[Contribution from the Armour Research Foundation of the Illinois Institute of Technology]

The Synthesis of ω-Trifluorostearic Acid and ω-Trifluoro-*n*-octadecyl Amine

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Received April 9, 1956

ω-Trifluorostearic acid was prepared in an eleven-step program based upon the synthesis of ω-trifluorobutyric acid *via* the intermediates 1,1,1,3-tetrachloropropane and 1,1,1-trifluoro-3-chloropropane, followed by chain-lengthening operations employing reactions between organocadmium compounds and acid chlorides. New compounds isolated pure, as intermediates, were ω-trifluoro-*n*-butyl alcohol, ω-trifluoro-*n*-butyl bromide, methyl 8,8,8-trifluoro-4-ketoöctanoate, ω-trifluorooctanoic acid, ω-trifluoro-*n*-octyl alcohol, ω-trifluoro-*n*-octyl bromide, methyl 18,18,18-trifluoro-10-ketoöctadecanoate, and ethyl 18,18,18-trifluoroöctadecanoate. Based on 1,1,1,3-tetrachloropropane the yield of ω-trifluorostearic acid was 1.7%. ω-Trifluoro-*n*-octadecyl amine was prepared by reduction of ω-trifluorostearamide.

INTRODUCTION

The contributions of fluorine substituents to the over-all physical properties of an organic compound are not fixed values as are those of the other halogens but vary widely depending upon the nature of the parent compound, the number of fluorine substituents, and the positions of these substituents relative to each other and to the functional groups. Syntheses of ω-trifluorostearic acid and ω-trifluoro-*n*-octadecyl amine were undertaken to serve an over-all program to study these factors.

The over-all scheme employed to effect these syntheses is shown in the accompanying illustration. The key intermediate is ω-trifluorobutyric acid (III). In this compound the fluorine is oriented properly and the trifluoromethyl group is sufficiently removed from the functional group to prevent interference with chain lengthening operations.

Each reaction was chosen because it was known to yield the desired product unambiguously, free from difficultly separated by-products. To check the validity of the postulated transformations butyric acid was carried through the same series to stearic acid and *n*-octadecyl amine. These reactions were repeated with the corresponding ω-trifluoro- derivatives without the formation of fluoride ion detectable by the Steiger-Merwin Test.[1]

DISCUSSION

ω-Trifluorobutyric acid. Formation of ω-trifluorobutyric acid from 1,1,1-trifluoro-3-chloropropane *via* Grignard reactions was carried out essentially as reported by McBee and Truchan.[2] Attention is directed here to the methods of synthesis used for precursors, I and II.

The formation of 1,1,1,3-tetrachloropropane (I) by polymerization of ethylene in carbon tetrachloride solution under vigorous conditions of chain transfer has been described by Joyce, Hanford, and Harmon.[3] Their conditions were modified only to the extent of reducing the reaction temperature from 90–120° to 70–80°. At the higher temperature, ethylene absorption by the carbon tetrachloride solution was found to virtually cease within a few hours with the formation of just a few grams of polymer. At 70–80° the absorption of ethylene continued for 48 to 72 hours. These data can be correlated with the half-life of the reaction chain initiator, benzoyl peroxide, which is of the order of 0.5 hour at 100° and 15 hours at 70°. The most readily isolatable product is the desired one, 1,1,1,3-tetrachloropropane, the boiling point differential between it and the ethylene dimer, 1,1,1,5-tetrachloropentane, being 53° at 24 mm. To prevent thermal degradation during fractional distillation, the pressure was reduced as necessary to maintain a distilland boiling point below 110°.

The conversion of 1,1,1,3-tetrachloropropane to 1,1,1-trifluoro-3-chloropropane was effected by a fluorinating agent comprising a preheated mixture of antimony trifluoride and antimony pentachloride. The use of antimony trifluoride in conjunction with antimony pentachloride, without preheating, as a fluorinating agent for highly halogenated compounds is standard. However, that method generally fails for partially halogenated compounds because of concurrent degradation and tar formation. Vigorous decomposition of 1,1,1,3-tetrachloropropane was observed at 0° when the unheated salt mixture was used. After the pretreatment, the fluorinating agent and 1,1,1,3-tetrachloropropane are compatible without visible decomposition to at least 50°. Since antimony trifluoride alone will not cause the degradative side reactions noted, and since the chief function of the pretreatment is presumably halogen interchange, antimony pentachloride is indicated to be a more severe reagent than any pentavalent antimony fluorochloride.

Whether or not the fluorinating activity of antimony trifluoride-antimony pentachloride is enhanced by preheating is uncertain. It is quite certain that there is no decrease. In the present case,

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[1] W. W. Scott, *Standard Methods of Chemical Analysis*, D. Van Nostrand Co., Inc., 1939, Vol. I, pp. 410–413.

[2] McBee and Truchan, *J. Am. Chem. Soc.*, **70**, 2911 (1948).

[3] Joyce, Hanford, and Harmon, *J. Am. Chem. Soc.*, **70**, 2529 (1948).

$$CCl_4 + CH_2{=}CH_2 + \text{Peroxide} \longrightarrow CCl_3CH_2CH_2Cl \qquad \text{I}$$

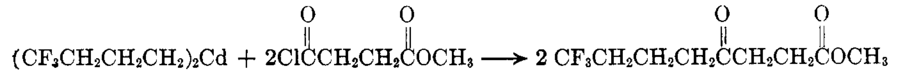
$$CCl_3CH_2CH_2Cl \xrightarrow{SbF_3\ +\ SbCl_5} CF_3CH_2CH_2Cl \qquad \text{II}$$

$$CF_3CH_2CH_2Cl \xrightarrow[(2)\ CO_2]{(1)\ Mg} CF_3CH_2CH_2COOH \qquad \text{III}$$

$$CF_3CH_2CH_2COOH \xrightarrow{LiAlH_4} CF_3CH_2CH_2CH_2OH \qquad \text{IV}$$

$$CF_3CH_2CH_2CH_2OH \xrightarrow{PBr_3} CF_3CH_2CH_2CH_2Br \qquad \text{V}$$

$$2\ CF_3CH_2CH_2CH_2Br \xrightarrow[(2)\ CdCl_2]{(1)\ Mg} (CF_3CH_2CH_2CH_2)_2Cd$$



$$(CF_3CH_2CH_2CH_2)_2Cd + 2Cl\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow 2\ CF_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3 \qquad \text{VI}$$

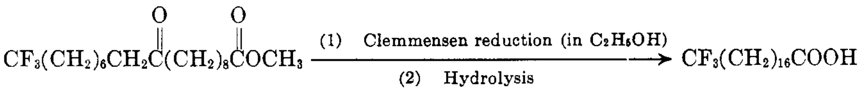
$$CF_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow{\text{Clemmensen reduction (in } H_2O)} CF_3(CH_2)_6COOH \qquad \text{VII}$$

$$CF_3(CH_2)_6COOH \xrightarrow{LiAlH_4} CF_3(CH_2)_6CH_2OH \qquad \text{VIII}$$

$$CF_3(CH_2)_6CH_2OH \xrightarrow{PBr_3} CF_3(CH_2)_6CH_2Br \qquad \text{IX}$$

$$2\ CF_3(CH_2)_6CH_2Br \xrightarrow[(2)\ CdCl_2]{(1)\ Mg} (CF_3(CH_2)_6CH_2)_2Cd$$

$$(CF_3(CH_2)_6CH_2)_2Cd + 2Cl\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OCH_3 \longrightarrow 2\ CF_3(CH_2)_6CH_2\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OCH_3 \qquad \text{X}$$



$$CF_3(CH_2)_6CH_2\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}OCH_3 \xrightarrow[(2)\ \text{Hydrolysis}]{(1)\ \text{Clemmensen reduction (in } C_2H_5OH)} CF_3(CH_2)_{16}COOH \qquad \text{XI}$$

$$CF_3(CH_2)_{16}COOH \xrightarrow[(2)\ NH_3]{(1)\ SOCl_2} CF_3(CH_2)_{16}CONH_2 \qquad \text{XII}$$

$$CF_3(CH_2)_{16}CONH_2 \xrightarrow{LiAlH_4} CF_3(CH_2)_{16}CH_2NH_2 \qquad \text{XIII}$$

replacement of chlorine by fluorine set in readily at 0° and the temperature range 0–45° was sufficient to complete the desired reaction.

ω-Trifluorostearic acid and ω-trifluoro-n-octadecyl amine. The chain-lengthening operations applied to ω-trifluorobutyric acid are based upon the reaction between dialkyl cadmium and ω-carbomethoxyalkanoyl chloride, illustrated in the over-all reaction scheme by the formation of VI and X. The preparation of keto-esters in this way was reported first by Gilman and Nelson[4] and subsequently brought to its present stage of refinement by Cason and his co-workers.

Cason and Prout[5] pointed out that the diester arising from reaction of the ester acid chloride with ether could be largely eliminated by exchange of the ether for benzene after preparation of the dialkyl cadmium. Recently, Cason, Sumrell, and Mitchell[6] further established that occasional erratic results are due to thermal cracking of the dialkyl cadmium reagent during this exchange. Prolonged boiling in ether was not harmful. However appreciable pyrolysis was noted on stripping the ether to dryness on a steam-bath.

In the present work, this information was applied to an improvement in reactor design and reaction procedure that insured against pyrolysis as well as interference due to ether. The reaction flask was provided with a Trubore stirring unit having an aluminum packing gland with Teflon packing. The tolerance of the bearing section was close enough to limit the leak to 5 mm. Hg per minute at a pressure differential of 650 mm. In place of the usual take-off condenser an 18-inch helix-packed Fenske-type fractionating column was used. It was thus possible to effect solvent exchange by fractional distillation under a vacuum. Initially, ether was stripped at atmospheric pressure to a distilland boiling point of 40°. Then the benzene was added and the exchange was completed by fractional distillation at 100 mm., at which pressure the benzene boiling point is 30°. Cason[7] has stated that keto-ester yields based on the alkyl halide ranged from 30 to 64%; whereas in the present synthesis yields ranged from 69 to 77%; 70–75% was obtained regularly. It is suggested that solvent ex-

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[4] Gilman and Nelson, *Rec. trav. chim.*, **55**, 518 (1936).

[5] Cason and Prout, *J. Am. Chem. Soc.*, **66**, 46 (1944).

[6] Cason, Sumrell, and Mitchell, *J. Org. Chem.*, **15**, 850 (1950).

[7] Cason, *Chem. Revs.*, **40**, 15 (1947).

change under a vacuum be applied to the preparation of a cadmium di-*sec*-alkyl from which yields are reputedly low.[8] Low yields due to thermal sensitivity of the cadmium reagent thus may be avoided.

Reduction of the keto-esters, VI and XI, was carried out by the Clemmensen technique[9] rather than by the more generally reliable Huang-Minlon-Wolf-Kishner procedure.[10] It was found that treatment of ω-trifluorobutyric acid under the experimental conditions of the latter reaction, 190° in a ten per cent solution of potassium hydroxide in diethylene glycol, caused equimolecular elimination of hydrogen fluoride. With regard to the hydrolytic stability of the trifluoro methyl group—prolonged refluxing of a solution of ω-trifluorobutyric acid in either 50% aqueous potassium hydroxide (*ca.* 120°) or in concentrated hydrochloric acid (*ca.* 120°) did not produce any detectable fluoride ion. The conditions for Clemmensen reduction are within these limits.

The preparation of the alkyl bromides, V and IX, was carried out by addition of the alcohol to phosphorus tribromide in reverse of the customary procedure.[11] The purpose was to avoid dehydration and/or rearrangement of the alcohol by anhydrous phosphoric acid. By performing the addition at 0° and subsequently raising the temperature about 10° per hour for ten hours, yields of 90% were obtained.

Itemized yields for all conversions, except the first, appear in Table I. No value is given for I, since the reactants are common reagents that may be used in unlimited quantities.

TABLE I

REACTION SUMMARY

Product	Yield, mole-%[a]	Over-all Yield, mole-%[b]
I	—	—
II	75	75
III	68	51
IV	95	48
V	90	43
VI	69	30
VII	72	22
VIII	67	15
IX	89	13
X	73	9.5
XI	17.5	1.7
XII	87	1.5
XIII	31	0.47

[a] Based on preceding product. [b] Based on I.

EXPERIMENTAL

β-Carbomethoxypropionyl chloride was prepared as described in *Organic Syntheses*,[12] yield 300 g., (90%), b.p. 94–95° (20 mm.), reported: 92–93° (18 mm.).

ω-Carbomethoxynonanoyl chloride was prepared by the procedure reported;[13] b.p. 156° (10 mm.), reported b.p. 143° (3.5 mm.). The dimethyl sebacate used as starting material was redistilled to a constant boiling point, 145° (10 mm.) and was crystallized from the melt to ensure use of a single species.

1,1,1,3-Tetrachloropropane (I). A standard Pyrex pressure bottle (capacity 450 ml.) for use in a Parr low-pressure hydrogenation apparatus was wrapped with asbestos paper and wound with a 600-watt Nichrome element. It was charged with 400 g. of a 1% solution of benzoyl peroxide in carbon tetrachloride. A neoprene stopper carrying a thermocouple well and a gas inlet tube was inserted and the bottle was placed in the rocker of the Parr apparatus. The use of neoprene was important since ordinary rubber stoppers swelled badly during the reaction.

The system was flushed with ethylene and then filled to a pressure of 60 p.s.i. The reaction bottle and contents were maintained at 70–80°. The reservoir pressure was readjusted to 60 p.s.i. manually each time it had dropped to 50 p.s.i. The reaction was terminated when the ethylene absorption became slow, ordinarily within 48 to 72 hours. The entire reaction product was washed with aqueous sodium bicarbonate and water, dried over Drierite, and cut by simple distillation into three fractions, the main cut occurring in the boiling range 80° (atmospheric) to 110° (4 mm.). Fractional distillation of all three cuts yielded the principal fraction, b.p. 90–97° (100 mm.); yield, 50 to 100 g. per run. Products from eleven runs were combined and subjected to refractionation through the same column. The 1,1,1,3-tetrachloropropane used in subsequent work had a boiling range of 93.8 to 94.0° (100 mm.).

1,1,1-Trifluoro-3-chloropropane (II). The size of each fluorination was limited to the treatment of 126 g. (0.69 mole) of 1,1,1,3-tetrachloropropane by the capacity of the laboratory stirrers available to handle the necessary antimony salts. It was possible to accelerate the work, however, by carrying out two fluorinations concurrently and working up the reaction products together.

The fluorination vessels consisted of Pyrex three-necked round-bottom flasks, each fitted with a scraping stirrer driven by a laboratory motor geared to 300 r.p.m. Stirrers of the Hershberg[14] design made of No. 14 B & S gage Nichrome wire, and glass paddle stirrers of the type sold by Ace Glass, Incorporated were found to be satisfactory.

Each flask was charged with 375 g. (2.1 moles) of antimony trifluoride and 315 g. (1.05 moles) of antimony pentachloride. The mixtures were heated to 165° and maintained at that temperature for two to three hours. Then the stirring motors were stopped, and the antimony salt mixtures were allowed to cool undisturbed to room temperature and then to 0° by cooling with ice. At that point the antimony salt mixture was a highly viscous supercooled liquid with a melting point of 85° Cooling without stirring was critical, since otherwise a solid cake was obtained which could not be dispersed in ethylene chloride at low temperatures. Dispersion below the melting point was necessary because the antimony salt mixture attacked the solvent vigorously at 85°. Ethylene chloride (300 ml.) was added on top of the molten antimony salt, and stirring was begun. Crystal-

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(8) *Ann. Rep. on Progress Chem.* (*Chem. Soc., London*), **46**, 159 (1949).

(9) Roger Adams, *Org. Reactions*, **1**, 155–209 (1942).

(10) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2847–2848 (1946).

(11) A. H. Blatt, *Org. Syntheses*, Coll. Vol. **2**, 358–359 (1943).

(12) E. C. Horning, *Org. Syntheses*, Coll. Vol. **3**, 169–171 (1955).

(13) Soffer, Straus, Trail, and Sherk, *J. Am. Chem. Soc.*, **69**, 1684 (1947).

(14) L. F. Fieser, *Experiments in Organic Chemistry*, D. C. Heath and Company, New York, 1941, p. 308.

lization began immediately, but a fine crystalline suspension was produced before caking could occur. After cooling to an equilibrium temperature in an ice-bath, the charge of 1,1,1,3-tetrachloropropane (126 g., 0.69 mole) was added dropwise over a period of 3 to 4 hours. The ice-bath was removed, and the reaction mixture was stirred at room temperature for 15 to 20 hours.

The reaction product was cooled with ice and treated with 175 ml. each of 5 *N* hydrochloric acid and 5 *N* sulfuric acid. Hydrochloric acid alone was unsatisfactory because it favored distillation of antimony salts during subsequent steam-distillation. Sulfuric acid alone was unsatisfactory because it caused precipitation of antimony salts during hydrolysis.

The acidified mixtures were combined and steam-distilled. Traces of antimony were eliminated from the product with a final acid wash. After drying, the 1,1,1-trifluoro-3-chloropropane was stripped from the ethylene chloride through a 60-cm. helix-packed fractionating column; yield 137 g., 75%. Before use in the subsequent Grignard reaction, the product was redistilled twice, first through the same fractionating column and then from phosphorus pentoxide. Observed: b.p. 45.1°; n^{25}_{D} 1.3280. Reported[15] b.p. 45.1°; n^{20}_{D} 1.3350.

ω-Trifluorobutyric acid (III). The reaction assembly comprised a 1-liter, three-neck flask provided with a Friedrichs condenser, a dropping-funnel with a pressure-equalizing side tube, and a mercury seal stirrer of the Hershberg type made of B & S gage 16 tantalum wire. All closures were made through standard taper joints lubricated with chlorofluorocarbon grease.[16] The condenser outlet was joined to a Dry Ice trap sealed with nitrogen and a mercury valve.

The Grignard reagent was prepared with 100 g. (0.75 mole) of 1,1,1-trifluoro-3-chloropropane using the usual technique.[17] The reaction flask was immersed in a thermostat at −15° and "bone dry" carbon dioxide was admitted at a rate commensurate with a reaction temperature of −5°. When the Gilman test[18] showed negative the carbon dioxide addition was terminated. Absorption of excess carbon dioxide caused precipitation of a taffy-like mass that fouled the stirrer. The crude product was isolated as recommended[17] after which ethylene dichloride was added and stripped to azeotropically eliminate water.

The residue was distilled through an efficient fractionating column at 100 mm.; yield 72 g.; 68%. Observed for ω-trifluorobutyric acid, b.p. 112° (100 mm.) m.p. 32–33°; reported:[1] b.p. 166.6° (760 mm.), m.p. 33.2°. *p*-Bromophenacyl ω-trifluorobutyrate: m.p. 100–100.5°. *p*-Nitrobenzyl ω-trifluorobutyrate: m.p. 72–73.5°.

ω-Trifluoro-n-butyl alcohol (IV). The reaction assembly consisted of a 3-liter, three-neck, round-bottom flask provided with a dropping-funnel having a pressure-equalizing side tube, a Trubore mercury seal paddle stirrer, and a Friedrich condenser protected from moisture with a nitrogen seal. Before use, the apparatus was flushed thoroughly with nitrogen.

A solution of lithium aluminum hydride was prepared by refluxing a mixture of 33.6 g. (0.88 mole) with 1 liter of ether for four to six hours. Through the dropping-funnel a solution of 56.8 g. (0.4 mole) of ω-trifluorobutyric acid in 450 ml. of ether was added at a rate such as to produce gentle refluxing. Refluxing was continued with external heating for one hour after the addition was completed. Sufficient water, 50–100 ml., was added to decompose the excess hydride followed by 1800 ml. of 10% sulfuric acid to completely dissolve the precipitated inorganic basic salts. The aqueous layer was extracted with six 100-ml. portions of ether which then were added to the main ether fraction. The combined ether solutions were dried for 24–48 hours over potassium carbonate to remove the bulk of the water and over Drierite for a final drying. The ether was stripped through a 36-inch fractionating column to a residue of approximately 100 ml. Three such residues were combined and fractionated through an 18-inch helices-packed column at a pressure of 100 mm. Yield: 145 g., 1.14 moles, 95%; b.p. 75° (100 mm.), 125° (755 mm.). ω-Trifluoro-*n*-butyl 3,5-dinitrobenzoate: m.p. 86.5–87.0°. ω-Trifluoro-*n*-butyl *p*-nitrobenzoate: m.p. 47.5–48.0°.

ω-Trifluoro-n-butyl bromide (V). Phosphorus tribromide (40.6 g., 0.15 mole) was placed in a round-bottom flask provided with a reflux condenser, a calcium chloride drying tube, an addition funnel with pressure equalizing connection, and a stirrer. After the flask and contents had been cooled to 0° in an ice-bath, ω-trifluoro-*n*-butyl alcohol (38.4 g., 0.3 mole) was added dropwise over a one-hour period. The reaction temperature was raised about 10° per hour over a ten-hour period by heating with an oil-bath. When the reaction mixture had cooled, it was poured into 500 ml. of ice-water. The organic layer was washed with three portions of concentrated sulfuric acid followed by water until free of acid. The products of two such runs were combined, dried over Drierite, and distilled through an efficient fractionating column away from phosphorus pentoxide. Yield: 106 g., 90%, b.p. 104° (755 mm.).

Methyl 8,8,8-Trifluoro-4-ketoöctanoate (VI). The reaction was carried out in a 2-liter four-neck (standard taper joints), round-bottom flask equipped with: (a) A Trubore stirring unit with an aluminum packing gland, packed with Teflon packing and lubricated with fluocarbon grease. The impeller was a Hershberg type and made with B&S No. 16 gage tantalum wire. Power was furnished by a Waco power stirrer in which the main shaft speed of 1200 rpm. is geared to 300 rpm. (b) A 500-ml. dropping-funnel with pressure-equalizing side tube. (c) A thermometer well. (d) A 30-cm. helices-packed partial take-off fractionating column sealed to the following train: a Dry Ice trap, a 2-liter ballast reservoir, an open-end manometer, and a manifold to permit maintaining system under slight positive pressure (with a mercury valve) or under controlled reduced pressure (oil vacuum-pump).

After making certain that the system could be operated at a pressure of 100 mm. (absolute) without leakage, 42.9 g. (0.244 mole) of ω-trifluorobutyl bromide was converted to the Grignard reagent in the accepted manner.[17]

The oil-bath used for heating was removed, and the reaction mixture was cooled to 0° by an ice-bath. Then the dropping-funnel was replaced by a 50-ml. Erlenmeyer flask containing 24.7 g. (0.135 mole) of anhydrous cadmium chloride and connected to the reaction flask by means of wide rubber tubing. After the cadmium chloride was added over a 20-minute period, the mixture was agitated at 0° for an additional 20 minutes; then the mixture was heated under reflux until Gilman's test[11] indicated that the Grignard reagent had been converted completely to the organocadmium compound.

The dropping-funnel was replaced, and ether was distilled from the reaction mixture at atmospheric pressure until the rate became slow at an oil-bath temperature of 50°. A 350-ml. portion of benzene was placed in the dropping-funnel. Half of the benzene was added to the reaction mixture and the pressure was reduced to 100 mm. The distillation was continued until an overhead temperature of 30° (100 mm.) indicated little or no ether remained in the reaction mixture. The remainder of the benzene was introduced and, to ensure complete ether removal, an additional 20 ml. was distilled. After cooling the reaction mixture to 20°, 36.3 g. (0.242 mole) of ω-carbomethoxypropionyl chloride dissolved in 50 ml. of benzene was added in essentially

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(15) Henne and Whaley, *J. Am. Chem. Soc.*, **64**, 1157 (1942).

(16) Halocarbon Products Corp., Hackensack, N. J.

(17) H. Gilman and A. H. Blatt, *Org. Syntheses*, **Coll. Vol. 1**, 2nd ed., 361 (1941).

(18) Gilman and Heck, *J. Am. Chem. Soc.*, **52**, 4949 (1930).

one batch. Ice cooling was used to prevent the reaction temperature from rising above 40°. When there was no longer any tendency for the reaction temperature to rise, an oil-bath was used to maintain the reaction mixture at 35–40° for one hour, at 50–60° for one hour and at reflux temperature for 30 minutes. The reaction product was cooled and 200 g. of ice was added, followed by sufficient 20% sulfuric acid to produce two clear liquid phases.

The aqueous phase was separated and extracted with two 50-ml. portions of benzene. The benzene extracts were washed successively with 100-ml. of water and 100-ml. of saturated sodium chloride solution.

After drying with Drierite, the solvent was stripped off and the residue was distilled at 20 mm. through a 30-cm. Vigreux partial take-off fractionating column. The keto-ester had a boiling range of 130–135° (20 mm.), at least 90% distilling at 134–135°; weight, 34.64 g. (yield 68.5%).

ω-Trifluoroöctanoic acid (VII). Clemmensen reduction of methyl 8,8,8-trifluoro-4-ketoöctanoate was carried out in a 2-liter, three neck, round-bottom flask fitted with a Liebig condenser surmounted by a Friedrichs condenser, a Hershberg stirrer with a Trubore bearing, and a 50-ml. dropping-funnel. The condensers were sealed with a Dry-Ice trap, and a gas washing bottle filled with petroleum ether (65–110°).

The flask was charged with 300 g. of amalgamated, reagent grade, mossy zinc, 100 ml. of water, 240 ml. of concentrated hydrochloric acid, and 93.0 g. (0.41 mole) of methyl 8,8,8-trifluoro-4-ketoöctanoate. The mixture was heated with an oil-bath at 120–130°. The reaction was continued for 112 hours, and an additional 50 g. of amalgamated zinc and 50 ml. of concentrated hydrochloric acid were added every 24 hours. The reaction mixture was extracted with four portions of isoöctane, and then the extract was washed with water and dried by azeotropic distillation with ethylene chloride. Fractional distillation of the residue through a Vigreux partial take-off, fractionating column yielded two main fractions: ω-trifluoroöctanoic acid, 31.6 g. (72% converted keto acid), b.p. 129° (10 mm.); and 8,8,8-trifluoro-4-ketoöctanoic acid, 36.0 g., b.p. 136° (2 mm.). ω-Trifluoroöctananilide: m.p. 85–86°. *p*-Bromophenacyl ω-trifluoroöctanoate: m.p. 74.5–75.5°.

ω-Trifluoro-n-octyl alcohol (VIII). Reduction of 16.3 g. (0.082 mole) of ω-trifluoroöctanoic acid with 6.9 g. of lithium aluminum hydride by the method used to prepare ω-trifluoro-*n*-butyl alcohol gave a yield of 12.3 g. (67%) of ω-trifluoroöctyl alcohol, b.p. 130° (10 mm.). ω-Trifluorooctyl N-phenylcarbamate, m.p. 80–81°.

ω-Trifluoro-n-octyl bromide (IX). Bromination of 12.0 g. (0.065 mole) of ω-trifluoro-*n*-octyl alcohol was carried out with 9.3 g. of phosphorus tribromide by the method described for the preparation of ω-trifluoro-*n*-butyl bromide. The crude product was distilled under a vacuum through a 6-inch Vigreux column equipped with a heating jacket. Yield of ω-trifluoro-*n*-octyl bromide: 13.95 g., 89%; b.p. 78–79° (10 mm.).

Methyl 18,18,18-trifluoro-10-ketoöctadecanoate (X). The method used in the preparation of methyl 8,8,8-trifluoro-4-ketoöctanoate from ω-trifluorobutyl bromide was applied for this synthesis. The organocadmium reagent was prepared from 13.8 g. (0.056 mole) of ω-trifluoro-*n*-octyl bromide and treated with 15.4 g. (0.05 mole) of ω-carbomethoxynonanoyl chloride. After working up the product, as previously described, the keto ester was distilled through the Vigreux fractionating column; b.p. 158-159° (0.2 mm.); yield 15.0 g., 73%.

ω-Trifluorostearic acid (XI). Clemmensen reduction of methyl 18,18,18-trifluoro-10-ketoöctadecanoate was carried out in alcoholic solution according to the method of Schneider and Spielman.[19] Dry hydrogen chloride was passed into 260 ml. of absolute alcohol, cooled to 3°, until saturated; 130 g. of amalgamated mossy zinc and 13 g. of methyl 18,18,18-trifluoro-10-ketoöctadecanoate were added. This mixture was refluxed (b.p. 80–90°) for a total of 80 hours, heating being interrupted about every 20 hours to resaturate the reaction mixture with hydrogen chloride and to make a 50-g. addition of amalgamated zinc. The reaction mixture was filtered and diluted with water. The water-insoluble fraction was taken up in ether and combined with an isooctane extract of the aqueous fraction. After drying, the solvents were stripped under a vacuum and the residue was distilled at 0.2 mm., through a 6-inch Vigreux column equipped with a heating jacket. The middle ester cut had a boiling range of 130–137° (0.3 mm.). All the ethyl ω-trifluorostearate in the boiling range of 120–140° (0.2 mm.) was recrystallized from 95% ethyl alcohol: melting point 47.5–48.0°.

Alcoholic sodium hydroxide was prepared by dissolving metallic sodium in absolute alcohol followed by addition of an equimolar amount of water. Ethyl ω-trifluorostearate was saponified in 0.5-g. batches. Each batch was heated under reflux for 2–3 hours with 25 ml. of 10% alcoholic sodium hydroxide. The reaction system was provided with a nitrogen atmosphere and a mercury valve. At the end of the saponification the alcohol was stripped under a vacuum; the residue was taken up in 50 ml. of distilled water and the ω-trifluorostearic acid was precipitated by the slow addition of 12 ml. of concentrated hydrochloric acid. Each batch of the ω-trifluorostearic acid was recrystallized ten times from 95% ethyl alcohol and absolute methyl alcohol including one decolorization with Norit. Five batches were combined and dissolved in 85 ml. of absolute methyl alcohol, treated with Norit once more, and chilled to −40 to −50°. The first crop of crystals was dried in a vacuum desiccator over calcium chloride. These crystals were subjected to two additional recrystallizations from *n*-hexane which previously had been passed through beds of activated alumina and silica gel. Melting point 70.0–70.5°; yield 2.1 g., 17.5%; Equivalent weight: calculated 338, found 339.

ω-Trifluorostearamide (XII). A ten-fold excess of thionyl chloride was added to 1.5 g. (0.0044 mole) of ω-trifluorostearic acid, after which the resulting solution was stirred at room temperature for 20 hours and heated to 35–45° for 7 hours. The thionyl chloride was stripped to a distilland temperature of 110°. The remainder of the thionyl chloride was separated by co-distillation with three 50-ml. portions of benzene. The residue was dissolved in 50 ml. of chloroform, treated with 75 ml. of chloroform saturated with dry ammonia, and filtered. After washing the precipitate with water, the filtrate was shaken with aqueous ammonia. The chloroform solution was dried and evaporated to a residue. The residue and precipitate were combined and recrystallized from 95% alcohol. The yield of ω-trifluorostearamide was 1.31 g., 87%; m.p. 103.5–104°.

ω-Trifluoro-n-octadecyl amine (XIII). ω-Trifluorostearamide was reduced to ω-trifluoro-*n*-octadecyl amine by the technique applied by Nystrom and Brown[20] to compounds of low ether solubility. An ether solution containing a ten-fold excess of lithium aluminum hydride was prepared. An extraction thimble containing 1.2 g. (0.0036 mole) of ω-trifluorostearamide was placed in a wide-bore tube between the reaction flask and condenser. Refluxing was initiated and continued until all of the amide had been dissolved (20–30 hours). The excess lithium aluminum hydride was decomposed with ethyl acetate; some water was added to ensure complete decomposition; then sufficient 20% aqueous

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[19] Schneider and Spielman, *J. Biol. Chem.*, **142**, 345 (1942).

[20] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197-1204 (1947).

sodium potassium tartrate to complex the aluminum was added. The ether layer was separated, washed with water, dried over sodium hydroxide and evaporated to crude amine. A chloroform solution of the amine was treated with excess dry hydrogen chloride and evaporated to dryness. The ω-trifluoro-*n*-octadecyl ammonium chloride thus obtained was recrystallized from mixtures of alcohol and acetone six times: yield 0.4 g., 31%.

Acknowledgment. The authors express thanks to Dr. W. A. Zisman of the Naval Research Laboratories, Washington 25, D.C., at whose suggestion this problem was undertaken, and to the Office of Naval Research for financial support of this work.

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