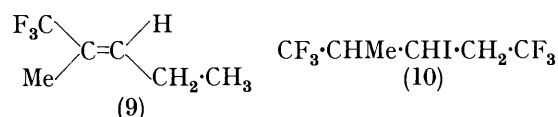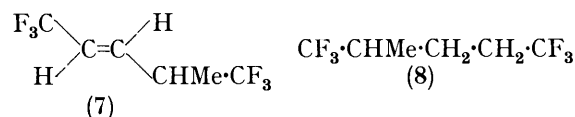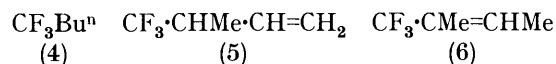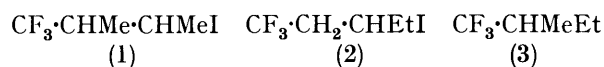# Addition of Free Radicals to Unsaturated Systems. Part 23.[1] Photochemical and Thermal Reactions of Trifluoroiodomethane with But-2-ene and But-1-ene

By **Terry Davies, Robert N. Haszeldine,** * and **Anthony E. Tipping,** * Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Photochemically-initiated addition of trifluoroiodomethane to but-2-ene gives as the major product the 1 : 1 adduct 2-iodo-3-trifluoromethylbutane as a mixture of the *erythro*- and *threo*-isomers together with compounds formed *via* dehydroiodination of the 1 : 1 adduct. Reduction of the 1 : 1 adduct to 2-trifluoromethylbutane is a major process when the reaction tube is shaken. Under thermal conditions fewer products arising *via* dehydroiodination of the 1 : 1 adduct are detected, but products formed *via* isomerisation of the reactant olefin to but-1-ene are present in low yield. With but-1-ene initial bidirectional $CF_3\cdot$ radical attack takes place to give the 1 : 1 adducts 1,1,1-trifluoro-3-iodopentane and 1-iodo-2-trifluoromethylbutane in the ratio *ca.* 19 : 1. Products are also formed *via* isomerisation of the reactant olefin and *via* dehydroiodination of the 1 : 1 adducts.

FREE-RADICAL additions of trifluoroiodomethane to olefins under thermal or photochemical conditions have been investigated widely and involve initial attack of the highly electrophilic [2,3] $CF_3\cdot$ radical on the double

$$CF_3\cdot CHMe\cdot CHMeI \quad CF_3\cdot CH_2\cdot CHEtI \quad CF_3\cdot CHMeEt$$
$$(1) \qquad\qquad (2) \qquad\qquad (3)$$

$$CF_3 Bu^n \quad CF_3\cdot CHMe\cdot CH{=}CH_2 \quad CF_3\cdot CMe{=}CHMe$$
$$(4) \qquad (5) \qquad\qquad (6)$$

$$\underset{H}{\overset{F_3C}{>}}C{=}C\underset{CHMe\cdot CF_3}{\overset{H}{<}}$$
$$(7)$$

$$CF_3\cdot CHMe\cdot CH_2\cdot CH_2\cdot CF_3$$
$$(8)$$

$$\underset{Me}{\overset{F_3C}{>}}C{=}C\underset{CH_2\cdot CH_3}{\overset{H}{<}}$$
$$(9)$$

$$CF_3\cdot CHMe\cdot CHI\cdot CH_2\cdot CF_3$$
$$(10)$$

$$CF_3\cdot CH_2\cdot CH_2\cdot CHMeI$$
$$(11)$$
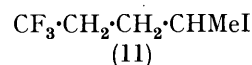
bond. With a number of unsymmetrical olefins, *e.g.* propene [4-6] and trifluoroethylene,[7] bidirectional $CF_3\cdot$ radical addition has been observed.

In the present work the thermal and photochemical reactions of trifluoroiodomethane with the butenes have been investigated. The expected major products, the 1 : 1 adducts (1) and (2), are precursors to the trifluoromethylalkanes (3) and (4), respectively, which were required in a study of the thermal reaction of hexafluoropropene with butanes and substituted butanes.[8]

(a) *But-2-ene.*—The conditions used and the results obtained from the reactions with (*E*)- and (*Z*)-but-2-ene are shown in Table 1.

Products (3) and (5)—(9), present in the low-boiling fractions from the photochemical reactions, were identified by elemental analysis, molecular-weight determination, and a consideration of their i.r. [(5), 6.06 μm (C=C str. in olefin of type $RCH{=}CH_2$); (6), (7), and (9), *ca.* 5.92 μm (C=C str. in olefins of type $CF_3\cdot CR^1{=}CHR^2$ and $CF_3\cdot CH{=}CHR$)], n.m.r., and mass spectra. The ^1H and ^{19}F n.m.r. spectra of compound (6) showed the presence of the (*E*)- (6a) and (*Z*)- (6b) isomers in the ratio 1 : 1 and these were differentiated by the CF_3 group chemical shifts [(*Z*)-isomer at lower field (-14.3 p.p.m.) than (*E*)-isomer (-6.4 p.p.m.), *cf.* $CF_3\cdot CH{=}CHMe$[4] and $CF_3\cdot CF{=}CHMe$[9]]. The olefin (7) was present

TABLE 1

Reaction of trifluoroiodomethane with (*E*)- and (*Z*)-but-2-ene

Experiment	1	2	3	4	5	6
Molar ratio (CF$_3$I : alkene)	5 : 3	4 : 3	4 : 3	4 : 3	3 : 1	3 : 1
Olefin	(*E*) + (*Z*)	(*Z*)	(*E*)	(*E*)	(*Z*)	(*E*)
Conditions	static, u.v.	static, u.v.	static, u.v.	shaken, u.v.	200 °C	200 °C
Time (h)	160	164	112	168	13	13
Recovered olefin (%)	10	14	11	9	48	51
Recovered CF$_3$I (%)	33	26	27	24	74	82
Products *,† (3)	4	8	18	48	31	18
(5)	2.5	4.5	5.5	0.5	1.5	0.5
(6)	3.5	7.5	1	1.5	1.5	Trace
(7)	1.5	1.5	0.5	0.5		
(4)					Trace	2
(8)	3.5	6	2	3		
(9)	Trace	Trace	Trace	0.5		
(1a)	29	28	24	19.5	24.5	43.5
C$_5$H$_6$F$_3$I	1	Trace	Trace	1.5		
(10a)	8	4	2.5	1		
(2)					4	3
(1b)	37	33	37	8.5	15	16
(10b)	6.5	4	5.5	1		
(11)					5.5	Trace
Total product yield (%)	96.5	96.5	96	85.5	85 ‡	84

* Yields based on olefin consumed and given to nearest 0.5%. † In order of g.l.c. retention time. ‡ Two unidentified products (total *ca.* 2%) also formed.

entirely as the *trans*-isomer (J_{H-H} 16.3 Hz) and the olefin (9) as the (E)-isomer (J_{CF_3-H} 2.0 Hz) in which the two bulkiest groups (CF_3 and $CF_3 \cdot CH_2$) are *trans*.

The higher-boiling fractions from the photochemical reactions consisted of two isomers of adduct (1), two isomers of compound (10), and small amounts of an unidentified compound of molecular formula $C_5H_6F_3I$ (1 : 1 adduct-H_2).

Dehydroiodination of the minor adduct (1) with powdered potassium hydroxide gave a mixture (99%) of olefins (6a) and (6b) in the ratio 5 : 95, while under similar conditions the major isomer gave a mixture (98%) of the same olefins in the ratio 95 : 5.

$$CF_3 \cdot CHMe \cdot CHMeI \xrightarrow{\text{KOH}}$$
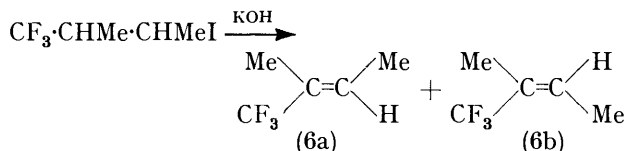
The major olefin from each reaction would be expected to be formed by an *E2 anti*-elimination of hydrogen iodide and so the minor isomer is assigned the *threo*-configuration and the major isomer the *erythro*-configuration. On the basis of the observed vicinal H–H couplings (2.4 and 3.6 Hz), in the range for *gauche* couplings, it would appear that the favoured conformations are (1a) and (1b), respectively, rather than the conformations (1c) and (1d) expected on steric grounds.
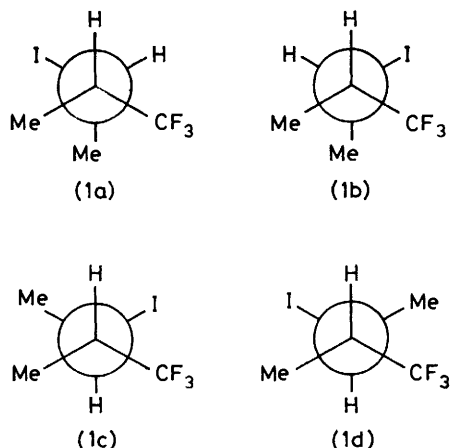

The configurations of the two isomers of compound (10) could not be determined from the n.m.r. spectra.
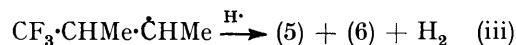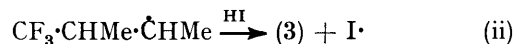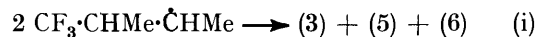
It is proposed that the products from the photochemical reactions are formed as shown in Scheme 1.

It is apparent from the results that considerable dehydroiodination of the initially formed 1 : 1 adduct (1) takes place under the conditions used. The photochemical dehydroiodination is bidirectional with cleavage of a C–H bond in the methyl group to give the olefin (5) favoured over cleavage of the methine C–H bond to afford olefin (6) by between *ca.* 3 : 1 (experiment 2) and *ca.* 17 : 1 (experiment 3). Such dehydroiodinations probably involve four-centre transition states and contrast with dehydroiodination by base which involves

elimination of the most acidic hydrogen atom (that adjacent to the CF_3 group) to give (6). Similar bidirectional photochemical dehydroiodination of compound (10) also occurs to give the olefins (7) and (9).

Scheme 1
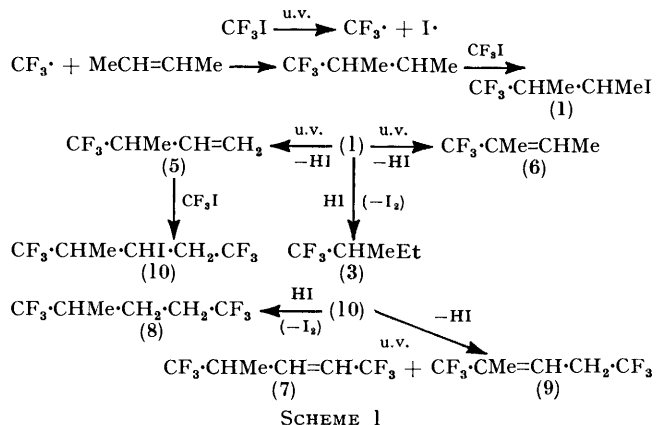
Although the stationary concentration of the reactive intermediate secondary radical $CF_3 \cdot CHMe \cdot \dot{C}HMe$ is likely to be low it is possible that a proportion of the products (3), (5), and (6) are formed *via* this radical [equations (i)—(iii)].

$$2\ CF_3 \cdot CHMe \cdot \dot{C}HMe \longrightarrow (3) + (5) + (6) \qquad \text{(i)}$$

$$CF_3 \cdot CHMe \cdot \dot{C}HMe \xrightarrow{\text{HI}} (3) + I \cdot \qquad \text{(ii)}$$

$$CF_3 \cdot CHMe \cdot \dot{C}HMe \xrightarrow{\text{H} \cdot} (5) + (6) + H_2 \qquad \text{(iii)}$$

The recovered olefin from the reactions involving pure (E)- or (Z)-but-2-ene was found to have isomerised to a small extent indicating that reversible addition (probably of $I \cdot$ or H^+) had taken place.

In experiment 4 the reaction tube was shaken and a much higher yield of the reduced compound (3) was observed. This can be rationalised on the basis that the gas phase is rich in olefin and trifluoroiodomethane and formation of the 1 : 1 adduct (1) takes place mainly in this phase. The relatively non-volatile adduct then dissolves in the liquid phase and further reaction in the static-tube experiments only occurs slowly. However, when the tube is shaken better mixing of the gas-phase and liquid-phase components takes place, which favours further reaction of the adduct (1). Compound (3) is formed mainly at the expense of the *erythro*-isomer (1b) which indicates that this isomer is more readily dehydroiodinated and reduced than the *threo*-isomer (1a).

In experiments 3 and, more especially, 4, hydrogen iodide eliminated in the formation of compounds (5), (6), (7), and (10) is insufficient to account for the yields of the reduced compounds (3) and (8). A proportion of the reactant olefin in each experiment (3% and 15% respectively) was not accounted for and it is probable that reactions involving this gave more hydrogen iodide and the tar observed.

In the thermal reactions as compared to the photochemical reactions new products, *i.e.* (2), (4), and (11)

werc formed, while compounds (7), (8), (9), and (10) were not detected. Adducts (2) and (11) are major products from the but-1-ene reactions and are discussed later, while the alkane (4) was identified by a comparison of its ^{1}H n.m.r. spectrum with that reported.[10] These products are considered to be formed via isomerisation of but-2-ene to but-1-ene (Scheme 2).

$$MeCH=CHMe + H^+ \rightleftharpoons MeCH_2 \cdot \overset{+}{C}HMe \rightleftharpoons MeCH_2 \cdot CH=CH_2$$

SCHEME 2
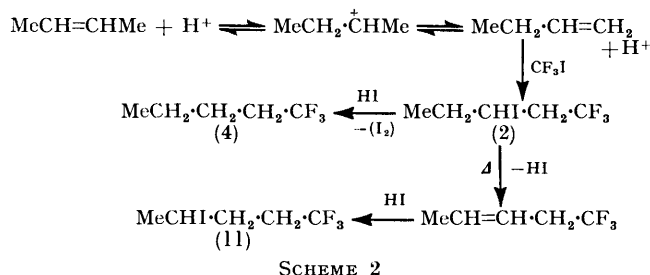
The relatively high yields of alkane (3) and the absence or formation in low yield only of compounds (5)—(10) indicates that reduction of adduct (1) is favoured under thermal conditions, while dehydroiodination is less favoured. However, thermal dehydroiodination of both adduct (1) isomers occurred readily at 260 °C, but the only volatile product was alkane (3) [47% from isomer (1a) and 64% from isomer (1b)] together with tar. The expected products were a mixture of olefins (5) and (6) and the alkane (3) in equimolar amounts if reduction of adduct (1) by hydrogen iodide occurred at a faster rate than did initial dehydroiodination. The absence of olefins (5) and (6) in the products indicates that they react further to give the tar observed and since the yield of alkane (3) from the erythro-isomer (1b) is >50% some interaction between iodine and olefins (5) and (6) or the tar is proposed to give the extra hydrogen iodide required.

Therefore, it is probable that in experiments 5 and 6 the low yields of products derived from dehydroiodination of adduct (1) [except alkane (3)] arose by further reaction of the olefins (5) and (6) to give tar. In these experiments, as in photochemical experiment 4, considerable amounts of reactant olefin consumed (ca. 15%) could not be accounted for by the products.

It was further shown that thermal reduction of the two adduct (1) isomers separately with hydrogen iodide at 200 °C resulted in near-quantitative yields of the alkane (3). Similarly, a mixture of adduct (1) and the iodide (10) on reduction under similar conditions gave the alkanes (3) [99% based on (1)] and (8) [95% based on (10)].

One surprising feature of the reactions was that the formation of the erythro-adduct (1b) was favoured in the photochemical static tube experiments while formation of the threo-adduct (1a) was favoured in the thermal reactions.

But-1-ene.—The conditions used and the results obtained are shown in Table 2. The olefins (12) and (13) were not separated but n.m.r. spectroscopy indicated the presence of three components in the ratio 2 : 1 : 1, i.e.
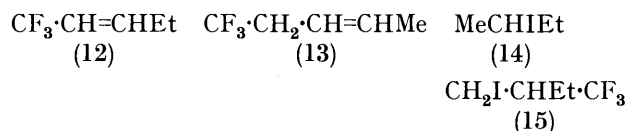
TABLE 2

Reaction of trifluoroiodomethane with but-1-ene

Experiment	1	2	3
Molar ratio (CF$_3$I : alkene)	ca. 8 : 5	ca. 8 : 5	ca. 3 : 1
Conditions	static, u.v.	shaken, u.v.	200 °C
Time (h)	164	164	90
Recovered olefin (%)	4	8	49
Recovered CF$_3$I (%)	44	46	77
Products *,† (3)	2		6
(6)			3.5
(4)	10.5	19	13.5
(12)	5	} 28	} 13.5
(13)	5		
(14)	1	16.5	
(1a)	2.5	1	11.5
(2)	57	7	37.5
(15)	4.5	2	3
(1b)	3.5	Trace	5.5
(11)	3.5	19.5	
Total product yield (%)	94.5	93	94

* Yields based on olefin consumed and given to nearest 0.5%.
† In order of g.l.c. retention time.

(12), probably trans-isomer (δ_{CF_3} — 12.3 p.p.m., $J_{CH_3-CH_3}$ 6.5 Hz), (13) cis- or trans-isomer (δ_{CF_3} — 9.5 p.p.m., $J_{CF_3-CH_2}$ 10.0 Hz), and (13) trans- or cis-isomer (δ_{CF_3} — 8.5 p.p.m., $J_{CF_3-CH_2}$ 10.0 Hz). Adducts (2), (11), and

$$CF_3 \cdot CH=CHEt \quad CF_3 \cdot CH_2 \cdot CH=CHMe \quad MeCHIEt$$
$$(12) \qquad\qquad (13) \qquad\qquad (14)$$

$$CH_2I \cdot CHEt \cdot CF_3$$
$$(15)$$

(15) were readily identified on the basis of their n.m.r. spectra. It is proposed that the products are formed as shown in Scheme 3.

SCHEME 3
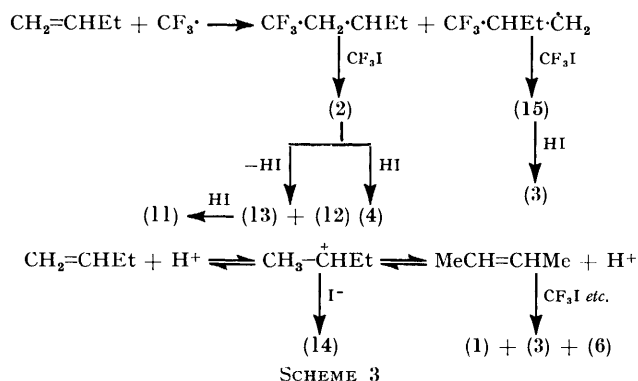
The isolation of adducts (2) and (15) shows that bi-directional CF$_3$· radical addition to but-1-ene takes place. Compounds (2), (4), (11), (12), and (13) arise via CF$_3$· radical addition at the CH$_2$ end of the olefin, while adduct (15) and possibly a proportion of compound (3) arise via attack at the CHEt group. The ratio of attack on the CH$_2$ and CHEt groups is then 94 ± 1 : 6 ± 1 (experiment 1), 97 : 3 (experiment 2) and 92 ± 4 : 8 ± 4 (experiment 3) allowing for the fact that compound (3) may or may not arise via adduct (15).

Comparable bidirectional CF$_3$· radical attack on the olefins CH$_2$=CHMe (Δ ratio 90 : 10,[4] u.v. ratio 96 : 4 [5]) and CH$_2$=CHF (Δ ratio 89 : 11,[4] u.v. ratio 96 : 4 [11]) have been reported previously.

The yield of adduct (2) was greatly reduced in the photochemical reaction when the tube was shaken (experiment 2) and the yields of products arising via dehydroiodination of the adduct were increased (cf. corresponding but-2-ene reaction, experiment 4).

A mixture consisting of adduct (2) with smaller amounts of adducts (1) and (11) when heated at 200 °C with an excess of hydrogen iodide afforded the trifluoromethylalkanes (3) [92% based on (1)] and (4) [99% based on (2) + (11)].

It has been reported [6] that some allylic hydrogen abstraction by $CF_3\cdot$ radicals took place in the reaction of trifluoroiodomethane with propene. Surprisingly, apart from trifluoromethane, products which could have arisen via such abstraction, e.g. (13) from but-2-ene and (5) from but-1-ene, were not detected in the present work. The trifluoromethane observed could have been formed by hydrogen abstraction from hydrogen iodide by $CF_3\cdot$ radicals.

EXPERIMENTAL

Reactants and products were manipulated in a conventional vacuum system. Photochemical reactions were carried out in silica tubes (ca. 300 cm³) which were irradiated at ca. 15 cm from a Hanovia S500 medium-pressure u.v. lamp and thermal reactions were carried out in Pyrex tubes (ca. 300 cm³). Products were separated by fractional condensation in vacuo or by preparative g.l.c. (columns as indicated in the text), with product ratios determined by analytical g.l.c. after prior calibration with standard mixtures of the same compounds, and were identified by elemental analysis, molecular-weight determination (Regnault's method), i.r. spectroscopy (Perkin-Elmer 257 spectrophotometer with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 spectrometer operating at 60 MHz for ¹H and 56.46 MHz for ¹⁹F, or a Varian HA100 instrument operating at 100 MHz for ¹H and 94.1 MHz for ¹⁹F, using internal tetramethylsilane and external trifluoroacetic acid as the respective references), and mass spectrometry (A.E.I. MS902 spectrometer).* Boiling points were determined by Siwoloboff's method.

Reactions of Trifluoroiodomethane.—(a) With a mixture of (E)- and (Z)-but-2-ene under photochemical conditions (static tube). A mixture of (E)- and (Z)-but-2-ene (1 : 1 molar; 1.68 g, 30.0 mmol) and trifluoroiodomethane (9.40 g, 48.0 mmol) was irradiated in vacuo (168 h) to give (i) a highly volatile mixture (3.40 g, 20.0 mmol; M, 170) which was shown [i.r. spectroscopy and g.l.c. (4 m TXP at 20 °C)] to be a mixture of unchanged olefin (0.17 g, 3.0 mmol, 10% recovered) and unchanged trifluoroiodomethane (3.14 g, 16.0 mmol, 33% recovered) contaminated with small amounts of silicon tetrafluoride, trifluoromethane, and hexafluoroethane; (ii) a volatile fraction (0.61 g, 4.13 mmol; M, 148), shown [g.l.c. (8 m TXP at 40 °C)] to contain six components in the ratio 15 : 8 : 12 : 8 : 18 : 1 and which was separated by g.l.c. (4 m TXP at 20 °C) into its individual components identified as 2-trifluoromethylbutane (3) * (0.14 g, 1.15 mmol, 4%) (Found: C, 47.4; H, 7.1; F, 44.8. $C_5H_9F_3$ requires C, 47.6; H, 7.2; F, 45.2%), M 126, b.p. 43 °C, 3-trifluoro-

methylbut-1-ene * (5) (0.08 g, 0.63 mmol, 2.5%) (Found: C, 48.1; H, 5.8. $C_5H_7F_3$ requires C, 48.4; H, 5.6%), M 124, b.p. 44 °C, a 1 : 1 mixture of (E)- and (Z)-2-trifluoromethylbut-2-ene (6) * (0.12 g, 0.94 mmol, 3.5%) (Found: C, 48.6; H, 5.8%), M 124, b.p. 44 °C, (E)-1,1,1-trifluoro-4-trifluoromethylpent-2-ene (7) * (0.08 g, 0.42 mmol, 1.5%) (Found: C, 37.3; H, 3.4. $C_6H_6F_6$ requires C, 37.5; H, 3.1%), M 192, b.p. 76.5 °C, 1,1,1-trifluoro-4-trifluoromethylpentane (8) * (Found: C, 37.4; H, 4.3; F, 59.0. $C_6H_6F_6$ requires C, 37.5; H, 3.1; F, 58.7%), M 194, b.p. 80 °C, and (E)-5,5,5-trifluoro-2-trifluoromethylpent-2-ene (9) * (0.01 g, 0.05 mmol, <0.5%), M 192; and (iii) a higher-boiling fraction (5.75 g, 21.9 mmol; M 262), shown [g.l.c. (8 m TXP at 115 °C)] to contain five components in the ratio 28 : 1 : 10 : 36 : 8, and which was separated by g.l.c. (4 m DNP at 110 °C) into its individual components identified as threo-2-iodo-3-trifluoromethylbutane (1a) * (1.96 g, 7.80 mmol, 29%) (Found: C, 24.0; H, 3.3. $C_5H_8F_3I$ requires C, 23.8; H, 3.2%), M 252, b.p. 130 °C, a component of molecular formula $C_5H_6F_3I$ (0.05 g, 0.2 mmol, 1%), M 250, 1,1,1-trifluoro-3-iodo-4-trifluoromethylpentane (diastereoisomer 1) (10a) * (0.68 g, 2.16 mmol, 8%) (Found: C, 22.8; H, 2.4. $C_6H_7F_6I$ requires C, 22.5; H, 2.2%), M 320, b.p. 133 °C, erythro-2-iodo-3-trifluoromethylbutane (1b) * (2.52 g, 10.0 mmol, 37%) (Found: C, 24.1; H, 3.2; F, 22.2. $C_5H_8F_3I$ requires C, 23.8; H, 3.2; F, 22.6%), M 252, b.p. 134 °C, and 1,1,1-trifluoro-3-iodo-4-trifluoromethylpentane (diastereoisomer 2) (10b) * (0.56 g, 1.77 mmol, 6.5%) (Found: C, 23.1; H, 2.6%; M, 320), b.p. 138 °C.

A small amount of iodine and tar remained in the reaction tube; this was not investigated further.

(b) With (Z)-but-2-ene under photochemical conditions (static tube). A mixture of the olefin (2.01 g, 36.0 mmol) and trifluoroiodomethane (9.40 g, 48.0 mmol) on irradiation in vacuo (164 h) gave, after treatment of the volatile products with mercury to remove iodine, (i) a mixture (2.76 g, 17.7 mmol; M 156) of unchanged (Z)-but-2-ene (0.28 g, 5.0 mmol, 14% recovered) and unchanged trifluoroiodomethane (2.45 g, 12.5 mmol, 26% recovered) contaminated with small amounts of (E)-but-2-ene, silicon tetrafluoride, trifluoromethane, and hexafluoroethane, (ii) a mixture (1.23 g, 8.55 mmol; M, 144) of (3), (5), (6), (7), (8), and (9) in the ratio 20 : 10 : 16 : 5 : 22 : 1 (g.l.c., 8 m TXP at 40 °C), and (iii) a mixture (5.70 g, 21.5 mmol; M 265) of (1a), $C_5H_6F_3I$, (10a), (1b) and (10b) present in the ratio 88 : 1 : 15 : 103 : 16 (g.l.c., 8 m TXP at 115 °C).

(c) With (E)-but-2-ene under photochemical conditions (static tube). A mixture of the olefin (14.78 g, 0.264 mol) and trifluoroiodomethane (73.52 g, 0.377 mol), sealed in vacuo in seven silica tubes (capacity ca. 2 100 cm³) and irradiated (112 h) and the volatile products treated with mercury to remove iodine, gave (i) a mixture (22.9 g, 0.140 mol; M 163) of unchanged (E)-but-2-ene (1.68 g, 30.0 mmol, 11% recovered) and unchanged trifluoroiodomethane (19.60 g, 100.0 mmol, 27% recovered) contaminated with small amounts of (Z)-but-2-ene, silicon tetrafluoride, trifluoromethane, and hexafluoroethane, (ii) a mixture (8.53 g, 64.5 mmol; M 132) of (3), (5), (6), (7), (8), and (9) present in the ratio 17 : 5 : 1 : 1 : 3 : trace (g.l.c., 8 m TXP at 40 °C), and (iii) a mixture (41.80 g, 0.162 mol) of (1a), (10a), (1b), and (10b), present in the ratio 7 : 1 : 11 : 2 (g.l.c., 8 m TXP at 115 °C).

(d) With (E)-but-2-ene under photochemical conditions (tube shaken). A mixture of the olefin (2.01 g, 36.0 mmol) and trifluoroiodomethane (9.40 g, 48.0 mmol), on irradiation

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* Spectroscopic data for compounds marked with an asterisk are available as Supplementary Publication No. SUP 22736 (8 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in J.C.S. Perkin I, 1979, Index issue.

in vacuo with the tube shaken continuously (168 h) and the volatile products treated with mercury to remove iodine, gave (i) a mixture (2.48 g, 15.0 mmol; M 165) of unchanged (E)-but-2-ene (0.18 g, 3.2 mmol, 9% recovered) and unchanged trifluoroiodomethane (2.20 g, 11.3 mmol, 24% recovered) contaminated with small amounts of (Z)-but-2-ene, silicon tetrafluoride, trifluoromethane, and hexafluoroethane, (ii) a mixture (2.36 g, 18.04 mmol; M 131) of (3), (5), (6), (7), (8), and (9), present in the ratio 90 : 1 : 3 : 2 : 9 : 1 (g.l.c., 8 m TXP at 40 °C), and (iii) a mixture (2.67 g, 10.38 mmol) of (1a), $C_5H_6F_3I$, (10a), (1b), and (10b), present in the ratio 14 : 1 : 1 : 6 : 1 (g.l.c., 8 m TXP at 115 °C).

(e) *With* (Z)-*but-2-ene under thermal conditions*. A mixture of the olefin (3.12 g, 56.0 mmol) and trifluoroiodomethane (31.4 g, 0.160 mol), sealed in four tubes (*ca.* 1 200 cm³) and heated *in vacuo* at 200 °C (13 h) and the volatile product treated with mercury to remove iodine, gave (i) a mixture (26.0 g, 0.152 mol; M 170) of unchanged (Z)-but-2-ene (1.52 g, 27.0 mmol, 48% recovered) and unchanged trifluoroiodomethane (23.1 g, 0.118 mol, 74% recovered) contaminated with small amounts of (E)-but-2-ene, trifluoromethane, and hexafluoroethane, (ii) a mixture (1.30 g, 10.5 mmol; M 125) of (3) (1.14 g, 9.0 mmol, 31%), (4) (trace), (5) (0.05 g, 0.40 mmol, 1.5%), (6) (0.05 g, 0.40 mmol, 1.5%), and two unidentified components (*ca.* 0.6 mmol, *ca.* 2%) present in the ratio 96 : trace : 4 : 4 : 3 : 3 (g.l.c., 8 m TXP at 40 °C), and (iii) a mixture (3.52 g, 13.97 mmol) of four components in the ratio 13 : 2 : 8 : 3 which were separated by g.l.c. (8 m TXP at 115 °C) and identified as (1a) (1.77 g, 7.04 mmol, 24.5%), 1,1,1-*trifluoro*-3-*iodopentane* (2) * (0.28 g, 1.10 mmol, 4%) (Found: C, 23.8; H, 3.3%. $C_5H_8F_3I$ requires C, 23.8; H, 3.2%), M 252, b.p. 133 °C, (1b) (1.08 g, 4.29 mmol, 15%), and 1,1,1-*trifluoro*-4-*iodopentane* (11) * (0.39 g, 1.54 mmol, 5.5%) (Found: C, 24.1; H, 3.2%), M 252, b.p. 135 °C.

A residue of iodine and carbonaceous material which remained in the tubes was not examined further.

(f) *With* (E)-*but-2-ene under thermal conditions*. A mixture of the olefin (3.36 g, 60.0 mmol) and trifluoroiodomethane (31.2 g, 0.160 mol), sealed in four tubes (*ca.* 1 200 cm²) and heated at 200 °C (13 h) and the volatile products treated with mercury to remove iodine, gave (i) a mixture (27.6 g, 0.166 mol; M 167) of unchanged (E)-but-2-ene (1.91 g, 34.0 mmol, 51% recovered) and unchanged trifluoroiodomethane (23.1 g, 0.118 mol, 74% recovered) contaminated with small amounts of (Z)-but-2-ene, trifluoromethane, and hexafluoroethane, (ii) a mixture (0.66 g, 5.22 mmol; M 126) of (3), (4), (5), and (6) present in the ratio 60 : 6 : 1 : trace [g.l.c. (8 m TXP at 40 °C)], and (iii) a mixture (4.09 g, 16.25 mmol) of (1a), (2), (1b), and (11) present in the ratio 14 : 1 : 5 : trace [g.l.c. (8 m TXP at 115 °C)].

(g) *With but-1-ene under photochemical conditions (static tube)*. A mixture of the olefin (2.80 g, 50.0 mmol) and trifluoroiodomethane (16.8 g, 86.0 mmol), irradiated *in vacuo* (164 h) and the volatile products treated with mercury to remove iodine, gave (i) a mixture (7.60 g, 40.4 mmol; M 188) of unchanged but-1-ene (0.11 g, 1.95 mmol, 4% recovered) and unchanged trifluoroiodomethane (7.44 g, 38.0 mmol, 44% recovered), contaminated with small amounts of silicon tetrafluoride, trifluoromethane, and hexafluoroethane [i.r. and g.l.c. (4 m TXP at 20 °C)], (ii) a volatile fraction (1.44 g, 11.4 mmol; M 127) which was separated by g.l.c. (8 m TXP at 40 °C) into its three components (ratio 1 : 5 : 5) which were identified as (3) (0.13 g,

1.04 mmol, 2%), (4) (0.65 g, 5.15 mmol, 10.5%), and a mixture, $C_5H_7F_3$, M 124, of 1,1,1-trifluoropent-2-ene (12) * (0.33 g, 2.60 mmol, 5%) and (E)- and (Z)-1,1,1-trifluoropent-3-ene (13) * (0.33 g, 2.60 mmol, 5%), and (iii) a mixture (8.66 g, 34.5 mmol) which was separated by g.l.c. (8 m TXP at 115 °C) into its six components (ratio 1 : 3 : 68 : 5 : 4 : 4) identified as 2-iodobutane (14) (0.10 g, 0.55 mmol, 1%), (1a) (0.30 g, 1.19 mmol, 2.5%), (2) (6.94 g, 27.5 mmol, 57%), 1-*iodo*-2-*trifluoromethylbutane* (15) * (0.51 g, 2.1 mmol, 4.5%) (Found: C, 23.9; H, 3.2. $C_5H_8F_3I$ requires C, 23.8; H, 3.2%), M 252, b.p. 133 °C, (1b) (0.40 g, 1.6 mmol, 3.5%), and (11) (0.40 g, 1.6 mmol, 3.5%). A residue of iodine and tar which remained in the tube was not examined further.

(h) *With but-1-ene under photochemical conditions (tube shaken)*. A mixture of the olefin (2.80 g, 50.0 mmol) and trifluoroiodomethane (16.8 g, 86.0 mmol), irradiated *in vacuo* (164 h) and the volatile products treated with mercury, gave (i) a mixture (8.24 g, 46.0 mmol; M 180) of unchanged but-1-ene (0.22 g, 4.0 mmol, 8% recovered) and trifluoroiodomethane (7.84 g, 40.0 mmol, 46% recovered) contaminated with small amounts of silicon tetrafluoride, trifluoromethane, and hexafluoroethane. (ii) a mixture (2.78 g, 21.8 mmol; M 126) of (4) and (12) + (13) in the ratio 2 : 3 [g.l.c. (8 m TXP at 40 °C)], and (iii) a mixture (4.80 g, 21.1 mmol) of (14), (1a), (2), (15), (1b) and (11) in the ratio 18 : 1 : 8 : trace : 2 : 20 [g.l.c., (8 m TXP at 115 °C)].

(i) *With but-1-ene under thermal conditions*. A mixture of the olefin (0.84 g, 15.0 mmol) and trifluoroiodomethane (7.84 g, 40.0 mmol), heated at 200 °C (90 h) and the volatile products treated with mercury, gave (i) a mixture (7.01 g, 41.0 mmol; M 171) of unchanged but-1-ene (0.41 g, 7.3 mmol, 49% recovered) and unchanged trifluoroiodomethane (6.08 g, 31.0 mmol, 77% recovered) contaminated with small amounts of trifluoromethane and hexafluoroethane, (ii) a mixture (0.35 g, 2.81 mmol; M 125) of (3), (6), (4), and (12) + (13) in the ratio 16 : 10 : 38 : 36 [g.l.c. (8 m TXP at 40 °C)], and (iii), a mixture (1.14 g, 4.44 mmol) of (1a), (2), (15), and (1b) in the ratio 4 : 13 : 1 : 2 [g.l.c. (8 m TXP at 115 °C)].

Dehydroiodination Reactions.—(a) threo-2-*Iodo*-3-*trifluoromethylbutane* (1a). The iodoalkane (0.21 g, 0.84 mmol) was condensed onto an excess of dry powdered potassium hydroxide (5 g) *in vacuo* and heated at *ca.* 70 °C (10 min) to give 2-trifluoromethylbut-2-ene (6a) (0.098 g, 0.79 mmol, 99%), $C_5H_7F_3$, M 124, as a mixture of the (E)-(6a) and (Z)- (6b) isomers in the ratio 5 : 95 (n.m.r.), and unchanged iodoalkane (0.01 g, 0.40 mmol, 5% recovered).

(b) erythro-*Isomer* (1b). Treatment of the iodoalkane (0.15 g, 0.59 mmol) with potassium hydroxide under the same conditions gave a mixture (0.07 g, 0.55 mmol, 98%; M 124) of the isomers (6a) and (6b) in the ratio 95 : 5 (n.m.r.) and unchanged (1b) (0.01 g, 0.025 mmol, 5% recovered).

Reduction with Anhydrous Hydrogen Iodide.—(a) threo-2-*Iodo*-3-*trifluoromethylbutane* (1a). The iodoalkane (0.25 g, 1.0 mmol) and anhydrous hydrogen iodide (0.26 g, 2.0 mmol), sealed *in vacuo* in a Pyrex tube (*ca.* 20 cm³) and heated at 200 °C (24 h) and the volatile products treated with mercury at room temperature (2 h) to remove iodine, gave (i) hydrogen (0.5 mmol), (ii) 2-trifluoromethylbutane (3) (0.12 g, 0.93 mmol, 99%), $C_5H_9F_3$, M 126, (iii) unchanged (1a) (0.02 g, 0.07 mmol, 70% recovered), and (iv) a residue of iodine (0.22 g).

(b) erythro-*Isomer* (1b). Treatment of isomer (1b) (0.31 g, 1.12 mmol) with hydrogen iodide (0.26 g, 2.0 mmol) under the same conditions gave (i) hydrogen (0.40 mmol), (ii) (3)

(0.13 g, 1.01 mmol, 100%; M 126), (iii) unchanged (1b) (0.03 g, 0.11 mmol, 10% recovered), and (iv) a residue of iodine (0.24 g).

(c) *A mixture of 2-iodo-3-trifluoromethylbutane* (1) *and 1,1,1-trifluoro-3-iodo-4-trifluoromethylpentane* (10). A mixture of the iodoalkanes (1a) and (1b) (3.84 g, 15.3 mmol, ratio 9 : 10) and (10a) and (10b) (1.03 g, 3.21 mmol), treated with hydrogen iodide (3.84 g, 30.0 mmol) under the same conditions (8 h), gave (i) hydrogen (5.2 mmol), (ii) (3) [1.90 g, 15.1 mmol, 99% based on (1)], (iii) 1,1,1-trifluoro-4-trifluoromethylpentane (8) [0.59 g, 3.05 mmol, 95% based on (10)], $C_6H_8F_6$, M 194, and (iv) a residue of iodine (2.2 g).

(d) *A mixture of 2-iodo-3-trifluoromethylbutane* (1), *1,1,1-trifluoro-3-iodopentane* (2), *and 1,1,1-trifluoro-4-iodopentane* (11). A mixture of the iodoalkanes (1a) and (1b) (3.00 g, 11.9 mmol, ratio 9 : 10), (2) (27.60 g, 109.5 mmol), and (11) (1.60 g, 6.3 mmol), treated with hydrogen iodide (23.1 g, 180.0 mmol) in a Pyrex tube (*ca.* 300 cm³) under the same conditions (12 h), gave (i) hydrogen (28.0 mmol), (ii) a mixture (16.38 g, 126.0 mmol), which was shown [g.l.c. (8 m-TXP at 40 °C) and n.m.r. spectroscopy] to consist of 2-trifluoromethylbutane (3) [1.38 g, 11.0 mmol, 92% based on (1)] and 1,1,1-trifluoropentane (4) [15.0 g, 115.0 mmol, 99% based on (2 + 11)], and (iii) a residue of iodine.

Pyrolysis of 2-Iodo-3-trifluoromethylbutane.—(a) threo-*Isomer* (1a). The iodoalkane (0.30 g, 1.17 mmol), heated *in vacuo* in a Pyrex tube (*ca.* 15 cm³) at 260 °C (40 h) and

the volatile product treated with mercury, gave 2-trifluoromethylbutane (3) (0.07 g, 0.55 mmol, 47%; M 126) and a residue of iodine and carbonaceous material.

(b) erythro-*Isomer* (1b). The iodoalkane (0.25 g, 0.98 mmol), heated under the same conditions, gave (3) (0.08 g, 0.63 mmol, 64%; M 126) and a residue of iodine and carbaceous material.

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