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	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

---

[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

---

[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).