$CF_3COCH_2COCH_3$, 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.

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[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.

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

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