280° with decomposition starting at 265° when heated at the rate of 5°/min.

Anal. Calcd. for $C_9H_{10}O_3NF$ (199): C, 54.3; H, 5.1; N, 7.0. Found: C, 54.3; H, 5.1; N, 6.9: $[\alpha]^{26}D = \frac{0.29 \times 1.95}{1 \times 0.100} = 5.7°$ (in 4% hydrochloric acid).

Toxicity Determinations.—The procedure employed was that described by Phillips, *et al.*,[1a] *i. e.*, single subcutaneous injections of solutions of the hydrochloride in both mature (150–300 g.) and immature (80–150 g.) rats. The toxic symptoms were identical with those reported[1a] and most of the deaths occurred during the first twenty-four hours although the period of observation was taken as forty-eight hours.

TABLE I

TOXICITY DATA

Substance	Moles/kg. $\times 10^{3a}$	Mortality per group Immature rat	Mortality per group Mature rat
3-Fluoro-*l*(−)-tyrosine	4.5	0/6	
	5.0	0/4	
	6.3	5/10	0/8
	7.5	4/4	4/8
3-Fluoro-*d*(+)-tyrosine	6.3	2/6	0/8
	7.5		4/8
3-Fluoro-*dl*-tyrosine	6.3	2/6	0/8
	7.5		6/8

[a] Mg./kg. = moles/kg. × 2 × 10^5.

GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIF.
RECEIVED MAY 20, 1946

Synthesis of 2,4-Dichloropropiophenone

BY JOHN T. SHEEHAN[1]

According to the available literature,[2,3] the Friedel–Crafts condensation of acyl halides with dihalogenated benzene derivatives proceeds with the formation of negligible or vanishing yields. Consequently it seemed worth while to note the present exception to this observed behavior, which was encountered in the course of another investigation. In this instance, the yield was found equal to that obtained in the usual Friedel–Crafts condensation between acyl halides and aromatic hydrocarbons, albeit a longer period of heating and a greater amount of anhydrous aluminum chloride than usual were employed.

Experimental

2,4-Dichloropropiophenone.—Forty grams (0.27 mole) of *m*-dichlorobenzene and 48 g. (0.50 mole) of propionyl chloride were dissolved in 300 cc. of carbon disulfide. The solution was refluxed on a steam-bath while stirring, and to it was added, over a period of ten minutes, 160 g. (1.20 moles) of anhydrous aluminum chloride. The heating and stirring were continued for twenty-four hours, during which time the evolution of hydrogen chloride was noticeable but never vigorous. The carbon disulfide was then distilled off and the residue poured into 300 cc. of 6 *N* hydrochloric acid in ice. The oily layer which separated was extracted with four 125-cc. portions of benzene. The combined benzene extract was washed twice with 300 cc. of water, once with 350 cc. of 10% sodium hydroxide, and finally three times with 300 cc. of water. It was then dried over anhydrous calcium chloride. The latter was filtered off, the solvent evaporated and the residue distilled. The main fraction boiled at 118–120° at 5 mm. On redistillation it boiled at 121–123° at 6.5–7 mm. The yield was 48.5 g. (89%). At 19 mm. the boiling point is 138–140°; $n^{25}D$ 1.5510 and d^{25} 1.2871.

Anal. Calcd. for $C_9H_8OCl_2$: C, 53.20; H, 3.95; Cl, 34.97. Found: C, 53.10; H, 3.89; Cl, 34.96.

On oxidation with potassium permanganate, the above compound yielded only one product, and that in almost quantitative yield. After recrystallization from water it melted at 158°. A mixed melting point with an authentic sample of 2,4-dichlorobenzoic acid gave no depression.

Anal. Calcd. for $C_7H_4O_2Cl_2$: C, 43.97; H, 2.09; Cl, 37.12. Found: C, 44.15; H, 2.30; Cl, 37.09.

WINTHROP CHEMICAL COMPANY, INC.
RENSSELAER, NEW YORK
RECEIVED MAY 2, 1946

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[1] Present address: Squibb Institute for Medical Research, New Brunswick, N. J.

[2] Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," A. C. S. Monograph 87, Reinhold Publishing Corp., New York, N. Y., 1941, pp. 226–228.

[3] Roberts and Turner, *J. Chem. Soc.*, 1832 (1927).

Carbonyl Chlorofluoride[1]

BY J. H. SIMONS, D. F. HERMAN AND W. H. PEARLSON

We have found that carbonyl chlorofluoride can be prepared readily by shaking a mixture of hydrogen fluoride and phosgene in a copper bomb at approximately 80° and 280 pounds per square inch pressure. Some fluorophosgene is simultaneously produced but as hydrogen chloride is one of the products and as this boils too close to fluorophosgene for separation by distillation, no significant amounts of fluorophosgene were prepared from these preparations.

The apparatus consisted of a heavy-wall copper bomb of about 250-cc. capacity which was connected to a copper condenser cooled by tap water. The condenser was fitted with a pressure gage and a valve through which the gaseous products could be removed. The bomb was placed in an electrically heated furnace located in a shaking machine. Hydrogen fluoride was removed from the exit gases by means of anhydrous sodium fluoride. After passage through a sulfuric acid bubbler the gases were condensed in traps cooled with liquid air. The procedure consisted of adding to the cooled bomb a charge of about 100 g. of phosgene and 200 g. of hydrogen fluoride. The apparatus was then assembled and heating and shaking begun. When the pressure reached the desired value, between 250 and 300 pounds per square inch, the exit gases were bled off at a rate to maintain the pressure constant. The rate of the reaction was usually negligible below 50° but increased rapidly with temperature so that at 70 to 90° a satisfactory rate of production could be maintained.

Phosgene from different sources gave different rates of production. A sample made by the method of Grignard and Urbain[2] and purified

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[1] This paper is based on work done for the Office of Scientific Research and Development under Contract No. NDCrc-167 with Pennsylvania State College.

[2] Grignard and Urbain, *Compt. rend.*, **169**, 17 (1919).

only by bubbling through sulfuric acid gave a satisfactory production of product at 125° with a pressure of 180 pounds per square inch without the use of added catalyst. A sample prepared from carbon monoxide and chlorine, and purified from excess chlorine by amalgamated mossy tin, required a temperature of 145° for an unsatisfactorily slow rate. The addition of 3 cc. of antimony pentachloride increased the rate so that satisfactory production was obtained at 80°.

Distillation of the condensate in the liquid air traps gave a middle fraction of relatively pure carbonyl chlorofluoride, representing about 25% of the initial phosgene. Redistillation of this fraction gave a material with the properties:

Melting point, °C.		−138
Boiling point (760 mm.), °C.		− 42
Vapor pressure to ±5%		$\log P_{\text{mm.}} = 7.93 - (1165/T)$
Molecular weight (by vapor density)		82.5
% Chlorine		43.6
Theoretical for COClF	Molecular weight	82.5
	% Chlorine	43.6

The gas has an odor similar to but distinguishable from that of phosgene. It is readily adsorbed by sodium hydroxide or soda lime. It shows no tendency to react with glass. Yields of approximately 50% COClF were obtained in some of the later preparations.

SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
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RECEIVED APRIL 6, 1946

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Unsaturated Alcohol Esters of the 9,10-Dihydroxystearic Acids. Preparation of Elaidyl Alcohol

BY DANIEL SWERN, E. F. JORDAN, JR., AND H. B. KNIGHT

During a recent investigation it was necessary to identify a series of by-products which appeared to be unsaturated alcohol esters of 9,10-dihydroxystearic acid. A search of the literature revealed that none of these compounds had been described previously. To facilitate their identification, we have prepared the allyl, methallyl, β-chloroallyl, furfuryl, cinnamyl, oleyl and elaidyl esters of both 9,10-dihydroxystearic acids, m. p. 95 and 130°, respectively.

Elaidyl alcohol is not a very well-known compound, since its preparation is extremely tedious. It is usually prepared by reduction of purified methyl or ethyl elaidate with metallic sodium and absolute alcohol, and purified by fractional distillation and crystallization.[2] We have worked out a convenient method for its preparation in fair yield from commercial or highly purified oleyl alcohol. Elaidyl alcohol, m. p. 36–37°, is obtained as glistening plates.

Experimental

Materials.—Low melting 9,10-dihydroxystearic acid (m. p. 95°) and its high-melting isomer (m. p. 130°), and their methyl esters (m. p. 70 and 104°, respectively) were prepared as previously described.[3,4] Purified oleyl alcohol was prepared from the commercial grade by low temperature solvent crystallization and fractional distillation.[5] The allyl, methallyl, β-chloroallyl, cinnamyl and furfuryl alcohols were the purest commercial grades and were fractionally distilled before use.

Two alternative procedures were employed for the preparation of elaidyl alcohol.

1. Commercial oleyl alcohol (oleyl alcohol content, 60 to 70%) was distilled through an 18-inch Vigreux column, and the fraction boiling at 165–205° (4.3 mm.), which amounted to about 85% of the starting material, was retained. Six hundred grams was dissolved in 9000 ml. of acetone, and the solution was cooled to −20° to precipitate solid (saturated) alcohols. The liquid alcohols (470 g.), obtained from the filtrate, were heated and stirred for two hours in a nitrogen atmosphere at 220–225° with 0.3% of powdered selenium.[6] The cooled reaction mixture was dissolved in 4700 ml. of acetone, treated with active carbon and filtered, and the filtrate was cooled to −20°. The precipitate, m. p. about 30°, consisted mainly of elaidyl alcohol and weighed 200 g. Pure elaidyl alcohol, m. p., 36–37° (lit. 35–35.5°),[2] was obtained after one additional crystallization from acetone at −20° and two at 0°. The yield was 56 g. *Anal.* Iodine number: Calcd., 94.5; Found, 93.4.

2. Purified oleyl alcohol[5] (270 g., oleyl alcohol content, 97%) was isomerized as described above. Crystallization from acetone at −20°, after treatment of the solution with active carbon, yielded 164 g. of fairly pure elaidyl alcohol m. p. about 33°; iodine number, about 91. Pure elaidyl alcohol, m. p., 36–37°, was obtained after two additional crystallizations from acetone at 0 to −5°. The yield was 110 g. Iodine number was 93.6.

Esterification Procedures.—The allyl, β-chloroallyl, oleyl and elaidyl esters were prepared by direct esterification of the corresponding alcohol with the dihydroxystearic acids, previously reported methods being employed.[3] In these preparations, with the exception of the allyl esters, the azeotropic method was used. Approximately 2–3 ml. of allyl and β-chloroallyl alcohol per gram of acid were employed, as compared with 20% molar excesses of oleyl and elaidyl alcohols. Yields of crude esters were quantitative.

The methallyl, furfuryl and cinnamyl esters were prepared by alcoholysis of methyl 9,10-dihydroxystearate with the appropriate alcohol. A typical preparation is as follows: To 0.5–1.0 mole of the freshly distilled alcohol, 0.4 g. (0.017 mole) of metallic sodium was added slowly at room temperature. When the sodium was completely dissolved, 0.05 mole of methyl 9,10-dihydroxystearate was added, and the mixture was heated on the steam-bath for three hours in a nitrogen atmosphere, with occasional shaking. The methyl alcohol formed in the reaction was permitted to escape. The reaction mixture was poured into a large quantity of hot water, and the aqueous layer was separated and discarded. The product was washed with hot water and cooled to room temperature. The solid product obtained was crystallized to constant melting point from 95% ethyl alcohol (2 to 5 ml./g.).

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(2) Toyama, *Chem. Umschau Fette, Öle, Wachse Harze*, **31**, 13 (1924).

(3) Swern and Jordan, THIS JOURNAL, **67**, 902 (1945).

(4) Swern, Billen, Findley and Scanlan, *ibid.*, **67**, 1786 (1945).

(5) Swern, Knight and Findley, *Oil & Soap*, **21**, 133 (1944).

(6) Bertram, *Chem. Weekblad*, **33**, 3 (1936).