bar which had an ASTM heat distortion of 110°. By comparison, a bar of poly-(methyl methacrylate), molded from polymer with an intrinsic viscosity of 0.72 and S.P. 144°, had an ASTM heat distortion of 102°.

Isopropyl Thiolmethacrylate Homopolymer.—A sample of 59 g. of isopropyl thiolmethacrylate was heated at 80° for 11 days without a catalyst, giving a transparent waxy solid. Gelation had occurred in 3 days. The material exhibited swelling in a variety of organic solvents, including chloroform, carbon tetrachloride, benzene, acetone, dimethylformamide and dimethyl sulfoxide. However, the major part of it did not dissolve. The entire mass (after evaporation of solvent) was treated with methanol, giving 37.5 g. (63%) of white solid which had S.P. 127°. The unpleasant odor of the monomer was not completely removed.

Another sample of 15 g. of this monomer was heated at 60° without a catalyst for 72 hours, giving a clear soft gel. This material also displayed swelling in chloroform, giving a jelly-like mass when allowed to stand with 900 ml. of the solvent. The polymer was distributed throughout the 900 ml. of chloroform, giving a gel which was too thick for pouring.

A third sample (15 g.) of this monomer was heated at 60° for 12 hours without a catalyst. The still fluid material was dissolved in 50 ml. of chloroform and poured with stirring into 250 ml. of methanol, giving 3 g. (20%) of white powdery material which had an intrinsic viscosity of 0.54 and S.P. 140°. This precipitated polymer was free of the odor of the monomer.

***t*-Butyl Thiolmethacrylate Polymers.**—A sample of 62 g. of *t*-butyl thiolmethacrylate was heated at 60° for 4 days with 0.1% of azodiisobutyronitrile. Gelation occurred in 12 hours. The material dissolved readily in 1200 ml. of chloroform. Precipitation from 6000 ml. of methanol gave 41 g. (66%) of white, odorless powder. This material had an intrinsic viscosity of 0.24 and S.P. 193°. Compression molding gave a clear brittle specimen which did not exhibit surface flow when heated in steam at 121°.

This monomer copolymerized readily with methyl methacrylate giving clear copolymers up to about 40 weight per cent. of the thiol ester. Larger amounts of thiol ester gave hazy and increasingly brittle materials. On one run, a mixture of 5 g. of *t*-butyl thiolmethacrylate and 45 g. of methyl methacrylate was heated at 60° for 5 days without a catalyst. Precipitation gave 36.7 g. (73%) of copolymer which had an intrinsic viscosity of 1.63 and S.P. 154°. Compression molding gave a clear tough bar which had an ASTM heat distortion of 112°.[8]

Pentachlorophenyl Thiolmethacrylate Homopolymer.—A sample of 10 g. of pentachlorophenyl thiolmethacrylate was heated at 105° for 48 hours with 0.5% of azodiisobutyronitrile, giving a yellow transparent solid which was quite brittle. This material was treated with 800 ml. or chloroform for several days, with no swelling and little solution occurring. Filtration gave back 6.5 g. of undissolved polymer which did not soften at 250°, the upper limit of our apparatus. An attempt to dissolve 0.1 g. in 100 ml. of chloroform failed. Compression molding gave a clear brittle specimen which did not show surface flow when heated in steam at 121°.

Cross-linking of Poly-(methyl Methacrylate) Using Methyl 2-Methyl-3-thiomethoxythiolpropionate.—Several runs were carried out in which methyl methacrylate was heated with a catalyst under varying conditions with 1–10% by weight of the methyl mercaptan addition product of methyl thiolmethacrylate, yielding insoluble polymers. When such experiments were carried out without a catalyst, the addition product proved to be an effective inhibitor to polymerization. The following run is illustrative of such runs:

A mixture of 20 g. of methyl methacrylate, 0.2 g. of the addition product and 0.02 g. of azodiisobutyronitrile was heated for 24 hours at 50°. The resulting solid was allowed to stand with 700 ml. of chloroform for several days. It soon swelled to several times its original size, giving a soft gel which did not further change. The supernatant chloroform was decanted and the gel stirred in a blender with methanol. The precipitated white solid was further washed with methanol and dried. It amounted to 14 g. (70%) and had S.P. 153°. An attempt to dissolve 0.1 g. in 100 ml. of chloroform gave swelling of the individual particles, but solution did not occur.

In another similar experiment, carried out at the same time under identical conditions, the amount of addition product was reduced to 0.07 g. This polymer was readily soluble in 400 ml. of chloroform. Precipitation in methanol gave 17 g. (85%) of polymer which had an intrinsic viscosity of 2.08 and S.P. 152°. A control, in which the addition product was omitted, gave 18 g. (90%) of poly-(methyl methacrylate) which had an intrinsic viscosity of 3.70 and S.P. 144°. Thus, at the lower concentration, the mercaptan addition product acted as a chain transfer agent, reducing the molecular weight of the polymer, but did not cross-link it.

Acknowledgments.—The authors wish to thank C. F. Hartman for technical assistance in this work, and Alfred Foulds for the sulfur analyses.

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[8] This material analyzed for 2.16% sulfur, indicating the incorporation of 10.7% of the thiol ester in the copolymer.

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

Preparation and Polymerization of Some New Aryl Methacrylates[1]

BY GENE SUMRELL,[2] PAUL G. CAMPBELL, GEORGE E. HAM AND CHARLES H. SCHRAMM

RECEIVED JANUARY 10, 1959

A number of new halogenated phenyl methacrylates have been prepared and polymerized. The relationship of softening points of the polymers to structure of the monomers is discussed. Difficulties experienced in the preparation of the 2,6-disubstituted phenyl esters is discussed, and a method of preparation is described. This method involves a modified Schotten-Baumann reaction in which methanolic sodium hydroxide is used instead of the aqueous reagent.

Although aliphatic esters of methacrylic acid have been extensively investigated, relatively few aryl methacrylates have been reported in the literature. We are aware of only two halogenated phenyl methacrylates having been previously prepared, *i.e.*, 4-chlorophenyl and 2,4-dichlorophenyl methacrylate.[3] The possibility that halogenated phenyl methacrylates could be used in the preparation of flame resistant polymers prompted us to prepare a series of chlorinated and brominated phenyl methacrylates. Some of the properties of homopolymers of these materials are presented here. We found that even the monomers containing one or more bromines were quite resistant to burning. At least three chlorines were necessary in the aryl methacrylates and their homopolymers to give marked resistance to burning. The halogenated phenyl methacrylates all gave clear transparent polymers when heated alone or in the pres-

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

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[3] S. Patai, M. Bentov and M. E. Reichmann, THIS JOURNAL, **74**, 845 (1952).

TABLE I

ARYL METHACRYLATE ESTERS, $CH_2{=}C(CH_3)COOR$

R in ester	M.p. or b.p., °C.	Mm.	$n^{25}D$	Yield, %	Calculated			Found		
					C	H	Halogen	C	H	Halogen
C_6H_5[d]	96–98	8	1.5138	89[a]						
2-ClC_6H_4	64–66	0.3	1.5246	62[a]	61.08	4.61	18.03	61.40	4.80	17.70
3-ClC_6H_4	85–86	1.3	1.5274	82[a]	61.08	4.61	18.03	61.10	4.66	18.04
4-ClC_6H_4[e]	122–124	8	1.5295	53[a]						
2,4-$Cl_2C_6H_3$[f]	55–56			83[b]						
2,4,5-$Cl_3C_6H_2$	60–61			86[b]	45.23	2.66	40.06	45.14	2.58	39.89
2,4,6-$Cl_3C_6H_2$	78–80	0.1	1.5504	59[c]	45.23	2.66	40.06	44.92	2.46	39.88
2,3,4,6-Cl_4C_6H	[c]			35[c]	40.04	2.02	47.28	39.74	2.05	47.66
C_6Cl_5	90–92			61[c]	35.91	1.51	53.01	35.83	1.77	52.94
4-BrC_6H_4	78–79	0.3	1.5483	86[a]	49.81	3.76	33.15	50.05	3.61	33.33
2,4-$Br_2C_6H_3$	63–65			83[b]	37.53	2.52	49.95	37.77	2.55	49.97
2,4,6-$Br_3C_6H_2$	123–125	0.2	1.6020	15[c]	30.11	1.77	60.10	29.98	1.84	59.99
C_6Br_5	138–140			31[c]	21.57	0.91	71.77	21.78	1.08	71.74

[a] Method A. [b] Method B. [c] See Experimental. [d] E. M. Filachione, J. H. Lengel and W. P. Ratchford, THIS JOURNAL, **72**, 839 (1950), use a more involved method for this compound; they report b.p. 47–50° (0.2 mm.), $n^{20}D$ 1.5147. [e] Lit.[4] b.p. 142–146° (23 mm.). [f] Lit.[4] m.p. 56°,

TABLE II

HOMOPOLYMERS OF ARYL METHACRYLATES[a]

Aryl group	Ester, grams	Polymer, %	Softening point, °C.	[η]	Conditions of polymerization		
					Temp., °C.	Time, days	AIBN, %
C_6H_5	20	65	152	1.20	60	2	0.1
2-ClC_6H_4	15	69	141	0.52	60	2	.1
3-ClC_6H_4	9	72	125	0.13	65	2	.15
4-ClC_6H_4	20	40[b]	154	4.40	60	9	None
2,4-$Cl_2C_6H_3$	10	80	154	0.84	65	2	0.1
2,4,5-$Cl_3C_6H_2$	32	75	160	.60	65	1	0.3
2,4,6-$Cl_3C_6H_2$	10	70	241	.42	75	7	None
2,3,4,6-Cl_4C_6H	7	86	237	.30[c]	95	1	0.07
C_6Cl_5	10	70	>250	.28[c]	95	2	0.2[d]
4-BrC_6H_4	20	40	164	1.52	65	10	None
2,4-$Br_2C_6H_3$	10	85	175	3.80	65	2	0.1
2,4,6-$Br_3C_6H_2$	5	56	>250	0.115	60	2	0.6

[a] See Experimental for processing procedure for polymers. [b] Difficulty in dissolving this polymer resulted in mechanical loss; solution of major portion was achieved in mixture of 300 ml. of xylene and 300 ml. of bromobenzene; precipitated with 3000 ml. of methanol. [c] These intrinsic viscosities were run in chloroform because of slight solubility of polymers in dioxane. [d] Benzoyl peroxide used as catalyst on this run.

ence of free radical catalysts. These polymers were hard and brittle.

The softening points of the polymers are presented in Table II. It is apparent that, in general, the softening points show an increase with increasing number of halogens, and that the brominated compounds give higher softening polymers than their chlorinated counterparts. A marked raising of the softening point is noted for both the chlorinated and brominated materials when substituents are in both *o*-positions of the phenyl group. This may result from hindrance to rotation in the polymer chains.

It is notable that whereas 2,4-dichlorophenyl and 2,4-dibromophenyl methacrylate, as well as 2,4,5-trichlorophenyl methacrylate all proved to be crystalline solids, both 2,4,6-trichlorophenyl and 2,4,6-tribromophenyl methacrylate proved to be liquids which did not crystallize even in a Dry Ice-bath. The failure of these materials to crystallize may be associated with hindrance to rotation which prevents the molecule from assuming a structure which would fit into a crystal lattice. That there is hindrance present when both *o*-positions of the phenyl group are substituted was noted by us in attempts to prepare 2,4,6-trichlorophenyl and pentachlorophenyl methacrylate by a Schotten–Baumann procedure involving addition of the acid chloride to a solution of the phenol dissolved in aqueous sodium hydroxide.[4] The reaction of methacrylyl chloride with an aqueous sodium hydroxide solution of pentachlorophenol was investigated in some detail since the desired methacrylate ester was a solid and small yields could be easily determined. When only a small excess of sodium hydroxide was present, pentachlorophenol quickly began precipitating as the methacrylyl chloride was added. With larger amounts of sodium hydroxide, traces of the desired ester up to about 8% could be obtained. The reaction was considerably more exothermic than those runs with phenols not having both *o*-positions substituted and which reacted smoothly to give the desired methacrylate ester; or than a run carried out in which the methacrylyl chloride was merely added to aqueous sodium hydroxide. This behavior suggested that the presence of the pentachlorophenylate ion facilitated hydrolysis of the acid chloride. A possible explanation is that, with both *o*-positions substituted, the approach of the phenylate ion to the acid chloride was sufficient to discharge the chloride ion, but hindered to the point that hydrolysis occurred in aqueous medium instead of

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(4) See ref. 3 for similar difficulties experienced by others.

ester formation. On this assumption a run was carried out using methanolic sodium hydroxide, giving a 61% yield of pentachlorophenyl methacrylate. The presence of one mole of water from the reaction of the phenol with sodium hydroxide did not appear to reduce the yield, since no increase in yield occurred when the sodium salt of the phenol was formed by the use of sodium methoxide instead of sodium hydroxide. However, when the sodium hydroxide was added in the form of a 50% aqueous solution, this extra amount of water caused as poor a result as if the reaction had been carried out in aqueous medium, *i.e.*, hydrolysis occurred instead of ester formation.

With these results in hand, preparations of 2,4,6-trichlorophenyl, 2,4,6-tribromophenyl, 2,3,4,6-tetrachlorophenyl and pentabromophenyl methacrylate were prepared in yields of 59, 15, 35 and 31%, respectively, using this modification of the Schotten–Baumann reaction where methanolic sodium hydroxide is used instead of the aqueous medium. It might be mentioned in passing that a preparation of 2,4,6-trichlorophenyl methacrylate using isopropyl alcohol as a solvent instead of methanol gave no improvement in yield.

In support of the suggestion that steric factors play a role in the difficulties experienced by us and others[3] in the reaction of methacrylyl chloride with 2,6-disubstituted sodium phenylates in aqueous medium, it might be pointed out that pentachlorophenyl thiolmethacrylate has been prepared in excellent yield by the Schotten–Baumann reaction in aqueous medium.[5] Thus, the larger sulfur atom apparently reduces the hindrance and allows the reaction to follow its normal course.

Experimental

Boiling points and melting points are uncorrected. Distillations were carried out through a Claisen head well wrapped with asbestos cord.

Starting Materials.—The phenols were commercial materials and were used without purification. The methacrylyl chloride was prepared as described by Rehberg, Dixon and Fisher.[6]

Processing Procedure for Polymers.—The monomers were polymerized in the bulk using screwcapped vials which were flushed with nitrogen after introduction of the monomer and catalyst. The resulting polymer was dissolved in enough chloroform to give approximately a 5% solution. The latter was poured with stirring into 5 volumes of methanol. The precipitated polymer was filtered, washed thoroughly with methanol and dried. The softening points were determined on a Parr melting point apparatus. The intrinsic viscosities were determined in the usual way[7] using dioxane as a solvent and a constant temperature bath regulated to 20 ± 0.02°. In the case of liquid monomers containing traces of iodine, the latter was removed prior to polymerization by shaking the monomer with a few drops of concentrated aqueous sodium thiosulfate solution. Then a small amount of sodium sulfate was added and the monomer was decanted. The polymerization conditions, amount of catalyst (usually azodiisobutyronitrile) and physical properties of the precipitated polymers are given in Table II.

2-Chlorophenyl Methacrylate (Illustrating Method A).—A solution of 1 mole of 2-chlorophenol in 1000 ml. of 5% sodium hydroxide was maintained at 0–5° by cooling with an ice–acetone-bath while 1 mole of methacrylyl chloride was added dropwise. The addition required one-half hour. Stirring was continued for 1 hour, then the mixture was rendered basic ($pH > 10$) by the addition of 50% sodium hydroxide. The bottom oily layer was separated, washed with water and placed in a flask containing sodium sulfate and 0.2 g. of iodine. The reaction mixture and water wash were extracted in series with 50 ml. of chloroform, which was added to the product. After drying, the chloroform was removed and the product distilled, yielding 122 g. (62%) of 2-chlorophenyl methacrylate at 64–66° (0.3 mm.), n^{20}_D 1.5273. The residue amounted to 6 g.

2,4-Dichlorophenyl Methacrylate (Illustrating Method B).—2,4-Dichlorophenyl methacrylate was prepared on a 0.5-mole scale in a similar manner to that described above as method A, except that the product separated as a solid. After the mixture was rendered basic, this white solid was filtered, washed well with water, and air-dried. The yield was 48 g. (83%) of material of m.p. 50–53°. Recrystallization from a mixture of isopropyl alcohol and water gave fine colorless needles of m.p. 55–56°.

2,4,6-Trichlorophenyl Methacrylate (I).—A mixture of 19.7 g. (0.1 mole) of 2,4,6-trichlorophenol, 6 g. of sodium hydroxide and 70 ml. of methanol was maintained at 0° while 11.5 g. (0.11 mole) of methacrylyl chloride was added dropwise. After 1 hour of additional stirring there was added 200 ml. of water, and the mixture was rendered basic. The organic layer was extracted into chloroform and dried over sodium sulfate containing 0.2 g. of iodine. Distillation gave 15.6 g. (59%) of product at 78–80° (0.1 mm.).

2,4,6-Tribromophenyl methacrylate was prepared essentially as described for I, using 0.25 mole of the phenol, 0.3 mole of the acid chloride and 20 g. of sodium hydroxide in 400 ml. of methanol. Distillation gave 14.8 g. (15%) of product at 123–125° (0.2 mm.).

2,3,4,6-Tetrachlorophenyl Methacrylate.—A mixture of 58 g. (0.25 mole) of 2,3,4,6-tetrachlorophenol, 15 g. of sodium hydroxide and 500 ml. of methanol was maintained at −5° while 26 g. (0.25 mole) of methacrylyl chloride was added dropwise. After 1 hour of additional stirring, 1000 ml. of water was added and the mixture was rendered basic. An oily layer had separated. Stirring was continued for 3 hours while cooling below 0°, at the end of which time the oil had crystallized. The solid was filtered, washed with water and air-dried; yield 26.4 g. (35%), m.p. 70–74°. Recrystallization from methanol gave material of m.p. 75–78°, unchanged by further recrystallization from methanol. However, three recrystallizations from isopropyl alcohol, with the mixture standing undisturbed while the crystals formed, slowly raised the m.p. to a final value of 89–92°. On a fourth recrystallization the mixture was swirled as the crystals formed. This material had m.p. 75–79°. When a sample of the material of m.p. 89–92° was recrystallized from methanol, the crystals which came down had m.p. 75–78° even though the mixture stood undisturbed during the crystallization.

Pentachlorophenyl Methacrylate.—A mixture of 26.7 g. (0.1 mole) of pentachlorophenol, 6 g. of sodium hydroxide and 200 ml. of methanol was maintained at −5° while 11.5 (0.11 mole) of methacrylyl chloride was added dropwise. After 1 hour of additional stirring, 250 ml. of water was added and the mixture was rendered basic. The solid was filtered, washed with water, and air-dried, giving 20.5 g. (61%) of material of m.p. 87–91°. Recrystallization from a mixture of 60 ml. of isopropyl alcohol and 15 ml. of water gave 17.2 g. of product with the constant m.p. 90–92°.

A sample of 10 g. of this monomer was heated at 95° for 48 hours with 0.2% of benzoyl peroxide, giving a hard clear brittle solid. Precipitation gave 7 g. (70%) of white powdery polymer which was relatively insoluble in dioxane, but gave an intrinsic viscosity of 0.28 in chloroform. The material did not soften at 250°, the upper limit of our apparatus.

Pentabromophenyl Methacrylate.—A mixture of 14.7 g. (0.03 mole) of pentabromophenol, 2.4 g. of sodium hydroxide and 100 ml. of methanol was maintained at 0–5° while 5.1 g. (0.05 mole) of methacrylyl chloride was added dropwise with stirring. After 20 minutes of additional stirring, 300 ml. of water was added and the mixture was rendered basic. The solid was filtered, washed with water and air-dried, yielding 5.2 g. (31%) of material of m.p. 132–137°. Acidification of the filtrate gave a recovery of 10 g. (68%) of pentabromophenol. Two recrystallizations of the crude

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(5) G. Sumrell, G. E. Ham and E. D. Hornbaker, THIS JOURNAL, **80**, 2509 (1958).

(6) C. E. Rehberg, M. B. Dixon and C. H. Fisher, *ibid.*, **67**, 208 (1945).

(7) See P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 308–310.

pentabromophenyl methacrylate from isopropyl alcohol gave colorless needles with the constant m.p. 138–140°.

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

Some New Thiol Esters. Preparation of Dithiolfumarates

BY GENE SUMRELL,[1] MORRIS ZIEF, EARL J. HUBER, GEORGE E. HAM AND CHARLES H. SCHRAMM

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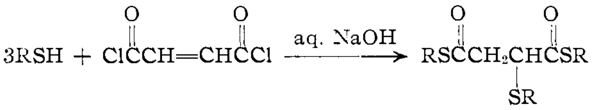
A number of new thiol esters have been prepared using a variety of methods. These new esters include six dithiolfumarates, the first compounds in this series to be reported. The fact that some of these compounds are colored, thus possessing a chromophoric grouping, is discussed.

We have prepared a number of new thiol esters. Current interest in the antifungal properties of similar compounds makes it desirable to report our work at this time.[2–4]

Of particular interest among the compounds prepared by us are several dithiolfumarates. As far as we are aware, compounds in this series have not been reported in the literature.[5] The fact that esters of fumaric acid in general have achieved their present industrial importance renders it desirable to know something of the properties of the sulfur analogs of these compounds.

Diphenyl and bis-(4-chlorophenyl) dithiolfumarate were readily prepared by the addition of fumaryl chloride to a solution of the appropriate thiophenol in a slight excess of aqueous 5% sodium hydroxide. The solubility of alkyl mercaptans in aqueous alkali allowed an attempt to extend this method to the preparation of the dialkyl dithiolfumarates. The attempt was successful in the case of *t*-butyl mercaptan, giving a 37% yield of di-*t*-butyl dithiolfumarate, which separated from the reaction mixture as a solid. When the reaction was carried out with methyl, ethyl and isopropyl mercaptan, oils resulted. Attempts to purify these by fractionation failed because of their high boiling points and a tendency to decompose. Simple distillation at reduced pressure gave materials which, judging from their sulfur analyses, evidently contained 50% or more of the product formed by addition of a mole of mercaptan to the double bond of the dialkyl dithiolfumarate



$$3RSH + Cl\overset{O}{\overset{\|}{C}}CH{=}CH\overset{O}{\overset{\|}{C}}Cl \xrightarrow{\text{aq. NaOH}} RS\overset{O}{\overset{\|}{C}}CH_2\underset{SR}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}SR$$

Dimethyl, diethyl and diisopropyl dithiolfumarate were successfully prepared by a method involving the reaction of the mercaptan and acid chloride using 1,2-dimethoxyethane as a solvent and pyridine as a hydrogen chloride acceptor. All of the dithiolfumarates reported here proved to be crystalline solids except the diethyl compound. This yellow oil crystallized readily on cooling, however, and melted at 14°.

It is surprising that some of these compounds proved to be distinctly yellow. While benzil and similar compounds, including those with one or more conjugated double bonds between the keto groups are colored, diphenyl oxalate and related compounds are colorless. Also, bis-(4-chlorophenyl) dithiolsuccinate and phenyl thiolcinnamate (see Experimental) proved to be colorless solids. However, bis-(4-chlorophenyl) dithioloxalate proved to be deep yellow. Similarly diphenyl and bis-(4-chlorophenyl) dithiolfumarate are also yellow solids. Even more surprising was the fact that di-*t*-butyl dithiolfumarate was yellow, though distinctly lighter in shade than the aryl dithiolfumarates. The remaining dialkyl dithiolfumarates were colorless in the solid state.

Marvel and co-workers have presented infrared spectral data indicating that the carbonyl group in a thiolacrylate has more of the character of a ketone carbonyl than does the carbonyl group in a normal ester.[6] The color noted in the bis-aryl dithiolfumarates is further evidence along this line for thiol esters in general. However, the question of the color in these compounds seems to be somewhat more complex. Pentachlorophenyl thiolmethacrylate, previously reported from these laboratories,[7] is a yellow crystalline solid. Pentachlorophenyl thiolacetate is also yellow (see Experimental). We have no explanation at present as to why these compounds are colored, whereas a more complexly conjugated system such as that in phenyl thiolcinnamate is colorless. Evidently the highly electronegative pentachlorophenyl group plays a role.

In addition to the thiol esters mentioned above, we are describing in the Experimental section of this paper the preparation of a number of thiol esters of various aliphatic acids, along with several

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[2] See K. Miyaki and S. Yamagishi, *J. Pharm. Soc.* (*Japan*), **76**, 436, 1196, 1200 (1956); *C. A.*, **51**, 3490 (1957).

[3] A. M. Shah, Ph.D. Thesis, State University of Iowa; *C. A.*, **52**, 4501 (1958).

[4] The antifungal and antibacterial properties of the compounds described in this paper are being reported elsewhere.

[5] While our manuscript was in the hands of the referees a paper appeared by C. S. Marvel and J. F. Porter, *J. Org. Chem.*, **24**, 137 (1959), describing the synthesis of dimethyl dithiolfumarate, m.p. 78–79°, by a several-step method. They report failure to obtain a homopolymer from this material, and also that no copolymerization with vinyl chloride could be achieved. We likewise were unable to obtain a homopolymer from dimethyl dithiolfumarate, or a copolymer with vinyl chloride. We thank Mr. Carl Miller for carrying out the latter experiments.

[6] C. S. Marvel, S. L. Jacobs, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **19**, 59 (1956).

[7] G. Sumrell, G. E. Ham and E. D. Hornbaker, THIS JOURNAL, **80**, 2509 (1958).