gether it was possible to induce the solvent to flow two or three times the length of the first strip. It was somewhat surprising to find that the R_f values of sugars using 1-butanol–ethanol–water were higher with thick sheets than those obtained using Whatman No. 1 paper. The reason for this is not apparent.

Some examples of the application of the above technique are given in Table I.

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Triesters of Carboxymethylmercaptosuccinic Acid[1]

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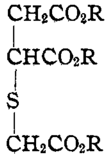
A number of esters of carboxymethylmercaptosuccinic acid have been described by Mulvaney, *et al.*[2] As part of a study on antioxidants, it was of interest to prepare several new trialkyl esters of this acid. These compounds and their physical properties are listed in Table I.

TABLE I

TRIALKYL ESTERS OF CARBOXYMETHYLMERCAPTOSUCCINIC ACID


$$\begin{array}{l}\mathrm{CH_2CO_2R}\\ |\\ \mathrm{CHCO_2R}\\ |\\ \mathrm{S}\\ |\\ \mathrm{CH_2CO_2R}\end{array}$$

R	B.p.[3] t, °C.	Mm.	$n^{25}D$	d^{25}_4	*MR* Calcd.	*MR* Found	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
Isobutyl	167–169	0.37	1.4583	1.042	98.0	98.6	8.54	8.65
n-Hexyl	200–203	.40	1.4644	1.013	125.7	125.6	6.96	7.32
2-Ethyl butyl	205–208	.40	1.4649	1.012	125.7	125.8	6.96	7.15
2-Ethyl hexyl	222–227	.37	1.4663	0.9801	153.4	153.6	5.88	5.92

Though somewhat unstable thermally, the esters may be distilled at the reduced pressures without appreciable decomposition. All of the esters are slowly hydrolyzed at room temperature by 5% aqueous potassium hydroxide. The tris-1,1-dihydroperfluorobutyl ester reacts rapidly with dilute potassium carbonate.[4] Esters of this fluoro alcohol which do not contain sulfur show no detectable hydrolysis under these conditions.[5]

Attempts to oxidize the triesters to sulfoxides or sulfones with chromic acid or potassium permanganate were unsuccessful. Hydrogen peroxide in acetic acid reacted with the tri-*n*-butyl ester,[6] but only a high yield of *n*-butyl acetate and a sulfur-containing residue, which may have been the original mercapto acid, were isolated. The formation of *n*-butyl acetate could result from oxidation or hydrolysis of the ester groups followed by esterification of the alcohol thus obtained by the acetic acid. Drastic oxidation with nitric or perchloric acids resulted in cleavage of the thioether linkages. In this manner, the sulfur could be determined quantitatively as sulfate. It is quite possible that the sulfones or the intermediate sulfoxides are formed but are unstable and react further.

Experimental

Preparation of Triesters of Carboxymethylmercaptosuccinic Acid.—The method used was similar to that described by Mulvaney,[2] except that sodium bisulfate was used as the catalyst, and is illustrated for the preparation of the triisobutyl ester. In a 300-ml. round-bottom flask fitted with a modified Dean and Stark apparatus used as a phase separator and to which was attached a reflux condenser, was placed 62.5 g. (0 3 mole) of carboxymethylmercaptosuccinic acid (Evans Chemetics, Inc.), 74 g. (1.0 mole) of isobutyl alcohol, 0.5 g. of sodium bisulfate and 50 ml. of benzene as a water entrainer. The mixture was heated under reflux for five hours, after which time the theoretical amount of water (16.4 ml.) had been collected. The reaction mixture was washed with three 50-ml. portions of a 10% sodium carbonate solution, then with water, and dried over anhydrous magnesium sulfate. The mixture was distilled and gave 90 g. (79.8%) of the triester, b.p. 167–169° (0.37 mm.). The other triesters, shown in Table I, were obtained in comparable yields.

Reaction of the Tri-*n*-butyl Ester with Hydrogen Peroxide in Acetic Acid.—In a 200-ml. round-bottom flask, fitted with a reflux condenser, was placed 22.6 g. (0.2 mole based on 100% H_2O_2) of 30% hydrogen peroxide and 50 ml. of glacial acetic acid. The mixture was heated with a Glas-Col mantle at 85° for one hour. The mixture was cooled to 25° and then 37.6 g. (0.1 mole) of the tri-*n*-butyl ester was added. The mixture was heated under reflux for two days. The upper, water-insoluble layer was separated and the lower acid layer was neutralized with a dilute solution of sodium bicarbonate and extracted with ether. The ether layer was combined with the original water-insoluble layer and dried over anhydrous sodium sulfate. The ether was removed by distillation and there was obtained 28.0 g. (80.5%) of *n*-butyl acetate, b.p. 121–124° and about 5 g. of a sulfur-containing residue, which decomposed on heating. This may have been carboxymethylmercaptosuccinic acid.

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[1] Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[2] J. F. Mulvaney, J. G. Murphy and R. L. Evans, THIS JOURNAL, **70**, 2428 (1948).

[3] Boiling points uncorrected.

[4] M. Hauptschein, private communication.

[5] R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien and M. Hauptschein, THIS JOURNAL, **75**, 2693 (1953).

[6] Hardesty Chemical Co., Inc., New York City.

Preparation and Properties of Pentamethyleneketene Monomer and Dimer

BY CARL M. HILL AND MARY E. HILL

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Recent studies[1,2] of mono- and disubstituted ketenes suggested investigation of the dehydrohalogenation products of hexahydrobenzoyl chloride.

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[1] C. M. Hill, H. I. Schofield, A. S. Spriggs and M. E. Hill, THIS JOURNAL, **73**, 1660 (1951).

[2] C. M. Hill and G. W. Senter, *ibid.*, **71**, 364 (1949).