lization of the resulting product from water gave 1.2 g. (24.5%) of benzoic acid, m.p. 120–121.5°, identified by mixture melting point.

The neutral organic layer was distilled and the residue chromatographed on alumina. The product eluted with petroleum ether (b.p. 60–70°) and carbon tetrachloride was recrystallized from petroleum ether of the same boiling point to give 4.05 g. (59%) of diphenylamine, m.p. 53–54°, identified by mixture melting point and infrared spectra.

When a mixture of 12.25 g. (0.05 mole) of triphenylamine, 1 g. (0.15 g.-atom) of lithium, and 50 ml. of THF was stirred for 1.5 hr. at room temperature and refluxed for 3 additional hours,[6a] a brown color had developed, but Color Test I[4] was still negative. After hydrolysis, 8.3% of diphenylamine was isolated, together with 58% of triphenylamine. In another experiment,[6a] employing the same amount of starting materials and solvent, a positive Color Test I was obtained after 3 hr. at reflux. Subsequent carbonation gave no benzoic acid, but diphenylamine in a 9.7% yield, together with unreacted triphenylamine (60%).

Cleavage of triphenylphosphine. To a stirred mixture of 10 g. (0.0382 mole) of triphenylphosphine and 1.4 g. (0.2 g.-atom) of finely cut lithium wire was added slowly 100 ml. of THF. The reaction started immediately, the solution turned dark red, heat was evolved, and Color Test I[4] was positive. Stirring was continued for 1 hr., at which time the mixture had cooled to room temperature. The solution was filtered through glass wool, hydrolyzed, and after the addition of some ether, extracted with dilute acid and water. The dried organic layer was distilled to give 5.2 g. (68.5%) of diphenylphosphine, b.p. 150–154° (11 mm.).[7] The infrared spectrum showed the characteristic P-H absorption band at 4.4μ.

In a second experiment 15.0 g. (0.0572 mole) of triphenylphosphine was cleaved with 1.4 g. (0.2 g.-atom) of lithium in 100 ml. of THF at −10° to 0° (stirring for 4 hr.). The work-up in the manner described above gave 4.95 g. (47%) of diphenylphosphine, b.p. 150–154° (11 mm.). The distillation residue was recrystallized from ethanol and yielded 2.5 g. (20.2%) of diphenylphosphinic acid, m.p. 190–191.5°, which was identified by its infrared spectrum.

In a third experiment the cleavage products were allowed to react with chlorotriphenylsilane. After hydrolysis, tetraphenylsilane, m.p. 232–234°, was isolated in a 64% yield from the ether insoluble part of the reaction mixture. Chromatography of the ether soluble part gave crude triphenylsilanol, diphenylphosphinic acid, and diphenylphosphine, which were identified by their infrared spectra.

Cleavage of triphenylarsine. To a stirred mixture of 10 g. (0.034 mole) of triphenylarsine and 1.4 g. (0.2 g.-atom) of finely cut lithium wire was added slowly 100 ml. of THF. The reaction started immediately, the solution turned red and showed a positive Color Test I.[4] After stirring for 1 hr. while cooling with ice and one additional hour at room temperature, a solution of 7.4 g. (0.068 mole) of chlorotrimethylsilane in 10 ml. of THF was added. The color of the solution faded after the addition of the second equivalent. The work-up by filtration through glass wool, addition of some ether, extraction with dilute acid, drying of the organic layer with sodium sulfate, and distillation gave 3.9 g. (76%) of trimethylphenylsilane, b.p. 166–169°, n_D^{20} 1.4870, which was identified by its infrared spectrum. The high boiling fractions, 1.5 g., b.p. 160–230° (0.1 mm.), and 5.1 g., b.p. 230–240° (0.1 mm.), both yellow oils, which slowly solidified, were treated with cold benzene. The benzene insoluble part was recrystallized from water to give 0.25 g. (3%) of diphenylarsinic acid, m.p. 171–172.[8] The benzene soluble part was recrystallized from ethanol to give 4.3 g. (54%) of bis-(diphenylarsenic) oxide, m.p. 92–93.5°.[8]

Cleavage of triphenylstibine. The cleavage of 10 g. (0.0283 mole) of triphenylstibine with 1.4 g. (0.2 g.-atom) of lithium in 80 ml. of THF was carried out as described in the previous experiment. The cleavage products were allowed to react with 6.5 g. (0.06 mole) of chlorotrimethylsilane. The deep red-brown color faded immediately, leaving a small amount of black precipitate (apparently metallic antimony). The reaction mixture was filtered through glass wool, hydrolyzed, and after the addition of some ether, washed with dilute acid. The dried organic layer deposited on standing a white precipitate, which was filtered off, washed with ether and water to give 5.25 g. (60%) of diphenylstibinic acid, m.p. 283–286°.[9] Distillation of the filtrate yielded 2.65 g. (62.5%) of trimethylphenylsilane, b.p. 55–60° (10 mm.), n_D^{20} 1.4865, which was identified by its infrared spectrum. The distillation residue upon treatment with benzene left 0.85 g. (9.5%) of insoluble diphenylstibinic acid, m.p. 282–286°. Addition of petroleum ether (b.p. 60–70°) to the benzene solution gave 0.2 g. (2%) of a colorless, crystalline compound, m.p. 170–172°, which is thought to be diphenylantimony trichloride.[9]

Relevant to the studies now reported are some experiments in progress on the reaction of triphenylsilyllithium with inorganic salts as well as with aryl derivatives like those described in this paper.

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(6) (a) Experiments of J. J. Dietrich.

(7) S. I. Vol'fkovich, V. K. Kustov, and K. F. Koroteeva, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, **1954**, 5 [*Chem. Abstr.*, **49**, 6859 (1955)] report a boiling point of 272° (760 mm.) and 170° (3 mm.) for diphenylphosphine.

(8) W. La Coste and A. Michaelis, *Ann.*, **201**, 229, 231 (1880), report a melting point of 174° for diphenylarsinic acid and a melting point of 91–92° for bis(diphenylarsenic) oxide.

(9) H. Schmidt, *Ann.*, **421**, 236 (1920) reports a melting point of 285° for diphenylstibinic acid and a melting point of 175° for diphenylantimony trichloride.

Reaction of Xanthates with β-Propiolactone

MARTIN W. FARRAR

Received January 10, 1958

The reaction of β-propiolactone with a variety of nucleophilic reagents has been described during the last decade. An excellent review on this subject has appeared recently.[1] As described in this article, β-propiolactone can react either at the carbonyl carbon to produce derivatives of β-hydroxypropionic acid or at the β-carbon to produce β-carboxyethyl derivatives of the nucleophile. The course of

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(1) H. E. Zaugg, *Org. Reactions*, **VIII**, 305 (1954).

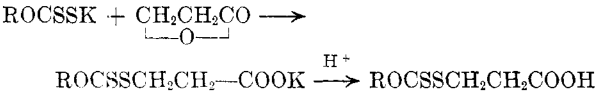
TABLE I

3-MERCAPTOPROPIONIC ACID, ALKYL XANTHATES

Potassium Alkyl Xanthate	Yield, %	Melting Point	Refractive Index (n_D^{25})	Calcd. for	Analysis					
					C	H	S	Found: C	H	S
Methyl	100	—	1.5511	$C_5H_8O_3S_2$	33.3	4.47	35.6	33.5	4.57	35.9
Ethyl	95	70–71°	—	$C_6H_{10}O_3S_2$	37.1	5.19	33.0	37.3	5.08	33.3
n-Propyl	99	50–53°	—	$C_7H_{12}O_3S_2$	40.3	5.81	30.8	40.2	5.81	30.8
Allyl	97	—	1.5505	$C_7H_{10}O_3S_2$	40.7	4.89	31.1	40.4	5.01	31.3
n-Butyl	100	—	1.5333	$C_8H_{14}O_3S_2$	43.2	6.35	28.8	43.3	6.46	29.2
2-Ethylhexyl	100	—	1.5177	$C_{12}H_{22}O_3S_2$	51.8	7.97	23.0	51.3	7.86	23.0

the reaction depends on a number of factors including the nature of the attacking reagent, solvent employed, and reaction conditions.

Although mercaptans and other organic sulfur compounds have been studied as nucleophiles, the reaction of xanthates with β-propiolactone has not been reported. In the present study it has been found that essentially quantitative yields of β-carboxyethyl xanthate esters are produced when β-propiolactone and potassium xanthates are allowed to react in aqueous solution at 20–30°.



$$ROCSSK + \underbrace{CH_2CH_2CO}_{O} \longrightarrow$$

$$ROCSSCH_2CH_2—COOK \xrightarrow{H^+} ROCSSCH_2CH_2COOH$$

Table I summarizes the results of this investigation.

Certain of these products possess interesting fungicidal, herbicidal, and microbiological activity.

EXPERIMENTAL

The potassium alkyl xanthates employed were freshly prepared from alcoholic potassium hydroxide and carbon disulfide. Freshly distilled β-propiolactone was used in these experiments. The reaction of potassium ethyl xanthate with β-propiolactone is typical of the general procedure employed and will be discussed in detail.

To a solution of 8.0 g. (0.05 mole) of potassium ethyl xanthate in 100 ml. of water at 15–20° was added 3.7 g. (0.05 mole) of β-propiolactone over a 10-min. period. Occasional cooling was necessary to maintain the temperature below 20°. After an additional 2-hr. period at room temperature, the solution was acidified with hydrochloric acid whereupon a white crystalline solid separated. This solid was removed by filtration and was washed with water. After drying in a vacuum desiccator, there was obtained 9.4 g. of product, m.p. 69–70°. Recrystallization from Skellysolve B yielded 9.2 g. (95%) of 3-mercaptopropionic acid, ethyl xanthate, m.p. 70–71°.

In a similar manner the potassium alkyl xanthates listed in Table I were reacted with β-propiolactone. In the case of liquid products, isolation was accomplished by solvent extraction after acidification, water washing, drying, and evaporation of the solvent. Analytical data in Table I are on the products as isolated in this manner. Purification by vacuum distillation was not entirely satisfactory as there was evidence of decomposition at temperatures above 140–150°.

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Reaction of Cyclohexanone and Hydrogen Peroxide with Ferrous Sulfate and Dimethyl Maleate

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The reaction of cyclohexanone peroxide (I) (formed *in situ* from cyclohexanone and hydrogen peroxide) with ferrous ion in the presence of butadiene to give dimethyl 8,12-eicosadiene-1,20-dioate was recently reported.[1]

We have now found that dimethyl maleate will also react with the intermediate radical A[2] to give a corresponding dimeric product, II. The latter was isolated, after esterification, as a reasonably pure distillation residue (38% yield based on unrecovered ketone, 39% based on unrecovered dimethyl maleate, 35% on hydrogen peroxide) after removal of the more volatile 1:1 products, III and IV (33% yield based on unrecovered ketone).[3] Analysis of the mixture of III and IV by carbon and hydrogen values, iodine number and by quantitative hydrogenation indicated it to contain 91% of III and 9% of IV.

Saponification of this hydrogenated ester mixture afforded the water-soluble 3-carboxyazelaic acid (V), an apparently novel compound.

When V was heated at 180° and 1 mm. for six hours, one molecule of water was lost and a water-insoluble anhydride was formed. The infrared spectrum of the latter was compatible with that expected for the substituted succinic anhydride, VI.

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(1) M. S. Kharasch and W. Nudenberg, *J. Org. Chem.*, 19, 1921 (1954).

(2) *Cf.* ref. 1, footnote 4, for a brief discussion of the possible existence of A.

(3) No comparable lower molecular weight products were observed in the reaction of I with iron and butadiene (ref. 1).