The acetals were purified by treatment of the reaction product with dilute sodium carbonate solution or solid magnesium carbonate, and subsequent fractionation in an efficient column. With few exceptions, they are colorless liquids; their molecular refraction is, within the limits of error, in accord with the theoretical values, as Table II shows. The same conclusion can be drawn from the date observed by Salmi and Kyrki.[4]

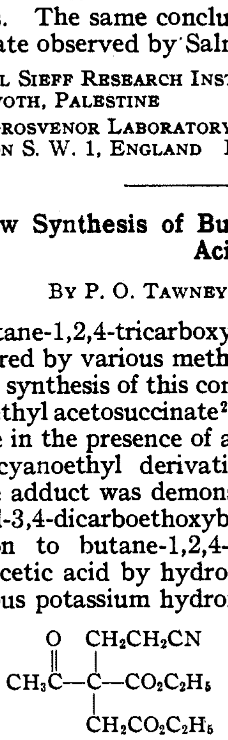
DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE
THE GROSVENOR LABORATORY
LONDON S. W. 1, ENGLAND RECEIVED JANUARY 13, 1948

A New Synthesis of Butane-1,2,4-tricarboxylic Acid

BY P. O. TAWNEY AND E. J. PRILL

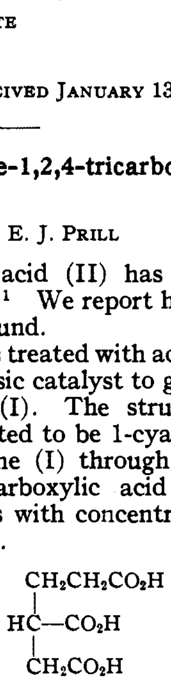
Butane-1,2,4-tricarboxylic acid (II) has been prepared by various methods.[1] We report herein a new synthesis of this compound.

Diethyl acetosuccinate[2] was treated with acrylonitrile in the presence of a basic catalyst to give a monocyanoethyl derivative (I). The structure of the adduct was demonstrated to be 1-cyano-3-acetyl-3,4-dicarboethoxybutane (I) through conversion to butane-1,2,4-tricarboxylic acid (II) and acetic acid by hydrolysis with concentrated, aqueous potassium hydroxide.



$$\begin{array}{c} \mathrm{O}\quad \mathrm{CH_2CH_2CN} \\ \mathrm{CH_3\overset{\|}{C}—\overset{|}{C}—CO_2C_2H_5} \\ \mathrm{\quad\ \ |} \\ \mathrm{\quad CH_2CO_2C_2H_5} \end{array}$$

I



$$\begin{array}{l} \mathrm{CH_2CH_2CO_2H} \\ \mathrm{\ \ |} \\ \mathrm{HC—CO_2H} \\ \mathrm{\ \ |} \\ \mathrm{CH_2CO_2H} \end{array}$$

II

Experimental

1-Cyano-3-acetyl-3,4-dicarboethoxybutane (I).—Potassium hydroxide (1.5 ml. of 50% aqueous solution) was added to a stirred solution of diethyl acetosuccinate[2] (164.8 g., 0.3 mole) and acrylonitrile (18.0 g., 0.34 mole). The temperature of the slightly exothermic reaction was kept at 30–35° by occasional cooling using an ice-bath. After three days at room temperature, the mixture was diluted with 2 vols. of chloroform. The resulting solution was washed successively with saturated sodium bicarbonate solution, dilute sulfuric acid and water. The solvent was removed by distillation at atmospheric pressure and the residue was fractionated at 1 mm.

Fraction I, b. p. 85–120°, 13.0 g. was recovered acetosuccinic ester. Fraction III, b. p. 154–160°, 55.0 g., (87% yield), n^{20}_D 1.4556, d^{20}_{20} 1.1186 was the desired 1-cyano-3-acetyl-3,4-dicarboethoxybutane.

Anal. Calcd. for $C_{13}H_{19}O_5N$: C, 58.0; H, 7.07; N, 5.2. Found: C, 58.15; H, 7.05; N, 5.07.

Butane-1,2,4-tricarboxylic Acid (II).—The ester (I) (68.0 g., 0.25 mole) was added in forty-five minutes with stirring to 120 ml. of 58% potassium hydroxide kept at 75–80°. The mixture was stirred for one hour at 75° and one hour at 100°. At the latter temperature ethanol and ammonia was removed by distillation. The solution was then cooled and acidified using 250 ml. of 35% sulfuric acid. The resulting mixture was subjected to continuous extraction with ether for forty-eight hours. After evaporation of the ether, acetic acid and water were removed from the residue by distillation under reduced pressure. The acetic acid was identified as *p*-phenylphenacyl acetate.[3] The crude product (40.5 g.) was crystallized from ethyl acetate to give 29.5 g. (62%) of white crystals, m. p. 120–121°. The reported[1] melting points for butane-1,2,4-tricarboxylic acid vary from 114° to 123–123.5°.

Anal. Calcd. for $C_7H_{10}O_6$: neut. equiv., 63.3. Found: neut. equiv., 63.5.

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[1] (a) "Beilstein," Vol. II, p. 819; 1st. Supp., p. 322; 2nd. Supp., p. 683; (b) Kiliani, *Ber.*, **62B**, 640–1 (1929); (c) Ruzicka, Borges de Almeida and Brack, *Helv. Chim. Acta*, **17**, 183–200 (1934); (d) Hardegger, *ibid.*, **29**, 1195–1198 (1946).

[2] Adkins, Isbell and Wojcik, "Organic Syntheses," **14**, 38 (1934).

[3] Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 181.

GENERAL LABORATORIES
UNITED STATES RUBBER COMPANY
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The Preparation of Fluoroacetyl Chloride

BY WILLIAM E. TRUCE

The synthesis of fluoroacetyl chloride was undertaken because of its potential value for directly introducing the group, $-COCH_2F$, into organic molecules. Such applications are being studied at this laboratory.

Experimental

Fluoroacetyl Chloride.—(Caution! Fluoroacetic acid, sodium fluoroacetate and fluoroacetyl chloride are potent poisons. The following reactions should be carried out under a hood.) Two hundred twenty grams (2.27 moles) of sodium fluoroacetate (Monsanto Chemical Co., 90% min. purity) and 530 g. (2.49 moles) of phosphorus pentachloride are mixed in a two-liter, round-bottom flask. The flask is immediately connected to a condenser arranged for downward distillation. The receiver is open to the atmosphere through a drying tube. When the initial reaction subsides, the flask is heated on a steam-bath until no further distillate comes over. The weight of distillate is 154 g. (1.60 moles). This material is redistilled through a 120-cm. helix-packed column. The fraction boiling at 70–71° (755 mm.) is collected. The colorless liquid weighs 123 g. and has n^{27}_D 1.3835.

Anal. Calcd. for C_2H_2ClFO: Cl, 36.7; neut. eq., 48.2. Found: Cl, 36.5; neut. eq., 47.9.

After standing for three weeks at room temperature, the compound was redistilled through the 120-cm. helix-packed column. Eighty-three per cent. of the material was recovered as a fraction boiling at 70–71° (755 mm.), signifying that fluorine–chlorine interchange was not great. A forerun, amounting to 6–7%, boiled at 62–70° (755 mm.). Since the column had a large hold-up, the rest of the material was accounted for in this way.

Fluoroacetamide.—This compound was prepared from fluoroacetyl chloride by the procedure used to make trifluoroacetamide.[1] The yield of crude fluoroacetamide is 73%. The product on recrystallization from chloroform melts at 107–108°. Fluoroacetamide has been prepared by other methods and the melting points reported are 104°,[2] 108°[3] and 108°.[4] This material gave no depression in melting point when mixed with an authentic sample of fluoroacetamide.[2]

Anal. Calcd. for C_2H_4FNO: N, 18.18. Found: N, 18.16.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA RECEIVED JANUARY 27, 1948

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[1] Simons and Ramler, THIS JOURNAL, **65**, 389 (1943).

[2] Swarts, *Bull. soc. chim.*, [3] **15**, 1134 (1896).

[3] U. S. Patent 2,403,576 (1946) [*C. A.*, **40**, 6498 (1946)].

[4] U. S. Patent 2,416,607 (1947).