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# Reactions of polyfluoroketones with unsaturated compounds

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**ABSTRACT.** **A review is presented on the reactions of polyfluoroketones with alkenes, alkynes, 1,2- and 1,3-dienes, and certain other unsaturated compounds. The reactivity of polyfluoroketones has been compared with that of diethyl oxomalonate. The characteristic dienophilic, enophilic and 1,2-dipolar properties of polyfluoroketones have been discussed.**

**The bibliography contains 156 references.**

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## I. Introduction

Among unsaturated organofluorine compounds, polyfluoroketones are second only to fluoroolefins in order of importance. The electrophilicity of ketones increases with introduction of fluorine atoms at the α-position, and such activity is at a maximum in polyfluoroketones and derivatives thereof in which one of the fluorine atoms in the α-position is replaced by an electron-accepting group: an alkoxy, carbonyl, nitro, sulphonic acid or fluorosulphonyl group. These are among the most powerful electrophilic agents known, possessing an extraordinary affinity for nucleophiles and towards π-systems with donor properties. Thus, depending on structural features, polyfluoroketones possess a wide range of chemical properties, exhibiting both the classical reactivity of aliphatic ketones.[1–3] and 'anomalous' behaviour specific to this class of functionalised ketone.

The unusual chemistry of polyfluoroketones and their derivatives is due, in part, to their extremely high electrophilicity and, in part, to the ability of perfluoroalkyl residues, especially the trifluoromethyl group, to stabilise adjacent δ-bonds. This explains the facile conversion of polyfluoroketones to stable hemiketals, hemiaminals, aldols, thermodynamically stable enols, α-fluoro-substituted alkoxides, oxetenes and other compounds with a small ring. The high electrophilicity and stabilising effect of polyfluoroalkyl groups is notably manifested in the reactions of polyfluoroketones with alkenes, alkynes, 1,2- and 1,3-dienes, and with a large number of other unsaturated compounds—the subject matter of the present review.

Up to now, there have been no review articles covering general aspects of the reactions of polyfluoroketones with unsaturated compounds; nor have the latter been examined in a critical sense. Previous reviews[4,5] and a monograph[6] in the field of organofluorine chemistry have included this aspect in part, as also has a more recent review.[7] In the authoritative survey of Witt et al.,[8] the authors collected and analysed information on the reactions of hexafluoroacetone with unsaturated elementoorganic and organometallic compounds.

In this article, we have compared the reactivity of highly electrophilic polyfluoroketones towards alkenes, cycloalkenes, alkynes, 1,3-dienes, cumulenes and a number of other unsaturated compounds. We have examined, in particular, the reactions of these unsaturated compounds with perfluorocyclobutanone, nitropentafluoroacetone, hexafluoroacetone (HFA), methyltrifluoropyruvate (MTFP), and with chloropentafluoro- and 1,3-dichlorotetrafluoroacetone. For comparison, information has also been gathered on the dienophilic, enophilic, and 1,2-dipolar properties of diethyl oxomalonate (DEOM)—an activated carbonyl compound with properties very similar to those of polyfluoroketones.

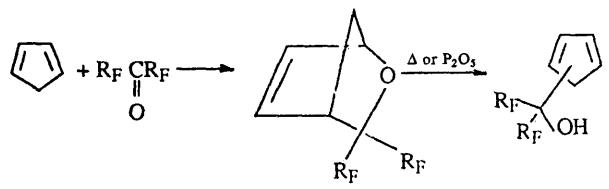
In an analysis of the collected information, an attempt has been made to assess the effect of the polyfluoroketone structure on the ability of these ketones to participate in Diels–Alder reactions, ene reactions, and in [2 + 2]-cycloaddition; the influence of the $CF_3$ group on these reactions has been examined by comparing the reactivity of hexafluoroacetone, methyltrifluoropyruvate, and diethyloxomalonate.

## II. [4 + 2]-Cycloaddition

Among the vast array of available heterodienophiles,[9] including activated carbonyl compounds, polyfluoroketones are particularly noteworthy in that they possess unusually high reactivity in Diels–Alder cycloaddition. Thus, [4 + 2]-cycloadducts are formed between polyfluoroketones and donor-type 1,3-dienes under mild conditions in the absence of a catalyst (Table 1). Furthermore, high reactivity is manifested towards certain 1,3-heterodienes.

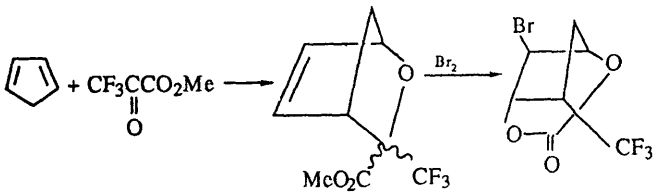
Perfluorocyclobutanone[10] and HFA [12,13] interact with cyclopentadiene even on mixing in the cold. The 2-oxabicyclo[2.2.1]hept-5-ene derivative obtained from perfluorocyclobutanone is relatively stable, and may be isolated pure by distillation under reduced pressure. However, fractionation under the normal conditions results in its conversion to 2-(α-hydroxyperfluorocyclobutyl)cyclopentadiene which readily polymerises. A similar

cycloadduct is formed from HFA, but undergoes retrodiene scission on heating above 20 °C. It is converted into a regioisomeric mixture of α-hydroxyhexafluoroisopropylcyclopentadienes in the presence of $P_2O_5$.[13]

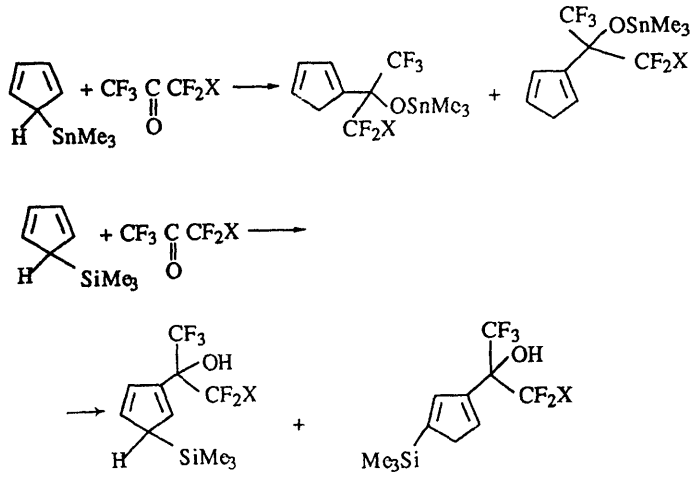


$R_F = CF_3$; $R_F$, $R_F = -(CF_2)_3-$

Methyl trifluoropyruvate (MTFP) has the same reactivity as HFA towards cyclopentadiene, affording a 2.5:1 mixture of *endo*- and *exo*-2-oxabicyclo[2.2.1]hept-5-enes.[21] The latter cycloadducts revert to the starting materials on heating, and are converted predominantly to a bromolactone on bromination.



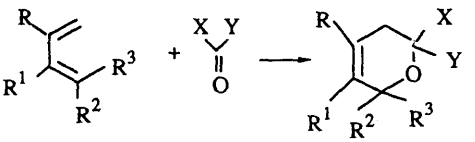
No cycloadduct is formed on reaction of HFA or chloropentafluoroacetone with cyclopentadienyltrimethyl-stannane or -silane. Instead, reaction of the cyclopentadienylstannane with these polyfluoroketones at 20 °C leads to insertion of the latter into a C–Sn bond, while reaction with the silyl analogue results in a mixture of 1,2-adducts.[23]



X = F, Cl.

Unlike polyfluoroketones, diethyl oxomalonate does not afford cycloadducts with cyclopentadiene in the temperature range −20 to 135 °C.[24]

Polyfluoroketones interact as readily with 1,3-butadiene and its alkyl and alkoxy derivatives as they do with cyclopentadiene (Table 1). The resulting 5,6-dihydro-2*H*-pyrans are stable and isolable in high yield. No information is available on the conditions required for retrodiene scission, nor on the manner of their decomposition.



R = $R^1$ = $R_2$ = $R^3$ = H; R = $CH_3$, $R^1$ = $R^2$ = $R^3$ = H;
R = $R^1$ = $CH_3$, $R^2$ = $R^3$ = H;
R = $R^1$ = $R^3$ = H, $R^2$ = $CH_3$; R = $R^1$ = $R^3$ = H; $R^2$ = OMe;
R = Cl, $R^1$ = $R^2$ = $R^3$ = H; R = $R^2$ = $R^3$ = $CH_3$, $R^1$ = H.
X, Y = $-(CF_2)_3-$; X = Y = $CF_3$; X = Y = $CF_2Cl$; X = $CF_3$,
Y = $CF_2NO_2$; X = $CF_3$, Y = $CO_2Me$.

**Table 1. Reaction conditions for the cycloaddition of polyfluoroketones to 1,3-dienes and the yield of 5,6-dihydro-2*H*-pyrans.**

| Polyfluoroketone | 1,3-Diene | *T*, °C | Time*, h | Yield, % | Refs. |
|---|---|---|---|---|---|
|  | 1,3-Butadiene | 0 | 24 | 100 | [10] |
| | Cyclopentadiene | 20 | – | 93 | [11] |
|  | " " | 20 | – | 54 | [12, 13] |
| | 1,3-Butadiene | 20 | 24 | 78 | [14] |
| | Isoprene | 20 | 16 | 75 | [15] |
| | " " | 100 | 16 | 83 | [12] |
| | Piperylene | 20 | 16 | 82 | [15] |
| | 2,3-Dimethyl-1,3-butadiene | 100 | – | 92 | [12] |
| | 1-Ethoxy-1,3-butadiene | 20 | 24 | 87 | [16] |
| | 2,4-Dimethyl-1,3-pentadiene | 170 | 24 | 86 | [17] |
| | 2-Methyl-6-methylene-,2-7-octadiene (myrcene) | 170 | 3 | 80 | [18] |
|  | 1,3-Butadiene | 100 | – | 87.5 | [12] |
| | Isoprene | 200 | 48 | 95 | [19] |
| | 2,3-Dimethyl-1,3-butadiene | 20 | 16 | 55 | [12] |
|  | | 200 | 10 | 76 | [12] |
| | 1,3-Butadiene | 20 | 24 | 90 | [15] |
| | Isoprene | −15 to −10 | – | 95.6 | [20] |
| | 2,3-Dimethyl-1,3-butadiene | −15 to −10 | – | 54.7 | [20] |
| | Chloroprene | 100 | 4 | 75.8 | [20] |
|  | Cyclopentadiene | 20 | 12 | 66.4 | [21] |
| | 1,3-Butadiene | 20 | 16 | 94 | [15] |
| | Isoprene | 20 | 24 | 84; 83 | [15, 22] |
| | 2,3-Dimethyl-1,3-butadiene | 20 | 24 | 88; 75 | [15, 22] |
| | Piperylene | 20 | 24 | 85 | [15] |
| | Chloroprene | 60 | 8 | 86 | [15] |

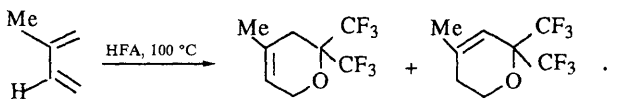
Footnote. A dash means that the reaction time has not been given.

Of the examined polyfluoroketones, perfluorocyclobutanone[10,11] and nitropentafluoroacetone[14,20] are the most reactive, the corresponding cycloadducts with 1,3-butadiene being formed in the cold or at 20 °C. Hexalfuoroacetone is slightly less reactive than nitropentafluoroacetone, interacting with 1,3-dienes at 20 °C.[14,15,20] The assertion of Ishihara et al.[25] that "HFA exhibits low reactivity towards the more familiar 1,3-dienes" is without foundation.

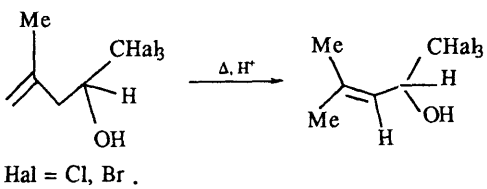
It should also be pointed out that it is not necessary to use harsh conditions for the cycloaddition of HFA or 1,3-dichlorotetrafluoroacetone with 1,3-dienes, as has been reported.[17,19] According to Linn,[12] [4 + 2]-cycloaddition with 1,3-dichlorotetrafluoroacetone at 20 °C is less facile than with HFA. It has recently been reported that MTFP is as reactive as HFA in such cycloaddition.[15]

A comparison of the reactivity of MTFP towards a number of 1,3-dienes has provided some interesting results.[15] Thus, it has been shown that cyclopentadiene, 1,3-butadiene, isoprene, piperylene (as a *cis/trans* mixture) and 2,3-dimethyl-1,3-butadiene interact with MTFP effectively under the same conditions (0–20 °C). It therefore follows that [4 + 2]-cycloaddition of these dienes with MTFP is little affected by structural variation within the dienes, by any variation in the transitional energy from transoid to cisoid form, or by the energy coefficients and degree of localisation of the frontier orbitals. As similar results are obtained with other polyfluoroketones (see Table 1), it is evident that such behaviour is characteristic of this family of dienophile.

The regioselectivity of the cycloaddition of polyfluoroketones with unsymmetrical 1,3-dienes is another characteristic feature. Thus, under all conditions, cycloaddition of the ketone proceeds in such a way that the carbon atom of the carbonyl group attacks the carbon atom of the conjugated system possessing the highest electron density. This is true under both mild and harsh conditions. The assertion that the thermal cycloaddition of polyfluoroketones with isoprene displays low regioselectivity[22] would appear to be unfounded since in the original work of Linn[12] it was shown that HFA affords only the *para*-isomer [sic] (85%) together with an isomer (15%) arising by prototropic shift:



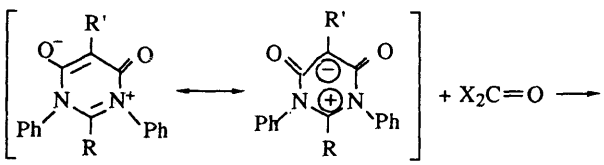

The latter product would be anticipated if traces of acid were present in the medium. Such acid-catalysed prototropic shfits, in fact, are characteristic of structures of the type:[26]

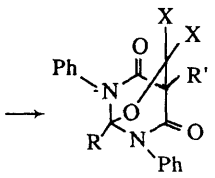



Hal = Cl, Br.

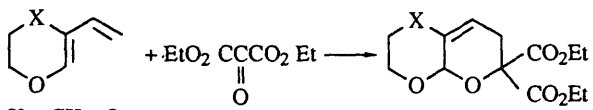
The somewhat anomalous cycloaddition of polyfluoroketones to 1,3-dienes is probably due to the electronic configuration of the carbonyl group and associated charged residues which make a large contribution to the formation of the pericyclic transition state. The high electronegativity of the carbonyl oxygen of the dienophile and the high electron-accepting ability of the perfluoroalkyl group leads to a significant decrease in the level of the LUMO and to its localisation primarily on the carbon atom of the carbonyl group, as has been demonstated with perfluorocyclobutanone.[27]

In this context, it is interesting to note that DEOM is noticeably more reluctant to participate in [4 + 2]-cycloaddition with 1,3-dienes than polyfluoroketones.[9] In fact, cycloaddition of DEOM with 1,3-butadiene and its alkyl derivatives can only be achieved at high temperatures (130–140 °C).[24,28–31] Cycloaddition at a lower temperature (50 °C) is only possible with electron-rich 1,3-dienes, such as 1-alkoxy-3-alkyl-1,3-butadienes,[32] 5-vinyl-3,4-dihydro-2*H*-pyran and 5-vinyl-2,3-dihydro-1,4-dioxin.[33] The notable difference in dienophilic reactivity between HFA and DEOM is apparent from the relative ease of cycloaddition of these compounds with 6-oxo-2,6-dihydro-1-pyrimidinium-4-olates [...3,6-dihydro? (Ed. of Translation)], involving a synchronous [$4\pi_s$ + $2\pi_s$]-mechanism: the former dienophile reacts at 0 °C, whereas cycloaddition with DEOM requires heating at 110 °C.[34] Oxadiazabicyclooctanediones are obtained as the reaction product:



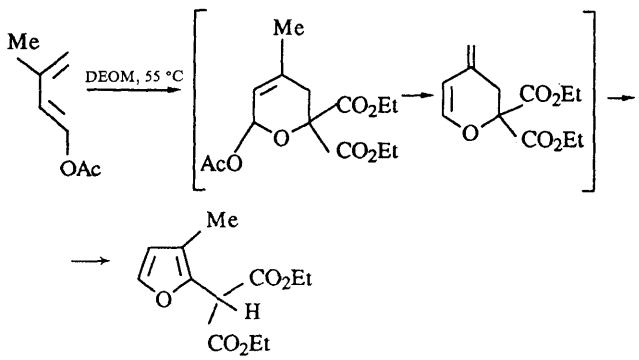




X = $CF_3$, $CO_2Et$.




X = $CH_2$; O.

1-Methoxy-3-methyl-1,3-butadiene forms an intermediate [4 + 2]-cycloadduct with DEOM on heating in THF. This subsequently eliminates acetic acid and rearranges to give a substituted furan.[35]

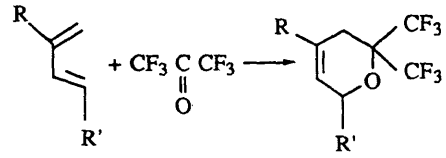



Coupled with the lower activity of DEOM is the somewhat reduced regioselectivity in its [4 + 2]-cycloaddition with unsymmetrical 1,3-dienes.[24] With isoprene, the para-isomer is formed predominantly together with around 10% of the meta-isomer. The regioselectivity of cycloaddition with piperylene is higher, the proportion of ortho- and meta-cycloadducts being 19 : 1.

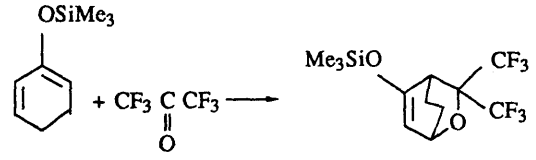
Further differences in the dienophilic activity of polyfluoroketones and DEOM are apparent in their reactions with siloxy-1,3-dienes, which have been extensively studied in the field of natural product synthesis,[36,37] notably in the context of asymemtric diene syntheses based on chiral organoaluminium catalysts.[38,39]

Hexafluoroacetone interacts regiospecifically with a variety of siloxy-1,3-dienes in the absence of catalysts at –40 to –45 °C. The sole regioisomer is that anticipated by considering the polarisation of

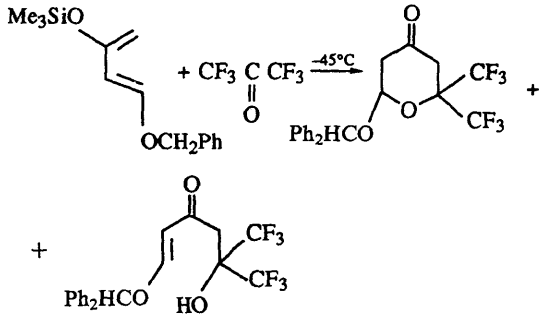
the carbonyl group and the 1,3-conjugated system.[25]



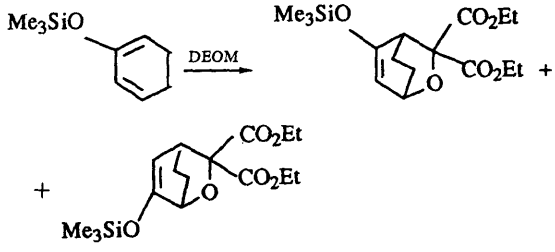
R = H, R' = $OSiMe_3$; R = $OSiMe_3$, R' = H.



However, the reaction of HFA with (*E*)-1-benzyloxy-3-trimethylsiloxy-1,3-butadiene yields both [4 + 2]-cycloadduct and an aldol-type by-product.[40]

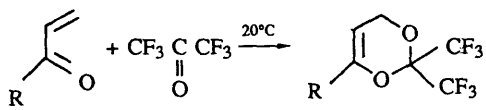


Diethyl oxamalonate (DEOM) normally participates in such reactions at 130–140 °C,[41] although a [4 + 2]-cycloadduct is obtainable on heating this dienophile with the electron-rich 1-methoxy-3-trimethylsiloxy-1,3-butadiene in refluxing THF over several hours.[35] However, the cycloaddition of DEOM with 1,3-dienes displays low regioselectivity. Thus, a 55 : 45 mixture of para- and meta-adducts is formed from 2-trimethylsiloxy-1,3-cyclohexadiene.[41]



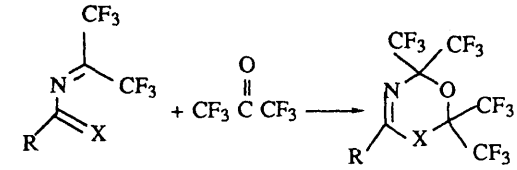
Low regioselectivity was also noted for the reaction of DEOM with 1-methyl-2-trimethylsiloxy-1,3-butadiene.

Dieles–Alder reactions with polyfluoroketones may also be performed with 1,3-heterodienes. Thus, mixing HFA with acrolein or methyl vinyl ketone at low temperature, followed by warming to 20 °C, leads to the corresponding [4 + 2]-adduct in quantitative yield.[42]



R = H, Me

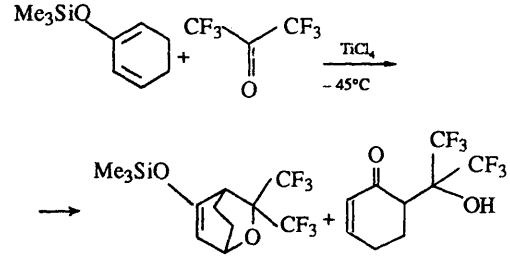
Heating HFA with highly electrophilic acylimine derivatives of HFA affords the corresponding 1,3,5-dioxazine,[43] while thioacylimine and iminoacylimine derivatives give the corresponding 1,3,5-oxathiazine and 1,3,5-oxadiazine derivatives.[44]



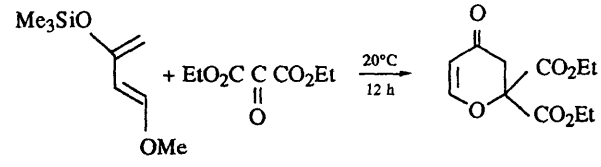
X = O, S, $NR^1$; R = Ph, 4–$ClC_6H_4$, $Bu^t$.

In all such heterodiene syntheses, reaction proceeds by attack of the carbonyl carbon of HFA at the most electron-rich atom of the 1,3-heterodiene component. It should be noted that such Diels–Alder reactions of HFA acylimine derivatives with non-fluorinated carbonyl compounds may be undertaken under milder conditions.[45]

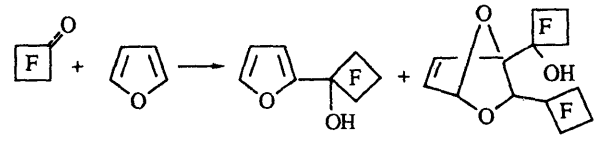
Little information is available on Lewis acid-catalysed cycloaddition of polyfluoroketones with 1,3-dienes. It is reported that the cycloaddition of HFA with 1-trimethylsiloxy-1,3-cyclohexadiene in the presence of $TiCl_4$ is accompanied by the formation of an aldol derivative as by-product.[25]



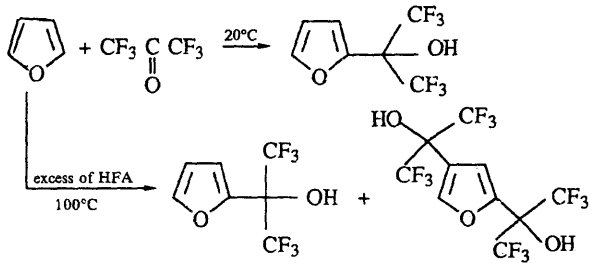
In the $SnCl_4$-catalysed reaction of isoprene with MTFP at –50 °C, an ene adduct is formed together with a [4 + 2]-cycloadduct (see below). The cycloaddition of DEOM with 1-ethoxy-3-alkyl-1,3-butadienes can be successfully carried out at 20 °C in the presence of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionato)-europium(III).[46] Zinc chloride (250 mol%) activates the cycloaddition of DEOM with 1-methoxy-3-trimethylsiloxy-1,3-butadiene.[47] This reaction is accompanied by removal of the silyl protective group and elimination of methanol.



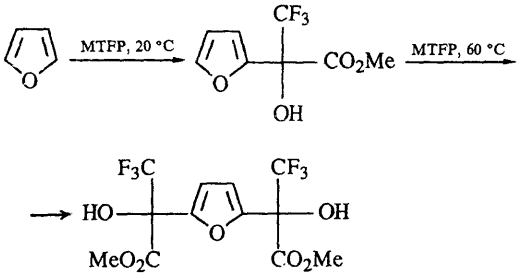
Normally, the interaction of polyfluoroketones with heterocyclic 1,3-dienes leads to 1,2-adducts rather than [4 + 2]-cycloadducts. However, in the reaction of perfluorocyclobutanone with furan, both 1,2- and [4 + 2]-adducts have been isolated.[48]



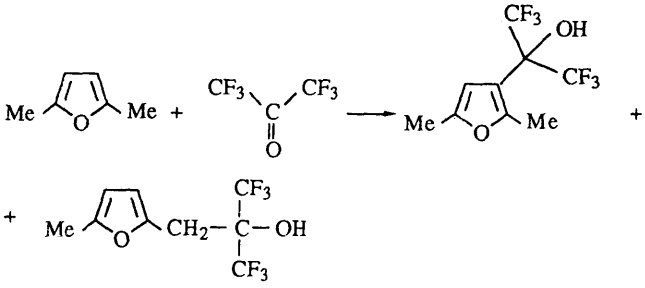
Depending on the temperature and ratio of the reactants, the interaction of HFA with furan leads to either a 2-substituted furan or a mixture of 2-substituted and 2,4-disubstituted furan.[48–50]



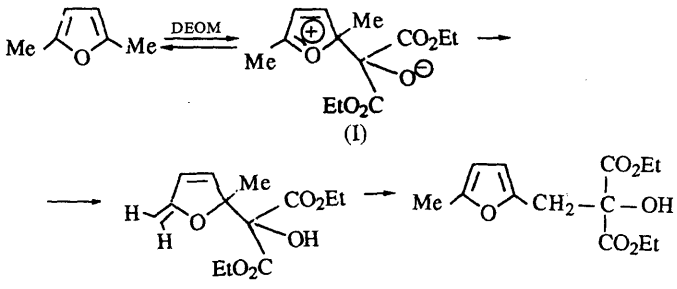
The reaction of furan with MTFP proceeds in a step-wise manner to give the corresponding 2,5-disubstituted furan via mono-substitution.[51,52]



The interaction of 2,5-dimethylfuran with HFA leads to a 3:1 mixture of side chain-substituted and ring-substituted derivatives.[49]



The reaction of DEOM with 2,5-dimethylfuran can only be conducted at elevated pressure.[53] In this instance, side-chain substitution is exclusive. It is thought that a zwitter-ion (I) is formed initially, and subsequently stabilised by a 1,5-sigmatropic shift.[54]

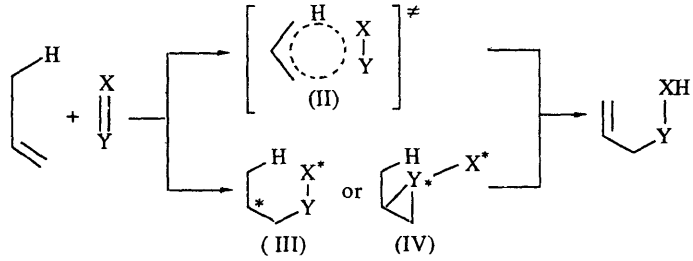


The reactions of *N*-methylpyrrole and thiophene with polyfluoroketones proceed by C-alkylation only.[48,49,51]

## III. Ene reactions

An ene reaction is defined as the addition of an electron-rich olefin (the ene component) having a allylic hydrogen to an electron-deficient double bond (the enophile), as a result of which the double bond of the olefin undergoes migration with transfer of the allylic hydrogen atom to the enophile.[55,56]

In his review, Hoffmann alludes to the possibility of there being a broad spectrum of transition states for an ene reaction.[55] One extreme is a symmetry-allowed concerted $[2\pi_s + 2\pi_s + 2\delta_s]$-process, as represented by transition state (II) (see below). However, the symmetry of the transition state is such that the other extreme, namely a step-wise pathway, is also possible. Here, the transition state could be represented by either a zwitter-ionic structure or a biradical having free (III) or restricted (IV) rotation.[56] A study of the several by-products formed during such ene reactions would tend to suggest that a step-wise mechanism is operative.[57,58]

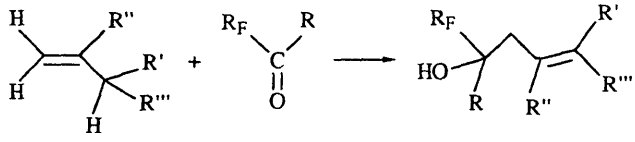


Synthetic applications of ene reactions have been legion in recent years. This is particularly true in the field of asymmetric synthesis in the presence of chiral catalysts.[59]

Polyfluoroketones are among the more interesting enophiles. In view of their high activity in ene reactions, they have sometimes been called "superenophiles",[62,63] as also have trifluoronitrosomethane,[60] DEOM,[62] and thionylimines with electron-accepting substituents.[61]

### 1. Ene reactions of polyfluoroketones with alkenes

Polyfluoroketones undergo ene reaction with terminal alkenes under mild conditions to give exclusively or predominantly homoallyl alcohols.[10,21,64,65]



R, $R_F$ = — $(CF_2)_3$ —, $CF_3$, $CF_2Cl$; $R_F$ = $CF_3$, R = $CF_2Cl$;
$R_F$ = $CF_3$, R = $CF_2NO_2$; $R_F$ = $CF_3$, R = $CO_2Me$.

Literature data on these reactions are summarised in Table 2. It should be noted that, contrasting with classical enophiles, polyfluoroketones participate in ene syntheses under mild conditions. Normally, the reaction can be conducted in the temprature range 20–100 °C, and in certain instances below 0 °C. For example, the following reactions can be carried out at 20–25 °C: polyfluorocyclobutanone with propene and 2-phenylpropene;[10,11] nitropentafluoroacetone with 2-methylpropene;[64] HFA with 2-methyl-, 2-methoxy- and 2-phenyl-propene;[64,65] and MTFP with 2-methylpropene and its homologues.[21] 1,3-Dichlorotetrafluoroacetone, HFA and MTFP each undergo ene reaction with active ene components, such as β-pinene and 3,7-dimethylenedicyclo[3.3.1]-nonane.[65,69]

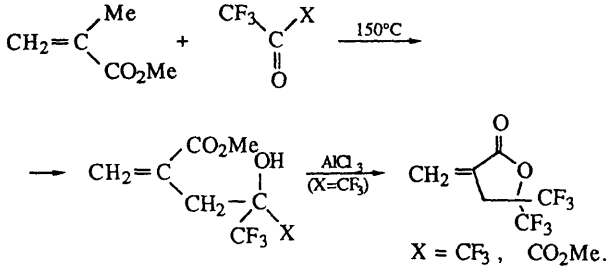
**Table 2.** Reaction conditions and yields of homoallyl alcohols obtained by reaction of polyfluoroketones with terminal alkenes.

| Polyfluoroketone | Alkene | T, °C | Time*, h | Yield, % | Refs. |
|---|---|---|---|---|---|
| O<br>F | Propene | 20 | – | 88 | [10] |
| | – | 175 | 12 | 87 | [11] |
| | 2-Phenylpropene | 20 | 1440 | 79 | [11] |
| $CF_3CCF_3$<br>O | Propene | 145 | 12 | 7.6 | [66] |
| | " " | 150 | 2.5 | 17 | [65] |
| | " " | 150 | 9 | 67 | [64] |
| | 2-Methylpropene | 20 | 24 | 97 | [64] |
| | " " | 35–40 | 12 | 62.1 | [66] |
| | " " | 50 | 3 | 36 | [67] |
| | " " | 25–30 | 78 | 60 | [68] |
| | 3,7-Dimethylene-bicyclo[3.3.1]nonane | 20 | – | 95.6 | [69] |
| | β-Pinene | 35 | 2 | 80 | [65] |
| | 2-Methoxypropene | 0–35 | 1 | 85 | [65] |
| | 2-Phenylpropene | 40 | 4 | 80 | [65] |
| | 2-Methyl-3-phenylpropene | 25–30 | 65 | 82 | [68] |
| | 3-(Triphenylsilyl)propene | 60 | 28 | 65 | [23] |
| | 3-(Trimethylsilyl)propene | 100 | 48 | 86 | [23] |
| | 1-Butene | 20 | 12 | 52 | [66] |
| | " " | 25 | 72 | 40 | [68] |
| | 1-Octene | 100 | 2 | 75 | [65] |
| | 2-Chloropropene | 165 | 4 | 10–20 | [65] |
| | 3-Chloropropene | 165 | 4 | 3 | [65] |
| | 2-Acetoxypropene | 25 | 56 | – | [66] |
| | 4-Allylanisole | 100 | 3 | 82.5 | [70] |
| | Allylbenzene | 120 | 5 | 80.7 | [70] |
| | Ally phenyl ether | 150 | – | 16.2 | [70] |
| | Allyl phenyl sulphide | 150 | 15 | 67.7 | [70] |
| | Methyl methacrylate | 165 | 6 | 16 | [65] |
| $CF_2ClCCF_3$<br>O | Methacrylonitrile | 165 | 4 | 3 | [65] |
| | Allybenzene | 25 | 72 | 53 | [68] |
| | 3-(Triphenylsilyl)propene | 80 | 24 | 53 | [23] |
| | 3-(Trimethylsilyl)propene | 100 | 24 | 89 | [23] |
| $CF_2ClCCF_2Cl$<br>O | 2-Phenylpropene | 45–100 | 72 | 93 | [71] |
| | – | 60 | 60 | 62 | [65] |
| | β-Pinene | −70–0 | 24 | 62 | [67] |
| | 2,4,4-Trimethylpent-1-ene | 66–71 | 5 | 50 | [67] |
| | 1,5-Hexadiene | 100 | 24 | 90 | [66] |
| | 3-(Triphenylsilyl)propene | 100 | 24 | 49 | [23] |
| | 3-(Trimethylsilyl)propene | 100 | 24 | 83 | [23] |
| $CF_3CCF_2NO_2$<br>O | Propene | 100 | 6 | 66 | [64] |
| | 3-Methylpropene | 20 | 24 | 96 | [64] |
| | 3-Methylpropene | −20 | 288 | 73.6 | [21] |
| $CF_3CCO_2Me$<br>O | 3,7-Dimethyl-ene-bicyclo[3.3.1] nonane | 20 | 0.5 | 94.6 | [69] |
| | 2-Methyl-1-pentene | 20 | 24 | 84 | [22] |
| | 1-Butene | 100 | 48 | 83 | [72] |
| | 1-Hexene | 100 | 5 | 90 | [72] |
| | – | 80–100 | 40–50 | 91 | [22] |
| | 1-Octene | 80–100 | 40–50 | 96 | [22] |
| | 1-Hexadecane | 80–100 | 40–50 | 79 | [22] |
| | Vinylcyclohexane | 80–100 | 40–50 | 74 | [22] |
| | Allylbenzene | 100 | 14 | 84 | [72] |
| | 2-Chloropropene | 120 | 12 | 61.4 | [72] |
| | 2-Methyl-3-chloropropene | 100 | 48 | 70 | [72] |
| | 3-Iodopropene | 150 | 48 | 21 | [72] |
| | Methyl methacrylate | 160 | 48 | 15 | [72] |

Footnote. A dash means that data are unavailable.

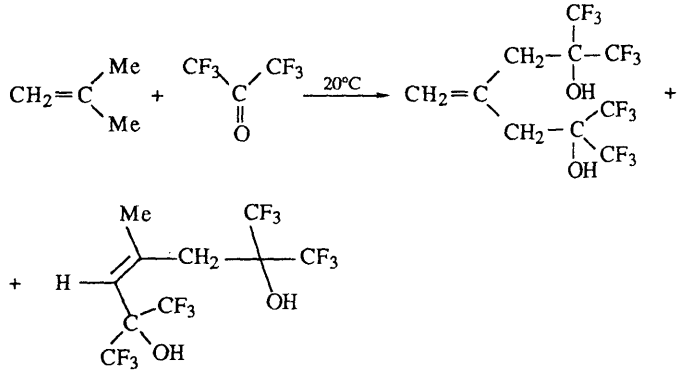
A further feature of polyfluoroketone chemistry is that their enophilic activity towards active ene components is as high as their dienophilic activity towards 1,3-dienes. This distinguishes polyfluoroketones from classical enophiles[55] which participate in ene reactions much less easily than in diene syntheses. It should be noted also that, in the family of highly electrophilic polyfluoroketones, the most active enophile (and dienophile) is perfluorocyclobutanone. This is evident from the reactivity of polyfluoroketones towards propene.[10] Hexafluoroacetone and methyl trifluoropyruvate display similar ene reactivity, while that of chloropentafluoro- and 1,3-dichlorotetrafluoro-acetone is lower and that of nitropentafluoro-acetone is somewhat higher.

It is also significant that polyfluoroketones participate in an unusually wide spectrum of ene reactions. For example, they react not only with classical ene components (differing in their donor properties and polarisation of the C=C bond but also with terminal 2-chloroalkenes, the unsaturation of which is deactivated by conjugation with the chlorine atom.[72] Ene reaction also takes place by interaction of polyfluoroketones with such 3-substituted propenes as 3-aryloxy- and 3-arylthio-propenes,[70] 3-iodopropene,[72] and 3-chloropropene,[65] which are normally unreactive as ene components or only weakly active. Even methyl methacrylate undergoes ene reaction with HFA [65] and MTFP.[72]




The ene adduct obtained with HFA is further converted to a λ-lactone on treatment with $AlCl_3$.[67] Bulky allylic substituents, such as trimethyl- and triphenyl-silyl, in the alkene component do not inhibit ene reaction with HFA or with chloropentafluoro- and 1,3-dichlorotetrafluoro-acetone.[23]

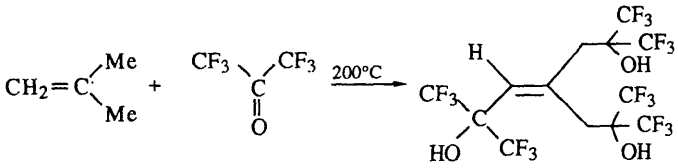
In certain instances the selectivity of the ene reaction between polyfluoroketones and alkenes is lower than normal because the initially formed homoallyl alcohol is itself a highly active ene component and undergoes a subsequent ene reaction to give a 2:1 adduct. The effect of the reaction conditions on such adduct formation has been studied in detail,[68] with particular reference to the reaction of HFA with 2-methylpropene.[66,68,73,74]




Similar products have also been observed on interaction of 2-methylpropene with 1,3-dichlorotetrafluoroacetone.[68,75] and MTFP.[21] In the latter instance, 2:1 adducts are even formed at −20 C.[72] The formation of such adducts also takes place on

reaction of HFA with propene,[68,76,77] 1-butene,2-phenylpropene, 2-methyl-1-pentene, 2-methyl-1-undecene, and 2-methyl-3-phenylpropene,[68] as well as on reaction of 1,3-dichlorotetrafluoroacetone with 2-phenylpropene and 1,5-hexadiene.[66]

A 3:1 adduct has been isolated by reacting 2-methylpropene with a four-fold excess of HFA.[68,78]

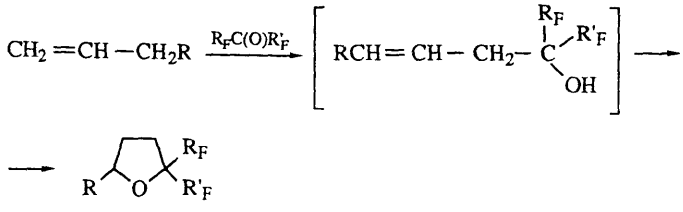


The ene reactions of polyfluoroketones with propenes having electron-donating allylic functionality afford tetrahydrofuran derivatives as by-product[64,70–72] the yield of which depends on the temperature and the reaction time. Under certain conditions such tetrahydrofurans are the main product (see Table 3).

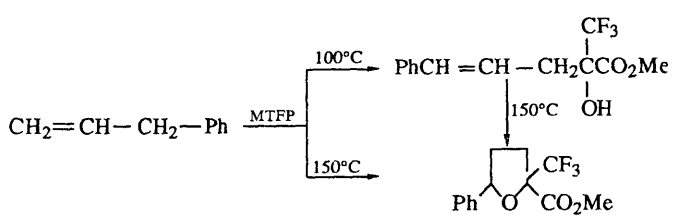
**Table 3.** Reaction conditions and yields of tetrahydrofurans obtained by reaction of polyfluoroketones with terminal alkenes.

| Polyfluoroketone | Alkene | *T*, °C | Time*, h | Yield, % | Refs. |
|---|---|---|---|---|---|
| $CF_3CCF_3$ ‖ O | Allyl methyl ether | 100 | 20 | 18 | [64] |
| | 4-Allylanisole | 150 | – | 79 | [70] |
| | Allyl phenyl sulphide | 150 | 15 | 17.8 | [70] |
| $CF_3CCF_2NO_2$ ‖ O | Allyl methyl ether | 100 | 10 | 30 | [64] |
| $CF_3CCO_2Me$ ‖ O | Allyl methyl ether | 110 | 30 | 57 | [72] |
| | Allylbenzene | 150 | 14 | 32.3 | [72] |
| $CF_2ClCCF_2Cl$ ‖ O | 4-Allylanisole | 45–100 | 144 | 91 | [71] |
| | Allyl phenyl ether | 45–100 | 310 | 67 | [71] |
| | Diallyl ether | 45–100 | 144 | 97 | [71] |

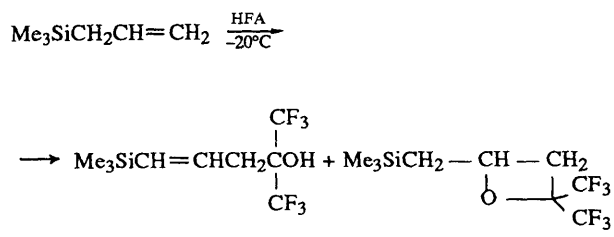
The formation of these products can be explained by cycloisomerisation of the initially formed homoallyl alcohols.



This was confirmed in a study of the reaction of HFA with 4-allylanisole[70] and of MTFP with allylbenzene.[72]

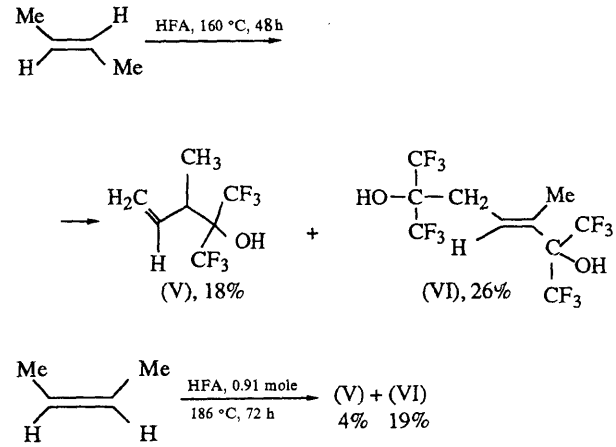


Only one example is known of a thermal reaction between a polyfluoroketone and a terminal alkene wherein by-product formation is kinetically independent of the primary ene reaction. Thus, it has been shown that HFA interacts with 3-(trimethylsilyl)propene to give a mixture of the corresponding homoallyl alcohol and an oxetane.[23]

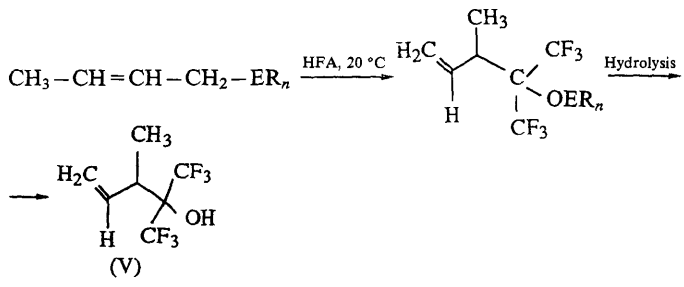


Here, [2 + 2]-cycloaddition coexists with ene reaction as a quite independent pathway.

Contrasting with terminal alkenes, internal alkenes interact with polyfluoroketones only under harsh conditions. For example, the reactions of *trans*- and *cis*-2-butene with HFA require heating at 160 and 180 °C, respectively. The resulting homoallyl alcohols, having a terminal vinyl group, readily participate in a subsequent ene reaction.[68]

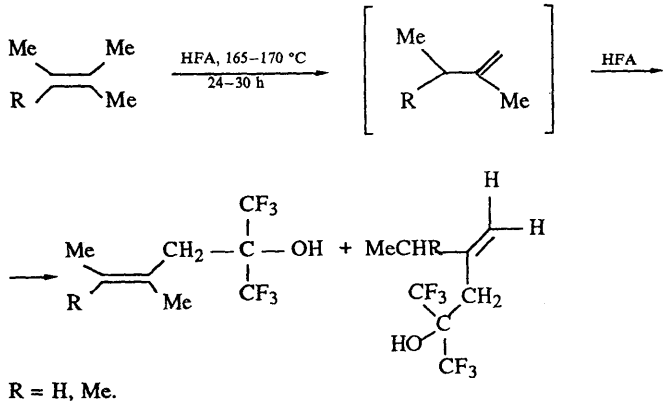


The homoallyl alcohols (V) and chloropolyfluoro analogues have also been prepared by reaction of the corresponding polyfluoroketones with crotyldibutylborane, tricrotylborane,[79] crotyltrimethylstannane or crotyltriphenylstannane.[23] The initial ene reaction proceeds regiospecifically at 20 °C with transfer of the organometallic residue to the oxygen atom of the carbonyl group.



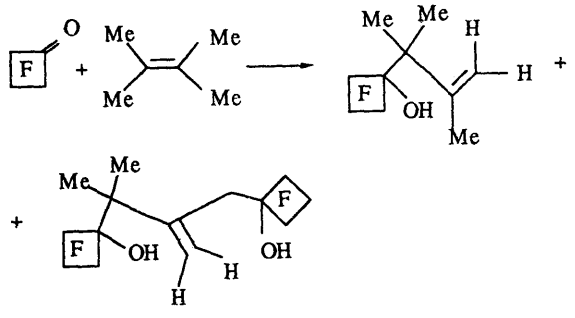
$ER_n = B(n\text{-}Bu)_2$, $B(CH_2{-}CH{=}CH{-}CH_3)_2$, $SnMe_3$, $SnPh_3$.

Treatment of HFA with trimethyl- or tetramethyl-ethene under harsh conditions initially produces a terminal alkene which then reacts with the ketone to give a mixture of two isomeric homoallyl alcohols.[68]

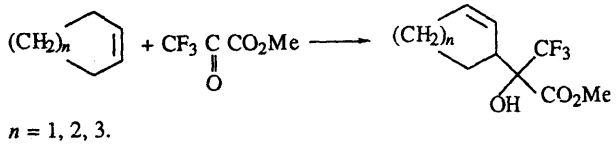


R = H, Me.

Perfluorocyclobutanone, however, reacts at 100 °C with tetramethylethene as a typical internal alkene, i.e. by formation of the corresponding homoallyl alcohol and a 2:1 adduct.[11]



Ene reactions of polyfluoroketones with cycloalkenes require the same forcing conditions as with internal acyclic alkenes. Thus, the interaction of MTFP with cyclohexene affords a preparatively useful yield of ene adduct at 170 °C, while cyclopentene and cycloheptene require heating at 150–160 °C.[21,72]

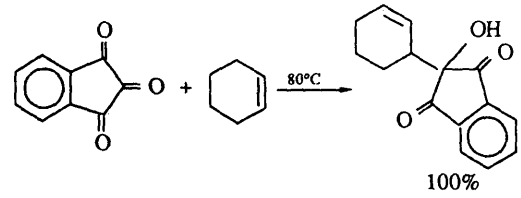


$n$ = 1, 2, 3.

However, only a small yield of ene adduct (up to 5%) is obtained on heating HFA with cyclohexene at 160 °C for 5 h.[65] It is worth noting that ene reactions of the pro-chiral MTFP with cycloalkenes afford a mixture of diastereoisomeric ene adducts. The ratio of diastereoisomers is quite high (up to 85% of one diastereoisomer in the mixture), so that these thermal ene reactions are stereoselective.[72]

The enophilic properties of DEOM are quite different from those of polyfluoroketones. Thus, DEOM reacts with terminal ene components to give the anticipated homoallyl alcohols but under noticeably more forcing conditions.[80–85] More to the point, 3-substituted propenes do not react at all with DEOM even under harsh conditions.[71]

In a comparative study of the reactions of DEOM, HFA and MTFP with 3,7-dimethylenebicyclo[3.3.1]nonane, it was found that DEOM is significantly less reactive than the two polyfluoroketones.[69] However, where ene reactions with internal alkenes and cycloalkenes are subject to steric control, there is little difference in the reactivity of polyfluoroketones[21,65] and DEOM.[30,80,85] From this it follows that ene reactions with polyfluoroketones (HFA and MTFP) and DEOM are equally affected by steric forces, and that the enophilicity of these ketones is less important with bulky ene components. In fact, where the carbonyl group is relatively unhindered, as in 1,2,3-indantrione, ene reaction proceeds under fairly mild conditions, even with cycloalkenes.[62]

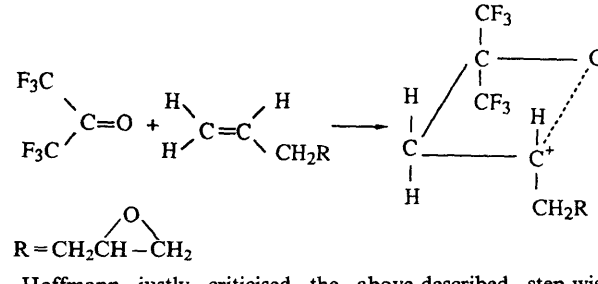


100%

It is evident that differences in the electronic state of the carbonyl group in polyfluoroketones and DEOM are more important. A molecular orbital study of ene reactions indicates that the energy and asymmetry of the LUMO of the enophile has a critical effect on the formation of a pseudoaromatic transition state.[86] It is very significant that, unlike DEOM, polyfluoroketones are characterised by a noticeably lower level for their LUMO which is predominantly localised on the carbon atom of the carbonyl group.[27]

Given the unusual electronic state of polyfluoroketones, one would not anticipate a concerted mechanism for their ene reactions, but rather the formation of a transition state wherein carbon–carbon bond formation has developed to a greater extent than hydrogen migration to the carbonyl group. However, from initial studies, it is evident that such ene reactions do involve a typical concerted pathway with the suprafacial formation of a pseudoaromatic six-membered transition state.[8,64] Gordon arrived at the same conclusion as a result of studying the kinetics of the reaction of HFA with propene in the gas phase.[87] At the same time, it was found that reaction is profoundly affected by steric hindrance, as reflected in the unusually low value for the kinetically derived pseudoexponential factor. It should be noted that thermal ene reactions with DEOM, which have been studied in more detail,[56,83–85,88,89] are also assumed to involve a concerted mechanism, wherein the six-membered transition state takes due account of the non-linear and aymmetric transfer of hydrogen.[56]

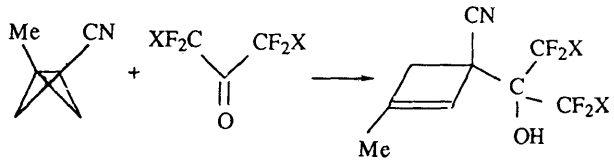
A step-wise mechanism has been proposed in one instance to explain the unexpected reaction of allyl glycidyl ether with HFA.[65] Here, it is thought that a four-centred bipolar ion is formed initially.



Later, Hoffmann justly criticised the above-described step-wise mechanism.[55] Nevertheless, the possibility still exists[56] that thermal ene reactions with polyfluoroketones may deviate from a concerted pathway, given that these enophiles are more reactive than DEOM towards classical ene components and that their behaviour towards 3-substituted propenes is distinctly different. The formation of a

[2 + 2]-cycloadduct from HFA and 3-(trimethylsilyl)propene under mild conditions would also lend weight to a non-concerted mechanism.

Only two examples are known to us where ene products are formed by interaction of polyfluoroketones with a strained δ-bonded system. This involves the reaction of HFA and 1,3-dichlorotetrafluoroacetone with 1-cyano-3-methylbicyclo[1.1.0]butane, as was outlined in Hoffmann's review.[55]



X = F, Cl.

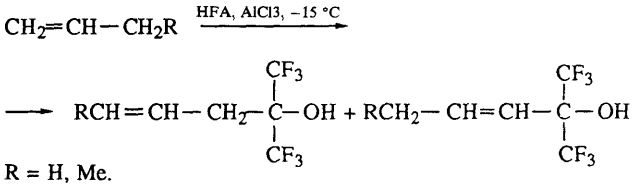
## 2. Reactions of polyfluoroketones with ene components in the presence of a Lewis acid

Like Diels–Alder cycloaddition, ene reactions are catalysed by Lewis acids.[55]

It has been shown that the lone pair-donating properties of the carbonyl oxygen atom of polyfluoroketones are largely nullified. This is evident from the fact that HFA is virtually unreactive towards electrophilic agents[4] and that the oxygen atom of HFA is not protonated by superacids.[90] It is also evident that no alternative sites in the polyfluoroketone molecule are available for interaction with Lewis acids. Hence only strong Lewis acids coordinate with polyfluoroketones, as is evident in the $AlCl_3$-catalysed reactions of nitropentafluoroacetone, HFA and chloropentafluoroacetone with unsaturated substrates, including ene components.[4,5]

Thus, HFA interacts with cyclohexene in the presence of $AlCl_3$ at −10 °C to give an ene adduct in 56% yield.[91] 1,1,1-Trifluoroacetone reacts similarly with cyclic olefins in the presence of $AlCl_3$ at −78 °C.[92] The $AlCl_3$-catalysed reaction of HFA or chloropentafluoroacetone with propene or 1-butene takes place at −15 °C.[93–95]

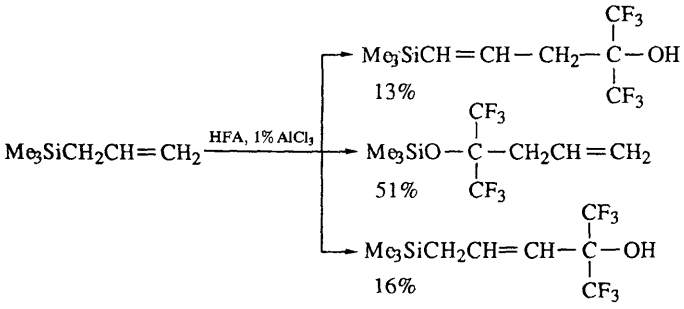
In these reactions, allyl alcohols are formed to a much greater extent than homoallyl alcohols.



R = H, Me.

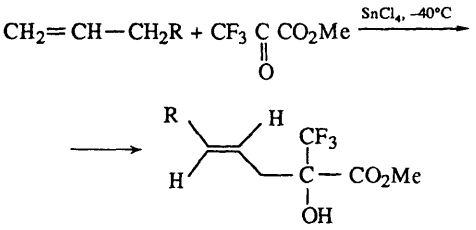
It has also been shown that the resulting allyl and homoallyl alcohols are formed in kinetically independent pathways.

The reaction of HFA with 3-(trimethylsilyl)propene can also be achieved in the presence of $AlCl_3$, but here the ene adduct predominates.[23]



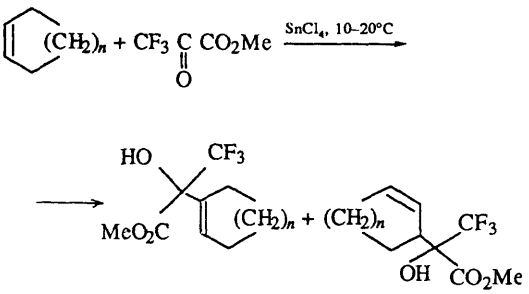
It is thought that the $AlCl_3$-catalysed reactions of polyfluoroketones with terminal alkenes involves the same activation as takes place in Friedel–Crafts reactions.[23,93] Thus, the donor–acceptor complex formed between the ketone and $AlCl_3$ attacks the terminal carbon atom of the unsaturation to give a carbocation, which is stabilised by elimination of a proton from an adjacent carbon atom.

The methoxycarbonyl group in MTFP provides a second site for complexation with the Lewis acid, so that ene reactions with this polyfluoroketone may be performed with $SnCl_4$. In fact, the $SnCl_4$ catalysed ene reactions of MTFP with propene and 1-butene afford exclusively ene adducts even at −40 °C.[21]



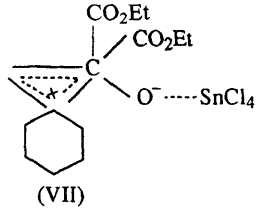
R = H, Me.

The $SnCl_4$-catalysed reactions of MTFP with cyclopentene and cyclohexene take place at 10–20 °C under steric control.[21] Here, the corresponding allyl alcohols are formed predominantly (60–65%), while the yield of ene adducts does not exceed 15%.



*n* = 1,2.

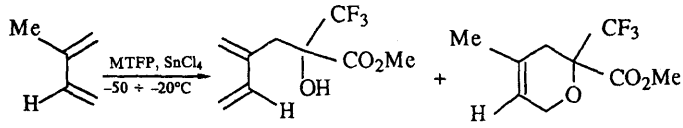
It should be noted that DEOM also reacts readily with terminal and internal alkenes in the presence of $SnCl_4$.[56,83,84] The mechanism of these processes has been studied in detail. A kinetic model has been proposed to explain the observed intramolecular and intermolecular isotope effects. This involves a three-membered intermediate having restricted rotation, exemplified below (VII) for the reaction of DEOM with methylenecyclohexane in the presence of $SnCl_4$.



(VII)

Although $SnCl_4$-catalysed reactions of DEOM and MTFP are apparently similar, one cannot assume that the rules and mechanism applicable to ene reactions with DEOM also hold true for ene reactions with MTFP.

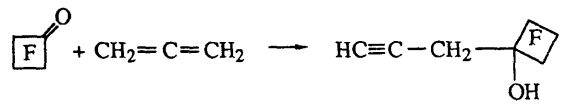
As mentioned above, $SnCl_4$ changes the course of the reaction of MTFP with isoprene in such a way that a 4:1 mixture of ene and Diels–Alder adducts is formed.[15]



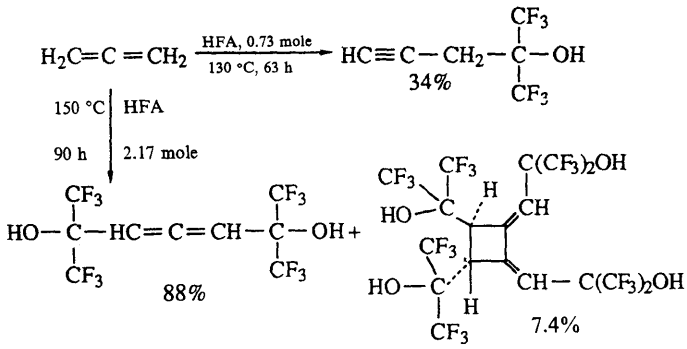

Similar results have been obtained previously for the reactions of chloral and *n*-butyl glyoxylate with isoprene and 2,3-dimethyl-1,3-butadiene.[96]

### 3. Ene reactions of polyfluoroketones with 1,2-dienes

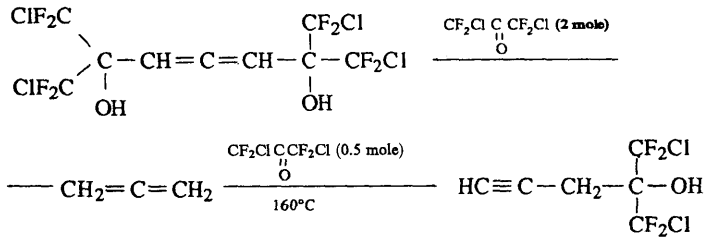
By analogy with the ene reactions considered above,[68] polyfluoroketones might be expected to form ene adducts with 1,2-dienes by a similar step-wise mechanism, taking into account the geometrical constraints of the reacting molecules. However, studies of isotopic effects on the reaction of perfluorocyclobutanone with allene[97,98] have shown clearly that the rate-limiting stage is consistent with a concerted mechanism involving a non-linear and asymmetric transfer of hydrogen. In fact, this reaction leads to an ene adduct (47% yield) even at 20 °C.[10]



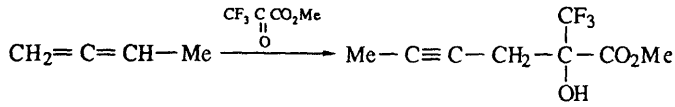

The reactions of allene with other polyfluoroketones can only be achieved on heating. Thus, heating HFA with allene at 130 °C affords an ene adduct (34% yield), which is almost completely transformed at 150 °C to a 2:1 adduct in the presence of an excess of HFA.[68]




Similarly, 1,3-dichlorotetrafluoroacetone interacts with allene at 160 °C to give 1:1 and 2:1 adducts depending on the proportion of the reactants.[99]

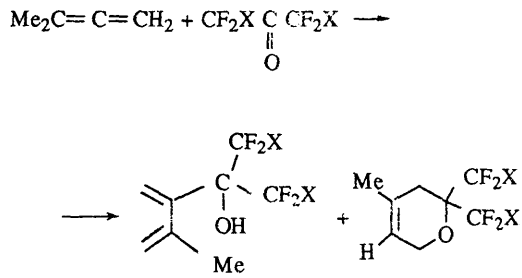



The ene reaction of MTFP with 1,2-butadiene proceeds under milder conditions (80 °C).[72]



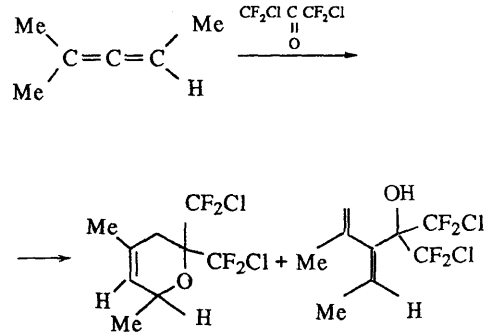

In the presence of polyfluoroketones, 3-methyl-1,2-butadiene and tri- and tetra-methylallene partly or completely isomerise into the corresponding 1,3-diene even at 20 °C. As a consequence, either Diels–Alder adducts or mixtures containing the latter and ene adducts are formed.[17,19]

Thus interaction of HFA or 1,3-dichlorotetrafluoroacetone with 3-methyl-1,2-butadiene at 175 °C affords a mixture of the corresponding hydroxy-1,3-diene and dihydropyran. Reaction is slow at 20 °C, but proceeds rapidly on heating.



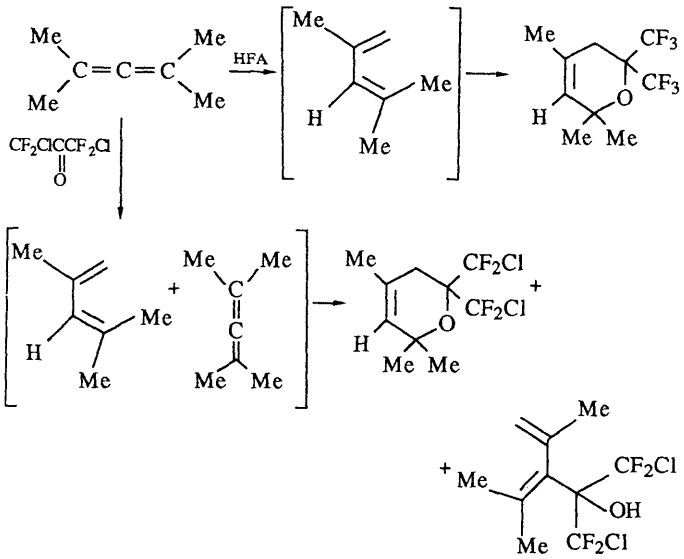

X = F or Cl.

The reason between trimethylallene and 1,3-dichlorotetrafluoroacetone affords the corresponding dihydropyran as the main product (56%) together with a 13% yield of an ene adduct.




Tetramethylallene isomerises completely in the presence of HFA at 20 °C to give 2,4-dimethyl-1,3-pentadiene which, under these conditions, readily undergoes diene synthesis. The isomerisation

proceeds more slowly in the presence of 1,3-dichlorotetrafluoroacetone to give both [4 + 2]-adduct and ene adduct (6%).

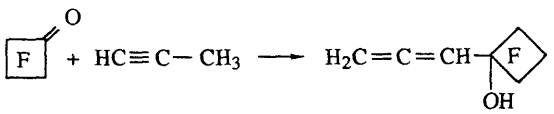


An unsuccessful attempt was made to minimise prototropic rearrangement of polymethyl-substituted allenes to conjugated dienes by carrying out the reaction in the gas phase at 100 °C.[19]

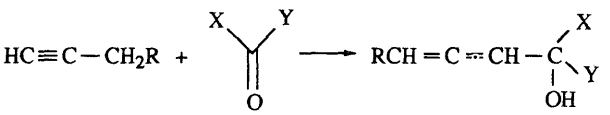
### 4. Ene reactions of polyfluoroketones with alkynes

Classical enophiles normally do not react with terminal alkynes as readily as they do with alkenes.[55] However, polyfluoroketones are an exception, reacting equally well with both alkynes and alkenes.

Thus, even at 20 °C, perfluorocyclobutanone reacts with propyne to give the corresponding allenealcohol in 43% yield.[10]

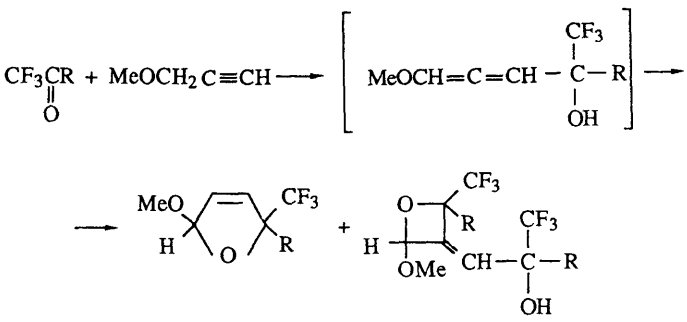


Allenealcohols are obtained similarly from the reaction of HFA with propyne,[99] from the reaction of MTFP with propyne and with 1-hexyne,[72] and from the reaction of 1,3-dichlorotetrafluoroacetone with propyne, 1-pentyne, or 1-undecyne at 50–100 °C. Ene adducts are also formed on interaction of 1,3-dichlorotetrafluoroacetone with propargyl chloride (140 °C),[99] and on interaction of MTFP with propargyl bromide (110 °C).[72]



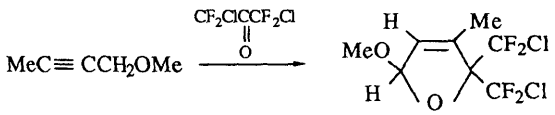
R = H, Et, $Pr^n$, n-$C_9H_{19}$, Cl, Br;
X = Y = $CF_3$, $CF_2Cl$, X = $CF_3$, Y = $CO_2Me$.

A mixture of dihydrofuran and oxetane derivatives was obtained on reaction of HFA, nitropentafluoroacetone or MTFP with methyl propargyl ether.[72,100] It is thought that an initial ene reaction affords the corresponding allenealcohol, which then undergoes cycloisomerisation or participates in [2 + 2]-cycloaddition with a second molecule of the ketone.

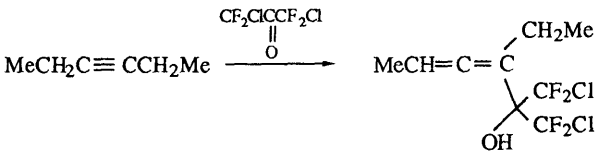


R = $CF_3$, $CF_2NO_2$, $CO_2Me$.

In the patent literature, it is reported that only dihydrofuran derivatives are formed on reaction of 1,3-dichlorotetrafluoroacetone with methyl propargyl ether and on reaction of HFA with ethyl propargyl ether.[101] The interaction of but-2-yn-1-yl methyl ether with 1,3-dichlorotetrafluoroacetone also affords the corresponding dihydrofuran exclusively.[101]



There are also references to ene reactions involving an internal alkyne. Thus, dichlorotetrafluoroacetone reacts with 3-hexyne during 20 h at 170 °C to give the expected allenealcohol.[99]



## IV. [2 + 2]-Addition

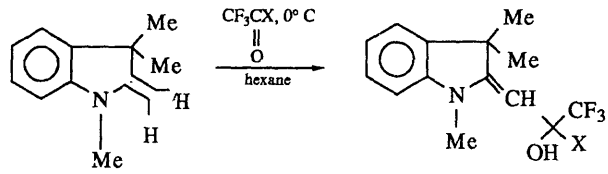
As has been mentioned previously (p. 786), it is the unusual electronic state of the C=O bond in polyfluoroketones which is responsible for their high reactivity with isolated, highly-polarised, electron-rich multiple bonds. As a consequence, several types of conversion are possible, the predominant ones being: [2 + 2]-cycloaddition; [2 + 2]-cycloaddition with subsequent ring opening or [2 + 2]-retroscission; and coupling to give an intermediate 1,4-dipolar zwitter-ion, stabilised by prototropic rearrangement or cycloaddition to the polyfluoroketone molecule. Furthermore, in certain instances, such reaction pathways are also possible with weakly polar and even polarised electron-deficient unsaturated compounds. Thus, the chemistry of [2 + 2]-addition with polyfluoroketones is far more extensive than with other 1,2-dipolarophiles.

All of the above-mentioned reaction types can be readily explained, in qualitative terms, by a step-wise [2 + 2]-addition which is consistent with molecular orbital calculations.[102–105] However, certain [2 + 2]-additions with polyfluoroketones may be interpreted in terms of a pericyclic pathway, the likelihood of which may be ascertained by the perturbation method.[106,107]

## 1. [2 + 2]-Addition across the C=C bond

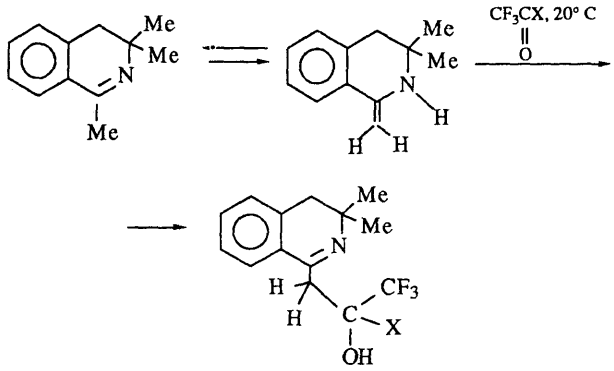
Enamines, ketene acetals, vinyl ethers, and ketenes are all highly reactive towards polyfluoroketones in [2 + 2]-addition. In certain instances, styrene and α,β-unsaturated carbonyl compounds also participate in this reaction.

Enamines interact the most smoothly with classical 1,2-dipolarophiles. Since the atom of nitrogen in the transition state is stabilised by an adjacent cationic centre, such reactions normally proceed via prototropic rearrangement of an intermediate zwitter-ion. This has been established for the reactions of HFA and MTFP with 2-methylene-1,3,3-trimethylindoline at 0 °C.[108]



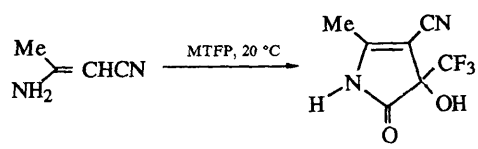

X = $CF_3$, $CO_2Me$.

Similarly, HFA and MTFP interact at 20 °C with the enamine form of 3,4-dihydro-1,3,3-trimethylisoquinoline.[109]

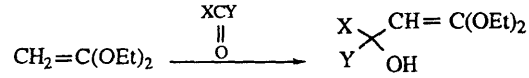



X = $CF_3$, $CO_2Me$.

MTFP reacts with 3-aminocrotononitrile in acetonitrile at 20 °C. The ketone initially interacts across the multiple bond, after which intramolecular ring closure takes place to give a lactam in 68% yield.[110]

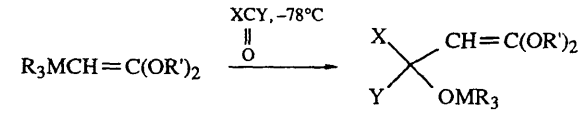



Ketene acetals react energetically with nitropentafluoroacetone, HFA and 1,1,3-trifluoro-1,3,3-trichloroacetone. However, no oxetanes were formed. Instead, reaction takes place at −30 to 20 °C to give the corresponding allylic tertiary alcohols.[111,112]



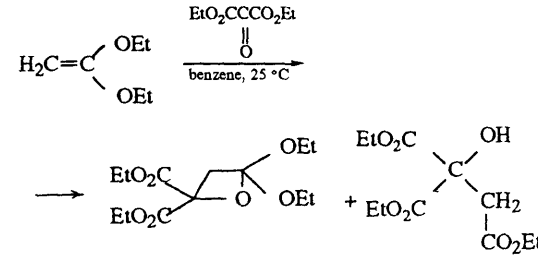

X = Y = $CF_3$; X = $CF_3$, Y = $CF_2NO_2$; X = $CF_2Cl$, Y = $CFCl_2$.

Acyclic products are also formed on reaction of silyl- and germylketene acetals with HFA, 1,3-dichlorotetrafluoroacetone and 1,1,3-trifluoro-1,3,3-trichloroacetone.[112,113]

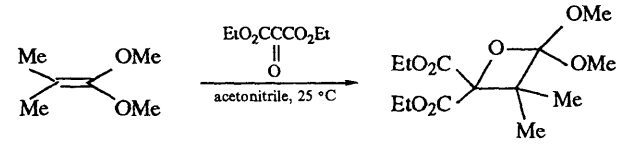



$MR_3$ = $Me_3Si$, $MeCl_2Ge$; X = Y = $CF_3$, $CF_2Cl$;
X = $CF_2Cl$, Y = $CFCl_2$; R' = Me, Et.

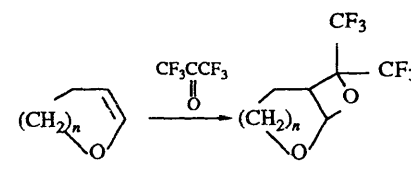
In a spectroscopic study of reactions of polyfluoroketones with 2-trimethylsilylketene acetals at −78 °C, it was shown that the initial product is the corresponding oxetane which is cleaved on raising the temperature. It is worth noting that interaction of DEOM with diethyl keteneacetal in benzene affords a mixture of the corresponding oxetane (58%) and a trace of an acyclic product.[114]




In the highly polar acetonitrile as solvent, this reaction gives a mixture of four products, none of which is the corresponding oxetane. However, the interaction of DEOM with 1,1-dimethoxy-2-methylpropene affords an oxetane exclusively, even in acetonitrile.[114]

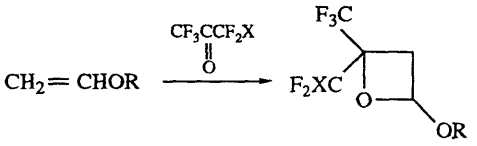



Stable oxetanes have been obtained by reaction of polyfluoroketones with a variety of vinyl ethers.[115–121] The most active of these is 2,3-dihydrofuran which yields a stable [2 + 2]-cycloadduct with HFA at −20 °C in 57% yield. With 3,4-dihydro-2*H*-pyran, however, such cycloaddition requires a higher temperature (50–60 °C).[121]



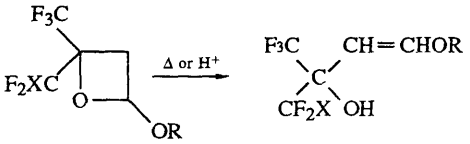

*n* = 1, 2

Alkyl vinyl ethers react with HFA more slowly at −20 °C. However, a preparative yield of oxetane derivatives is obtainable with HFA and nitropentafluoroacetone at 20 °C in dimethyl sulphate.[115]



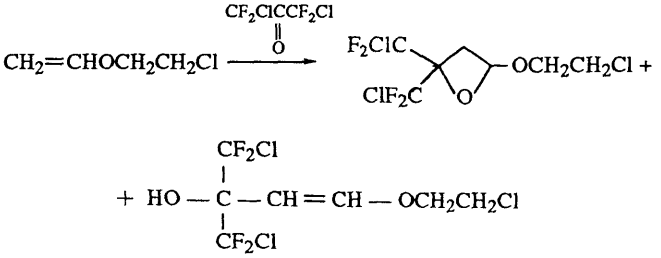
X = F, $NO_2$; R = Et, $Bu^n$.

Ring opening of the products takes place slowly at 100 °C, but noticeably faster in the presence of $H_2SO_4$.

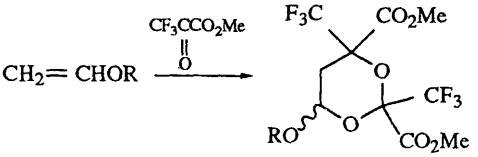


X = F, $NO_2$; R = Et, $Bu^n$.

In certain instances, e.g. on reaction of 1,3-dichlorotetrafluoroacetone with 2-chloroethyl vinyl ether, isomerisation of the oxetane takes place during the reaction.[116]

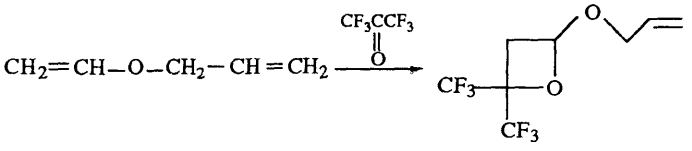


Contrasting with HFA, MTFP reacts with alkyl vinyl ethers in polar media to give products derived by 1,4-dipolar cycloaddition to an initially-formed zwitter-ion.[110] The course of the reaction is not affected by the proportion of the reactants.



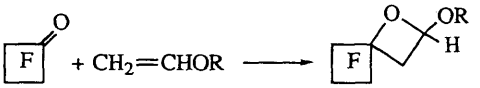
R = Et, $Bu^n$.

An interesting result was reported on studying the reaction of HFA with allyl vinyl ether.[120] Here, the sole product at 0 °C is an oxetane derivative, formed by exclusive attack of the vinylic unsaturation.



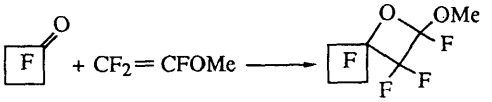
In such instances, polyfluoroketones undergo [2 + 2]-cycloaddition far more smoothly than ene reaction. Evidently, more information is required in order to elucidate the structures of the 2:1 and 3:1 adducts obtained on ene reaction of HFA and nitropentafluoroacetone with methyl allyl ether[64] and on reaction of *N*-methyl-*N*-allylaniline with HFA.[70]

Vinyl esters only participate in [2 + 2]-cycloaddition with perfluorocyclobutanone.[119] Thus, reaction with vinyl acetate and benzoate at 20 °C affords the corresponding oxetane in 54 and 45% yield, respectively.

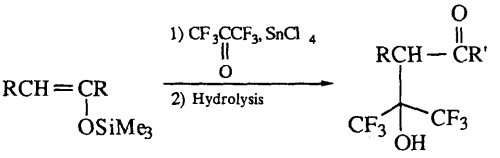


R = COMe, COPh.

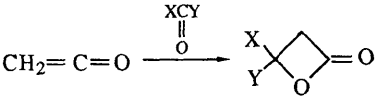
Perfluorocyclobutanone reacts similarly with methyl trifluorovinyl ether.[10]



A study has been made of the catalytic effect of Lewis acids on the reaction of HFA with trimethylsilyl enolethers. Reaction takes place at −45 °C in the presence of $SnCl_4$ or $TiCl_4$. The corresponding ketones were isolated on hydrolysis of the reaction mixture.[25]

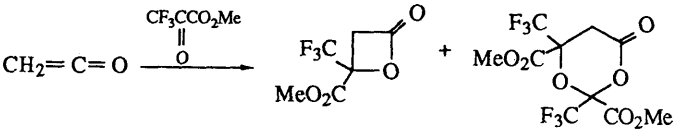


Contrasting with ketene acetals, ketenes form stable [2 + 2]-cycloadducts with polyfluoroketones. Thus 2-oxetanones are obtained in preparative yield by reaction of ketene itself with perfluorocyclobutanone,[119] nitropentafluoroacetone,[122] HFA [123] and with 1,3-dichlorotetrafluoroacetone.[124]

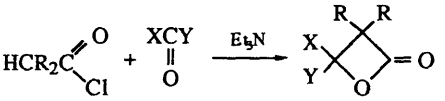


X = Y = −$(CF_2)_3$−, $CF_3$, $CF_2Cl$; X = $CF_3$, Y = $CF_2NO_2$.

A mixture of 2-oxetanone and 1,3-dioxan-4-one derivatives was obtained on passing ketene into a solution of MTFP in ether.[125]

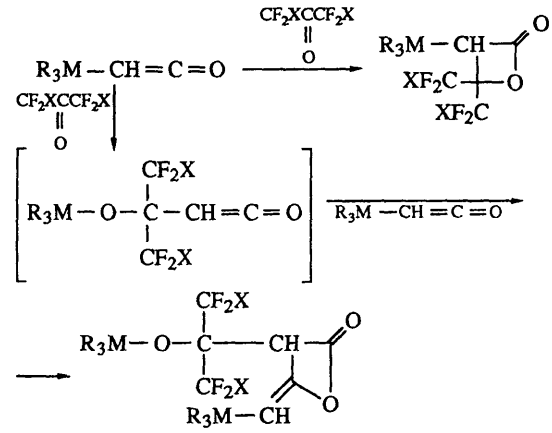


The isolation of 2-oxetanones on reaction of 1,1,3-trifluoro-1,3,3-trichloroacetone and MTFP with acetyl chloride[126] and dichloroacetyl chloride,[110] respectively, confirmed that ketenes are formed *in situ* [in the presence of base].



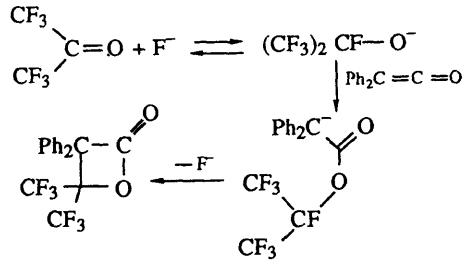
R = H, X = $CF_2Cl$, Y = $CFCl_2$; R = Cl, X = $CF_3$, Y = $CO_2Me$.

Silyl-, germyl- and stannyl-ketenes also interact with HFA and 1,3-dichlorotetrafluoroacetone to give 2-oxetanones.[127] An ionic [2 + 2]-addition takes place simultaneously to give an intermediate ketene which reacts with a second molecule of the starting ketene to give a 4-ene-2-oxetanone as by-product.

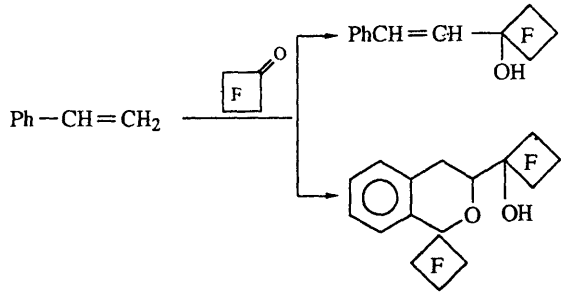


X = F, Cl; $R_3M$ = $SiMe_3$, $GeCl_2Me$, $SnBu^n_3$.

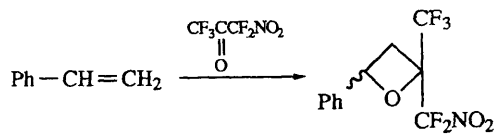
The steric effect of the phenyl groups in diphenylketene prevents reaction with HFA even at 100 °C. However, a 2-oxetanone derivative is obtained in preparative yield under nucleophilic catalysis.[128]



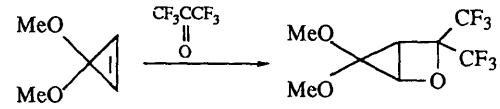
Only the most electrophilic polyfluoroketones react with weakly polarised alkenes. Thus, interaction of perfluorocyclobutanone with styrene at 20 °C yields an ionic [2 + 2]-adduct,[11] while an isochroman is formed in the presence of an excess of the ketone.



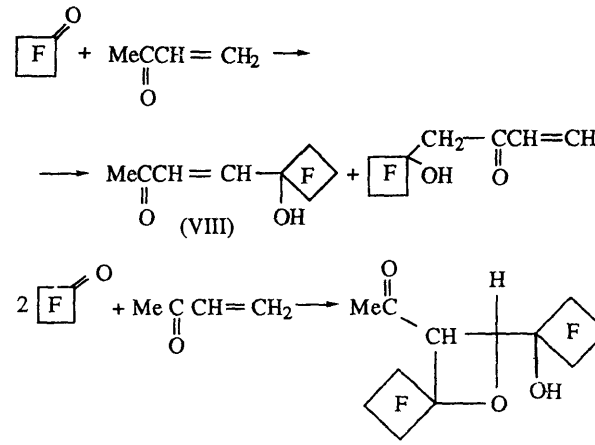
Heating a mixture of nitropentafluoroacetone and styrene at 100 °C for 10 h affords the corresponding oxetane in 37% yield.[129]



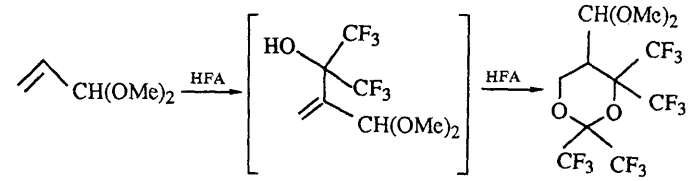
Under similar conditions, HFA initiates polymeristion of the alkene.[65] However, a [2 + 2]-cycloadduct is formed with the strained dimethyl ketal of cyclopropenone at 20 °C.[130]



Electron deficient α,β-unsaturated aldehydes, ketones, esters and nitriles react with polyfluoroketones under forcing conditions in the presence of a catalyst. Thus, treatment of methyl vinyl ketone with perfluorocyclobutanone at 100 °C affords a mixture of compounds, among which a ketol and the anomalous [2 + 2]-adduct (VIII) have been identified. An oxetane is obtained, however, in the presence of an excess of perfluorocyclobutanone. This has been shown to arise by cycloaddition of intermediate (VIII) with a second molecule of the ketone.[11]

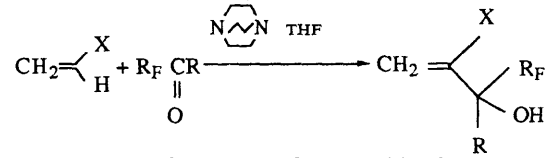


Reaction of acrolein dimethyl acetal with HFA at 150 °C produces a 1,3-dioxane (9%), which is thought to arise by the scheme shown below.[131]



The initial [2 + 2]-addition takes place in accordance with the polarisation of the C=C bond.

The same polarisation factors are at play in the reactions of HFA, MTFP, 1,3-dichlorotetrafluoroacetone and bromopentafluoroacetone with methyl acrylate, acrylonitrile, and acrolein in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO).[132]

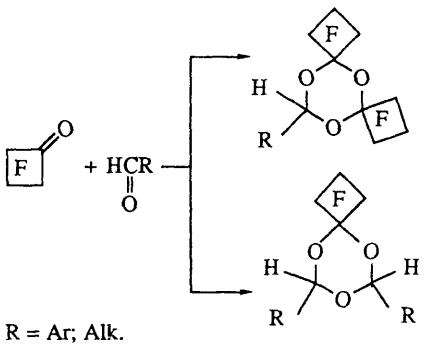


R = $R_F$ = $CF_3$, $CF_2Cl$; $R_F$ = $CF_3$, R = $CO_2Me$;
$R_F$ = $CF_3$, R = $CF_2Br$; X = $CO_2Et$, CN, CHO, COMe.

Among non-fluorinated carbonyl compounds, only DEOM participates readily in this conversion (known as the Baylis–Hillman reaction).[133] The addition of aliphatic and aromatic aldehydes requires more forcing conditions.[134] The mechanism of the Baylis–Hillman reaction involves addition of DABCO at the β-position of the α,β-unsaturated system, followed by interaction of the carbonyl compound with the generated anionic centre at the adjacent α-site.[135]

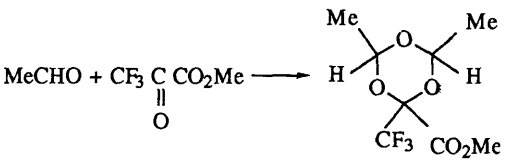
## 2. [2 + 2]-Addition across hetero-unsaturations, C=Y and X=Y

Polyfluoroketones interact with aliphatic and aromatic carbonyl compounds at room temperature or below. A zwitter-ion is formed initially, this being stabilised by 1,4-dipolar addition either to a second molecule of the polyfluoroketone or to the non-fluorinated component to give the corresponding 1,3,5-trixane. Thus, perfluorocyclobutanone reacts with aromatic aldehydes and certain ketones to give predominantly a 2:1 cycloadduct; a 1:2-cycloadduct, however, is formed with aliphatic aldehydes.[136]



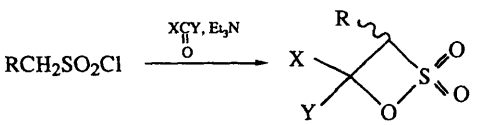
R = Ar; Alk.

Acetaldehyde interacts with MTFP at 20 °C to give a 1:2 cycloadduct exclusively.[110]



In the reactions of polyfluoroketones with aliphatic aldehydes, stable aldols are formed as by-products. The proportion of the latter increases with the length of the aliphatic chain. Enolisable ketones afford predominantly stable ketols with perfluorocyclobutanone,[11] while ketols are formed exclusively with HFA and MTFP.[137–140] The former initiates polymerisation of an acetone/formaldehyde mixture even at −78 °C.[141]

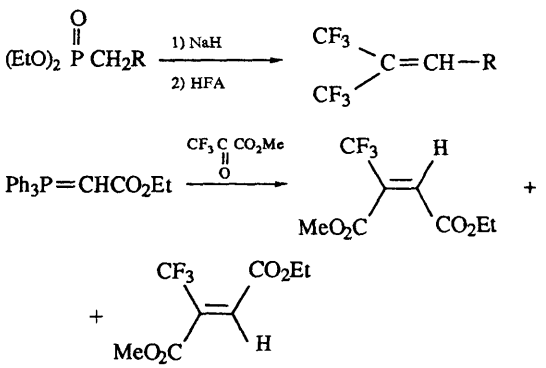
Chloropentafluoroacetone, 1,3-dichlorotetrafluoroacetone and MTFP yield β-sultones on reaction with sulphenes, generated *in situ* by treatment of the corresponding alkanesulphonyl chlorides with $Et_3N$ at 20 °C.[110,142–145]



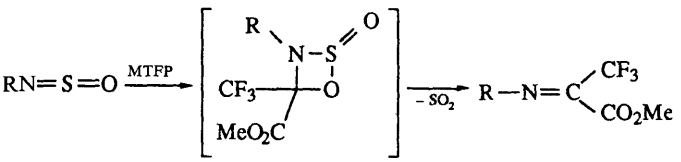
R = H, Cl; X = Y = $CF_2Cl$; R = H, X = $CF_3$, Y = $CF_2Cl$; R = H, X = $CF_3$, Y = $CO_2Me$.

A complex mixture of products was obtained with HFA, primarily because this ketone serves as a powerful dehydrogenating agent towards $Et_3N$.[146,147]

Witt's survey[8] provides extensive data on the reactions of HFA with unsaturated elementoorganic and organometallic compounds. Recently, new information on the use of polyfluoroketones in the Wittig and Horner–Emmons reactions has been made available.[148–150]



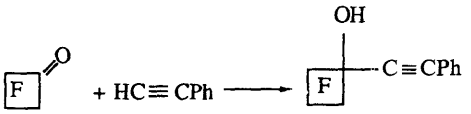
[2 + 2]-Cycloaddition-cycloreversion of polyfluoroketones with isocyanates and thionylimines has already been reviewed in the context of perfluoroketimine chemistry.[43,45] It is worth noting that, contrasting with HFA,[151] MTFP reacts with thionylimines in the absence of catalyst on warming.[152]



R = Ph, COPh, COMe.

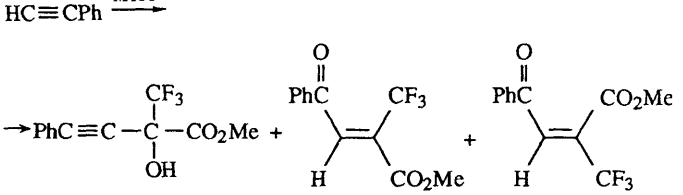
## 3. Addition across the C≡C bond

Terminal alkynes lacking a propargylic hydrogen atom react with polyfluoroketones to give either Favorskii products (tertiary acetylenealcohols) or [2 + 2]-cycloadducts (oxetenes), electrocyclic ring opening of which leads to α,β-unsaturated carbonyl compounds. For example, phenylacetylene reacts with perfluorocyclobutanone to give exclusively an acetylenealcohol even at 0 °C.[11]



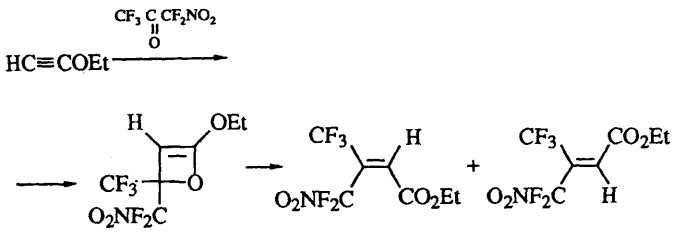
It should be noted that non-fluorinated ketones only participate in the Favorskii reaction in the presence of a strong base.[153]

Phenylacetylene reacts slowly at 20 °C with MTFP, or rapidly above 60 °C, to give a mixture of the corresponding acetylenealcohol and methyl α-trifluoromethyl-β-benzoylacrylate (as a mixture of *Z*- and *E*-isomers).[110]

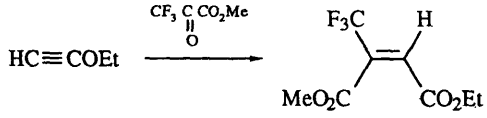


The products of this reaction were isolated pure and shown to be formed in kinetically independent pathways, i.e. no interconversions involving these products were observed, even under forcing conditions.

The reactions of ethoxyacetylene with HFA [154] and nitropentafluoroacetone[111] below room temperature lead to oxetenes, which rearrange at 20 °C to give substituted acrylates. A mixture of *Z*- and *E*-isomers was obtained from nitropentafluoroacetone.

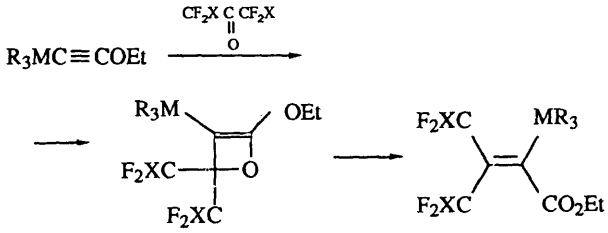


Ethoxyacetylene interacts with MTFP to give a trifluoromethylmaleic acid diester exclusively.[110]



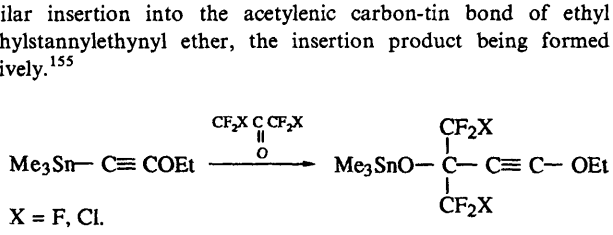
There was no intermediate formation of an extreme derivative under these conditions (20 °C).

Relatively stable oxetenes have been obtained by reaction of polyfluoroketones with trimethylsilyl and trimethylgermyl derivatives of ethoxyacetylene.[155] The resulting trimethylsilyloxete derivatives are converted to the corresponding acrylate at 20 °C over a period of 2 months or at 100 °C during 30 min.



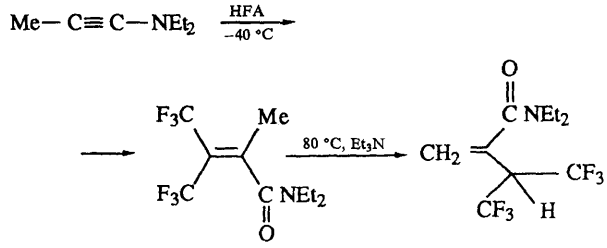
X = F, Cl; $MR_3$ = $SiMe_3$, $GeMe_3$, $SiEt_3$, $GeEt_3$.

Germyl-substituted acetylenealcohols are obtained as by-products on reaction of polyfluoroketones with ethyl trimethylgermylethynyl ether, i.e. the polyfluoroketones are inserted into the acetylenic carbon-germanium bond. 1,3-Dichlorotetrafluoroacetone undergoes a similar insertion into the acetylenic carbon-tin bond of ethyl trimethylstannylethynyl ether, the insertion product being formed exclusively.[155]



X = F, Cl.

1-Diethylaminoprop-1-yne reacts with HFA even at −40 °C to give an acrylamide derivative by ring opening of an intermediate oxetene. On heating in the presence of $Et_3N$, the product undergoes prototropic rearrangement to give α-(hexafluoroisopropyl)acrylic acid *N*,*N*-diethylamide.[156]



It was not possible to characterise the intermediate oxetene. Although there is a propargylic hydrogen atom in the starting ynamine, no simultaneous ene reaction was detected, i.e. the [2 + 2]-pathway is exclusive.

Polyfluoroketones (especially HFA) are seen as highly electrophilic ketones, which interact energetically with water, alcohols and amines to give stable hydrates, hemiketals and hemiaminals, respectively. This behaviour is typical of highly electrophilic carbonyl compounds. In fact, they are akin to certain aldehydes (formaldehyde, chloral, fluoral) and ketones with electron-accepting substituents (mesoxalates and certain 1,2-di- and 1,2,3-triketones, etc.).

***

The present review covers one particular aspect of the chemistry of polyfluoroketones—their unusually high affinity towards conjugated and unconjugated donor-type π-systems, with which they undergo uncatalysed [4 + 2]-cycloaddition, ene reaction and [2 + 2]-addition below or at room temperature. Non-fluorinated aliphatic ketones either do not participate in these reactions or do so only under forcing conditions. Even highly electrophilic, non-fluorinated ketones require heating (above 100 °C) or catalytic acitvation.

Recently, it has been shown that reactions of polyfluoroketones with unsaturated compounds are highly selective under certain circumstances. They may proceed regiospecifically with characteristically high stereoselectivity, in certain instances yielding only one stereoisomer. There is much to be gained by further studies in this area, notably with a view to designing effective routes to functionalised unsaturated compounds.

From a comparison of the reactivity of HFA, MTFP and DEOM towards unsaturated compounds, it is apparent that the characteristic properties of polyfluoroketones are a consequence of the lower level of their acceptor LUMO and its significantly higher asymmetry. The structure of the LUMO of polyfluoroketones is itself determined by interactive effects between the carbonyl oxygen atom and the $CF_3$ group. Thus, replacement of one of the carbalkoxy groups of DEOM by a $CF_3$ group leads to a qualitatively different electronic state for the C=O bond.

The anomalous electronic state of the C=O group in polyfluoroketones is responsible for the large contribution made by charged structures in the stabilisation of the transition state on reaction with unsaturated compounds. This determines the high affinity of polyfluoroketones towards polarised unsaturated compounds of a donor type. Among the many reactions discussed in this article, a number of charge-induced processes are particularly interesting from a theoretical standpoint; these proceed exothermically or with a low energy barrier, and differ in their regiospecificity and high stereoselectivity.

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