Addition of Free Radicals to Unsaturated Systems. Part IX. The Direction of Free-radical Addition to Allene and Allyl Chloride.*

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The photochemical reaction of trifluoroiodomethane with allene yields only the compound $CF_3\cdot CH_2\cdot CI:CH_2$, and radical attack is thus exclusively on the CH_2 group of allene. The synthesis of 4 : 4 : 4-trifluorobut-1-ene, 4 : 4 : 4-trifluorobuta-1 : 2-diene [(trifluoromethyl)allene], and 4 : 4 : 4-trifluorobut-1-yne is described. Trifluoroiodomethane reacts with allyl chloride to give only $CF_3\cdot CH_2\cdot CHI\cdot CH_2Cl$, thus establishing the direction of radical attack on this olefin. The results are discussed briefly.

When reagents react with allene, by a mechanism involving addition of ionic intermediates, it is known that the polarisation of the allene is represented as $\overset{\delta-}{CH_2}=\overset{\delta+}{C}=CH_2$ (*e.g.*, EtOH, H_2O, HOCl,HF; see Whitmore, "Organic Chemistry," Chapman and Hall, Ltd., London, 1937, p. 50; HF, Austin, U.S.P. 2,585,529/1952). The photochemical reaction of trifluoroiodomethane with allene has now been investigated in order to determine the direction of free-radical attack.

Trifluoroiodomethane and allene do not react in the dark, but a smooth reaction occurs on exposure to ultra-violet light, to give a high yield of a compound $CF_3\cdot(C_3H_4)\cdot I$ (b. p. 102°). This could be (I) or (II), formed by a chain reaction of the type described in earlier Parts, *e.g.*:

$$\text{(I)}\quad CF_3\cdot CH_2\cdot CI:CH_2 \qquad\qquad CF_3\cdot C(:CH_2)\cdot CH_2I\quad \text{(II)}$$

$$CF_3\cdot + CH_2:C:CH_2 \longrightarrow CF_3\cdot CH_2\cdot\dot{C}:CH_2$$

$$CF_3\cdot CH_2\cdot\dot{C}:CH_2 + CF_3I \longrightarrow CF_3\cdot CH_2\cdot CI:CH_2 + CF_3\cdot \longrightarrow \text{etc.}$$

The ultra-violet spectrum of the product is very similar to that of the known isomer 4 : 4 : 4-trifluoro-2-iodobut-2-ene (b. p. 94·5°), as shown in the annexed Table, and this strongly suggests that the product is (I), which also contains the $\cdot CH_2\cdot CI:CH_2$ system (with a vinylic iodine atom). The ultra-violet spectrum of (II) would be very similar to that of allyl iodide which has a single maximum at much longer wave-length and no high-intensity absorption at shorter wave-lengths (see Table).

Ultra-violet spectra (in light petroleum).

	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$		$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
$CF_3\cdot CH_2\cdot CI:CH_2$	261	315	242	150	$CF_3\cdot CH:CI\cdot CH_3$[1]	260	350	251·5	320
	223	3500	—	—		230	3800	221·5	3100
$CH_2I\cdot CH:CH_2$[2]	271	800	249·5	490		215	3500	—	—

[1] Leedham and Haszeldine (*J.*, 1954, 1634). [2] Haszeldine (*J.*, 1953, 1764).

Distinction between (I) and (II) can also be made on the basis of infra-red spectra. The product shows a strong C:C stretching absorption at 6·17 μ which is in the characteristic region for compounds containing a vinylic iodine atom. The C:C absorption in (II) would be close to that in 3 : 3 : 3-trifluoro-2-methylpropene, *i.e.*, near 6·0 μ. The $>C:CH_2$ group is also shown by the very strong band at 10·93 μ, which is displaced from its characteristic position in hydrocarbon olefins (11·24 μ).

Chemical evidence in favour of (I) is its reaction with zinc and mineral acid to give 4 : 4 : 4-trifluorobut-1-ene (III); (II) would have given 3 : 3 : 3-trifluoro-2-methylpropene (IV) by this reaction. The $\cdot CH:CH_2$ group is revealed by the bands in the infra-red at 3·22 (vinylic C–H), 6·06 (C:C stretching) (cf. $CH_3\cdot CH:CH_2$, C:C 6·06 μ), and 10·10, 10·75 μ (cf. compounds of type $R\cdot CH:CH_2$, 10·1, 10·9 μ). The b. p.s and double-bond stretching vibrations of the known isomeric trifluorobutenes are $CF_3\cdot CH:CH\cdot CH_3$ 17°, 5·90 μ; $CF_3\cdot CMe:CH_2$ 6·4°, 6·0 μ.

Since (III) was obtained in high yield, and with no contamination by (IV), the product

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* Part VIII, *J.*, 1954, 1634.

from trifluoroiodomethane and allene is exclusively (I), *i.e.*, attack of the trifluoromethyl radical is on the CH_2 group of allene. Final proof of constitution is given by the synthesis of (III) by an independent unambiguous route. Trifluoroiodomethane and allyl chloride,

$CF_3{\cdot}CH_2{\cdot}CH{:}CH_2$ (III) $CF_3{\cdot}CMe{:}CH_2$ (IV) $CF_3{\cdot}CH_2{\cdot}CHI{\cdot}CH_2Cl$ (V) $(CF_3)(CH_2Cl)CH{\cdot}CH_2I$ (VI)

on exposure to ultra-violet light, readily give 1-chloro-4 : 4 : 4-trifluoro-2-iodobutane (V). Dehalogenation by means of zinc and ethanol gives a high yield of a trifluorobutene which is spectroscopically identical with (III). It is to be noted that if the attack of the trifluoromethyl radical had been on the ${\cdot}CH{:}$ group of allyl chloride to give (VI), dehalogenation could have yielded neither (III) nor (IV). The direction of addition of the trifluoromethyl radical to allene and to allyl chloride is thus conclusively proved. Only very small amounts of fluoroform were detected in the reaction products from allene and allyl chloride, *i.e.*, hydrogen-abstraction is not a major reaction. The propagation step is not favoured (see earlier papers), since only small amounts of product with a higher b. p. were formed during reaction.

4 : 4 : 4-Trifluoro-2-iodobut-1-ene with ethanolic potassium hydroxide gives a mixture of 4 : 4 : 4-trifluorobuta-1 : 2-diene (VII) and 4 : 4 : 4-trifluorobut-1-yne (VIII). The

$CF_3{\cdot}CH{:}C{:}CH_2$ (VII) $CF_3{\cdot}CH_2{\cdot}C{\vdots}CH$ (VIII) $CF_3{\cdot}C{\vdots}C{\cdot}CH_3$ (IX)

latter is easily detected by its acetylenic carbon–hydrogen vibration at 3·00 μ and the $C{\vdots}C$ stretching absorption at 4·33 μ; it is separated from the trifluoromethylallene (VII) by formation of a silver salt, from which it can be regenerated on treatment with acid. The allene (VII) shows the ${\cdot}CH{:}C{:}CH_2$ bands in the infra-red at 5·00, 5·08 (doublet), and 5·90 μ (cf. methylallene 5·10, 5·88 μ); there are no bands corresponding to the $C{\vdots}C$ stretching vibration or to an acetylenic carbon–hydrogen absorption. The isomeric 1 : 1 : 1-trifluorobut-2-yne (IX) was described in Part VIII. The b.p.s of the isomers are similar: (VII), 16°; (VIII), 15°; (IX), 18·0—18·5°. The alkyne (VIII) is doubtless formed by isomerisation of the allene (VII) in the alkaline medium, just as allene is isomerised to propyne when treated with sodium.

By adopting the concept that intermediate radical stability determines the direction of radical addition to an unsaturated compound (see earlier papers), it follows that relative radical stabilities are: $CF_3{\cdot}CH_2{\cdot}\dot{C}{:}CH_2 > CH_2{:}C(CF_3){\cdot}CH_2{\cdot}$; $CF_3{\cdot}CH_2{\cdot}CH{\cdot}CH_2Cl > (CF_3)(CH_2Cl)CH{\cdot}CH_2{\cdot}$. Full discussion is deferred until a later paper.

EXPERIMENTAL

Allene was prepared from allyl bromide and was shown to be free from impurities (particularly methylacetylene) by infra-red spectroscopic examination. Allyl chloride was a commercial sample distilled in nitrogen immediately before use; it was peroxide-free. Oxygen, moisture, etc., which might catalyse ionic or free-radical reactions were excluded. Silica or Pyrex vessels were thoroughly cleaned, and were filled and sealed *in vacuo*. A Hanovia S-250 ultra-violet lamp was used.

Reaction of Trifluoroiodomethane with Allene.—Trifluoroiodomethane (37·9 g., 0·193 mole) and allene (7·80 g., 0·195 mole), sealed in a silica tube, were exposed to ultra-violet light for 48 hr. to give products (15·25 g.) of b. p. >0°. When distilled, they gave 4 : 4 : 4-*trifluoro*-2-*iodobut*-1-*ene* (14·61 g., 96%), b. p. 101—102·5°, 58—59°/160 mm., n_D^{20} 1·4312 (Found: C, 20·8; H, 2·0. $C_4H_4IF_3$ requires C, 20·4; H, 1·7%), and a small amount of material of higher b. p. which was not examined.

4 : 4 : 4-Trifluoro-2-iodobut-1-ene (5·28 g.) was added to zinc powder (25 g.), magnesium (2 g.), and 50% hydrochloric acid (10 ml.) in a flask fitted with reflux water-condenser leading *via* rubber tubing to a trap cooled in liquid oxygen. The temperature was raised to 100° during 3 hr. and the volatile product was distilled *in vacuo*, to give 4 : 4 : 4-trifluorobut-1-ene (82%), b. p. (isoteniscope) 10·6°, shown to be identical with the material prepared below by comparison of infra-red spectra.

In control experiments, allene was irradiated alone, or in presence of iodine, for 3 days; infra-red spectroscopic examination showed that allene did not isomerise to propyne under these conditions.

Reaction of Trifluoroiodomethane with Allyl Chloride.—Freshly distilled allyl chloride (5·6 g., 0·073 mole; b. p. 45·5°/769 mm.) and trifluoroiodomethane (15·3 g., 0·078 mole) in a Pyrex tube were exposed to ultra-violet light (14 days). The volatile products were distilled, to give trifluoroiodomethane (8·6 g., 56%). Distillation of the liquid products in an atmosphere of nitrogen gave allyl chloride (3·5 g., 60%) and 1-*chloro*-4 : 4 : 4-*trifluoro*-2-*iodobutane* (8·3 g., 89%), b. p. 88°/69 mm., n_D^{20} 1·476 (Found : C, 18·0; H, 1·7. $C_4H_5ClIF_3$ requires C, 17·6; H, 1·8%).

4 : 4 : 4-*Trifluorobut*-1-*ene.*—1-Chloro-4 : 4 : 4-trifluoro-2-iodobutane (2·80 g.) and ethanol (3 ml.), added slowly to zinc dust (10 g.) and refluxing ethanol (20 ml.), gave volatile products, which were washed with water and distilled to give 4 : 4 : 4-*trifluorobut*-1-*ene* (0·92 g., 80%), b. p. 10·5° (Found : C, 43·5; H, 5·6%; *M*, 111. $C_4H_5F_3$ requires C, 43·6; H, 4·5%; *M*, 110).

4 : 4 : 4-*Trifluorobuta*-1 : 2-*diene.*—To 4 : 4 : 4-trifluoro-2-iodobut-1-ene (2·90 g.) was slowly added, with stirring, ethanolic potassium hydroxide (10 ml. of 10%). After 2 hr. at room temperature the mixture was refluxed for 2 hr. The combined volatile products, which had passed through a reflux water-condenser and been condensed in a trap cooled by liquid oxygen, were distilled *in vacuo,* to give a mixture (0·98 g.) of an allene and an acetylene. This product was repeatedly shaken with a solution of silver nitrate (2 g.) in 50% aqueous ethanol (10 ml.) until the volatile material was shown by its infra-red spectrum to be free from acetylenic compounds. Redistillation gave 4 : 4 : 4-*trifluorobuta*-1 : 2-*diene* (0·581 g., 44%), b. p. 16·0° (Found : C, 44·2%; *M*, 108·5. $C_4H_3F_3$ requires C, 44·5%; *M*, 108).

The white precipitate obtained from the above reaction with silver nitrate was treated with sulphuric acid (3 ml. of 30%), and the gaseous product was distilled *in vacuo,* to give 4 : 4 : 4-*trifluorobut*-1-*yne* (0·290 g., 22%), b. p. 15° (Found : F, 52·4%; *M*, 108. $C_4H_3F_3$ requires F, 52·7%; *M*, 108).

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