was removed and 0.6 mole of diethyl carbonate, dissolved in 50 cc. of absolute ether, was added to the stirred reaction mixture as rapidly as the ether was efficiently condensed. The reaction mixture was again placed on a steam-bath and the mixture stirred and refluxed for two hours longer. The reaction mixture was poured into a mixture of 50 g. of ice and 100 cc. of concentrated hydrochloric acid and the phases separated. The ethereal phase was dried over Drierite, the solvent distilled and most of the diethyl carbonate distilled off at atmospheric pressure. The residue was fractionated *in vacuo*, collecting diethyl α-phenylmalonate, b. p. 127–130° at 2 mm.[3]; yield 64%.

Diethyl α-Phenyl-α-ethylmalonate.—The reaction of 0.1 mole of ethyl α-phenyl-*n*-butyrate, 0.2 mole of sodium amide and 0.2 mole of diethyl carbonate was carried out essentially as described above, except that the reaction mixture was refluxed for eight hours instead of two hours.[9] The product, diethyl α-phenyl-α-ethylmalonate, boiled at 169–171° at 19 mm. in agreement with that reported in the literature[4]; yield 40%.

Anal.[10] Calcd. for $C_{15}H_{20}O_4$: C, 68.12; H, 7.63. Found: C, 67.80; H, 7.84. A sample of the product was converted to phenobarbital, m. p. 173–174°, essentially as described by Nelson and Cretcher,[4] except that Mathieson sodium methoxide was used instead of sodium ethoxide.

An ether suspension of the sodium derivative of ethyl α-phenyl-*n*-butyrate, prepared from 0.1 mole of the ester and 0.1 mole of sodium amide, was refluxed until essentially all of the ammonia had been driven off, and 15% excess of ethyl chlorocarbonate in 50 cc. of absolute ether was then added. After stirring for one hour, the mixture was shaken with ice and water. The ether phase was washed with sodium bicarbonate solution, dried with Drierite and the solvent distilled. The residue was fractionated, collecting the fraction boiling at 169–171° at 19 mm., presumably diethyl α-phenyl-α-ethylmalonate; yield 30%. The product was colored yellow. Similar results were obtained using a 100% excess of ethyl chlorocarbonate.

Summary

1. Ethyl phenylacetate and ethyl α-phenyl-*n*-butyrate have been carbethoxylated with diethyl carbonate by means of sodium amide to form diethyl α-phenylmalonate and diethyl α-phenyl-α-ethylmalonate, respectively.

2. The carbethoxylation of certain other esters is considered.

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(9) When the reaction mixture was refluxed for two hours, the yield of carbethoxylation product was only 16%, 70% of the ester being recovered. No α-phenyl-*n*-butyramide was found in either of the carbethoxylation experiments. Ethyl α-phenyl-*n*-butyrate appears to be converted readily to its sodium derivative in the presence of sodium amide in liquid ammonia, since, when this ester is added to an equivalent of sodium amide in liquid ammonia containing a trace of sodium triphenylmethide as indicator,[6] the deep red color of the mixture is discharged almost immediately.

(10) Microanalysis by Arlington Laboratories, Fairfax, Virginia.

[CONTRIBUTION FROM THE ARMY INDUSTRIAL HYGIENE LABORATORY[1]]

Preparation of 2,4,6-Trichlorophenyl Isocyanate

BY ROBERT R. McNARY[2] AND LOUIS MAGID[3]

In the course of a special investigation, it was desired to synthesize 2,4,6-trichlorophenyl isocyanate, and its corresponding methyl and ethyl alcohol derivatives, namely, 2,4,6-trichlorophenyl ethyl carbamate and 2,4,6-trichlorophenyl methyl carbamate. The preparation or properties of these compounds have not heretofore been reported in the literature.

The method used for the synthesis of 2,4,6-trichlorophenyl isocyanate was based upon the method developed for the preparation of *p*-nitrophenyl isocyanate by Shriner, Horne and Cox.[4]

Experimental

Preparation of 2,4,6-Trichlorophenyl Isocyanate. ($Cl_3C_6H_2N{=}C{=}O$) (mol. wt. 222.5).—Carbonyl chloride was prepared by the action of fuming sulfuric acid on carbon tetrachloride[5] and then passed through concentrated sulfuric acid to remove the sulfur trioxide and sulfuryl chloride vapors. Seventy-five cc. of dry benzene was saturated with carbonyl chloride at room temperature and a solution of 5 g. of 2,4,6-trichloroaniline in 25 cc. of dry benzene was run in slowly over a period of one hour. During this time a steady stream of carbonyl chloride was passed through the solution to ensure an excess. After the addition of the last of the trichloroaniline, the stream of carbonyl chloride was continued for five minutes and then shut off. The benzene solution was then filtered and quickly evaporated at room temperature with a stream of dry air. The residue was recrystallized from dry carbon tetrachloride and the product obtained in the form of white needles melting at 66–67° (uncor.).

Properties and Reactions of 2,4,6-Trichlorophenyl Isocyanate.—2,4,6-Trichlorophenyl isocyanate has a characteristic but not unpleasant odor. It sublimes on heating. It is not hygroscopic, but in contact with the moisture of the air, or when dissolved in undried organic solvents, 2,4,6,2′,4′,6′-hexachlorocarbanilide (m. p. 320–325°, uncor.), which was first prepared by Chattaway and Orton,[6] is formed. Trichlorophenyl isocyanate is insoluble in water but soluble in benzene, petroleum ether, ether, carbon tetrachloride, chloroform, mineral spirits, alcohol, methyl alcohol and acetone. On hydrolysis with water or aqueous alkaline solutions, 2,4,6-trichloroaniline and 2,4,6,2′,4′,6′-hexachlorocarbanilide are formed. When dissolved in acetone and precipitated by the addition of water, the product formed is almost entirely 2,4,6-trichloroaniline. Trichlorophenyl isocyanate reacts with methyl and ethyl alcohols to form the corresponding urethans.

Preparation of 2,4,6-Trichlorophenyl Ethyl Carbamate. ($Cl_3C_6H_2NHCOOC_2H_5$) (mol. wt. 268.5).—When 2,4,6-trichlorophenyl isocyanate is dissolved in an excess of ethyl alcohol, 2,4,6-trichlorophenyl ethyl carbamate

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(1) Present location: Edgewood Arsenal, Md.

(2) Present address: U. S. Citrus Products Station, Winter Haven, Florida.

(3) Present address: The Wm. S Merrell Co., Cincinnati, 15, Ohio.

(4) R. L. Shriner, W. H. Horne and R. F. B. Cox, "Organic Syntheses," Vol. XIV, John Wiley and Sons, Inc., New York, N. Y., 1934, p. 72.

(5) H. Erdmann, *Ber.*, **26**, 1993 (1893).

(6) Chattaway and Orton, *ibid.*, **34**, 1077 (1901).

(m. p. 118°, uncor.) is formed and may be precipitated from its alcoholic solution by the addition of water. It is a white, crystalline, almost odorless compound, insoluble in water and soluble in all the usual organic solvents. Hydrolysis cannot be effected by boiling in strong aqueous acid or alkaline solutions.

2,4,6-Trichlorophenyl ethyl carbamate could not be synthesized from the action of ethyl chlorocarbonate on 2,4,6-trichloroaniline.

Preparation of 2,4,6-Trichlorophenyl Methyl Carbamate ($Cl_3C_6H_2NHCOOCH_3$) (mol. wt. 254.5).—When 2,4,6-trichlorophenyl isocyanate is dissolved in an excess of methyl alcohol, 2,4,6-trichlorophenyl methyl carbamate (m. p. 132°, uncor.) is formed and may be precipitated from its alcoholic solution by the addition of water. It is a white, crystalline, almost odorless compound, insoluble in water and soluble in all the usual organic solvents.

Summary

A method of preparation and properties of 2,4,6-trichlorophenyl isocyanate and its corresponding methyl and ethyl alcohol derivatives, namely, 2,4,6-trichlorophenyl methyl carbamate and 2,4,6-trichlorophenyl ethyl carbamate, have been presented.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

The Use of Liquid Phase Oxidation for the Preparation of Nuclearly Substituted Styrenes. I. Methyl *p*-Vinylbenzoate[1]

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS, EARL C. CHAPIN, GRAFTON R. OWENS AND ROBERT W. SHORTRIDGE

The air oxidation of substituted ethylbenzenes to the corresponding acetophenones offers a direct and convenient route to many otherwise difficultly obtainable compounds. While, in the case of ethylbenzene itself, quite a few studies have been made employing oxygen as the oxidizing agent,[2,3,4,5,6] only four examples employing air are mentioned in the literature. As catalysts, copper oxide,[7,8] iron oxide[8,9] and cobalt acetate[10] in acetic acid solution have been used. In the case of cobalt acetate[10] about half as much by-product benzoic acid was obtained as the desired acetophenone.

We have found that in the presence of chromium oxide and calcium carbonate both ethyl *p*-ethylbenzoate and methyl *p*-ethylbenzoate are smoothly oxidized by air to ethyl *p*-acetylbenzoate (41% conversion and 70% yield) and methyl *p*-acetylbenzoate (54% conversion and 66% yield). These ketones were then treated with hydrogen in the presence of copper chromite to give the corresponding carbinols in 63–80% yields.

When ethyl *p*-(α-hydroxyethyl)-benzoate was passed, together with steam, through a column packed with alumina[11] and heated to 300–350°, the product, in two runs, was a low yield of what may be impure ethyl *p*-vinylbenzoate. In a third run there was isolated a small amount of crystalline material having the correct analysis for *p*-vinylbenzoic acid and a larger portion of polymeric material of the same constitution. This latter product swelled to a voluminous gel on long-continued treatment with aqueous alkali, and shrank to its original proportions when again treated with acid.

On the basis of these experiments methyl *p*-(α-hydroxyethyl)-benzoate was heated with potassium bisulfate essentially according to the procedure of Brooks.[12] In this way there was obtained a 49% yield of methyl *p*-vinylbenzoate.

The authors are grateful to Mr. E. L. Ringwald for the preparation of considerable quantities of methyl *p*-ethylbenzoate.

Experimental

Ethyl *p*-Ethylbenzoate.[13]—A solution of 500 g. of HTH (70% $Ca(ClO)_2$ in 2 liters of water and one of 350 g. of potassium carbonate and 100 g. of potassium hydroxide in 1 liter of water were mixed, thoroughly shaken and filtered. The filtrate was placed in a 5-liter, three-necked flask equipped with a stirrer, thermometer, dropping funnel and refluxing condenser, and heated to 65°. While the mixture was stirred and held at 75–80° by the occasional application of a water-bath, 160 g. of *p*-ethylacetophenone was added over a forty-five-minute period. The mixture was stirred thirty minutes more at this temperature and then cooled. A solution of 100 g. of sodium bisulfite in 400 cc. of water was added with continued cooling and the stirring continued for fifteen minutes. This solution was finally acidified with 400 cc. of concentrated hydrochloric acid and the precipitated acid was removed by filtration, washed with water and dried in a 50° oven. This product together with 36 g. from another experiment was refluxed for one and one-half hours with 800 cc. of absolute ethyl alcohol while a vigorous stream of hydrogen chloride was introduced into the boiling mixture. At this

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[1] Since the completion of this work an article has appeared by Marvel and Overberger, THIS JOURNAL, **67**, 2250 (1945), which describes the preparation of this compound by an alternate route.

[2] Stephens, THIS JOURNAL, **48**, 2920 (1926).

[3] Stephens, *ibid.*, **50**, 2523 (1928).

[4] King, Swann and Keyes, *Ind. Eng. Chem.*, **21**, 1227 (1929).

[5] Senseman and Stubbs, *ibid.*, **25**, 1286 (1933).

[6] Newitt and Burgoyne, *Proc. Roy. Soc.* (London), **A153**, 448 (1936); *C. A.*, **30**, 2555^{9} (1936).

[7] Binapfl and Krey, U. S. Patent 1,813,606; *Chem. Zentr.*, **102**, II, 2058 (1931).

[8] I. G. Farbenindustrie, A.-G., French Patent 646,078; *Chem. Zentr.*, **100**, I, 1507 (1929).

[9] I. G. Farbenindustrie, A. G., U. S. Patent 1,815,985; see French Patent 676,826; *Chem. Zentr.*, **101**, I, 3831 (1930).

[10] Loder, U. S. Patent 2,245,528; *C. A.*, **35**, 5912^{8} (1941).

[11] Emerson and Agnew, THIS JOURNAL, **67**, 518 (1945).

[12] Brooks, *ibid.*, **66**, 1295 (1944).

[13] This is an adaptation of the method of Newman and Holmes, "Organic Syntheses," Coll. Vol. II, p. 428.