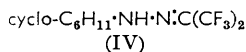#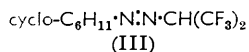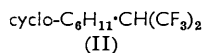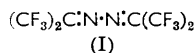 Unsaturated Nitrogen Compounds containing Fluorine. Part II.[1] The Reactions of Hexafluoroacetone Azine with cis- or trans-But-2-ene and Cyclohexene [2]

By T. P. Forshaw and A. E. Tipping,* Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Hexafluoroacetone azine reacts with but-2-ene or cyclohexene under thermal conditions to give products formally derived from the intermediacy of bis(trifluoromethyl)carbene. Thus cis- or trans-but-2-ene afford a mixture of cis- and trans-2,3-dimethyl-1,1-bis(trifluoromethyl)cyclopropane in the ratio ca. 1:4 and cyclohexene gives 7,7-bis(trifluoromethyl)norcarane and the allylic insertion compound, 3-(2,2,2-trifluoro-1-trifluoromethylethyl)-cyclohexene, in the ratio ca. 2:5. Pyrolysis of the trans-cyclopropane gives 1,1,1-trifluoro-2-methyl-2-trifluoromethylpent-2-ene and 1,1-bis(trifluoromethyl)propa-1,2-diene among the products.

HEXAFLUOROACETONE AZINE (I) has been observed [1,2] to react with acetylene under thermal conditions and with hydrocarbon terminal olefins under thermal or photochemical conditions to afford 2 : 1 adducts (acetylene or olefin to azine) (>50%) formed by criss-cross addition; electron-deficient olefins or acetylenes did not react under comparable conditions.

It has also been reported [3] that the azine (I) reacts with cyclohexane at 160° to give nitrogen and the insertion product 2,2,2-trifluoro-1-trifluoromethylethylcyclohexane (II) (40%); benzene did not react under comparable conditions. Later work [4] showed that cyclohexane reacts to afford three major products: (II) (36—71%), the azo-compound (III) (11—17%), and the hydrazone (IV) (3—18%), in relative yields depending on the conditions. A radical double-chain mechanism was proposed.

$$(CF_3)_2C{:}N{\cdot}N{:}C(CF_3)_2$$
$$(I)$$

$$cyclo\text{-}C_6H_{11}{\cdot}N{:}N{\cdot}CH(CF_3)_2$$
$$(III)$$

$$cyclo\text{-}C_6H_{11}{\cdot}CH(CF_3)_2$$
$$(II)$$

$$cyclo\text{-}C_6H_{11}{\cdot}NH{\cdot}N{:}C(CF_3)_2$$
$$(IV)$$

In a continuation of an investigation into the chemistry

The cyclopropanes (V) and (VI) have been prepared previously [5] by the reaction of bis(trifluoromethyl)-

$$(CF_3)_2CH_2 \qquad (CF_3)_2C{:}CHMe$$
$$(VII) \qquad (VIII)$$
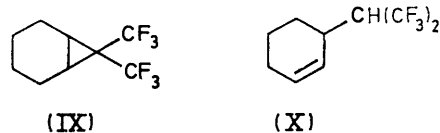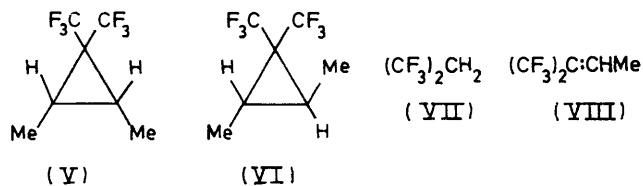
diazomethane (XI) or bis(trifluoromethyl)diazirine (XII) with the but-2-enes, and the products (IX) and (X) have

$$(CF_3)_2CN_2 \qquad (CF_3)_2C{\cdot}N{:}N$$
$$(XI) \qquad (XII)$$

Olefin	Molar ratio olefin : azine	Conditions	Recovered azine (%)	Recovered olefin (%)	Products (%)			
						(CF₃)₂C–Olefin adducts *		
					N_2	Cyclopropanes	Insertion	Others †
trans-CHMe:CHMe	2 : 1	Heat		33	70	(V) (6, 10) (VI) (26, 39)		(VII) (8) (VIII) (3)
trans-CHMe:CHMe	2 : 1	U.v.	81	96	29	(V) (1·5, 6) (VI) (6, 29)		
cis-CHMe:CHMe	1 : 1	Heat	3	21 ‡	44	(V) (6, 15) (VI) (26, 63)		(VII) (8)
CH₂·CH₂·CH:CH·CH₂·CH₂	2 : 1	Heat	6	40	51	(IX) (9, 14)	(X) (22, 35)	(VII) (18)

* The two yields given are based on (i) azine reacted, assuming azine (1 mol) gives $(CF_3)_2C{:}$ (2 mol), and (ii) olefin reacted, respectively.   † Yields based on azine reacted.   ‡ Mixture of cis- and trans-olefin in ratio ca. 3 : 5.

of the azine (I) its reaction with three hydrocarbon internal olefins under thermal conditions and with trans-but-2-ene under photochemical conditions are now reported. The results are summarised in Table 1.

[1] Part I, T. P. Forshaw and A. E. Tipping, J. Chem. Soc. (C), 1971, 2404.
[2] Preliminary communication, T. P. Forshaw and A. E. Tipping, Chem. Comm., 1969, 816.

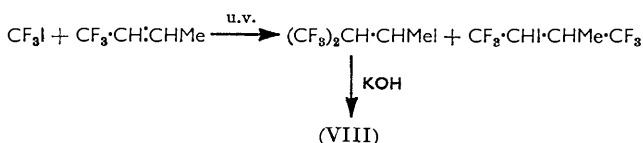been prepared by the reaction of (XII) with cyclohexene.[5]

1,1,1,3,3,3-Hexafluoropropane (VII) was identified by

[3] W. J. Middleton, D. M. Gale, and C. G. Krespan, J. Amer. Chem. Soc., 1968, 90, 6813.
[4] W. J. Middleton, J. Amer. Chem. Soc., 1971, 93, 423.
[5] D. M. Gale, W. J. Middleton, and C. G. Krespan, J. Amer. Chem. Soc., 1966, 88, 3617.

a comparison of its n.m.r. spectra with those obtained [6] previously and 1,1,1-trifluoro-2-trifluoromethylbut-2-ene (VIII) has been prepared previously by the illustrated route.[7] This olefin, isolated from the thermal reaction

$$CF_3I + CF_3\cdot CH\!:\!CHMe \xrightarrow{u.v.} (CF_3)_2CH\cdot CHMeI + CF_3\cdot CHI\cdot CHMe\cdot CF_3$$

$$\downarrow KOH$$

(VIII)

with *trans*-but-2-ene, probably arose by decomposition of the criss-cross adduct (XIII) formed in small amount. Such adducts, formed by reaction of the azine (I) with terminal olefins, $CH_2\!:\!CHR$ ($R = H$, Me, or Et), are observed to decompose at a temperature (*ca.* 210°) only slightly higher than that (190°) employed in the present reaction.[1]

$$(I) + CHMe\!:\!CHMe \longrightarrow$$

(XIII)

$$heat \downarrow$$

$$2(CF_3)_2C\!:\!CHMe + [MeCH\!:\!N\cdot N\!:\!CHMe]$$
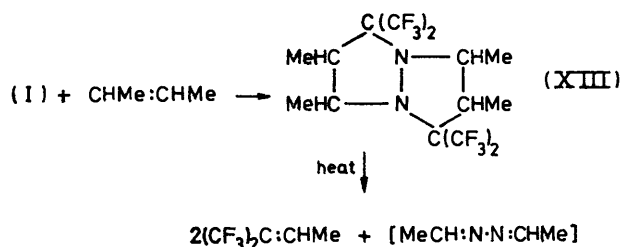
Mechanism of Reaction of the Azine (I) *with Internal Olefins.*—The reactions all gave considerable amounts of involatile brown oils, nitrogen (29—70%), and products formally derived from the reaction of bis-(trifluoromethyl)carbene with the olefins. However, the carbene [or its precursors (XI) or (XII)] is not formed by direct decomposition of the azine (I); the latter is stable when heated alone to 240°. At higher temperatures (570°) it decomposes to give trifluoroacetonitrile (2 parts) and hexafluoroethane (1 part) rather than products expected if the carbene were formed as an intermediate.[8] The azine is reported also not to react with carbon tetrachloride under conditions where the diazirine (XII) reacts to afford the carbene insertion product, $(CF_3)_2CCl\cdot CCl_3$.[4]

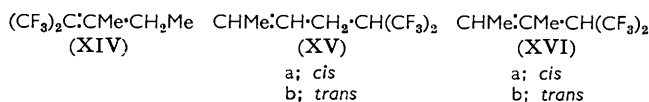TABLE 2

Reaction of carbene precursors with the but-2-enes

Olefin	Carbene precursor	Total product (%)	Products (% relative yields)
cis- *	(XI)	57	(V) (39); (VI) (8); (XIV) (49)
trans-	(XI)	53	(VI) (100)
cis-	(XII)		(V) (55); (VI) (8); (XIV) (2); (XVa) (27); (XVIa) (8)
trans-	(XII)		(VI) (57); (XVb) (39); (XVIb) (4)

* Recovered olefin contained <1·5% of *trans*-isomer.

There remains the possibility that the carbene, perhaps *via* its precursor (XI) or (XII), is formed by a secondary reaction. However, the reported reactions [5] of the carbene precursors (XI) and (XII) with the but-2-enes gave products (Table 2) which differ considerably

from those observed in the present work. The differences in the products of the present reactions, *i.e.* (i) isomeris-

$$\underset{\text{(XIV)}}{(CF_3)_2C\!:\!CMe\cdot CH_2Me} \quad \underset{\substack{\text{(XV)}\\ \text{a; } cis\\ \text{b; } trans}}{CHMe\!:\!CH\cdot CH_2\cdot CH(CF_3)_2} \quad \underset{\substack{\text{(XVI)}\\ \text{a; } cis\\ \text{b; } trans}}{CHMe\!:\!CMe\cdot CH(CF_3)_2}$$

tion of *cis-* to *trans*-olefin, (ii) exclusive formation of cyclopropanes (V) and (VI), (iii) formation of cyclopropanes (V) and (VI) in the ratio *ca.* 1 : 4 irrespective

$$(I) \xrightarrow{\text{MeCH:CHMe}}$$

(XVII)

$$\text{MeCH:CHMe} \downarrow$$

(XVIII)
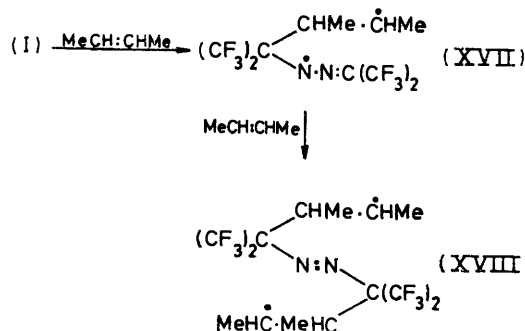
of reactant olefin isomer, and (iv) isolation of the propane (VII), can be explained by two alternative mechanisms. Either (*a*) bis(trifluoromethyl)carbene is formed by secondary reactions, but its reactivity is modified compared to that reported or, more likely, (*b*) the products arise mainly by radical reactions. In support of the latter mechanism it has been shown that the reaction of the azine (I) with cyclohexane under comparable conditions takes place mainly by a radical mechanism, and bis(trifluoromethyl)carbene is involved only in a minor capacity.[4]

The reaction of the azine (I) with the but-2-enes is thus considered to involve the formation of a diradical (XVII), which reacts further with a second molecule of olefin to afford the diradical (XVIII) rather than decomposing to give the diazoalkane (XI) and a mixture of the cyclopropanes (V) and (VI).


(XIX)   (XX)
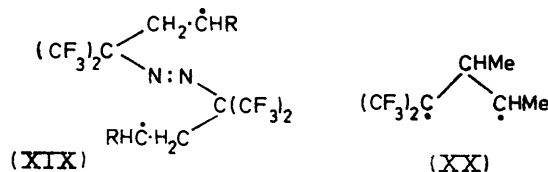
Diradicals similar to (XVIII), *i.e.* of type (XIX), formed by reaction of the azine (I) with terminal olefins, are possible precursors of the criss-cross adducts. With diradical (XVIII) ring closure is not favoured relative to decomposition because of steric interactions. Decomposition of the diradical could occur to give nitrogen and either the diradical (XX) or a mixture of cyclopropanes (V) and (VI). The two diradicals of structure (XX) [the *cis-* (XXa) and *trans-* (XXb) isomers] have been proposed as intermediates in the reactions of the

[6] D. D. Elleman, L. C. Brown, and D. Williams, *J. Mol. Spectroscopy*, 1961, **7**, 393; R. N. Haszeldine, J. R. McAllister, and A. E. Tipping, unpublished results.

[7] R. Gregory, R. N. Haszeldine, and A. E. Tipping, *J. Chem. Soc. (C)*, 1971, 1216.

[8] T. P. Forshaw and A. E. Tipping, unpublished results.

diazoalkane (XI) with *cis*- and *trans*-but-2-ene, respectively.[5] The diradicals react, as shown in the Scheme, to give products different from those observed in the present work.


SCHEME
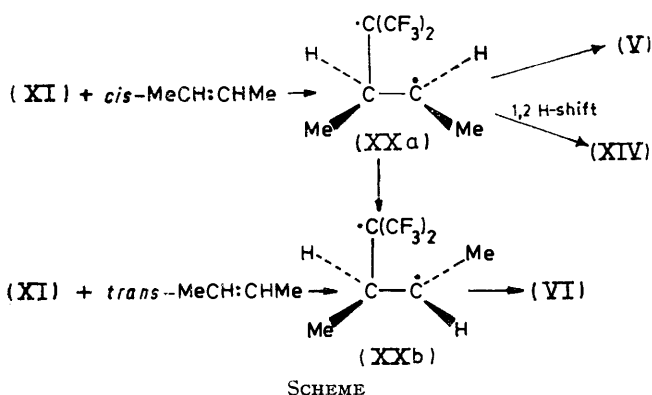
Diradical (XVIII), which is considered to be a mixture of the diradical with *trans*-vicinal methyl groups and that with *cis*-vicinal methyl groups in the ratio *ca.* 4 : 1, then decomposes, either in the two-step manner shown or alternatively by a one-step concerted mechanism, to afford nitrogen and a mixture of the cyclopropanes (VI) and (V) in the ratio *ca.* 4 : 1.
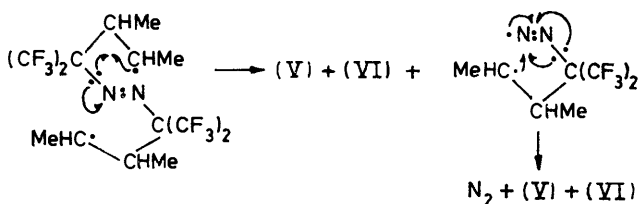
The observed isomerisation of *cis*- to *trans*-but-2-ene, which does not take place in the absence of azine (I), probable occurs *via* reversible formation of the diradical (XVII).

The formation of the other observed product, the propane (VII), probably involves the intermediacy of $(CF_3)_2CH\cdot$ radicals. These radicals could be formed *via* hydrogen abstraction reactions involving the azine (I) and the allylic hydrogen atoms present in the but-2-enes.

The reaction of the diazoalkane (XI) with cyclohexene has not been reported, although the diazirine (XII) reacts to give the norcarane (IX), the insertion product (X), and the vinylic insertion product (XXI), in the ratio 47 : 44 : 9.[5] In the present work compound (XXI) was not observed.

$(CF_3)_2CH\cdot C\!:\!CH\cdot[CH_2]_3\cdot CH_2$
(XXI)
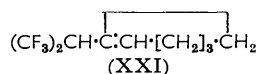
Adduct (IX) is considered to arise by a mechanism analogous to that proposed for cyclopropane formation from the but-2-enes.

The insertion product (X) could be formed *via* an allylic hydrogen abstraction reaction which is more favourable with cyclohexene (secondary allylic C–H

bonds) than with the but-2-enes (primary allylic C–H bonds).
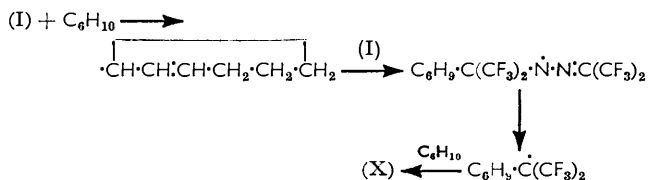
In accordance with this the yield of the propane (VII) is also higher (18%) than observed from the but-2-ene reactions (8%).

Pyrolysis of the Cyclopropane (IV).—Flow pyrolysis of the cyclopropane at 720° gave 1,1-difluoroethylene and a higher boiling mixture which contained at least eight components (g.l.c.) and from which only the major and one of the minor components could be separated. The major component was identified as 1,1,1-trifluoro-3-methyl-2-trifluoromethylpent-2-ene (XIV) by comparison of its n.m.r. spectra with those reported.[5]

The minor component was identified as 1,1-bis(trifluoromethyl)propa-1,2-diene (XXII) by a consideration of spectral evidence. The i.r. spectrum contained a band at 4·99 μm (C:C:C str.), the [19]F n.m.r. spectrum showed one absorption (t) at −16·0 p.p.m. (relative to external $CF_3\cdot CO_2H$) in the region expected for allylic CF_3 groups, and the ^{1}H spectrum showed one absorption (septet) at τ 4·42 in the region expected for vinylic protons. The mass spectrum contained a parent peak at *m/e* 176 and the breakdown pattern was consistent with the proposed structure.

The olefin (XIV) is formed by opening of the cyclopropane ring to give the diradical (XX), in which the lone electrons are situated on a tertiary and a secondary carbon atom, rather than the alternative opening of the ring to give the diradical (XXIII), in which the two lone electrons are each situated on a secondary carbon atom.

$(CF_3)_2C\!:\!C\!:\!CH_2$ $\dot{C}HMe\cdot C(CF_3)_2\cdot\dot{C}HMe$
(XXII)   (XXIII)
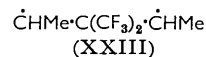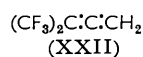
Hydrogen migration in (XX) then gives the olefin (XIV). It has been previously observed that in trifluoromethyl-substituted cyclopropanes the ring cleaves adjacent to a trifluoromethyl group rather than adjacent to a methyl group.[9] As expected, a hydrogen atom migrates in the diradical (XX) rather than a methyl group.[10]

The mechanisms of formation of the allene and of 1,1-difluoroethylene are uncertain. The allene cannot be formed by a concerted loss of ethane from the diradical (XX) because ethane is not one of the products.

EXPERIMENTAL

Techniques used were as described previously.[1] The azine (I) was prepared from the corresponding imine by

[9] D. H. Placzek and B. S. Rabinovitch, *J. Phys. Chem.*, 1965, **69**, 2141.
[10] H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 1963, 5717.

treatment with potassium fluoride and bromine [11] to give the *N*-bromo-imine which was then photolysed.[12]

Reaction of Hexafluoroacetone Azine (I) *with Olefins.*—(a) *Thermal reaction with* trans-*but-2-ene.* The azine (11·60 g, 35·4 mmol) and the olefin (3·86 g, 70·8 mmol), sealed in a Pyrex tube (*ca.* 300 ml) and heated at 190° (48 h), gave (i) nitrogen (0·70 g, 25·0 mmol, 70%) (Found: *M*, 28); (ii) a mixture (2·18 g, 29·0 mmol; *M*, 75), shown by i.r. spectroscopy to contain unchanged olefin (1·30 g, 23·2 mmol, 33% recovered) and 1,1,1,3,3,3-hexafluoropropane (0·88 g, 5·8 mmol, 8%); (iii) a higher-boiling volatile fraction (5·14 g, 25·3 mmol; *M*, 202) shown by g.l.c. (8m Kel-F 10 oil at 100°) to contain three components in the ratio 9 : 73 : 18; and (iv) an involatile brown oil (6·1 g) which was not investigated further.

The three-component mixture was separated by g.l.c. (as above) into 1,1,1-trifluoro-2-trifluoromethylbut-2-ene (0·41 g, 2·3 mmol, 3%) (Found: *M*, 178. Calc. for $C_5H_4F_6$: *M*, 178), identified by a comparison of its i.r. spectrum with that reported; [7] *trans*-2,3-dimethyl-1,1-bis(trifluoromethyl)-cyclopropane (3·78 g, 18·4 mmol, 26% based on azine, 39% based on olefin) (Found: C, 41·5; H, 4·0%; *M*, 206. Calc. for $C_7H_8F_6$: C, 40·6; H, 3·9%; *M*, 206), b.p. (Siwoloboff) 89—90° (lit.,[5] b.p. 87°), identified by a comparison of its ^{1}H and [19]F n.m.r. spectra with those reported; [5] and *cis*-2,3-dimethyl-1,1-bis(trifluoromethyl)cyclopropane (0·95 g, 4·6 mmol, 6% based on azine, 10% based on olefin) (Found: C, 40·2; H, 4·2%; *M*, 206), b.p. (Siwoloboff) 92·5° (lit.,[5] b.p. 95·5°), identified by a comparison of its ^{1}H and [19]F n.m.r. spectra with those reported.[5]

The *trans*-cyclopropane did not isomerise, even partially, to the *cis*-isomer at 195° (24 h).

(b) *Photochemical reaction with* trans-*but-2-ene.* The azine (7·20 g, 22·0 mmol) and *trans*-but-2-ene (2·44 g, 44·0 mmol), sealed in a silica tube (*ca.* 300 ml) and irradiated with a Hanovia S500 lamp at a distance of 30 cm (48 h) then at a distance of 4 cm (96 h), gave (i) nitrogen (0·03 g, 1·2 mmol, 29%) (Found: *M*, 28); (ii) unchanged but-2-ene (2·35 g, 42·0 mmol, 96% recovered); and (iii) a higher-boiling fraction (5·96 g, 18·5 mmol; *M*, 310) which was shown by g.l.c. (as before) to consist of unchanged azine (5·82 g, 17·8 mmol, 81% recovered) and a mixture of *cis*- and *trans*-2,3-dimethyl-1,1-bis(trifluoromethyl)cyclopropane (0·14 g, 0·7 mmol, 8% based on azine, 35% based on olefin) in the approximate ratio 1 : 5.

A small amount of an involatile brown oil remained in the reaction tube.

(c) *Thermal reaction with* cis-*but-2-ene.* The azine (1·64 g, 5·0 mmol) and *cis*-but-2-ene (0·28 g, 5·0 mmol), treated as in experiment (a) at 190° (60 h), gave (i) nitrogen (0·06 g, 2·1 mmol, 44%); (ii) a mixture (0·10 g, 1·3 mmol) (Found: *M*, 76) which was shown by i.r. spectroscopy and g.l.c. [4 m dimethylsulpholan (DMS) at 22°] to consist of *cis*- and *trans*-but-2-ene (0·06 g, 1·0 mmol, 21%) in the ratio *ca.* 3 : 5 and 1,1,1,3,3,3-hexafluoropropane (0·04 g, 0·3 mmol, 3%); (iii) a higher-boiling fraction (0·69 g, 3·3 mmol; *M*, 210) which was shown by g.l.c. (8 m Kel-F 10 oil at 100°) to consist of unchanged azine (0·05 g, 0·2 mmol, 3% recovered), *trans*-2,3-dimethyl-1,1-bis(trifluoromethyl)cyclopropane (0·51 g, 2·5 mmol, 26% based on azine, 63% based on olefin), and *cis*-2,3-dimethyl-1,1-bis(trifluoromethyl)cyclopropane

(0·13 g, 0·6 mmol, 6% based on azine, 15% based on olefin); and (iv) an involatile brown oil (0·8 g).

It was shown by i.r. spectroscopy and g.l.c. (4 m DMS at 25°) that *cis*-but-2-ene did not isomerise at 190° (36 h).

(d) *Thermal reaction with cyclohexene.* The azine (5·80 g, 17·7 mmol) and cyclohexene (2·90 g, 35·4 mmol), treated as in experiment (a) at 180° (96 h), gave (i) nitrogen (0·26 g, 8·5 mmol, 51%); (ii) 1,1,1,3,3,3-hexafluoropropane (0·94 g, 6·1 mmol, 18%) (Found: *M*, 154. Calc. for $C_3H_2F_6$: *M*, 152); (iii) a higher-boiling fraction (3·90 g) which was separated by g.l.c. (4 m Silicone MS550 oil at 120°) into its four components: unchanged azine (0·33 g, 1·0 mmol, 6% recovered), unchanged cyclohexene (1·17 g, 14·3 mmol, 40% recovered), 3-(2,2,2-trifluoro-1-trifluoromethylethyl)-cyclohex-1-ene (1·71 g, 7·4 mmol, 22% based on azine, 35% based on olefin) (Found: *M*, 232. Calc. for $C_9H_{10}F_6$: *M*, 232), identified by a comparison of its ^{1}H and [19]F n.m.r. spectra with those reported,[5] and 7,7-bis(trifluoromethyl)-norcarane (0·69 g, 3·0 mmol, 9% based on azine, 14% based on olefin) (Found: *M*, 232), identified by a comparison of its ^{1}H and [19]F n.m.r. spectra with those reported; [5] and (iv) an involatile brown oil (3·6 g).

Pyrolysis of trans-2,3-*Dimethyl*-1,1-bis(trifluoromethyl)-*cyclopropane.*—The cyclopropane (1·66 g, 8·0 mmol), pyrolysed by passage (30 min) *in vacuo* through a silica tube (heated length 55 cm; i.d. 12 mm) at 720°, gave (i) 1,1-difluoroethylene (0·11 g, 1·7 mmol) (Found: *M*, 65. Calc. for $C_2H_2F_2$: *M*, 64), which was identified by i.r. spectroscopy; (ii) an unidentified fraction (0·5 mmol), $\lambda_{max.}$ 3·40w (C–H str.), 5·75m (C:C str.), 7·62m, 8·10s, 8·70s, 9·05s, 10·30m, 10·90m, 11·08m, and 14·10m (CF$_3$ def.) μm; and (iii) a higher-boiling fraction (1·43 g) which was shown by g.l.c. (4 m silicone at 60°) to contain at least eight components and from which only two components, the major and one of the minor ones, could be separated. The minor component was identified as 1,1-bis(trifluoromethyl)propa-1,2-diene (*ca.* 0·18 g, *ca.* 1·0 mmol, *ca.* 12%) [Found: *M* (mass spectrometry), 176. Calc. for $C_5H_2F_6$: *M*, 176], $\lambda_{max.}$ 4·99m (C:C:C str.), 6·95w (C–H bend), 7·12w, 7·51s, 7·70s, 7·92m, 8·10m, 8·40vs, 8·60vs, 8·90w, 10·30s, 11·50m, and 14·00m (t, CF$_3$ def.) μm; [19]F n.m.r. band at 16·00 p.p.m. (t, *J* 2·9 Hz) to low field of external trifluoroacetic acid and [1]H n.m.r. band at τ 4·42 (sept, *J* 3·0 Hz); *m/e* 176 (100%, *M*+), 157 [51%, (*M* − F)+], 156 [6%, (*M* − HF)+], 145 (6%, $C_4H_2F_5^+$); 137 [31%, (*M* − HF$_2$)+], 126 [6%, (*M* − CF$_2$)+], 125 [6%, (*M* − CHF$_2$)+], 112 (12%, $C_3F_4^+$), 107 [17%, (*M* − CF$_3$)+], 106 [17%, (*M* − CHF$_3$)+], 100 (6%, $C_2F_4^+$), 93 (6%, $C_3F_3^+$), 88 [26%, (*M* − CF$_4$)+], 87 (12%, $C_4HF_2^+$), 75 (17%, $C_3HF_2^+$), 69 (67%, CF$_3^+$ and $C_4H_2F^+$), 57 (26%, $C_3H_2F^+$), 51 (9%, CHF$_2^+$), 50 (6%, CF$_2^+$), and 38 (20%, $C_3H_2^+$), *m** 119·6 (137^2/157) [$C_5H_2F_5^+$ (157) ⟶ $C_5HF_4^+$ (137) + HF (20)]. The major component was identified as 1,1,1-trifluoro-3-methyl-2-trifluoromethylpent-2-ene (*ca.* 0·54 g, *ca.* 2·6 mmol, *ca.* 33%) (Found: *M*, 205. Calc. for $C_7H_8F_6$: *M*, 206) by a comparison of its i.r. and n.m.r. spectra with those reported.[5]

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