

Ene Reactions of Allenes. Part 5.¹ Regio- and Stereo-selective Ene Reactions of a Trialkylallene

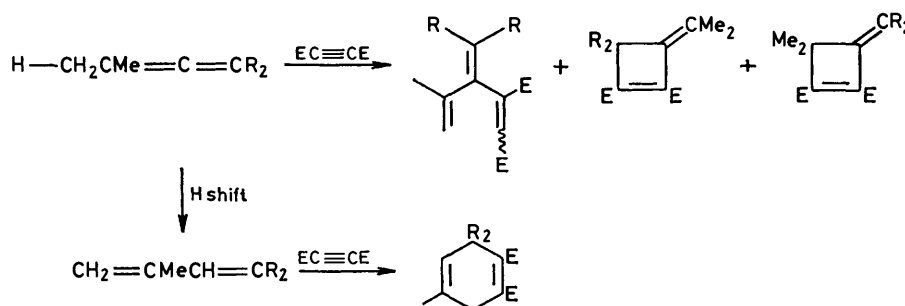
By Chan Boo Lee, R. John J. Newman, and David R. Taylor,* Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Thermal ene insertion reactions have been achieved between 2-methylpenta-2,3-diene and the reactive enophiles diethyl azodicformate, hexafluorobut-2-yne, dimethyl acetylenedicarboxylate, and 1,3-dichlorotetrafluoroacetone. In each case the ene adduct isolated arises by regioselective attack at the more substituted allenic π -bond, and the ¹H n.m.r. spectra of the adducts also suggest that the reaction is stereoselective. Whereas the azodicformate converts the allene cleanly to the dienyldicarbamate (1d), the other enophiles also cause numerous side-reactions to occur, leading to the formation of [2 + 2] cycloadducts, rearrangement of the allene to 2-methylpenta-1,3-diene, and Diels-Alder cycloaddition. Related reactions between dichlorotetrafluoroacetone and 2,4-dimethylpenta-2,3-diene and 3-methylbuta-1,2-diene, and between hexafluoroacetone and 2,4-dimethylpenta-2,3-diene are discussed.

We have previously reported ene reactions² between symmetrically substituted allenic hydrocarbons, such as 2,4-dimethylpenta-2,3-diene and cyclonona-1,2-diene, and terminally disubstituted Allenes, such as 3-methylbuta-1,2-diene, and a variety of electron deficient enophiles.^{1,3-5} Such reactions frequently lead to mixtures of 1 : 1 adducts in which the ene insertion product

and 1,3-dialkylallenes and acetylenes,^{4,6} in which [2 + 2] cycloaddition mainly occurs, and between hexafluoroacetone and the tetrasubstituted 2,4-dimethylpenta-2,3-diene, a reaction in which prototropic rearrangement followed by [4 + 2] cycloaddition dominates all other processes.³

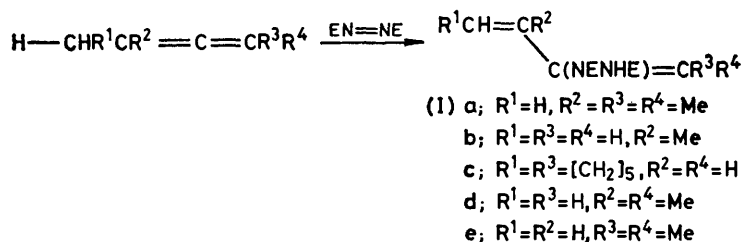
This series of reactions has now been extended to



SCHEME 1 R = H, Me; E = CF₃, CO₂Me

is accompanied by varying proportions of [2 + 2] cycloadduct(s) and/or a Diels-Alder adduct which stems from a competing prototropic rearrangement of

include a trisubstituted allene, 2-methylpenta-2,3-diene, since no previous study of the ene reaction appears to have included such a substrate. Particular objectives



SCHEME 2 E = CO₂Et

the allene to a conjugated diene (Scheme 1). In some instances these competing reactions supplant ene-insertion altogether, notably in reactions between 1,1-

were the observation of any regio- and stereo-selectivity in the ene insertion process, for the study of which the structure of this allene is well suited.

¹ Part 4, C. B. Lee and D. R. Taylor, *J. Chem. Research (S)*, 1977, 136.

² For a review see H. M. R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, 8, 556.

³ D. R. Taylor and D. B. Wright, *J.C.S. Perkin I*, 1973, 956.

⁴ H.-A. Chia, B. E. Kirk, and D. R. Taylor, *J.C.S. Perkin I*, 1974, 1209.

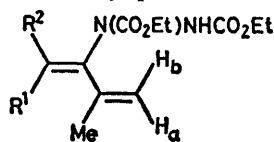
⁵ C. B. Lee and D. R. Taylor, *J.C.S. Perkin I*, 1977, 1463.

⁶ B. E. Kirk and D. R. Taylor, *J.C.S. Perkin I*, 1974, 1844.

Reaction of 2-Methylpenta-2,3-diene with Diethyl Azodicarbonate.—The most effective of the enophiles tested previously against alkylallenes proved to be diethyl azodicarbonate, which converted the three allenes investigated into the ene adducts (Ia—c) in very high yields

more, application of the principle of additivity of vinyl substituent shielding constants,^{8,9} which gives generally good predictions of the values of the chemical shifts of the other vinyl protons in these dicarbamoylbutadienes (Table),* leads to predicted values of the ethylidene

Observed and calculated vinyl proton chemical shifts (δ) in (A)



(A)

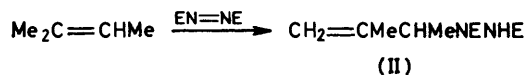
Adduct (A)	R ¹	R ²	Calc. δ ^a				Observed δ			
			H _a	H _b	R ¹	R ²	H _a	H _b	R ¹	R ²
(Ia)	Me	Me	4.81	4.95			4.83	5.06		
(E)-(Id)	Me	H	4.81	4.95		5.47	4.87	5.08		5.68
(Z)-(Id)	H	Me	4.81	4.95	5.06					
(Ib)	H	H	4.81	4.95	4.57	5.03	4.94	5.18	5.12	5.40
(Ic) ^b		H	5.78			5.74	5.82			5.77

^a Calculated on the principle of additivity of substituent shielding constants^{8,9} taking the N-CO group to be equivalent to OAc.

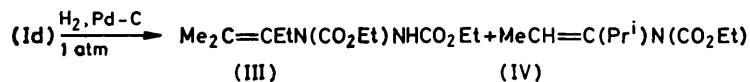
^b In (Ic) H_b and R¹ are replaced by [CH₂]_s.

(Scheme 2). 2-Methylpenta-2,3-diene also reacts readily with this enophile at 80 °C; simple competition experiments⁵ indicate that its rate of reaction is intermediate between those of 2,4-dimethylpenta-2,4-diene and 3-methylbuta-1,2-diene under the same conditions, and that the allene is a little more than twice as reactive as the correspondingly substituted alkene, 2-methylbut-2-ene.

The product, initially a viscous oil but crystallizing when pure, was identified spectroscopically as the ene adduct (Id). The reaction is thus apparently regio-specific: none of the isomeric adduct (Ie) which would be formed by hydrogen transfer from the monosubstituted terminus was detected. In this respect the allene resembles closely its olefinic counterpart, 2-methylbut-2-ene, which reacts with similar regioselectivity, giving



only the dicarbamate (II) produced by N-C bond formation at the least alkylated terminus of the π -bond.⁷



Furthermore, the ¹H n.m.r. spectrum of the adduct (Id) indicates that it has exclusively *E*-geometry at the nitrogen-substituted double bond. This point was established, albeit with reservations, by consideration of the chemical shift of the ethylidene proton, δ 5.68, which lies substantially downfield of all of the vinyl protons in the methylbutadiene adduct (Ib),⁵ and is close to that of the corresponding proton in the cyclononadiene adduct (Ic), δ 5.77,¹ which is forced to adopt an *E*-configuration because of the ring structure. Further-

* There being no available substituent constant for the N(CO₂Et)NHCO₂Et group, the value generally used for OAc was assumed.⁹

proton shift of δ 5.06 for a *Z*-configuration and 5.47 for the suggested *E*-configuration. This apparent stereoselectivity of ene insertion will be discussed in more detail below.

Mild catalytic hydrogenation (Pd-C; 1 atm.) of the adduct (Id) gave mainly the dicarbamate (III) formed by 1,4-addition of hydrogen, together with ca. 10% of an isomer, identified as (IV) on the basis of a n.m.r. doublet attributable to an isopropyl group. No attempt was made to force the reaction to completion.

Reactions of 2-Methylpenta-2,3-diene with Alkynes.—The behaviour of 2-methylpenta-2,3-diene towards electron-deficient acetylenes was then studied, initially using hexafluorobut-2-yne. At 80 °C a mixture of 1 : 1 adducts and an involatile oil were obtained, the former containing at least five components of which the four largest were isolated by preparative g.l.c. The major products proved to be the cyclohexa-1,4-diene (Va) (36%), presumed by analogy with earlier work⁴ to arise by acid-catalysed rearrangement of the allene to 2-methylpenta-1,3-diene followed by Diels-Alder cycloaddition of

the acetylene, and the alkylidenecyclobutenes (VIa) (31%) and (VIIa) (16%) formed by [2 + 2] cycloaddition without rearrangement. Only one (VIIIa) of several possible isomeric ene adducts was isolated, and in rather meagre yield (8%) (Scheme 3a).

The corresponding reaction of 2-methylpenta-2,3-diene with dimethyl acetylenedicarboxylate also gave a mixture of 1 : 1 adducts, only three of which could be isolated in amounts adequate for identification. The

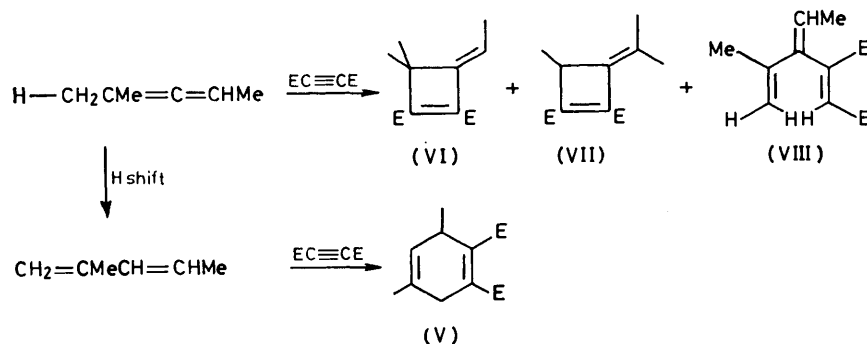
⁷ W. A. Thaler and B. Franzus, *J. Org. Chem.*, 1964, **29**, 2226.

⁸ C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, 1966, **49**, 164.

⁹ S. W. Tobey, *J. Org. Chem.*, 1969, **34**, 1281.

main products were the two [2 + 2] cycloadducts (VIb) (27%) and (VIIb) (36%); the only ene adduct isolated was (VIIIb) (18%) (Scheme 3b). The non-appearance of a Diels-Alder adduct (Vb) is attributed to the use of a

δ 5.82, and is well removed from the corresponding resonance in the available *E*-isomer (Xb), δ 6.23.⁴ Furthermore, the value of $^5J_{\text{FF}}$ (11.2 Hz) confirms the *cis*-disposition of the trifluoromethyl groups in (VIIIa),



SCHEME 3 a; E = CF₃, b; E = CO₂Me

hydrocarbon solvent and to the absence of traces of acidic decomposition products such as those likely to arise when hexafluorobutylene is heated in glass vessels.⁴

The structure of the ene adducts (VIII) establishes the regioselective nature of the insertion, though the low yield of adducts is disappointing. There remain two significant structural features to establish, however: the geometries of the two trisubstituted double bonds. With the information now available we do not feel able to assign firmly the geometry of the ethylidene terminus, although the chemical shift of the methyl doublet, δ 1.76 in (VIIIa) and 1.50 in (VIIIb), is to highfield of the position expected for a methyl *syn* to a C(CF₃)= or C(CO₂Me)= group ($\delta \geq 1.80$ in our experience^{4,6}), which suggests an *E*-configuration comparable with that of (Id). However the chemical shifts of the vinyl quartets, δ 5.82 in (VIIIa) and 5.80 in (VIIIb), do not necessarily indicate proximity to deshielding groups. An important compound for comparison is the pentadienylamide (IX),¹⁰ of which the n.m.r. spectra of the *Z*- and *E*-isomers* have been published. Prediction of the vinyl proton shifts by the Pascual-Meier-Simin approach⁹ shows that in the *E*-isomer (IXa) ($\delta_{\text{calc.}}$ 6.44, $\delta_{\text{obs.}}$ 6.65) the observed deshielding relative to the *Z*-isomer (IXb) ($\delta_{\text{calc.}}$ 6.03, $\delta_{\text{obs.}}$ 5.67) is twice as large as that predicted, and this implies that a value of δ 5.80–5.82 in (VIII) is possibly lower than that to be expected for a proton *syn* to an electron-deficient π -bond. Reliable substituent shift constants for such π -systems are not available, unfortunately.

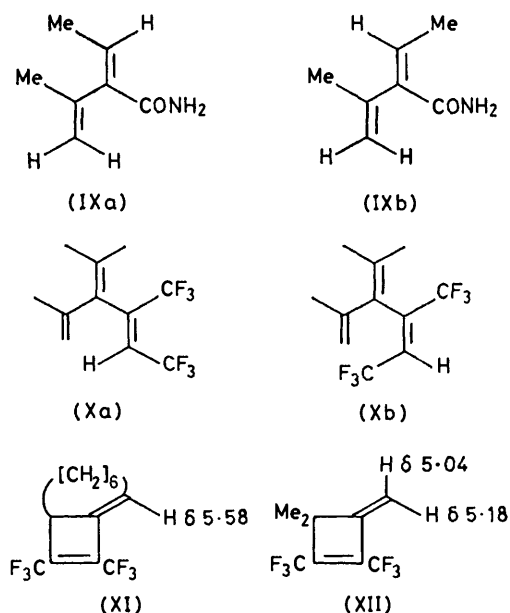
The geometries of the electron-deficient 2,3-double bonds in (VIIIa and b) are, by contrast, reliably assignable as *Z*-structures since 2-H, δ 5.90 in (VIIIa) and 5.80 in (VIIIb), resonates close to that in the *Z*-isomer of the tetramethylallene-hexafluorobutylene adduct (Xa),

* We find a discrepancy between the text definition and the structural diagram which depicts the *cis* and *trans* (*sic*) isomers of (IX).¹⁰ We take Chart I to be in error, and assume '*cis*' corresponds to (IXb).

¹⁰ E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, 1968, **33**, 3036.

¹¹ J. C. Sauer and G. N. Sausen, *J. Org. Chem.*, 1962, **27**, 2730.

and there are numerous citations of the chemical shift of the analogous vinyl protons in 2-alkylmaleates (δ values in the range 5.68–6.05)^{11–14} and 2-alkyl fumarates (δ 6.71–6.72).^{13,14} This structural feature is of some importance, since the corresponding reactions of 2,4-dimethylpenta-2,3-diene yield significant proportions of the *trans*-ene adducts, e.g. (Xb).^{4,14}



The *E*-geometry of the 3-ethylidene groups in (VIa and b) is indicated by their n.m.r. spectra on a similar basis to that described for (Id), the predicted shift values for the vinyl proton being δ 5.38 (*E*-isomer) and 5.18 (*Z*-isomer). The values observed, δ 5.39 in (VIa), 5.35 in (VIb), besides being close to that predicted for an *E*-isomer, are very similar to that of the corresponding

¹² P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, 1968, **90**, 1517.

¹³ P. J. Collin and S. Sternhell, *Austral. J. Chem.*, 1966, **19**, 317.

¹⁴ J. C. Martin, P. L. Carter, and J. L. Chitwood, *J. Org. Chem.*, 1971, **36**, 2225.

adduct of cyclonona-1,2-diene (XI), δ 5.58,¹ a compound which must adopt the *E*-configuration.

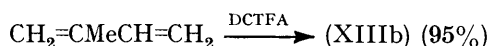
However, it is disappointing that shift values predicted on the same basis for the exocyclic vinyl protons in the 2-methylbuta-1,2-diene adduct (XII) are 0.3 p.p.m. lower than the observed values,⁶ an amount sufficient to place the geometrical assignment for (VIa and b) in doubt. In the absence of the *Z*-isomers, this structural point is difficult to establish; in cases where both isomers are available the chemical shift of the geminal 4-methyl groups has been used.¹⁵ A g.l.c.-m.s. analysis of the mixed 1:1 adducts from the hexafluorobutynemethylpentadiene reaction indicated that the *Z*-isomer of (VIa) may indeed be present, but it could not be isolated in quantities sufficient for n.m.r. analysis owing to poor g.l.c. resolution.

Reactions of 1,3-Dichlorotetrafluoroacetone (DCTFA).—
(a) *With 2-methylpentadiene.* A very rapid reaction occurs when DCTFA and 2-methylpenta-2,3-diene are

(XIIIb and c), which are symmetrical with respect to the heterocyclic ring, display 12-line AA'BB' multiplets. In (XIIIa) the two CF₂Cl groups are also chemically non-equivalent due to the 6-methyl group, and its ¹⁹F n.m.r. spectrum appears as a 28-line pattern interpreted as two overlapping AB systems.

The spectroscopic data of the ene adduct (XIVa) convincingly establish that the insertion is regioselective in favour of the more substituted double bond, as in the previous reactions. The low conversion (69%) into volatile products should be assessed against the high recovery; negligible amounts of unidentified 1:1 adducts were detected. To assess whether the reaction is also stereoselective, the geometry of the ethylidene group must be established, and therefore the n.m.r. spectra of (XIVa and b) were compared. The comparison suggests, as it did for the azodiformate adduct of this allene, that the *E*-isomer is formed preferentially. Thus, the vinyl proton quartet in (XIVa), δ 6.14, is the expected 0.46 p.p.m.⁹ to low field of even the most deshielded vinyl proton in (XIVb), which is taken to be the one nearest the electron-withdrawing methanol substituent (for which no shielding constant is available). This assignment is supported by the position of the methyl doublet, δ 1.71, in (XIVa), *i.e.* to highfield of the position expected for a *Z*-isomer.

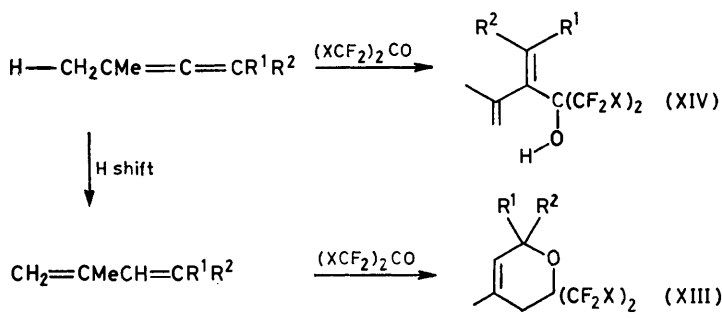
(b) *With 3-methylbuta-1,2-diene.* This reaction, previously reported in the patent literature,¹⁶ was repeated to prepare (XIVb) for spectroscopic analysis. In addition to the reported product (53% yield) we obtained an isomeric 1:1 adduct identified as the dihydropyran (XIIIb) (21%), presumed to arise by spontaneous rearrangement of the allene to isoprene. The latter was shown in a separate experiment to undergo a Diels-Alder reaction with DCTFA yielding (XIIIb), which appears to be a compound hitherto unreported, though two close homologues were synthesised in the same way during a study of diene-fluoroketone cycloadditions.¹⁷



The orientation of addition leading to (XIIIb), a 4-rather than a 3-methyldihydropyran, is established from the position of the methyl n.m.r. resonance (δ 1.76; a 3-methyl group should resonate at $\delta \leq 1.65$).¹⁷

(c) *With 2,4-dimethylpenta-2,3-diene.* This tetraalkylallene and DCTFA, kept at 80 °C in a Pyrex tube, gave in high yield two 1:1 adducts, of which the major isomer was readily identified as (XIIIc) (79%). Its 4-methyl group resonates at δ 1.75, supporting the structural assignment of (XIIIb); in (XIIIc) the orientation is fixed by the chemical shift of the ring methylene.¹⁷

In an attempt to increase the yield of the minor product, spectroscopically identified as the dienol (XIVc) (6%), by minimising the prototropic rearrangement leading to (XIIIc), the reaction was carried out in the gas phase at 100 °C. In addition to the dihydropyran (XIIIc) (61%), two new products were detected by gas



- a; X = Cl, R¹ = H, R² = Me
b; X = Cl, R¹ = R² = H
c; X = Cl, R¹ = R² = Me
d; X = F, R¹ = R² = Me

SCHEME 4

mixed at ambient temperature, and a red colour develops in the liquid phase. The main product (56%) is the dihydropyran (XIIIa), but some of the ene adduct, the pentadienylmethanol (XIVa) (13%), was also isolated. The spontaneous development of a red colour is attributed to formation of a charge-transfer complex between the ketone and either the allene or its conjugated isomer. Such a complex of the allene could explain its ready rearrangement, a reaction believed to precede formation of (XIIIa) by Diels-Alder cycloaddition of DCTFA to the conjugated diene, and previously noted to occur when alkylallenes are treated with hexafluoroacetone (Scheme 4).³ Like all the dihydropyrans produced in such reactions, (XIIIa) displays an intense, very characteristic, i.r. doublet at 1340–1370 cm⁻¹. Another characteristic property of the dihydropyrans (XIIIa–c) prepared from DCTFA is the complexity of their ¹⁹F n.m.r. spectra, which arises from non-equivalence of the fluorines in each CF_ACF_BCl group. Thus the adducts

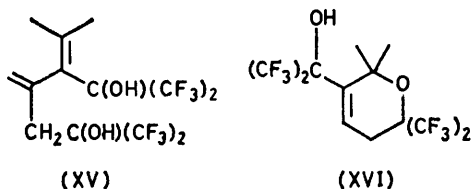
¹⁵ J. E. Baldwin and R. H. Fleming, *J. Amer. Chem. Soc.*, **1973**, **95**, 5249 and references cited therein; see also M. Bertrand, R. Maurin, J. L. Gras, and G. Gil, *Tetrahedron*, **1975**, **31**, 849.

¹⁶ H. R. Davis, U.S.P. 3 284 516/1966.

¹⁷ W. J. Linn, *J. Org. Chem.*, **1964**, **29**, 3111.

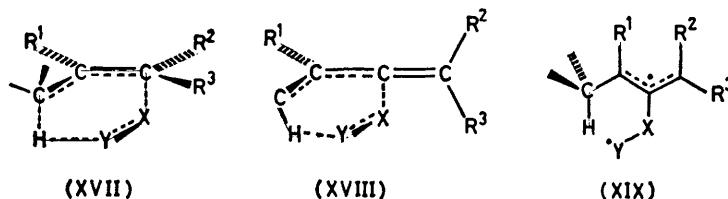
chromatography and shown by g.l.c.-m.s. to be 2 : 1 ketone-allene adducts. Although these products have not yet been fully characterised, their formation suggests that ene insertion occurs but is followed under these conditions by Diels-Alder addition of another molecule of ketone or by further ene insertion. Related 2 : 1 adducts are formed in the reactions of 3-methylbuta-1,2-diene³ and 2,4-dimethylpenta-2,3-diene (below) with hexafluoroacetone.

Since prototropic rearrangement of the allene might be triggered off by acidic surfaces, the reaction was repeated in a stainless steel reactor. No significant difference in product distribution was noted between this and the



liquid phase reaction in Pyrex: the dihydropyran (XIIIc) was still the main product.

Reaction of 2,4-Dimethylpenta-2,3-diene with Hexafluoroacetone.—This reaction was previously found to yield the dihydropyran (XIIIc) in high yield, without detection of products attributable to ene insertion.³ Repetition of the reaction in Pyrex but in the gas phase at 100 °C now yielded, in addition to the dihydropyran (46%), a solid, m.p. 100–101 °C. Its mass spectrum and elemental composition showed it to be a 2 : 1 adduct, and its ¹⁹F n.m.r. spectrum displays two types of CF₃ group. It is believed to be the hydroxydienol (XV), rather than the Diels-Alder cycloadduct (XVI), on the basis of its



n.m.r. spectrum which reveals the presence of (i) Me₂C= (δ 1.48 and 1.51), (ii) =CCH₂ (δ 2.94), and (iii) CH₂= functions (δ 5.33–5.55), accompanied by a broad, two-proton signal (δ 4.04) which is ascribed to two hydroxy groups since it is exchanged out when D₂O is added.

DISCUSSION

Concertedness has been recently demonstrated for azodiformate insertions into acyclic olefins,¹⁸ and evidence is accumulating that the concerted [$\pi 2_s + \pi 2_s + \sigma 2_s$] pathway is preferred for other types of enophiles.^{19–22}

¹⁸ L. M. Stephenson and D. L. Mattern, *J. Org. Chem.*, 1976, **41**, 3614.

¹⁹ J. A. Berson, R. G. Wall, and H. D. Perlmutter, *J. Amer. Chem. Soc.*, 1966, **88**, 187.

²⁰ L. E. Friedrich, J. A. Kampeier, and M. Good, *Tetrahedron Letters*, 1971, 2783.

²¹ R. K. Hill, J. W. Morgan, R. V. Shetty, and M. E. Synerholm, *J. Amer. Chem. Soc.*, 1974, **96**, 4201.

Such conclusions do not necessarily apply to allenic substrates, which are recognized to follow two-step cycloaddition pathways,²³ and which have been shown to undergo non-stereospecific ene insertions with electron-deficient alkynes, compatible with a two-step mechanism.^{4,6,14}

Steric effects in ene reactions are not well understood, though it is known (i) that *trans*-olefins react faster than their *cis*-isomers,⁷ (ii) that olefins like β -pinene react preferentially at their less hindered face,²⁴ and (iii) that *endo*-transition states are favoured.^{19,21} The 100% regioselectivity of ene insertions by azodiformates into 2-methylbut-2-ene⁷ and now reported for ene insertions into 2-methylpenta-2,3-diene cannot, however, be ascribed wholly to steric control. Both hydrocarbons react faster than less alkylated compounds, and the 100% selectivity in the case of 2-methylbut-2-ene would not be compatible with a rate ratio for *trans*- over *cis*-but-2-ene of only 4 : 1. Rather, the regioselectivity points to the favourable effect of 2-alkyl substituents in the transition state [*e.g.* (XVII; R¹ ≠ H)]. The high insertion rates of isobutene⁷ and of allenes relative to comparably substituted olefins^{1,5} indicate that the absence of 1-alkyl substituents [*e.g.* (XVII; R² = R³ = H) or (XVIII)] is also favourable.

The stereoselectivity of insertion (*syn*) of alkynes into 2-methyl penta-2,3-diene is not to be regarded as convincing evidence of concertedness, since not all the 1 : 1 adducts could be characterised. However, the preferential formation of isomers with *E*-geometry at the ethylidene terminus [(Id), (XIVa), and possibly (VIIIa and b)] is noteworthy, and seems to be more compatible with the operation of a steric effect in a concerted pathway *via* (XVIII) than in a stepwise pathway *via* a

diradical intermediate such as (XIX), since work on stepwise cycloadditions would suggest the opposite stereochemical outcome for a stepwise ene-insertion.^{23,25–27}

EXPERIMENTAL

Pure products were identified by i.r. (Perkin-Elmer models 137 with NaCl and 257 with grating optics), n.m.r. (Perkin-Elmer R10 or Hitachi-Perkin-Elmer R20 operated at 60 MHz for ¹H and 56.5 MHz for ¹⁹F, or Perkin-Elmer R32 operated at 90 MHz for ¹H, or, for highest resolution, Varian HA-100 operated at 100 MHz for ¹H and 94.1 MHz for ¹⁹F; shift values, positive downfield, from internal

²² H. H. Wasserman and L. S. Keller, *Tetrahedron Letters*, 1974, 4355.

²³ J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, 1970, **15**, 281.

²⁴ R. T. Arnold and J. S. Showell, *J. Amer. Chem. Soc.*, 1957, **79**, 419.

Me₄Si or external CF₃CO₂H), u.v. (Hilger-Watts Ultrascan SP 700), and mass spectrometry (AEI MS902 with AEI DS10 data acquisition; only the most intense bands of *m/e* > base peak are reported). Analytical g.l.c. was carried out on Pye-Unicam model 104 chromatographs (dual flame ionization detector, 4 mm i.d. columns) and preparative g.l.c. separations were achieved either on Pye 104 with 3/8 in columns or on Perkin-Elmer F21 chromatographs with 3.5 × 6 mm columns.

2-Methylpenta-2,3-diene, prepared in 55% yield by Skattebøl's method,²⁸ was purified by fractional distillation (30 cm Fenske packed column), b.p. 72.5 °C, *n*_D²⁵ 1.434 5 (lit.,²⁹ b.p. 72.5 °C, *n*_D²⁵ 1.435 0). Diethyl azodiformate,⁵ dimethyl acetylenedicarboxylate,⁴ and hexafluorobut-2-yne⁴ were prepared as described previously. 1,3-Dichlorotetrafluoroacetone and hexafluoroacetone were obtained commercially and redistilled.

Reactions of 2-Methylpentadiene.—(a) *With diethyl azodiformate.* 2-Methylpenta-2,3-diene (4.6 g, 56.1 mmol), diethyl azodiformate (5.05 g, 29.0 mmol), and polymerization inhibitor (mixed terpenes; 0.15 g), kept at 80 °C for 48 h in a sealed Pyrex tube (base rinsed; 300 cm³), gave on fractional distillation unchanged methylpentadiene (25.6 mmol, 46%), a viscous oil, b.p. 110 °C at 0.1 mmHg, and a brown residue (0.6 g). The oil solidified on standing; recrystallization (hexane) gave a solid identified spectroscopically as *diethyl (E)-1-isopropenylprop-1-enyldicarbamate* (Id) (6.7 g, 26.2 mmol, 90% on RN:NR), m.p. 61–62 °C (Found: C, 56.1; H, 7.9; N, 10.2%; *M*⁺, 256.142 1. C₁₂H₂₀N₂O₄ requires C, 56.2; H, 7.8; N, 10.9%; *M*, 256.142 2), *v*_{max} (mull) 3 280m (NH str.), 3 090w, 2 990m, 2 920m, 2 870w, 2 740w, 1 750vs (C:O str.), 1 700vs and 1 660vs (C:C str.), 1 640w, 1 520s, 1 480m, 1 470w, 1 450s, 1 400s, 1 380vs, 1 330s, 1 300m, 1 240s, 1 190m, 1 100w, 1 060m, 1 020w, 910w, 840w, 765w, and 720w cm⁻¹, *λ*_{max} (hexane) 230 nm (ε 9 600), δ_H (100 MHz; CCl₄) 7.14 (NH), 5.68 (q, :CHMe), 5.08br and 4.87br (2 × s, :CH₂), 4.10 (2 overlapping q, OCH₂Me × 2), 1.87 (s, :CMe), 1.75 (nsym, d, ³J_{HH} 6.8 Hz, :CHMe), and 1.23 (t, ³J_{HH} 7 Hz, OCH₂Me × 2), *m/e* 256 (6%, *P*) and 94 (100, C₆H₈N).

(b) *With hexafluorobutylene.* 2-Methylpenta-2,3-diene (4.1 g, 50 mmol), hexafluorobut-2-yne (8.1 g, 50 mmol), and inhibitor (0.2 g), kept in a Pyrex tube (300 cm³) at 80 °C for 48 h, gave a sticky involatile resin (0.6 g) and a volatile liquid (11.7 g) shown by g.l.c. (2 m Apiezon L; 80 °C) to contain five components in the ratio (in order of elution) 32 : 5 : 8 : 17 : 38 (by area). Preparative g.l.c. (Apiezon L; 100 °C) yielded samples of components 1 and 3–5 which were identified spectroscopically as: (component 1) (E)-3-ethylidene-4,4-dimethyl-1,2-bis(trifluoromethyl)cyclobutene (VIa) (3.74 g, 15.3 mmol, 31% by g.l.c.), a liquid, b.p. 107 °C (Found: C, 48.2; H, 4.2; F, 44.9%; *M*⁺, 244. C₁₀H₁₀F₆ requires C, 49.1; H, 4.1; F, 46.8%; *M*, 244), *v*_{max} (liquid) 2 980w, 2 930w, 2 850w, 1 715w (C:CF₃ str.), 1 650m (C:CMe str.), 1 460w, 1 440w, 1 360sh, 1 355s, 1 320s, 1 290vs, 1 275s, 1 250vs, 1 180vs, 1 140vs, 1 130vs, 1 065w, 1 030w, 980m, 965m, 825m, 730m, 710w, and 700s cm⁻¹, δ_H (100 MHz; CDCl₃) 5.39 (q, ³J_{HH} 7.5 Hz, :CHMe), 1.77 (d, :CHMe), and 1.32 (s, CMe₂), δ_F (94.1 MHz; CDCl₃) 14.5 (q) and 16.7 (q, ⁵J_{FF} 7.2 Hz), *m/e* 244 (74%, *P*), 229 (94, *P* – Me), and 175 (100, *P* – CF₃); (component 3)

(Z,?)-1,1,1-trifluoro-4-(prop-2-enyl)-3-trifluoromethylhexa-2,4-diene (VIIIa) (0.94 g, 3.8 mmol, 8%), a liquid, b.p. 118 °C (Found: C, 48.1; H, 4.0; F, 45.3%; *M*⁺, 244. C₁₀H₁₀F₆ requires C, 49.1; H, 4.1; F, 46.8%; *M*, 244), *v*_{max} (liquid) 3 050w, 2 970w, 2 900w, 2 810w, 1 690w and 1 650m (C:C str.), 1 620w, 1 435w, 1 340s, 1 330s, 1 280sh, 1 270vs, 1 250sh, 1 230s, 1 210m, 1 180s, 1 130vs, 1 080s, 1 060w, 1 030w, 980w, 905m, 860w, 835w, 810w, 729w, 700m, and 680m cm⁻¹, δ_H (100 MHz; CCl₄) 5.90 (q, ³J_{HF} 9 Hz, :CHCF₃) over-lapping a band at 5.82 (q, ³J_{HH} 7.6 Hz, :CHMe), 5.20br and 4.83br (2 × s, :CH₂), 1.80 (s, :CMe), and 1.76 (d, :CHMe), δ_F (94.1 MHz; CCl₄) 18.9 (q, ⁵J_{FF} 11.2 Hz, :CCF₃) and 21.1 (qd, :CHCF₃), *m/e* 244 (28%, *P*), 229 (11, *P* – Me), 175 (28, *P* – CF₃), and 40 (100, C₃H₄); (component 4) 3-isopropylidene-4-methyl-1,2-bis(trifluoromethyl)cyclobutene (VIIa) (1.97 g, 8.1 mmol, 16%), b.p. 125 °C (Found: C, 48.6; H, 4.2; F, 46.0%; *M*⁺, 244. C₁₀H₁₀F₆ requires C, 49.1; H, 4.1; F, 46.8%; *M*, 244), *v*_{max} (liquid) 2 959w, 2 899w, 2 849w, 1 718w (endocyclic C:C str.), 1 639m (exocyclic C:C str.), 1 451m, 1 433w, 1 364m, 1 344s, 1 302s, 1 279vs, 1 239s, 1 199vs, 1 179vs, 1 144vs, 1 076m, 1 066m, 1 041m, 991m, 918w, 869w, 788w, 757w, 726m, and 700s cm⁻¹, *λ*_{max} (hexane) 260 nm (ε 6 590), *λ*_{min} 229 nm (ε 2 740), δ_H (100 MHz; CDCl₃) 3.37br (m, CHMe), 1.80 and 1.73 (2 × s, :CMe₂), and 1.32 (d, ³J_{HH} 6 Hz, CHMe), δ_F (94.1 MHz) 15.1 [qd, ⁵J_{FF} 7.4, ⁴J_{FF} 2.2 Hz, :C(CF₃)CHMe] and 17.0 (q, :CCF₃), *m/e* 244 (66%, *P*), 229 (19, *P* – Me), 209 (12, C₉H₈F₅), and 175 (100, *P* – CF₃); and (component 5) 3,5-dimethyl-1,2-bis(trifluoromethyl)cyclohexa-1,4-diene (Va) (4.4 g, 18 mmol, 36%), b.p. 139 °C (Found: C, 48.6; H, 4.1; F, 45.3%; *M*⁺, 244. C₁₀H₁₀F₆ requires C, 49.1; H, 4.1; F, 46.8%; *M*, 244), *v*_{max} (liquid) 2 970m, 2 900m, 2 850m, 1 690w and 1 660m (C:C str.), 1 490m, 1 420m, 1 380w, 1 370w, 1 340w, 1 280vs, 1 210sh, 1 190vs, 1 160vs, 1 135vs, 1 075vs, 1 035s, 1 000s, 975vs, 900w, 840m, 825m, 755m, 720s, and 705w cm⁻¹, δ_H (100 MHz; CDCl₃) 5.37br (s, :CH), 3.14 (poorly resolved q, CHMe), 2.82br (s, CH₂), 1.70 (s, :CMe), and 1.15 (d, ³J_{HH} 6.4 Hz, CHMe), δ_F (94.1 MHz) 15.3 (q, ⁵J_{FF} 14 Hz) and 18.9 (q), *m/e* 244 (47%, *P*), 229 (78, *P* – Me), and 209 (100, C₉H₈F₅). Component 2, although not isolated, is believed to be a 1 : 1 adduct (Found: *M*⁺, 244. Calc. for C₁₀H₁₀F₆: *M*, 244), possibly the *Z*-isomer of (VIa), on the basis of g.l.c.–m.s. analysis, *m/e* 244 (100%, *P*), 229 (80, *P* – Me), and 175 (93, *P* – CF₃). The three major products (Va)–(VIIa) were separately kept at 80 °C for 48 h without change by g.l.c. (50 m Apiezon L capillary; 80 °C).

With dimethyl acetylenedicarboxylate. 2-Methylpenta-2,3-diene (5.75 g, 70 mmol), dimethyl acetylenedicarboxylate (9.96 g, 70 mmol), benzene (30 cm³), and inhibitor (0.2 g), kept in a Pyrex tube (300 cm³) for 72 h at 80 °C, gave, on distillation under nitrogen, benzene, a yellow oil (14.1 g), b.p. 80–82° at 0.1–0.2 mmHg, and a residue (1.6 g). The oil was shown by g.l.c. (2 m Apiezon L; 190°) to consist of four compounds in the ratio (in order of elution) of 3 : 1 : 2 : 4 (by area), and was separated by preparative g.l.c. (Apiezon L; 200°) to give the following samples: (component 1) a liquid identified spectroscopically as (E)-3-ethylidene-1,2-bis(methoxycarbonyl)-4,4-dimethylcyclobutene (VIb) (4.23 g, 18.9 mmol, 27% by g.l.c.) (Found: C, 64.0; H, 6.8%; *M*⁺, 224. C₁₂H₁₆O₄ requires C, 64.3; H, 7.2%; *M*, 224)

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ν_{\max} . (liquid) 2 990s, 2 790sh, 1 740vs (C:O str.), 1 710vs and 1 690s (C:C str.), 1 610s, 1 440vs, 1 340m, 1 280vs, 1 230vs, 1 190m, 1 160m, 1 140m, 1 090m, 980m, 945w, 910w, 860w, 820w, and 770w cm^{-1} , δ (60 MHz; CCl_4) 5.35 (q, :CHMe), 3.65 and 3.58 ($2 \times s$, OMe $\times 2$), 1.50 (d, $^3J_{\text{HH}}$ 7.4 Hz, :CHMe), and 0.94 (s, CMe_2), m/e 224 (19%, P), 193 (29, $P - \text{OMe}$), and 192 (100, $\text{C}_{11}\text{H}_{12}\text{O}_3$); (component 2) an unidentified 1 : 1 adduct (Found: M^+ , 224. Calc. for $\text{C}_{12}\text{H}_{16}\text{O}_4$: M , 224), ν_{\max} . (liquid) 1 730s (C:O str.) and 1 710s and 1 620s (C:C str.), δ (60 MHz; CCl_4) 3.7 and 1.5—1.0; (component 3) a yellow oil identified spectroscopically as methyl (Z,?)-3-methoxycarbonyl-4-(prop-2-enyl)hexa-2,4-dienoate (VIIIb) (2.82 g, 12.6 mmol, 18%) (Found: C, 62.8; H, 6.7%; M^+ , 224. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires C, 64.3; H, 7.1%; M , 224), ν_{\max} . (liquid) 2 940m, 2 850sh, 1 750vs (C:O str.), 1 730vs and 1 650s (C:C str.), 1 620w, 1 440s, 1 380m, 1 350s, 1 290s, 1 240s, 1 210s, 1 170vs, 1 110m, 1 070w, 1 040w, 990m, 900m, 880w, 865m, and 830w cm^{-1} , δ (60 MHz; CCl_4) (sample contaminated by component 2) 5.8 (m, :CHCO₂Me) overlapped by 5.8 (m, :CHMe), 5.3br and 4.8br ($2 \times s$, :CH₂), 3.7 and 3.6 ($2 \times s$, OMe $\times 2$), 1.6 (s, :CMe), and 1.5 (d, $^3J_{\text{HH}}$ 7.2 Hz, :CHMe), m/e 224 (11%, P), 193 (31, $P - \text{OMe}$), 192 (26), 165 (28, $P - \text{CO}_2\text{Me}$), 164 (92), 149 (27), 133 (68), and 105 (100, C_8H_8); and (component 4) a viscous oil identified spectroscopically as 3-isopropylidene-4-methyl-1,2-bis(methoxycarbonyl)cyclobutene (VIIb) (5.64 g, 25.2 mmol, 36%) (Found: C, 64.4; H, 6.7%; M^+ , 224. $\text{C}_{12}\text{H}_{16}\text{O}_4$ requires: C, 64.3; H, 7.1; M , 224), ν_{\max} . (liquid) 2 930vs, 2 870sh, 1 750vs (C:O str.), 1 730vs and 1 700m (C:C str.), 1 610m, 1 450m, 1 380w, 1 340m, 1 280vs, 1 210s, 1 160s, 1 110m, 1 090w, 1 070w, 1 030w, 800w, and 770w cm^{-1} , δ (60 MHz; CCl_4) 3.70 and 3.65 ($2 \times s$, OMe $\times 2$), *ca.* 2 (q, CHMe), 1.55 and 1.48 ($2 \times s$, :CMe₂), and 1.13 (d, $^3J_{\text{HH}}$ 7 Hz, CHMe), m/e 224 (17%, P), 209 (13, $P - \text{Me}$), 193 (43, $P - \text{OMe}$), and 192 (100, $\text{C}_{11}\text{H}_{12}\text{O}_3$).

Hydrogenation of the Dicarbamate (Id).—The dicarbamate (Id) (363 mg, 1.42 mmol) in ethanol (10 cm^3) was stirred with 5% palladium on charcoal (1 mg) while hydrogen was admitted from a conventional 1 atm. manifold. After 4 h, when hydrogen uptake had ceased, gas adsorbed measured 35 cm^3 (1.4 mmol); the mixture was filtered and the filtrate evaporated to give an oil which, by molecular distillation, gave diethyl 1-isopropylidenepropylidicarbamate (III) (338 mg, 1.31 mmol, 92%) (Found: C, 55.7; H, 8.4; N, 10.0%; M^+ , 258.159 4. $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_4$ requires C, 55.8; H, 8.5; N, 10.8%; M , 258.157 9), ν_{\max} . (liquid) 3 280m (NH str.), 2 990m, 2 880sh, 1 750 (C:O str.), 1 720vs, 1 650w, 1 500w, 1 450m, 1 440m, 1 395m, 1 360s, 1 330s, 1 240sh, 1 230sh, 1 220vs, 1 175m, 1 085m, 1 060s, 1 025w, 930w, and 760w cm^{-1} , δ (100 MHz; CCl_4) 7.70 (NH), 4.10 (q, $^3J_{\text{HH}}$ 7 Hz, $\text{OCH}_2\text{Me} \times 2$), 2.17 (q, $^3J_{\text{HH}}$ 7.2 Hz, :CCH₂-Me), 1.70 and 1.64 ($2 \times s$, :CMe₂), 1.23 (t, $\text{OCH}_2\text{Me} \times 2$), and 0.96 (t, :CCH₂Me) [the spectrum showed the presence of *ca.* 10% of an impurity believed to be MeCH:CPriN(CO₂Et)-NHCO₂Et, with resonances at δ 7.36 (NH), 5.24 (q, :CHMe), and 1.07 (d, CHMe₂)], m/e 258 (13%, P), 186 (51), 170 (36), 169 (23), 145 (43), 142 (24), 140 (29), 139 (24), and 125 (100).

Competition Experiments.—The relative reactivity of 2-methylpenta-2,3-diene towards diethyl azodiformate was measured at 80 °C by the previously described technique.⁵ Two determinations were carried out, comparing the methylpentadiene with (a) 2,3-dimethylbut-2-ene (k_{rel} for methylpentadiene 1.3 \pm 0.1) and (b) 2-methylbut-2-ene (k_{rel} for

methylpentadiene 2.2 \pm 0.2). The extent of consumption of the reagents (30 mmol each of methylpentadiene and olefin, 3 mmol of diethyl azodiformate) were measured by triplicate g.l.c. analysis using a 50 m capillary Apiezon L column programmed from 50 to 100 °C, using n-pentane as internal standard.

Reaction of DCTFA with Dimethylpentadiene.—(a) *Liquid phase, Pyrex reactor.* 2,4-Dimethylpenta-2,3-diene (3.17 g, 33 mmol) and DCTFA (5.97 g, 30 mmol), kept in a sealed Pyrex tube (300 cm^3) for 48 h at 80 °C, gave a mixture shown by g.l.c. (2 m PEG-A; 145°) to consist of four components in the ratio (in order of elution) 2 : 36 : 3 : 2 (by area). Components 1 and 4 were identified as, respectively, DCTFA (0.4 g) and the known dimer of 2,4-dimethylpenta-1,3-diene [1,3,3,5,5-pentamethyl-4-(prop-2-enyl)cyclohexene]³⁰ (0.4 g, 13%) by comparison with authentic samples. The remaining components were isolated by g.l.c. (4 m PEG-A, 190°) and identified spectroscopically as (component 2) 2,2-bis(chlorodifluoromethyl)-3,6-dihydro-4,6,6-trimethyl-2H-pyran (XIIIc) (7.70 g, 26.1 mmol, 79% from the allene), a liquid, b.p. 215 °C [Found: C, 41.2; H, 4.5; F, 24.7; Cl, 23.8%; M^+ , 294. $\text{C}_{10}\text{H}_{12}\text{Cl}_2\text{F}_4\text{O}$ requires C, 40.7; H, 4.1; F, 25.8; Cl, 24.1%; M (for ^{35}Cl), 294], ν_{\max} . (liquid) 3 020s, 2 980s, 2 900m, 1 665w (C:C str.), 1 440m, 1 430s, 1 370s, 1 350s, 1 290m, 1 270s, 1 240m, 1 220s, 1 205vs, 1 175vs, 1 160vs, 1 125vs, 1 080vs, 1 035s, 1 020s, 980s, 960s, 935s, 920s, 890m, 848s, 824s, 795m, 782s, 735m, and 708 cm^{-1} , δ_{H} (100 MHz; CDCl_3) 5.47 (q, $^4J_{\text{HH}}$ 1.5 Hz, :CH) 2.41 (s, CH₂), 1.75 (m, :CMe), and 1.32 m (s, CMe_2O), δ_{F} (94.1 MHz) 12 line AA'BB' m centred at 18.1, m/e (^{35}Cl only) 294 (10%, P), 279 (36, $P - \text{Me}$), 209 (23), 131 (23, $\text{C}_9\text{H}_7\text{O}$), 95 (14, C_7H_{11}), and 43 (100, C_3H_5), and (component 3) 1-chloro-2-(chlorodifluoromethyl)-1,1-difluoro-4-methyl-3-(prop-2-enyl)pent-3-en-2-ol (XIVc) (0.62 g, 2.1 mmol, 6%), b.p. 220 °C [Found: C, 41.2; H, 4.5%; M^+ , 294. $\text{C}_{10}\text{H}_{12}\text{Cl}_2\text{F}_4\text{O}$ requires C, 40.7; H, 4.1%; M (for ^{35}Cl), 294], ν_{\max} . (liquid) 3 530s (OH str.), 3 000s, 2 940s, 2 850m, 1 695w (asym. C:C str.), 1 645m (sym. C:C str.), 1 450s, 1 390s, 1 370s, 1 325m, 1 285m, 1 110—1 240vs, 1 090vs, 1 040s, 975s, 950s, 885s, 818s, and 735s cm^{-1} (insufficient material for n.m.r.). An otherwise identical reaction at 95 °C for 96 h gave (g.l.c.) the pentamethylcyclohexene (25%) the dihydropyran (XIIIc) (68%), and the pentenol (XIVc) (7%).

(b) *Liquid phase, stainless steel reactor.* The dimethylpentadiene (4.3 g, 45 mmol) and DCTFA (8.2 g, 41 mmol), kept at 100 °C for 28 h in a stainless steel autoclave (25 cm^3) gave a mixture shown (g.l.c.) to consist of (XIIIc) (57%) and two other components (14 and 28% by area) later identified as 2 : 1 adducts (see below).

(c) *Gas phase, Pyrex reactor.* A Pyrex flask (3 l) was fitted with a sealed inlet leading *via* a greaseless stopcock and a ball-joint to a cold-finger and thence *via* a second greaseless stopcock to the vacuum manifold. DCTFA (8.0 g, 40.4 mmol) was placed in the bulb and 2,4-dimethylpenta-2,3-diene (4.0 g, 41.7 mmol) was condensed *in vacuo* into the cold-finger. The bulb was heated to 100 °C by immersion in stirred Lissapol, and the cold finger was warmed to 30 °C. The dimethylpentadiene was rapidly introduced into the bulb by inverting the cold-finger section and opening the connecting stopcock, and the mixed vapours were kept at 100 °C for 20 h. The bulb was inverted and liquid drained into the chilled cold-trap, giving a product shown (g.l.c.) to consist of a 40 : 11 : 15 (by area) mixture of the dihydropyran (XIIIc) (7.16 g,

³⁰ M. L. Poutsma, *J. Org. Chem.*, 1968, **33**, 4080.

24.3 mmol, 61%), b.p. 215 °C, and two unidentified components. Distillation at low pressure gave a fraction (3.8 g), b.p. 75–80 °C at 3 mmHg, consisting of (XIIIc) (14%) and two components (34 and 52% by g.l.c.) identified by g.l.c.–m.s. (4 m SE30; 220 °C) as 2:1 DCTFA–dimethylpentadiene adducts (Found: M^+ , 492–498. Calc. for $C_{13}H_{12}^{35}Cl_4F_8O_2$: M , 492) (estimated yields 13 and 20% on DCTFA, respectively), which could not be isolated by distillation. No significant alteration in product distribution was noted when the reagents were admitted to the reactor in the reverse order.

Reaction of DCTFA with 2-Methylpenta-2,3-diene.—The methylpentadiene (3.6 g, 44 mmol) and DCTFA (7.96 g, 40 mmol) were mixed by condensation *in vacuo* into a –196 °C trap and transferred after a few min at 25 °C into a Pyrex tube (200 cm³) which was sealed and kept at 70 °C for 12 h. A high boiling red liquid remained in the mixing trap; a colourless liquid was isolated by g.l.c. separation of the red liquid, and identified spectroscopically as 2,2-bis(chlorodifluoromethyl)-3,6-dihydro-4,6-dimethyl-2H-pyran (XIIIa) (2.04 g) [Found: C, 38.3; H, 3.4; F, 27.6; Cl, 25.0%; M^+ , 280. $C_9H_{10}Cl_2F_4O$ requires C, 38.4; H, 3.6; F, 27.0; Cl, 25.3%; M (for ^{35}Cl), 280], b.p. 206 °C, ν_{max} (liquid) 2 950s, 2 900s, 2 860s, 1 645m (C:C str.), 1 420s, 1 355s, 1 340s, 1 270m, 1 250s, 1 220m, 1 160vs, 1 060vs, 1 030s, 955s, 915s, 840s, 810s, and 694 cm⁻¹, δ_H (100 MHz; $CDCl_3$) 5.45 (dq, :CH, J_q 1.5, J_d 1.6 Hz), 4.46br (s, OCHMe), 2.39br (m, :CCH₂), 1.76 (s, :CMe), and 1.28 (d, $^3J_{HH}$ 6.5 Hz, OCHMe), δ_F (94.1 MHz; $CDCl_3$) a 28-line spectrum consisting of two AB portions centred at 20.04 (ddt, J_{AB} 174, J_t 11.8 Hz in the downfield portion and 15.0 Hz in the upfield portion) and 16.12 (dddd, J_{AB} 165, J_d 12–16 Hz), m/e (^{35}Cl) 280 (24%, P), 265 (79, $P - Me$), 195 (9, $P - CClF_2$), 163 (34), 96 (11, C_6H_8O), 85 (76, $CClF_2$), 82 (53, C_6H_{10}), 81 (20), 69 (14), 67 (99), 65 (13), 54 (14), 53 (18), 50 (17), and 43 (100). The contents of the sealed reactor (9.4 g) were shown (g.l.c.) to consist of four components in the area ratio 8:12:4:1, and the first two were mixed starting materials (*ca.* 3 g) and the dihydropyran (XIIIa) (total yield 6.35 g, 22.6 mmol, 56% from DCTFA). The third component was isolated by g.l.c. (4 m Apiezon L; 170 °C) and identified spectroscopically as (E)-1-chloro-2-(chlorodifluoromethyl)-1,1-difluoro-3-(prop-2-enyl)pent-3-en-2-ol (XIVa) (1.5 g, 5.3 mmol, 13% from DCTFA), b.p. 210 °C [Found: C, 39.2; H, 3.8; F, 26.5; Cl, 24.5%; M^+ , 280. $C_9H_{10}Cl_2F_4O$ requires C, 38.4; H, 3.6; F, 27.0; Cl, 25.3%; M (^{35}Cl), 280], ν_{max} (liquid) 3 590s (OH str.), 3 120w, 3 010s, 2 960s, 2 900m, 1 705w, 1 630m (C:C str.), 1 440m, 1 380s, 1 340s, 1 250m, 1 185vs, 1 150vs, 1 040vs, 1 020s, 995s, 975s, 925s, 890m, 865m, 830s, 810s, 780s, and 744s cm⁻¹, δ_H (100 MHz; $CDCl_3$) 6.14 (qm, J_q 7, J_M 1.5 Hz, :CHMe), 5.41 (q, J_q 1.65 Hz, :CH), 5.08 (s, :CH), 3.59br (s, OH), 1.90 (s, :CMe), and 1.71 (d, $^3J_{HH}$ 7 Hz, :CHMe). δ_F (94.1 MHz) 19.6 (s), m/e (^{35}Cl) 280 (23%, P), 265 (16, $P - Me$), 195 (68, $P - CClF_2$), 110 (10, $C_6H_{10}O$), 109 (50), 97 (11), 96 (23), 95 (13), 91 (23), 85 (43, $CClF_2$), 81 (73, C_6H_8), 79 (34), 78 (50), 69 (18), and 67 (100).

Reaction of DCTFA with 3-Methylbuta-1,2-diene.—The methylbutadiene (2.99 g, 44 mmol) and DCTFA (7.96 g, 40 mmol), kept at 140 °C for 96 h in a sealed Pyrex tube (200 cm³), gave a liquid (9.41 g) shown by g.l.c. (2 m Apiezon L; 140 °C) to consist mainly of two components (60 and 24% by area), which were isolated (4 m Apiezon

L; 170 °C) and identified spectroscopically as 1-chloro-2-(chlorodifluoromethyl)-1,1-difluoro-4-methyl-3-methylene-pent-4-en-2-ol (XIVb) (5.65 g, 21.2 mmol, 53% from DCTFA), b.p. 202 °C [Found: C, 36.0; H, 3.4; F, 28.4; Cl, 26.1%; M^+ , 266. $C_8H_8Cl_2F_4O$ requires C, 36.0; H, 3.0; F, 28.5; Cl, 26.1%; M (^{35}Cl), 266], ν_{max} (liquid) 3 390vs (OH str.), 3 010w, 2 970s, 2 950m, 2 850w, 1 640s (C:C str.), 1 460vs, 1 435s, 1 375vs, 1 280m, 1 190vs, 1 160vs, 1 070s, 1 020s, 960s, 940s, 848vs, 795s, 785vs, and 708w cm⁻¹, δ_H (100 MHz; $CDCl_3$) 5.68, 5.50, 5.21, and 5.09 (all incompletely resolved m, possibly dq, $J_d \approx J_q$ 1–2 Hz, :CH₂ × 2), 3.65 (s, OH), and 1.98 (m, :CMe), δ_F (94.1 MHz) 18.6 (s), m/e (^{35}Cl) 266 (11%, P), 215 (15), 195 (23), 181 (47, $P - CClF_2$), 167 (13), 147 (17), 145 (12), 131 (78), 97 (32), 85 (27, $CClF_2$), 77 (17), 67 (86), 65 (23), 53 (33), 51 (22), and 43 (100), and 6,6-bis(chlorodifluoromethyl)-5,6-dihydro-4-methyl-2H-pyran (XIIIb) (2.26 g, 8.5 mmol, 21% from DCTFA), a liquid, b.p. 195 °C [Found: C, 35.8; H, 3.0; F, 28.5; Cl, 26.5; M^+ , 266. $C_8H_8Cl_2F_4O$ requires C, 36.0; H, 3.0; F, 28.5; Cl, 26.6%; M (^{35}Cl), 266], ν_{max} (liquid) 2 950s, 2 870s, 2 750w, 1 710m (C:C str.), 1 450s, 1 380s, 1 360m, 1 280s, 1 260s, 1 225s, 1 160vs, 1 105s, 1 060s, 1 035s, 1 010s, 1 000s, 985s, 960s, 925s, 915s, 850m, 810s, 790s, and 704s cm⁻¹, δ_H (100 MHz; $CDCl_3$) 5.55 (tq, J_t 4.5, J_q 1.5 Hz, :CH), 4.34br (s, OCH₂), 2.40br (s, :CCH₂), and 1.76br (s, :CMe), δ_F (94.1 MHz) 18.3 (12 line AA'BB' m), m/e (^{35}Cl) 266 (66%, P), 251 (56, $P - Me$), and 181 (100, $P - CClF_2$).

Reaction of DCTFA with Isoprene.—DCTFA (3.98 g, 20 mmol), isoprene (1.48 g, 22 mmol), and inhibitor (mixed terpenes; 0.1 g) were kept at 200 °C for 48 h in a sealed Pyrex tube (200 cm³) to give a liquid (5 g), b.p. 195 °C shown to consist mainly of the dihydropyran (XIIIb) (95%) identified by i.r. and g.l.c. comparison with authentic material.

Reaction of Hexafluoroacetone with 2,4-Dimethylpenta-2,3-diene.—Using the technique described above for DCTFA, hexafluoroacetone (2.0 g, 12 mmol) was placed in a Pyrex flask (3 l), heated to 100 °C, and then rapidly mixed with 2,4-dimethylpenta-2,3-diene (1.3 g, 13 mmol). The mixture of gases was kept at 100 °C for 28 h, liquid product removed, and a solid adhering to the walls of the flask was washed out and identified spectroscopically as 1,1,1,7,7,7-hexafluoro-5-isopropylidene-4-methylene-2,6-bis(trifluoromethyl)-heptane-2,6-diol (XV), m.p. 100 °C (0.7 g, 1.7 mmol, 28% from ketone) (Found: C, 36.7; H, 3.0; F, 53.9%; M^+ , 428. $C_{13}H_{12}F_{12}O_2$ requires C, 36.5; H, 2.8; F, 53.5%; M , 428), ν_{max} (mull) 3 370m (OH str.), 2 950s, 2 860s, 2 810w, 1 650w (C:C str.), 1 470s, 1 370s, 1 280s, 1 230s, 1 210s, 1 175s, 1 160s, 1 125m, 1 060m, 1 020m, 985s, 975s, 894w, 880w, 838m, 746m, 730m, 717m, and 680m cm⁻¹, δ_H (100 MHz; C_6D_6) 5.55 and 5.33 (2 × s, :CH₂), 4.04br (s, OH × 2), 2.94 s, :CCH₂), and 1.51 and 1.48 (2 × s, :CMe₂) δ_F (94.1 MHz) 1.89(s) and 0.54 (s), m/e 428 (17%, P), 261 (18), 94 (11), 79 (11), 69 (15, CF_3), and 43 (100, C_6H_6). The liquid product (2.4 g) was analysed by g.l.c. (2 m Apiezon L; 120 °C) and shown to consist mainly (60% by area) of the known 3,6-dihydro-4,6,6-trimethyl-2,2-bis(trifluoromethyl)-2H-pyran³ (XIIIId) (1.44 g, 46% from ketone), identified by comparison of the i.r. spectrum with that of an authentic sample.