190. *Reactions of Fluorocarbon Radicals. Part VIII.* Alternative Syntheses for γγγ-Trifluorocrotonic Acid.*

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Alternative syntheses for γγγ-trifluorocrotonic acid from trichloroiodomethane and 3 : 3 : 3-trifluoropropene or 3 : 3 : 3-trifluoropropyne are described. The acid has $K_{25} = 7 \pm 0{\cdot}5 \times 10^{-4}$.

Trifluorocrotonic acid has been prepared from 3 : 3 : 3-trifluoropropyne by addition of hydrogen cyanide followed by hydrolysis, and from acrylonitrile by reaction with trifluoroiodomethane followed by dehydroiodination and hydrolysis (Haszeldine, *J.*, 1952, 3490). Alternative syntheses are now reported.

Addition of trichloroiodomethane to 3 : 3 : 3-trifluoropropene yields 1 : 1 : 1-trichloro-4 : 4 : 4-trifluoro-3-iodobutane which, when treated with a base and then with concentrated acid, yields γγγ-trifluorocrotonic acid:

$$CF_3\cdot CH{:}CH_2 + CCl_3I \xrightarrow[\text{light}]{\text{Heat or}} CF_3\cdot CHI\cdot CH_2\cdot CCl_3 \xrightarrow{-\text{HI}} CF_3\cdot CH{:}CH\cdot CCl_3 \xrightarrow{H_2SO_4} CF_3\cdot CH{:}CH\cdot CO_2H$$

Dehydroiodination and hydrolysis can also be effected by direct reaction of the trichlorotrifluoroiodobutane with concentrated sulphuric acid.

In a second synthesis, trichloroiodomethane and 3 : 3 : 3-trifluoropropyne yielded 1 : 1 : 1-trichloro-4 : 4 : 4-trifluoro-3-iodobut-2-ene, which gave 1 : 1 : 1-trichloro-4 : 4 : 4-trifluorobut-2-ene on mild treatment with zinc and hydrochloric acid. Acid hydrolysis of the allylic trichloromethyl group yielded γγγ-trifluorocrotonic acid.

The synthesis of the known trifluorocrotonic acid establishes the structure of 1 : 1 : 1-trichloro-4 : 4 : 4-trifluoro-3-iodo-butane and -but-2-ene, and thus proves the direction of addition of trichloroiodomethane to the olefin and alkyne. On the assumption that the trichloromethyl radical initiates the reaction, it follows that its direction of addition is the same as for the trifluoromethyl radical or bromine atom (Haszeldine, *J.*, 1952, 2504; K. Leedham, unpublished data on 3 : 3 : 3-trifluoropropyne).

The ionisation constant of γγγ-trifluorocrotonic acid is $7 \pm 0{\cdot}5 \times 10^{-4}$ at 25°, and is of interest for qualitative comparison with K_{25} for related acids. The influence of the trifluoromethyl group is apparently relayed to an appreciable extent through the vinylic system by induction and resonance of the type postulated earlier (*J.*, 1952, 3490) ($F^- \; CF_2{:}CH\cdot\overset{+}{C}H\cdot CO_2H$), since for crotonic acid $K_{25} = 2{\cdot}0 \times 10^{-5}$ (Dippy, *Chem. Reviews*, 1939, **25**, 151). Henne and Fox (*J. Amer. Chem. Soc.*, 1951, **73**, 2323) measured K_{25} for βββ-trifluoropropionic acid (1×10^{-3}) and γγγ-trifluorobutyric acid (7×10^{-5}) and thus showed that the effect of the trifluoromethyl group is shielded only partly by one methylene group and incompletely even by two such groups, since the ionisation constants are some 70 and 5 times those of propionic and butyric acids, respectively. In γγγ-trifluorocrotonic acid the –CH:CH– group (with *trans*-substituents) thus has about the same shielding effect as a CH_2 group.

Experimental

γγγ-Trifluorocrotonic Acid.—(*a*) Trichloroiodomethane (b. p. 141°, by isoteniscope) (3·1 g.), prepared from bromotrichloromethane and aluminium tri-iodide, was heated to 200° for 24 hours in a sealed tube with 3 : 3 : 3-trifluoropropene (1·2 g.), prepared as already described (*J.*, 1952, 2504). Distillation gave 1 : 1 : 1-*trichloro*-4 : 4 : 4-*trifluoro*-3-*iodobutane* (57%), b. p. 120°/53 mm., *ca.* 210°/760 mm. (micro) (Found: C, 13·9; H, 0·8. $C_4H_3Cl_3F_3I$ requires C, 14·1; H, 0·9%), hexachloroethane (15%), and starting material. To the chlorofluoroiodobutane (4·3 g.) in ethanol (12 ml.), cooled in ice, was slowly added with stirring a 10% excess of 10% ethanolic potassium hydroxide. After dilution with ice-water, the lower layer was removed, sealed with concentrated sulphuric acid (5 ml.), and slowly heated to 80° for

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* Part VII, Haszeldine, *J.*, 1952, 3490.

6 hours. After dilution with water, ether-extraction followed by purification as described earlier (*J.*, 1952, 3490), gave γγγ-trifluorocrotonic acid (51%). Chloride ion is formed during the dehydroiodination step, but the product (presumably CF_3·CHI·CH:CCl_2) does not give interfering acid products during the subsequent hydrolysis.

By an alternative procedure 1 : 1 : 1-trichloro-4 : 4 : 4-trifluoro-3-iodobutane (3·2 g.) [prepared by exposure of trichloroiodomethane (4·0 g.) and 3 : 3 : 3-trifluoropropene (1·4 g.) to ultra-violet light at room temperature for 24 hours, followed by distillation] was heated at 100° with concentrated sulphuric acid (7 ml.) for 15 hours. Dilution with water, followed by ether-extraction, extraction of the acid fraction from the ethereal extract by aqueous sodium hydroxide, re-acidification, and ether-extraction, followed by purification as earlier, gave γγγ-trifluorocrotonic acid (48%). The residual ethereal extracts gave unchanged trichlorotrifluoroiodobutane (17%) on distillation.

(*b*) Trichloroiodomethane (4·5 g.) and 3 : 3 : 3-trifluoropropyne (*J.*, 1951, 2495) were exposed to a " Hanovia " ultra-violet lamp for 36 hours at room temperature to give, after distillation, 1 : 1 : 1-*trichloro*-4 : 4 : 4-*trifluoro-3-iodobut-2-ene* (74%), b. p. 108°/27 mm. (Found: C, 14·2; H, 0·2. $C_4HCl_3F_3I$ requires C, 14·1; H, 0·3%). The butene (2·8 g.) was heated under reflux with dilute hydrochloric acid (15 ml.) and zinc (*ca.* 1 g.) during 3 hours. Extraction with ether, followed by drying (P_2O_5) and distillation of the ethereal extracts, gave 1 : 1 : 1-*trichloro*-4 : 4 : 4-*trifluorobut-2-ene* (63%), b. p. 128—130° (Found: C, 22·6; H, 0·7. $C_4H_2Cl_3F_3$ requires C, 22·5; H, 0·9%). By comparison with *cis*- and *trans*-1 : 1 : 1 : 4 : 4 : 4-hexafluorobutenes, b. p. 33·5° and 8·5°, it would appear that the trichlorotrifluorobutene is the *trans*-isomer. Hydrolysis of the butene with concentrated sulphuric acid as described under (*a*) above gave γγγ-trifluorocrotonic acid (68%).

Ionisation Constant of γγγ-Trifluorocrotonic Acid.—An initial potentiometric titration of γγγ-trifluorocrotonic acid solution against carbonate-free sodium hydroxide solution by use of a Cambridge Instrument Co. pH meter gave $K_{25} = 7·0 \pm 0·2 \times 10^{-4}$, it being assumed that at half-neutralisation point pH = p*K* (see, however, Bennett, Brooks, and Glasstone, *J.*, 1935, 1821). A second value was obtained by conductimetric measurements on γγγ-trifluorocrotonic acid (made up by weight in carbonate-free distilled water) and sodium γγγ-trifluorocrotonate (made by exact neutralisation with carbonate-free sodium hydroxide solution by using the potentiometric titration data obtained earlier). The conductivity apparatus and techniques described earlier (Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544; Emeléus and Haszeldine, *J.*, 1949, 2953) were used to obtain the following results at 25·0° ± 0·1° :

C (g.-equiv./l.)	0·10	0·05	0·025	0·010	0·001
Λ	31·66	43·91	60·61	91·11	217·8

For sodium γγγ-trifluorocrotonate, dilution by weight being used, $\Lambda = 86·1$ ($C = 1 \times 10^{-3}$) and 86·3 ($C = 5 \times 10^{-4}$); a second determination with a fresh solution of the sodium salt ($C = 6·67 \times 10^{-4}$) gave $\Lambda = 86·4$. Application of Onsager's equation gave $\Lambda_0 = 88·6$, 88·1, and 88·6, respectively, whence a value of $\Lambda_0 = 88·5$ was taken. By using ionic conductivities $Na^+ = 50·1$, $H^+ = 349·7$ (McInnes, Shedlovsky, and Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2758), Λ_0 for CF_3·CH:CH·CO_2H is calculated as 388·1. A precise calculation of K_{25} is not merited by the experimental method used. The good agreement between values of K_{25} calculated by using Ostwald's equation at the various concentrations ($7·2 \pm 0·1 \times 10^{-4}$) is purely fortuitous, and, allowing a much larger experimental error, $K_{25} = 7·0 \pm 0·5 \times 10^{-4}$. The degree of ionisation (Λ/Λ_0) at $C = 0·10$ is 0·082, and should be compared with CF_3·CO_2H, 0·88; C_3F_7·CO_2H, 0·88; CF_3·CH_2·CO_2H, 0·093; CF_3·$[CH_2]_2$·CO_2H, 0·026; C_2H_5·CO_2H, 0·012, and C_3H_7·CO_2H, 0·012.

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[*Received, October 23rd,* 1952.]