and the solvent removed *in vacuo* at 35°. The dark, sirupy residue was dissolved in ether (150 ml.) and decolorization completed by filtration again through Norit and Celite. Removal of the ether left 6.1 g. (55%) of clear, amber sirup having a high, positive rotation, $[\alpha]^{25}_{\mathrm{D}}$ 130.6° (*c*, 6.530; chloroform). This compound was unstable on standing, but did not decompose as rapidly as the corresponding bromide.

Anal. Calcd. for $C_{18}H_{27}O_9Cl$: Cl, 8.41. Found[14]: Cl, 8.66.

Summary

Crystalline 2,3,4,6-tetrapropionyl-β-D-glucose has been prepared by controlled hydrolysis of tetrapropionyl-α-D-glucosyl bromide. The crystalline nature is striking, since D-glucose pentapropionate and others are sirups.

The mutarotation of 2,3,4,6-tetrapropionyl-β-D-glucose has been studied at two temperatures, the sum of the rate constants for these mutarotations calculated, and these data compared with the corresponding values for 2,3,4,6-tetraacetyl-β-D-glucose.

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RECEIVED APRIL 9, 1947

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[14] Analyzed by the procedure of Vaughn and Nieuwland. *Ind. Eng. Chem., Anal. Ed.*, **3**, 294 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Alkaline Condensation of Fluorinated Esters with Esters and Ketones[1]

BY ALBERT L. HENNE, MELVIN S. NEWMAN, LAURENCE L. QUILL AND ROBERT A. STANIFORTH

A series of alkaline condensations have been performed, linking a fluorinated ester with another ester, a ketone or a fluorinated ketone. At that time (1942–1943) the only known condensation of this kind was the preparation of a trifluoroacetoacetate, $CF_3COCH_2CO_2R$, by Swarts,[1a] who also obtained trifluoroacetone, CF_3COCH_3, from it by decomposition with 10% sulfuric acid; recently a similar work has been reported.[2]

First, Swarts' work was repeated, using an improved technique. Next, ethyl difluoroacetate was successfully condensed with ethyl acetate to yield the difluoroacetoacetate. In contrast it was not found possible to condense a trifluoro- with a difluoroacetate, nor was it found possible to condense a difluoroacetate with itself. With ketones, two condensations were tried, which both succeeded well: a trifluoroacetate and acetone yielded trifluoroacetylacetone, $CF_3COCH_2COCH_3$, while a trifluoroacetate and trifluoroacetone yielded hexafluoroacetylacetone, $CF_3COCH_2COCF_3$.

In all cases, the condensed compounds gave stable chelated derivatives with such ease, that it became advantageous to separate the condensates from the reaction mixtures as their crystalline copper derivatives. These chelated derivatives were easily recrystallized from paraffin hydrocarbons or from alcohol; they proved more stable, lower melting and more volatile than their unfluorinated analogs. A number of metal derivatives were prepared which will be reported separately.[3]

Experimental

Preparation of Fluorinated Esters.—Trifluoroacetic and difluoroacetic acids were obtained by oxidation of a propene derivative.[4] They were esterified either by treatment of their sodium salt with ethyl sulfate, or by heating their salt in an excess of alcohol with a small amount of sulfuric acid, distilling the azeotropic mixture of ester and alcohol as formed, and ultimately washing off the alcohol by means of calcium chloride. It was noted that an appreciable amount of ether was formed when trifluoroacetic acid reacted with ethanol or with butanol but that the amount of ether formed in the case of difluoroacetic acid was small. This is well in line with the known strength of these acids. Properties observed were: $CF_3CO_2C_2H_5$: b. p. 60.5°, n_{D} 1.3093 at 15° and $CHF_2CO_2C_2H_5$: b. p. 99°, n_{D} 1.3463 at 20°. The yield of pure ester was 75 to 80% and additional impure fractions were obtained which accounted for all of the material used.

Condensation and Isolation Procedures.—All condensations were performed in ether, with sodium ethylate freshly prepared by treating one equivalent of absolute ethanol with one equivalent of finely dispersed sodium. To the resulting suspension was added one equivalent of dry fluorinated ester, whereupon solution took place with a slight evolution of heat. The second compound (ester or ketone) was then added, and the mixture refluxed for about fifty hours, a period of time which may be unnecessarily long. On account of the avidity of the condensates for water, the following procedure of isolation was adopted. The reaction mixture was treated with a concentrated solution of sodium bisulfate in very slight excess over neutralization requirements, then with a clear aqueous solution of cupric acetate. The organic layer was distilled off, then the crystalline copper derivative was filtered and recrystallized from a suitable solvent. The dry copper derivative was suspended in dry ether, in which it partly dissolved, and was subjected to a stream of hydrogen sulfide. After removal of the cupric sulfide, the condensed compound was separated from the ether by fractional distillation, with rigorous precautions to avoid losses by volatility.

$CF_3COCH_2CO_2Et$, b. p. 131.8°; over-all yield 54%; copper chelate as green crystals from alcohol, m. p. 189°, Cu % 33.4 found, 33.5 calcd.

CF_3COCH_3, b. p. 21°, 75% yield by refluxing the preceding compound for two hours with 10% sulfuric acid, collecting the vapors on phosphoric anhydride to destroy the hydrate, and distilling therefrom; 2,4-dinitrophenylhydrazone, m. p. 139°, N % 19.06 found, 18.98 calcd.

$CHF_2COCH_2CO_2Et$, b. p. 72° at 30 mm., n_{D} 1.4018 at 20°, 35% over-all yield. F % found 22.3, calcd. 22.9; copper chelate as blue crystalline prisms m. p. 183–184°. Low yield attributed to faulty technique.

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[1] This paper is based on work performed under Contract W-7405-eng-95 for the Manhattan Project and the information therein will appear in Division VII of the Manhattan Project Technical Series, as part of the contribution of the Department of Chemistry, Ohio State University.

[1a] Swarts, *Bull. class sci. Acad. roy. Belg.*, [5] **12**, 692 (1926).

[2] Breslow and co-workers, THIS JOURNAL, **68**, 100 (1946).

[3] Quill and Staniforth, private communication.

[4] Henne, Alderson and Newman, THIS JOURNAL, **67**, 918–919 (1945); Henne, U. S. Patent 2,371,757, March 20, 1945.

$CF_3COCH_2COCH_3$, b. p. 107°, 70% net yield; copper chelate as blue-violet crystals from alcohol, C % 32.52, H % 2.20 found, C % 32.48, H % 2.18 calcd.

$CF_3COCH_2COCF_3$, b. p. 63–65°, 72% net yield, F % 54.0 found, 54.9 calcd.; copper chelate as bright green crystals m. p. 113–115° with sublimation.

Summary

Alkaline condensations of a fluorinated ester with another ester or a ketone were used to synthesize $CF_3COCH_2CO_2Et$, $CHF_2COCH_2CO_2Et$, $CF_3COCH_2COCH_3$ and $CF_3COCH_2COCF_3$ in 70–75% net yields. All form chelated metal derivatives which are very stable and can be distilled.

COLUMBUS, OHIO RECEIVED FEBRUARY 7, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Improved Preparation of Trifluoroacetic Acid

BY ALBERT L. HENNE AND PAUL TROTT

A practical preparation of trifluoroacetic acid based on the sequence $CCl_3CCl{=}CCl_2$ to $CF_3CCl{=}CCl_2$ to CF_3CO_2H has been described in a preceding article.[1] The last step of this sequence consumes an oxidizing agent not only to cut the double bond, but also to burn off the one-carbon fragment. To correct this waste, it would be better to start from a butene derivative $CF_3CCl{=}CClCF_3$, the oxidation of which supplies two moles of trifluoroacetic acid per mole without loss of carbon, as we have shown before.[2] We are now describing a very simple and economical synthesis of this butene. Starting from a cheap commercial product $CCl_2{=}CClCCl{=}CCl_2$, a single fast operation brings about the 1,4-addition of one mole of chlorine to make $CCl_3CCl{=}CClCCl_3$ and the substitution of the six end-atoms of chlorine to make $CF_3CCl{=}CClCF_3$. Our preferred procedure follows.

Commercial antimony trifluoride (1225 g. or 6.76 moles) is placed in a steel vessel equipped with an assembly bearing a needle valve and 300 p. s. i. steel gage. The vessel, maintained at 135° by an electric jacket, is strapped to a mechanical shaker, and flexibly connected to a chlorine tank. Chlorine (480 g. or 6.76 moles) is allowed to be absorbed, with continued shaking. The operation is completed in one and one-half hours and requires no attention, as absorption stops automatically when the formation of SbF_3Cl_2 is completed.

The vessel is disconnected from the tank and cooled to room temperature; the unabsorbed chlorine is vented into a hood through the needle valve; the vessel is opened; more antimony trifluoride (305 g. or 1.7 mole) is added, then the perchlorobutadiene, C_4Cl_6, (1044 g. or 4 moles) is poured in. The vessel is closed, then heated in a steam-bath to 95–100° for half an hour, a time-saving step due to better heat transfer; it is then strapped in the heating jacket of the shaker and rocked at 155° for two hours. At this temperature, the working pressure is about 90 p. s. i.

After cooling, the gage and valve assembly is replaced by a 0.5-inch vertical pipe 45 cm. long which acts as a dephlegmator. This pipe is connected to a descending metal condenser which delivers the distillate into a receiver half filled with water. Loss of volatile material is prevented by a tail trap cooled with Dry Ice. Distillation can be performed by heating directly with a gas burner and is pursued to about 200°, where the distillate is practically all antimony chloride.

The organic material is steam-distilled, to give crude $CF_3CCl{=}CClCF_3$ (886 g. or 96% yield). Fractional distillation with a ten plate column gives 85 mole per cent. of good material boiling 65–66° at 745 mm. and 8.5 mole per cent. of a heptafluorobutene b. p. 32–35° (745 mm.) presumed to be $CF_3CF{=}CClCF_3$.

In a five-liter, three-necked round-bottom flask equipped with a mercury sealed stirrer, a 12-bulb reflux condenser protected by a tail Dry Ice trap, and a dropping funnel are placed potassium permanganate (460 g. or 2.6 moles), commercial potassium hydroxide (315 g. or 5.5 moles) and water (3500 cc.). The solids are dissolved by heating to 60° with constant stirring. Crude $CF_3CCl{=}CClCF_3$ is dropped continuously into the reaction mixture as fast as the capacity of the reflux condenser will permit. After completing the addition of the organic halide, the dropping funnel is replaced by a thermometer dipping in the liquid and the solution is heated until its temperature reaches 95°. The time required is from eight to ten hours.

The solution is cooled to 40°. A stream of sulfur dioxide is bubbled through, with stirring and cooling below 60° until the permanganate color just fades. The solution is acidified with just enough 50% sulfuric acid to neutralize the potassium hydroxide used, and sulfur dioxide is again passed through until the solution clears. Continuous extraction with ether is then applied, or else the solution is extracted three times with a 500-cc. portion of ether tumbled for two hours. Distillation of the ether extract yields 480 g. of the (80/20) azeotropic mixture of CF_3CO_2H and water boiling at 103–105° (745 mm.) This is a 87% yield for the oxidation.

The net over-all yield of trifluoroacetic acid from commercial material is therefore 83%.

Summary

Practical directions for making trifluoroacetic acid from commercial C_4Cl_6 with an 83% over-all yield are described.

COLUMBUS, OHIO RECEIVED MARCH 14, 1947

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[1] Henne, Alderson and Newman, THIS JOURNAL, 67, 918 (1945).

[2] Henne and Zimmerschied, *ibid.*, 67, 1906 (1945).