B. Mole Ratio AlCl$_3$/C$_4$H$_9$C$_6$H$_5$ = 0.40.—Three disproportionations were run as before using n-butyl-α-C^{14}-benzene of 1.17 μc./mmole activity. In the first two, 15 g. of hydrocarbon and 6 g. of aluminum chloride were used. The amounts of dibutylbenzene obtained by fractional distillation were too small to allow oxidative degradation and accurate radioassay, so in the third disproportionation the amounts of hydrocarbon and catalyst were doubled. After decomposition of this third reaction mixture and extraction in the usual way, the ether and benzene were distilled at atmospheric pressure and the higher-boiling products were fractionated through a 50-cm. glass helix-packed column. The following fractions were obtained.

No.	B.p. °C.	Mm.	Reflux ratio	Wt., g.
1	97.5–100	49–51	1/1	8.21
2	100–132	51	9/1	0.40
3	132–145	51	9/1	0.78
4	145–153	51	1/1	2.64
Residue				3.50
			Total	15.53

Oxidation of 1 ml. of fraction 1 gave benzoic acid with an activity of 1.12 μc./mmole, after sublimation and resublimation. Oxidation of 1 ml. of fraction 4 gave phthalic acid with an activity of 2.23 μc./mmole after recrystallization and sublimation.

EXTENT OF ISOTOPIC REARRANGEMENT IN DISPROPORTIONATIONS

Disproportionation	Isotopic rearrangement, % in Butylbenzene	Dibutylbenzene
1	5.0	..
2	4.3	..
3	4.3	4.3

Disproportionation of Ethyl-β-C^{14}-benzene.—The ethyl-β-C^{14}-benzene was prepared as described previously.[5] Small liquid samples (*ca.* 3 mg.) were radioassayed.[4] The activity of the material used in the disproportionations was 0.431 μc./mmole.

A. **Single Disproportionation.**—An 11.9-g. sample of ethyl-β-C^{14}-benzene and 4.86 g. of aluminum chloride (AlCl$_3$/C$_2$H$_5$C$_6$H$_5$, mole ratio 0.32) were heated and stirred at 100° for 6.5 hours. The reaction mixture was decomposed, extracted and distilled as before. A 50-cm. glass helix-packed column was used to separate the products. The fractions collected included benzene, b.p. 76–85°, 0.88 g.; ethylbenzene, b.p. 130–137°, 2.36 g.; and diethylbenzene, b.p. 170–183°, 1.23 g.

Oxidation of the ethylbenzene fraction gave benzoic acid with a radioactivity of 4.4 × 10^{-3} μc./mmole, corresponding to 1.0% isotopic rearrangement. Oxidation of the diethylbenzene fraction gave phthalic acid with a radioactivity of 8.2 × 10^{-3} μc./mmole, corresponding to 1.0% isotopic rearrangement per alkyl group.[7]

B. **Triple Disproportionation.**—The same amounts of materials used in the experiment above were heated and stirred as before for 6.5 hours at 100°. The reaction mixture was worked up as before, through the step in which ether was removed from the hydrocarbons by distillation through a 50-cm. glass helix-packed column. The hydrocarbon mixture was not distilled, however, but to it was added 4.86 g. of fresh aluminum chloride, and the mixture was heated and stirred for 6.5 hours at 100°. This procedure was repeated once more and then the hydrocarbon mixture was distilled through a 50-cm. glass helix-packed column. The fractions collected included benzene, b.p. 77–86°, 1.20 g.; ethylbenzene, b.p. 131–138°, 1.26 g.; and diethylbenzene, b.p. 176–177°, 1.40 g. (After the first disproportionation the reaction mixture was orange, after the second, purple, and after the third, black.)

Oxidation of the ethylbenzene fraction gave benzoic acid with a radioactivity of 3.44 × 10^{-2} μc./mmole (32- and 47-mg. samples assayed), corresponding to 8.0% isotopic rearrangement. Oxidation of the diethylbenzene fraction gave phthalic acid with a radioactivity of 6.55 × 10^{-2} μc./mmole (22- and 19-mg. samples assayed), corresponding to 7.6% isotopic rearrangement per alkyl group.

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[7] In the radioassay of these weakly radioactive products, large samples were assayed—36 to 46 mg. of benzoic acid and 26 to 38 mg. of phthalic acid—in order to increase the accuracy of the assay.

AUSTIN 12, TEXAS

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF J. T. BAKER CHEMICAL CO.]

Preparation of Thiolmethacrylate Esters. A Study of the Reaction of Sodium Mercaptides with Methacrylyl Chloride[1]

BY GENE SUMRELL, GEORGE E. HAM AND EDWIN D. HORNBAKER

RECEIVED JANUARY 8, 1958

The usefulness of the reaction of sodium mercaptides with methacrylyl chloride as a means of preparing aryl and alkyl thiolmethacrylates has been investigated. This method was quite successful when the group attached to sulfur was phenyl, 4-chlorophenyl, pentachlorophenyl, isopropyl and t-butyl, but failed with methyl mercaptan and 2-mercaptobenzothiazole. The anomalous reaction which occurred in the case of the latter mercaptan is discussed. The alkyl mercaptides displayed a tendency to react at the double bond, with this tendency decreasing in the order: methyl >>> isopropyl > t-butyl. The reaction of the sodium mercaptides of benzenethiol and t-butyl mercaptan with acrylyl chloride also is reported.

The widespread usefulness which has been found for acrylic type esters led us to a desire to study the sulfur analogs of some of these compounds. The first extensive study of the thiol esters of acrylic acid was reported by Marvel and coworkers.[2] They prepared seven alkyl thiolacrylates by a method involving the reaction of 2,3-dibromopropionyl chloride with a mercaptan, followed by the removal of bromine with sodium iodide. The ease with which the mercaptans added to the double bond prevented the preparations from being carried out directly from acrylyl chloride and the mercaptans.

Recently Koton and co-workers reported the preparation of phenyl thiomethacrylate and benzyl thiolmethacrylate by a procedure involving the addition of the acid chloride to a cold solution of the mercaptan in a small excess of 5% aqueous sodium hydroxide.[3] This method appeared to be of considerable interest if generally applicable to the preparation of thiolmethacrylates and has been further investigated by us. Its shortcomings were im-

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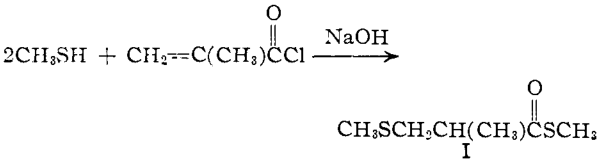
[1] The antibacterial and antifungal properties of some of the compounds described in this paper will be reported elsewhere.

[2] (a) C. S. Marvel, S. L. Jacobs, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **19**, 59 (1956); see also (b) S. L. Jacobs, Ph.D. Thesis, University of Illinois; *C.A.*, **49**, 10894 (1955).

[3] M. M. Koton, T. M. Kiselyeva and K. S. Podgorskaya, *Zhur, Obshchei Khim.*, **26**, 475 (1956); *C.A.*, **50**, 13815 (1956).

mediately apparent when a run carried out with methyl mercaptan gave a 76% yield of the methyl thiol ester containing a mole of the mercaptan added across the double bond

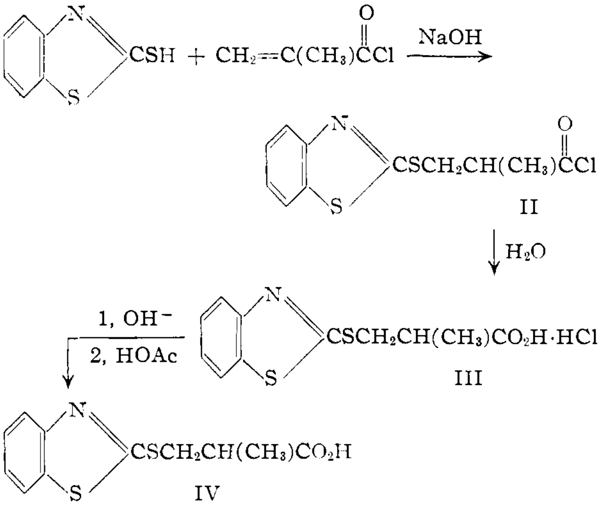


$$2CH_3SH + CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}Cl \xrightarrow{NaOH} CH_3SCH_2CH(CH_3)\overset{O}{\overset{\|}{C}}SCH_3$$

I

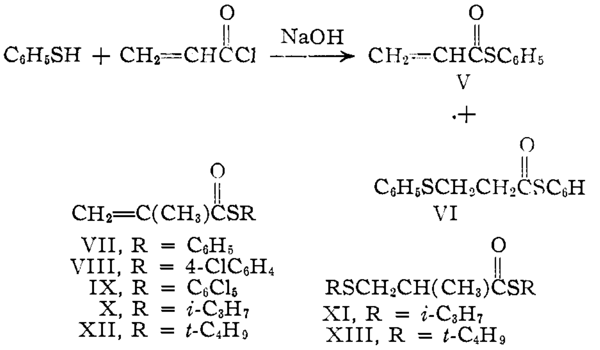
Compound I was quite stable, distilling undecomposed at atmospheric pressure. A small forerun probably contained traces of the desired methyl thiolmethacrylate.

It was thought that a mercaptan with a bulkier group might have less tendency to add to the double bond. Accordingly, the reaction was carried out using 2-mercaptobenzothiazole. A solid precipitate formed as the acid chloride was added dropwise to the cold alkaline solution of the mercaptan. When this solid was filtered, washed free of alkali, and allowed to stand at room temperature for several hours, it slowly liquefied. Then, over the next day or two it slowly solidified again. Most of the material now dissolved readily in aqueous sodium bicarbonate solution. Acidification with acetic acid gave compound IV. Another sample of the crude wet material which was stored at about 5° exhibited no change in appearance, and lost no weight. However, it was quite dry after several days, and was now soluble in sodium bicarbonate solution. This material evidently was composed primarily of hydrochloride III, resulting from the slow hydrolysis of II. A benzene solution of crude III slowly evolved hydrogen chloride. Attempts to cause crystallization from various solvents led to oiling out. After long standing a solution of III in a mixture of benzene and petroleum ether eventually gave crystalline material which proved to be a higher melting polymorph of IV. The purest samples of these two forms melted at 74–76° and 98.5–100°, respectively. Either form could be obtained moderately readily by seeding molten IV with the proper seed. When melted, IV showed little tendency to crystallize even at room temperature without seeding.



At this point we decided to attempt to repeat the work reported by Koton,[3] using benzenethiol. No difficulty was encountered except for extensive polymerization during the reaction and working up period. Rapid work and the use of iodine as an inhibitor allowed us to obtain yields up to 84% of phenyl thiolmethacrylate, with no indication of addition to the double bond. Similar results were obtained with 4-chlorobenzenethiol and with pentachlorobenzenethiol.

That reaction at the double bond can occur also with benzenethiol in alkaline solution was shown by using acrylyl chloride in the place of methacrylyl chloride. The yield of phenyl thiolacrylate (V) from such a run was 24%, and a yield of 36% of addition product VI also was obtained.[4]



$$C_6H_5SH + CH_2{=}CH\overset{O}{\overset{\|}{C}}Cl \xrightarrow{NaOH} \underset{V}{CH_2{=}CH\overset{O}{\overset{\|}{C}}SC_6H_5} + \underset{VI}{C_6H_5SCH_2CH_2\overset{O}{\overset{\|}{C}}SC_6H}$$

$$CH_2{=}C(CH_3)\overset{O}{\overset{\|}{C}}SR$$

VII, R = C_6H_5
VIII, R = 4-ClC_6H_4
IX, R = C_6Cl_5
X, R = i-C_3H_7
XII, R = t-C_4H_9

$$RSCH_2CH(CH_3)\overset{O}{\overset{\|}{C}}SR$$

XI, R = i-C_3H_7
XIII, R = t-C_4H_9

With this information in hand, further runs were made using more hindered alkyl mercaptans. Isopropyl mercaptan gave a 57% yield of thiolmethacrylate X, and a 26% yield of addition product XI. When the reaction was carried out with *t*-butyl mercaptan using 5% sodium hydroxide, the usual procedure in most of these runs, the yield of thiolmethacrylate XII was 68% and no addition product was detected. Considerable polymerization during the distillation accounted for the low yield. On another run in which the alkali concentration was increased to 10% (resulting in doubling the concentration of sodium mercaptide), the yield of XII was reduced to 59%, and a yield of 26% of addition product XIII was obtained. The use of iodine as an inhibitor on this run reduced the amount of polymerization during distillation to a negligible amount.

The reaction of a 5% sodium hydroxide solution of *t*-butyl mercaptan with acrylyl chloride gave a 20% yield of *t*-butyl thiolacrylate and a 54% yield of the thiol ester containing mercaptan added across the double bond. In this case an intermediate fraction proved to be the acid chloride formed by addition of a mole of *t*-butyl mercaptan across the double bond of acrylyl chloride. The yield of this acid chloride was 8%.

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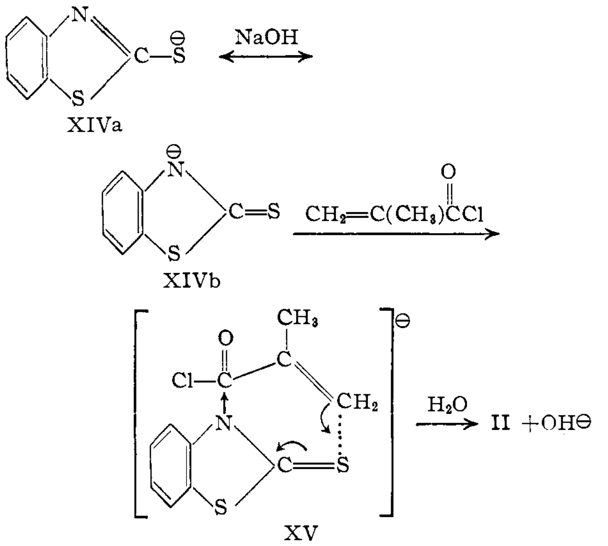
[4] The assignment of attachment of the sulfur atom at the β-carbon in these addition compounds is somewhat arbitrary, but is supported by the following facts: (a) The narrow boiling ranges found for most of the compounds suggests the absence of isomers; (b) the work of B. Holmberg and E. Schjanberg, *Arkiv Kemi, Mineral. Geol.*, **14A**, No. 7 (1940) (see *C.A.*, **35**, 2113 (1941)) showed that when thioacetic acid adds to the double bond of unsaturated acids, the AcS group goes distant from the carboxyl group; and (c) no infrared absorption band occurred in the region of 3.37 μ for compound VI, whereas such a band was present in the spectra of the compounds derived from methacrylic acid, which has a branching methyl group. These spectra were determined and interpreted for us by Mr. Francis Joy.

The tendency of mercaptans and other compounds with an active hydrogen to add to the double bond of acrylate and methacrylate esters in the presence of basic catalysts is well known.[5]

However, the behavior of 2-mercaptobenzothiazole is anomalous compared with results obtained with other mercaptans in our work. It is of interest to note that when pentachlorobenzenethiol was used, the resulting pentachlorophenyl thiolmethacrylate (IX) gave a precipitate as the reaction proceded in much the same manner that acid chloride II precipitated when 2-mercaptobenzothiazole was used. In one case, however, the reaction was predominantly at the double bond; in the other a high yield of the desired thiolmethacrylate was obtained. The explanation probably lies in the fact that the mercaptide ion of 2-mercaptobenzothiazole can be represented by the resonance forms pictured as XIV, with XIVb probably being the larger contributor to the actual structure.[6] The anomalous reaction of this mercaptide with methacrylyl chloride is thus represented by the initial attack of ion XIVb at the carbonyl carbon. A cyclic mechanism then involves the formation of complex XV. Electron shifts as indicated, along with acquisition of a hydrogen ion from the reaction medium gives compound II.



XIVa

XIVb

XV

In the course of this work a sample of methyl thiolmethacrylate was desired. Since the attempt to prepare it by reaction of the sodium mercaptide with methacrylyl chloride failed, a method similar to that of Marvel[2] employing the dibromo acid chloride and methyl mercaptan, followed by removal of bromine was used, resulting in an over-all yield of 63% of methyl thiolmethacrylate. Further work (see Experimental) gave a more convenient procedure for making this thiol ester (45% yield) involving the slow addition of pyridine to a cold solution of methyl mercaptan and methacrylyl chloride in 1,2-dimethoxyethane. Ethyl thiolmethacrylate was similarly prepared in 47% yield.

Experimental

Unless otherwise indicated, distillations were carried out through an 80-cm. Podbielniak-type column with heated jacket and partial reflux head similar to that described by Cason and Rapoport.[7] Boiling points and melting points are uncorrected.

Starting Materials.—The mercaptans were commercial materials and were used without purification. The methacrylyl chloride and acrylyl chloride were prepared in a similar manner to that described by Rehberg, Dixon and Fisher.[8]

Methyl 2-Methyl-3-thiomethoxythiolpropionate (I).—A solution of 48 g. (1 mole) of methyl mercaptan in 1000 ml. of aqueous 5% sodium hydroxide was prepared. To this solution with stirring and cooling was added dropwise 110 g. (1.04 moles) of methacrylyl chloride, maintaining the temperature below 10°. Stirring was continued for one hour. On stopping the stirrer, an oily bottom layer separated. The aqueous layer proved to be acidic. The oil was extracted into ether, washed with 10% sodium carbonate solution, then with water until neutral, and dried over sodium sulfate. Fractionation gave a small forerun followed by 62.7 g. (76% based on mercaptan) of material at 99–101° (10 mm.), n^{22}_{D} 1.5190, leaving a viscous residue of 6.8 g. The product distilled without decomposition at 223–224° at atmospheric pressure.

Anal. Calcd. for $C_6H_{12}OS_2$: C, 43.86; H, 7.36; S, 39.03. Found: C, 43.50; H, 7.26; S, 39.02.

Methyl Thiolmethacrylate.[9]—A solution of 96 g. (2 moles) of methyl mercaptan in 200 ml. of anhydrous 1,2-dimethoxyethane was added ice-cold to 209 g. (2 moles) of methacrylyl chloride at 0°. Then, with stirring and cooling, 161 g. (2.04 moles) of pyridine was added dropwise during 2 hours. After an hour of additional stirring, water was added and the organic layer was extracted into ether and dried over sodium sulfate. Then 0.5 g. of iodine was added and the material was fractionated.[10] After removal of solvent there was obtained 104 g. (45%) of methyl thiolmethacrylate at 58–59° (32 mm.), n^{25}_{D} 1.4936, leaving 40 g. of viscous residue.

Anal. Calcd. for C_5H_8OS: C, 51.69; H, 6.94; S, 27.60. Found: C, 52.04; H, 7.09; S, 27.20.

Methyl thiolmethacrylate was also prepared by the following procedure: To a solution of 2 moles of methacrylyl chloride in 165 ml. of carbon tetrachloride, with stirring and cooling to −10° with an ice-acetone mixture, was added dropwise 2 moles of bromine (freshly washed with concd. sulfuric acid). The cooling bath was removed and stirring continued for 5 hours. Then the mixture was warmed slowly to 70°, at which point the bromine fumes had disappeared. The mixture was then chilled to 0° and an ice-cold solution of 100 g. (2.08 moles of methyl mercaptan in 200 ml. of 1,2-dimethoxyethane was added dropwise with stirring. There was little or no exothermic reaction. The mixture was allowed to stand overnight. Then 250 ml. of material was distilled from the mixture, removing most of the hydrogen chloride and leaving about 400 ml. of brownish-colored residue. This material was washed until neutral with 15% sodium chloride solution and dried over sodium sulfate. It was then added dropwise to a solution of 4 moles of sodium iodide in 2500 ml. of acetone, and left stirring overnight. The mixture was then reduced to one-

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[5] See E. H. Riddle, "Monomeric Acrylic Esters," Reinhold Publishing Corp., New York, N. Y., 1954, pp. 146–186.

[6] Evidence has been advanced to show that 2-mercaptobenzothiazole probably exists in a thioketone form with the hydrogen attached to nitrogen. See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 293, and references cited there.

[7] J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 238.

[8] C. E. Rehberg, M. B. Dixon and C. H. Fisher, THIS JOURNAL, **67**, 208 (1945).

[9] While our manuscript was in the hands of the referee a paper appeared by G. Braude, *J. Org. Chem.*, **22**, 1675 (1957), describing the preparation of methyl and ethyl thiolmethacrylate and certain other unsaturated thiol esters by a procedure involving the reaction of the lead mercaptides with the acid chloride in ether. Braude reports for ethyl thiolmethacrylate a 57% yield, b.p. 50–51° (13 mm.), d^{20}_{4} 0.973; for methyl thiolmethacrylate, b.p. 58° (36 mm.), d^{20}_{4} 1.032. No yield is given for the latter compound.

[10] An attempt to distil material from a similar run using hydroquinone (1 g.) as an inhibitor instead of iodine led to extensive polymerization in the column and flask and very little distillate was obtained.

half its volume by distillation. One liter of ether was added and the precipitated sodium bromide was removed by washing with water, followed by removal of iodine by washing with 10% sodium thiosulfate solution. Fractionation gave 147 g. (63%) of methyl thiolmethacrylate.[11]

Ethyl Thiolmethacrylate.[9]—A mixture of 35.5 g. (0.57 mole) of ethyl mercaptan, 0.1 g. of iodine and 50 ml. of anhydrous 1,2-dimethoxyethane was chilled to −5° and 60 g. (0.57 mole) of methacrylyl chloride was added. Then 50 ml. of pyridine was added dropwise to the stirred mixture at such a rate that the temperature remained below 5°. The mixture was stirred 2 hours and worked up as described in the preparation of the methyl thiol ester. Fractionation gave 35 g. (47%) of ethyl thiolmethacrylate at 65–66° (25 mm.), n^{25}_{D} 1.4856. The yellow, viscous residue amounted to 17 g.

Anal. Calcd. for $C_6H_{10}OS$: C, 55.35; H, 7.74; S, 24.62. Found: C, 55.47; H, 7.78; S, 24.47.

Reactions Involving 2-Mercaptobenzothiazole.—A solution of 0.5 mole of 2-mercaptobenzothiazole in 600 ml. of 5% aqueous sodium hydroxide was prepared. The temperature was maintained at 15–20° by external cooling while 0.55 mole of methacrylyl chloride was added dropwise with stirring. A solid began separating almost immediately. The stirred mixture was chilled to 0°, filtered, and washed with water until the washings were neutral. On standing at room temperature, the material slowly liquefied over a period of several hours, but in a few days was solid again. At this point it was mostly soluble in aqueous sodium bicarbonate solution, having become increasingly soluble as time went on. The solid was treated with an excess of 10% sodium carbonate solution and filtered to remove a small amount of insoluble material (which proved to be 2-mercaptobenzothiazole). After a charcoal treatment, the nearly colorless solution was chilled to 0–5° and acetic acid was added with stirring. The addition was extremely slow at first to avoid oiling out, but more rapid after crystallization started. The yield was 90 g. (71%) of **2-methyl-3-(2-mercaptobenzothiazolyl)-propionic acid** (IV), m.p. 74–76°.

Anal. Calcd. for $C_{11}H_{11}NO_2S_2$: C, 52.15; H, 4.39; N, 5.53; S, 25.31. Found: C, 52.10; H, 4.28; N, 5.66; S, 25.69.

On another similar run, a portion of the moist solid obtained by filtration of the reaction mixture was stored at 5°. It did not liquefy on standing. The only change noted was that after several days it had become quite dry.[12] No loss in weight had occurred. Attempts to recrystallize this material were rendered difficult by oiling out. On solution in benzene, hydrogen chloride was noted to evolve. Eventually crystalline material of m.p. 94–99° was obtained from a mixture of benzene and petroleum ether (30–60°); several more recrystallizations gradually raised the m.p. to 98.5–100°. This material proved to be a higher melting form of IV. Either polymorph formed predominantly when molten IV was seeded with the desired form. The molten material was observed to stand many hours at room temperature without crystallizing unless seeded. When crystallization did occur spontaneously, the lower-melting form usually resulted.

On one run methacrylic acid was substituted for the acid chloride to see whether the sodium mercaptide would add to the double bond of the acid under these conditions. The solid which precipitated as the acid was added proved to be 2-mercaptobenzothiazole. Further addition of the acid gave a quantitative recovery of the mercaptan.

Phenyl Thiolmethacrylate (VII).—Two moles of benzenethiol were dissolved in 2000 ml. of 5% sodium hydroxide solution. The stirred mixture was maintained at 0–5° while 220 g. (2.1 moles) of methacrylyl chloride was added dropwise. Stirring was continued for one-half hour, then the organic bottom layer was separated from the basic aqueous layer, washed once with water, and run directly into a flask containing sodium sulfate and 0.4 g. of iodine. The aqueous phases in the two separatory funnels were washed in series with 50 ml. of chloroform, which was added to the flask containing the product. After drying, the chloroform was removed and the product distilled rapidly through a simple Claisen head at 80–90° (1 mm.), yielding 301 g. (84%) of product, n^{25}_{D} 1.5755. There remained a residue of 37 g. which proved to be polymeric in nature. Fractionation of the product revealed no significant impurities and gave a boiling range of 103–104° (3 mm.) (lit.[3] b.p. 107° (4 mm.), n^{20}_{D} 1.5774).

Phenyl Thiolacrylate (V).[13]—To a solution of one mole of benzenethiol in 1000 ml. of 5% sodium hydroxide was added dropwise, with stirring and cooling to 0–10°, 133 g. (1.47 moles) of acrylyl chloride. The organic phase was extracted with ether, washed with 10% sodium carbonate solution, and then with water until neutral and dried over sodium sulfate containing 0.2 g. of iodine. Distillation through a simple Claisen head at water-pump pressure gave 40.2 g. (24%) of phenyl thiolacrylate. Fractionation led to extensive polymerization, but gave a boiling range of 115–116° (6 mm.) for this material; n^{24}_{D} 1.5869.

Anal. Calcd. for C_9H_8OS: C, 65.84; H, 4.91; S, 19.53. Found: C, 65.70; H, 4.80; S, 19.40.

A residue of 75 g. of material remained from the distillation of the phenyl thiolacrylate. Fractionation of this material gave 65 g. (47% based on benzenethiol) of **phenyl 3-thiophenoxythiolpropionate** (VI) at 233–235° (7 mm.), n^{23}_{D} 1.6238.

Anal. Calcd. for $C_{15}H_{14}OS_2$: C, 65.66; H, 5.14; S, 23.37. Found: C, 65.69; H, 5.05; S, 23.62.

4-Chlorophenyl thiolmethacrylate (VIII) was prepared on a 0.3-mole scale by a procedure essentially like that described for VII. It proved to be even more susceptible to polymerization. The yield was 35.7 g. (56%) at 90–92° (0.3 mm.), n^{23}_{D} 1.5876, leaving 17.7 g. of residue which was polymeric in nature.

Anal. Calcd. for $C_{10}H_9ClOS$: C, 56.47; H, 4.27; Cl, 16.67; S, 15.07. Found: C, 56.30; H, 4.25; Cl, 16.55; S, 15.14.

Pentachlorophenyl Thiolmethacrylate (IX).—A mixture of 1 mole of pentachlorobenzenethiol in 1500 ml. of 4% sodium hydroxide was maintained at 15–20° while 1 mole of methacrylyl chloride was added dropwise with stirring. A solid began precipitating immediately. The mixture was stirred 1 hour, filtered, and washed well with water. Drying yielded 305 g (87%) of crude pentachlorophenyl thiolmethacrylate of m.p. 92–100°. Two recrystallizations from acetone gave material with the constant m.p. 101–102°.

Anal. Calcd. for $C_{10}H_5Cl_5OS$: C, 34.27; H, 1.44; Cl, 50.58; S, 9.15. Found: C, 34.17; H, 1.40; Cl, 50.81; S, 9.28.

Isopropyl Thiolmethacrylate (X).—This preparation was carried out on a 2-mole scale essentially by the procedure described for VII. Fractionation from 0.1 g. of iodine gave 166 g. (57%) of isopropyl thiolmethacrylate at 55–56° (9 mm.), n^{25}_{D} 1.4790.

Anal. Calcd. for $C_7H_{12}OS$: C, 58.29; H, 8.39; S, 22.23. Found: C, 58.21; H, 8.25; S, 21.98.

Fractionation of the higher-boiling material from the above run gave 57 g. (26% based on mercaptan) of **isopropyl 2-methyl-3-(2-thiopropoxy)-thiolpropionate** (XI) at 120–121° (8 mm.), n^{24}_{D} 1.4906, leaving 12 g. of viscous yellow residue.

Anal. Calcd. for $C_{10}H_{20}OS_2$: C, 54.49; H, 9.15; S, 29.09. Found: C, 54.89; H, 8.99; S, 29.10.

t-**Butyl Thiolmethacrylate** (XII).—A preparation of this compound was carried out on a 0.5-mole scale by essentially the procedure described for VII, except that hydroquinone (1 g.) was added as an inhibitor before distillation instead of

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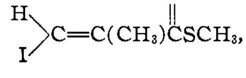
[11] A residue of 121 g. of material was not successfully purified by fractionation. It mostly distilled at 100–120° (8 mm.), without any sharp cuts and appeared to be largely a mixture of the dibromo thiol ester and an iodo compound, possibly



$$\overset{\mathrm{H}}{\underset{\mathrm{I}}{>}}\mathrm{C{=}C(CH_3)}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{SCH_3},$$

or an isomer, which might form by the splitting out of hydrogen iodide from the diiodo compound.

[12] This crude material had m.p. 70–80°. It analyzed for 9.23% chlorine; theory for the hydrochloride of IV, 12.24%.

[13] The only reference to phenyl thiolacrylate which we have found in the literature is the report by W. Reppe, *Ann.*, **582**, 13 (1953), that this compound resulted from the reaction of acetylene, carbon monoxide and benzenethiol. He reports a b.p. of 150–180° (10 mm.), but gives no experimental details, yield or analysis.

iodine. The yield was 54 g. (68%) of XII distilling at 62–63° (13 mm.), $n^{24}_{\rm D}$ 1.4783.

Anal. Calcd. for $C_8H_{14}OS$: C, 60.71; H, 8.92; S, 20.26. Found: C, 60.84; H, 8.80; S, 19.98.

There remained 26 g. of residue from the above distillation which solidified on cooling and was polymeric in nature. On another run 2 moles of methacrylyl chloride was added dropwise at 0–10° to a stirred solution of 2 moles of *t*-butyl mercaptan in 1000 ml. of 10% sodium hydroxide. The organic phase was separated, washed with water, and dried over sodium sulfate. Distillation was carried out from 0.2 g. of iodine, yielding 187 g. (59%) of XII at 56–57° (8 mm.), followed by 65 g. (26% based on mercaptan) of **t-butyl 2-methyl-3-(2-methyl-2-thiopropoxy)-thiolpropionate** (XIII) at 128–129° (8 mm.), $n^{24}_{\rm D}$ 1.4865, leaving 7 g. of hard yellow residue.

Anal. Calcd. for $C_{12}H_{24}OS_2$: C, 58.01; H, 9.74; S, 25.81. Found: C, 58.35; H, 9.67; S, 25.50.

Illustrating the fact that the *t*-butyl mercaptide could react at the double bond of methacrylyl chloride prior to reaction at the acid chloride function was another 2-mole run in which the acid chloride was added in one portion to the chilled solution of mercaptan in 5% sodium hydroxide. The mixture was stirred with cooling for 2 hours and worked up in the usual manner. Fractionation from 0.1 g. of iodine gave a 47% yield of *t*-butyl thiolmethacrylate and a 21% yield of addition compound XIII. An intermediate fraction of 25 g. (6%) proved to be **2-methyl-3-(2-methyl-2-thiopropoxy)-propionyl chloride**, b.p. 91–92° (12 mm.), $n^{24}_{\rm D}$ 1.4740.

Anal. Calcd. for $C_8H_{15}ClOS$: C, 49.34; H, 7.77; Cl, 18.21; S, 16.46. Found: C, 49.55; H, 7.97; Cl, 18.29; S, 16.44.

Reaction of the *t*-Butyl Mercaptide with Acrylyl Chloride.—To 1000 ml. of 5% sodium hydroxide was added 90.2 g. (1 mole) of *t*-butyl mercaptan. The solution was maintained at 0–5° while 100 g. (1.1 moles) of acrylyl chloride was added dropwise with stirring. The organic phase was then separated and washed with 10% sodium carbonate, then with water, and run into a flask containing sodium sulfate and a trace of iodine. After drying, the material was decanted and fractionally distilled, yielding 29 g. (20%) of *t*-butyl thiolacrylate at 50–51° (12 mm.), $n^{23}_{\rm D}$ 1.4786 (lit.[2] b.p. 44.5–45° (8 mm.), $n^{21.2}_{\rm D}$ 1.4808). An intermediate fraction of 15 g. (8%) of **3-(2-methyl-2-thiopropoxy)-propionyl chloride** followed at 88–89° (11 mm.), $n^{23}_{\rm D}$ 1.4788.

Anal. Calcd. for $C_7H_{13}ClOS$: C, 46.53; H, 7.25; Cl, 19.62; S, 17.74. Found: C, 46.56; H, 7.10; Cl, 19.99; S, 17.65.

Continuation of the distillation yielded 63 g. (54%) of **t-butyl 3-(2-methyl-2-thiopropoxy)-thiolpropionate** at 135–136° (11 mm.), $n^{23}_{\rm D}$ 1.4900.

Anal. Calcd. for $C_{11}H_{22}OS_2$: C, 56.36; H, 9.46; S, 27.35. Found: C, 56.27; H, 9.34; S, 27.18.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Reactions of Elemental Sulfur. II. The Reaction of Alkali Cyanides with Sulfur, and Some Single-Sulfur Transfer Reactions[1]

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The reaction of sulfur, S_8, with cyanide has been studied kinetically in homogeneous solution. The reaction is of second order, first order in each reactant. The effects of salts and solvents upon the rate has been interpreted as evidence for the rate-determining step being the opening of the S_8 ring by cyanide ion. Two other forms, hexatomic sulfur and irradiated sulfur, react immeasurably fast with cyanide ion. Ferricyanide and ferrocyanide ions do not attack sulfur at a measurable rate. Several sulfur transfer reactions have been studied.

Introduction

When sulfur reacts with an ionic cyanide the product is exclusively the thiocyanate; the reaction has been used as an analytical method for sulfur. The thiocyanate produced can be titrated with silver nitrate[3,4] or measured spectrophotometrically as the ferric–thiocyanate complex.[5] The reaction is fast enough at 40° to permit the titration of sulfur with cyanide using potentiometric *p*H measurements.[6]

Triarylphosphines,[1] like cyanide ion, react cleanly with sulfur to yield a single product, the phosphine sulfide, which is produced in a second-order reaction. The rate of the reaction is markedly increased by anion-solvating solvents

$$8\mathrm{Ar_3P} + \mathrm{S_8} \longrightarrow 8\mathrm{Ar_3PS} \qquad (1)$$

and by electron-releasing substituents in the phenyl groups ($\rho = -2.5$ in the Hammett equation). Two other forms of sulfur, the hexatomic form[7] and the amorphous form produced by irradiation,[8] react immeasurably fast with triphenylphosphine in benzene. From these facts it was concluded that the rate-determining step was the opening of the sulfur ring on attack by the phosphine giving a dipolar ion which then reacts rapidly in a series of further displacement reactions.

The reaction of sulfur, S_8, with cyanide represents the attack of a strongly nucleophilic anion on sulfur–sulfur bonds. The reaction can easily be

$$8\mathrm{CN^-} + \mathrm{S_8} \longrightarrow 8\mathrm{SCN^-} \qquad (2)$$

followed using the strong ultraviolet absorption of sulfur.[9]

Another reagent which attacks elemental sulfur in similar fashion is the sulfite ion. We find that either triphenylphosphine or cyanide ion will take an atom of sulfur from thiosulfate ion, but there is no measurable reaction of sulfur transfer between

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