Reactions Involving Fluoride Ion. Part 29.[1] Reactions of Perfluoro-2,3-dimethylbuta-1,3-diene

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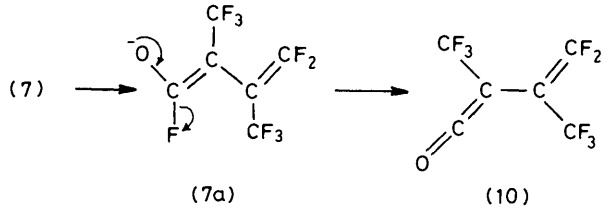
Reactions of perfluoro-2,3-dimethylbutadiene (1) with methanol, phenol, and sodium methoxide yield products arising from substitution; with methanol a 1,2-addition product is also observed. Reactions of (1) with enolate anions derived from ethyl acetoacetate and acetylacetone yield pyran derivatives, and an oxepine. The diene (1) undergoes free radical addition with methanol, and cycloaddition with diazomethane. Except under strongly nucleophilic conditions, reactions occur at only one of the double bonds of the diene (1) and, on the basis of this and u.v. spectral data, the diene (1) is considered to be conjugated, contrary to other conclusions.

In previous papers we have described the synthesis of fluorinated dienes by pyrolytic elimination of CF_4 and by metal-induced, thermolytic defluorination of perfluoro-3,4-dimethylhex-3-ene, an oligomer of tetrafluoroethylene.[2] By the former method, perfluoro-2,3-dimethylbutadiene (1) is now readily accessible; although first prepared over 20 years ago [3] the chemistry of (1) is largely unexplored. In earlier work it was established that no reaction occurs between the diene (1) and bromine but reaction with water occurs at room temperature to yield a mixture of acids, the major product being (2).[4] We have shown [5] that (1) dimerises readily in the presence of fluoride ion to afford (3) and (4), as the main products, and in this paper we describe a wide range of reactions of the diene (1).

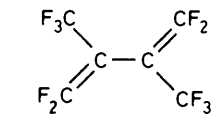
Reaction of the diene (1) with an excess of neutral methanol occurred slowly at room temperature to give a 1,2-addition product (5) (17%) and a substitution product (7) (39%), the structure of which follows simply from ^{19}F n.m.r. data. In contrast, reaction of (1) with phenol, in the presence of sodium carbonate and solvent dimethylformamide (DMF), yielded only one product (8) (26%) which almost certainly arises by addition of HF to the double bond of the initial substitution product (6). It is probable that the addition of HF occurred in this case because reaction was carried out in an aprotic solvent in which fluoride ion is a strong nucleophile, whereas in neutral methanol fluoride ion is a weaker nucleophile.

Reaction of (1) with sodium methoxide afforded a complex mixture of products from which only the disubstituted product (9) (30%) could be isolated as a mixture of isomers; no product resulting from addition to (1) could be identified. The same product (9) (although in a different isomer ratio) was obtained from reaction of NaOMe with the mono-substituted product (7). From these results it is clear that once one of the double bonds in (1) has reacted, far stronger nucleophilic conditions are required to bring about reaction with the second double bond.

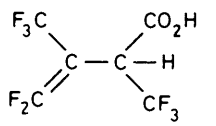
Treatment of (7) with iodotrimethylsilane under conditions known to cleave ethers,[6] led to the formation of the ketene (10)



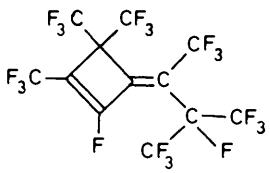
(7a) (10)



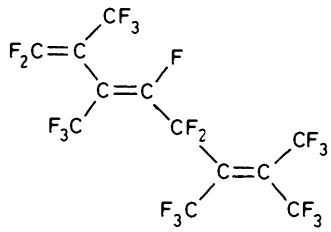
(1)



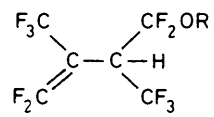
(2)



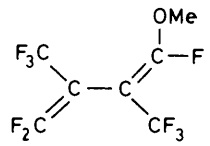
(3)



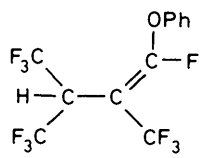
(4)



(5) R = Me
(6) R = Ph



(7) (*cis* / *trans*)



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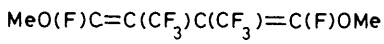
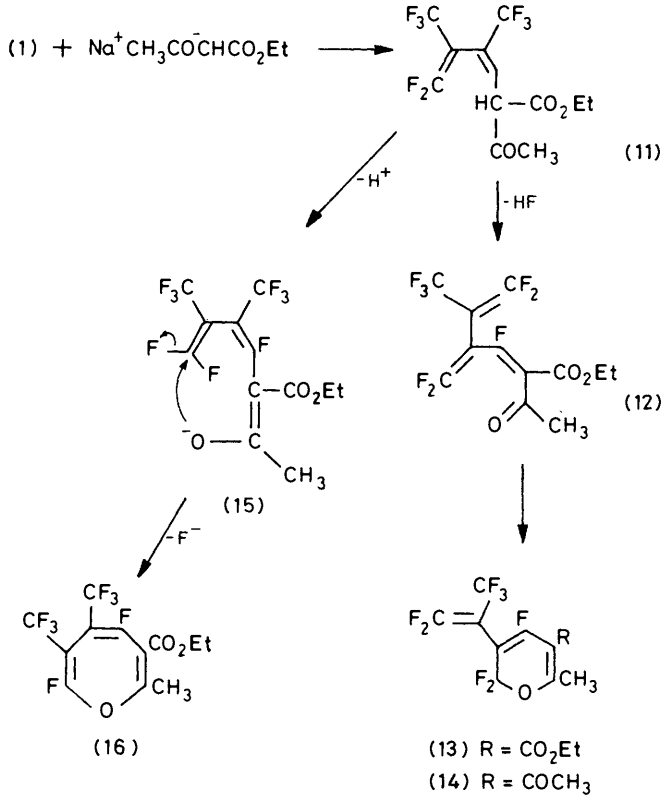


(9)

(20%). This can be accounted for by a novel elimination of fluoride ion from a position α to the incipient oxyanion (7a). Compound (10) has been prepared previously by dehydration of the acid (2).[4] Attempts to prepare a diketene from (9) and iodotrimethylsilane resulted in a complex mixture of products, none of which could be identified.

We have recently shown that enolate anions react with appropriate fluoro-olefins, initially by replacement of a vinylic fluorine atom, to give a variety of heterocyclic products.[7] Reaction of the diene (1) with the anion derived from ethyl acetoacetate in tetraglyme at room temperature yielded two isomeric products. The major product (30%) was the pyran derivative (13) which presumably arises by electrocyclic



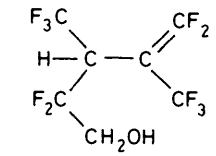
Scheme.

ring closure of (12) in accord with the previously proposed mechanism.[7b] The minor product (2%) significantly did not contain a terminal difluoromethylene group, and all spectroscopic data are consistent only with the oxepine structure (16). The formation of (16) can be explained by proton loss from (11), followed by cyclisation through the oxyanion (15) (Scheme). In an attempt to improve the yield of oxepine, the anion derived from acetylacetone was treated with (1). It was anticipated that the relative amounts of charge on oxygen *versus* carbon in the intermediate enolate anion should favour cyclisation through oxygen, but, conversely, the only isolated product was the pyran (14).

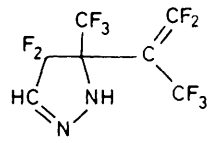
We have also demonstrated that the diene (1) reacts readily under free radical conditions, as in the presence of an excess of methanol and with γ-irradiation, the 1 : 1 adduct (17) being formed in high yield. Notably, there was no evidence for the formation of compounds (2) or (3) by competing nucleophilic attack.

The reaction of (1) with an excess of diazomethane yielded the Δ^2-pyrazoline (18) (50%) as the only isolable product; the structure of (18) is in accord with our recent investigation of regioselectivity in reactions of diazomethane with fluorinated alkenes.[8]

The reaction of the diene (1) with even neutral methanol, albeit slowly, places (1) more in common with $(CF_3)_2C{=}CF_2$ than $CF_3CF{=}CF_2$ in reactivity towards nucleophiles.[8] However, only the 1 : 1 adduct (5) is formed from (1), showing that (5) is of considerably lower reactivity than (1). Likewise, reaction with only one double bond occurs in the free radical addition of methanol, and with the addition of diazomethane. Collectively, this suggests that the double bonds of (1) are conjugated and the u.v. spectrum of (1) supports this ($\lambda_{max.}$ 242 nm), even though this is not reflected in the formation of 1,4-addition products which might have been expected,



(17)



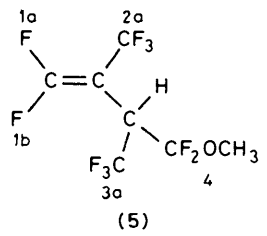
(18)

especially for the radical reaction. Previous workers[4] have considered (1) to be non-conjugated, but on the basis of reactions described above, and the u.v. spectrum, this seems to be unjustified.

Experimental

^1H and ^{19}F N.m.r. spectra were recorded at 40 °C using either a Varian A56/60D or a Bruker HX90E spectrometer, with trichlorofluoromethane as solvent, and either this or tetramethylsilane as reference. For ^{19}F spectra upfield shifts are quoted as positive. I.r. spectra were recorded on a Perkin-Elmer 577 instrument as liquid films unless otherwise stated. Mass spectra were recorded on an A.E.I. MS9 spectrometer. γ-Irradiation was produced using a ^{60}Co source. G.l.c. columns were packed with 30% silicone rubber SE-30 on Chemsosorb P.

Reaction of the Diene (1) *with Methanol.*—A mixture of the diene (1) (7.8 g, 29.8 mmol) and methanol (4.0 g, 125 mmol) was stirred at room temperature for 7 days. Water was added and the fluorocarbon layer dried over $MgSO_4$. After filtration, preparative scale g.l.c. separated compounds (5) and (7). Compound (5), *4-methoxy-2,3-bistrifluoromethyltetrafluorobut-1-ene* (1.5 g, 17%) was obtained as a colourless liquid, b.p. 95 °C (Found: C, 28.7; F, 64.0. $C_7H_4F_{10}O$ requires C, 28.6; F, 64.6%); *m/z* 294 (M^+); δ_F 59.4br (1b-F), 63.2br (d, $J_{1a,2a}$ 19 Hz, 2a-CF_3), 67.2br (3a-CF_3), 69.0br (1a-F), and 77.3br (4-F); δ_H 3.5 (s, CH_3) and 3.6br (CH); $\nu_{max.}$ 1 700 cm^{-1} (C=C). Compound (7), cis-, trans-*1-methoxy-2,3-bistrifluoromethyltrifluorobutadiene* (isomers could not be separated; isomer ratio *cis* : *trans* = 1.6 : 1) (3.1 g, 39%) was obtained as a colourless liquid, b.p. 114 °C (Found: C, 30.9; F, 61.9. $C_7H_3F_9O$ requires C, 30.7; F, 62.4%); *m/z* 274 (M^+); $\nu_{max.}$ 1 745 and 1 700 (both C=C). *cis*-Isomer (7a): δ_F 61.1 (d, $J_{1,2a}$ 12 Hz 2a-CF_3), 63.1 (m, 3a-CF_3), 73.6 (q, $J_{3a,4a}$ 19 Hz, 4a-F), and 74.5 (m, 1-F and 4b-F); δ_H 4.03 (s). *trans*-Isomer (7b): δ_F 60.4 (d, $J_{1,2a}$ 19 Hz, 2a-CF_3), 63.1 (m, 3a-CF_3), 73.3 (q, $J_{3a,4a}$ 19 Hz, 4a-F), 74.5 (m, 4b-F), and 76.1 (q, $J_{1,2a}$ 9 Hz, 11-F); δ_H 3.98 (s).



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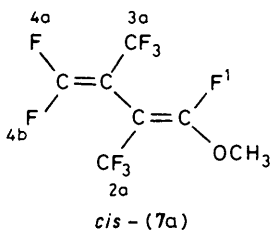
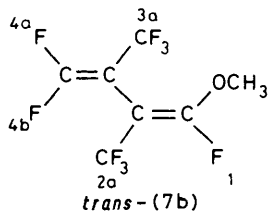
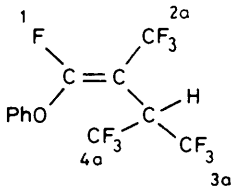


cis - (7a)

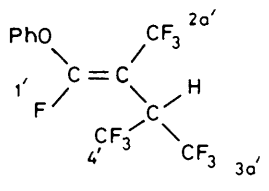


trans - (7b)

Reaction of the Diene (1) *with Phenol.*—A mixture of diene (1) (4.1 g, 15.6 mmol), phenol (1.5 g, 15.9 mmol), sodium carbonate (1.75 g, 16.5 mmol), and *N,N*-dimethylformamide (25 mol) was stirred at room temperature for 36 h. The reaction mixture was poured onto water and the product extracted with diethyl ether. The ether layer was washed successively with dilute NaOH, dilute HCl, and water, and then dried (Na_2SO_4). Filtration and evaporation of ether left a liquid (3.6 g) containing one main component by g.l.c. Purification using preparative scale g.l.c. afforded *1-phenoxy-2,3-bistrifluoromethyltetrafluorobut-1-ene* (8) (1.3 g, 23%), as an inseparable mixture of isomers (ratio *cis* : *trans* 1 : 2) (Found: C, 40.1; H, 1.8; F, 53.7. $C_{12}H_6F_{10}O$ requires C, 40.45; H, 1.7; F, 53.4%); *m/z* 356 (M^+); δ_F 60.7 (d, $J_{1,2a}$ 22 Hz, 2a-CF_3), 61.3 (d, $J_{1',2a'}$ 10 Hz, 2a'-CF_3), and 65.7 and 66.0 (m, 3a-CF_3, 4a-CF_3, 1-F, 3a'-CF_3, 4a'-CF_3, and 1'-F); δ_H 7.0 (5 H, m, ArH) and 4.1br (1 H, s); $\nu_{max.}$ 1 700 cm^{-1} (C=C).



trans - (8)



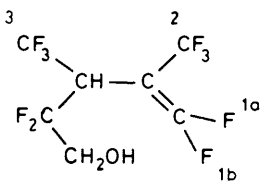
cis - (8)

Reaction of the Diene (1) *with Sodium Methoxide.*—A mixture of the diene (1) (2.6 g, 10 mmol) and sodium methoxide (1.2 g, 21 mmol) in methanol (10 ml) was stirred at room temperature for 48 h. Water was added and the fluorocarbon layer separated and dried over $MgSO_4$. After filtration, distillation yielded 1,4-dimethoxy-2,3-bistrifluoromethyldifluorobuta-1,3-diene (9) (0.86 g, 30%) as a complex mixture of *cis,cis-*, *cis,trans-*, and *trans,trans*-isomers, which could not be separated (Found: C, 33.4; H, 1.8; F, 53.2. Calc. for $C_8H_6F_8O_2$. C, 33.6; H, 2.1; F, 53.2%); *m/z* 286 (M^+); δ_F 61.4 (d, *J* 19 Hz), 63.2 (d, *J* 14 Hz), 64.6 (m), 72.3 (m), 76.1 (m), and 78.4 (m); δ_H 4.10 (s) and 4.00 (s); $\nu_{max.}$ 1 740 (C=C). The same product (9) was formed in a different isomer ratio from reaction of compound (7) with sodium methoxide (1 equiv.) under the conditions described above.

Reaction of the Diene (1) *with Ethyl Acetoacetate.*—The diene (1) (2.6 g, 10 mmol) was added to tetraglyme (5 ml) containing the anion derived from the reaction of ethyl acetoacetate (2.7 g, 21.0 mmol) with an equimolar amount of sodium hydride. The reaction mixture was stirred at room temperature for 17 h after which water was added and the fluorocarbon layer dried ($MgSO_4$) and then transferred *in vacuo* to a cold trap. The resultant colourless oil (2.8 g) was shown by g.l.c. to consist of one major product and one minor product. Preparative scale g.l.c. separated (13) and (16). *Pyran* (13) (1.06 g, 30%) (Found: C, 40.7; H, 2.4; F, 43.6. $C_{12}H_8F_8O_3$ requires C, 40.9; H, 2.3; F, 43.2%), *m/z* 352 (M^+); δ_F 56.8br (2 F, exocyclic CF_2), 59.4 (3 F, m, CF_3), 64.0 (2 F, br, ring CF_2), and 134br (1 F); δ_H 4.20 (2 H, q, *J* 7 Hz), 2.05 (3 H, s), and 1.10 (3 H, t, *J* 7 Hz); $\nu_{max.}$ 1 740, 1 705, 1 660, and 1 585 cm^{-1}. *Oxepine* (16) (70 mg, 2%) (Found: C, 41.2; H, 2.3; F, 42.8%); *m/z* 352 (M^+); δ_F 59.4 (3 F, m), 62.1 (1 F, q, *J* 19 Hz), 65.8 (3 F, m), and 157.4 (1 F, q, *J* 20 Hz); δ_H 3.84 (2 H, q, *J* 7 Hz), 2.50 (3 H, s), and 1.01 (3 H, t, *J* 7 Hz); $\nu_{max.}$ 1 730 and 1 655 cm^{-1}.

Reaction of the Diene (1) *with Acetylacetone.*—Reaction of the diene (1) (2.6 g, 10 mmol), acetyl acetone (2.5 g, 25 mmol), sodium hydride (25 mmol), and tetraglyme (10 ml), under conditions detailed above, yielded the *pyran* (14) (0.90 g, 28%) (Found: C, 40.7; H, 2.1; F, 47.3. $C_{11}H_6F_8O_2$ requires C, 41.0; H, 1.9; F, 47.2%); *m/z* 322 (M^+); δ_F 55.6br (2 F, exocyclic CF_2), 59.0 (3 F, m), 62.0br (2 F, ring CF_2), and 130.5br (1 F); δ_H 2.30 and 2.15 (both 3 H, s); $\nu_{max.}$ 1 705, 1 695, and 1 640 cm^{-1}.

Reaction of the Diene (1) *with Methanol under γ Irradiation.*—A mixture of diene (1) (2.6 g, 10 mmol) and methanol (2.0 g, 62 mmol) was sealed in a Pyrex tube and irradiated with γ rays at 20 °C for 150 h. Volatile material was transferred under vacuum into a cold trap. The resultant liquid was identified as *1,1,4,4-tetrafluoro-2,3-bistrifluoromethylpent-1-en-5-ol* (17) (2.2 g, 76%) (Found: C, 28.4; H, 1.4; F, 64.2. $C_7H_4F_{10}O$ requires C, 28.6; H, 1.4; F, 64.6%); *m/z* 294 (M^+); δ_F 59.4br and 61.6br (1a-F and 1b-F), 67.7 (s, 2-CF_3), 74.8 (s, 3-CF_3), and



(17)

115.0 (m, $J_{F,H}$ 216 Hz, 4-F_2); δ_H 4.2—3.3 (m); $\nu_{max.}$ ($CHCl_3$) 3 450br and 1 690 cm^{-1}.

Reaction of the Diene (1) *with Diazomethane.*—A solution of diazomethane in diethyl ether was added dropwise with stirring to the diene (1) (2.6 g, 10 mmol) at room temperature until the yellow colour persisted. After a further 10 min at room temperature, ether was removed under reduced pressure and the crude product distilled b.p. 55 °C/15 mmHg to yield the 4,4-difluoro-5-perfluoroisopropenyl-5-trifluoromethyl-2-pyrazoline (18) (1.70 g, 56%) obtained as a colourless oil (Found: C, 28.6; N, 8.9; F, 62.0. Calc. for $C_7H_2N_2F_{10}$: C, 27.6; N, 9.2; F, 62.5%), *m/z* 304 (M^+); δ_F 57.9br (C=CF_2), 62.5 and 63.4 (both m, CF_3), 67.0br (ring CF_2); δ_H 8.70br (NH), and 7.07 (dd, *J* 12 Hz, CH); $\nu_{max.}$ 3 290 (NH) and 1 695 cm^{-1}.

Reaction of Compound (7) *with Iodotrimethylsilane.*—A mixture of compound (7) (1.4 g, 0.5 mmol) and iodotrimethylsilane (1.5 g, 0.75 mmol) was stirred at room temperature for 12 h. G.l.c. showed a small amount of unchanged (7), one major product, and several minor components. Preparative-scale g.l.c. separated the ketene (10) (0.24 g, 20%) (Found: C, 29.8; F, 63.3. Calc. for C_6F_8O; C, 30.0; F, 63.3%); $\nu_{max.}$ 2 170 cm^{-1} (C=C=O), identified by close agreement of i.r. and ^{19}F n.m.r. data with those reported previously for (10).[4]

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