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.

DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY
UNIVERSITY OF MINNESOTA
ST. PAUL, MINNESOTA

Triesters of Carboxymethylmercaptosuccinic Acid[1]

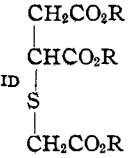
BY ROBERT FILLER AND RICHARD W. SNEED

RECEIVED DECEMBER 24, 1952

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



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

	B.p.[3]				*MR*		Sulfur analyses, %	
R	*t*, °C.	Mm.	n^{25}_D	d^{25}_4	Calcd.	Found	Calcd.	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.

MATERIALS LABORATORY
WRIGHT AIR DEVELOPMENT CENTER
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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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

RECEIVED JANUARY 14, 1953

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).

Treatment of the acid chloride in dilute ether solution with triethylamine resulted in formation of pentamethyleneketene monomer and dimer in satisfactory yields. The relative yields of the monomer and dimer varied with the number of hours the reaction mixture was allowed to stand at room temperature; prolonged reaction time seemed to favor formation of the dimer.

The monomer was a slightly yellow colored liquid; the dimer a white solid which sublimed to form needle-like crystals. The monomer gave positive reaction with bromine in carbon tetrachloride and potassium permanganate, and reacted with aniline to form hexahydrobenzoanilide and with dilute alkali to yield hexahydrobenzoic acid.

The dimer reacted with hydroxylamine to form the monoxime and with hot dilute alkali to give dicyclohexyl ketone. Catalytic hydrogenation of the dimer at elevated temperature and high pressure produced a hydroxy ketone, which upon reaction with alkali formed dicyclohexyl ketone and formic acid.

Experimental[3]

Hexahydrobenzoyl Chloride.—The chloride was prepared from hexahydrobenzoic acid, m.p. 30–31°, by use of thionyl chloride. Boiling point of chloride was 65–65.5° (5 mm.) and 180–181° (750 mm.); reported b.p. 179° (760 mm.).[4] Observed m.p. of amide was 183–184°; reported m.p. 184°.[5]

Pentamethyleneketene Monomer and Dimer.—The monomer was prepared by treating 14.6 g. (0.10 mole) of hexahydrobenzoyl chloride dissolved in 300 ml. of diethyl ether with 11.4 g. (0.11 mole) of triethylamine. At the end of 16 hours, the hydrochloride was removed by inverted filtration. Removal of the ether by distillation left a dark colored residue which when distilled from a Claisen flask gave 3.6 g. (32%) of the monomer, b.p. 40–41° (3 mm.), d^{20}_{4} 1.0617, n^{20}_{D} 1.4680. *Anal.* Calcd. for $C_7H_{10}O$: mol. wt., 110. Found: mol. wt., 108.

The dimer was prepared by treating a solution of 36.6 g. (0.25 mole) of hexahydrobenzoyl chloride in 400 ml. of diethyl ether with 30.3 g. (0.30 mole) of triethylamine. The reaction mixture was allowed to stand for four days. At the end of this period, the precipitated triethylamine hydrochloride was separated by filtration. The filtrate was then concentrated by evaporation of the ether with a stream of dry, oxygen-free nitrogen. Prolonged chilling of the concentrated filtrate produced crystals of the dimer, which were removed by suction filtration. Repeated chilling of the filtrate caused additional crops of the dimer to separate. Finally, the filtrate was distilled, and 2 g. of the dimer, b.p. 175–180° (15 mm.), collected. The crude dimer was recrystallized from ethanol; yield was 15.5 g. (55%); m.p. 164–165°.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.36; H, 9.09; mol. wt., 220. Found: C, 75.90; H, 9.00; mol. wt., 218.

Reaction of Monomer with Aniline.—One gram of pure monomer was added slowly to an equivalent amount of aniline in 10 ml. of anhydrous diethyl ether. The crude anilide was recrystallized from petroleum ether. Observed m.p. was 139–140°; reported[6] m.p. for hexahydrobenzoanilide is 141°; mixed m.p. was 140–141°.

Reaction of Monomer with Alkali.—To 1 g. of the monomer was added dropwise 10 ml. of 10% sodium hydroxide. The alkaline solution was extracted with diethyl ether and acidified with dilute hydrochloric acid. The acid solution was extracted with several small portions of ether and the combined extracts dried. Evaporation of the solvent left 0.7 g. of hexahydrobenzoic acid, m.p. 29.5–30.5°. Mixed m.p. with authentic sample of hexahydrobenzoic acid was 30–31°.

Reaction of Dimer with Hydroxylamine.—One gram of dimer, 10 ml. of ethanol and 1 g. of pyridine were warmed under reflux to 60°; and a solution of 0.3 g. of hydroxylamine in 5 ml. of water was added slowly. After heating for two hours, the reaction mixture was evaporated by a stream of dry air. The residue was triturated with a small portion of hot chloroform and filtered. Chilling of the filtrate precipitated 0.3 g. of the monoxime, m.p. 171–172°.

Anal. Calcd. for $C_{14}H_{21}O_2N$: N, 5.95. Found: N, 5.93.

Catalytic Hydrogenation of Dimer.—Two grams of the dimer and 50 ml. of ethanol, mixed with 0.5 g. of Raney nickel, were treated with hydrogen at 1,000 p.s.i. and 80° for two hours. After removal of the catalyst by filtration, the solution was concentrated by distillation. The solid residue was recrystallized from dilute ethanol. The hydrogenated product was further purified by sublimation; m.p. 121–122°; yield 1.64 g. (77%). This product formed a semicarbazone, m.p. 141–142°, and a phenylurethan, m.p. 151–152°.

Alkaline Hydrolysis of Hydrogenated Product.—To 2 g. of the hydrogenated product was added 10 ml. of 10% sodium hydroxide solution. The mixture was warmed over a water-bath. The oil which formed was extracted with ether. Removal of the ether left 1 g. of an oily liquid, b.p. 211–213° (755 mm.), which formed an oxime, m.p. 157–158°. Melting point of the oxime prepared from an authentic sample of dicyclohexyl ketone was 157–158°; mixed m.p. 158–159°.

Anal. Calcd. for $C_{13}H_{23}ON$: N, 6.70. Found: N, 6.77.

The alkaline solution from above was acidified with sirupy phosphoric acid and distilled. The distillate reacted acid to litmus, reduced potassium permanganate and mercuric nitrate solutions and gave a negative test with the Schiff reagent.

Reaction of Dimer with Sodium Hydroxide.—Two grams of the dimer was refluxed with 50 ml. of 15% sodium hydroxide solution for 48 hours. The cooled reaction mixture was extracted with diethyl ether. Removal of the ether by distillation gave 0.9 g. (53%) of an oil, b.p. 145–147° (12 mm.). Treatment of this oil with hydroxylamine produced an oxime, m.p. 158–159°; mixed m.p. with an authentic sample of dicyclohexyl ketone oxime was 157–158°.

DEPARTMENT OF CHEMISTRY
TENNESSEE A. AND I. STATE UNIVERSITY
NASHVILLE 8, TENNESSEE

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[3] All melting points are corrected.

[4] V. Meyer, *Ber.*, **30**, 1941 (1897).

[5] J. S. Lumsden, *J. Chem. Soc.*, **87**, 92 (1905).

[6] N. J. Edson, *J. Soc. Chem. Ind.*, **53**, 138 (1934).

Cyclization of N-β-Cyanoethylanilines

BY WILLIAM S. JOHNSON AND WILLIAM DEACETIS[1]

RECEIVED FEBRUARY 2, 1953

A recent publication of Braunholtz and Mann,[2] in which the monocyclization of N,N-bis-(β-cyanoethyl)-*m*-toluidine, II ($R = CH_3$) was mentioned, prompts us to announce our interest in this problem. Our studies, which are yet at a preliminary stage, have been aimed at finding a facile synthesis of 4-keto-7-chloro-1,2,3,4-tetrahydroquinoline III (R = Cl), which has recently been shown[3] to be easily converted to the important antimalarial, chloroquine.

We have been able to obtain III (R = Cl) by direct cyclization of I (R = Cl),[4] but since we have found that cyclizations of this type proceed more readily with cyanoethyl derivatives of alkylanilines (having a tertiary nitrogen atom),[5] we have considered the feasibility of monocyclization of II (R = Cl) to IV (R = Cl) followed by β-elimination of the N-cyanoethyl group to give III (R = Cl). Some of our experiments are reported below.

The addition of acrylonitrile to aniline and to *m*-

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1950–1952.

[2] J. T. Braunholtz and F. G. Mann, *J. Chem. Soc.*, 3046 (1952).

[3] W. S. Johnson and B. G. Buell, THIS JOURNAL, **74**, 4513 (1952).

[4] Details of this work will be reported in a future publication.

[5] *Cf.* French patent 806,715 [*C. A.*, **31**, 4991 (1937)].