disulfide. The mixture was heated under reflux for 15 minutes and poured onto a mixture of ice and hydrochloric acid. Extraction with benzene and removal of the benzene gave the crude ketone which after recrystallization from 95% ethanol amounted to 16 g. (67%), m.p. 90–90.5°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.1; H, 7.0.

The **2,4-dinitrophenylhydrazone** melted at 197–198° (a mixture with 2,4-dinitrophenylhydrazine showed a depression).

Anal. Calcd. for $C_{22}H_{20}N_4O_5$: C, 62.9; H, 4.8; N, 13.3. Found: C, 63.6, 63.2, 63.0; H, 4.7, 5.0, 5.3; N, 11.8, 13.2, 13.0.

***p*-Methoxybenzyl *p*-Tolyl Ketone.**—To a Grignard solution prepared from 3.0 g. (0.12 mole) of *p*-bromotoluene in 200 ml. of dry ether was added 11.0 g. (0.060 mole) of anhydrous cadmium chloride in small portions. After 1 hour of stirring at room temperature a part of the ether was distilled and replaced by benzene after which 15.4 g. (0.084 mole) of *p*-methoxyphenylacetyl chloride was added at a rate just fast enough to maintain gentle reflux. The solution was heated for 15 minutes after the addition was complete, then poured onto ice and hydrochloric acid. Removal of the solvent from the organic layer gave 12.3 g. (62%) of crude ketone which after three recrystallizations from methanol and one from hexane–benzene melted at 99.5–100°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.7. Found: C, 80.8, 80.1, 79.9; H, 7.0, 7.6, 6.5.

The **2,4-dinitrophenylhydrazone** melted at 224.5–225°.

Anal. Calcd. for $C_{22}H_{20}O_5N_4$: C, 62.9; H, 4.8; N, 13.3. Found: C, 63.2; H, 4.9; N, 13.3.

Benzyl *p*-chlorophenyl ketone was prepared in 78% yield from phenylacetyl chloride and chlorobenzene and, after recrystallization from 95% ethanol and benzene–hexane, melted at 104.5–105°. Additional recrystallizations did not raise the m.p. (reported[22] 107.5°).

***p*-Chlorobenzyl phenyl ketone** was prepared in 89% yield from *p*-chlorophenylacetyl chloride and benzene. The m.p. was 136.5–137.5° (reported[22] 138°).

Rearrangement of the Amino Alcohols I, II, III and IV with Nitrous Acid.—The rearrangements were carried out by treating 500 mg. of the amino alcohol in 35 ml. of 50% acetic at 0–2° with a threefold excess of aqueous sodium nitrite (0.4 g. in 5 cc. of water). After the addition of sodium nitrite was completed, stirring was continued at 1–2° for 24 hours. Excess nitrous acid was then destroyed by addition of 10% sulfamic acid until the mixture did not darken starch–iodide paper. The solution was then diluted with 75 ml. of water and the neutral fraction extracted with pentane. The pentane layer was dried over anhydrous sodium carbonate and evaporated to dryness. In each case a white solid was obtained which amounted to 97–100% of the theoretical weight of ketones. This solid was accurately weighed, dissolved in ethanol and the solution diluted to 100.0 ml. A 5.00-ml. portion of the solution was further diluted until the final concentration (accurately known) was about 20 mg./l. This solution was used for the ultraviolet spectra as described below.

The ethanol was removed from the remaining ethanol solution and the infrared spectrum of the mixture was determined in carbon tetrachloride as described below. Duplicate runs of each rearrangement were carried out.

Ultraviolet Spectral Analyses of the Ketone Mixtures.—The data were obtained using a Beckman DU spectrophotometer. The spectra of the eight *p*-substituted benzyl phenyl ketones described above were determined in 95% ethanol at concentrations of 30 and 15 mg./ml. and Beer's law appears to hold at the concentrations used.

The method of analysis is illustrated by a description of its application to a mixture of *p*-methoxybenzyl phenyl ketone and *p*-anisyl benzyl ketone obtained in the rearrangement of the amino ketone I. Extinction coefficients of the two pure ketones and of the unknown mixture were obtained at each of four wave lengths (229, 237, 243 and 278 mμ). Five of the six possible pairs of simultaneous equations expressing the extinction coefficients of the mixtures of products as functions of the concentrations and independently determined extinction coefficients of the product ketones were solved for the ketone concentrations, and the percentage composition of the ketone mixture calculated. The maximum error was determined and used to weight the values of the percentage composition in computing the average value.[23] These weighted averages together with their probable errors are reported in Table I.

The infrared spectra were obtained with a model 21 Perkin–Elmer double beam recording spectrophotometer. In general, 5% solutions in carbon tetrachloride were employed. However, because of the low solubilities, the *p*-chlorobenzyl phenyl ketone and benzyl 4-chlorophenyl ketone solutions were 2.5% in carbon tetrachloride.

The curves used to check the analysis of the mixture obtained by the rearrangement of the *p*-methyl amino alcohol II, the ketone mixture of which showed the largest probable errors on ultraviolet analysis, are recorded in Fig. 1.

Urbana, Illinois

---

[22] S. S. Jenkins and E. M. Richardson, This Journal, **55**, 1618 (1933).

[23] N. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 487 ff.

[Contribution from the Department of Chemistry, Purdue University]

The Ionization Constants of Some New Fluorine-containing Acids[1a]

By E. T. McBee, O. R. Pierce and D. D. Smith[1b]

Received January 18, 1954

The acids $CF_3CH{=}CHCO_2H$ and $C_3F_7CH{=}CHCO_2H$ are stronger than $CF_3CH_2CH_2CO_2H$ and $C_3F_7CH_2CH_2CO_2H$; and considerably stronger than their non-fluorinated analogs, but they are much weaker acids than CF_3CO_2H or $C_3F_7CO_2H$. Thus it is shown that the inductive effect of fluorine in the CF_3– and C_3F_7– groups is transmitted only partially through a vinyl group.

Compounds having the general formula $CF_3(CH_2)_nCO_2H$ show a marked decrease in acid strength as "*n*" increases from zero to two,[2] but the effect of a vinyl group or C_3F_7– group (except for $C_3F_7CO_2H$[2]) had not been studied prior to the start of this work. Therefore it was of interest to synthesize acids of this type and compare their acidity with that of their saturated analogs as well as their non-fluorine-containing analogs.

The acids selected for study were $C_3F_7CH_2CH_2CO_2H$, $C_3F_7CH{=}CHCO_2H$, $CF_3CH{=}CHCO_2H$ and, as a check on the method, $CF_3CH_2CH_2CO_2H$ inasmuch as its strength was already known.[2] The ethyl esters of these acids were synthesized starting with trifluoroacetic or heptafluorobutyric acids, reducing them to the perfluorinated aldehydes,[3] subjecting these aldehydes to the Reformatsky

---

[1] (a) Part of a paper presented before the Division of Organic Chemistry, 124th National Meeting of the American Chemical Society, Chicago, Ill., September, 1953. (b) Abstracted from the doctoral dissertation of D. D. Smith, Purdue University.

[2] A. L. Henne and C. J. Fox, This Journal, **73**, 2323 (1951).

[3] D. R. Husted and A. H. Ahlbrecht, *ibid.*, **74**, 5422 (1952).

procedure[4a,b] with zinc and ethyl bromoacetate to yield the ethyl β-hydroxy esters which—while they are much more stable than their non-fluorine-containing analogs—could be dehydrated readily to the unsaturated esters by heating them with phosphorus pentoxide. These last were reduced to the saturated esters with Adams catalyst and hydrogen.

Three of the acids, $CF_3CH_2CH_2CO_2H$, $C_3F_7CH_2CH_2CO_2H$ and $C_3F_7CH{=}CHCO_2H$, were obtained from their esters by saponification with dilute base, but $CF_3CH{=}CHCO_2H$ was obtained by this method only in very poor yield because the β-hydroxy acid also was formed as a product of hydrolysis. Consequently, this acid was prepared by acidolysis of the ester with formic acid as described by Rehberg[5] which resulted in much better yields. (Walborsky and Schwarz,[6] in a paper published subsequent to the completion of this work, also noted that trifluorocrotonic ester was subject to hydration. However, they attributed this to the addition of formic acid to the double bond, followed by alkaline hydrolysis.) The acid strength was measured by determination of the *p*H curve during neutralization and calculation of K from the midpoint of the plot.

The transmittance of an inductive effect in the fluorine-containing unsaturated acids by means of vinylogy is slight as evidenced by a comparison of ionization constants (Table Ib). This, together with the evidence of a normal mode of addition to such an unsaturated system,[6] would indicate that the resonance effect is predominant in the fluorine-containing system. The inductive effect is noticeable, however, probably accounting for hydration of ethyl 4,4,4-trifluorocrotonate during aqueous, alkaline hydrolysis. The ease of nucleophilic attack depends upon the polarized state of the double bond.[7]

TABLE Ia

IONIZATION CONSTANTS ($K_{25°}$) DETERMINED

Acid	$K_{25°} \times 10^5$
$CF_3CH_2CH_2CO_2H$	7.0[a]
$CF_3CH{=}CHCO_2H$	33[b]
$C_3F_7CH_2CH_2CO_2H$	6.6
$C_3F_7CH{=}CHCO_2H$	59

[a] Henne and Fox[2] reported 6.98×10^{-5} for this acid by the method of limiting conductance, and 1.0×10^{-4} by the method used in this paper. [b] In good agreement with those reported previously.[6,10a,b]

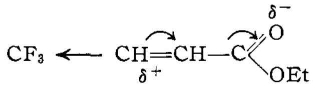
TABLE Ib

COMPARISON OF SOME FLUORINE-CONTAINING ACIDS WITH THEIR NON-FLUORINE-CONTAINING ANALOGS

Acid[a]	$K_{25°} \times 10^5$	Acid	$K_{25°}$
CH_3CO_2H	1.8	CF_3CO_2H	0.588[b]
$CH_3CH_2CH_2CO_2H$	1.5	$C_3F_7CO_2H$	0.678[b]
		$CF_3CH_2CH_2CO_2H$	7.0×10^{-5}
$CH_3CH{=}CHCO_2H$	2.0	$CF_3CH{=}CHCO_2H$	3.3×10^{-4}
$CH_3(CH_2)_4CO_2H$	1.3	$C_3F_7CH_2CH_2CO_2H$	6.6×10^{-5}
$CH_3(CH_2)_2CH{=}CHCO_2H$	2.0	$C_3F_7CH{=}CHCO_2H$	5.9×10^{-4}

[a] Taken from a review article by J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939). [b] Values reported by Henne and Fox.[2]

It seems likely that the competition of the inductive effect acting in one direction *vs.* the resonance effect acting in the opposite direction produces the necessary polarization to allow attack by an OH^- group upon the B-carbon atom, *viz.*



In a non-fluorine-containing crotonate ester, polarization does not occur to such an extent, and nucleophilic attack does not occur during hydrolysis. That it does not occur in the case of ethyl 4,4,5,5,-6,6,6-hexenoate may be attributable to the steric effect offered by the bulky C_3F_7- group.

Acknowledgment.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio, for their financial support of this work.

Experimental[8]

Perfluoroacetaldehyde and Perfluorobutyraldehyde.—These compounds were prepared in a manner similar to that described by Husted and Ahlbrecht.[3] However, yields were increased to as high as 60% by adding the perfluoro acid to cold lithium aluminum hydride solution at such a rate that the ether was not refluxed; also the intermediate aldehydrol was not isolated.

Ethyl 3-Hydroxy-4,4,4-trifluorobutyrate[9] (Reformatsky Procedure[4a,b]).—A 5-liter, 3-necked flask was equipped with a cold finger condenser (60 mm. i.d., 95 mm. o.d., 37 cm. high), cooled by means of a Dry Ice–trichloroethylene mixture, an efficient Hershberg type stirrer and a gas inlet tube. Ether (400 ml., Mallinckrodt anhydrous grade) and benzene (400 ml.) were pipetted into the flask, which was then chilled in an ice–water-bath while perfluoroacetaldehyde (206 g., 2.10 moles) was added by distillation (b.p. −19°). The gas inlet tube was removed, ethyl bromoacetate (345 g., 2.07 moles) and zinc dust (146 g., 2.25 moles) were added, the open neck was stoppered and the contents of the flask were heated by means of a heating mantle. (The mixture refluxed at room temperature, but additional heat was required to initiate the reaction.) When the reaction became spontaneous, usually in 0.5 to 1 hour, the mantle was removed and the reaction was moderated by immersing the flask for short intervals in ice-water. When the reaction ceased to be spontaneous, more zinc dust (*ca.* 20 g.) was added and the mixture was refluxed until the odor of ethyl bromoacetate was no longer apparent. At this point the contents of the flask were chilled and added to a solution made by pouring 100 ml. of concentrated sulfuric acid onto 1 kg. of ice. The acid layer was separated and washed twice with 200-ml. portions of ether and discarded. The ether washings were combined with the organic layer, washed once with 100 ml. of saturated sodium bicarbonate solution, once with water then dried over Drierite.

The ether and benzene were removed by distillation at atmospheric pressure and the product was distilled through a 1 ft. high Vigreux column at reduced pressure. There was obtained 336 g. (1.81 moles, 87%) of ethyl 3-hydroxy-4,4,4-trifluorobutyrate, b.p. 81–83° (15 mm.), m.p. 25.5°, n^{25}_D 1.3720, d^{25}_4 1.259.

Anal. Calcd. for $C_6H_9O_3F_3$: C, 38.71; H, 4.84. Found: C, 38.78; H, 4.82.

Ethyl 3-Hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate.—The procedure followed in this experiment was identical with that described for the preparation of ethyl 3-hydroxy-4,4,4-

---

[4] (a) S. Reformatsky, *Ber.*, **20**, 1210 (1887); (b) R. Adams, ed., "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 1–37.

[5] C. E. Rehberg, *Org. Syntheses*, **29**, 5 (1949).

[6] H. M. Walborsky and M. Schwarz, THIS JOURNAL, **75**, 3241 (1953).

[7] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 235–236.

[8] Analyses by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

[9] H. M. Walborsky and M. Schwarz, *op. cit.*, also reported the synthesis of this compound using a different procedure.

trifluorobutyrate except that it was not necessary to add the aldehyde (b.p. 30–32°) by distillation. From 473 g. (2.39 moles) of perfluorobutyraldehyde, 375 g. (2.25 moles) of ethyl bromoacetate and 163 g. (2.50 moles) of zinc dust there was obtained 602 g. (2.12 moles, 94%) of product, b.p. 90–92° (15 mm.), m.p. 17.3°, $n^{20}\text{D}$ 1.3538, d^{25}_4 1.431.

Anal. Calcd. for $C_8H_9O_3F_7$: C, 33.57; H, 3.15. Found: C, 33.59; H, 3.24.

Ethyl 4,4,4-Trifluorocrotonate.—Ethyl 3-hydroxy-4,4,4-trifluorobutyrate (150 g., 0.81 mole) was placed in a 500-ml. round-bottomed flask and phosphorus pentoxide (55 g., 0.39 mole) was added in one portion. The flask was stoppered and shaken intermittently for a one-hour period during which time a sirupy, transparent, brown-colored liquid was formed and heat was evolved. The mixture was allowed to cool, the flask was arranged for distillation and the volatile contents distilled (b.p. 112–118°). The crude distillate was rectified yielding 109 g. (0.65 mole, 80%) of product, b.p. 112.5°, $n^{20}\text{D}$ 1.3600, d^{25}_4 1.125.

Anal. Calcd. for $C_6H_7O_2F_3$: C, 42.86; H, 4.17. Found: C, 42.74; H, 4.08.

Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate.—The procedure employed was exactly that described for the crotonate ester; but the mixture of reactants formed a "gel" rather than a sirupy liquid. From 150 g. (0.53 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate and 43 g. (0.30 mole) of phosphorus pentoxide there was obtained 114 g. (0.42 mole, 80%) of product, b.p. 139.5–140.0°, $n^{20}\text{D}$ 1.3444, d^{25}_4 1.352.

Anal. Calcd. for $C_8H_7O_2F_7$: C, 35.82; H, 2.61. Found: C, 35.86; H, 2.61.

3-Hydroxy-4,4,4-trifluorobutyric Acid.—Ethyl 3-hydroxy-4,4,4-trifluorobutyrate (30 g., 0.16 mole) was added to 100 ml. of 10% aqueous sodium hydroxide solution contained in a 200-ml. round-bottomed flask and the mixture was refluxed for one hour, then washed with two 50-ml. portions of ether to remove ethanol and traces of unreacted ester. The aqueous layer was acidified with sulfuric acid, extracted with two 100-ml. portions of ether and discarded. The combined ether washings were distilled to remove the ether, dried by azeotropic distillation with benzene, and the residue, which solidified on cooling, was recrystallized from benzene. There was obtained 18 g. (0.11 mole, 70%) of the hydroxy acid, m.p. 78.0–79.0°, b.p. 98.0° (3 mm.); neut. equiv.: calcd. 158, found 158.

Anal. Calcd. for $C_4H_5O_3F_3$: C, 30.38; H, 3.16. Found: C, 30.43; H, 3.26.

3-Hydroxy-4,4,5,5,6,6,6-heptafluorohexanoic Acid.—By the procedure described above, 28.6 g. (0.10 mole) of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate yielded 23 g. (0.09 mole 90%) of acid, m.p. 75.0–76.0°; neut. equiv. calcd. 258, found 254.

Anal. Calcd. for $C_6H_5O_3F_7$: C, 27.91; H, 1.94. Found: C, 27.83; H, 2.06.

4,4,4-Trifluorocrotonic Acid.[9,10a,b] A. **By Acidolysis of the Ester with Formic Acid.**[5]—A 100-ml., 3-necked flask was fitted with a glass helices-packed column 1 ft. in height having a variable take-off head and a thermometer well. The third neck was used to charge the flask and was stoppered during the reaction. Ethyl 4,4,4-trifluorocrotonate (56.0 g. 0.33 mole), formic acid (46 g. of 98–100% acid, 1.0 mole) and 1 ml. of concentrated sulfuric acid were mixed in the flask which was heated by means of a heating mantle. After about 1 hour, the system had reached equilibrium and the temperature at the top of the column was 55°. (Ethyl formate boils at 54°, but this temperature was never achieved, even when using a more efficient column.) A slow take-off was maintained over a 16-hour period (reflux ratio 70:1) such that the fraction removed had a boiling range of 55–56°, except at the end when it was allowed to reach 65° for a short time, at which point the pot temperature was 110°. The contents of the flask were transferred to a 100-ml. flask equipped with a short Vigreux column, the excess formic acid was distilled at a pressure of 20 mm. and the residue was distilled. There was obtained 30 g. (0.21 mole, 65%) of acid, which was recrystallized once from 90–100° ligroin, m.p. 55.0–56.0°, b.p. 68.0–69.0°; neut. equiv.: calcd. 140, found 139.

Anal. Calcd. for $C_4H_3O_2F_3$: C, 34.29; H, 2.14. Found: C, 34.25; H, 2.06.

It is of interest to note that the ester was recovered quantitatively when trifluoroacetic acid was used in place of formic acid.

B. **By Hydrolysis of the Ester with Aqueous Base.**—Ethyl 4,4,4-trifluorocrotonate (40 g., 0.24 mole) was refluxed with 135 ml. of 10% aqueous sodium hydroxide until the mixture became homogeneous, whereupon it was washed twice with ether to remove ethanol and traces of unreacted ester, discarding the washings. The aqueous solution was acidified with sulfuric acid (25 ml. of concd. acid in 50 ml. of ice-water), then extracted twice with 100-ml. portions of ether and discarded. The combined ether washings were dried over Drierite, the ether was removed by distillation and the last traces of water were removed by azeotropic distillation with benzene. Distillation of the residue through a 1-ft. Vigreux column at reduced pressure yielded 14 g. (0.10 mole, 42.2%) of trifluorocrotonic acid, b.p. 68–69° (20 mm.), and 16 g. (0.10 mole, 41.7%) of 3-hydroxy-4,4,4-trifluorobutyric acid, b.p. 96–98° (3 mm.).

4,4,5,5,6,6,6-Heptafluoro-2-hexenoic Acid.—The procedure followed was the same as that described in part B, for the hydrolysis of ethyl trifluorocrotonate, but only one acid was obtained. From 40 g. (0.15 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate there was obtained 31 g. (0.13 mole, 86%) of the acid, m.p. 48.5–49.0°, b.p. 80.0–81.0° (10 mm.); neut. equiv: calcd. 240, found 242.

Anal. Calcd. for $C_6H_3O_2F_7$: C, 30.00; H, 1.25. Found: C, 29.94; H, 1.37.

Ethyl 4,4,4-Trifluorobutyrate and Ethyl 4,4,5,5,6,6,6-Heptafluorohexanoate.—These compounds were prepared by low pressure hydrogenation of an ether solution of the corresponding unsaturated esters, with Adams catalyst. A shaker type hydrogenation apparatus was employed, using an initial hydrogen pressure of 50 p.s.i. The ether was removed by distillation and the product was fractionally distilled.

From 40 g. (0.24 mole) of ethyl 4,4,4-trifluorocrotonate there was obtained 35.1 g. (0.21 mole, 86%) of ethyl 4,4,4-trifluorobutyrate, b.p. 126.5–127.0°, $n^{20}\text{D}$ 1.3520 (revised constant).[11]

From 60 g. (0.22 mole) of ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate there was obtained 54 g. (0.20 mole, 89%) of ethyl 4,4,5,5,6,6,6-heptafluorohexanoate, b.p. 152.0–152.2°, $n^{20}\text{D}$ 1.3360, d^{25}_4 1.342.

Anal. Calcd. for $C_8H_9O_2F_7$: C, 35.55; H, 3.33. Found: C, 35.61; H, 3.41.

4,4,4-Trifluorobutyric Acid and 4,4,5,5,6,6,6-Heptafluorohexanoic Acid.—The ethyl esters were refluxed with dilute base until solution was effected, the basic solutions were washed with ether to remove ethanol then acidified with excess dilute sulfuric acid and extracted with two 100-ml. portions of ether. The combined ether washings were dried over Drierite, the ether was removed by distillation and the acids were distilled under reduced pressure through a short column packed with glass helices.

From 52.0 g. (0.31 mole) of ethyl 4,4,4-trifluorobutyrate there was obtained 33.0 g. (0.23 mole, 76%) of 4,4,4-trifluorobutyric acid, b.p. 83.0–84.5° (25 mm.), m.p. 30–31°; neut. equiv.: calcd. 142, found 143.

From 50 g. (0.19 mole) of ethyl 4,4,5,5,6,6,6-heptafluorohexanoate there was obtained 35.0 g. (0.15 mole, 79%) of 4,4,5,5,6,6,6-heptafluorohexanoic acid, b.p. 102.5–104.0° (25 mm.), m.p. 38.0–39.0°; neut. equiv.: calcd. 242, found 243.

Anal. Calcd. for $C_6H_5O_2F_7$: C, 29.75; H, 2.06. Found: C, 29.69; H, 2.16.

Determination of the Ionization Constants, K_{25°.—Ionization constants were determined for $CF_3CH_2CH_2CO_2H$ (used as a control), $C_3F_7CH_2CH_2CO_2H$, $CF_3CH{=}CHCO_2H$ and $C_3F_7CH{=}CHCO_2H$. They were purified by distillation through a column followed by recrystallization from ligroin. In addition, $CF_3CH_2CH_2CO_2H$ and $CF_3CH{=}CHCO_2H$ were sublimed under a pressure of less than 1 mm. The purified acids had the following melting points: CF_3-

---

[10] (a) While this work was in progress R. N. Haszeldine, *J. Chem. Soc.*, 3495 (1952), reported the synthesis of this compound by another method; (b) see also A. L. Henne and C. J. Fox, This Journal, **76**, 479 (1954).

[11] This compound was prepared previously by E. T. McBee, A. Kelly and E. Rapkin, This Journal, **72**, 5071 (1950), who reported b.p. 127°, $n^{25}\text{D}$ 1.3620.

TABLE II

LIST OF DERIVATIVES

Compound	Derivative	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
$CF_3CHOHCH_2CO_2C_2H_5$	Phenylurethan	70.0–70.5					4.58	4.62
$C_3F_7CHOHCH_2CO_2C_2H_5$	Phenylurethan	77.5–78.0	44.44	44.51	3.46	3.52	3.46	3.58
$CF_3CHOHCH_2CO_2H$	*p*-Bromophenacyl ester	110.0–111.0	40.28	40.28	2.96	2.96		
$C_3F_7CHOHCH_2CO_2H$	*p*-Bromophenacyl ester	127.0–127.5	36.92	36.59	2.20	2.33		
$CF_3CH{=}CHCO_2H$	Anilide	125.0–126.0					6.52	6.42
$C_3F_7CH{=}CHCO_2H$	Anilide	130.0–131.0					4.44	4.44
$C_3F_7CH_2CH_2CO_2H$	Anilide[a]	100.0	45.43	45.34	3.15	3.13	4.42	4.58

[a] Also prepared from the ester.

$CH_2CH_2CO_2H$, m.p. 32.5–33.0°; $CF_3CH{=}CHCO_2H$, m.p. 55.5–56.0°; $C_3F_7CH_2CH_2CO_2H$, m.p. 38.5–39.0°; C_3F_7-$CH{=}CHCO_2H$, m.p. 48.5–49.0°.

The apparatus was a Beckman Model H-2 *p*H meter which was standardized before each titration with standard buffer solutions of *p*H 4.00 and 7.00. Titrations were conducted at 25.00 ± 0.02° in a Sargent constant temperature bath having a mercury thermoregulator.

Two of the acids ($CF_3CH_2CH_2CO_2H$ and $CF_3CH{=}CHCO_2H$) were readily soluble in water and a sample of each was easily prepared for titration by dissolving a small amount in approximately 200 ml. of water. The other two were not as soluble and it was necessary to prepare saturated solutions of each by allowing them to stand for 24 hours in one liter of water (contained in an erlenmeyer flask stoppered and protected with an Ascarite filled drying tube) with occasional swirling, then pipetting samples for titration. The water was prepared by passing distilled water through an ion exchange resin and had a *p*H range of 6.90–7.00.

The acid solution to be titrated was contained in a 400-ml. beaker which was placed in the constant temperature bath at least 20 minutes prior to titration, with a slow stream of nitrogen maintained over its surface to ensure exclusion of CO_2. Titrations were conducted by adding a measured amount of standard base and mechanically stirring until the *p*H remained constant.

The ionization constants were calculated from the midpoints of the curves, at which point $pH = pK$, and at other points on the curves by the use of Henderson's equation as described by Glasstone.[12] The results obtained are presented in Table Ia; and in Table Ib these values and those of perfluoroacetic and perfluorobutyric acids are compared with their non-fluorine containing analogs.

Preparation of Derivatives.—These were prepared in the usual manner.[13,14] Melting points were determined with a Fisher-Johns melting point stage and the values reported are corrected. The derivatives are listed in Table II.

---

[12] S. Glasstone, "Textbook of Physical Chemistry," 2nd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1003.

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

[14] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Preparation and Properties of Some Compounds Containing the 4,4,4-Trifluorocrotyl Group[1]

BY E. T. MCBEE, O. R. PIERCE AND D. D. SMITH[2]

RECEIVED JANUARY 18, 1954

The preparation and reactions of several compounds containing the 4,4,4-trifluorocrotyl group are described, and an unusual reaction of lithium aluminum hydride—the reduction of an α,β-dibromoester to an α,β-unsaturated alcohol at *ca.* −80°—is reported.

In a previous paper[3] it was reported that the hydrolysis of ethyl 4,4,4-trifluorocrotonate with aqueous base resulted in hydration of the double bond. This gave substance to the belief that the 4,4,4-trifluorocrotonyl group was unusually reactive, and prompted further investigation. The present paper describes some new reactions of ethyl 4,4,4-trifluorocrotonate, and the use of both the ester and 4,4,4-trifluorocrotonic acid in the preparation of other compounds containing the 4,4,4-trifluorocrotonyl group.

The preparation of ethyl 4,4,4-trifluorocrotonate and 4,4,4-trifluorocrotonic acid have been reported previously.[4] Ethyl 2,3-dibromo-4,4,4-trifluorobutyrate was synthesized by refluxing a solution of bromine, ethyl 4,4,4-trifluorocrotonate and carbon tetrachloride. The reaction of this dibromoester with excess lithium aluminum hydride at *ca.* −80° produced unexpected results. Instead of obtaining the di- or monobrominated alcohol or the saturated alcohol,[5] 4,4,4-trifluorocrotyl alcohol was obtained in yields of 50%. An alternative synthesis of this alcohol was achieved by the reaction of sodium trimethoxyborohydride with 4,4,4-trifluorocrotonyl chloride. This latter compound was prepared from either 4,4,4-trifluorocrotonic acid or a mixture of this acid and formic acid (obtained as the residue from the acidolysis of ethyl 4,4,4-trifluorocrotonate) and benzoyl chloride, a procedure reported by Brown.[6] An attempt to prepare this same alcohol by the dehydration of 4,4,4-trifluoro-1,3-butanediol

---

[1] Part of a paper presented before the Division of Organic Chemistry, 124th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1953.

[2] Abstracted from the doctoral dissertation of D. D. Smith, Purdue University.

[3] E. T. McBee, O. R. Pierce and D. D. Smith, THIS JOURNAL, **76**, 3722 (1954).

[4] (a) H. M. Walborsky and M. Schwarz, *ibid.*, **75**, 3241 (1953); (b) R. N. Haszeldine, *J. Chem. Soc.*, 3495 (1952), reported the acid, only; (c) A. L. Henne and C. J. Fox, THIS JOURNAL, **76**, 479 (1954).

[5] L. W. Trevoy and W. G. Brown (THIS JOURNAL, **71**, 1675 (1949)) obtained styrene from dibromostyrene and lithium aluminum hydride using a reaction medium of refluxing tetrahydrofuran; but under the same conditions they found that ethyl 2,3-dibromo-3-phenylpropionate was reduced to hydrocinnamyl alcohol.

[6] H. C. Brown, *ibid.*, **60**, 1325 (1938).