benzenesulfenate. Both hydroxysteroids had absorption bands in the hydroxyl region, near 3625 cm.$^{-1}$ These absorption bands were not present in the spectra of either derivative, indicating that the reaction occurred at the hydroxyl group, rather than at some other point in the hydroxysteroid molecule.

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Thiocarboxylic Esters and Related Compounds[1]

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The reaction of unsaturated acid chlorides with lead mercaptides gave the corresponding thiolesters. Polymerization of thiolacrylates and thiolmethacrylates yielded glasslike materials, comparable in properties to the corresponding ester polymers. Attempts to prepare thionoacrylates by dehydrohalogenation of halothionopropionates failed. The stability of the intermediate halo- and dihalopropionimidates to decomposition was found to decrease markedly with increasing halogen substitution. The reaction of unsaturated acid chlorides with sodium sulfhydrate yielded polymeric material, equivalent in analytical composition to the corresponding thioacids.

In spite of the abundant literature published in recent years on lower unsaturated acids and esters, unsaturated thioacid derivatives received remarkably little attention. Previous work in this field was in fact limited to the investigations of Reppe[3] and Jacobs.[4]

In the present study, a number of new thiolesters and thionoesters were prepared, and their physical and chemical properties determined and evaluated. Since this work was completed, Jacobs[4] made a series of thiolacrylates by debromination of dibromothiolpropionates. His attempts to obtain thiolacrylates directly from acrylyl chloride and a mercaptan in presence of sodium carbonate were not successful, due presumably to the addition of the mercaptan to the double bond and the formation of a mercapto thiolpropionate.

In the present work, thiolesters of unsaturated carboxylic acids were prepared directly from the corresponding acid chloride and lead mercaptide, by a modification of the method first described by Obermeyer,[5] which is based on the reaction:

$$2\ \mathrm{RCOCl} + \mathrm{Pb(SR')_2} \longrightarrow 2\ \mathrm{RCOSR'} + \mathrm{PbCl_2}$$

Attempts to prepare ethyl thiolmethacrylate from methacrylyl chloride and lead ethyl mercaptide by Obermeyer's method without a solvent resulted in a violet, exothermic reaction and the formation of a dark, polymerized product. This difficulty was overcome by using anhydrous ether, in which the lead mercaptide was slurried up initially, and by adding the acid chloride gradually with good agitation and cooling. An excess of lead mercaptide (10%) was used to avoid the troublesome separation of unreacted acid chloride.

Properties and analyses of a number of unsaturated thiolesters made by this procedure are listed in Table I.

Samples of the thiolesters were heated in bulk, or in a solvent, or irradiated with ultraviolet light to obtain polymers. As could be expected by analogy with the corresponding esters, only thiolacrylates and thiolmethacrylates were found to polymerize under the conditions employed, yielding transparent, colorless materials.

Saturated thionoesters have been made by Matsui[6] and by Sacurada[7] from an iminoester and hydrogen sulfide:

$$\mathrm{RC(OR')NH} + 2\ \mathrm{H_2S} \longrightarrow \mathrm{RCSOR'} + \mathrm{NH_3}$$

Unsaturated thionoesters have not been described before, and it was an object of this work to attempt their preparation by dehydrohalogenation of halothionopropionates.

A modification of Matsui's method was used for the preparation of a series of halothionopropionates from the corresponding halopropionimidates. The analyses and physical properties of these new compounds are listed in Table II.

Dichloro- and dibromothionopropionates intended for dehalogenation trials, could not be prepared from the corresponding iminoesters, as dihalopropionimidates are not sufficiently stable for reaction with hydrogen sulfide.

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(1) Includes some data from "Unsaturated Thioacids and Derivatives" by G. Braude and T. Lieser (Doctoral Dissertation), University of Halle.

(2) Present address: Grace Research & Development Co., Curtis Bay, Baltimore, Md.

(3) W. Reppe, *Ann.*, **582**, 1 (1939). German Patent **856,293**, July 8, 1949.

(4) L. Jacobs, "Thioacrylic Esters," Doctoral Dissertation, University of Illinois, 1955.

(5) J. Obermeyer, *Ber.*, **20**, 2920 (1887).

(6) M. Matsui, *Mem. Coll. Sci. Kyoto*, **1**, 285 (1908); **3**, 247 (1912).

(7) Y. Sacurada, *Mem. Coll. Sci. Kyoto*, **9**, 237 (1925/26).

TABLE I

UNSATURATED THIOLESTERS

Compound	Boiling Point °C.	Mm. Hg	Spec. Grav., d_{D}^{20}	Analyses Calculated C	H	S	Found C	H	S
Methyl thiolacrylate[a] $CH_2{=}CHCOSCH_3$	65	110	1.052	46.8	5.90	31.2	46.9	5.93	30.8
Ethyl thiolacrylate $CH_2{=}CHCOSC_2H_5$	58	30	1.012	51.7	6.93	27.6	51.2	7.23	27.4
Methyl thiolmethacrylate[b] $CH_2{=}C(CH_3)COSCH_3$	58	36	1.032	51.7	6.93	27.6	51.2	7.40	27.1
Ethyl thiolmethacrylate[b] $CH_2{=}C(CH_3)COSC_2H_5$	50–51	13	0.973	55.3	7.77	24.6	55.1	7.75	24.8
Ethyl thiolcrotonate[b,c] $CH_3CH{=}CHCOSC_2H_5$	74–75 66–67	20 13	1.003	55.3	7.77	24.6	55.3	7.78	24.6
Ethyl thiocinnamate $C_6H_5CH{=}CHCOSC_2H_5$	290 171–173 129–130	752 21 0.5	1.098	68.7	6.30	16.65	68.1	6.13	16.49

[a] Yield: 53%. Irritating white liquid, horseradish odor. [b] Not described before. [c] Oily, slightly yellowish liquid.

TABLE II

THIONOESTERS

Compound	Boiling Point, °C./mm.	Analyses Calculated C	H	Cl	S	Found C	H	Cl	S
Methyl β-chlorothionopropionate $CH_2ClCH_2CSOCH_3$	63–65/13	34.7	5.06	25.6	23.1	34.7	4.94	26.4	23.8
Ethyl β-chlorothionopropionate[a] $CH_2ClCH_2CSOC_2H_5$	81–83/20 55–56/3	39.4	5.94	23.3	21.0	40.3	6.19	23.2	20.2
Ethyl β-bromothionopropionate $CH_2BrCH_2CSOC_2H_5$	121–124/15	30.5	4.57	Br 40.6	16.25	30.2	4.76	Br 39.8	15.71

[a] Specific Gravity d_4^{20} 1.133.

Attempts to dehydrohalogenate the halothionopropionates by treatment with alkali or amines resulted in hydrolysis and decomposition with the formation of dark, tarry materials. Thionoacrylates could not be isolated and identified in any of these reaction products.

In the course of this work, a number of new β-halopropionimidates and dihalopropionimidate hydrohalides were synthesized as intermediates.

Attempts to prepare the free iminoesters from the hydrohalides revealed interesting differences in their stability. Unsubstituted propionimidates are reported as quite stable at room temperature, but β-chloropropionimidates decompose within a few minutes on storage above 0°. Ethyl β-bromopropionimidate had to be prepared with the utmost care below 0° from the hydrohalide, and ethyl dichloropropionimidate decomposed on formation immediately. It is evident that the stability of propionimidates is adversely affected by an increasing halogen substitution.

A number of trials were carried out in the course of this study with the object of preparing unsaturated thioacids.

Hydrolysis of unsaturated thiolesters with sodium hydroxide or sodium sulfhydrate did not yield any thioacid, but an acid and a mercaptan instead, or only polymeric material. In another series of trials, acrylyl or methacrylyl chloride were reacted at room temperature with anhydrous sodium sulfhydrate in ether solution. However, monomeric thioacid or thioacid salt could not be isolated even from reactions run in presence of hydroquinone as an inhibitor.

After the elimination of ether and inorganic salts from the reaction products of acrylyl chloride and sodium sulfhydrate, a water-insoluble solid residue remained. This was separated into several fractions of increasing molecular weight and melting point by extraction with a series of hot solvents and crystallization. Elemental analyses of these fractions gave nearly identical values, which were close to theory for thioacrylic acid.

This material can therefore be considered a mixture of polymers of a molecular weight of over about 400, formed under milder conditions than required for the polymerization of acrylic acid.

This raises the question as to structure, and the following may be a possible explanation. Sherlin,[8] in attempts to polymerize acrylic acid in furan at

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(8) Sherlin, *J. Gen. Chem.* (*U.S.S.R.*), 8, 7–15 (1938).

160°, obtained a dimer of the structure:

$$CH_2{=}CHCOOCH_2CH_2COOH$$

A trimer and higher polymers were formed under similar conditions in benzene.

Sulfhydryl groups, on the other hand, are known to be very reactive. Holmberg,[9] for instance, reported a very exothermic reaction between thioacidic acid and acrylic acid at room temperature, yielding a thiolester structure:

$$CH_3COSH + CH_2{=}CHCOOH \longrightarrow CH_3COSCH_2CH_2COOH$$

By analogy, it was considered conceivable that thioacrylic acid, formed initially, polymerized in the following way:

$$CH_2{=}CHCOSH + CH_2{=}CHCOSH \longrightarrow CH_2{=}CHCOSCH_2CH_2COSH$$

and finally to:

$$CH_2{=}CHCOS(CH_2CH_2COS)_nCH_2CH_2COSH$$

Titration of samples of this material with an alcoholic caustic solution gave values equivalent to one acid group for 5–7 moles, or $n = 5$–7. This is roughly equivalent to apparent molecular weights obtained, and confirms the structure concept expressed.

Further attempts to clarify the identity of these compounds were not conclusive. A more complete structure determination could not be carried out in the course of this work, but would certainly be of interest.

EXPERIMENTAL

Ethyl thiolmethacrylate. The preparation of ethyl thiolmethacrylate is typical for all the reactions in this series.

Lead ethyl mercaptide was prepared by adding ethyl mercaptan to an excess of lead acetate solution under stirring, then filtering off the yellow precipitate, which was washed successively with water, alcohol, and ether. Samples of the mercaptide were made immediately before use to avoid decomposition on storage. Methacrylyl chloride was prepared from methacrylic acid and thionyl chloride and purified by vacuum-distillation.

Lead ethyl mercaptide (36.2 g., 0.11 mole) was slurried in 200 ml. of anhydrous ether, and 21 g. (0.2 mole) of methacrylyl chloride was added over a period of 2–3 hr., stirring continuously. The temperature was maintained between 10° and 20° by cooling and agitation was continued for 1 hr. after the reaction was completed. The salts, consisting of lead chloride and some unreacted lead mercaptide, were then filtered off and washed with ether. All filtrates were combined and the ether was distilled off, leaving a yellow liquid.

Hydroquinone (1%) was then added to prevent polymerization, and the product was distilled under vacuum. The bulk of the material distilled at 50–51° under 13 mm., and weighed 14.8 g., corresponding to a yield of 57% (based on methacrylyl chloride).

All thiolesters listed in Table I were prepared in an analogous manner from the acid chlorides and lead mercaptides in ether solution, using the corresponding molar ratios of starting materials.

Bromination. Methyl thiolacrylate (10 g.) was dissolved in carbon tetrachloride and 15.5 g. of bromine was added gradually under agitation. The solution, which became light yellow a few minutes after the end of the bromine addition, was distilled under vacuum. Methyl dibromothiolpropionate distilled at 92° (13 mm.) as a light yellow oil, which turned red on storage.

Anal. Calcd. for $C_4H_6Br_2OS$: C, 18.32; H, 2.29; Br, 61.0; S, 12.22. Found: C, 18.08; H, 2.29; Br, 58.8; S, 11.31.

Hydrolysis. Ethyl thiolacrylate was refluxed for 3 hr. with an excess of 30% sodium hydroxide solution. The ethyl mercaptan liberated was passed into lead acetate solution and identified as lead ethyl mercaptide.

Anal. Calcd. for $C_4H_{10}PbS_2$: for Pb: 62.8. Found 62.0.

The remaining solution was acidified cautiously with dilute sulfuric acid and extracted with ether. The residue remaining after evaporation of the ether was free of sulfur and was identified as acrylic acid by the silver salt method, according to Biilman.[10]

Ethyl thiolcrotonate could not be saponified readily with caustic solution and was identified by a method described by Sachs.[11] Mercuric acetate was reacted with the thiolester in alcoholic solution at room temperature to form ethyl mercapto mercuric chloride, which crystallized readily.

Anal. Calcd. for C_2H_5ClHgS: for S, 10.75. Found: 10.60.

Polymerization. Samples of the distilled thiolesters were heated in test tubes to 60° or 130° with or without benzoyl peroxide (1%) as a catalyst. Another series of samples was irradiated with ultraviolet light.

Ethyl thiolcrotonate and ethyl thiolcinnamate did not polymerize under any of the conditions employed. Hard to rubbery, transparent materials were obtained from all thiolacrylates and thiolmethacrylates with the exception of methyl thiolmethacrylate, which yielded a very hard, glasslike polymer.

Methyl β-chloropropionimidate hydrochloride. This compound was prepared in 88% yield by the general method described by Clemo[12] from acrylonitrile, anhydrous methanol, and hydrogen chloride, and purified by recrystallization from a warm acidic acid, ether mixture.

Anal. Calcd. for $C_4H_9Cl_2NO$: C, 30.4; H, 5.74; Cl, 44.9; N, 8.87. Found: C, 30.7; H, 5.62; Cl, 45.8; N, 8.61.

Ethyl β-chloropropionimidate hydrochloride was prepared in an analogous way from acrylonitrile, ethanol, and hydrogen chloride.

Ethyl β-bromopropionimidate hydrobromide. Acrylonitrile (53 g., 1 mole) was dissolved in 250 g. of anhydrous ether and dried hydrogen bromide was passed through the solution. The crystalline material which precipitated was filtered off and washed with ether. It was then reprecipitated from warm glacial acetic acid by the addition of ether. This new compound crystallized in the form of needles and melted at 110° (dec.). The yield was 72%.

Anal. Calcd. for $C_5H_{11}Br_2NO$: C, 23.1; H, 4.27; Br, 61.2; N, 5.40. Found: C, 23.5; H, 4.17; Br, 62.1; N, 5.49.

Ethyl dichloropropionimidate hydrochloride was prepared by saturating a solution of α,β-dichloropropionitrile in anhydrous ethanol with dry hydrogen chloride, and separating the resulting crystalline iminoester hydrochloride. This new compound could not be recrystallized from glacial acetic acid due to a lack of solubility. Analyses gave consistently high chlorine values, a fact reported previously for other iminoester hydrochlorides.

Anal. Calcd. for $C_5H_{10}BrClNO$: C, 20.3; H, 3.41; Br, 54.2; Cl, 12.02; N, 4.74. Found: C, 19.74; H, 3.15; Br, 54.8; Cl, 16.24; N, 4.91.

Methyl β-bromopropionimidate. Preparation of free iminoesters. Due to the ease with which halopropioniminoesters hydrolyze in solution, it was found necessary to cool all reagents and glass equipment to below −10° before use.

One hundred twenty-four grams (0.5 mole) of ground

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(9) B. Holmberg, *Arkiv Kemi*, **14A**, No. 7 (1940); **15A**, No. 20 (1942).

(10) Biilman, *J. prakt. Chem.*, (2), 61, 493 (1900).

(11) G. Sachs, *Ber.*, **54**, 1851 (1921).

(12) G. R. Clemo, *J. Chem. Soc.*, 729 (1928).

methyl β-bromopropionimidate hydrobromide was suspended in 500 ml. of anhydrous ether and cooled to −10°. This suspension was then treated in portions with a cold, aqueous solution of potassium carbonate (40%) in a jacketed, brine-cooled separatory funnel. The ether solution of free iminoester obtained was then dried with anhydrous sodium sulfate and used for the preparation of the thionoester without delay. The identity of this iminoester was established by its conversion to the thionoester, as all attempts to eliminate the ether under vacuum led to decomposition. All other iminoesters were prepared in an analogous manner from the corresponding hydrogen halide salts.

Methyl β-chlorothionopropionate. An ether solution of methyl β-chloropropionimidate was prepared from 79 g. (0.5 mole) of methyl β-chloropropionimidate hydrochloride by the general method described, and saturated with hydrogen sulfide. The solution turned yellow, and a white precipitate separated, which was filtered off and washed with ether. It consisted of ammonium hydrogen sulfide and was discarded. The filtrates were combined, dried with sodium sulfate, and distilled under vacuum to yield 42 g. (61%) of a yellow liquid, b.p. 63–65° (13 mm.).

Ethyl β-chlorothionopropionate and ethyl β-bromothionopropionate were prepared in an analogous manner from the corresponding propionimidates. In Table II analyses and boiling points are listed.

Reaction of acrylyl chloride with sodium sulfhydrate. Anhydrous sodium sulfhydrate (62 g., 1.1 moles), prepared from sodium ethoxide and hydrogen sulfide in alcoholic solution and separated by addition of ether, was suspended in 250 ml. of ether, and 90 g. (1.0 mole) of acrylyl chloride was added gradually, stirring and cooling continuously. The temperature was kept below 20°. Stirring was continued for 1 hr. after the end of the reaction, and the solid precipitate obtained was separated from the ether solution by filtration. The latter was discarded, as it was found to contain only traces of material.

Treating of a part of the yellow solid obtained with dilute hydrochloric acid, followed by ether extraction did not yield any ether soluble material. The main portion was extracted repeatedly with water to dissolve inorganic salts. An ash-free residue remained after filtration and drying, which was extracted successively with hot methanol, benzene, and toluene. Much remained undissolved. Cooling of the solutions yielded white powders, which were analyzed.

Starting with 10 g. of dried crude material, extraction with boiling benzene yielded 3 g. of purified product.

Anal. Calcd. for C_3H_4OS (thioacrylic acid): C, 40.9; H, 4.57; S, 36.3. Found: C, 41.0; H, 4.90; S, 35.2.

Molecular weights (Rast) and melting points were determined for the different fractions separated from solvents:

Methanol extract:	Mol. Wt. 316	m.p. 87–88°
Toluene extract:	Mol. Wt. 542	m.p. 118–120°
Benzene extract:	Mol. Wt. 698	m. p. —
Residue:	(insoluble)	m.p. 130–135°

Methacrylyl chloride and sodium sulfhydrate. Methacrylyl chloride (52 g., 0.5 mole) was reacted with 34 g. (0.6 mole) of sodium sulfhydrate in 250 ml. of ether at room temperature. The resulting material was separated into a salt residue and an ether solution, which contained the organic part of the reaction products. After evaporation of the ether, a yellow semisolid material was obtained, which solidified on standing. Soluble in ether and benzene when freshly prepared, it became partly insoluble after 1 to 2 days. The residue remaining after extraction with benzene was analyzed:

Anal. Calcd. for C_4H_6OS (thiomethacrylic acid): C, 47.1; H, 5.93; S, 31.4. Found: C, 46.9; H, 5.91; S, 30.2.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF WICHITA AND THE RESEARCH LABORATORY OF THE VETERANS ADMINISTRATION, WICHITA, KANSAS]

Reaction of *N*-Bromosuccinimide with Secondary Alcohols

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When aliphatic secondary alcohols are oxidized with *N*-bromosuccinimide under anhydrous conditions, subsequent bromination occurs *via* debromination of *N*-bromosuccinimide by hydrogen bromide, followed by bromination of the ketone by free bromine. This bromination can be suppressed by addition of a proton acceptor such as pyridine or calcium carbonate.

N-bromosuccinimide has been used as an oxidizing agent for the conversion of secondary aliphatic alcohols to the corresponding ketones.[3,4] *N*-bromosuccinimide[5] and *N*-chlorosuccinimide[6] have been shown to react with the aromatic secondary alcohol, benzhydrol, to give benzophenone. When Kruse *et al.*[7] attempted to oxidize ethyl lactate to ethyl pyruvate, they obtained a mixture of ethyl pyruvate and ethyl bromopyruvate from equimolecular quantities of *N*-bromosuccinimide and ethyl lactate, whereas twice the quantity of *N*-bromosuccinimide gave a 64% yield of ethyl bromopyruvate. The latter result was obtained with several other secondary alcohols. Ethyl mandelate was oxidized to ethyl phenylglyoxylate in satisfactory yields.

Our interest in the preparation of α-ketoesters and their halogenated derivatives prompted us to investigate the mode of formation of α-brominated ketones from secondary aliphatic alcohols, with a view to finding a method for repressing the bromi-

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