The unusually high strength of the carbon-to-oxygen bond in trichloromethylpropanol is demonstrated by our isolation of 26% of $Cl_3C{-}C(CH_3)_2O{-}P({=}O)(OH)_2$.[3,4] The unusual volatility of 1,1-1-trichloro-2-methyl-2-bromopropane prevented its isolation in more than 5% conversion from I.

Experimental Part

1,1,1-Trichloro-2-methylpropyl-2-phosphoric Acid (IV).—Preparation of IV is attended by extreme lachrymatory effects. All operations should be carried out in a hood, and with a gas mask and rubber gloves.

Freshly prepared phosphorus pentabromide (295 g., 0.685 mole) and 121.8 g. (0.685 mole) of purified anhydrous 1,1,1-trichloro-2-methyl-2-propanol (I) were mixed in a flask bearing a drying tube, and heated at 100° for 8 hours. The anhydrous reaction mixture and became dark amber in color and was cooled and allowed to stand at 25–30° for two weeks; then it was hydrolyzed slowly at 30–35° (2 to 4 hours) by taking it up with ether and with mechanical stirring, adding dropwise 100 ml. of distilled water. While the hydrolyzed mixture was allowed to stand at room temp., a crystalline mass formed which was collected after six days, and washed repeatedly with 10-ml. portions of carbon tetrachloride until the washes gave no residue on evaporation. The remaining crystals were dried under 20 mm. pressure, wt. 45.8 g. (26%) of IV, m.p. 159–163°, which analyzed for 11.3% phosphorus (calcd. 12.0%). The yield of pure IV, after recrystallization from water, was 30.4 g. (17%), m.p. 181–182.5°. Three recrystallizations of IV from water gave analytically pure IV, m.p. 184.5–185.5°, the m.p. of which did not change upon a fourth recrystallization. IV is slightly soluble in cold water, moderately soluble in boiling water, and insoluble in carbon tetrachloride. It is acid to congo red and liberates carbon dioxide from bicarbonate solutions.

Anal. Calcd. for $C_4H_8Cl_3O_4P$: Cl, 41.3; P, 12.0; neut. equiv., 257.5. Found: Cl, 41.7, 41.1; P, 12.0, 12.1, 12.2, 12.1, 12.2; neut. equiv., 259.5, 256.1, 261.8.

When this substance is cleaved by 60% aqueous potassium hydroxide at 25–40°, carbon monoxide (molybdenum blue test), phosphate ion (ammonium phosphomolybdate test) and acetone are produced. The last was identified after distillation of the diluted reaction mixture as its 2,4-dinitrophenylhydrazone, m.p. 127.5–128°, undepressed by an authentic sample, and by a positive iodoform test (m.p. 118.5–119.5°).

The combined carbon tetrachloride washes were concentrated and the residue was sublimed to give II, m.p. 160–169°, which after recrystallizing from ether was found to be analytically pure, m.p. 169–170° (sealed tube).

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[3] This finding agrees with the observation reported by W. Gerrard and P. L. Wyvill in *Research* **2**, 536 (1949), that phosphorus trichloride does not interact with I under mild conditions in which *t*-butyl alcohol readily affords the chloride, and that much more rigorous treatment affords the chlorophosphites $ROPCl_2$, $(RO)_2PCl$, but still no chloride; also, that an unusually vigorous treatment with phosphorus pentachloride is required to convert I into the corresponding chloride, RCl. Gerrard and Wyvill did convert I into the chloride in apparently about 90% yield only by refluxing I with phosphorus pentachloride for several hours. No product other than the chloride was mentioned.

[4] No method has yet been described, until the present, for converting the hydroxyl of I to a derivative of phosphoric acid.

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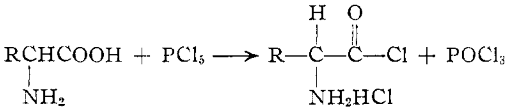
Synthesis of Glycyl and Alanyl Chlorides[1]

BY SUMNER LEVINE

RECEIVED OCTOBER 15, 1953

Fischer[2] has reported a fairly general method for the synthesis of amino acid chlorides. However, this method suffers from the disadvantage of requiring a preliminary recrystallization of the amino acids and in addition, the reaction is conducted in acetyl chloride as the solvent. Because of these disadvantages and the relatively low yield obtained by Fischer's procedure, a modified method was developed. The synthesis was conducted as a heterogeneous reaction in the more convenient solvent carbon tetrachloride, in which the phosphorus pentachloride is dissolved. Since carbon tetrachloride is hydrophobic and less volatile than acetyl chloride, the product is less sensitive to atmospheric moisture during the filtration operation. In addition, the yield obtained by the present method is considerably higher than that of the earlier procedure. The reaction proceeds smoothly according to the equation



$$\underset{\displaystyle NH_2}{RCHCOOH} + PCl_5 \longrightarrow R{-}\overset{\displaystyle H}{\underset{\displaystyle NH_2HCl}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}Cl + POCl_3$$

Because of the salt formation at the amino nitrogen further condensation of the product to polypeptides does not occur under these conditions. In addition, since hydrochloric acid generated during the course of the reaction is bound, very little, if any, pressure build-up was noticed.

Experimental Part

Glycyl Chloride Hydrochloride.—The reaction was conducted in a glass-stoppered vessel. Five grams of glycine was suspended in 200 ml. of purified carbon tetrachloride.[3] Fifteen grams of phosphorus pentachloride was added and the tightly (wired) stoppered vessel shaken vigorously for ten hours at room temperature. The product was filtered on a long necked sintered glass filter. During the filtration, the top of the sintered glass filter was protected with a stopper containing a drierite filled tube. The product was washed three times with carbon tetrachloride and then three times with anhydrous petroleum ether. After a final washing with anhydrous ether, the product was dried on the filter; yield 90 to 95%. The product was recrystallized from redistilled acetyl chloride; yield 75 to 80%.

Anal. Calcd. for $C_2H_5ONCl_2$: C, 18.48; H, 3.88; N, 10.78; Cl, 54.56. Found: C, 18.50; H, 3.85; N, 10.75; Cl, 54.53.

Alanyl Chloride Hydrochloride.—This compound was prepared by the same method given above; yield 92%.

Anal. Calcd. for $C_3H_7NOCl_2$: C, 25.02; H, 4.90; N, 9.73; Cl, 49.24. Found: C, 25.05; H, 4.85, N, 9.75; Cl, 49.28.

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[1] This work was supported by an institutional grant from the Damon Runyon Memorial Fund for Cancer Research.

[2] E. Fischer, *Ber.*, **38**, 2914 (1905).

[3] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Inc., New York, N. Y., 1941.

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Oxymercuration of *trans*-1,2-Diphenyl-1-propene

BY ALAN RODGMAN AND GEORGE F WRIGHT

RECEIVED NOVEMBER 25, 1953

Studies in progress in this Laboratory show that a previous report of a single product from oxymercuration of 1-phenyl-1-propene is erroneous.[1] Since oxymercurations of related compounds such as styrene and 1-phenyl-2-methyl-1-propene give

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[1] G. F Wright, THIS JOURNAL, **57**, 1993 (1935).