Allene Cycloadditions. Part V.[1] Temperature Dependence of Product Distribution in Alkylallene–Alkyne Reactions

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3-Methylbuta-1,2-diene reacts with hexafluorobut-2-yne at 80° to give a 3:1 mixture of 3,3-dimethyl-4-methylene-1,2-bistrifluoromethylcyclobutene and 3-isopropylidene-1,2-bistrifluoromethylcyclobutene, the product ratio remaining constant up to 150°. (Z)-1,1,1-trifluoro-5-methyl-4-(prop-2-enyl)-2-trifluoromethylhexa-2,4-diene isomerises at 100—140° to give 3,3-dimethyl-2-(prop-2-enyl)-1,4-bistrifluoromethylcyclobutene. The temperature dependence of the product distribution in the reaction between hexafluorobut-2-yne and 2,4-dimethylpenta-2,3-di-ene is reported and discussed.

CYCLOADDITIONS between alkylallenes and alkynes are not common,[2,3] and for this reason are not widely employed to prepare alkylidenecyclobutenes.[4] From a mechanistic viewpoint, however, such cycloadditions are of particular interest, because of their similarity to allene–olefin [2 + 2] cycloadditions, which have been extensively studied and are widely believed to be energetically non-concerted.[5] The supposed intermediates are diradicals, claimed to be formed and converted into products in an orbitally concerted fashion, in order to explain why such two-step reactions are nevertheless stereospecific.[5] It is therefore of interest to ascertain whether acetylene–allene cycloadditions tread the same mechanistic ' tightrope ' or whether the presence of an additional but seemingly non-participating π-bond modifies the reaction profile.

Another interesting feature of reactions between polyalkylallenes and electron-deficient acetylenes is their diversion from cycloaddition to ene-insertion, recent examples of which were found to be non-stereo-specific,[6,7] producing mixtures of (Z)- (I) and (E)-trienes (II) [equation (1)]. These observations have raised

the question of how apparently antarafacial (*i.e.*, *transoid*) additions to the alkyne take place, producing the (E)-isomers.

$$Me_2C:C:CMe_2 + RC:CR \longrightarrow$$ (I) + (II) (1)

a; R = CF_3
b; R = CO_2Me
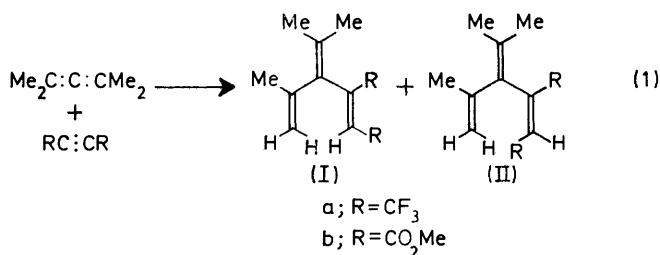
In one of these ene reactions [equation (1), R = CF_3] the products included the cycloadduct (IIIa),[6] an

(III) a; R^1 = R^2 = Me
b; R^1 = Me, R^2 = H
c; R^1 = H, R^2 = Me
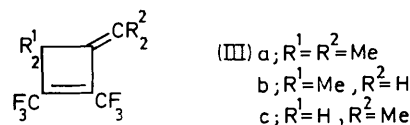
observation which has in the past been taken to indicate that a stepwise mechanism operates, and that in such circumstances all three primary products (two

[1] Part IV, D. R. Taylor and D. B. Wright, *J.C.S. Perkin I*, 1973, 445.

[2] J. D. Roberts and D. E. Applequist, *J. Amer. Chem. Soc.*, 1956, **78**, 4012.

[3] R. E. Banks, W. R. Deem, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.* (C), 1966, 2051.

[4] D. R. Taylor, M. R. Warburton, and D. B. Wright, *J.C.S. Perkin I*, 1972, 1365, and references therein.

[5] J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsh.*, 1970, **15**, 281.

[6] H.-A. Chia, B. E. Kirk, and D. R. Taylor, *J.C.S. Perkin I*, 1974, 1209.

[7] J. C. Martin, P. L. Carter, and J. L. Chitwood, *J. Org. Chem.*, 1971, **36**, 2225.

ene-adducts and one cycloadduct) arise *via* a common intermediate, presumed to be a diradical.[8,9]

During attempts to uncover further examples of non-stereospecific ene-insertions of alkynes into alkyl-allenes, we treated 3-methylbuta-1,2-diene with di-methyl acetylenedicarboxylate and with hexafluorobut-2-yne. The former reaction gave only intractable tar, but the latter yielded two isomeric adducts, both of which arise by [2 + 2] cycloaddition. Subsequently we investigated this reaction and that between the butyne and 2,4-dimethylpenta-2,3-diene reported pre-viously,[6] over a range of temperatures, in an attempt to ascertain whether intermediate diradicals are involved.

Hexafluorobut-2-*yne*-3-*Methylbuta*-1,2-*diene Reaction.*— A smooth reaction occurred when 3-methylbuta-1,2-diene and hexafluorobut-2-yne were kept at 80° in the presence of polymerisation inhibitor. The product consisted of a mixture of 1 : 1 adducts, formed almost quantita-tively, two of which (97%) were isolated by preparative g.l.c.

The most abundant isomer, a liquid, b.p. 92°, evidently contains an exocyclic methylene group [intense C:C str. 1720 and 1710 and CH_2 out-of-plane def. 898 cm^{-1}, τ 4·82—4·96 (2H)], whereas the last-eluted isomer, b.p. 105°, contains an isopropylidene group [weak C:C str. 1733 and 1680 cm^{-1}, τ 8·14—8·27 (6H)]. Both isomers display ^{19}F n.m.r. spectra characteristic of *cis*-$CF_3C:CCF_3$ groups ($^5J_{FF}$ 6—7 Hz).[10] These and their remaining spectroscopic properties are only consistent with structures (IIIb) and (IIIc). Isomer (IIIb) is the more abundant, rather surprisingly in view of the preferential formation of isomers with exocyclic isopropylidene groups analogous to (IIIc) in related cycloadditions between this allene and fluoro-olefins.[11-13]

The effect of temperature upon the isomer ratio was investigated in a very simple manner, using individual point sealed tubes of identical internal volume and con-taining equal amounts of reagents. The reaction was too slow for accurate measurement at 50°, but satis-factory average analyses were obtained at 80—150° (data in Table 1). By-product formation tended to increase at 115—150° and became significant at reaction times longer than 24 h. At the shorter reaction times, no significant variation was observed in the (IIIb) : (IIIc) ratio.

The lack of a pronounced variation in product ratio over a 70° range makes it appear unlikely that the two isomers arise by completely independent pathways, because the different reactivities of the two double bonds in this unsymmetrically substituted allene imply that such pathways would have rather different activation parameters.

[8] P. D. Bartlett, *Science*, 1968, **159**, 833.
[9] H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 556.
[10] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolu-tion Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Per-gamon, London, 1966, p. 871.
[11] H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 2723.

TABLE 1

Average g.l.c. areas of isomers (IIIb) and (IIIc) from the hexafluorobut-2-yne–3-methylbuta-1,2-diene reaction

$T/^\circ C$	t/h	(IIIb) (%)	(IIIc) (%)	By-products (%)	$\frac{(IIIb)}{(IIIc)}$
50	72	<1	<0·1		
80	48	73·0	24·0	3	3·04
115	24	69·5	22·2	8·3	3·13
115	48	61·6	23·9	14·5	2·58
115	72	64·7	23·2	12·1	2·79
150	24	73·3	22·0	4·7	3·33
150	48	64·0	18·0	18·0	3·56
150	72	61·2	17·3	21·5	3·54

A more natural explanation is that the bond to the central carbon atom of the allene forms first, as is believed to be the case in allene–olefin and allene-allene cyclisations.[5] The resulting diradical (IVc) may adopt any of the configurations [(A), (B), or (C)], which equilibrate only if free-rotation is permitted about the first-formed bond; such equilibration is thought *not* to occur in cycloadditions between allenes and olefins,[5] in which the favoured configuration is that corresponding to (B).[14]
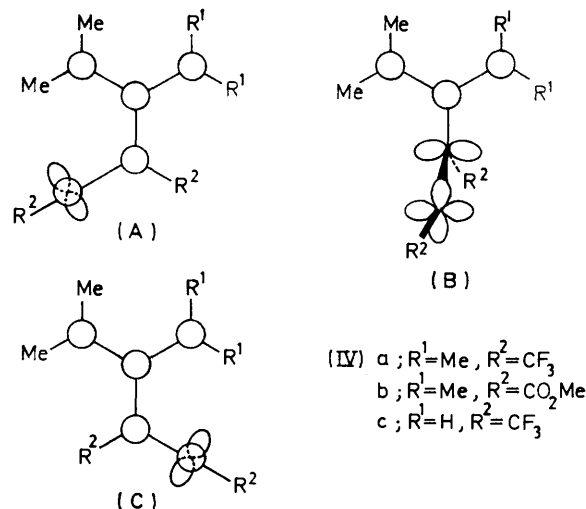
Vinyl radicals are believed to be bent planar species,[15,16] capable of equilibration between *cis*- and *trans*-forms at rates possibly an order of magnitude faster than diffusion controlled processes such as re-combination or abstraction.[17] Each configuration[17] (A)—(C) of (IV) must therefore be viewed as mixtures of (*E*)- and (*Z*)-isomeric diradicals, *i.e.* [R = ($Me_2C \cdots C \cdots CH_2$)·].
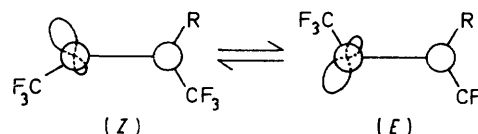
[12] D. R. Taylor, M. R. Warburton, and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 385.
[13] D. R. Taylor and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 391.
[14] J. E. Baldwin and U. V. Roy, *Chem. Comm.*, 1969, 1225.
[15] R. C. Neuman, jun., and G. D. Holmes, *J. Org. Chem.*, 1968, **33**, 4317.
[16] L. A. Singer, *Selective Org. Transformations*, 1972, **2**, 239.
[17] G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, 1971, **93**, 1379.

A MO computation of the most favourable structure for diradicals of this type has not been reported and is obviously desirable.

Hexafluorobut-2-yne–2,4-Dimethylpenta-2,3-diene Reaction.—As recently reported,[6] hexafluorobut-2-yne also reacts readily with the tetra-alkylallene 2,4-dimethylpenta-2,3-diene. At 80° this reaction gives a mixture of three isomers, one of which (IIIa) arises by [2 + 2] cycloaddition and the others (Ia) and (IIa) by suprafacial and antarafacial ene-insertion, respectively.

To test whether (IIa) was a primary reaction product, or a secondary product arising by isomerisation of (Ia), the latter isomer was heated alone. At 140° it yielded not (IIa) but a fourth isomer, equilibrium being achieved after 3 days when 26% (Ia) remained. The new
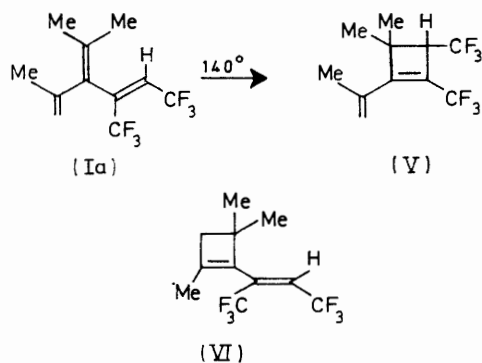
material was isolated and its elemental composition shown to be unchanged. Its n.m.r. spectra showed that two vinyl protons and three allyl protons remained, features only compatible with an electrocyclic ring closure to the isopropenylcyclobutene (V). Isomerisation cannot have taken the alternative course to give (VI), because the CHCF₃ proton resonance has moved too far upfield [τ 6·8, $^3J_{HF}$ 9 Hz in (V), *cf.* τ 3·8, $^3J_{HF}$ 9 Hz in (Ia)[6]].

Four-electron electrocyclic rearrangements normally proceed in the reverse direction, converting cyclobutenes into acyclic dienes;[18] usually ground-state butadienes have lower energies than ground-state cyclobutenes.[19] Exceptions to this generalisation arise when severe steric interactions destabilise the open chain isomer, as in *cis,trans*-cyclo-octa-1,3-diene,[20] or when lone pair repulsions operate, as in hexafluorobutadiene.[21] In the present case steric factors seem likely to promote ring closure of the triene (Ia), because repulsions between methyl and trifluoromethyl groups occur in all its coplanar configurations. Since the (E)-isomer (IIa) suffers additional steric destabilisation, any rearrangement equilibria of the type:

$$\text{(Ia)} \rightleftharpoons \text{(V)} \rightleftharpoons \text{(IIa)}$$
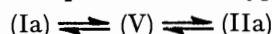
will not serve for the formation of (IIa) from (Ia) *via* (V), which in any case has not achieved its equilibrium

[18] R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H.-A. Brune, *Chem. Ber.*, 1965, **98**, 2339.

[19] W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, 1969, **91**, 6042.

[20] K. M. Shumate, P. N. Neuman, and G. J. Fonken, *J. Amer. Chem. Soc.*, 1965, **87**, 3996.

concentration with (Ia) even after 114 h at 122° (see Table 2), by which time (IIa) has reached a steady concentration. Therefore, (IIa) must be a primary reaction product of the ene-insertion of hexafluorobutyne.

TABLE 2

Average g.l.c. areas of isomers (Ia), (IIa), (IIIa), and (V) from the hexafluorobut-2-yne–2,4-dimethylpenta-2,3-diene reaction

T/°C	t/h	(Ia) (%)	(IIa) (%)	(IIIa) (%)	(V) (%)
80 [a]	48	80·8	7·8	11·5	
100	24	79·2	10·7	10·3	
100	96	73·9	15·0	10·5	0·5
122	24	72·6	5·5	11·6	10·2
122	48	60·2	6·4	12·1	21·5
122	114	40·4	7·5	13·1	39·5
140	24	18·1	7·3	13·9	60·4

[a] Large-scale run, in which two minor components (4%) were detected.[6]

In a series of small-scale reactions, the effect of temperature in the range 80—140° on the product distribution in the hexafluorobutyne–dimethylpentadiene reaction was examined in the same way as described above for the butyne-methylbutadiene reaction. The average relative g.l.c. areas for the isomers (Ia), (IIa), (IIIa), and (V) are shown in Table 2. The primary feature of interest in these data is the constancy of the proportion of the [2 + 2] cycloadduct (IIIa) at *ca.* 12%. The difference between the transition states for an allowed $[_\pi 2_s + _\pi 2_a]$ cycloaddition[22] and a concerted $[_\pi 2_s + _\pi 2_s + _\sigma 2_s]$ ene-insertion[9] renders such a small variation in percentage cycloaddition over 60°
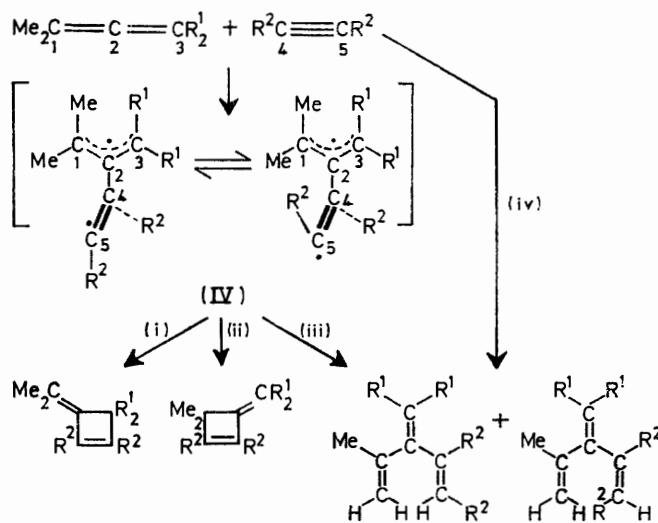
SCHEME (i) Rotation about C(2)–C(3) and C(2)–C(4); (ii) rotation about C(1)–C(2) and C(2)–C(4); (iii) C(5) abstracts H from CH₃–C(1); (iv) concerted pathways.

most improbable. Therefore, cycloaddition and ene-insertion most probably share a common reaction intermediate in a two-step mechanism (see Scheme).

[21] E. W. Schlag and W. B. Peatman, *J. Amer. Chem. Soc.*, 1964, **86**, 1676.

[22] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

The suggested structure for the intermediate is, as in the butyne–methylbutadiene reaction, a diradical (IVa). As with (IVc), geometrical inversion is expected to be rapid at the vinylic centre, so that both (E)- and (Z)-forms should be present in (IVa).

Conclusions about the variation in the (Ia) : (IIa) ratio over the temperature range studied are less reliable, owing to the increasingly rapid leakage of these isomers to (V) and to the large experimental error in the observed proportion of (IIa), the less abundant isomer. Data reported previously by Martin and his co-workers [7] and by ourselves [6] have shown that quite large variations in the (I) : (II) ratio can occur. The reaction studied was that between dimethylpentadiene and dimethyl acetylenedicarboxylate in arene solvents

TABLE 3

Isomer ratio in dimethyl acetylenedicarboxylate–dimethylpentadiene reaction in arene solvents

Solvent	T/°C	Time	(Ib) (%)	(IIb) (%)	(Ib)/ (IIb)	Ref.
Benzene	25	25 days	47	53	0·887	7
Benzene	60	4 days	57	43	1·326	6
Benzene	80	42 h	73	27	2·705	7
Toluene	110	7 h	85	15	5·670	7

at 25—110° (data in Table 3), the only products isolated being the ene adducts (Ib) and (IIb). The temperature dependence of the (Ib) : (IIb) ratio is large enough to be compatible with a difference in activation energies for the formation of the two isomers as large as 20—25 kJ mol⁻¹. This indicates that if (IVb) is a common intermediate in their formation, its collapse to one isomer must proceed rather differently from that to the other isomer. Models of (IV) show that whereas intramolecular H-abstraction can easily occur when leading to (Z)-isomers, intramolecular H-abstraction in (E)-diradicals is likely to be difficult. Whether (II) can arise by other means from (IV) will depend upon the lifetime and concentration of (IV). An alternative pathway to (II) is the allowed but geometrically awkward $[_{\pi}2_a + _{\pi}2_s + _{o}2_a]$ ene-insertion,[6] a route which should become more accessible as steric hindrance to more coplanar pathways increases.

In conclusion, the hexafluorobutyne–methylbutadiene reaction appears to proceed by formation of an allyl-vinyl diradical (IVc), probably in its orthogonal configuration (B) as in other types of allene cycloadditions.[5] The hexafluorobutyne–dimethylpentadiene reaction is believed to proceed via the corresponding diradical (IVa), the lower proportion of cycloadduct formed in this case being attributed to greater steric hindrance to rotation towards coplanarity, as well as to the greater availability of allylic hydrogen atoms suitably placed for ene-insertion. The absence of detectable amounts of cycloadduct in the dimethyl acetylenedicarboxylate–dimethylpentadiene reaction is in accord with this proposal, and points to a mechanistic continuum shifted from predominantly cycloaddition to pre-

dominantly ene-insertion by structural features in the reagents.

EXPERIMENTAL

General manipulative and analytical procedures, and the preparation of (Z)-1,1,1-trifluoro-5-methyl-4-(prop-2-enyl)-2-trifluoromethylhexa-2,4-diene, have been described previously.[6] 3-Methylbuta-1,2-diene was prepared from 3-chloro-3-methylbut-1-yne,[23] and hexafluorobut-1-yne from 2,2,3,3-tetrachlorohexafluorobutane.[24]

Reaction of 3-Methylbutadiene with Hexafluorobutyne.—(a) *At 80°.* Hexafluorobut-2-yne (8·1 g, 50 mmol), 3-methylbuta-1,2-diene (3·4 g, 50 mmol), and Terpene B polymerisation inhibitor (equal parts by volume of dipentene and α-terpinolene, 0·2 cm³) were sealed *in vacuo* into each of two Pyrex ampoules (300 cm³), and kept at 80° for 48 h. The combined pale yellow liquid products (23 g) were shown by g.l.c. (2 m Apiezon L, 90°) to contain three components in the ratio 1 : 29·2 : 9·6; distillation was not attempted. The two major components were isolated by preparative g.l.c. (Perkin-Elmer F21, 6 m Apiezon L, 90°) and identified spectroscopically as 3,3-di-methyl-4-methylene-1,2-bistrifluoromethylcyclobutene (IIIb) (estimated 16·8 g, 73 mmol, 73%), a liquid, b.p. 92° at 758 mmHg (Found: C, 47·0; H, 3·8; F, 49·9%; M⁺, 230. C₉H₈F₆ requires C, 47·0; H, 3·5; F, 49·5%; M, 230), ν_max. (film) 3595w, 3110w, 2980s, 2940m, 2885m, 2720w, 2310w, 1805w, 1720s (C:C str.), 1710s (C:C str.), 1670w, 1650m, 1470m, 1455m, 1420m, 1393m, 1375m, 1362s, 1295s, 1267s, 1185s, 1145s, 1059m, 1040s, 1015s, 950s, 898s (:CH₂ out-of-plane def.), 838m, 771m, 756m, 724m, and 701s cm⁻¹, τ (CFCl₃ soln.) 8·59 (6H, s, CMe₂). 4·96 (1H, m, :CH), and 4·82br (1H, s, :CH), ¹⁹F n.m.r, (in CFCl₃) −13·6 (qdd, ⁵J_{FF} 6·04 Hz, :CCF₃·C:CH₂) and −15·1 p.p.m. (q, :CCF₃·CMe₂) (rel. to ext. CF₃CO₂H, positive upfield), λ_max. (EtOH) 211 (ε *ca.* 2800) and 244 nm (4510), λ_min. 219 nm (ε 2700), and 3-isopropylidene-1,2-bis-trifluoromethylcyclobutene (IIIc) (estimated 5·5 g, 24 mmol, 24%), also a liquid, b.p. 105° at 755 mmHg (Found: C, 46·9; H, 3·7; F, 50·0%; M⁺, 230. C₉H₈F₆ requires C, 47·0; H, 3·5; F, 49·5%; M, 230) ν_max. (film) 2985w, 2930w, 2870w, 1733w (C:C str.), 1680w (C:C str.), 1685w, 1651m, 1648m, 1460w, 1450m, 1425w, 1379m, 1359m, 1294s, 1250m, 1205m, 1185m, 1145s, 1079w, 1055m, 995m, 959w, 939m, and 790w cm⁻¹, τ (neat) 8·27 (3H, s, :CMe), 8·14 (3H, s, :CMe), and 7·0br (2H, s, CH₂), ¹⁹F n.m.r. (neat) −13·8 (asymmetric q, J_{FF} *ca.* 7 Hz) and −13·6 p.p.m. (asymmetric m, possibly qt, J_{FH} *ca.* 3 Hz), λ_max. (EtOH) 212 (ε *ca.* 3600) and 262 nm (7700), λ_min. 227 nm (ε 2010).

(b) *At various temperatures.* Thick-walled Pyrex ampoules (internal vol. 5 cm³) were loaded and sealed *in vacuo* with identical mixtures of polymerisation inhibitor (0·04 cm³), 3-methylbuta-1,2-diene (68 mg, 1·0 mmol), and hexafluorobutyne (162 mg, 1·0 mmol). Duplicated runs were performed by rapidly heating six tubes to each temperature (see Table 1) and removing two tubes for rapid quenching to −196° after each time shown. Immediately prior to g.l.c. analysis (2 m Apiezon L, 90°), the tubes were opened and allowed to reach ambient temperature. Each product mixture was analysed in triplicate, and peak areas were determined electronically (Kent Chromalog Mark II) and by graphical methods.

²³ G. F. Hennion, J. Sheenan, and L. Maloney, *J. Amer. Chem. Soc.*, 1950, **72**, 3545.

²⁴ A. L. Henne and W. G. Finnegan, *J. Amer. Chem. Soc.*, 1949, **71**, 298.

The average relative areas so obtained are shown in Table 1, including unidentified by-products as a gross figure.

Thermal Isomerisation of (Z)-1,1,1-Trifluoro-5-methyl-4-(prop-2-enyl)-2-trifluoromethylhexa-2,4-diene.—The (Z)-hexadiene (Ia) [1] (7·74 g, 30 mmol), containing small amounts (*ca.* 2—3%) of the (*E*)-isomer (IIa) and the isopropylidenecyclobutene (IIIa), was kept in a sealed evacuated Pyrex ampoule (50 cm³) for 48 h at 140° to give a liquid shown by g.l.c. (2 m PEGA, 100°) to contain four components in the ratio 1 : 3 : 16 : 40, and identified by comparison of retention times with authentic samples [1] as, in order of elution, the (*E*)-hexatriene (IIa), the isopropylidenecyclobutene (IIIa), the (*Z*)-hexatriene (Ia) (26% recovery), and an unknown. The unknown component was then isolated by g.l.c. (F21, 6 m PEGA, 80°) and identified spectroscopically as 3,3-*dimethyl*-2-(*prop*-2-*enyl*)-1,4-*bistrifluoromethylcyclobutene* (V) (94% based on hexadiene consumed) (Found: C, 52·1; H, 5·1%; M^+, 258. $C_{11}H_{12}F_6$ requires C, 51·2; H, 4·7%; M, 258), b.p. 156° at 758 mmHg, $\nu_{max.}$ (film) 3580w, 3110w, 2975m, 2939m, 2880m, 1830w (C:C str.), 1650m (C:C str.), 1609m, 1470m, 1445m, 1410m, 1391m, 1375s, 1365s, 1349s, 1299vs, 1278vs, 1245s, 1215s, 1189vs, 1160vs, 1125vs, 1096vs, 1070s, 1040w, 1005m, 980m, 928m, 915m, 840m, 791w, 770w, 734w, 708m, and 685s cm⁻¹, τ (CCl₄) 8·52 (3H, q, MeC·CCF₃, $^5J_{HF}$ 2 Hz) 8·50 (3H, s, >CMe), 7·95 (3H, m, MeC:), 6·83 (1H, q, $^3J_{HF}$ 9 Hz), and 4·65br (2H, s, :CH₂), ¹⁹F n.m.r. (CCl₄) −13·3 (dqq, $^3J_{FH}$ 9, $^5J_{FF}$ 4, $^5J_{FH}$ 2, CF₃CH), and −17·95 p.p.m. (qm, J_{FF} 4 Hz, CF₃C:).

Hexafluorobutyne–Dimethylpentadiene Reaction at Various Temperatures.—Duplicate runs were performed as described above, using Pyrex ampoules (5 cm³) containing 2,4-dimethylpenta-2,3-diene (96 mg, 1·0 mmol), hexafluorobut-2-yne (162 mg, 1·0 mmol), and inhibitor (0·04 cm³). G.l.c. analyses (2 m PEGA, 100°) were performed in triplicate and average relative areas, determined as above, are shown in Table 2 for each of the four products, (*E*)-hexatriene (IIa), (*Z*)-hexatriene (Ia), isopropylidenecyclobutene (IIIa), and propenylcyclobutene (V), which were identified by comparison of retention times with authentic samples. No significant unidentified components were detected.