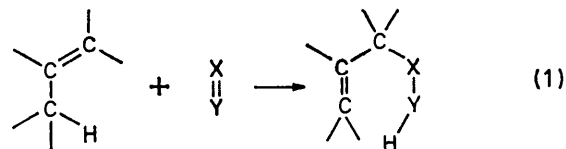


Ene Reactions of Allenes. Part I. Reactions of Alkylallenes with Hexafluoroacetone

By David R. Taylor* and D. Bruce Wright, Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

The reaction of 2,4-dimethylpenta-2,3-diene with hexafluoroacetone proceeds by rearrangement of the allene to 2,4-dimethylpenta-1,3-diene followed by a Diels-Alder reaction to give 3,6-dihydro-4,6,6-trimethyl-2,2-bis(trifluoromethyl)-2*H*-pyran under thermal or photochemical conditions. Treatment of 3-methylbuta-1,2-diene with hexafluoroacetone at ambient temperature gave a 4:1 mixture of 1,1,1-trifluoro-4-methyl-3-methylene-2-trifluoromethylpent-4-en-2-ol and 3,6-dihydro-4-methyl-2,2-bis(trifluoromethyl)-2*H*-pyran. At 175 °C, an additional product is 3,6-dihydro-5-methyl-4-(2,2,2-trifluoro-1-hydroxy-1-trifluoromethylethyl)-2,2-bis(trifluoromethyl)-2*H*-pyran.

ALDER'S ene reaction¹ usually involves the interaction of an electron-rich mono-olefin, termed the ene component and preferably bearing primary allylic hydrogen atoms, with an electron-deficient enophile [X:Y; equation (1)]. Such reactions will be exothermic² if $D(C_{sp^2}-X) + D(Y-H)$ exceeds $D_{\pi}(X:Y) + D(C_{sp^2}-H)$, since when the ene component is a mono-olefin there is little change in $D_{\pi}(C:C)$. On the basis of such considerations, alkylallenes should be especially prone to

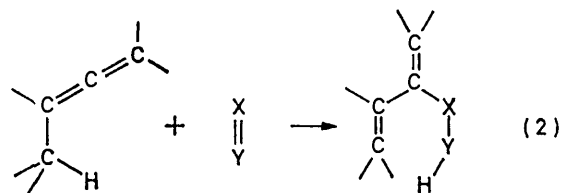


ene reactions [equation (2)] because of their more favourable change in $D_{\pi}(C:C)$, and because of the stronger $C_{sp^2}-X$ bond formed.

¹ K. Alder, F. Pascher, and A. Schmitz, *Ber.*, 1943, **76**, 27.

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

In 1968, reactions of 2,4-dimethylpenta-2,3-diene with nitrosobenzene and chlorosulphonyl isocyanate were



reported,^{3,4} which, though not so interpreted at the time, may involve ene reactions (Scheme 1). We therefore initiated a study^{5,6} of potential ene reactions of 3-methylbuta-1,2-diene and 2,4-dimethylpenta-2,3-diene with a series of enophiles, commencing with hexafluoro-

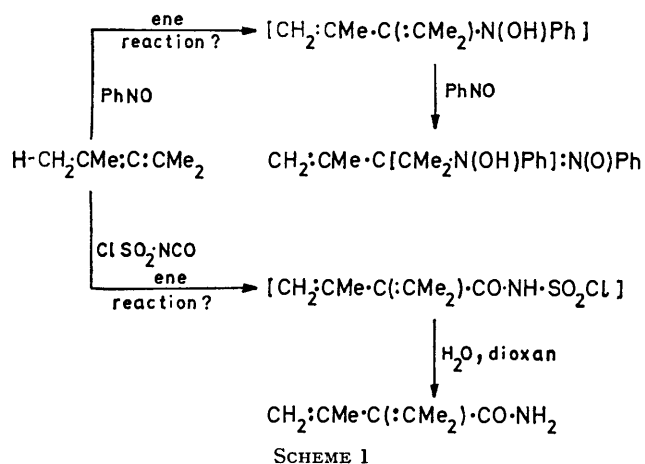
³ R. K. Howe, *J. Org. Chem.*, 1968, **33**, 2848.

⁴ E. J. Moriconi and J. F. Kelly, *J. Org. Chem.*, 1968, **33**, 3036.

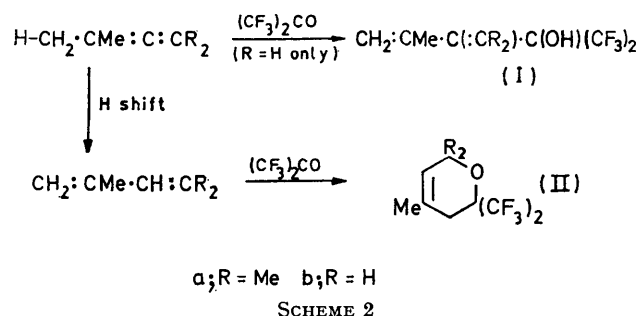
⁵ H. A. Chia, B. E. Kirk, and D. R. Taylor, *Chem. Comm.*, 1971, 1144.

⁶ D. R. Taylor and D. B. Wright, *Chem. Comm.*, 1968, 434.

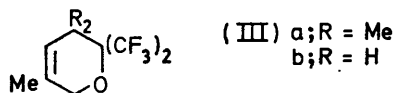
acetone.^{7,8} Subsequently, several related reactions of alkylallenes have been reported.⁹⁻¹³



2,4-Dimethylpenta-2,3-diene-Hexafluoroacetone Reaction.—Despite the well-established propensity of hexafluoroacetone for undergoing ene reactions, the expected adduct (Ia) was not isolated. Instead, the allene isomerises to 2,4-dimethylpenta-1,3-diene which then achieves a Diels–Alder cycloaddition (Scheme 2; R = Me).



The 1 : 1 adduct (IIa), obtained in almost quantitative yield at 170°, displays none of the characteristic properties of a conjugated diene. Its ¹H n.m.r. spectrum shows signals for a single vinyl and five (3 + 2) allylic hydrogen atoms, thereby indicating the dihydro-2H-pyran structure (IIa) or (IIIa).



The structure (IIa) was adopted on the basis of comparison of the n.m.r. data with those reported by Linn,¹⁴

⁷ R. L. Adelman, *J. Org. Chem.*, 1968, **33**, 1400.

⁸ W. H. Urry, J. H. Y. Niu, and L. G. Lundsted, *J. Org. Chem.*, 1968, **33**, 2302.

⁹ See ref. 2, footnote [51d].

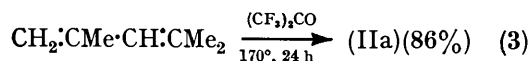
¹⁰ H. H. Wasserman and L. S. Keller, *Chem. Comm.*, 1970, 1482.

¹¹ D. C. England and C. G. Krespan, *J. Org. Chem.*, 1970, **35**, 3322.

¹² J. C. Martin, P. L. Carter, and J. L. Chitwood, *J. Org. Chem.*, 1971, **36**, 2225.

who systematically studied the Diels–Alder reactions of fluoro-ketones with isoprene and 2,3-dimethylbutadiene. He showed that in the 3,6-dihydro-2H-pyrans produced, a 5-methyl group resonates at τ ca. 8.4, detectably to higher field than a 4-methyl group (τ 8.21–8.26). The methyl band appears at τ 8.23 in the spectrum of (IIa), indicating a 4-methyl group, an orientation fully in accord with the proven structures of products of related reactions.¹⁵⁻¹⁹

The intermediate formation of the conjugated diene in the reaction of 2,4-dimethylpenta-2,3-diene with hexafluoroacetone is strongly indicated: it is detected in the recovered hydrocarbon, and separate treatment of the conjugated pentadiene with hexafluoroacetone [equation (3)] gives compound (IIa) in high yield. It was also



established that hexafluoroacetone catalyses the isomerisation of 2,4-dimethylpenta-2,3-diene to the conjugated pentadiene. When the allene–hexafluoroacetone reaction was conducted at ambient temperature, (IIa) was again the major (ca. 75%) product; the allene is stable in Pyrex at room temperature. Although strictest precautions were taken to exclude moisture, the prototropic rearrangement, which is known to be acid-catalysed,²⁰ is most probably initiated by traces of the ketone hydrate, (CF₃)₂(OH)₂, a strong acid,²¹ or by an analogous species (CF₃)₂C(OH)– formed on the glass reactor's surface.

Attempts to effect a photochemical [2 + 2] cycloaddition between this allene and hexafluoroacetone, such as that reported with acetone,^{22,23} were unsuccessful. The dihydro-2H-pyran (IIa) was again the major product (65%) and the recovered hydrocarbon contained a high proportion of the conjugated isomer. Almost no hexafluoroacetone was recovered, presumably because its photochemical decomposition competes with the [4 + 2] cycloaddition, which did not appear to be accelerated or otherwise by light.

3-Methylbuta-1,2-diene-Hexafluoroacetone Reaction.—The unsymmetrically substituted allene reacts smoothly with hexafluoroacetone in the dark at 175°, leaving little of the ketone remaining after 24 h. Two liquids and one

¹³ H. Gotthardt, *Tetrahedron Letters*, 1971, 2343.

¹⁴ W. J. Linn, *J. Org. Chem.*, 1964, **29**, 3111.

¹⁵ E. I. Klimova, E. G. Treshchova, and Yu. A. Arbizov, *J. Org. Chem. (U.S.S.R.)*, 1970, **6**, 411, 417.

¹⁶ I. N. Nazarov and M. V. Mavrov, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk*, 1959, 1068 (*Chem. Abs.*, 1960, **54**, 1407).

¹⁷ N. P. Sopov, *Zhur. org. Khim.*, 1965, **1**, 446 (*Chem. Abs.*, 1965, **63**, 1712).

¹⁸ K. Alder and W. Vogt, *Annalen*, 1949, **564**, 120.

¹⁹ J. C. Lunt and F. Sondheimer, *J. Chem. Soc.*, 1950, 2957.

²⁰ T. L. Jacobs and P. Prempre, *J. Amer. Chem. Soc.*, 1967, **89**, 6177.

²¹ R. E. Banks, 'Fluorocarbons and Their Derivatives,' Macdonald, London, 1970, 2nd edn., p. 91.

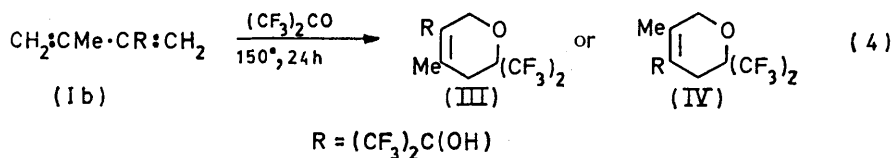
²² D. R. Arnold and A. H. Glick, *Chem. Comm.*, 1966, 813.

²³ H. Gotthardt, R. Steinmetz, and G. S. Hammond, *Chem. Comm.*, 1967, 480.

solid product were isolated, the main product being readily identified as the sought-for diene alcohol (Ib), formed by an ene reaction. It is a colourless liquid which slowly becomes viscous and discoloured. The remaining liquid was shown by ^1H n.m.r. to be identical with the dihydro-2*H*-pyran (IIb) first prepared by Linn from the perfluoro-ketone and isoprene.¹⁴

The reasons why this allene, but not 2,4-dimethylpenta-2,3-diene, undergoes an ene reaction are not understood, though they may involve steric factors. The more alkylated allene reacts readily with electron-deficient acetylenes by the ene reaction,⁵ whereas 3-methylbuta-1,2-diene does not.²⁴

The solid product was a 2 : 1 adduct, accounting for the slightly greater consumption of the ketone. A separate experiment showed that it arises by reaction of hexafluoroacetone with the diene alcohol (Ib) [equation (4)], indicating that it is one of the dihydro-2*H*-pyrans (III) and (IV). Of the two, (IV) is preferred marginally,



since its 3-methylene protons would be expected to show a greater downfield shift than the 6-methylene protons, relative to the hexafluoroacetone adduct of 2,3-dimethylbutadiene.¹⁴

Treatment of 3-methylbuta-1,2-diene with hexafluoroacetone at ambient temperature in the dark leads, by a slower reaction, to the diene alcohol (Ib) and the dihydro-2*H*-pyran (IIb) in a similar ratio to that observed at 175°; the 2 : 1 adduct was not detected, however. The bulky group R is likely to place a constraint upon the diene (Ib) to adopt a *trans*-configuration unfavourable to a Diels-Alder reaction.

Irradiation of a mixture of the perfluoro-ketone and 3-methylbuta-1,2-diene did not lead to oxetan formation.^{22,23} In this and the previous methylbutadiene reactions, recovered hydrocarbon material was not found to contain isoprene, the presumed intermediate product in the formation of (IIb). However, since this allene is far less readily isomerised than 2,4-dimethylpenta-1,3-diene, its isomerisation may be the rate-limiting process, so that little or no isoprene accumulates in the reaction mixture.

EXPERIMENTAL

Gaseous reagents and products were handled by conventional vacuum-transfer techniques in a Pyrex vacuum system. Crude liquid products were purified by precise fractional distillation or preparative g.l.c. (Perkin-Elmer F21 Fractometer), and pure products were identified by i.r. (Perkin-Elmer models 137, with sodium chloride optics, and 257, with diffraction grating), n.m.r. (Perkin-Elmer R10 spectrometer, operating at 60 MHz for ^1H and at 56.5

MHz for ^{19}F), and mass spectrometry (A.E.I. MS 902 spectrometer). ^{19}F Chemical shifts are quoted relative to external $\text{CF}_3\cdot\text{CO}_2\text{H}$ (high field positive). Analytical g.l.c. was carried out using Perkin-Elmer 451 and F11 and Pye 104 Fractometers. 3-Methylbuta-1,2-diene and 2,4-dimethylpenta-2,3-diene were prepared from 3-chloro-3-methylbut-1-yne and the lactone dimer of dimethylketen, respectively, as described previously.²⁵ Temperatures are in degrees Celsius unless otherwise stated.

Reaction of 2,4-Dimethylpenta-2,3-diene with Hexafluoroacetone.—(a) *At 170° in the dark.* In a typical experiment, hexafluoroacetone (4.98 g, 30 mmol) and 2,4-dimethylpenta-2,3-diene (3.0 g, 30 mmol), kept at 170° for 24 h in a sealed Pyrex tube (200 cm³), gave hexafluoroacetone (1% recovery), 2,4-dimethylpenta-1,3-diene (2% yield), and 3,6-dihydro-4,6,6-trimethyl-2,2-bis(trifluoromethyl)-2*H*-pyran (IIa) (7.3 g, 28 mmol, 93%) as a liquid, b.p. 154° at 760 mmHg, n_D^{20} 1.3781 (Found: C, 46.3; H, 4.7%; *M*, 262. $\text{C}_{10}\text{H}_{12}\text{F}_6\text{O}$ requires C, 45.8; H, 4.6%; *M*, 262), readily purified by distillation (10 cm Vigreux), ν_{max} (film) 2994s (CH_3), 2945m (CH_2), 2875w (CH_3), 1710w (C=C), 1470m

(CH_3), 1450s, 1390s, 1370s, 1330s, 1305s, 1240s, 1210s, 1175s, 1165s, 1125s, 1080s, 1052s, 1030m, 988s, 963s, 940w, 860m, 830m, 812w, 778w, 730s, and 690s cm⁻¹, τ (neat liq.) 4.42 (1H, m, CH), 7.66 [2H, m, $\text{CH}_2\cdot\text{C}(\text{CF}_3)_2$], 8.23 (3H, m, CMe), 8.70 (6H, s, $\text{CMe}_2\cdot\text{O}$), ^{19}F n.m.r. δ (neat liq.) 0.22br p.p.m. (s).

(b) *At 20—25° in the dark.* 2,4-Dimethylpenta-2,3-diene (5 mmol) and hexafluoroacetone (5 mmol), kept in the dark at ambient temperature for 72 h in a sealed Pyrex tube (50 cm³), gave a liquid (1.2 g) shown by g.l.c. (2 m Apiezon L, 150°) to contain the dihydro-2*H*-pyran (IIa) (65%, ca. 0.98 g, 75% yield) and unidentified higher-boiling products.

(c) *In u.v. light.* A mixture of 2,4-dimethylpenta-2,3-diene (2.50 g, 26 mmol) and hexafluoroacetone (3.32 g, 20 mmol) was sealed *in vacuo* in a silica tube (300 cm³) and irradiated for 72 h, with shaking, by means of a 500 W Hanovia lamp (Hg) placed 25 cm away. Volatile products were passed through a -78° trap *in vacuo* to give, in the -196° trap (0.20 mmol, 1%) hexafluoroacetone, identified by i.r., and, in the -78° trap, a liquid (0.3 g) shown by g.l.c. (2 m Apiezon L, 65°) to contain 2,4-dimethylpenta-2,3-diene (8 mg), 2,4-dimethylpenta-1,3-diene (120 mg), and the dihydro-2*H*-pyran (IIa) (150 mg). The liquid residue (5.1 g), analysed by g.l.c. (as before) and i.r., was found to contain the same three compounds; combined yields (by g.l.c.), 2,4-dimethylpenta-2,3-diene (0.09 g, 4%), the penta-1,3-diene (0.92 g, 35%), and the dihydro-2*H*-pyran (IIa) (4.2 g, 16 mmol, 64%).

Reaction of Hexafluoroacetone with 2,4-Dimethylpenta-1,3-diene.—Hexafluoroacetone (0.83 g, 5 mmol) and 2,4-dimethylpenta-1,3-diene (0.5 g, 5 mmol) were kept at 170° for 24 h in a sealed Pyrex tube (50 cm³) to give, after vola-

²⁴ B. E. Kirk and D. R. Taylor, unpublished results.

²⁵ D. R. Taylor, M. R. Warburton, and D. B. Wright, *J. Chem. Soc. (C)*, 1971, 385.

tile material had been vented, a liquid (1.2 g) shown by g.l.c. (2 m Apiezon L, 65° or 2 m SE30, 60°) to contain the dihydropyran (IIa) (86% yield by g.l.c.), identical (i.r., g.l.c.) with authentic material.

Reaction of Hexafluoroacetone with 3-Methylbuta-1,2-diene.

—(a) *At 175° in the dark.* Hexafluoroacetone (4.98 g, 30 mmol) and 3-methylbuta-1,2-diene (2.02 g, 30 mmol) were kept in a sealed Pyrex tube (250 cm³) in the dark at 175° for 24 h to give hexafluoroacetone (1%), 3-methylbuta-1,2-diene (5%), a liquid (5.2 g) not passing a -78° trap *in vacuo*, and an involatile residue (1.6 g) which slowly solidified. The liquid was shown by g.l.c. (2 m PEGA, 85°) to consist of a 86:13:1 mixture of three components, the first two of which were collected by preparative g.l.c. (6 m Carbowax 20M, 110°) and identified spectroscopically as 1,1,1-trifluoro-4-methyl-3-methylene-2-trifluoromethylpent-4-en-2-ol (Ib) (estimated yield 4.5 g, 19 mmol, 65% based on C₈H₈F₆O) (Found: C, 40.4; H, 3.8%; M, 234. C₈H₈F₆O requires C, 41.0; H, 3.4%; M, 234), b.p. (Siwoloboff) 123—124° at 755 mmHg, n_D^{20} 1.3636, v_{max} (film) 3610—3590m (OH), 3100w (:CH₂), 2990m (CH₃), 2970w (CH₃), 2935w, 2860w, 1890w, 1630m (C=C), 1455m (CH₃), 1440m, 1385m, 1270s, 1215s, 1180s, 1150s, 1140s, 1050w, 1018m, 987s, 970s, 950s, 930m, 810m, 782s, 750m, 700m, and 650m cm⁻¹, τ (neat liq.) 4.35 (1H, m, :CH), 4.52 (1H, m, :CH), 4.80 (1H, m, :CH), 5.04 (1H, m, :CH), 6.50 (1H, s, OH), and 8.08 (3H, m, :CMe), ¹⁹F n.m.r. δ (neat liq.) -0.81 p.p.m. (m), and the known¹⁴ 3,6-dihydro-4-methyl-2,2-bis(trifluoromethyl)-2H-pyran (IIb) (estimated yield 0.7 g, 3 mmol, 10% based on C₈H₈F₆O) (Found: M, 234.0478. Calc. for C₈H₈F₆O: M, 234.0479),²⁶ τ (CCl₄) 4.44 (1H, m, :CH), 5.72br (2H, s, CH₂·O), 7.67br (2H, s, :C·CH₂), and 8.21 (3H, m, :CMe), ¹⁹F δ (CCl₄) -1.2 p.p.m.(s). The low-melting white solid was purified by vacuum sublimation and identified as 3,6-dihydro-5-methyl-4-(2,2,2-trifluoro-1-hydroxy-1-trifluoromethylethyl)-2,2-bis(trifluoromethyl)-2H-pyran (IV) (4 mmol, 13% based on C₈H₈F₆O), m.p. 25—30° (Found: C, 34.1; H, 2.6. C₁₁H₈F₁₂O requires C, 33.2; H, 2.0%), v_{max} (CCl₄) 3700w, 3585s (OH), 3360m, 2990m (CH₃), 2940m (CH₂), 2888m (CH₃), 1665m (C=C), 1470m, 1442s, 1368s, 1340s,

1300s, 1281s, 1260s, 1238s, 1212s, 1183s, 1151s, 1100s, 1068s, 1045m, 990s, 967s, 949s, 870m, 700s, and 660m cm⁻¹, τ (CCl₄) 5.70 (2H, s, CH₂·O), 6.55br (1H, s, OH), 7.40 (2H, s, :C·CH₂), and 7.81 (3H, s, :CMe), ¹⁹F δ (CCl₄) -0.76 (6F, s, CF₃·C·OH) and -3.14 p.p.m. (6F, s, O·C·CF₃).

(b) *At 20—25° in the dark.* An otherwise identical reaction between these two compounds at ambient temperature for 19 days gave hexafluoroacetone (21 mmol, 70% recovery), 3-methylbuta-1,2-diene (22 mmol, 74% recovery), and a liquid fraction condensing *in vacuo* at -64° (1.8 g) which was shown by g.l.c. (2 m SE30; 85°) to consist of a 4:1 mixture of the diene alcohol (Ib) (estimated yield 1.4 g, 6 mmol, 67% based on ketone consumed) and the dihydro-2H-pyran (IIb) (estimated yield 0.4 g, 1.7 mmol, 19% based on ketone consumed). The solid dihydro-2H-pyran (IV) was not detected.

(c) *In u.v. light.* A mixture of hexafluoroacetone (4.1 g, 25 mmol) and 3-methylbuta-1,2-diene (1.7 g, 25 mmol) was sealed *in vacuo* in a silica tube (300 cm³) and irradiated for 96 h by means of a 500 W Hanovia lamp (Hg) placed 15 cm away, to give a liquid (2.7 g) shown by g.l.c. (2 m SE30; 85°) and i.r. to contain the diene alcohol (Ib) (estimated yield 2.2 g, 9 mmol, 36%) and the dihydro-2H-pyran (IIb) (estimated yield 0.5 g, 2 mmol, 9%).

Reaction of Hexafluoroacetone with the Diene (Ib).—The diene alcohol (Ib) (0.5 g, 2 mmol) and hexafluoroacetone (0.5 g, 3 mmol), kept in a sealed Pyrex tube (50 cm³) for 24 h at 150°, gave hexafluoroacetone (40%) and a pale yellow solid (0.7 g), purified by vacuum sublimation and identified spectroscopically (i.r., n.m.r.) as the dihydro-2H-pyran (IV) [or (III)] (1.8 mmol, 90%) by comparison with authentic material isolated from the hexafluoroacetone-3-methylbuta-1,2-diene reaction.

We thank the S.R.C. for financial support (for D. B. W.), and Dr. M. G. Barlow for discussions and for assistance in interpretation of the n.m.r. spectra.

[2/2221 Received, 25th September, 1972]

²⁶ B. E. Kirk, Ph.D. Thesis, University of Manchester, 1972.