *C. A.*, **45**, 3420i (1951).

(17) F. P. Doyle, British Patent 640,127, June, 1950; *C. A.*, **45**, 6519e (1951).

(18) J. von Braun and G. Kirschbaum, *Ber.*, **53B**, 1407 (1920).

(19) E. Rothstein, *J. Chem. Soc.*, 1550 (1940).

(20) E. Rothstein, *ibid.*, 1553 (1940).

TABLE I

PHENYL THIOETHERS

Halogen compound	Reaction product[f]	Yield, %	M.p. or b.p., °C.	Mm.	$n^{25}D$		Analyses, % Calcd.	Found
5-Bromofuroic acid	5-Phenylmercaptofuran	90	97–98	2.5	1.5976	C	68.15	68.21
						H	4.57	4.69
2-Bromopyridine[a]	2-Phenylmercaptopyridine[b]	41	121–122	0.7	1.6368	C	70.55	70.78
		13[c]				H	4.84	4.88
						N	7.48	7.51
β-Bromostyrene	β-Phenylmercaptostyrene	93	134–135	0.3	1.6676	C	79.20	79.12
						H	5.70	5.76
1-Bromo-2-methyl-1-propene[d]	1-Phenylmercapto-2-methyl-1-propene	100	111–112	9	1.5782	C	73.12	73.28
						H	7.37	7.49
1-Bromododecane	1-Phenylmercaptododecane	84	33–34[e]			C	77.63	77.76
						H	10.86	10.73

[a] 2-Bromopyridine was prepared from 2-aminopyridine as described in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 136. [b] Lit. b.p. 160–162° at 8 mm.; L. G. S. Brooker, *et al.*, THIS JOURNAL, **73,** 5326 (1951). [c] Preparation in dimethylformamide. [d] 1-Bromo-2-methyl-1-propene was prepared from 1,2-dibromo-2-methylpropane as described by E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3328 (1955). [e] Crystallized from ethanol. [f] All reaction products in Table I were extracted from the copper salts with ether.

TABLE II

n-BUTYL THIOETHERS

Halogen compound	Reaction product[g]	Yield, %	M.p. or b.p., °C.	Mm.	$n^{25}D$		Analyses, % Calcd.	Found
p-Bromobenzanilide	*p*-*n*-Butylmercaptobenzanilide	83	153–154[a]			C	71.54	71.54
						H	6.71	6.46
						N	4.91	4.99
3-Bromonitrobenzene	3-*n*-Butylmercaptonitrobenzene[b]	77	128–130	0.7	1.5721	C	56.85	56.96
						H	6.20	6.11
						N	6.63	6.93
o-Dibromobenzene	*o*-Di-*n*-butylmercaptobenzene	67	137–138	1	1.5680	C	66.08	66.01
						H	8.72	8.76
p-Dibromobenzene	*p*-Di-*n*-butylmercaptobenzene[c]	75	143–144	0.6		C	66.08	65.97
						H	8.72	9.04
p-Iodobenzoic acid	*p*-*n*-Butylmercaptobenzoic acid[d]	100	121–122[a]			C	62.82	62.66
						H	6.71	6.66
2-Chloronitrobenzene	2-*n*-Butylmercaptonitrobenzene	37	137–138	0.7	1.5975	C	56.85	57.22
						H	6.20	6.30
						N	6.63	6.86
		85	100–101	27	1.5012	C	61.49	61.09
5-Bromofuroic acid	5-*n*-Butylmercaptofuran		98–99	26		H	7.74	7.68
2-Bromothiophene	2-*n*-Butylmercaptothiophene	92	116–117	15	1.5508	C	55.76	55.92
			85	3.5		H	7.02	6.76
1-Bromo-2-methyl-1-propene	1-*n*-Butylmercapto-2-methyl-1-propene	88	88–89	26	1.4782	C	66.60	66.91
						H	11.18	11.30

[a] Crystallized from ethanol. [b] Lit. b.p. 135° at 3 mm.; J. J. Donleavy and J. English, Jr., THIS JOURNAL, **62,** 2965 (1940). [c] Lit. b.p. 142° at 0.3 mm.; ref. 1. [d] Lit. m.p. 122°; N. P. Buu-Hoï and J. Lecocq, *Bull. soc. chim. France,* 475 (1946); and m.p. 115°, T. Kurihara, H. Niwa, K. Ro and K. Chiba, *J. Pharm. Soc. Japan,* **73,** 725 (1953). [e] For extraction from the copper salts, ethanol was used in the reaction involving *p*-bromobenzanilide, chloroform in the case of *o*-dibromobenzene, and ether for all other compounds in Table II.

Although sodium mercaptides are reported to react with long chain alkyl halides to give thioethers,[21] the use of cuprous mercaptides, both aliphatic and aromatic, is probably a preferable procedure.

Cuprous hexamethylenedimercaptide reacts slowly with two moles of bromobenzene or *p*-bromotoluene to give the corresponding dithioethers in good yield.

Cuprous benzylmercaptide and cuprous ethylxanthate did not give the expected products with a variety of halogen compounds. These cuprous mercaptides, like the *t*-butyl analog, decompose before reacting with the halogen compounds. The cuprous benzylmercaptide gives a mixture of dibenzyl sulfide and *cis*- and *trans*-stilbene, though with β-bromonaphthalene β-dinaphthyl sulfide was isolated. β-Dinaphthyl sulfide was also obtained from cuprous ethyl xanthate and β-bromonaphthalene.

In the early work,[1] the condensation of hexachlorobenzene with cuprous phenylmercaptide was reported to yield hexaphenylmercaptobenzene, m.p. 182–184°. This experiment has now been repeated and two isomeric products have been isolated, the first, m.p. 184–185° (cor.) which was identical with that previously isolated, and a second product, m.p. 149.5–150° (cor.). Both have identical empirical formulas as shown by analysis. The infrared spectrum of the lower-melting form is similar to that of the higher-melting form except that it shows an additional band at 1520 cm.$^{-1}$. The higher-melting isomer by careful oxidation gives the corresponding hexabenzenesulfonylbenzene, but by oxi-

(21) R. W. Bost and J. E. Everett, THIS JOURNAL, **62,** 1752 (1940).

TABLE III

ETHYL THIOETHERS

Halogen compound	Reaction product	Yield, %	M.p. or b.p., °C.	Mm.	$n^{25}D$	Analyses, % Calcd.		Found
p-Bromoaniline	*p*-Ethylmercaptoaniline[a,m]	44	102–103	0.7	1.6123	C	62.70	63.05
						H	7.24	7.12
						N	9.14	9.09
p-Bromoanisole	*p*-Ethylmercaptoanisole[b,m]	64	77–78	0.8	1.5604	C	64.24	64.18
						H	7.19	7.25
9-Bromoanthracene	9-Ethylmercaptoanthracene[n]	48	171	0.5		C	80.63	80.69
						H	5.92	6.22
α-Bromo-β-methoxynaphthalene	α-Ethylmercapto-β-methoxynaphthalene[n]	70	125–126	0.5	1.6420	C	71.52	71.54
						H	6.46	6.64
β-Bromonaphthalene	β-Ethylmercaptonaphthalene[c,n]	73	105–107	0.3	1.6496	C	76.54	76.66
						H	6.43	6.52
o-Bromo-*p*-nitrotoluene	*o*-Ethylmercapto-*p*-nitrotoluene[n]	58	118–119	0.7		C	54.80	54.74
			40–41[k]			H	5.62	5.51
p-Bromotoluene	*p*-Ethylmercaptotoluene[d,m]	69	91–93	8	1.5558	C	71.00	70.95
						H	7.95	7.74
o-Bromo-*p*-toluic acid	*o*-Ethylmercapto-*p*-toluic acid[m]	60	170–171[l]			C	61.20	61.41
						H	6.16	6.29
o-Dibromobenzene	*o*-Diethylmercaptobenzene[n]	58	103–104	0.5	1.6048	C	60.56	60.58
						H	7.11	7.20
p-Dibromobenzene	*p*-Diethylmercaptobenzene[e,m]	96	46.5–47.5[k]			C	60.56	60.43
						H	7.11	7.24
4,4′-Dibromobibenzyl	4,4′-Diethylmercaptobibenzyl[m]	94	64.5–65.5[k]			C	71.46	71.17
						H	7.33	7.43
2,6-Dibromo-4-nitrophenol	2,6-Diethylmercapto-4-nitrophenol[n]	23	170–171	0.7				
1,3,5-Tribromobenzene	1,3,5-Triethylmercaptobenzene[n]	35	147–148	0.4	1.6182	C	55.77	55.59
						H	7.02	6.87
5-Bromofuroic acid	5-Ethylmercaptofuran[m]	61	154–155	760	1.5104	C	56.22	56.27
						H	6.29	6.59
2-Bromothiophene	2-Ethylmercaptothiophene[f,n]	56	103–105	38	1.5670	C	49.96	49.85
						H	5.59	5.79
β-Bromostyrene	β-Ethylmercaptostyrene[m]	62	135–136	11	1.6133	C	73.11	72.94
						H	7.37	7.45
1-Chlorododecane	1-Ethylmercaptododecane[g,n]	39	107–108	0.5	1.4592	C	72.97	72.97
						H	13.12	13.06
2,4,6-Tribromomesitylene	2,4,6-Triethylmercaptomesitylene[m]	79	162	0.5	1.5994	C	59.95	60.01
						H	8.05	7.94
2-Bromomesitylene	2-Ethylmercaptomesitylene[m]	90	79	1	1.5465	C	73.27	73.60
						H	8.95	8.92
2,5-Dibromotoluene	2,5-Diethylmercaptotoluene[m]	75	112	0.5	1.5962	C	62.21	62.43
						H	7.59	7.47
4,4′-Dibromobiphenyl	4,4′-Diethylmercaptobiphenyl[h,m]	96	135–136[k]			C	70.02	69.90
						H	6.61	6.57
3-Bromo-1-nitrobenzene	3-Ethylmercapto-1-nitrobenzene[i,m]	78	108	1	1.5952	C	52.44	52.37
						H	4.95	4.98
						N	7.65	7.79
	3-Ethylmercaptoaniline[j]		112	1	1.6152	C	62.70	62.92
						H	7.24	7.21
						N	9.14	9.12
2,4,6-Trichloro-1-iodobenzene	2,4,6-Trichloro-1-ethylmercaptobenzene[m]	34	101	0.8	1.5990	C	39.77	40.16
						H	2.92	2.99

[a] Lit. b.p. 280–281°; G. W. Monier-Williams, *J. Chem. Soc.*, **89**, 278 (1906). [b] Lit. b.p. 103° at 5 mm.; C. M. Suter and H. L. Hansen, THIS JOURNAL, **54**, 4100 (1932). [c] Lit. m.p. 16°, b.p. 170.5° at 15 mm.; F. Kraff and R. Schönherr, *Ber.*, **22**, 824 (1889). [d] Lit. b.p. 105° at 15 mm.; K. Auwers and F. Arndt, *ibid.*, **42**, 2712 (1909); b.p. 218–220° at 760 mm.; F. Taboury, *Bull. soc. chim. France*, [3] **31**, 1187 (1904). [e] Lit. m.p. 46.5°; M. Bennett and F. S. Stathman, *J. Chem. Soc.*, 1684 (1931). [f] Lit. b.p. 196–197°; W. Steinkopf and P. Leonhardt, *Ann.*, **495**, 166 (1932). [g] Lit. m.p. −6 to −5°; b.p. 167–171° at 18 mm.; ref. 21. [h] Lit. m.p. 135°; R. Leuckart, *J. prakt. Chem.*, [2] **41**, 214 (1890). [i] Lit. b.p. 117° at 3 mm.; ref. *b*, Table II. [j] Prepared in 73% yield from 3-ethylmercaptonitrobenzene by reduction with Sn and HCl; lit. b.p. 103° at 3 mm.; see ref. in footnote *i*. [k] Crystallized from ethanol. [l] Crystallized from ether. [m] Extracted from copper salts with ether. [n] Extracted from copper salts with chloroform.

dation of the lower-melting isomer no such product could be isolated. Drastic oxidation of the higher-melting isomer converts it chiefly to succinic acid.

Models indicate that the hexaphenyl thioether may exist in more than one form, but that the hexasulfone can exist in only one form without extraordinary crowding. The hexasulfone has the oxygens and benzene rings of each of the benzenesulfonyl groups alternately above and below the plane of the central benzene ring. It is a fair assumption

TABLE IV

t-BUTYL THIOETHERS

Halogen compound	Reaction product	Yield, %	M.p. or b.p. °C.	Mm.	Analyses, %	Calcd.	Found
1,2,4,5-Tetrabromobenzene	1,2,4-Tribromo-5-*t*-butylmercaptobenzene[a]	*ca.* 20	88.5–89.5[d]		C	29.80	30.29
					H	2.75	2.95
p-Dibromobenzene	*p*-*t*-Butylmercaptobromobenzene[b]	*ca.* 20	75	0.5	C	48.99	49.96
					H	5.34	5.43

TABLE V

1,6-DIARYLMERCAPTOHEXANES

Bromobenzene	1,6-Diphenylmercaptohexane[b]	60	81–82[e]		C	71.47	71.63
					H	7.33	7.51
p-Bromotoluene	1,6-Di-*p*-tolylmercaptohexane[c]	58	63.5–64.5[e]		C	72.67	73.00
					H	7.93	8.00

[a] Extracted from copper salts with benzene. [b] Extracted from copper salts with ether. [c] Extracted from copper salts with acetone and ether. [d] Recrystallized from methanol. [e] Recrystallized from ethanol.

that the higher-melting hexaphenyl thioether has its phenylmercapto groups alternated in a similar way. No evidence is available for establishing the relative positions of the phenylmercapto groups in the lower-melting form. The resistance to oxidation of the lower-melting form indicates the probability of at least two adjacent phenylmercapto groups being present in the *cis* configuration since two adjacent benzenesulfonyl groups *cis* to each other are sterically very unlikely.

In Tables I–V are assembled the compounds synthesized and their physical constants.

Experimental

All melting points are corrected.

Cuprous Mercaptides.—Cuprous phenylmercaptide, benzylmercaptide and *n*-butylmercaptide were prepared in ethanol as previously described.[1]

Cuprous ethylmercaptide was made similarly but ether was used as solvent in place of ethanol. The reaction was completed in 12 hours. Upon addition of absolute ethanol 2 hours prior to completion of the reaction, a perfectly white mercaptide results. Otherwise the product may be pinkish in color. The mercaptide was washed with methanol. It darkens at 260° and decomposes completely at 280°.

Anal. Calcd. for C_2H_5SCu: C, 19.26; H, 4.04. Found: C, 19.52; H, 4.08.

Cuprous *t*-butylmercaptide was prepared in methanol as solvent. It melts with decomposition at about 170°.

Cuprous Hexamethylenedimercaptide.—This preparation required a different procedure. To a stirred solution of 40 g. (4 mole equivs.) of cuprous chloride, in a mixture of 300 ml. of concentrated aqueous ammonia and 300 ml. of ethanol was added 15 g. of hexamethylenedimercaptan drop by drop. The reaction was conducted in a vigorous stream of nitrogen. Stirring was continued for 5 minutes after all the mercaptan had been added, the precipitate was then collected on a sintered glass funnel, washed in succession with aqueous ammonia, water, ethanol and ether.

Reaction of Halogen Compounds with Cuprous Thiophenolate, Cuprous Thiobutylate, Cuprous Thioethylate and Cuprous Hexamethylene Dimercaptide.—The general procedure[1] previously described is repeated here on account of the inaccessibility of the journal where it appeared.

General Procedure.—A quantity of halogen compound corresponding to 0.1 g. atom of halogen, 0.108 mole of cuprous mercaptide (or 0.054 mole of hexamethylenedimercaptide), 80–90 ml. of quinoline and 2–8 ml. of pyridine were heated at 200° for 4 to 5 hours longer than was necessary to obtain a completely homogeneous solution (1 to 10 hours). The warm solution was poured into cracked ice and excess hydrochloric acid. After standing for some hours, the acid mixture was filtered through a sintered glass funnel, and the solid freed as much as possible from water. The powdery, gummy or tarry solid was extracted in a soxhlet, or digested with a solvent overnight, according to its consistency. Ether, acetone, benzene or chloroform was used as a solvent; ethanol was used to extract *p*-butylmercaptobenzanilide. When the product obtained was a liquid, part of it passed through the filter; in this case the acid waters containing the oil were extracted twice with the solvent. The combined extracts were washed twice with dilute hydrochloric acid (1:10), twice with water and dried. After evaporation of the solvent the residue was crystallized from ethanol or ether, or distilled *in vacuo*. When acetone was used to extract the product from the copper salts, the solution was poured into ether which caused precipitation of tars.

For the preparation of 2-phenylmercaptopyridine and *p*-ethylmercaptoaniline the general procedure was modified as described below.

2-Phenylmercaptopyridine.—The initial heating of 23.9 g. of cuprous phenylmercaptide and 20 g. of 2-bromopyridine was carried out in the usual way, and after pouring into ice and hydrochloric acid, the solid residue was removed after several hours standing. The aqueous solution was made alkaline and an oil contaminated with cuprous oxide resulted. The latter was separated by filtration, and the filtrate was extracted three times with ether, the ether was removed, and the residue distilled with steam. When no more oil distilled, the distillate was extracted with ether, the ether solution dried, the solvent removed, and the product distilled. After the quinoline had been removed 3.5 g. of 2-phenylmercaptopyridine distilled, b.p. 138–140° at 2.5 mm.

The residue that did not distil with steam was dissolved in dilute hydrochloric acid, the solution extracted with ether to remove any insoluble product, then realkalinized with sodium hydroxide and extracted with ether. After removal of the solvent, the oil weighing 6 g., was added to that obtained above and redistilled *in vacuo*.

Since steam distillation does not afford a means of separation of quinoline and the product, the first part of the preparation described above could be perhaps advantageously eliminated.

A less satisfactory yield was obtained when dimethyl formamide was used as solvent.

***p*-Ethylmercaptoaniline.**—The directions for synthesis of 2-phenylmercaptopyridine were used in this preparation. From 51.6 g. of *p*-bromoaniline and 44 g. of cuprous ethylmercaptide, 20 g. of *p*-ethylmercaptoaniline was obtained of which 11.3 g. came from the steam distillation and 8.7 g. was recovered from the residue.

***cis*- and *trans*-1,2-Diphenylmercaptoethylene.**—The condensation of cuprous phenylmercaptide and 1,2-dibromoethylene was carried out according to the general procedure. Ether was used to separate the product from copper salts. The oily residue from the ether was cooled and crystals separated after 24 hours in 42% yield. After four crystallizations from ethanol the product melted at 63–64° (*trans* form) (lit.[22] m.p. 62°).

Anal. Calcd. for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95. Found: C, 69.31; H, 5.06.

(22) W. E. Truce and R. J. McManimie, THIS JOURNAL, **76**, 5745 (1954).

The oily filtrate from the crystals was distilled, b.p. 170–171° at 1 mm. (*cis* form) (lit.[5] b.p. 235–242° at 760 mm. for mixture of *cis* and *trans*), yield 18%.

Anal. Calcd. for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95. Found: C, 69.05; H, 4.98.

The higher-melting form has been assigned the *trans* structure by Truce[22] as deduced from its oxidation to the higher-melting sulfone. However, oxidation experiments of either isomer in this Laboratory gave only the *trans*-sulfone.

***trans*-1,2-Dibenzenesulfonylethylene.**—To a cold solution of 3 g. of 1,2-diphenylmercaptoethylene (*cis* or *trans*) in 40 ml. of glacial acetic acid and 10 ml. of acetic anhydride, was added 11 ml. (twice the required amount) of 30% hydrogen peroxide during a period of one hour. After standing overnight, 2.7 ml. more of hydrogen peroxide was added and the reaction mixture was heated at 100° for 2 hours. On cooling, long needles precipitated which were separated by filtration. The yield of product, after purification from glacial acetic acid, m.p. 228–229°, was 72% from the higher-melting sulfide and 35% from the lower-melting sulfide.

Anal. Calcd. for $C_{14}H_{12}O_4S_2$: C, 54.53; H, 3.92. Found: C, 54.41; H, 3.88.

Reaction of 1,2-Dibromoethylene and Cuprous Ethylmercaptide.—The reagents were heated for 8 hours and the product, b.p. 61° at 1 mm., was isolated in the usual way. The analysis indicated that this product was impure ethylmercaptoacetylene.

Anal. Calcd. for C_4H_6S: C, 55.76; H, 7.02. Found: C, 56.60; H, 8.00.

Further distillation did not improve the product. The band characteristic of acetylenic derivatives (3300 $cm.^{-1}$) or the stretching absorption of monosubstituted acetylenes (2100–2140 $cm.^{-1}$) in the infrared spectrum were absent. However, a strong band at 1260 $cm.^{-1}$, which has been assigned to an acetylene bending vibration, was present.

Ethylmercaptocarboxylic Acid.—When the crude ethylmercaptoacetylene was heated in glacial acetic acid with 30% hydrogen peroxide ethylmercaptocarboxylic acid separated. It was purified by crystallization from ethanol, m.p. 145–146°.

Anal. Calcd. for $C_3H_6O_2S$: C, 33.95; H, 5.70; S, 30.20. Found: C, 34.13; H, 5.75; S, 30.29.

Hexaphenylmercaptobenzene.—The preparation was conducted as previously described.[1] After pouring into acid and standing, the precipitate was collected and washed with three 200-ml. portions of acetone. The insoluble residue was dried and extracted with chloroform in a soxhlet for 48 hours. From the chloroform solution, 25 g. (38%) of product resulted which, after crystallization from carbon tetrachloride, melted at 184–185°.

Anal. Calcd. for $C_{42}H_{30}S_6$: C, 69.38; H, 4.15. Found: C, 69.50; H, 4.40.

The acetone washings of the crude hexaphenylmercaptobenzene deposited, after 7 days in a refrigerator, 9.9 g. of crystals. After purification by several crystallizations from glacial acetic acid they melted at 149.5–150°, yield 5 g. (7.6%).

Anal. Calcd. for $C_{42}H_{30}S_6$: C, 69.38; H, 4.15. Found: C, 69.25; H, 4.08.

Hexabenzenesulfonylbenzene.—A solution of 5 g. of hexaphenylmercaptobenzene (m.p. 184–185°) in 400 ml. of glacial acetic acid was treated with 110 ml. (12 times theory) of 30% hydrogen peroxide, added in thirteen portions during 7 days. After addition of each portion, the mixture was slowly heated to 120° and the temperature maintained there for 2 hours before allowing to cool. At the end of the oxidation 0.9 g. of product separated on cooling. After three recrystallizations from glacial acetic acid it melted at 264–266°. The infrared spectrum showed peaks at 1148 and 1333 $cm.^{-1}$.

Anal. Calcd. for $C_{42}H_{30}O_{12}S_6$: C, 54.89; H, 3.29; S, 20.93. Found: C, 55.10; H, 3.57; S, 20.6.

The mother liquors on concentration did not yield any more product.

By oxidation in a similar manner of the lower-melting hexaphenylmercaptobenzene, no pure product could be isolated.

Reaction of β-Bromonaphthalene and Cuprous Benzylmercaptide and with Cuprous Ethyl Xanthate.—The reaction of β-bromonaphthalene and cuprous benzylmercaptide, or cuprous ethyl xanthate, was carried out in the usual way. The product in less than 10% yield that could be separated from the unchanged β-bromonaphthalene proved to be β-naphthyl sulfide, m.p. 150–151°. This was identified by analysis and by oxidation with hydrogen peroxide in acetic acid to give β-dinaphthyl sulfone, m.p. 177–178°.

Anal. Calcd. for $C_{20}H_{14}O_2S$: C, 75.45; H, 4.43. Found: C, 75.55; H, 4.66.

Acknowledgment.—The authors thank the A. P. Sloan Foundation for financial help which made this investigation possible. The authors are indebted to Mr. J. Nemeth, Miss C. Higham and Mrs. Ruby Liu for the microanalyses and to Mr. P. E. McMahon and Mr. B. A. Shoulders for the determination of the infrared spectra.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Stereochemistry of the Base-catalyzed Addition of *p*-Toluenethiol to Propiolic Acid[1,2]

BY WILLIAM E. TRUCE, DAVID L. GOLDHAMER AND ROBERT B. KRUSE

RECEIVED MARCH 27, 1959

An exception to the Rule of *trans*-Nucleophilic Addition has been reported for the base-catalyzed addition of *p*-toluenethiol to sodium propiolate to give *trans*-*p*-tolylmercaptoacrylic acid. Rates of cyclization of the *cis*- and *trans*-*p*-tolylmercaptoacrylic acids together with infrared spectral data and dipole moment measurements of the corresponding *cis*- and *trans*-*p*-tolylsulfonylacrylic acids have elucidated the configurations of *cis*- and *trans*-*p*-tolylmercaptoacrylic acids.

Montanari and Negrini have reported the formation of "*cis*"- and "*trans*"-*p*-tolylmercaptoacrylic acids (II) and (I), respectively, as shown[3] The melting points of the assigned "*cis*"-(II) and "*trans*"-(I) were 143–144° and 137–138°, respectively. Their "bases"[3] for assignment of configurations were: (a) the rule, formulated by Montanari, that substitution of the halogen of a vinylic-type halide by a nucleophilic agent proceeds with "retention of configuration," (b) isomer II may be converted to isomer I by thermal isomerization: the von Auwers–Skita rule states that the *trans* isomer would be more thermally stable, (c) the

(1) This constitutes Paper X in the series, "Stereospecific Reactions of Nucleophilic Agents with Acetylenes and Vinyl-type Halides"; for preceding paper see THIS JOURNAL, **81**, 592 (1959).

(2) Taken from the Ph.D. theses of Mr. Goldhamer and Mr. Kruse.

(3) F. Montanari and A. Negrini, *Gazz. chim. ital.*, **87**, 1073 (1957).