Ene Reactions of Allenes. Part II.[1] Non-stereospecific Ene Insertions into an Alkylallene by Electron Deficient Acetylenes

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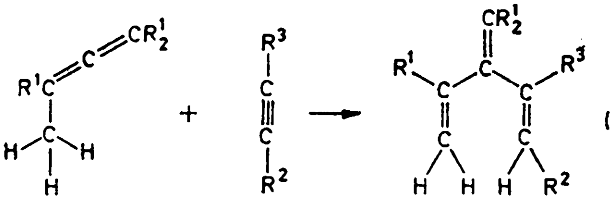
2,4-Dimethylpenta-2,3-diene reacts with dimethyl acetylenedicarboxylate in benzene to give a mixture of the (*E*)- and (*Z*)-isomers of methyl 4-isopropenyl-3-methoxycarbonyl-5-methylhexa-2,4-dienoate, and in tetrachloroethane by prototropic rearrangement and Diels–Alder cycloaddition to give dimethyl 3,3,5-trimethylcyclohexa-1,4-diene-1,2-dicarboxylate; with hexafluorobut-2-yne it gives a mixture of the [2 + 2] cycloadduct 4-isopropylidene-3,3-dimethyl-1,2-bistrifluoromethylcyclobutene and the ene adducts (*E*)- and (*Z*)-1,1,1-trifluoro-4-isopropenyl-5-methyl-3-trifluoromethylhexa-2,4-diene; and with 3,3,3-trifluoropropyne it gives a mixture containing *trans*-1,1,1-trifluoro-4-isopropenyl-5-methylhexa-2,4-diene.

Ene reactions between alkylallenes and acetylenes [equation (**1**)] are expected to be favoured energetically because of the stability gained in transforming an allenic π-bond system into a cross-conjugated triene, and by the formation of a C_{sp^2}–C_{sp^2} σ-bond. Calculations based upon the heats of formation of reagents and products suggest that the ene reaction between buta-1,2-diene and acetylene should be 220 kJ mol^{-1} exothermic, compared to the archetypal ene reaction between propene and ethylene from which a mere 96 kJ mol^{-1} is to be expected; neither reaction has yet been achieved.[2]

Surprisingly few examples of alkylallene–alkyne ene reactions have been reported hitherto,[2-4] and the only systematic study with a variety of allenic substrates involved benzyne as enophile.[5]



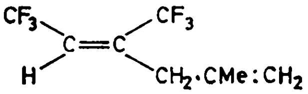
Such reactions, in which the enophile abstracts an allylic proton from the allene, may well proceed by mechanisms quite different from those of ene reactions between propadiene and electron-deficient ketones [equation (2)],[6-8] in which the enophile abstracts a vinylic proton from propadiene in a polar, one-step, process.[8]

$$\mathrm{H{-}CH{:}C{:}CH_2 + (R_F)_2CO \longrightarrow HC{:}C{\cdot}CH_2{\cdot}C(OH)(R_F)_2} \quad (2)$$

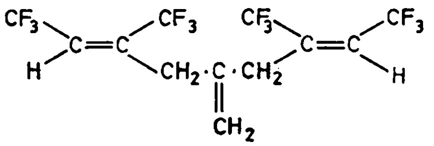
$$\mathrm{R_F = CF_3 \text{ or } (R_F)_2 = CF_2{\cdot}CF_2{\cdot}CF_2}$$

Three examples of ene reactions between 2,4-dimethylpenta-2,3-diene and electron-deficient acetylenes are reported here [equation (1): $R^1 = Me$, $R^2 = R^3 = CF_3$ or CO_2Me; $R^1 = Me$, $R^2 = CF_3$, $R^3 = H$]. Two of these display an unexpected non-stereospecificity of addition with respect to the alkyne and produce mixtures of (*E*)- and (*Z*)-isomers, an observation which has important mechanistic implications. Related reactions between electron-deficient alkynes and cyclonona-1,2-diene, 3-methylbuta-1,2-diene, and 2-methylpenta-2,3-diene have been investigated,[9] but no further examples of non-stereospecific insertion have yet emerged.

Dimethylpentadiene–Hexafluorobutyne Reaction.—Hexafluorobut-2-yne is a well-known and powerful enophile. It reacts suprafacially with isobutene at 145° to produce the (*Z*)-diene[10] (I) in 80% yield, and if the temperature is raised and more butyne admitted a 2 : 1 adduct (II) forms, the second ene reaction being reported[11] as at least predominantly a suprafacial (*cisoid*) addition to the alkyne, although other products were present.



(I)



(II)

Hexafluorobutyne reacts even more readily when the ene-component is 2,4-dimethylpenta-2,3-diene (tetramethylallene) and complete conversion into a five-component mixture occurs at 80° after only 80 h. No attempt was made to obtain pure adducts by distillation; instead, preparative g.l.c. was used to obtain pure samples of the three main components, which were originally present in the ratio 7·5 : 11 : 77·5. Elemental analysis and mass spectrometry proved that each of the

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[1] Part I, D. R. Taylor and D. B. Wright, *J.C.S. Perkin I*, 1973, 956.

[2] H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 556.

[3] H. A. Chia, B. E. Kirk, and D. R. Taylor, *Chem. Comm.*, 1971, 1144.

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

[5] H. H. Wasserman and L. S. Keller, *Chem. Comm.*, 1970, 1483.

[6] D. C. England, *J. Amer. Chem. Soc.*, 1961, **83**, 2205.

[7] W. H. Urry, J. H. Y. Niu, and L. G. Lundsted, *J. Org. Chem.*, 1965, **33**, 2302.

[8] S.-H. Dai and W. R. Dolbier, jun., *Chem. Comm.*, 1971, 166; *J. Amer. Chem. Soc.*, 1972, **94**, 3953.

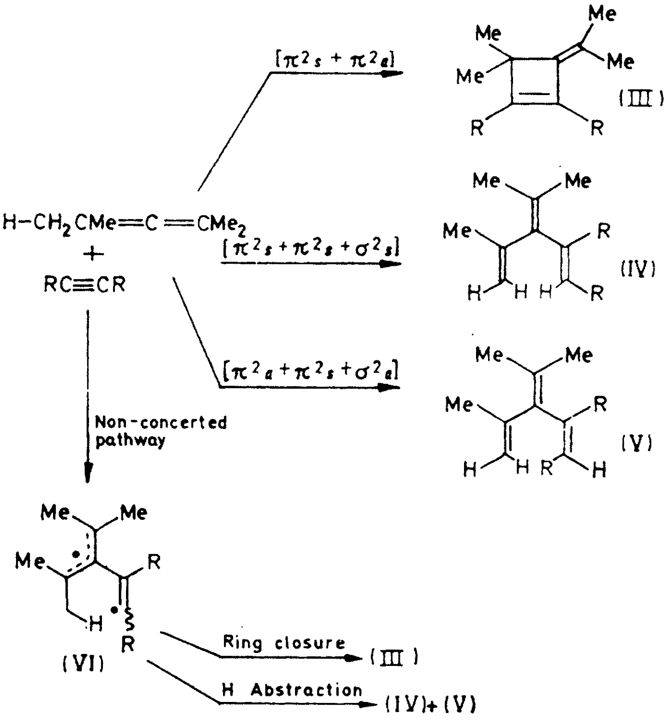
[9] B. E. Kirk, C. B. Lee, and D. R. Taylor, unpublished results.

[10] Trifluoromethyl takes precedence over H and RCH$_2$ substituents (see E. L. Eliel, *J. Chem. Educ.*, 1971, **48**, 163 and references cited therein).

[11] J. C. Sauer and G. N. Sansen, *J. Org. Chem.*, 1962, **27**, 2730.

isolated products was a 1 : 1 adduct, but, contrary to expectation, none arises by cycloaddition of the alkyne to the allene's conjugated isomer, namely 2,4-dimethylpenta-1,3-diene, which so readily occurs when this allene is treated with fluoro-olefins.[12,13]

The second most abundant isomer, b.p. 144°, was readily identified by spectroscopic comparison with related compounds[14] as the alkylidenecyclobutene (IIIa), formed by a [2 + 2] cycloaddition of the alkyne to the allene. The ^{1}H n.m.r. spectra of the remaining two isomers indicate that both contain three vinyl protons, one of which is attached to $\dot{C}\cdot CF_3$ ($^3J_{HF}$ 7·2 and 8·6 Hz); they are both apparently ene-insertion adducts. The major adduct, b.p. 152·5°, is assigned the (*Z*)-geometry (IVa), arising by the usual suprafacial addition process. The remaining isomer, b.p. 136°, is characterised by (i) a much lower value of the F–F coupling constant ($^5J_{FF}$ $\leqslant$2 Hz) and (ii) stronger deshielding of the downfield $CF_3C\dot{H}$ proton (τ 3·77), compared to the corresponding values for (IVa) ($^5J_{FF}$ 11 Hz, τ 4·18). These features require a *trans*-arrangement of CF_3 groups,[15] and indicate the (*E*)-isomer (Va), apparently arising by antarafacial addition to the enophile (Scheme 1).

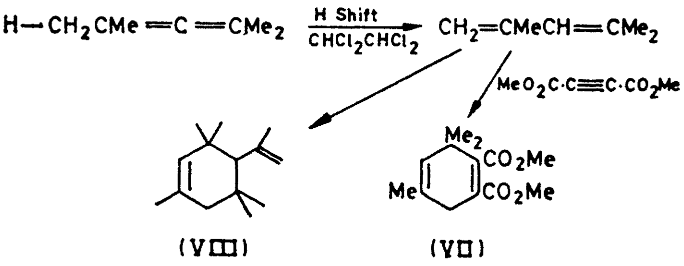


a, R = CF_3; b, R = CO_2Me

Scheme 1

The formation of the (*E*)-isomer was totally unexpected and was therefore initially supposed to be a result of thermal isomerisation of the (*Z*)-isomer (IVa), a hypothesis conclusively ruled out by unsuccessful attempts to convert (IVa) into (Va) at 80° and above.[16] Therefore, (Va) is a primary product of the reaction of hexafluorobutyne and the allene.

Dimethylpentadiene–Dimethyl Acetylenedicarboxylate Reaction.—Observation of a *transoid* ene reaction between 2,4-dimethylpenta-2,3-diene and hexafluorobutyne prompted a re-investigation of a reaction between this allene and dimethyl acetylenedicarboxylate, which had been previously abandoned after preliminary study indicated that intractable tars resulted.



Scheme 2

Rapid distillation of the tarry material obtained when the reaction was conducted without a solvent showed that low yields of 1 : 1 adducts ($\leqslant$20%) were indeed formed. Repetition of the reaction in *sym*-tetrachloroethane gave, disappointingly, the cyclohexa-1,4-diene derivative (VII) as the major product. The most likely mode of formation for the diester (VII), which does not appear to have been reported previously, is by Diels–Alder addition of the acetylenedicarboxylate to 2,4-dimethylpenta-1,3-diene produced *in situ* by prototropic isomerisation of the alkylallene. The conjugated pentadiene was indeed present and could be isolated from the more volatile fraction, along with its dimer (VIII)[17] (Scheme 2).

Isomerisation of the tetra-alkylallene persisted even when the tetrachloroethane was rigorously purified, and is supposed to be caused by traces of HCl liberated from the solvent during the reflux period. When the allene was warmed under nitrogen in pure *sym*-tetrachloroethane in the absence of the acetylenedicarboxylate, isomerisation was complete in 2 h. Chloroform had a similar effect.

When a more suitable solvent, benzene, was adopted, the hoped-for ene reaction took place and yielded a mixture of at least two 1 : 1 adducts. Precise fractional distillation yielded the pure (*Z*)-isomer (IVb) and a slightly impure sample of the (*E*)-isomer (Vb). G.l.c. analysis of the crude product indicated an initial (*Z*) : (*E*) ratio of 57 : 43, the ratio decreasing during work-up owing to decomposition of the higher-boiling (*Z*)-isomer.

These identifications are based on the pronounced difference in chemical shift [τ 4·30 in (IVb), 3·34 in (Vb)]

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[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.C.S. Perkin I*, 1973, 445.

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

[15] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' vol. 2, Pergamon, London, 1966, p. 871.

[16] B. E. Kirk and D. R. Taylor, *J.C.S. Perkin I*, in the press.

[17] M. L. Poutsma, *J. Org. Chem.*, 1968, **33**, 4080.

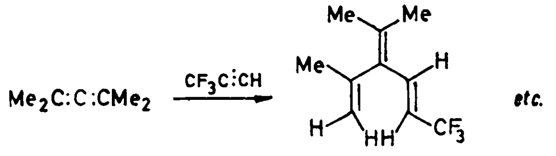
of the downfield vinyl proton, which is usually deshielded by *ca.* 1 p.p.m. in fumarates relative to maleates.[18]

Concurrently with our preliminary communication,[3] Martin and his co-workers reported a study of this reaction at 25—110° in a series of solvents.[4] Their spectroscopic data for the (*E*)- and (*Z*)-isomers which they isolated by g.l.c. are in excellent agreement with those reported here.

We could not induce thermal interconversion of (IVb) and (Vb) in refluxing benzene, thus demonstrating that both are primary products of the ene reaction. Nor could we isolate the [2 + 2] cycloadduct (IIIb), though it may be present amongst the minor unidentified products.

Dimethylpentadiene–Trifluoropropyne Reaction.—3,3,3-Trifluoropropyne has received less attention than its symmetrical homologue C_4F_6 as an enophile, although it is quite easily prepared.[19-21] It has been assessed to be less potent than the butyne as an enophile towards mono-olefins, requiring quite high temperatures (*ca.* 225°) to be effective.[2,11]

Nevertheless it reacts with 2,4-dimethylpenta-2,3-diene at 140° giving a complex mixture containing at least seven components. Only the most abundant product (35%) has so far been isolated, namely, the expected *trans*-hexadiene (IX). This product was identified principally on the basis of its n.m.r. spectra, the geometry of the trifluoromethyl-substituted double bond being assigned by consideration of the coupling constants ($^3J_{HH}$ 15, $^3J_{HF}$ 7, and $^4J_{HF}$ 2 Hz). This structure agrees with earlier work on ene reactions with unsymmetrical alkynes,[11] which revealed a regioselectivity in favour of hydrogen-capture by the substituted acetylenic carbon atom.

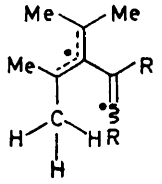


(IX)

Attempts to isolate other components led only to the detection of the prototropic isomerisation product 2,4-dimethylpenta-1,3-diene (16%). Its formation may be due to the relatively high acidity of this alkyne, since it did not arise when hexafluorobutyne was used.

Treatment of 1-chloro-3-methylbuta-1,2-diene with hexafluorobutyne yielded an even more complex mixture from which no pure adducts were obtained.

Mechanism of Allene–Alkyne Ene Reactions.—Ene reactions are widely held to be concerted processes, designated as $[_\pi2_s + {}_\pi2_s + {}_\sigma2_s]$ in orbital symmetry terms, although there is little symmetry on the molecular scale.[2,22] Thus, observation of the (*E*)-isomers (V) as primary products of these ene reactions poses the problem: do these arise by a concerted antarafacial pathway, parallel but distinct from the formation of the (*Z*)-isomers by the conventional suprafacial pathway, or are both types of ene adduct produced *via* a common intermediate, for example the diradical (VI)? An additional attraction of the hypothesis that diradical (VI) is formed transiently is that it could collapse to the [2 + 2] adduct (III) (Scheme 1), thereby avoiding the symmetry-allowed but rarely followed $[_\pi2_s + {}_\pi2_a]$ pathway. Evidence pertaining to this problem will be advanced in a further paper.[16]



(VI)

EXPERIMENTAL

Gaseous reagents and products were manipulated in a Pyrex vacuum manifold with calibrated storage facilities and mercury-filled manometers. Crude liquid products were purified by precise fractional distillation through (i) a 100 cm Haage spinning band still (column A) or (ii) a 60 cm Buchi spinning band still (column B), or by preparative g.l.c. (Perkin-Elmer F21 Fractometer). Pure products were identified by i.r. (Perkin-Elmer models 137, NaCl optics, and 257, diffraction grating), n.m.r. (Perkin-Elmer R10, operating at 60 MHz for ^{1}H and 56·5 MHz for ^{19}F, and Varian HA-100, operating at 100 MHz for ^{1}H and 94·1 MHz for ^{19}F) (^{19}F chemical shifts cited relative to external $CF_3{\cdot}CO_2H$, high field positive), u.v. (Hilger and Watts Ultrascan SP700), and mass spectrometry (A.E.I. MS902, with high resolution facilities computed with an A.E.I. data acquisition and analysis system DS10). Analytical g.l.c. was carried out using a Perkin-Elmer F11 fractometer with 50 m wall-coated capillary columns or a Pye model 104 fractometer fitted with 2 m × 4·5 mm i.d. columns, both fitted with FID detectors coupled to a Kent Chromalog Mark 2 electronic integrator. 2,4-Dimethylpenta-2,3-diene was prepared as described previously;[12] dimethyl acetylenedicarboxylate was either prepared by esterification of acetylenedicarboxylic acid or, if obtained commercially, was redistilled prior to use (b.p. 96—98° at 20 mmHg); hexafluorobut-2-yne[23] and 3,3,3-trifluoropropyne[19] were prepared by literature procedures and purified by fractional condensation *in vacuo*.

Reaction of 2,4-*Dimethylpenta*-2,3-*diene with Dimethyl Acetylenedicarboxylate*.—(a) *Without solvent.* No detectable reaction occurred between 2,4-dimethylpenta-2,3-diene and dimethyl acetylenedicarboxylate in the dark at ambient temperature after 24 h. In a further experiment, dimethyl acetylenedicarboxylate (14·2 g, 100 mmol), 2,4-dimethylpenta-2,3-diene (9·6 g, 100 mmol), and Terpene B inhibitor

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[18] R. M. Kellog, *J. Amer. Chem. Soc.*, 1971, **93**, 2344, and references cited therein.

[19] R. N. Haszeldine, *J. Chem. Soc.*, 1951, 588, 2495.

[20] A. L. Henne and M. Nager, *J. Amer. Chem. Soc.*, 1951, **73**, 1042.

[21] W. C. Smith, *Angew. Chem. Internat. Edn.*, 1962, **1**, 467.

[22] T. L. Gilchrist and R. Storr, ' Organic Reactions and Orbital Symmetry,' Cambridge University Press, Cambridge, 1972, p. 242.

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

{0·3 cm^3 of a 1 : 1 mixture of dipentene and α-terpinolene-[*p*-mentha-1,4(8)-diene]} were kept in the dark at 150 °C for 6 h in a sealed, base-rinsed Pyrex tube (300 cm^3) to give a yellow viscous liquid, which was rapidly distilled at low pressure through a short Vigreux column to give a liquid (6·3 g) (Found: C, 65·4; H, 7·5%. Calc. for $C_{13}H_{18}O_4$: C, 65·6; H, 7·6%), b.p. 100—130° at 0·1 mmHg, shown by g.l.c. (2 m Apiezon L, 180°) and 60 MHz n.m.r. to contain a 2 : 1 ratio of the (*Z*)- and (*E*)- somers of methyl 4-isopropenyl-3-methoxycarbonyl-5-methylhexa-2,4-dienoate (IVb) and (Vb) (*ca.* 20% yield), contaminated with unidentified by-products [not the trimethylcyclohexadiene (VII)]. Attempted g.l.c. separations (7 m SE30, MS550, and Apiezon L, 180—200°) were unsuccessful.

(b) *In benzene.* 2,4-Dimethylpenta-2,3-diene (9·6 g, 100 mmol) and dimethyl acetylenedicarboxylate (7·1 g, 50 mmol) were kept in anhydrous benzene (40 cm^3) at 62° for 4 days. The solution was shown by g.l.c. (50 m capillary, Apiezon L, 175°) to contain a 57 : 43 mixture of (IVb) and (Vb). Distillation (column B) at reduced pressure gave benzene, 2,4-dimethylpenta-2,3-diene, a fraction (2·35 g), b.p. 110—112° at 2 mmHg, n_D^{20} 1·4773, shown by g.l.c. (as above) to consist of a 4 : 89 : 7 mixture of an unknown, *methyl* (E)-*4-isopropenyl-3-methoxycarbonyl-5-methylhexa-2,4-dienoate* (Vb) (Found: C, 65·6; H, 7·6%; M^+, 238·1199. $C_{13}H_{18}O_4$ requires C, 65·6; H, 7·6%; *M*, 238·1205), $\lambda_{max.}$ (EtOH) 217·5 nm (ε ~12,200), $\nu_{max.}$ (film) 2900m, 2800w, 1725vs (C:O str., d), 1630m (C:C str.), 1430s, 1360w, 1340w, 1250vs (CO str.), 1200s, 1170s, 1120w, 1080w, 1030s, and 900w cm^{-1}, τ (100 MHz, CCl_4) 3·34 (s, :C*H*CO$_2$Me), 5·08 (dq) and 5·24 (dq) (inner members of AB system, :CH$_2$), 6·34 (s) and 6·40 (s) (2 × CO$_2$Me), 8·26 (s, :CMe), 8·32 (dd, H$_2$C:C*Me*), and 8·50 (s, :CMe), and the (*Z*)-isomer (IVb), an intermediate fraction (3·0 g) shown by g.l.c. to be a 1 : 1 mixture of (Vb) (total yield estimated at 3·6 g, 15 mmol, 30% based on alkyne) and (IVb), and a liquid (0·6 g), b.p. 142° at 2 mmHg, n_D^{20} 1·4911, identified spectroscopically as *methyl* (Z)-*4-isopropenyl-3-methoxycarbonyl-5-methylhexa-2,4-dienoate* (IVb) (Found: C, 65·3; H, 7·7%; M^+, 238·1199. $C_{13}H_{18}O_4$ requires C, 65·6; H, 7·6%; *M*, 238·1205) (total yield estimated at 9 mmol, 18%, after distillation), $\lambda_{max.}$ (EtOH) 212 (ε ~10,800) and 286 nm (ε 6400), $\lambda_{min.}$ 253 nm (ε 3200), $\nu_{max.}$ (film) 2900m, 2800w, 1725vs (C:O str., d), 1630m (C:C str.), 1600m, 1430s, 1360m, 1340m, 1250s (CO str.), 1200m, 1160s, 1090w, 990m, and 900m cm^{-1}, τ (100 MHz, CCl_4) 4·30 (s, :C*H*·CO$_2$Me), 5·00 (m, :CH), 5·34 (m, :CH), 6·36 (s, CO$_2$Me), 6·39 (s, CO$_2$Me), 8·26 (s, 2 × :CMe), and 8·29 (m, :CMe). A distillation residue (3·9 g) was not investigated

(c) *In tetrachloroethane.* The dimethylpenta-2,3-diene (19·2 g, 200 mmol), dimethyl acetylenedicarboxylate (14·2 g, 100 mmol), and *sym*-tetrachloroethane (100 cm^3) were stirred under dry nitrogen at 65° for 7 days. Distillation gave 2,4-dimethylpenta-1,3-diene (6·2 g, 65 mmol, 32%), b.p. 92—94° (lit.,[24] 93°) identified by i.r. and g.l.c. comparison with an authentic sample, and a residue which was distilled at reduced pressure (column A) to give tetrachloroethane, a $C_{14}H_{24}$ hydrocarbon identified by n.m.r.[17] as 4-isopropenyl-1,3,3,5,5-pentamethylcyclohexene (VIII) (1·09 g, 6%) (Found: C, 87·8; H, 12·7. Calc. for $C_{14}H_{24}$: C, 87·5; H, 12·5%), b.p. 94—98° at 7 mmHg (lit.,[17] 99° at 16 mmHg), and a fraction (16·5 g), b.p. 95—100° at 1 mmHg shown by g.l.c. to contain two components (9 : 1). The major component was isolated by g.l.c. (4·5 m Apiezon L, 190°) and identified spectroscopically as *dimethyl 3,3,5-trimethylcyclohexa-1,4-diene-1,2-dicarboxylate* (VII) [14·8 g (estimated), 0·062 mol, 62%] (Found: C, 64·8; H, 7·6%; M^+, 238·1212. $C_{13}H_{18}O_4$ requires C, 65·6; H, 7·6%; *M*, 238·1205), $\nu_{max.}$ (film) 2900s, 2800m, 1740vs, (C:O str.), 1630m (C:C str.), 1460m, 1430s, 1370w, 1350w, 1320m, 1270—1230vs (CO str.), 1200m, 1150m, 1120m, 1050s, 1030m, 1020w, 990w, 940m, 860w, 850w, 835w, 800m, 770m, 755m, and 715m cm^{-1}, τ (60 MHz, CCl_4) 4·86 (qm, :CH), 6·31 (s, 2 × OMe), 7·19 (dm, :CCH$_2$), 8·30 (m, :CMe), and 8·86 (s, CMe$_2$). The minor component was isolated similarly and identified as a 1 : 1 adduct (Found: M^+, 238·1197. Calc. for $C_{13}H_{18}O_4$: *M*, 238·1205) (4%). A high-boiling residue (5·2 g) was not examined.

Reaction of 2,4-*Dimethylpenta*-2,3-*diene with Hexafluorobutyne.*—Hexafluorobut-2-yne (8·1 g, 50 mmol), the dimethylpenta-2,3-diene (4·8 g, 50 mmol), and inhibitor (0·2 cm^3) were kept in a sealed Pyrex reactor (base-rinsed, 300 cm^3) at 80° for 48 h to give a yellow liquid (12·9 g) shown to contain five components in the ratio 7·5 : 11 : 77·5 : 2 : 2. The first three were isolated by g.l.c. (6 m polyethylene glycol adipate, 100°) and identified spectroscopically as (E)-*1,1,1-trifluoro-4-isopropenyl-5-methyl-3-trifluoromethylhexa-2,4-diene* (Va) (0·9 g, 4 mmol, 8%) (Found: M^+, 258·0828. Calc. for $C_{11}H_{12}F_6$: *M*, 258·0842), b.p. 136°, n_D^{20} 1·3904, $\nu_{max.}$ (film) 3010m, 2920m, 2870m, 1660m (C:C str.), 1625m (C:C str.), 1420m, 1360m, 1340m, 1290m, 1260s, 1180s, 1145s, 1110m, 1070w, 1019w, 1005m, 979w, 965m, 952w, 909m, 880m, 854m, 748m, 737w, 722m, and 699m cm^{-1}, τ (60 MHz, neat), 3·77 (qm, $^3J_{HF}$ 7·2 Hz, :CHCF$_3$), 4·85 (m, :CH), 5·11 (m, :CH), 8·17 (s, :CMe), 8·21 (s, :CMe), and 8·30 (s, :CMe), ^{19}F n.m.r. (56·46 MHz, neat) −15·6 (d, $^3J_{FH}$ 7 Hz, :CH·CF$_3$) and −10·8 p.p.m. (s, :CCF$_3$), (Z)-*1,1,1-trifluoro-4-isopropenyl-5-methyl-3-trifluoromethylhexa-2,4-diene* (IVa) (9·5 g, 37 mmol, 74%) (Found: C, 51·2; H, 4·7; F, 44·0%; *M*, 258. $C_{11}H_{12}F_6$ requires C, 51·2; H, 4·7; F, 44·2%; *M*, 258), b.p. 152·5 °C, n_D^{20} 1·39127, $\nu_{max.}$ (film) 3090w, 2995m, 2979m, 2942m, 2920s, 2862m, 2735w, 1825w, 1670m (C:C str.), 1635m (C:C str.), 1448m, 1365vs, 1293vs, 1277vs, 1250s, 1185vs, 1159vs, 1123vs, 1085m, 1040m, 1009w, 965w, 909m, 850w, 814m, 771w, 725w, 704w, 675m, and 650s cm^{-1}, τ (60 MHz, neat) 4·18 (q, $^3J_{HF}$ 8·6 Hz, :CHCF$_3$), 4·87 (dq, :CH), 5·14br (s, :CH), 8·20 (s, :CMe), 8·23 (m, :CMe), and 8·27 (s, :CMe), ^{19}F n.m.r. (94·1 MHz, neat) −18·06 (dq, $^3J_{FH}$ 8·8, $^5J_{FF}$ 11 Hz, :CHCF$_3$) and −17·14 p.p.m. (q, $^5J_{FF}$ 11 Hz, :CCF$_3$), $\lambda_{max.}$ (EtOH) 215 and 264 nm (ε 1355), $\lambda_{min.}$ 250 (ε 1225), and *4-isopropylidene-3,3-dimethyl-1,2-bistrifluoromethylcyclobutene* (IIIa) (1·3 g, 5 mmol, 10%), b.p. 144° (Found: C, 51·2; H, 4·8; F, 44·2%. $C_{11}H_{12}F_6$ requires C, 51·2; H, 4·7; F, 44·2%), $\nu_{max.}$ (film) 3095w, 2983vs, 2941vs, 2880vs, 2740w, 2698w, 2315w, 2050w, 1985w, 1789w, 1729s, 1682m (C:C str.), 1651vs (C:C str.), 1470s, 1455s, 1390s, 1375vs, 1355vs, 1305vs, 1270vs, 1232vs, 1200vs, 1181vs, 1144vs, 1087s, 1043w, 1010vs, 984vs, 962m, 920m, 878m, 859m, 814m, 789m, 751m, 720vs, 704vs, 655s, and 630m cm^{-1}, τ (60 MHz, CDCl$_3$) 8·20 (s, :CMe), 8·25 (s, :CMe), and 8·60 (s, CMe$_2$), ^{19}F n.m.r. (56·46 MHz, CHCl$_3$) −18·0 (q, $^5J_{FF}$ 8·1 Hz, :CCF$_3$) and −15·0 (q, :CCF$_3$) p.p.m.

Reaction of Trifluoropropyne with 2,4-*Dimethylpenta*-2,3-*diene.*—3,3,3-Trifluoropropyne (4·51 g, 48 mmol), 2,4-dimethylpenta-2,3-diene (4·61 g, 48 mmol), and inhibitor (0·2 cm^3) were kept at 140° in a sealed Pyrex tube (300 cm^3)

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[24] H. I. Waterman and W. J. L. de Kok, *Rec. Trav. chim.*, 1933, **52**, 234.

for 5 days to give trifluoropropyne (4%), and a liquid (8·9 g) shown by g.l.c. (2 m polyethylene glycol adipate, 100°) to contain seven components of relative areas (in order of elution) 10·6 : 8·5 : 12·7 : 11·2 : 35·8 : 10·6 : 10·6. Component 2 was shown by i.r. and g.l.c. to be 2,4-dimethylpenta-1,3-diene (16% yield). Component 5 was isolated by g.l.c. and identified spectroscopically as 1,1,1-*trifluoro-4-isopropenyl-5-methyl*-trans-*hexa-2,4-diene* (IX) (*ca.* 35% yield) (Found: C, 63·0; H, 6·9; F, 30·0%; *M*, 190. $C_{10}H_{13}F_3$ requires C, 63·2; H, 6·9; F, 30·0%; *M*, 190), b.p. 149° at 740 mmHg, n_D^{20} 1·43598, $\nu_{max.}$ (film) 3080m, 3055m, 2970m, 2940m, 2920m, 2860m, 1820—1800w, 1650s (C:C str.), 1640s (C:C str.), 1442m, 1378m, 1303vs, 1269s, 1159s, 1120vs, 1090s, 1040w, 1008w, 969s, 940m, 905s, 895m, 850m, 833w, 760m, 700m, and 650s cm^{-1}, τ (60 MHz, neat) 3·13 (dq, $^3J_{H_aH_b}$ 15·4, $^4J_{H_aF}$ 1·7 Hz) and 4·72 (dq, $^3J_{H_bF}$ 7·0 Hz) (*trans*-H_aC:CH_bCF_3), 5·10 (dq) and 5·61 (dq) (MeC:C*H*$_2$), and 8·30—8·50 (m, 3 × :CMe), ^{19}F n.m.r. (56·46 MHz, neat) −14·8 p.p.m. (dd).

Isomerisation of 2,4-Dimethylpenta-2,3-diene in Tetrachloroethane.—Technical *sym*-tetrachloroethane (B.D.H.) was purified carefully.[25] A mixture of pure solvent (10 cm^3) and 2,4-dimethylpenta-2,3-diene (1·9 g) was stirred at 65° and samples were removed for g.l.c. analysis (2 m Apiezon L, 80—190°) after (*a*) 1 h (10·9% penta-2,3-diene, 89·1% penta-1,3-diene) and (*b*) 2 h (100% 2,4-dimethylpenta-1,3-diene). Distillation of the mixture after 17 h at 65° afforded a 70% isolated yield of 2,4-dimethylpenta-1,3-diene. Isomerisation of the allene also occurred in chloroform at 62°, but was not detected in carbon tetrachloride.

Attempted Thermal Isomerisations of (IVb) *and* (Vb).—Small samples (0·3 g) of isomers (IVb) and (Vb) were separately dissolved in benzene (1 cm^3) containing naphthalene (0·1 g) as g.l.c. standard. Each solution was divided into two portions, one of each being kept at 0° and the others at 65° for 96 h under reflux. All four mixtures were then analysed by g.l.c. (50 m Apiezon L capillary, 170°). Both isomers appeared to decompose, as evidenced by 12—33% loss of area relative to naphthalene, but no (Vb) appeared in the solution of (IVb) or *vice versa*.

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[25] A. I. Vogel, ' A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 176.