Heterocyclic Polyfluoro-compounds. Part 31.[1] Photochemical Oxetan Formation from Fluoroketones and Perfluoroaldehydes and 1,2-Difluoroethylene

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The photochemical addition of five fluoroketones (hexafluoro-, chloropentafluoro-, 1,3-dichlorotetrafluoro-, 1,1,3-trichlorotrifluoro-, and 1,1,1-trifluoro-propan-2-one) and the perfluoroaldehydes $R_F CHO$ ($R_F = CF_3$, C_2F_5, or n-C_3F_7) to (Z)- or (E)-1,2-difluoroethylene at $\lambda > 300$ nm has been studied. Oxetan formation dominates with hexafluoropropan-2-one, but there is increasing competition from reactions involving free radicals arising from photolysis of the ketone as the chlorine content is increased. Oxetan formation occurs with little stereo-specificity. The aldehydes give r-2-perfluoroalkyl-t-3,c-4-, -c-3,t-4-, and -t-3,t-4-difluoro-oxetans, in the ratio 1.0 : 1.7 ± 0.2 : 1.3 ± 0.1, respectively, and in high yield (78—94%). A small amount of olefin isomerisation occurred.

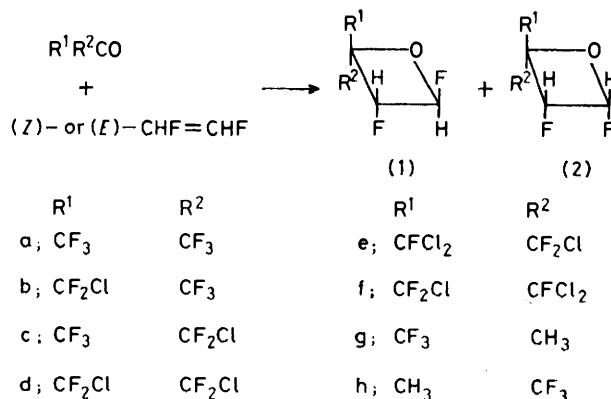Flow pyrolysis of the oxetans from hexafluoroacetone yields (Z)- and (E)-1,2-difluoroethylene and the olefin $(CF_3)_2C=CHF$, the oxetan cis-$(CF_2Cl)_2\overline{CCHFCHFO}$ yields the olefins (Z)- and (E)-$CHF=CHF$ and $(CF_2Cl)_2C=CHF$, and r-2-pentafluoroethyl- or heptafluoro-n-propyl-c-3,t-4-difluoro-oxetans yield mainly the olefins (Z)- and (E)-$R_FCH=CHF$ ($R_F = C_2F_5$ or n-C_3F_7).

THE well known Paterno-Büchi reaction,[2] where oxetans are formed by the photochemical addition of carbonyl compounds to olefins, has been studied extensively in the hydrocarbon field, but there have been few studies of fluorinated substrates. Harris and Coffman reported in 1962 that oxetans were obtained from fluoro-alde-hydes, -ketones, and -acid fluorides and highly fluorinated olefins.[3] The reaction was regio- but not stereo-selective, and the products were rationalised in terms of the most stable diradical intermediate. With acetalde-hyde, only very low yields of oxetans were obtained from fluoro-olefins [4] and the reaction of hexafluoroacetone with vinyl fluoride and 1,1-difluoroethylene showed little regioselectivity.[5] Additions of hexafluoro-, chloro-pentafluoro-, and 1,3-dichlorotetrafluoro-propan-2-ones to the 1,2-difluoroethylenes $XCF = CFY$ ($X = H$ or Cl, $Y = Br$, Cl, or F; $X = Y = Br$ or I) have been described in the patent literature.[6]

1,2-Difluoroethylene is a highly suitable substrate for study in this type of reaction. Its (Z)- and (E)-isomers are readily separated,[7] differences in the polarity of isomeric products should aid their separation, and their stereochemistry should be amenable to spectroscopic definition. We here describe a study of the addition of the ketones $(CF_3)_2CO$ CF_3COCF_2Cl, $(CF_2Cl)_2CO$, $CF_2ClCOCFCl_2$, and CF_3COCH_3, to 1,2-difluoroethylene. The emphasis rests upon product characterisation, but mechanistic implications are made where possible.

Since aliphatic aldehydes, unlike ketones, add to hydrocarbon olefins to give oxetans where the configur-ation of the olefin is largely retained in the product, and the first excited singlet state of the aldehyde appears to be involved,[8,9] a study of the reactions of the fluoro-aldehydes R_FCHO ($R_F = CF_3$, C_2F_5, or n-C_3F_7) with 1,2-difluoroethylene was also made, to see whether this dichotomy prevailed among the fluorinated counter-parts.

Irradiation with u.v. light in Pyrex ($\lambda > 300$ nm) of gaseous mixtures of the chlorofluoroketones and either (Z)- or (E)-1,2-difluoroethylene gave all possible oxetans (1a—f) and (2a—f) (see Scheme 1). The (Z)-olefin showed essentially no stereoselectivity whereas the (E)-olefin gave products where the configuration of the fluorines was retained to some 70%. For example, chloropentafluoroacetone gave equimolar amounts of the oxetans (1b), (1c), (2b), and (2c) with (Z)-1,2-difluoroethylene, but with (E)-1,2-difluoroethylene, the

| R^1R^2CO			
R^1	R^2	R^1	R^2
a; CF_3	CF_3	e; $CFCl_2$	CF_2Cl
b; CF_2Cl	CF_3	f; CF_2Cl	$CFCl_2$
c; CF_3	CF_2Cl	g; CF_3	CH_3
d; CF_2Cl	CF_2Cl	h; CH_3	CF_3

SCHEME 1

trans-oxetans (1b) and (1c) comprised 74% of the oxetan fraction. The (E)-olefin appeared to be somewhat more reactive and gave a higher yield of oxetans. The yield of oxetans diminished rapidly with increasing chlorine content, and free-radical products resulting from photo-lysis of the ketone [10] became more and more important. The lower-boiling trans-oxetans (1) were readily sepa-rated from the corresponding cis-oxetans (2) by g.l.c., but isomeric pairs such as (1b) and (1c) proved impossible to separate. However, their [19]F n.m.r. spectra in particular proved distinctive.

Olefin isomerisation did not appear to be important in the early stages of a reaction, particularly where the (Z)-olefin was involved, but it was detected for reactions involving the (E)-olefin. In the addition of hexa-fluoroacetone to (E)-CHF=CHF, the ratio of oxetans (1a) : (2a) showed little change from the ratio 2.3 : 1 up to 53% reaction, and small amounts of (Z)-CHF= CHF were detected only after 32% reaction. The addition of cis-piperylene to a reaction involving hexa-fluoroacetone and (Z)-CHF=CHF completely suppressed the formation of oxetans.

A reaction involving 1,1,1-trifluoropropan-2-one proved rather different from the rest. With the (Z)-olefin the reaction was slow and gave only 10% of oxetans. With the (E)-olefin, reaction occurred to the extent of 90% after 6 days, a 63% yield of oxetans was obtained [(1g) : (1h) : (2g) = 13 : 25 : 25]; the product mixture was very similar to that obtained from the (Z)-olefin, and the cis-oxetan (2h) did not appear to be formed.

Irradiation of gaseous mixtures of the aldehydes with either (Z)- or (E)-1,2-difluoroethylene yielded mixtures of three oxetans (Scheme 2) (3) to (5), in the ratio
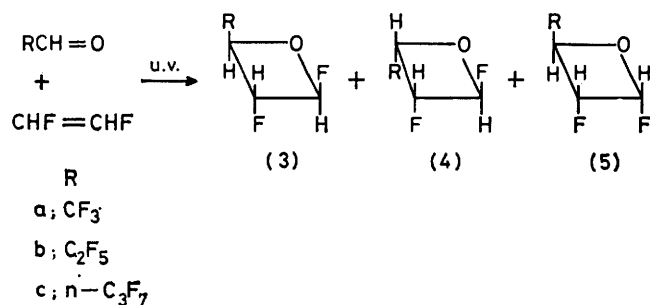

SCHEME 2

1.0 : 1.7 ± 0.2 : 1.3 ± 0.1. This ratio was, within the experimental error, essentially independent of the nature of the R group and of the configuration of the olefin. Yields of oxetans were high, ranging from 78% for the addition of heptafluoro-n-butyraldehyde to (Z)-1,2-difluoroethylene to 94% for the addition of pentafluoropropionaldehyde to (E)-1,2-difluoroethylene, the remainder being largely accounted for in terms of products derived from photolysis of the aldehydes and reactions of the free radicals so produced, and although a little (E)- to (Z)-isomerisation was detected in the recovered olefin from reactions involving the (E)-olefin,

(6)
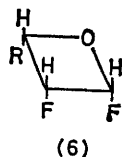
this did not appear to be important. A careful search was made by gas-liquid chromatography, coupled with mass spectrometry, and by ^{19}F n.m.r. spectroscopy, for the missing cis-oxetan (6), but no trace was detected.

In all these reactions, the carbonyl compound is clearly the species excited, since the olefin is completely transparent to the wavelength used ($\lambda > ca.$ 300 nm); irradiations were carried out in Pyrex. An electron-impact determination of the triplet excitation energy of 1,2-difluoroethylene indicates that there is insufficient energy to excite the olefin by sensitisation.[11]

So far as the reactions with the ketones are concerned, the complete suppression of the reaction of hexafluoro-acetone with (Z)-1,2-difluoroethylene by cis-piperylene is evidence for involvement of the ketone triplet state. The greater reactivity of the (E)-olefin may well be a reflection of ground state stabilities, since the (Z)-olefin is more stable.[12] So the reaction may be pictured as involving initial excitation of the ketone, intersystem crossing to the ketone triplet state, and reaction with the olefin to form a biradical (7) in its triplet state. Spin
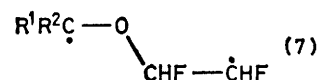
inversion and cyclisation completes the oxetan formation. Clearly rotation about the C–C bond is competitive with cyclisation, particular with the (Z)-olefin, but cyclisation would appear to be faster than in the comparable reaction of acetone with but-2-ene, where the configuration of the olefin is completely lost in the product;[13] the heavy-atom effect of the halogens, particularly chlorine, should enhance this rate of spin inversion and hence of cyclisation.

In the formation of the biradical (7), and its subsequent cyclisation, there is little or no stereochemical preference so far as the differing groups R^1 and R^2 of the ketone with respect to neighbouring fluorines are concerned, apart from the reaction with 1,1,1-trifluoro-acetone, where the oxetan (8) is absent from the product.
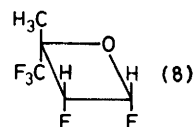
However, this product is disfavoured on steric grounds, since the more bulky trifluoromethyl group is cis to the ring fluorines, and on polarity grounds, because of the alignment of like bond-dipoles.

Minor amounts of olefin isomerisation products were observed. These could result from a limited reversion of biradical (7) to the reactants, i.e., to a Schenck-type mechanism.[14]

The above reactions of 1,2-difluoroethylene with fluoroketones resemble the reactions of acetone with simple alkyl-substituted olefins [13,15] in that a triplet mechanism is involved, rather than those with electron deficient olefins where the ketone singlet is involved.[16]

For the reactions with fluoroaldehydes, the absence of stereospecificity indicates that any diradical intermediate must be relatively long-lived, more so than

those from the chlorofluoroketones. Of the *trans*-oxetans, the more favoured one (4) has the perfluoroalkyl group and 3-fluorine situated *cis* to each other, indicating that steric repulsion is not important here,


(9)
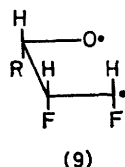
but the missing oxetan (6) has the bulky substituents situated *cis* to each other, and with like bond-dipoles aligned, so that steric and polar effects may be of some importance at the cyclisation step from, for example, diradical (9). Like the fluoroketone reactions, a triplet 1,4-diradical seems likely so that the fluoroaldehydes resemble benzaldehyde [17] in their reactions, rather than aliphatic aldehydes. The missing oxetans (6), and (8) from the reaction of 1,1,1-trifluoroacetone with 1,2-difluoroethylene, all have the perfluoroalkyl group and fluorines situated *cis* to each other.

A limited study was made of the flow pyrolysis of the oxetans (1a), (2a), (2d), (4b), and (4c) for the following reasons (see Scheme 3). The cleavage *a* might provide

SCHEME 3
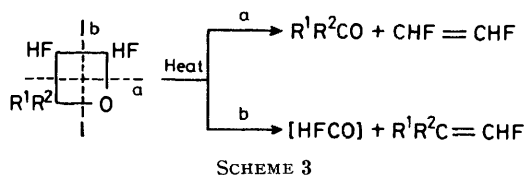
independent evidence of the stereochemistry of the ring fluorines, and the alternative cleavage *b* a route to olefins of the type $R^1R^2C=CHF$.*

Flow pyrolysis at 670 °C of the *trans*-oxetan (1a) gave both (*E*)- and (*Z*)-1,2-difluoroethylene (13 and 12%, respectively), the olefin $(CF_3)_2C=CHF$ (37%), and recovered oxetan (37%), no oxetan isomerisation being observed. Pyrolysis of the *cis*-oxetan (2a) at 675 °C gave (*E*)- (11%) and (*Z*)-1,2-difluoroethylene (27%), the olefin $(CF_3)_2C=CHF$ (47%), and recovered oxetan (16%). The *cis*-oxetan (2d) at 665 °C gave (*E*)- (21%) and (*Z*)-1,2-difluoroethylene (44%), and the olefin $(CF_2Cl)_2C=CHF$ (20%). So far as regiospecificity is concerned path b is favoured over path a for oxetans (1a) and (2a), but not for the chloro-oxetan (2d). For the *trans*-oxetans (4b) and (4c) at 680—690 °C, again cleavage b was favoured over a, but to a greater extent, the product containing the olefins $R_FCH=CHF$ [$R_F = C_2F_5$, 67% from (4b), or n-C_3F_7, 63% from (4c)], and $CHF=CHF$ [32% from (4b) and 30% from (4c)].

In no case was the reaction stereospecific for either mode of cleavage. For the pyrolyses of the oxetans from the fluoroketones, there is limited stereoselectivity so far as the *cis*-oxetans (2a) and (2d) are concerned, but

this presumably is because the (*Z*)-isomer of 1,2-difluoroethylene is more stable.† For the pyrolyses of the *trans*-oxetans (4b) and (4c), the configuration of the oxetan was retained in the product to a certain extent [for example, the olefins (*Z*)- and (*E*)-$C_2F_5CH=CHF$ were obtained in the ratio 23 : 44]. The reactions would appear to involve a two-step process, with irreversible formation of an intermediate diradical.

The Structure of the Oxetans.—The structures of the isomeric oxetans were decided upon spectroscopic grounds. Their i.r. spectra demonstrated the absence of unsaturation. In their mass spectra, the molecular ions were of negligible intensity, and sets of isomers showed spectra differing only in the intensities of various ions. The ions of highest mass corresponded to $M - F$ and $M - Cl$ for the hexafluoroacetone and chloropentafluoroacetone adducts, respectively. All the chlorofluoroacetone adducts showed prominent ions corresponding to $[CFXC(CF_2X)CHF]^+$ (X = F or Cl), the oxetans from trifluoroacetone showed the analogous ion $[CH_2C(CF_3)CHF]^+$, and the $[CHFCHF]^{+\cdot}$ ion was shown by all the oxetans. For the perfluoroaldehyde adducts, in the trifluoromethyl-substituted oxetans, the ion of highest mass ($m/e = 143$) with appreciable intensity (4.8—13.8%) corresponded to loss of F_2 from the molecular ion, the $C_3H_2F_4^{+\cdot}$ and $C_3HF_4^+$ ions were intense (62—80 and 51—81%, respectively), as was the $\overset{+}{C}F_2CH=CHF$ ion (24—37%) and CF_3^+ ion (35—51%), and the base peak corresponded to $C_2H_2F_2^{+\cdot}$. In the pentafluoroethyl-substituted oxetans also, the $(M - F_2)^{+\cdot}$ ion was observed, but of diminished intensity (1.3—2.5%), the base peak corresponded to $\overset{+}{C}F_2CH=CHF$, and the ions CF_3^+ (29—39%) and $C_2H_2F_2^{+\cdot}$ (36—52%) were prominent. In the heptafluoro-n-propyl-substituted oxetans, ions of the highest observed mass corresponded to $C_5H_2F_7^+$ (*ca.* 1%) and the base peak again corresponded to $\overset{+}{C}F_2CH=CHF$, with the CF_3^+ and $C_2H_2F_2^{+\cdot}$ ions prominent.

G.l.c. provided two oxetan fractions for each reaction of a ketone, and ^{1}H and [19]F n.m.r. spectroscopy indicated that these were single compounds from the symmetrical ketones, but inseparable mixtures of two compounds from the unsymmetrical ketones. The product from 1,1,1-trifluoroacetone was anomalous, in that the first eluted fraction was a single compound, but the second was a mixture of two. The oxetan fractions obtained from the aldehydes by g.l.c. appeared to be single compounds by n.m.r. spectroscopy.

Rather more useful for structural elucidation were the ^{1}H and [19]F n.m.r. spectra, and it is convenient to discuss firstly the spectra of the oxetans obtained from the ketones, and then to consider the spectra of the oxetans obtained from the perfluoroaldehydes.

The n.m.r. spectra of the ketone adducts were highly

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* The sequence of photochemical formation and thermolysis of oxetans has been described as carbonyl-olefin metathesis.[18]

† Shimizu and Nishida [19] describe the stereospecific thermolysis of *trans*-2-phenyl-3-n-propyloxetan to give *trans*-1-phenylpent-1-ene, and non-stereospecific thermolysis of its *cis*-isomer; the more-stable olefin isomer is formed specifically.

complex, rendering difficult the extraction of all the coupling constants, particularly some of the F,F-coupling constants. In general, the spectra were first-order, and absorptions due to the ^{19}F nuclei of the CHF-CHF grouping fell into two sets, one of which showed absorptions in the ranges -117.3 to -126.1 p.p.m. for

$|J_{trans}|$ should be less than $|J_{cis}|$.[20] The observed ranges: $|J_{trans}^{HH}| = 2$—2.5 Hz and $|J_{cis}^{HH}| = 3$—4 Hz, are similar, but distinct. The trends of vicinal H,F-coupling parallel those of H,H-coupling constants,[21] and here the ranges for J_{cis}^{HF} are 6—8 Hz for the CCFCHO grouping and 10—12 Hz for the OCFCHC grouping,
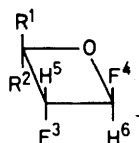
R¹
├──── O
R²\H⁵ \F⁴
│   │
F³   H⁶

TABLE 1

N.m.r. chemical shifts of 2-substituted trans-3,4-difluoro-oxetans ^{a}

		Chemical shifts (p.p.m.)					
R¹	R²	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
CF₃	CF₃	-1.5	2.8	-122.6	-38.8	4.96	5.68
CF₂Cl	CF₃ ^{b}	12.0	5.2	-121.1	-38.7	5.04	5.83
CF₃	CF₂Cl ^{b}	1.1	15.8	-121.1	-38.9	5.04	5.92
CF₂Cl	CF₂Cl	15.3	18.9	-119.4	-38.5	5.30	6.02
CFCl₂	CF₂Cl ^{b}	4.3	12.2	-117.6	-38.3	5.45	6.10
CF₂Cl	CFCl₂ ^{b}	18.8 ^{c}	18.2	-117.3	-38.6	5.45	6.18
CF₃	CH₃	-6.7	1.21	-126.1	-42.9	4.86	5.55
CH₃	CF₃ ^{d}	1.29	-1.7	-120.1	-38.0	4.63	5.72
CF₃	H	-3.7	4.3	-119.2	-39.9	4.84	5.57
C₂F₅	H	-53.9 ^{e}	4.42	-118.4	-39.6	4.91	5.60
n-C₃F₇	H	-51.1 ^{f}	4.50	-118.5	-39.8	4.94	5.62
H	CF₃	4.53	0.8	-124.5	-38.1	4.98	5.86
H	C₂F₅	4.61	-51.4 ^{g}	-123.4	-37.4	5.05	5.86
H	n-C₃F₇	4.75	-47.9 ^{h}	-123.1	-37.5	5.05	5.86

^{a} All examined as neat liquids, and positive values are to low field of the reference, external CF_3CO_2H or internal $SiMe_4$. ^{b} 1 : 1-Mixture of isomers. ^{c} AB-type multiplet with $|J_{AB}| = 180$ Hz. ^{d} 1 : 1-Mixture with the cis-isomer of Table 3. ^{e} For the CF_2 group, and the CF_3 group has δ -7.4 p.p.m. ^{f} For the CF_2 group attached to the ring, the other CF_2 group has δ -51.5, and the CF_3 group δ -5.3 p.p.m. ^{g} For the CF_2 group, and the CF_3 group has δ -7.6 p.p.m. ^{h} For the CF_2 group attached to the ring, the other CF_2 group has δ -51.1, and the CF_3 group δ -5.1 p.p.m.

the CCHFC group and -38.0 to -42.9 p.p.m. for the CCHFO group, and the other where the respective ranges were -129.8 to -133.7 p.p.m. and -54.2 to -56.3 p.p.m. (see Tables 1 to 4). The former set corresponded to the lower boiling fraction for the adducts of the fully halogenated ketones, and are assigned to the trans-3,4-difluoro-oxetans on the following grounds. The trans-oxetans should be the less polar and lower boiling. For the vicinal H,H-coupling constants,

whereas the respective ranges for J_{trans}^{HF} are 3—4 and 6.5—10 Hz. As expected,[22] the smaller values are associated with the attachment of the electronegative oxygen to the CH end of the fragment.

In the trans-oxetans, the ring fluorine absorptions, where hydrogen is cis to fluoride, occur well to low-field of the corresponding absorptions in the cis-isomer. This appears to be of diagnostic value in small-ring compounds. For example, the fluorine nuclei of cis-

TABLE 2

Coupling constant magnitudes of 2-substituted trans-3,4-difluoro-oxetans

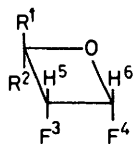|		Coupling constants (Hz) ^{a}								
R¹	R² ^{b}	J_{12}	J_{23}	J_{24}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
CF₃	CF₃	9	15	3	c	51	6.5	11	65	2.5
CF₂Cl	CF₃	10	15.5	3	c	51	6	11	65	2.5
CF₃	CF₂Cl	10	17	2	c	51	6	11	65	2.5
CF₂Cl	CF₂Cl	9	17.5	2.5	c	51	6	11.5	65	2.5
CFCl₂	CF₂Cl	9	18	2	c	51	6	12	66	2
CF₂Cl	CFCl₂	6 ^{d}	25		c	51	6	12	66	2
CF₃	CH₃	9	2		c	52.5	8	10	67	2
CH₃	CF₃		14	2	7	52	7	12	68	2.5
CF₃ ^{e,f}	H	6	14	3.7	?	52	8	10	65	2
C₂F₅ ^{f}	H	11	13		?	52	8	10.5	66	1.5
n-C₃F₇ ^{f}	H	11	13	?	?	52	8	10	66	2
H	CF₃ ^{g}	7	12	2.5	2.5	51	7	11	67	2
H	C₂F₅ ^{h,i}	10	?	?	?	52	7.5	11	68	2
H	n-C₃F₇ ^{h,j}	10	$\sim$10	?	?	52	7	11	68	2

^{a} Where determined, and coupling constants involving perfluoroalkyl groups refer to the fluorine nuclei adjacent to the ring. ^{b} See Table 1. ^{c} Ca. 7 Hz estimated from the appropriate band envelopes. ^{d} Distinct couplings involving non-equivalent fluorines of the CF_2Cl-group, where the upper value refers to the low-field half of the absorption. ^{e} $J_{13} = J_{14} = 2$ Hz. ^{f} $J_{25} = 4$ Hz. ^{g} $J_{14} = 2.5$, $J_{15} = 6.5$ Hz. ^{h} Strongly coupled AB-type multiplet for the CF_2–CH group. ^{i} $J_{14} = 3$, $J_{15} = 6$, $J_{3,CF_3} = 5$ Hz. ^{j} $J_{14} = 3$, $J_{15} = 7$, $J_{3,CF_2} = 7$ Hz.

1,1-dichloro-2,3-difluorocyclopropane absorb at -145 p.p.m. (relative to CF_3CO_2H), and at -130 p.p.m. in the *trans*-isomer.[23]

Assignment of the absorptions of the alkyl groups, and hence of distinguishing individual isomers from the unsymmetrical ketones, is more difficult. For each

oxetans, only one shows a substantial coupling constant involving the CF_3 group, and it is the other isomer where the CH_3 group shows coupling to the ring fluorine.

The above spectral parameters for the oxetans obtained from chlorofluoroacetones then allowed the structures of the oxetans obtained from perfluoroalde-

TABLE 3

N.m.r. chemical shifts of 2-substituted *cis*-3,4-difluoro-oxetans

		Chemical shifts (p.p.m.) [a]					
R¹	R²	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6
CF_3	CF_3	-1.5	3.0	-133.7	-55.4	5.12	5.66
CF_2Cl	CF_3 [b]	12.0	5.7	-133.2	-54.9	5.32	5.84
CF_3	CF_2Cl [b]	1.3	16.1	-132.3	-55.9	5.32	5.84
CF_2Cl	CF_2Cl	15.4	19.2	-131.5	-55.4	5.46	5.97
$CFCl_2$	CF_2Cl [b]	14.3	22.8 [c]	-129.8	-55.0	5.50	6.09
CF_2Cl	$CFCl_2$ [b]	18.8 [e]	19.6	-129.8	-56.3	5.60	6.09
CF_3	CH_3 [d]	-6.6	1.35	-132.7	-54.2	4.98	5.58
CF_3	H	-3.6	4.79	-124.7	-56.0	4.91	5.61
C_2F_5	H	-54.2 [e]	4.91	-123.8	-56.9	4.99	5.60
$n\text{-}C_3F_7$	H	-51.4 [f]	4.94	-123.9	-56.9	5.02	5.64

[a] Examined as neat liquids, and positive values are to low-field of the reference. [b] 1 : 1-Mixture of isomers. [c] AB-Type multiplet. [d] 1 : 1-Mixture with a *trans*-isomer. [e] For the CF_2 group, the CF_3 group has $\delta - 7.5$ p.p.m. [f] For the CF_2 group adjacent to the ring, the other CF_2 group has $\delta -51.5$, and the CF_3 group $\delta -5.2$ p.p.m.

isomer from the chlorofluoro-ketones, the fluorines of one of the alkyl groups are quite strongly coupled (14—25 Hz) to the adjacent ring fluorine (J_{23} of Tables 2 and 4); this coupling constant increases in magnitude with increasing chlorine substitution, and for any particular alkyl group, CF_3, CF_2Cl, or $CFCl_2$, within an isomer, or pair of *cis*-isomers or of *trans*-isomers, this is the absorption δ_2, to lower field. If there is a 'through space'

hydes to be determined. For the latter set, we expect no great variation for the coupling constants within the CHFCHF fragment, the [19]F n.m.r. chemical shifts of the CHFO fluorine should be very similar, but the remaining CHF fluorine should be affected by the relative disposition of the substituents on the remaining ring carbon atom. In addition, three-bond couplings to the remaining ring proton should follow similar trends of

TABLE 4

Coupling constant magnitudes of 2-substituted *cis*-3,4-difluoro-oxetans

		Coupling constants (Hz) [a]								
R¹	R² [b]	J_{12}	J_{23}	J_{24}	J_{34}	J_{35}	J_{36}	J_{45}	J_{46}	J_{56}
CF_3	CF_3	9.2	15	7.5	8	51	3.5	8	65	3.5
CF_2Cl	CF_3	10	16	8	8	51	3.5	8	65	3.5
CF_3	CF_2Cl	9	22	5.5	c	51	3.5	8	65	3.5
CF_2Cl	CF_2Cl	9.5	19.5	5.5	c	50.5	4	8	64	4
$CFCl_2$	CF_2Cl	8.5	21	?	c	51	3	6.5	64	3
CF_2Cl	$CFCl_2$	8	24	?	c	51	3	6.5	64	3
CF_3	CH_3		2.5		c	52	3.5	10	68	3.5
CF_3 [e]	H	6 [d]	?		10	52	3.5	10	68	3.5
C_2F_5 [f]	H	11 [d]	12		?	52	3.5	10	68	3.5
$n\text{-}C_3F_7$ [g]	H	10 [d]	13		?	52	3	10	68	3

[a] Where determined and distinct from zero. [b] See Table 3. [c] *Ca.* 8 Hz from the band envelopes. [d] For the fluorines adjacent to the ring. [e] $J_{13} = 2$, $J_{25} = 3.5$ Hz. [f] $J_{25} = 4$ Hz. [g] $J_{25} = 3.5$, $^4J_{CF_3,CF_2} = 9$ Hz.

contribution to this coupling,[24] then this should involve the alkyl group *cis* to the ring fluorine. The low-field shift of this alkyl group may be a result of steric compression.[25] On this basis, the assignments are then complete.

For the 1,1,1-trifluoropropan-2-one adducts, the single *cis*-isomer shows no substantial coupling of the CF_3 group to ring fluorines and hence this group is *cis* to protons. It is noteworthy that here the CH_3 group is noticeably coupled (2.5 Hz) to F-3. For the *trans*-

$|J_{cis}| > |J_{trans}|$, but be larger since fluorine is replaced by the less electronegative perfluoroalkyl groups.[22,26]

For the oxetans from perfluoro-aldehydes, the very distinctive ^{19}F chemical shifts of the CHFO fluorines allowed an immediate distinction between *trans*- and *cis*-3,4-difluoro-oxetans to be made (*cf.* δ_4 of Tables 1 and 3). The *trans*-oxetans then fell into two sets distinguished by the ^{19}F chemical shifts of the remaining ring fluorine (δ_3), and separated by *ca.* 5 p.p.m. A hydrogen at C-2 is expected to result in a low field shift

of a fluorine *cis* to it—compare the *cis*- and *trans*-oxetans from chlorofluoroketones above—so that the last three entries of Table 1 were assigned configurations with the fluorine at C-3 *cis* to the perfluoroalkyl group. This was confirmed by the magnitudes of the coupling constants, where determined. Within the CHFCHF fragment, the magnitudes resembled closely the values for the oxetans from chlorofluoro-ketones. For coupling constants involving the proton at C-2, the H,H-coupling constants have $|J_{trans}|$ (4 Hz) $< |J_{cis}|$ (6—7 Hz), and for the H,F-coupling constants, $|J_{cis}|$ is large (13—14 Hz) but unfortunately $|J_{trans}|$ was not obtained. The spectra were complicated by the fluorine spectra showing highly complex and not well resolved multiplets for certain absorptions, and complex proton spectra which were not first-order, particularly for the R_FCH-CH absorptions. However, J_{trans} was clearly considerably less than 13 Hz, so the assignment is assured. This is further supported by the observation of long-range coupling constants, presumably through-space in origin, involving the perfluoroalkyl group and the adjacent *cis*-fluorine in the last three entries of Table 1.

The identity of the *cis*-oxetans is confirmed by the coupling constants within the CHFCHF fragment (Table 4). Again, only a partial analysis was possible, and the proton spectrum of the CF₃-substituted compound, in particular, was far from first-order. However, compared with the *cis*-oxetans from the chlorofluoro-ketones, the fluorine at C-3 (δ_3) shows a distinct low-field shift, suggesting a *cis*-proton at C-2, and no long-range F,F-coupling constants involving the perfluoroalkyl group were apparent. The presumed *trans*-H,H coupling constant, J_{25}, is relatively small (3.5—4 Hz), and the *cis*-H,F coupling constant, J_{23}, fairly large (12—13 Hz) and they are very similar in magnitude to the corresponding coupling constants for the *trans*-oxetans with the same relative configuration at C-2 and C-3, so there seems no doubt as to the assignment.

EXPERIMENTAL

Volatile materials were manipulated in a Pyrex vacuum system, and products were identified by elemental analysis,

1,2-Difluoroethylene was prepared as follows: [28]

$$CFCl_2CFCl_2 \xrightarrow[\text{Bun}_2O]{\text{LiAlH}_4} CHFClCHFCl \xrightarrow[\text{Me}_2NCHO]{\text{Zn}} CHF{=}CHF$$

and distilled using a semi-automatic low-temperature still to give (*E*)- (>99.5% pure by g.l.c.) and (*Z*)-isomers (pure by g.l.c.). U.v. irradiations were carried out using a Hanovia UVS 500 medium-pressure mercury lamp.

Photochemical Addition of Fluoroketones to 1,2-*Difluoroethylene.*—(a) *Hexafluoroacetone.* (i) *With* (*Z*)-1,2-*difluoroethylene.* (*Z*)-1,2-Difluoroethylene (1.086 g, 16.97 mmol) and hexafluoroacetone (2.685 g, 16.17 mmol), sealed in a Pyrex ampoule (300 cm³) and irradiated for 6 d at a distance of 25 cm from the lamp, gave carbon monoxide (0.90 mmol) and, after fractionation by trap-to-trap distillation *in vacuo*, hexafluoroethane (8 mg, 0.06 mmol), a mixture of (*Z*)-1,2-difluoroethylene (0.214 g, 3.34 mmol, 20% recovery) and hexafluoroacetone (0.410 g, 2.47 mmol, 15% recovery), and a fraction (3.11 g) which condensed at −78 and −45 °C. This was shown by g.l.c. to consist of 3 components, and the major components were separated (3 m, 20% trixylyl phosphate on Celite at 30 °C) to give trans-2,2-*bistrifluoromethyl-3,4-difluoro-oxetan* (1a) (1.452 g, 6.32 mmol, 37%) (Found: C, 26.1; H, 1.0; F, 65.7%; *M*, 230. $C_5H_2F_8O$ requires C, 26.1; H, 0.9; F, 66.1%; *M*, 230), b.p. (Siwoloboff) 79.5 °C/761 mmHg, and cis-2,2-*bistrifluoromethyl-3,4-difluoro-oxetan* (2a) (1.489 g, 6.48 mmol, 38%) (Found: C, 26.1; H, 0.9; F, 65.7%; *M*, 229. $C_5H_2F_8O$ requires: C, 26.1; H, 0.9; F, 66.1%; *M*, 230), b.p. (Siwoloboff) 86.5 °C/761 mmHg. The minor component (2 g.l.c. peaks) was identified as (±)- and *meso*-1,1,1,2,3,4,4,4-octafluorobutanes (0.168 g, 0.83 mmol, 6%) by mass spectrometry.

Addition of *cis*-piperylene (7 mole %) to a similar mixture, completely suppressed oxetan formation.

(ii) *With* (*E*)-1,2-*difluoroethylene.* (*E*)-1,2-Difluoroethylene (1.413 g, 22.12 mmol) and hexafluoroacetone (3.665 g, 22.09 mmol), similarly irradiated for 6 d, gave a trace of carbon monoxide, hexafluoroethane (7 mg, 0.05 mmol), (*Z*)-1,2-difluoroethylene (5 mg, 0.07 mmol), (*E*)-1,2-difluoroethylene (37 mg, 0.57 mmol), hexafluoroacetone (75 mg, 0.45 mmol), and a mixture (4.954 g) comprising the *trans*-oxetan (1a) (3.516 g, 15.29 mmol, 69%), the *cis*-oxetan (2a) (1.316 g, 5.72 mmol, 26%), and 1,1,1,2,3,4,4,4-octafluorobutane (15 mg, 0.07 mmol, 0.3%). A small amount (0.107 g) remained unidentified.

A series of similar small-scale reactions were carried out

TABLE 5

Photochemical addition of hexafluoroacetone to (*E*)-1,2-difluoroethylene

Time (h)	7	11	16	22	28	36	48
% (*E*)-CHF=CHF recovered	86	84	74	68	65	53	47
% (*Z*)-CHF=CHF formed				1.4	2.8	1.6	3.0
% *trans*-Oxetan (1a)	9.6	11.0	18.2	20.8	22.5	31.7	35.4
% *cis*-Oxetan (2a)	4.4	5.0	7.8	9.8	9.8	13.7	14.6

i.r. spectroscopy (Perkin-Elmer model 257), n.m.r. spectroscopy [Varian HA 100 instrument operating at 100 MHz for ¹H nuclei (external tetramethylsilane reference) and 94.1 MHz for ¹⁹F nuclei (external trifluoroacetic acid reference)], where samples were examined as capillaries, mass spectrometry (A.E.I. MS902 spectrometer, coupled to a g.l.c. instrument), and g.l.c. (Pye 104 for analytical and Perkin-Elmer F21 for preparative separation). The perfluoroaldehydes were prepared by reducing the corresponding acid with lithium aluminium hydride in diethyl ether. [27]

for periods ranging from 7 to 48 h. The results are summarised in Table 5.

(b) *Chloropentafluoroacetone.* (i) *With* (*Z*)-1,2-*difluoroethylene.* (*Z*)-1,2-Difluoroethylene (0.864 g, 13.50 mmol) and chloropentafluoroacetone (2.555 g, 14.00 mmol), irradiated for 2 d, gave carbon monoxide (0.60 mmol), chloropentafluoroethane (trace), (*Z*)-1,2-difluoroethylene (0.479 g, 7.49 mmol, 56% recovery), chloropentafluoroacetone (1.210 g, 6.63 mmol, 47% recovery), and a mixture (1.668 g), condensing at −78 and −45 °C, which comprised

two major and several minor components by g.l.c. Preparative separation (4 m, 25% SE30 silicone oil on Embacil at 87 °C) gave an inseparable 1 : 1 mixture of r-2-chlorodifluoromethyl-2-trifluoromethyl-t-3,c-4-difluoro-oxetan (1b) and r-2-chlorodifluoromethyl-2-trifluoromethyl-c-3,t-4-difluoro-oxetan (1c) (0.700 g, 2.84 mmol, 38% based upon chloropentafluoroacetone consumed) (Found: C, 24.6; H, 1.1; F, 54.2%; M, 245.5. Calc. for $C_5H_2ClF_7O$: C, 24.3; H, 0.8; F, 54.0%; M, 246.5), b.p. (Siwoloboff) 80.5—82.0 °C/759 mmHg, and an inseparable 1 : 1 mixture of r-2-chlorodifluoromethyl-2-trifluoromethyl-t-3,t-4-difluoro-oxetan (2b) and r-2-chlorodifluoromethyl-2-trifluoromethyl-c-3,c-4-difluoro-oxetan (2c) (0.700 g, 2.84 mmol, 38%) (Found: C, 24.2; H, 1.0; F, 54.3%; M, 246.5. Calc. for $C_5H_2ClF_7O$: C, 24.3; H, 0.8; F, 54.0%; M, 246.5), b.p. (Siwoloboff) 94.0—95.0 °C/759 mmHg. The minor components were identified by g.l.c.-coupled mass-spectrometry as 1,1,1,2,3,4,4,4-octafluorobutane (26 mg, 0.13 mmol, 2%), 1-chloro-1,1,2,3,4,4,4-heptafluorobutane (16 mg, 0.07 mmol, 0.5%), 1,4-dichloro-1,1,2,3,4,4-hexafluorobutane (26 mg, 0.11 mmol, 1.5%), and unchanged chloropentafluoroacetone (0.200 g, 1.10 mmol, 8% recovery).

(ii) *With* (E)-1,2-*difluoroethylene*. (E)-1,2-Difluoroethylene (1.497 g, 23.40 mmol) and chloropentafluoroacetone (4.270 g, 23.40 mmol), similarly irradiated for 5 d, gave carbon monoxide (3.86 mmol), a mixture of hexafluoroethane (83 mg, 0.60 mmol) and chloropentafluoroethane (62 mg, 0.40 mmol), a mixture (condensing at −130 °C) of 1,2-dichlorotetrafluoroethane (0.103 g, 0.60 mmol) and 1-chloroheptafluoropropane (0.102 g, 0.50 mmol), which was identified by i.r. spectroscopy and mass spectrometry, and a mixture (condensing at −78 and −45 °C) from which the major components, *trans*-oxetans (1b) and (1c) (3.553 g, 14.42 mmol, 62%) and *cis*-oxetans (2b) and (2c) (1.242 g, 5.04 mmol, 22%), were separated by g.l.c. The minor components were identified by g.l.c.-mass spectrometry as 1,1,1,2,3,4,4,4-octafluorobutane (42 mg, 0.21 mmol, 2%), 1-chloro-1,1,2,3,4,4,4-heptafluorobutane (33 mg, 0.15 mmol, 0.5%), 1,4-dichloro-1,1,2,3,4,4-hexafluorobutane (26 mg, 0.11 mmol, 1%), and 1-chloro-1,2,3,3,4,4,4-heptafluorobutane (20 mg, 0.09 mmol, 0.5%). Less-volatile material (0.394 g) remained unidentified.

(c) 1,3-*Dichlorotetrafluoropropan-2-one*. (i) *With* (Z)-1,2-*difluoroethylene*. (Z)-1,2-Difluoroethylene (1.268 g, 19.80 mmol) and 1,3-dichlorotetrafluoropropan-2-one (3.951 g, 19.85 mmol) were irradiated for 5 d, with the liquid phase shielded from the lamp, to give carbon monoxide (11.00 mmol), a mixture (condensing at −130 °C) of (Z)-1,2-difluoroethylene (0.122 g, 1.90 mmol, 10% recovery), 1,2-dichlorotetrafluoroethane (0.609 g, 3.58 mmol, 18%), and dichlorodifluoromethane (43 mg, 0.36 mmol), which was identified by g.l.c. and i.r. spectroscopy, and a mixture (4.137 g) condensing at −45 and −78 °C, from which two major components were separated by g.l.c. (2 m, 20% MS550 silicone oil on Chromosorb at 30 °C) to give trans-2,2-*bis*(chlorodifluoromethyl)-3,4-*difluoro-oxetan* (1d) (1.320 g, 5.04 mmol, 25%) (Found: C, 22.8; H, 1.1. $C_5H_2Cl_2F_6O$ requires C, 22.8; H, 0.8%), b.p. (Siwoloboff) 123 °C/766 mmHg, and cis-2,2-*bis*(chlorodifluoromethyl)-3,4-*difluoro-oxetan* (2d) (0.998 g, 3.81 mmol, 19%) (Found: C, 22.6; H, 0.9; F, 43.5. $C_5H_2Cl_2F_6O$ requires C, 22.8; H, 0.8; F, 43.3%), b.p. (Siwoloboff) 133.5 °C/765 mmHg. Three of the minor components were tentatively identified by g.l.c.-mass spectrometry as 1,3-dichlorohexafluoropropane

(0.103 g, 0.41 mmol), 1,4-dichloro-1,1,2,3,4,4-hexafluoro-butane (89 mg, 0.38 mmol, 2%), and 1,6-dichloro-1,1,2,3,-4,5,6,6-octafluorohexane (0.319 g, 1.07 mmol, 12%). Some 1.308 g of material remained unidentified.

(ii) *With* (E)-1,2-*difluoroethylene*. (E)-1,2-Difluoroethylene (1.451 g, 22.68 mmol) and 1,3-dichlorotetrafluoropropan-2-one (4.513 g, 22.68 mmol), irradiated for 6 d, gave carbon monoxide (14.8 mmol), (E)-1,2-difluoroethylene (0.163 g, 2.72 mmol, 12% recovery), a mixture of (Z)-1,2-difluoroethylene (31 mg, 0.49 mmol, 2%), 1,2-dichloro-tetrafluoroethane (34 mg, 0.20 mmol), and dichlorodifluoromethane (12 mg, 0.10 mmol), and a fraction (5.294 g) in which the above *trans*-oxetan (1.235 g, 4.72 mmol, 22%) and *cis*-oxetan (0.410 g, 1.56 mmol, 7%) were identified, together with (by mass-spectrometry) the compounds 1,2-dichlorotetrafluoroethane (21 mg, 0.12 mmol), 1,3-dichlorohexafluoropropane (48 mg, 0.22 mmol), 1,3-dichlorotetrafluoropropan-2-one (0.325 g, 1.63 mmol, 7% recovery), and 1,4-dichloro-1,1,2,3,4,4-hexafluorobutane (0.192 g, 0.82 mmol, 4%). Material amounting to 3.060 g (at least seven components) remained unidentified.

(d) 1,1,3-*Trichlorotrifluoropropan-2-one*. (Z)-1,2-Difluoroethylene (1.920 g, 31.00 mmol) and 1,1,3-trichlorotrifluoropropan-2-one (6.853 g, 32.80 mmol), irradiated for 6 d, gave carbon monoxide (27.80 mmol), a mixture (condensing at −78 °C) comprising, by g.l.c.-mass spectrometry, 1,1,2-trichlorotrifluoroethane (93 mg, 0.50 mmol), 1,2-dichloro-tetrafluoroethane (0.684 g, 4.00 mmol), and traces of unidentified material, and a fraction (6.944 g), which was distilled to give a fraction (2.510 g), b.p. < 100 °C, shown by g.l.c.-mass spectrometry to comprise 1,1,2-trichlorotrifluoroethane (1.026 g, 5.50 mmol), 1,1,2,2-tetrachloro-difluoroethane (0.222 g, 1.10 mmol), 1,1,3-trichloropenta-fluoropropane (47 mg, 0.20 mmol), 1,2,3-trichloropenta-fluoropropane (47 mg, 0.20 mmol), 1,4-dichloro-1,1,2,3,4,4-hexafluorobutane (0.164 g, 0.70 mmol), 1,1,4-trichloro-1,2,3,4,4-pentafluorobutane (0.103 g, 0.41 mmol), and unidentified material (0.901 g). The fraction, b.p. >100 °C (4.434 g) was further separated by g.l.c. (2 m, MS550 at 105 °C) to give fractions shown by g.l.c.-mass spectrometry, and n.m.r. spectroscopy, to comprise 1,1,2,2-tetrachloro-difluoroethane (0.465 g, 2.30 mmol), 1,1,4-trichloro-1,2,3,4,4-pentafluorobutane (0.373 g, 1.49 mmol), 1,1,4,4-tetrachloro-1,2,3,4-tetrafluorobutane (0.160 g, 0.60 mmol), and 1,6-dichloro-1,1,2,3,4,5,6,6-octafluorohexane (90 mg, 0.30 mmol), a 1 : 1-mixture of r-2-dichlorofluoromethyl-2-chlorodifluoromethyl-t-3,c-4-difluoro-oxetan (1e) and r-2-dichlorofluoromethyl-2-chlorodifluoromethyl-c-3-t-4-difluoro-oxetan (1f) (0.612 g, 2.20 mmol, 7%), and a 1 : 1 mixture of r-2-dichlorofluoromethyl-2-chlorodifluoromethyl-t-3,t-4-difluoro-oxetan (2e) and r-2-dichlorofluoromethyl-2-chlorodifluoromethyl-c-3,c-4-difluoro-oxetan (2f) (0.612 g, 2.20 mmol, 7%). Material amounting to 2.122 g remained unidentified.

Acetone-soluble material (0.203 g) remained in the reaction vessel.

(e) *With* 1,1,1-*trifluoropropan-2-one*. (i) *With* (Z)-1,2-*difluoroethylene*. (Z)-1,2-Difluoroethylene (1.518 g, 23.71 mmol) and 1,1,1-trifluoropropan-2-one (2.640 g, 23.57 mmol), irradiated for 16 d with the liquid phase shielded from the lamp, gave a trace of carbon monoxide, (Z)-1,2-difluoroethylene (72 mg, 1.12 mmol), (E)-1,2-difluoroethylene (56 mg, 0.88 mmol), and 1,1,1-trifluoropropan-2-one (1.388 g, 12.39 mmol, 53% recovery), and a mixture (1.482 g), condensing at −45 °C, which was separated by g.l.c

(3.5 m, 20% trixylyl phosphate on Celite at 40 °C) to give further 1,1,1-trifluoropropan-2-one (0.651 g, 5.81 mmol, 25% recovery), r-2-*trifluoromethyl-2-methyl*-t-3,c-4-*difluoro-oxetan* (1g) (84 mg, 0.48 mmol, 2%) (Found: C, 34.3; H, 2.9; F, 54.0. $C_5H_5F_5O$ requires C, 34.1; H, 2.8; F, 54.0%), b.p. (Siwoloboff) 75.5 °C/770 mmHg, and an inseparable 1 : 1 mixture of r-2-trifluoromethyl-2-methyl-t-3,t-4-difluoro-oxetan (2g) and r-2-trifluoromethyl-2-methyl-c-3,t-4-difluoro-oxetan (1h) (0.345 g, 1.96 mmol, 8%) (Found: C, 34.2; H, 3.0; F, 53.7. Calc. for $C_5H_5F_5O$: C, 34.1; H, 2.8; F, 54.0%), b.p. (Siwoloboff) 84 °C/760 mmHg. Minor components (0.402 g) were not identified and a brown, acetone-soluble, solid (1.16 g) which remained in the tube, was not further examined.

(ii) *With* (E)-1,2-*difluoroethylene*. (E)-1,2-Difluoroethylene (1.411 g, 22.05 mmol) and 1,1,1-trifluoropropan-2-one (2.496 g, 22.29 mmol), irradiated for 6 d with the liquid phase shielded from the lamp, gave carbon monoxide (0.17 mmol), (E)-1,2-difluoroethylene (0.116 g, 1.82 mmol), (Z)-1,2-difluoroethylene (24 mg, 0.37 mmol), 1,1,1-trifluoropropan-2-one (1.046 g, 9.34 mmol, 42% recovery), the *trans*-oxetan (1g) (0.467 g, 2.65 mmol, 13%) and an inseparable 1 : 1 mixture of the *cis*- (2g) and *trans*-oxetans (1h) (1.784 g, 10.14 mmol, 50%). Four minor components (estimated 42 mg) remained unidentified, and an acetone-soluble gum (0.423 g) remained in the reaction tube.

Photochemical Addition of Perfluoroaldehydes to 1,2-Difluoroethylene.—(a) *Trifluoroacetaldehyde*, (i) *With* (Z)-1,2-*difluoroethylene*. (Z)-1,2-Difluoroethylene (0.561 g, 8.76 mmol) and trifluoroacetaldehyde (0.585 g, 8.76 mmol), sealed in a Pyrex ampoule (*ca.* 100 cm³) and irradiated for 89 h with light from a u.v. lamp placed at a distance of 25 cm, gave carbon monoxide (0.70 mmol) and, after fractionation by trap-to-trap distillation *in vacuo*, a mixture of recovered (Z)-1,2-difluoroethylene (8 mg, 0.12 mmol, 1% recovery) and trifluoroacetaldehyde (trace), and a liquid fraction (1.311 g). This fraction was shown by g.l.c. to consist of three major components and a number of minor components. The major components were separated by g.l.c. (3.5 m, trixylyl phosphate on Celite at 30 °C) to give r-2-*trifluoromethyl*-t-3,c-4-*difluoro-oxetan* (3a) (0.303 g, 1.87 mmol, 21%) (Found: C, 29.9; H, 2.1; F, 58.2%; M, 162. $C_4H_3F_5O$ requires C, 29.6; H, 1.8; F, 58.6%; M, 162), b.p. (Siwoloboff) 59 °C/763 mmHg, r-2-*trifluoromethyl*-t-3,t-4-*difluoro-oxetan* (5a) (0.356 g, 2.20 mmol, 25%) (Found: C, 29.9; H, 2.1; F, 58.4%; M, 162. $C_4H_3F_5O$ requires C, 29.6; H, 1.8; F, 58.6%; M, 162), b.p. (Siwoloboff) 69.5 °C/763 mmHg, and r-2-*trifluoromethyl*-c-3,t-4-*difluoro-oxetan* (4a) (0.509 g, 3.14 mmol, 36% yield) (Found: C, 29.7; H, 1.8; F, 58.3%; M, 162.5. $C_4H_3F_5O$ requires C, 29.6; H, 1.8; F, 58.6%; M, 162), b.p. (Siwoloboff) 76 °C/763 mmHg. The minor components of the liquid fraction were identified by g.l.c. coupled mass spectrometry as 1,1,1,2,3,4,4,4-octafluorobutane (30 mg, 0.15 mmol, 2%), 1,1,1,2,3,4,5,6,6,6-decafluoropropane (19 mg, 0.14 mmol, 2%), and 1,1,1,2,3,4,5,6,6,6-decafluorohexane (12 mg, 0.05 mmol, 1%). Material amounting to 82 mg remained unidentified, and a transparent viscous gum (76 mg), soluble in ethanol, remained in the reaction tube.

(ii) *With* (E)-1,2-*difluoroethylene*. (E)-1,2-Difluoroethylene (0.870 g, 13.60 mmol) and trifluoroacetaldehyde (1.343 g, 13.70 mmol), similarly irradiated for 4 days, gave a trace of carbon monoxide, a mixture of (E)-(11 mg, 0.17 mmol, 1% recovery), and (Z)-1,2-difluoroethylenes (3 mg, 0.04 mmol, 0.3%), a trace of trifluoromethane,

and a liquid graction (2.101 g) comprising mainly the oxetans (3a) (0.567 g, 3.50 mmol, 26%), (5a) (0.635 g, 3.92 mmol, 29%), and (4a) (0.782 g, 4.83 mmol, 36%), the minor components 1,1,1,2,3,4,4,4-octafluorobutane (38 mg, 0.19 mmol, 1%), 1,1,1,2,3-pentafluoropropane (12 mg, 0.09 mmol, 0.7%), and 1,1,1,2,3,4,5,6,6,6-decafluorohexane (8 mg, 0.03 mmol, 0.2%), and unidentified material (59 mg). Involatile material (95 mg) remained in the ampoule.

(b) *Pentafluoropropionaldehyde*. (i) *With* (Z)-1,2-*Difluoroethylene*. (Z)-1,2-Difluoroethylene (1.070 g, 16.73 mmol) and pentafluoropropionaldehyde (2.462 g, 16.84 mmol), sealed in a Pyrex ampoule (300 cm³) and irradiated for 7 days, gave carbon monoxide (0.82 mmol), a mixture, condensing *in vacuo* at −130 °C, of (Z)-1,2-difluoroethylene (64 mg, 1.00 mmol, 6% recovery) and traces of pentafluoropropionaldehyde, pentafluoroethane, and decafluorobutane, and a liquid fraction (3.282 g). The major components from this last fraction were separated by g.l.c. (3.5 m, trixylyl phosphate on Celite at 30 °C) to give r-2-*pentafluoroethyl*-t-3,c-4-*difluoro-oxetan* (3b) (0.761 g, 3.59 mmol, 21%) (Found: C, 28.7; H, 1.6; F, 62.4%; M, 211. $C_5H_3F_7O$ requires C, 28.3; H, 1.4; F, 62.7%; M, 212), b.p. (Siwoloboff) 77.5 °C/768 mmHg, r-2-*pentafluoroethyl*-t-3,t-4-*difluoro-oxetan* (5b) (0.990 g, 4.67 mmol, 28%) (Found: C, 28.6; H, 1.6; F, 63.1%; M, 212. $C_5H_3F_7O$ requires C, 28.3; H, 1.4; F, 62.7%; M, 212), b.p. (Siwoloboff) 89.0 °C/768 mmHg, and r-2-*pentafluoroethyl*-c-3,t-4-*difluoro-oxetan* (4c) (1.140 g, 5.38 mmol, 32%) (Found: C, 28.3; H, 1.6; F, 62.7%; M, 211. $C_5H_3F_7O$ requires C, 28.3; H, 1.4; F, 62.7%; M, 212), b.p. (Siwoloboff) 93.5 °C/768 mmHg, and the minor components 1,1,1,2,2,3,4-heptafluorobutane (53 mg, 0.29 mmol, 2%), 3H,4H-dodecafluorohexane (10 mg, 0.03 mmol, 0.2%), and 3H,4H,5H,6H-tetradecafluoro-octane (48 mg, 0.13 mmol, 2%), were identified by g.l.c.-coupled mass spectrometry, leaving 0.28 g of unidentified components. An ethanol-soluble gum (0.156 g) remained in the ampoule.

(ii) *With* (E)-1,2-*difluoroethylene*. (E)-1,2-Difluoroethylene (1.435 g, 22.43 mmol) and pentafluoropropionaldehyde (3.562 g, 23.86 mmol), similarly irradiated for 5 days, gave carbon monoxide (1.60 mmol), pentafluoroethane (28 mg, 0.23 mmol), decafluorobutane (69 mg, 0.29 mmol), a liquid fraction (4.620 g) containing the oxetans (3b) (1.091 g, 5.15 mmol, 23%), (5b) (1.406 g, 6.63 mmol, 30%), and (4b) (1.971 g, 9.30 mmol, 41%), the minor components 1,1,1,2,2,3,4-heptafluorobutane (66 mg, 0.36 mmol, 2%), 3H,4H-dodecafluorohexane (24 mg, 0.08 mmol, 0.4%), and 3H,4H,5H,6H-tetradecafluoro-octane (17 mg, 0.05 mmol, 0.2%), and unidentified material (45 mg). Gum (0.205 g) remained in the ampoule.

(c) *Heptafluorobutyraldehyde*. (i) *With* (Z)-1,2-*difluoroethylene*. (Z)-1,2-Difluoroethylene (0.818 g, 12.77 mmol) and heptafluorobutyraldehyde (2.359 g, 11.91 mmol), similarly irradiated for 4 days, gave a trace of carbon monoxide and of 1H-heptafluorobutane, and a liquid fraction (3.020 g) from which the major components were separated by g.l.c. (3.5 m, trixylyl phosphate on Celite at 45 °C) to give r-2-*heptafluoro-n-propyl*-t-3,c-4-*difluoro-oxetan* (3c) (0.622 g, 2.37 mmol, 19%) (Found: C, 27.7; H, 1.2; F, 65.2. $C_6H_3F_9O$ requires C, 27.5; H, 1.1; F, 65.3%), b.p. (Siwoloboff) 95.2 °C/760 mmHg, r-2-*hepta-fluoro-n-propyl*-t-3,t-4-*difluoro-oxetan* (5c) (0.928 g, 3.54 mmol, 28%) (Found: C, 27.8; H, 1.2; F, 64.9. $C_6H_3F_9O$ requires C, 27.5; H, 1.1; F, 65.3%), b.p. (Siwoloboff) 105 °C/760 mmHg, and r-2-*heptafluoro-n-propyl*-c-3,t-4-

difluoro-oxetan (4c) (1.054 g, 4.02 mmol, 31%) (Found: C, 27.4; H, 1.1; F, 65.0. $C_6H_3F_9O$ requires C, 27.5; H, 1.1; F, 65.3%), b.p. (Siwoloboff) 107.5 °C/760 mmHg. Mass spectrometry indicated that one of the minor components was 1,1,1,2,2,3,3,4,5-nonafluoropentane (43 mg, 0.18 mmol, 1%), and at least six components (total 0.373 g) remained unidentified. An ethanol-soluble gum (0.152 g) remained in the ampoule.

(ii) *With* (E)-1,2-*difluoroethylene*. (E)-1,2-Difluoro-ethylene (1.519 g, 23.73 mmol) and heptafluorobutyralde-hyde (4.700 g, 23.73 mmol), similarly irradiated for 2 days, gave carbon monoxide (0.40 mmol), a mixture of 1*H*-heptafluoropropane (39 mg, 0.23 mmol), (E)- (4 mg, 0.06 mmol), and (Z)-1,2-difluoroethylenes (1 mg, 0.01 mmol), a trace of heptafluorobutyraldehyde, and a liquid fraction (5.924 g) containing the oxetans (3c) (1.269 g, 4.84 mmol, 20%), (5c) (1.681 g, 6.42 mmol, 27%), and (4c) (2.422 g, 9.24 mmol, 39%), 1,1,1,2,2,3,3,4,5-nonafluoro-pentane (67 mg, 0.28 mmol, 1%), and unidentified material (0.485 g), together with a gum (0.238 g) which remained in the ampoule.

Pyrolysis of Oxetans.—(a) *Of* trans-2,2-*bis(trifluoro-methyl)-3,4-difluoro-oxetan*. The title oxetan (0.136 g, 0.60 mmol) was passed at 2—3 mmHg pressure through a silica tube (0.7 cm i.d., heated length 51 cm) at 670 °C during 7 min (contact time ca. 0.6 s) to give (Z)-1,2-difluoro-ethylene (4 mg, 0.07 mmol, 12%), (E)-1,2-difluoroethylene (5 mg, 0.08 mmol, 13%), 1,1,1,3-tetrafluoro-2-trifluoro-methylpropene (40 mg, 0.22 mmol, 37%) identified by n.m.r. spectroscopy,[29] an unidentified component (0.04 mmol), and recovered *trans*-oxetan (51 mg, 0.22 mmol, 37% recovery).

(b) *Of* cis-2,2-*bis(trifluoromethyl)-3,4-difluoro-oxetan*. The title oxetan (0.563 g, 2.45 mmol), passed through the silica tube at 675 °C during 28 min (contact time ca. 0.6 s), gave (Z)-1,2-difluoroethylene (42 mg, 0.66 mmol, 27%), (E)-1,2-difluoroethylene (17 mg, 0.26 mmol, 11%), 1,1,1,3-tetrafluoro-2-trifluoromethylpropene (0.207 g, 1.14 mmol, 47%), an unidentified component (0.25 mmol), and recovered *cis*-oxetan (90 mg, 0.39 mmol, 16%).

(c) *Of* cis-2,2-*bis(chlorodifluoromethyl)-3,4-difluoro-oxetan*. The title oxetan (0.213 g, 0.81 mmol), passed at 5—6 mmHg through the silica tube at 665 °C during 15 min (contact time ca. 2 s), gave (Z)-1,2-difluoroethylene (23 mg, 0.36 mmol, 44%), (E)-1,2-difluoroethylene (11 mg, 0.17 mmol, 21%), 1-chloro-1,1,3-trifluoro-2-chlorodifluoro-methylpropene (45 mg, 0.21 mmol, 26%), $\nu_{max.}$ 1 724 cm^{-1}, identified by n.m.r. spectroscopy and its analogy to the olefin $(CF_3)_2C=CHF$, and unidentified material consisting of at least three other components (ca. 0.12 mmol).

(d) *Of* r-2-*pentafluoroethyl*-c-3,t-4-*difluoro-oxetan*. The title oxetan (0.197 g, 0.93 mmol) was passed at 2—3 mmHg pressure through a Pyrex tube (1.0 cm i.d., heated length 51 cm) at 680 °C during 4.5 min (contact time ca. 0.25 s) to give, after fractionation by trap-to-trap distillation *in vacuo* and examination by i.r. and n.m.r. spectroscopy, mass spectrometry, and g.l.c., a product estimated to comprise silicon tetrafluoride (0.02 mmol), (E)- (10 mg, 0.15 mmol, 19%) and (Z)-1,2-difluoroethylenes (6 mg, 0.10 mmol, 13%), pentafluoropropionaldehyde (10 mg, 0.07 mmol, 9%), (E)- (29 mg, 0.18 mmol, 23%) and (Z)-1,3,3,4,-4,4-hexafluorobut-1-enes (55 mg, 0.34 mmol, 44%), and recovered oxetan (30 mg, 0.14 mmol, 15% recovery).

(e) *Of* r-2-*heptafluoro-n-propyl*-c-3,t-4-*difluoro-oxetan*. The title oxetan (0.794 g, 3.03 mmol) was passed at 3—4

mmHg pressure through a silica tube (0.7 cm i.d., heated length 51 cm) at 690 °C during 21 min (contact time ca. 0.5 s) to give a product similarly estimated to comprise traces of silicon tetrafluoride and trifluoromethane, hexa-fluoroethane (22 mg, 0.16 mmol) (E)- (26 mg, 0.42 mmol, 17%) and (Z)-1,2-difluoroethylenes (19 mg, 0.31 mmol, 13%), heptafluorobutyraldehyde (26 mg, 0.13 mmol, 5%), (E)- (0.120 g, 0.56 mmol, 23%) and (Z)-1,3,3,4,4,5,5,5-octafluoropent-1-enes (0.207 g, 0.97 mmol, 40%), recovered oxetan (0.160 g, 0.61 mmol, 20% recovery), and liquid material (0.102 g) which remained unidentified.

The structures of the olefins $R_FCH=CHF$ were largely determined by n.m.r. spectroscopy. (E)-1,3,3,4,4,4-Hexa-fluorobut-1-ene had δ_F (positive values to low-field of external CF_3CO_2H) −10.8 (CF_3), −39.0 (CF_2, $^3J_{HF} = 12$ Hz), and −40.4 p.p.m. (CF, $^2J_{HF} = 77$, $^3J_{HF} = 14$, $^4J_{FF} = 3$ Hz) and δ_H (external SiMe$_4$) 6.56 (CHF, $^3J_{HH} = 11$, $^4J_{HF} = 1.5$ Hz) and 5.00 p.p.m. (=CH), and the (Z)-isomer had δ_F −10.9 (CF_3, $^5J_{FF} = 6$ Hz), −36.0 (CF_2, $^4J_{FF} = 22$, $^3J_{HF} = 14$ Hz), and −32.8 p.p.m. (CF, $^2J_{HF} = 77$, $^3J_{HF} = 37$ Hz), and δ_H 6.16 (CHF, $^3J_{HH} = 5.5$, $^4J_{HF} = 1.5$ Hz) and 4.46 p.p.m. (=CH). The configuration follows from the magnitudes of the olefinic coupling constants, and the similarities to the compounds $(CF_3)_2CFCH=CHF$ [30] and $CF_3CH=CHF$.[29] Analogously, the isomers of the 1,3,3,-4,4,4,5,5,5-octafluoropent-1-ene were identified largely on the basis of the n.m.r. parameters of the olefinic nuclei.

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