was obtained, a yield of about 90% based on the amount of formaldehyde and hydrochloric acid used. The crude THPC melted at about 145°. The pure compound, which melts at 151°, can be obtained by recrystallizing from acetic acid.[3]

At about 25°, the absorption of phosphine and its reaction with formaldehyde and hydrochloric acid are rapid until about 85 to 90% of these materials are converted to THPC. In order to avoid the escape of unused phosphine, which is likely to occur near the end of the reaction, the reaction should be discontinued when an amount of THPC has been made that is equivalent to about 85 to 90% of the formaldehyde originally present in the solution. This end-point can be determined conveniently by removing a small sample of the solution, evaporating the volatile components and weighing the crystalline THPC. The maximum temperature at which the evaporation can be carried out and still obtain crystals is not known, but when the solution is evaporated on a hot-plate at relatively high temperatures, a viscous sirup is obtained which is difficult, if not impossible, to crystallize. The sirup is probably a mixture of THPC and tris-(hydroxymethyl)-phosphine oxide since it is known that phosphonium compounds are converted to phosphine oxides by heat.

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[4] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

Some Halophenoxyacetic Anhydrides

BY GEORGE SVARNAS AND WILLIAM L. HOWARD

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Interest in the herbicidal properties of 2,4-dichlorophenoxyacetic acid and related compounds[1] suggested that the preparation of the anhydrides of some phenoxyacetic acids might prove useful. Accordingly, three representative anhydrides have been prepared: 2,4-dichlorophenoxyacetic anhydride, 4-fluorophenoxyacetic anhydride and 2,4-difluorophenoxyacetic anhydride. Thompson, *et al.*,[2] have reported 2,4-dichlorophenoxyacetic anhydride, but, since no details are given, its preparation is presented herewith. 4-Fluorophenoxyacetyl chloride and 2,4-difluorophenoxyacetyl chloride, prepared as intermediates, and the corresponding amides have not been reported previously.

TABLE I

Compound	M.p. or b.p. (mm.), °C.	Carbon, %		Nitrogen, %		Hydrogen, %		Yield, %
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
4-$FC_6H_4OCH_2COCl$	106–107 (9)	50.94	50.80	....	....	3.21	3.06	73.3
2,4-$F_2C_6H_3OCH_2COCl$	96 (7)	46.51	46.51	....	....	2.44	2.57	69.0
4-$FC_6H_4OCH_2CONH_2$	109.5–110.5	...	...	8.29	8.35	..	..	75.5
2,4-$F_2C_6H_3OCH_2CONH_2$	123.5–125	...	...	7.49	7.55	..	..	83.0
(4-$FC_6H_4OCH_2CO)_2O$	54.5–56	59.63	59.86	161^a	159^a	3.75	3.93	47.5
(2,4-$F_2C_6H_3OCH_2CO)_2O$	73.5–74.5	53.66	53.69	179^a	177^a	2.81	2.97	75.0
(2,4-$Cl_2C_6H_3OCH_2CO)_2O$	76.5–77.5	45.32	45.52	212^a	212^a	2.38	2.31	42.5

[a] Saponification equivalent.

Qualitative observations during the preparation of these compounds indicated that the acid chlorides and anhydrides are intermediate in reactivity between the corresponding derivatives of the typical aromatic and aliphatic acids. Because of their sensitivity to hydrolysis, moisture was carefully excluded throughout the preparations.

It is of interest to note that phenoxyacetic acid melts at a considerably higher temperature than its anhydride. The anhydrides reported here exhibit the same relationship.

All pertinent data concerning the compounds prepared are listed in Table I. The melting points were determined on a Fisher–Johns melting point apparatus and are uncorrected.

Experimental

Preparation of the Acid Chlorides.—The acid[3] is refluxed with about two equivalents of thionyl chloride for 2–3 hours. After the excess thionyl chloride has been removed at the aspirator the residual liquid is vacuum distilled.

Preparation of the Amides.—A benzene solution of the acid chloride is added portionwise with stirring to a flask containing benzene into which dry ammonia is being passed, an excess of ammonia being maintained during the entire addition. After being allowed to stand overnight the mixture is filtered and the solid is washed thoroughly with water. Concentration of the benzene filtrate yields more product, after which the crops are combined and recrystallized from benzene or acetone–benzene.

Preparation of the Anhydrides.—The silver salt of the phenoxyacetic acid is prepared by converting the acid to the sodium salt with the equivalent amount of aqueous sodium hydroxide, after which the equivalent amount of aqueous silver nitrate is added to the hot solution with vigorous stirring. The precipitated silver salt is filtered off without delay, washed successively with water, ethanol, and ether, and then dried *in vacuo*.

Slightly more than one mole of the freshly prepared, finely divided silver salt is refluxed with a mole of the acid chloride in ligroin (d. 0.72–0.74) for one to three days. The hot supernatant liquid then is decanted into a flask, the flask is stoppered, and the solution is allowed to cool to room temperature during which time an oil separates and eventually solidifies. The solid product is then recrystallized from benzene–ligroin.

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[1] M. E. Synerholm and P. W. Zimmerman, *Contrib. Boyce Thompson Inst.*, **14**, 91 (1945); R.L. Weintraub, *J. Agr. Food Chem.*, **1**, 250 (1953).

[2] H. E. Thompson, C. P. Swanson and A. G. Norman, *Botan. Gaz.*, **107**, 476 (1946).

[3] The fluorophenoxyacetic acids were prepared from the corresponding phenols obtained from the Illinois State Geological Survey. The 2,4-dichlorophenoxyacetic acid was obtained from the Eastman Kodak Co.

Rates of Aminolysis

BY C. GARDNER SWAIN AND DONALD C. DITTMER[1]

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Table I records first-order rate constants for the solvolysis of seven compounds in various amine solutions. The results are striking from the point of view of the Brönsted catalysis law for bases. The ratio of rate constants for *n*-butylamine and aniline

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[1] National Science Foundation Fellow, 1952–1953. For further experimental data see D. C. Dittmer, Ph.D. thesis, M.I.T., September, 1953.