remaining beryllium chloride and again dried. The bright yellow solid was infusible at 360°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Be_{1.5}$: Be, 3.67. Found: Be, 3.5.

The Mn and Co ions have coordinated with the ligand in approximately the 1:1 ratio; however, the true valency of the metal ions is in doubt. They may be trivalent, carrying a hydroxyl or other small ion. It is obvious that the metal content of the linear polymer has the ligand metal ratio 1:1 only when the chain length is infinite. In the actual cases shown in Table I the metal content depends on the chain length and the nature of the terminal groups. For short chains of five to twenty ligand units the metal content will be too low if the terminal groups are ligand molecules and will be too high if the chains end with metal ions. The conditions required for production of long chain polymers are being investigated.

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Synthesis of Some Thiol Esters of *dl-cis-trans*-Chrysanthemummonocarboxylic Acid

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A number of new thiol esters of *dl-cis-trans*-chrysanthemummonocarboxylic acid have been synthesized. The 1,4-piperazonium dichrysanthemummonocarboxylate and chrysanthemummonocarboxypiperidide were also made.

Some of the esters of *dl-cis-trans*-chrysanthemummonocarboxylic acid (*dl-cis-trans*-2,2-dimethyl 3-isobutenylcyclopropane-1-carboxylic acid) possess potent insecticidal properties.[1-4] However, thiol esters of chrysanthemummonocarboxylic acid have not been described in the literature.

The present paper deals with the synthesis of the following thiol esters: methyl, ethyl, propyl, isopropyl, *n*-butyl, allyl, furfuryl, piperonyl, and 6-bromopiperonyl.

The thiol esters were made by a modification of the procedure described by Harper and Reed[5] for the preparation of ethyl *dl-trans*-carbomethoxythiocaronate. The yields of the thiochrysanthemummonocarboxylates were uniformly good except for the piperonyl and 6-bromopiperonyl compounds, which were unstable to heat, and troublesome to prepare, purify, and analyze. The infrared spectra of the thiol esters in chloroform solution exhibited the characteristic band for the carbonyl frequency of a thiol ester in the region of 1675 cm.$^{-1}$ [6]

Piperonal, dissolved in absolute ethanol, yielded on treatment with dry ammonia and hydrogen sulfide gas dipiperonyldisulfide sulfhydrate as the principal product. This is contrary to the findings of Manchot and Zahn,[7] who obtained mainly the disulfide under similar conditions and the sulfhydrate under more drastic experimental conditions. The reduction of this compound to the piperonyl mercaptan proceeded smoothly with lithium aluminum hydride, using the general procedure of Arnold *et al.*[8] for reducing disulfides to mercaptans. 6-Bromopiperonal subjected to the same reaction as piperonal yielded a mixture of 6,6′-dibromodipiperonyl disulfide and 6,6′-dibromodipiperonyl disulfide sulfhydrate. These two compounds were separated by fractional crystallization. On subsequent reduction with lithium aluminum hydride, both yielded 6-bromopiperonyl mercaptan which, unlike the piperonyl mercaptan, proved to be unstable to heat, since it lost bromine and sulfur on attempted purification by distillation with steam. These three bromine intermediates have not been previously described.

1,4-Piperazonium dichrysanthemummonocarboxylate and chrysanthemummonocarboxypiperidide were also made. The former is a well defined crystalline solid which can be used as a derivative for the characterization of chrysanthemummonocarboxylic acid. The piperidide is a liquid possessing possible synergistic properties in insecticides.

The results of the insecticidal testing of the present compounds will be reported separately.

EXPERIMENTAL[9]

Alkyl thiochrysanthemummonocarboxylates. In a typical preparation (*n*-butyl thiol ester), a solution of 0.027 mole of freshly distilled *dl-cis-trans*-chrysanthemummonocarbonyl chloride in 7 ml. of dry benzene was added dropwise during the course of 1 hr. to a mechanically stirred solution of 0.032 mole of the mercaptan in 7 ml. of dry benzene to which 2.6

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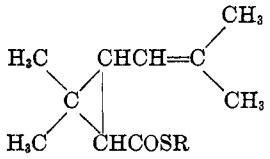
TABLE I

THIOL ESTERS OF *dl-cis-trans* CHRYSANTHEMUMMONOCARBOXYLIC ACID



R	B.P.	Mm.	Formula	Yield, %	n_D^{25}	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
Methyl	48–53	0.80	$C_{11}H_{16}OS$	67.1	1.5090	66.61	9.15	16.16	66.55	9.05	16.30
Ethyl	71–72	0.80	$C_{12}H_{20}OS$	56.0	1.5023	67.85	9.49	15.10	67.85	9.50	15.09
n-Propyl	114–115	0.94	$C_{13}H_{22}OS$	46.3	1.5009	68.89	9.79	14.17	68.90	9.70	14.22
Isopropyl	97.0–99.5	0.96	$C_{13}H_{22}OS$	62.5	1.4973	68.89	9.79	14.17	68.90	9.60	14.08
n-Butyl	126.8–127.2	0.92	$C_{14}H_{24}OS$	69.2	1.4980	69.94	10.06	13.34	70.10	10.12	13.28
Allyl	95.7–96.2	0.22	$C_{13}H_{20}OS$	60.0	1.5128	69.59	8.99	14.29	69.58	9.01	14.25
Furfuryl	148.5–154	0.96	$C_{15}H_{20}O_2S$	61.9	1.5342	68.14	7.63	12.13	68.05	7.63	12.23
Piperonyl	Decomposes		$C_{18}H_{22}O_3S$	9.6	1.5526	67.89	6.96	10.07	68.23	6.69	10.51
6-Bromo-piperonyl	Decomposes		$C_{18}H_{21}O_3BrS$	92.9[a]	...	54.41	5.33	8.07	52.30[a]	5.00[a]	7.80[a]

[a] Values are for the crude thiol ester which decomposed on attempted purification by different conventional methods.

ml. of anhydrous pyridine had been added. The reaction mixture was held at a temperature of 0 to 2° throughout the addition. White, crystalline pyridine hydrochloride soon precipitated. The flask, after it had warmed to room temperature, was stoppered and allowed to stand overnight. Fifty milliliters of water was then added and the mixture shaken. The benzene layer was removed and washed successively with 40 ml. of sulfuric acid (1*N*), 40 ml. of sodium bicarbonate (1*N*), and twice with 40-ml. portions of water. After drying the benzene solution of the thiol ester over anhydrous sodium sulfate, the solvent was removed at 80° under slight vacuum and the crude ester was fractionated at a pressure of 1 mm.

In the case of piperonylthiol and of 6-bromopiperonylthiol equimolecular quantities of the reactants were used instead of a 20 per cent excess of the thiol. The thiol esters prepared are listed in Table I.

Dipiperonyl disulfide sulfhydrate. The preparation of this intermediate was essentially the same as that described by Manchot and Zahn[7] for dipiperonyl disulfide. Anhydrous hydrogen sulfide was passed through 400 ml. of absolute ethanol, which had previously been saturated with anhydrous ammonia at 25°, until fine crystals began to appear. To this suspension was added 30 g. of piperonal, the mixture was stoppered, and it was allowed to stand in a refrigerator at 3° for three weeks. From this reaction 18.2 g. of crude product was obtained, which was purified by fractional crystallization in 0.5 g. portions from boiling ethanol-acetone (9 : 1) using 15 ml. per portion. It was found necessary to decant the supernatant liquid within 5–10 min. after filtration of the hot solution of the crude product. The decanted liquid on cooling gave dipiperonyl disulfide sulfhydrate (containing some dipiperonyl disulfide), which could be used for reduction to piperonyl mercaptan. The yield of crude material was 4.3 g. (11.6%). Recrystallization from ethanol-acetone (1:1) gave pure sulfhydrate, m.p. 114.7–115.6° (lit.[7] m.p. 113°).

Anal. Calcd. for $C_{16}H_{14}O_4S_2 \cdot H_2S$: C, 52.15; H, 4.38; S, 26.11. Found: C, 52.36; H, 3.95; S, 25.92.

Piperonyl mercaptan was obtained from this compound. A solution of 0.13 g. of lithium aluminum hydride[8] in 75.5 ml. of anhydrous ether was prepared, and 1.9 g. of dipiperonyl disulfide sulfhydrate was added. The excess reducing agent was decomposed with 1.9 ml. of water, and the mercaptan was liberated from the lithium aluminum complex with 3.8 ml. of a 15% sulfuric acid solution. The reaction gave 1.6 g. (91%) of crude mercaptan which was found to be suitable for esterification with chrysanthemummonocarbonyl chloride.

6,6′-Dibromodipiperonyl disulfide and its sulfhydrate. Anhydrous hydrogen sulfide was bubbled through 132 ml. of absolute ethanol, which had previously been saturated with anhydrous ammonia at 25°, until fine crystals began to appear.[7] To this suspension was added 9.9 g. of 6-bromopiperonal. After standing, as described above for piperonal, 10.3 g. (about 94.0%) of a crude solid mixture of disulfide and sulfhydrate was obtained. These were separated by fractional crystallization from a boiling mixture of ethanol-acetone (1:1) utilizing a 1.0 g. portion (with 72 ml. of solvent mixture) of crude solid at a time. After filtration, the hot solution was allowed to stand 45 min. to allow for the complete crystallization of the sulfhydrate, before decanting carefully the supernatant liquid containing the disulfide. The crystals of the sulfhydrate were washed on a Büchner funnel and air-dried. This yielded 4.3 g. (39.2%) of long white rods, m.p. 136.4–138.2°, which had a correct analysis for the sulfhydrate.

Anal. Calcd. for $C_{16}H_{12}O_4Br_2S_2 \cdot H_2S$: C, 36.51; H, 2.68; Br, 30.38; S, 18.27. Found: C, 36.82; H, 2.41; Br, 30.00; S, 18.14.

The decanted solution containing the disulfide was evaporated under slight vacuum to one-third its original volume and the crystals which separated were filtered, washed rapidly with ethanol, and air-dried. This process was repeated a second time. There was obtained 2.7 g. (24.9%) of practically pure disulfide suitable for reduction to the mercaptan. Two crystallizations from ethanol gave white microcrystals, m.p. 115.2–118.7°.

Anal. Calcd. for $C_{16}H_{12}O_4Br_2S_2$: C, 39.06; H, 2.46; Br, 32.47; S, 13.03. Found: C, 39.23; H, 2.82; Br, 31.94; S, 13.65.

6-Bromopiperonyl mercaptan. Both 6-bromopiperonyl disulfide and its sulfhydrate were reduced to the mercaptan with lithium aluminum hydride in anhydrous ether.[8] Reduction was performed with 1.0-g. portions. A typical example is as follows: To a solution of 0.05 g. of lithium aluminum hydride in 60 ml. of absolute ether was added 1.0 g. of the sulfhydrate. The excess reductant was decomposed with 0.7 ml. of water and the mercaptide complex was treated with 1.3 ml. of 15% sulfuric acid to liberate the mercaptan.

(9) The mercaptans, used as starting materials, were available from commercial sources, except for the piperonyl and 6-bromopiperonyl mercaptans. We are indebted to Mr. C. Di Pietro of the Analytical Laboratory for the microanalyses, and to Mr. F. Bissett of our laboratory for the spectrophotometric determinations. Melting points and boiling points are uncorrected.

The ether was removed under a slight vacuum at room temperature in a nitrogen atmosphere. The residue consisted of 0.46 g. (48.8% from the sulfhydrate) of minute clusters of opaque white crystals, m.p. 103.7–106.7°. An infrared spectrum showed the characteristic weak band of a thiol group at 2565 cm.$^{-1}$

Anal. Calcd. for $C_8H_7O_2BrS$: C, 38.88; H, 2.86; Br, 32.34; S, 12.98. Found: C, 38.56; H, 2.50; Br, 32.34; S, 13.20.

1,4-Piperazonium di-dl-cis-trans-chrysanthemummonocarboxylate. A solution of 1.65 g. of piperazine hexahydrate in 7 ml. of absolute ethanol was added to a solution of 2.87 g. of chrysanthemummonocarboxylic acid in 7 ml. of absolute ethanol and the resultant clear yellow liquid was allowed to stand overnight at room temperature. Concentration to about 10 ml. caused crystallization to occur. After the mixture had been cooled in a refrigerator, the crystals were collected by suction filtration, washed with ether, and air-dried. Crystallization from acetone afforded 1.25 g. (27.8%) of colorless needles, m.p. 129.5–130.5°.

Anal. Calcd. for $C_{24}H_{42}N_2O_4$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.61; H, 10.04; N, 6.48.

dl-cis-trans-Chrysanthemummonocarboxypiperidide. A solution of 1.45 g. of piperidine in 8 ml. of dry benzene was added to a solution of 1.59 g. of chrysanthemummonocarbonyl chloride in 10 ml. of the same solvent at room temperature. After standing overnight, the reaction mixture was filtered and the solvent removed in vacuum. The yellow residual oil was dissolved in 15 ml. of ether and washed successively with water, sulfuric acid (1*N*), sodium bicarbonate (1*N*), and water. Removal of the solvent gave 1.58 g. of crude product as a yellow oil. Vacuum distillation afforded 0.57 g. (28.5%) of colorless oil, b.p. 127° (0.33 mm.).

Anal. Calcd. for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.35; H, 11.10; N, 6.45.

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NATICK, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY UNIVERSITY OF GHENT]

Studies of the Grignard Reaction. II. Kinetics of the Reaction of Dimethylmagnesium with Benzophenone and of Methylmagnesium Bromide–Magnesium Bromide with Pinacolone

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The reaction of dimethylmagnesium with benzophenone is shown to occur with the transfer of only one of the two potentially reactive methyl groups, and proceeds faster than the corresponding reaction of methylmagnesium halides. Second order kinetics are found for the reaction of methylmagnesium bromide with pinacolone in the presence of equivalent amounts of magnesium bromide. These findings appear to support the mechanism proposed by Swain and Boyles.[1a]

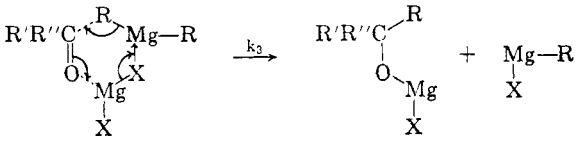
In a previous paper[1b] it was shown that the reaction of methylmagnesium halide with benzophenone and pinacolone follows a third-order law

$$V = k_3(\text{Grignard})^2(\text{ketone})$$

One possible way of explaining this result is to assume that the reactive species is $R_2Mg \cdot MgX_2$, which is believed to be a constituent of Grignard solutions.[2–8] According to the possible equilibrium

$$2\ RMgX \rightleftharpoons R_2Mg \cdot MgX_2, \text{ with } K = \frac{(RMgX)^2}{R_2Mg \cdot MgX_2},$$

the reaction could be of third order and consistent with the process



$$V = k_3(\text{ketone})(R_2Mg \cdot MgX_2) = \frac{k_3}{K}(\text{ketone})(\text{Grignard})^2$$

This scheme can be excluded, however, as we have found[1b] that the reaction slows down with increasing concentration of Grignard reagent. Furthermore, it has been shown[9] that the equilibrium $2\ RMgX \longleftrightarrow R_2Mg \cdot MgX_2$ is established very slowly, if at all.

Another possibility is that dialkylmagnesium is the reactive species:

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