The dibasic acids have been computed by the method of Speakman,[6] working out the activity coefficient terms as above and employing an analytical rather than graphical method of extrapolating the resulting functions.

These measurements and those of Speakman and Michaelis and Mizutani assign a ΔpK ($= pK' - pK$) from 50 weight per cent. aqueous ethanol to water of about 1.6 units for benzoic acid. Of eight monobasic acids studied by Michaelis and Mizutani and Mizutani,[7] ΔpK's varied from 1.1 to 1.6 with a mean of 1.4. Employing Michaelis and Mizutani's value of $pK' = 5.62$ for benzoic acid in 50 volume per cent. aqueous ethanol, it is possible to compute ΔpK's from this latter solvent to water from Halford's[8] tabulation. Within a group of twenty-one acids ΔpK's range from 0.2 for *p*-nitrophenol to 1.5 for α-naphthoic with a mean of 1.1. Comparison of the strengths of two acids, the one in water, the other in these aqueous ethanol mixtures, appears on the basis of incomplete data experimentally justified only if an uncertainty of the order of one pK unit is accepted. Fundamental difficulties introduced by specific solvent effects in acid strength comparison have been discussed elsewhere by Brönsted,[9] Hall,[10] Halford,[11] Speakman,[5] Wynne-Jones,[12] and others. Comparison is of particular interest, however, in relating the strengths of alcohol soluble higher members of homologous series, not in general sufficiently soluble in water for measurement, to the known strengths in water of lower water-soluble homologs. A convenient device for making such comparison is to arbitrarily adopt an average ΔpK ($= 1.4$) from 50 weight per cent. aqueous ethanol to water and, from this, to compute what may be termed "water equivalent" values of pK for acids whose pK's are determined in the aqueous ethanol solvent, recognizing that these water equivalent values embrace the very considerable solvent effect uncertainties.

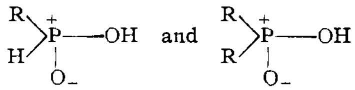
Kumler and Eiler[13] report pK_1 values in water for diesters of orthophosphoric acid increasing from 1.29 for dimethyl to 1.72 for dibutyl; the water equivalent values for di-*n*-decyl and di-*n*-dodecyl esters are 1.9 and 2.0, respectively. The same investigators find pK_1 and pK_2 values for mono esters of orthophosphoric acid increasing from $pK_1 = 1.54$, $pK_2 = 6.31$, for monomethyl to $pK_1 = 1.89$, $pK_2 = 6.84$, for monobutyl; the water equivalent values for the mono-*n*-decyl ester are $pK_1 = 2.2$, $pK_2 = 7.4$.

Rumpf and Chavane[14] present pK values in water for phosphonic acids increasing from $pK_1 = 2.35$, $pK_2 = 7.1$ for methane, to $pK_1 = 2.6$, $pK_2 = 7.9$ for hexane; the water equivalent values for dodecanephosphonic acid are $pK_1 = 2.8$, $pK_2 = 8.4$.

From the measurements here reported the water equivalent values of pK for palmitic and oleic acids are 5.06 and 5.02, respectively. These are to be compared with pK values in water from 4.75 for acetic acid to 4.85 for caprylic acids. From measurements in assorted alcohol–water mixtures Jukes and Schmidt[15] infer that the pK's in water of capric, lauric, myristic, palmitic, stearic and oleic acids are approximately 4.9 to 5.0.

In all three homologous series, fatty acids, partial esters of orthophosphoric acid and phosphonic acids, the higher alkyl members differ in acidic dissociation constants from the lower alkyl members by no more than the errors in comparison inherent from solvent effects. This is in full accord with the principles of inductive transmission through an alkyl chain summarized by Branch and Calvin.[16]

It is convenient to regard dodecanephosphonous acid and di-2-ethylhexylphosphinic acid, respectively, as the mono- and dialkyl analogs of hypophosphorous acid. The formal structures



appear not to offer a ready explanation for the differences in dissociation constants observed.

Acknowledgment.—The writer desires to thank Mrs. Margaret E. Cattrall and Mr. Emil B. Mower for assistance in the measurements.

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[6] Speakman, *ibid.*, 855 (1940).

[7] Mizutani, *Z. physik. Chem.*, **116**, 350 (1925).

[8] Halford, This Journal, **53**, 2948 (1931).

[9] Brönsted, *Chem. Revs.*, **5**, 291 (1928).

[10] Hall, *ibid.*, **8**, 191 (1931).

[11] Halford, This Journal, **53**, 2944 (1931).

[12] Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A140**, 440 (1933).

[13] Kumler and Eiler, This Journal, **65**, 2355 (1943).

[14] Rumpf and Chavane, *Compt. rend.*, **224**, 919 (1947).

[15] Jukes and Schmidt, *J. Biol. Chem.*, **110**, 9 (1935).

[16] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 217.

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A New Method of Preparation of Esters of Difluoroacetic Acid[1]

BY JOHN A. YOUNG AND PAUL TARRANT

Difluoroacetic acid has been prepared recently by the oxidation of 1,2-dichloro-3,3-difluoropropene[2,3] while methyl difluoroacetate has been formed by the reaction of methyl dichloroacetate and potassium fluoride.[4] The latter method, although requiring only one step, gives a yield of about 18% when the reaction is carried out at 220–30° for twenty-five hours. The preparation of the acid by the oxidation of the olefin necessi-

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[1] The material in this paper is abstracted from a portion of a thesis to be submitted by John A. Young to the Graduate Council of the University of Florida in partial fulfilment of the requirements for the Degree of Doctor of Philosophy.

[2] Henne, Alderson and Newman, This Journal, **67**, 919 (1945).

[3] Whaley and Davis, *ibid.*, **70**, 1026 (1948).

[4] Gryszkiewicz-Trochimovsky, Sporzynski and Wnuk, *Rec trav. chim.*, **66**, 427 (1947).

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.

CONTRIBUTION FROM THE
DEPARTMENT OF CHEMISTRY C. A. BUEHLER
UNIVERSITY OF TENNESSEE BURTON P. BLOCK
KNOXVILLE 16, TENNESSEE
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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.