Reactions of Fluorocarbon Radicals. Part XV. Synthesis and Hydration of* 1 : 1 : 1-*Trifluorobut-2-yne.*

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1 : 1 : 1-Trifluorobut-2-yne has been synthesised from trifluoroiodomethane and propyne *via* 1 : 1 : 1-trifluoro-3-iodobut-2-ene and 2 : 3-dibromo-1 : 1 : 1-trifluorobut-2-ene. Hydration of the butyne catalysed by a mercury salt yields only 4 : 4 : 4-trifluorobutan-2-one, and the significance of this on the mechanism of hydration of acetylenes is discussed.

In Parts VI and VII (*J.*, 1952, 3483, 3490) the reaction of HX (X = F, Cl, Br, I, OMe, OEt, or NR_2) with 3 : 3 : 3-trifluoropropyne under conditions favouring a reaction with ionic intermediates was shown to yield $CF_3{\cdot}CH{:}CHX$, *i.e.*, there was a reversal of the direction of addition with respect to propyne, indicating a polarisation $F_3C \longleftarrow \overset{\delta-}{C}{\vdots}\overset{\delta+}{C}H$. Hydration of trifluoropropyne was thus expected to yield exclusively the aldehyde $CF_3{\cdot}CH_2{\cdot}CHO$, but it was found that a mixture of the aldehyde and the ketone $CF_3{\cdot}CO{\cdot}CH_3$ was produced in the ratio 1 : 2 :

$$CF_3{\cdot}C{\vdots}CH \longrightarrow CF_3{\cdot}CH_2{\cdot}CHO + CF_3{\cdot}CO{\cdot}CH_3$$

Since a mercury-salt catalyst was essential to bring about hydration, it was suggested that two competing reactions were involved in the hydration of an acetylene $R{\cdot}C{\vdots}CH$ (R = electron-withdrawing group such as CF_3, C_2F_5, or COPh) : (*a*) formation of the aldehyde *via* an intermediate complex formed by addition of the mercury salt to the triple bond, and (*b*) formation of the ketone *via* a compound of the type $R{\cdot}C{\vdots}C{\cdot}HgY$ (Y = HSO_4, say, in sulphuric acid solution). Full details are given in Part VI (*loc. cit.*). Since the acetylenic hydrogen atom is essential in scheme (*b*), the catalysed hydration of 1 : 1 : 1-trifluorobut-2-yne should take place in the direction predicted from the inductive effects of the methyl and the trifluoromethyl and yield only 4 : 4 : 4-trifluorobutan-2-one :

$$CF_3{\cdot}C{\vdots}C{\cdot}CH_3 \longrightarrow CF_3{\cdot}CH_2{\cdot}CO{\cdot}CH_3$$

Trifluoroiodomethane reacts with propyne when exposed to ultra-violet light, to give 1 : 1 : 1-trifluoro-3-iodobutene :

$$CF_3{\cdot} + CH_3{\cdot}C{\vdots}CH \longrightarrow CH_3{\cdot}\dot{C}{:}CH{\cdot}CF_3 \xrightarrow{CF_3I} CH_3{\cdot}CI{:}CH{\cdot}CF_3 + CF_3{\cdot}$$

This compound reacts vigorously with bromine at low temperature to give, by addition to the double bond and replacement of iodine, 2 : 2 : 3-tribromo-4 : 4 : 4-trifluorobutane. Dehydrobromination of the tribromo-compound is predominantly in one direction to give 2 : 3-dibromo-1 : 1 : 1-trifluorobutene, since the hydrogen atom α to the trifluoromethyl group is preferably eliminated as a proton (see *J.*, 1951, 2495); debromination of the dibromotrifluorobutene completes the synthesis :

$$CF_3{\cdot}CH{:}CI{\cdot}CH_3 \xrightarrow{Br_2} CF_3{\cdot}CHBr{\cdot}CBr_2{\cdot}CH_3 \xrightarrow{-HBr} CF_3{\cdot}CBr{:}CBr{\cdot}CH_3$$

$$CF_3{\cdot}CBr{:}CBr{\cdot}CH_3 \xrightarrow{Zn-EtOH} CF_3{\cdot}C{\vdots}C{\cdot}CH_3$$

The 1-alkyne, 4 : 4 : 4-trifluorobut-1-yne, is a major impurity in the product, and is easily detected by its characteristic infra-red spectrum, and notably the acetylenic C–H band at 3·0 μ. It is formed by isomerisation during the debromination step, but can be separated from the but-2-yne by formation of the silver or copper acetylide.

If the temperature is allowed to rise too high during the initial bromination step, hydrogen bromide is evolved and unidentified polybromo-compounds are formed.

The dehydrobromination step is best effected at *ca.* 0° since at higher temperatures two dibromotrifluorobutenes, which could not be separated by distillation on the scale used,

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* Part XIV, Haszeldine and Jander, *J.*, 1954, 919.

are formed. Infra-red spectroscopic examination shows that one is 2 : 3-dibromo-1 : 1 : 1-trifluorobut-2-ene which, when pure, has only one $C{:}C$ stretching vibration in the 6-μ region (6·18 μ); the other is 2 : 3-dibromo-4 : 4 : 4-trifluorobut-1-ene, since a second $C{:}C$ stretching vibration at 6·05 μ and a vinylic C–H stretching vibration band at 3·25 μ can be observed in the spectrum of the mixture, *i.e.*:

$$CF_3\cdot CHBr\cdot CBr_2\cdot CH_3 \longrightarrow CF_3\cdot CBr{:}CBr\cdot CH_3 + CF_3\cdot CHBr\cdot CBr{:}CH_2$$

Since debromination of the mixture gives only the trifluorobut-1- and -2-yne as volatile products, it appears that either the trifluoromethylallene expected from 2 : 3-dibromo-4 : 4 : 4-trifluorobut-1-ene is isomerised to the alkynes, or the second dibromo-compound yields products which do not contaminate the alkyne fraction. The compound $CF_3\cdot CH{:}C{:}CH_2$ has been synthesised by an alternative route (B. R. Steele, unpublished work), and comparison of infra-red spectra shows that it is not formed in the above debromination. It should be noted that debromination of *pure* 2 : 3-dibromo-1 : 1 : 1-trifluorobutene gives a mixture of the two butynes.

Dehydrobromination is incomplete at temperatures below 0° and 2-bromo-4 : 4 : 4-trifluorobut-2-ene then becomes a major product:

$$CF_3\cdot CH{:}CI\cdot CH_3 \xrightarrow{Br_2} CF_3\cdot CHBr\cdot CBr_2\cdot CH_3 \xrightarrow{Zn-EtOH} CF_3\cdot CH{:}CBr\cdot CH_3$$

This compound shows $C{:}C$ stretching absorption at 6·00 μ (cf. $CF_3\cdot CH{:}CH\cdot CH_3$, 5·90 μ; $CF_3\cdot CH{:}CCl\cdot CF_3$, 5·98 μ; $CF_3\cdot CH{:}CI\cdot CF_3$, 6·07 μ; *trans*-isomers).

The effect of hydrogen substitution on the boiling point of fluoroacetylenes is shown in the annexed Table. Replacement of three hydrogen atoms in but-2-yne by fluorine causes only a slight decrease in boiling point (9°), but replacement of the remaining three hydrogen atoms causes a very marked decrease (43°); the corresponding variation in boiling point in the but-2-ene series is much smaller. The corresponding propyne and propene compounds are also shown in the Table (see earlier papers for details).

	B. p.		B. p.		B. p.		B. p.
$CH_3\cdot C{\vdots}C\cdot CH_3$	27·2°	*trans*-$CH_3\cdot CH{:}CH\cdot CH_3$	2·5°	$CH_3\cdot C{\vdots}CH$	−23°	$CH_3\cdot CH{:}CH_2$	−48°
$CF_3\cdot C{\vdots}C\cdot CH_3$	18·5	,, $CF_3\cdot CH{:}CH\cdot CH_3$	16·5	$CF_3\cdot C{\vdots}CH$	−48	$CF_3\cdot CH{:}CH_2$	−22
$CF_3\cdot C{\vdots}C\cdot CF_3$	−25	,, $CF_3\cdot CH{:}CH\cdot CF_3$	9				

The acetylenic carbon–hydrogen stretching vibration is at 3·04 μ in propyne, and is shifted appreciably to shorter wave-length (3·01 μ) in fluorine-substituted alk-1-ynes, as shown in the following Table.

	$C{\vdots}C$	C–H		$C{\vdots}C$	
$CH_3\cdot C{\vdots}CH$	4·63	3·04	$CH_3\cdot C{\vdots}C\cdot CH_3$	4·47 4·33	Raman
$CF_3\cdot C{\vdots}CH$	4·65	3·01	$CF_3\cdot C{\vdots}C\cdot CH_3$	4·34(m) 4·40(s)	doublet
$C_2F_5\cdot C{\vdots}CH$	4·66	3·01	$CF_3\cdot C{\vdots}C\cdot CF_3$	4·23	probably

Monosubstituted acetylenes with fluorine on the α-carbon atoms show a $C{\vdots}C$ stretching vibration at longer wave-length than that of propyne, and this can be attributed to hyperconjugation involving fluorine, *e.g.*, $CF_3\cdot C{\vdots}CH \longleftrightarrow F^- \; CF_2{:}C{:}CH^+$. When the triple bond is flanked by one or two trifluoromethyl groups as in 1 : 1 : 1-trifluoro- or hexafluoro-but-2-yne, its stretching vibration moves to shorter wave-length, as would be predicted from the inductive effect.

1 : 1 : 1-Trifluorobut-2-yne fails to react with aqueous sulphuric acid even when catalytic amounts of mercuric sulphate are added. When greater than molar quantities of the mercury salt are used, the formation of an intermediate solid complex can be observed. This is not completely decomposed to the ketone when heated, but only 4 : 4 : 4-trifluorobutan-2-one (b. p. 95°) is produced. The isomeric 1 : 1 : 1-trifluorobutan-2-one, which would be formed by addition in the opposite direction, has been prepared from reaction of trifluoromethylmagnesium iodide with propionyl chloride or ethyl propionate; it boils at 46°, and would thus be readily separated from 4 : 4 : 4-trifluorobutan-2-one. The products from the hydration were examined by infra-red spectroscopy for the carbonyl groups: 4 : 4 : 4-trifluorobutan-2-one shows the $C{:}O$ stretching vibration at 5·72 μ, the characteristic position for compounds of the type $CF_3\cdot[CF_2]_n\cdot CH_2\cdot CO\cdot Alk$ (cf. $Alk\cdot CO\cdot Alk$, 5·75 μ).

The C:O stretching vibration in the known 1 : 1 : 1-trifluorobutan-2-one is at 5·62 μ (cf. CF_3·CO·CH_3, 5·61 μ), showing the characteristic shift to shorter wave-length; this shift is a maximum in compounds of the type CF_3·$[CF_2]_n$·CO·$[CF_2]_n$·CF_3, where the C:O vibration is at 5·56 μ. The spectroscopic examination failed to reveal any 1 : 1 : 1-trifluorobutan-2-one, or the presence of more than one carbonyl-containing compound.

4 : 4 : 4- and 1 : 1 : 1-Trifluorobutan-2-one cannot be distinguished by their ultra-violet spectra, which are very similar (see Table below), but the ketones give 2 : 4-dinitrophenylhydrazones which are easily distinguished by their melting points and by their ultra-violet spectra, as shown in the annexed Table. Examination of the ultra-violet and infra-red spectra of 2 : 4-dinitrophenylhydrazones prepared from various fractions of the hydration product showed that only 4 : 4 : 4-trifluorobutan-2-one was present. Control experiments showed that 1 : 1 : 1-trifluorobut-2-yne does not isomerise to 4 : 4 : 4-trifluorobut-1-yne under the conditions used, *i.e.*, the ketone isolated does not arise by CF_3·C⋮C·CH_3 ⟶ CF_3·CH_2·C⋮CH ⟶ CF_3·CH_2·CO·CH_3.

	Solvent	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
CF_3·CO·C_2H_5	Vapour	286·5	8·9	236·5	2·2
CF_3·CH_2·CO·CH_3	Vapour	286	7·5	242	2·9
CF_3·CO·C_2H_5 2 : 4-dinitrophenylhydrazone, m. p. 93°	EtOH	336	20,000	288	4,500
		254	12,000	238	11,400
		220	13,500	—	—
CF_3·CH_2·CO·CH_3 2 : 4-dinitrophenylhydrazone, m. p. 131—132°	EtOH	350	19,900	291	2,500
		225	14,500	Inflection 249	11,000

The polarisation of 1 : 1 : 1-trifluorobut-2-yne during attack by an ionic reagent is $CF_3\cdot\overset{\delta-}{C}\equiv\overset{\delta+}{C}\cdot CH_3$, since reaction with hydrogen chloride in presence of aluminium chloride yields 2-chloro-4 : 4 : 4-trifluorobut-2-ene, which is identical with the product prepared from 1 : 1 : 1-trifluoro-3-iodobut-2-ene :

$$CF_3\cdot C\vdots C\cdot CH_3 \xrightarrow[AlCl_3]{HCl-} CF_3\cdot CH{:}CCl\cdot CH_3$$

$$CF_3\cdot CH{:}CI\cdot CH_3 \xrightarrow{Cl_2} CF_3\cdot CHCl\cdot CCl_2\cdot CH_3 \xrightarrow{Zn-EtOH} CF_3\cdot CH{:}CCl\cdot CH_3$$

The ketone formed by the hydration of 1 : 1 : 1-trifluorobut-2-yne is thus that predicted from the inductive effects of the trifluoromethyl and methyl groups :

$$CF_3\cdot\overset{\delta-}{C}\equiv\overset{\delta+}{C}\cdot CH_3 \xrightarrow{HgY_2} CF_3\cdot C(HgY){:}CY\cdot CH_3 \xrightarrow[-\,HgY_2]{+\,H_2O} CF_3\cdot CH{:}C(OH)\cdot CH_3 \rightleftharpoons CF_3\cdot CH_2\cdot CO\cdot CH_3$$

where Y = HSO_4, say, in acid solution. This gives appreciable support to the ideas put forward in Part VI to explain the apparently anomalous hydration of perfluoroalkylacetylenes, and it should be noted that these ideas can be applied to any acetylene, not necessarily containing fluorine.

EXPERIMENTAL

1 : 1 : 1-*Trifluoro*-3-*iodobut*-2-*ene*.—Trifluoroiodomethane (28·7 g., 0·15 mole; for preparation see *J.*, 1951, 584), mixed with propyne (5·83 g., 0·15 mole) in a sealed 200-ml. Pyrex tube and exposed to ultra-violet radiation for 17 hr., gave 1 : 1 : 1-trifluoro-3-iodobut-2-ene (31·3 g., 91%), b. p. 95·0°, n_D^{20} 1·4352 (cf. Leedham and Haszeldine, *J.*, 1954, in the press).

2 : 3-*Dibromo*-1 : 1 : 1-*trifluorobut*-2-*ene*.—In a typical experiment 1 : 1 : 1-trifluoro-3-iodobut-2-ene (11·32 g., 0·05 mole) was cooled to −40° to −20° in a flask fitted with stirrer and reflux condenser, and to it was added dropwise (4 hr.) bromine (16·00 g., 0·10 mole); the reaction is vigorous if the temperature is allowed to rise. A slight excess of 25% ethanolic potassium hydroxide was then added dropwise at −10°, followed by an excess of 10% aqueous sulphuric acid. The lower layer (9·70 g., 76%) was distilled from phosphoric anhydride, to give 2 : 3-*dibromo*-1 : 1 : 1-*trifluorobut*-2-*ene*, b. p. 133—134° with partial decomposition (Found : C, 18·0; H, 1·2. $C_4H_3Br_2F_3$ requires C, 18·0; H, 1·1%). In other experiments the bromo-compound was distilled under reduced pressure, and had b. p. 62°/71 mm., 57·5°/45 mm., n_D^{19} 1·4568.

A by-product was 3-*bromo*-1 : 1 : 1-*trifluorobut*-2-*ene* (16%), b. p. 79—82°, n_D^{20} 1·403 (Found :

C, 25·6; H, 2·0%; *M*, 188. $C_4H_4BrF_3$ requires C, 25·4; H, 2·1%; *M*, 189). Other by-products (probably ethers formed during reaction with ethanolic potassium hydroxide) were not investigated.

1 : 1 : 1-*Trifluorobut-2-yne*.—2 : 3-Dibromo-1 : 1 : 1-trifluorobut-2-ene (2·0 g.) was added dropwise (1 hr.) to zinc (6 g.) and refluxing ethanol (20 ml.), and refluxing was continued for a further 8 hr. The volatile products passed through a reflux condenser and were condensed in traps cooled by liquid oxygen. Distillation *in vacuo* gave a mixture (0·60 g., 75%) of 1 : 1 : 1-trifluorobut-2-yne and 4 : 4 : 4-trifluorobut-1-yne (Found : *M*, 109. Calc. for $C_4H_3F_3$: *M*, 108). An experiment with 4·04 g. of the bromo-compound gave an 81% yield of the mixed alkynes.

The 4 : 4 : 4-trifluorobut-1-yne was removed by passing the mixed alkynes through aqueous-ethanolic silver nitrate (3 times) and ammoniacal cuprous chloride (2 times), and the residual gas was washed with 10% sulphuric acid and distilled *in vacuo*. The purification procedure was repeated if an infra-red spectrum showed the acetylenic C–H absorption at 3·0 μ. The product was 1 : 1 : 1-*trifluorobut-2-yne* (39%), b. p. (isoteniscope) (18·0—18·5° (Found : F, 52·7%; *M*, 108. $C_4H_3F_3$ requires F, 52·7%; *M*, 108).

The infra-red spectrum of 1 : 1 : 1-trifluorobut-2-yne was unchanged after treatment of the alkyne with acid catalysts at 110° for 10 hr.

Hydration of 1 : 1 : 1-*Trifluorobut-2-yne*.—The alkyne was substantially unchanged (94%) when heated with mercuric sulphate (1 mol. %) and 10% sulphuric acid at 120° for 8 hr.

In a typical experiment, the butyne (3·14 g., 0·03 mole) was heated with mercuric sulphate (12·0 g., 0·04 mole) and 25% sulphuric acid (8 ml.) at 45—55° for 20 hr. The volatile products were unchanged butyne (0·26 g., 8%), identified spectroscopically, carbon dioxide, and an unknown fraction (0·23 g.) (*M*, 125) shown by spectroscopic examination to contain no carbonyl group. The aqueous and the solid products were extracted with butyl ether, and the ethereal extract was dried (P_2O_5) and distilled, to give a fraction, b. p. 95—98°, which was redistilled, to give 4 : 4 : 4-*trifluorobutan*-2-*one*, b. p. 95—96° (Found : C, 38·3; H, 4·7%; *M*, 125. $C_4H_5OF_3$ requires C, 38·1; H, 4·0%; *M*, 126). The material of b. p. higher and lower than that shown above was treated with 2 : 4-dinitrophenylhydrazine, to give the 2 : 4-*dinitrophenylhydrazone* (1·68 g.), m. p. 131—132°, of 4 : 4 : 4-trifluorobutan-2-one, since the ketone could not be completely separated from butyl ether by distillation (Found: C, 39·0; H, 3·2; N, 18·3. $C_{10}H_9O_4N_4F_3$ requires C, 39·2; H, 2·9; N, 18·3%). The infra-red spectra of the 2 : 4-dinitrophenylhydrazones of 4 : 4 : 4-trifluorobutan-2-one and 1 : 1 : 1-trifluorobutan-2-one are distinctly different.

The ketone can also be isolated by extraction with ethyl ether, followed by distillation and treatment with phosphoric anhydride. Butyl ether was used in the first experiment so that any 1 : 1 : 1-trifluorobutan-2-one, b. p. 46°, formed could be detected. There is no reason to believe that the breakdown products arise preferentially from 1 : 1 : 1-trifluorobutan-2-one. All fractions were examined by infra-red spectroscopy, and tested for formation of a 2 : 4-dinitrophenylhydrazone.

3-*Chloro*-1 : 1 : 1-*trifluorobut*-2-*ene*.—Chlorine (4·07 g., 0·057 mole) and 1 : 1 : 1-trifluoro-3-iodobut-2-ene (13·60 g., 0·058 mole) in a sealed Carius tube were kept at −10° for 1 hr., then treated with a slight excess of 10% aqueous potassium hydroxide at 10—20° to remove precipitated iodine halides. The lower layer was added dropwise (3 hr.) to zinc (20 g.) and refluxing ethanol (125 ml.); the ethanol was slowly distilled off during the reaction and added to an excess of ice-water. The lower layer so obtained was dried (P_2O_5) and distilled, to give 3-chloro-1 : 1 : 1-trifluorobut-2-ene (6·2 g., 76%), b. p. 58—60° (Found : *M*, 142. Calc. for $C_4H_4ClF_3$: *M*, 144·5).

1 : 1 : 1-Trifluorobut-2-yne (0·69 g.) failed to react with anhydrous hydrogen chloride (0·26 g.) after 2 days at 140°. Addition of aluminium chloride (0·8 g.) brought about an immediate reaction at room temperature, completed at 95° (10 hr.), to give 1 : 1 : 1-trifluoro-3-chlorobut-2-ene (Found : *M*, 144. Calc. for $C_4H_4ClF_3$: *M*, 144·5) and unchanged butyne (56%). The infra-red spectra of the chlorofluorobutenes made by the two routes were identical.

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