tates the following: a Prins type reaction, a dehydrohalogenation, a fluorination with antimony trifluoride and finally the oxidation with potassium permanganate. It has been found that esters of difluoroacetic acid, from which other derivatives may be readily prepared, can be obtained in good yields by a simple two-step process using a commercially available fluorine compound as the starting material.

This method consists of the preparation of 1-ethoxy-1,1,2,2-tetrafluoroethane by the reaction of sodium ethoxide on 1-chloro-1,1,2,2-tetrafluoroethane (Freon 124A) followed by the hydrolysis of the ether to ethyl difluoroacetate with concentrated sulfuric acid. The tetrafluoroether has also been prepared in a yield of 90% by the addition of ethanol to tetrafluoroethylene.[5]

The ether hydrolysis gives slightly lower yields than with other α-difluoro ethers,[6] but the over-all yield of ester is in the neighborhood of 40%. Since the total time involved is only about six hours, the method offers a very convenient preparation of difluoroacetate esters.

Experimental

1-Ethoxy-1,1,2,2-tetrafluoroethane.—Fifty-six g. (1 mole) of technical potassium hydroxide was dissolved in 150 ml. of 95% ethanol, the solution added to a pressure vessel and cooled thoroughly in a Dry Ice–acetone-bath. A conventional type, high pressure rocking autoclave was used in these experiments since it was available. The pressure in the bomb was so low that it failed to register on a 5000 lb. gage and, therefore, it is probable that simpler and lighter equipment could be used for this reaction. Sixty-eight g. (0.5 mole) of CHF_2CF_2Cl was added, the vessel sealed and heated with shaking for three hours at 120°. The loss of liquefied Freon (b. p −12°) at Dry Ice temperatures was negligible. After washing, the crude product may be used directly for the hydrolysis. Distillation gave 66–70% of $CHF_2CF_2OC_2H_5$, boiling at 57–58°, with no appreciable forerun or residue.

Ethyl Difluoroacetate.—Hydrolysis of the tetrafluoroether at 10° as previously described[6] for α-difluoroethers gives 40–50% yields of ester but is difficult to control. The following method is preferable. To a suitable flask equipped with thermometer, stirrer, and reflux condenser were added 29 g. (0.2 mole) $CHF_2CF_2OC_2H_5$, 10 g. of 96% sulfuric acid, and 5–10 g. powdered glass or quartz. If enough siliceous material is present, damage to glassware is almost entirely prevented. Unpleasant fumes can be avoided by absorbing the evolved gases in water if the bubbles emerge through a layer of mercury to prevent clogging in the delivery tube with silica. The reaction began immediately and the mixture was refluxed with stirring until the liquid temperature climbed at least 20° above the original 55–57°; about three hours were required for this operation. The mixture was then poured onto ice and the layers separated. After washing and drying, the product was distilled to give 4–5 g. of unreacted ether and 15 g. of ethyl difluoroacetate, b. p. 99–100°, corresponding to a yield of 60%. The yields can probably be increased when the reaction is carried out on a larger scale.

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[5] Rigby and Schroeder (to du Pont) U. S. Patent 2,409,315 1946).

[6] Young and Tarrant, This Journal, 71, 2432 (1949).

NEW COMPOUNDS

Degradation Products of the Lactone of 6-Hydroxymethyl-1,3-benzodioxan-7-carboxylic Acid

6-Hydroxymethyl-1,3-benzodioxan-4-one-7-carboxylic Acid Lactone.—One and one-tenth grams of 6-hydroxymethyl-1,3-benzodioxan-7-carboxylic acid lactone[1] was dissolved in 50 cc. of glacial acetic acid by heating. When the solution was just starting to boil, it was removed from the hot-plate and 3.5 g. of chromium trioxide was added at such a rate as to keep the mixture boiling vigorously. When boiling had ceased, 175 cc. of water was added and the dark green solution was cooled overnight in the refrigerator. Filtration and thorough washing gave 0.45 g. of white needles, which after several crystallizations from benzene melted at 215–216°. The compound gave positive dioxanoyl and phthalide ring tests.[1]

Anal. Calcd. for $C_{10}H_6O_5$: C, 58.26, H, 2.93. Found: C, 58.27, 58.05; H, 3.29, 3.40.

5-Carboxy-6-hydroxyphthalide.—Two-tenths gram of the dioxanonyl phthalide was saponified in 10% sodium hydroxide solution and after acidification and cooling 0.18 g. of a white solid was recovered. Several crystallizations from a minimum amount of methanol gave 0.15 g., m. p. 275–276° with darkening. The compound gives a deep red color with ferric chloride and in aqueous sodium hydroxide exhibits a blue fluorescence.

Anal. Calcd. for $C_9H_6O_5$: C, 55.67; H, 3.12. Found: C, 55.16, 55.34; H, 3.15, 3.24.

5-Carbomethoxy-6-hydroxyphthalide.—The hydroxy acid, 0.42 g. in 100 cc. of methanol, was treated with an ethereal solution of diazomethane,[2] both at 5° in the usual manner. The residue was taken up in methanol and thrown out with water to give 0.26 g., m. p. 166–167°. An additional crystallization by the same procedure elevated the melting point to 170.0–170.4°. Saponification gave the original hydroxy acid.

Anal. Calcd. for $C_{10}H_8O_5$: C, 57.66; H, 3.84. Found: C, 57.61, 57.73; H, 3.95, 4.08.

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[1] Buehler, Harris, Shacklett and Block, This Journal, 68, 574 (1946).

[2] "Organic Syntheses," Vol. XV, John Wiley and Sons, Inc., New York, N. Y., 1935, p. 4, note 7.

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2-Sulfanilylimino-3-butylbenzothiazoline

2-(N-Acetylsulfanilyl)-imino-3-butylbenzothiazoline.—To a solution of 41.2 g. (0.2 mole) of 3-butylbenzothiazolone imide[1] in 150 ml. of pyridine, 46.6 g. (0.2 mole) of acetylsulfanilyl chloride was gradually added. After standing overnight, the mixture was warmed on a steam-bath for twenty minutes. The white crystalline material which had formed was collected on a Buchner funnel, washed with water and recrystallized from alcohol. The yield of dry product was 68 g. (84%); m. p. 179–181°. Recrystallization from Cellosolve did not change the melting point.

Anal. Calcd. for $C_{19}H_{21}N_3O_3S_2$: N, 10.42. Found: N, 10.65.

2-Sulfanilylimino-3-butylbenzothiazoline (I).—A mixture of 50 g. (0.124 mole) of 2-(N-acetylsulfanilyl)-imino-3-butylbenzothiazoline, 135 ml. of concentrated hydrochloric acid, 300 ml. of alcohol and 300 ml. of water was

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[1] Obtained through the courtesy of Sharples Chemicals, Inc.