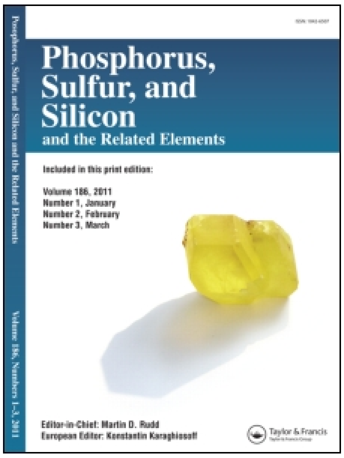

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FLUOROPHOSPHAALKENES-PREPARATION AND REACTIVITY

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FLUOROPHOSPHAALKENES—PREPARATION AND REACTIVITY[‡§]

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A novel preparative route to perfluoroheteroalkenes $F_3CE{=}CF_2$ (E = P, As) and $E'{=}CF_2$ (E′ = S, Se) has been developed using the trimethyltin compounds $Me_2SnE(CF_3)_2$ and $Me_3SnE'CF_3$ as precursors. After a short information about the characterization of these heteroalkenes, the results of self-addition, HX-additon and [2 + 4] cycloaddition reactions of $F_3CP{=}CF_2$ (**1**) [and in part of $F_3CAs{=}CF_2$ (**2**)] are presented and discussed. A one-pot procedure could be developed for the Diels-Alder type reactions of **1** and **2**, keeping a mixture of $Me_3SnE(CF_3)_2$ and the corresponding diene at 70°C until the ^{19}F signals of the tin compound disappeared. The enthalpy of dissociation of the dimer $(CF_3PCF_2)_2$ as well as that of the retrodiene cleavage of the [2 + 4] cycloadduct, formed from **1** and cyclopentadiene, are deduced from appearance potentials and used for an estimate of the PC σ- and π-bond energy of **1**. A one-pot process for the production of the labile diphosphene $F_3P{=}PCF_3$ (**23**) and its trapping by dienes are reported. The observed reactivity of **1** and **23** support the view that these compounds show a remarkable similarity to alkenes.

INTRODUCTION

Phosphorus carbon (p–p)π compounds show a surprising similarity to alkenes.[2] The proof of this relationship faces some difficulties, because most of the known phosphaalkenes are kinetically stabilized by bulky substituents. Therefore, their low reactivity is not due to the genuine properties of the PC double bond, but to steric hindrance. This is particularly valid for [2 + 4] cycloaddition reactions.[3] Some successful experiments with heterosubstituted phosphaalkenes, reported on in literature[4] demonstrate the importance of substituent effects. This result led us to the investigation of the dienophilic properties of the perfluorophosphaalkene $F_3CP{=}CF_2$ (**1**) in some detail. Because of the so-called perfluoro effect,[5] a comparatively high stability of the P=C system together with a pronounced dienophilicity of **1** can be expected. Prerequisite to a systematic study is a reliable preparative route to **1**. This short review reports on a new method of preparation for and reactivity studies with **1** concentrating on Diels-Alder type reactions. Table I gives a rough survey of the historical development of the chemistry of $F_3CP{=}CF_2$.

PREPARATION AND PROPERTIES OF 1

The various reactions listed in Table I are not very well suited for the preparation of pure **1**, because it is usually formed together with other volatile products, or is

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[‡] This is a slightly expanded version of a lecture first presented at the 4th International Symposium on Inorganic Ring Systems in the University of Paris-Sud on 4th September 1985.

[§] Part VIII of the series "Reactive E=C (p-p)π Systems".[1]

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TABLE I

Literature information on $F_3CP{=}CF_2$ (**1**)

Year	Information	Lit.
1965	Reaction of $(CF_3)_2PH$ with MeOH in the presence of MeONa: Main product $F_3CP(OMe)CF_2H$. Postulate of **1** as reactive intermediate.	6
1968-1973	Preparation of $Me_3M'E(CF_3)_2$ (E = P, As); decomposition at moderate temperature to give $Me_3M'F$ and $(CF_3ECF_2)_x$ via **1**.	7-9
1972	Reaction of $(CF_3)_2PH$ with $ZnMe_2$ yielding the trans-dimer of **1** (KANG-Reaction)	10
1976	Base reaction of $(CF_3)_nPH_{3-n}$ to produce the unsaturated species **1**, $HP{=}CF_2$ and $P{\equiv}CF$. Spectroscopic studies (NMR, microwave).	11
1981-1984	Studies of KANG and base reactions producing **1** and its dimers and trimers	10,12

contaminated with the starting phosphane $(CF_3)_2PH$. There was a good chance of improvement, however, in a renewed study of the decomposition of silyl, germyl and stannyl derivatives of trifluoromethylphosphanes and arsanes of the type $Me_3M'E(CF_3)_2$ (M' = Si, Ge, Sn; E = P, As),[7-9] which undergo slow thermolysis at moderate temperatures to give $Me_3M'F$ and oily oligo- and polymers according to equation (1):

$$Me_3M'E(CF_3)_2 \rightarrow Me_3M'F + \{F_3CE{=}CF_2\} \rightarrow \frac{1}{x}(F_3CECF_2)_x \qquad (1)$$

Remembering these results of the early 70s, we came to the conclusion that the trimethyltin compound $Me_3SnP(CF_3)_2$ would be the best precusor for the preparation of pure **1**, since Me_3SnF is known to form solid polyadducts. Therefore, separation problems are minimized for this system. So we developed a simple thermolysis procedure according to equation (2) to produce **1** in mmol amounts and almost quantitative yield.

$$Me_3SnP(CF_3)_2 \xrightarrow[10^{-3}\text{ torr}]{300\text{-}340°C} \underset{\mathbf{1}}{F_3CP{=}CF_2} + Me_3SnF \qquad (2)$$

The apparatus used for this reaction is shown in Figure 1. The phosphaalkene formed at 10^{-3} torr is quenched from the gas phase at −196°C. Unreacted $Me_3SnP(CF_3)_2$ is repeatedly fed through the hot zone until the conversion into **1** is complete.[13]

In the meantime, the new method proved to be a quite general way to fluorinated E=C (p—p)π compounds as demonstrated by the examples $F_3CAs{=}CF_2$ (**2**), $C_2F_5P{=}C(F)CF_3$ (**3**), $S{=}CF_2$ (**4**), $Se{=}CF_2$ (**5**) and $Me_3SnP{=}CF_2$ (**6**).

The kinetic stability observed for **1** in a dilute gas or liquid phase is surprising: thus, in ca. 10% toluene or pentane solutions the dimer is first detectable after about 10 hr, even at 25°C. Therefore, handling in vacuum lines and reactivity studies in organic solvents are possible under ordinary conditions.

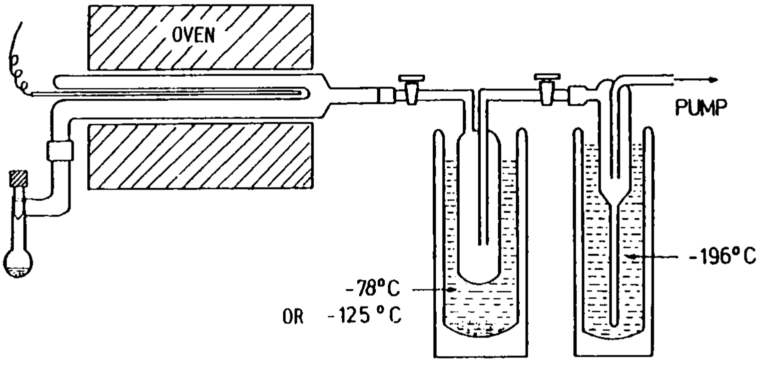


FIGURE 1 Pyrolysis apparatus for the preparation of $CF_3P{=}CF_2$ (**1**).

TABLE II

Intensities (%) and appearance potentials for the molecular ions M^+ of several heteroalkenes and their dimers.

No.	Compound	M^+	%	AP (eV)
1	$CF_3P{=}CF_2$	150	8.9	8.8
2	$CF_3As{=}CF_2$	194	1.4	8.5
4	$S{=}CF_2$	82	100.0	10.3
5	$SeCF_2$	130	81.3	9.4
6	$(F_3CPCF_2)_2$	300	0.3	8.3
7	$(F_3CAsCF_2)_2$	388	29.2	—

On this basis, the spectroscopic data of **1**, as reported by Nixon[11] and Burg,[12] could be confirmed and completed. A thorough mass spectroscopic study of **1** and several other E=C compounds including the dimers $(F_3CECF_2)_2$ (E = P, As) was performed.[14] The determination of appearance potentials (AP) for molecular and characteristic fragment ions allowed the calculation of a reasonable value of 36.9 kcal/mol for the enthalpy of dissociation of the phosphaalkene dimer $(F_3CPCF_2)_2$ from a thermochemical cycle. The results of the AP measurements, summarized in Table II, support the unsaturated character of the compounds.

An electron-diffraction study by Oberhammer[15] confirms the structure of **1** in the gas phase and the presence of a double bond by a PC distance of 1.686 Å. In all investigations carried out so far, ^{19}F-NMR data proved to be of particular value for the characterization of **1** and its derivatives. This is demonstrated in Figure 2 by the ^{31}P- and ^{19}F-NMR spectra of **1**. The difference $\Delta\delta_F$ observed for the chemical shifts of the nonequivalent fluorine atoms of the CF_2 group amounts to about 33 ppm, a value indicative of the position of the F nuclei with respect to the CF_3 substituent or the phosphorus lone pair. Following the assignment of coupling constants by Becker et al.,[16] we attribute the high field signal to the F atom cis and the low field resonance to the F atom trans to the CF_3 group. Table III shows that similar $\Delta\delta_F$

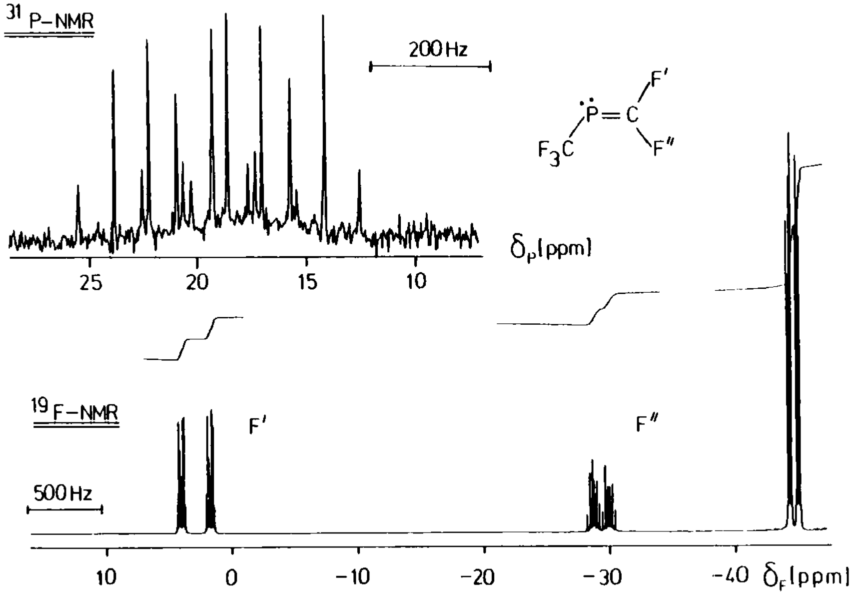


FIGURE 2 ^{31}P- and ^{19}F-NMR spectra of **1**.

TABLE III

Characteristic ^{19}F and ^{31}P-NMR-Data of Fluorophosphaalkenes $F_3CP{=}C(X)F$

Compound No.	X	δ_F	$\Delta\delta_F$	$^2J_{(PF)}$	δ_P	Assignment
1	F_a	2.9	–	192	20.0	F_a trans to CF_3
	F_b	–29.9	32.8	103		F_b cis to CF_3
8	NMe_2	–31.0	–	149	–9.0	Z (100%)
9	NEt_2	–34.1	–	148	–9.9	Z (100%)
10a	OMe	0.7	–	171	5.0	E (97%)
10b	OMe	–33.4	34.1	158		Z (3%)
11a	OEt	1.4	–	173	2.7	E (95%)
11b	OEt	–32.0	33.4	165		Z (5%)

values are obtained for the CF resonance of the E and Z isomers of phosphaalkene derivatives $F_3CP{=}C(F)X$.

In addition to the NMR data briefly discussed above, a photoelectron spectroscopic study on several fluorophosphaalkenes is underway at present in cooperation with Prof. R. Gleiter.[17]

REACTIVITY STUDIES

The isolation of the pure phosphaalkene **1** in preparative amounts offered the possibility of a systematic investigation of its reactivity. Of particular interest are reactions which can prove or disprove the assumed relationship to alkene chemistry.

Therefore we concentrated on three typical reactions:

(a) The self-addition giving dimers and trimers of **1**,
(b) the addition of proton acidic compounds HX, and
(c) the [2 + 4] cycloaddition, as a proof of the dienophilic properties of **1**.

(a) Self-addition Reaction

Concerning the self-addition of the monomer, our results confirm a report published by Burg[12] according to which the trans head-to-tail dimer **6a** is the main product if **1** is passed through a U-tube cooled to $-78°C$ at 10^{-3} torr. However, the cis isomer **6b** and the head-to-head trans dimer **6c** are formed, too, along with small amounts of trimeric species. The thawing of the monomer in the condensed phase from $-196°C$ to room temperature leads to polymers $(F_3CPCF_2)_x$. The rate of the [2 + 2] cycloaddition reaction of the perfluoroheteroalkenes $F_3CE{=}CF_2$ (E = P, As) and $E'{=}CF_2$ (E' = S, Se) strongly depends on the heteroatoms: As ≫ P; Se > S. In the case of the phosphorus and arsenic compounds this difference gives rise to divers

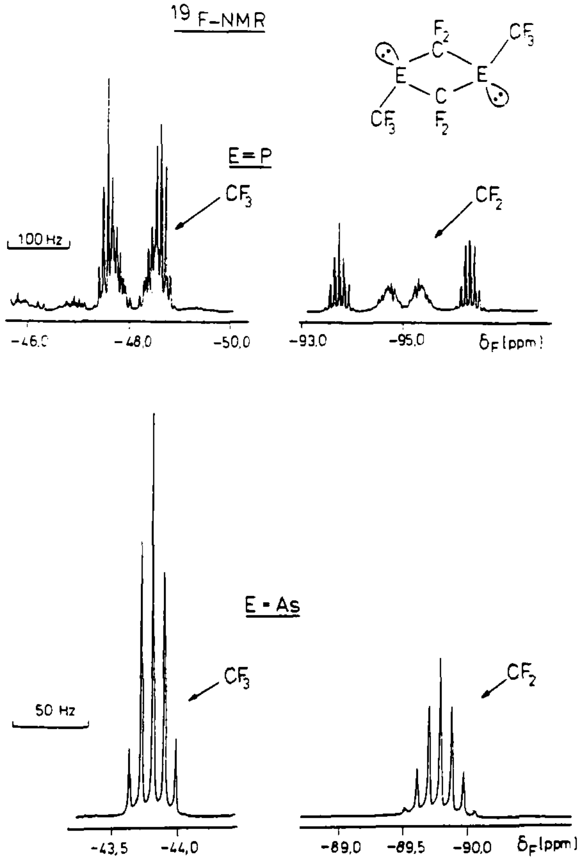


FIGURE 3 ^{19}F-NMR spectra of the trans head-to-tail dimers of $CF_3E{=}CF_2$ (E = P, As).

product patterns:

$E = P$; **6a** : **6b** : **6c** : trimers = 85 : 9 : 2 : 4
$E = As$; **7a** : **7b** : **7c** : trimers = 64 : 21 : 3 : 12

As an example of the cycloaddition products, Figure 3 shows the 1,3-diphospha- and 1,3-diarsacyclobutane derivatives with trans-oriented CF_3 groups together with their ^{19}F-NMR spectra. A simple first-order pattern (quintet for CF_3, septet for CF_2) is observed for the arsenic compound, whereas fairly complicated signals have been obtained in case of the phosphorus analogue due to strong PP′ coupling of the magnetically different P nuclei.

(b) Addition of HX Compounds to 1

The second type of reaction we studied in some detail, deals with the addition of proton acidic compounds HX to the P=C double bond of **1**, which in principle can proceed along two different lines giving chiral phosphane derivatives with either a PX or a PH bond. According to recent literature information,[18] the usual direction of HX addition of P=C systems results in the combination of the anionic group X with the phosphorus and of the proton with the carbon atom. Therefore, it was of great interest how CF_3 and F substituents would affect this behavior. Haszeldine's work[6] on the base-induced reaction of $(CF_3)_2PH$ with methanol, repeated and confirmed by Nixon et al.,[19] suggested an analogous pathway for the addition of methanol to **1**. The results of our study using a variety of HX compounds are summarized in Figure 4 showing that both directions of addition are observed. The pathway is obviously determined mainly by the properties of the HX partner pointing to a fairly low polarity of the P=C bond in **1**.

Referring to a full account to be published shortly,[20] only the reaction of **1** with secondary amines (Me_2NH, Et_2NH) ought to be discussed briefly, because of its

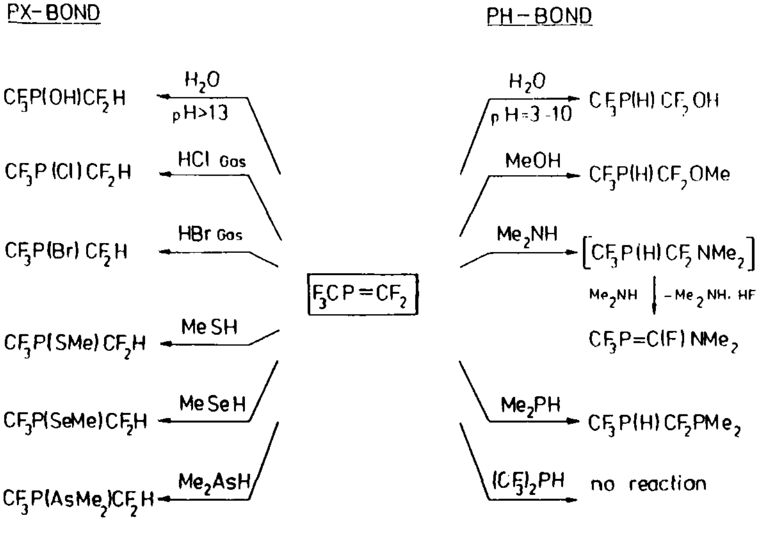


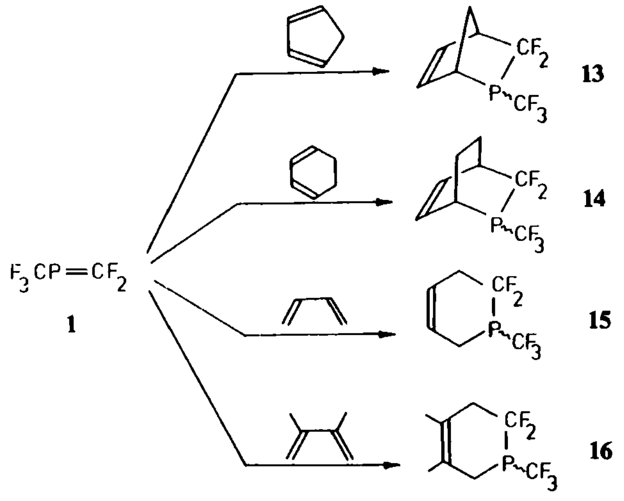
FIGURE 4. Reactions of 1 with proton acidic compounds HX.

general importance for the preparation of heterosubstituted perfluorophosphaalkenes. Independent of the stoichiometry of phosphaalkenes $F_3CP{=}CF(NR_2)$ (R = Me, **8**; R = Et, **9**) are formed showing that these derivatives contain stabilized P=C double-bond systems. With a 1 : 2 molar ratio of the reactants, a quantitative yield of the new phosphaalkenes is obtained. While the addition of HX with formation of PX derivatives leads to interesting functional phosphanes $F_3CP(X)CF_2H$, the reverse addition yields chiral secondary phosphanes $F_3CP(H)CF_2X$, which can serve as precursors for further substituted phosphaalkenes as demonstrated by the reaction of **1** with HNR_2. In fact, this prediction could be confirmed recently by 1,2-elimination of HF from the precursors $F_3CP(H)CF_2OR$ (R = Me, **10**; Et, **11**) and $F_3CP(H)CF_2PMe_2$ (**12**) using trimethylamine as a base.

(c) [2 + 4] Cycloaddition Reactions

The strong relationship between phosphaalkenes and alkenes is expected to be clearly proved by the dienophilic properties of **1**. Therefore, we investigated its reactions with cyclopentadiene, cyclohexadiene, butadiene and 2,3-dimethylbutadiene. In all cases the [2 + 4] cycloaddition proceeds under mild conditions, with cyclopentadiene and 2,3-dimethylbutadiene even at −20°C, with cyclohexadiene and butadiene at −10 and +15°C, respectively, demonstrating the pronounced dienophilicity of **1**. Figure 5 shows the products obtained together with the ratio of conformers or diastereomers as observed at room temperature by ^{19}F-NMR measurements immediately after the Diels-Alder reactions had come to an end. Compounds **13**, **14**, and **16** are formed quantitatively, whilst **15** is produced in about 75% yield together with small amounts of the dimers.

In general one can state that **1** strongly resembles the alkene dienophiles, but is much more reactive. Thus, during the first step of the reaction the sterically unfavorable compound is produced which afterwards rearranges to the thermodynamically stable isomer or conformer. Of particular importance is the result that **13**



Nr.	(a′)	:	b(b′)
13	96		4
14	2	:	98
15	80	:	20
16	100	:	0

FIGURE 5 Diels-Alder cycloaddition products of **1**.

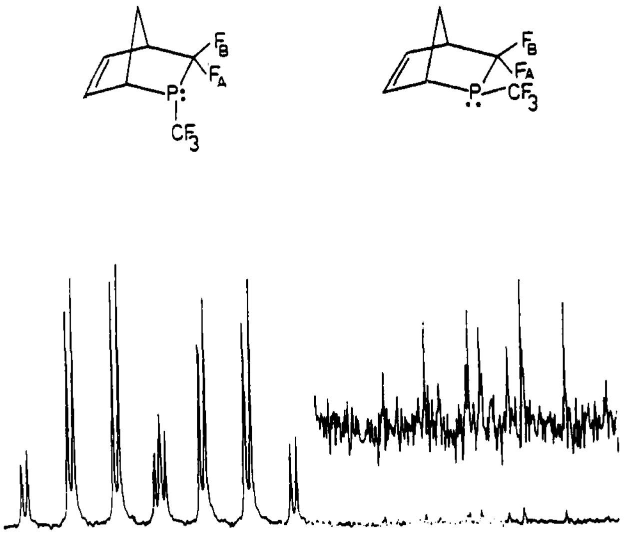


FIGURE 6 $^{31}P\{^1H\}$-NMR spectrum of the [2 + 4] cycloadduct **13** formed by the reaction of **1** with cyclopentadiene.

can be used as a storage compound and source of **1** by retrodiene cleavage. This possibility will be discussed in a more general context below.

The assistance of NMR data in the identification of the new compounds is demonstrated by the $^{31}P\{^1H\}$-NMR spectrum of **13** (Figure 6) showing a doublet of quartets of doublets due to coupling with the nonequivalent F nuclei of the CF_2 and the three equivalent F atoms of the CF_3 group.

The readiness and unambiguity of the decomposition reaction of the $Me_3SnE(CF_3)_2$ compounds encouraged us to investigate the question whether or not they can be used as $CF_3E{=}CF_2$ equivalents in Diels-Alder type reactions. The result is an effective one-pot procedure for the preparation of cyclic organophosphorus or arsenic compounds from $Me_3SnE(CF_3)_2$ and dienes. In this process (equation 3) use is made of the fact that the tin compounds slowly decompose at moderate temperatures to give polymeric $(Me_3SnF)_x$ and $CF_3E{=}CF_2$ ($E = P, As$) which are captured in situ by the diene molecules. Figure 7 demonstrates the results of this simple method in case of **1** as dienophile.

$$Me_3SnE(CF_3)_2 + 1{,}3\text{-Diene} \xrightarrow[CHCl_3]{70°C} \text{Diels-Alder Adduct} + Me_3SnF \qquad (3)$$

For all the examples studied so far, the yields of the cycloaddition products amount to 80 to 95%. A study at controlled reaction time at 70°C led to the following reactivity series of dienes:

Cyclopentadiene > pentamethylcyclopentadiene, 2,3-diphenyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene > 1,3-butadiene, 1,3-cyclohexadiene, anthracene.

The conformers and diastereomers are formed in similar ratios as found for the [2 + 4] cycloaddition of the isolated P=C system. The product of 2-methylfurane (compound **20** in Figure 7) after a reaction time of 30 hrs. consists of the isomers

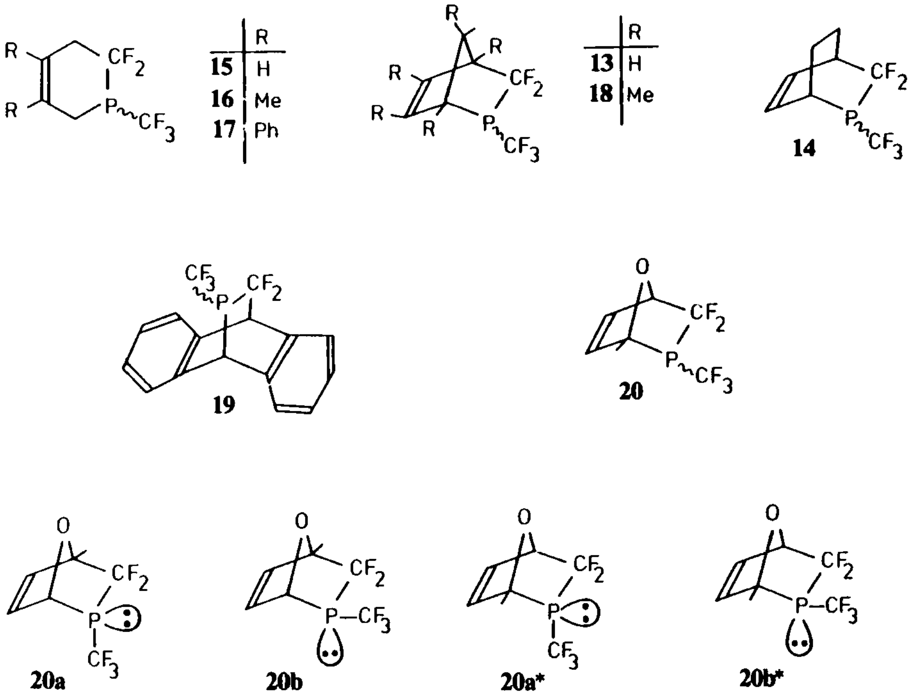


FIGURE 7 [2 + 4] Cycloadducts of the one-pot reaction of $Me_3SnP(CF_3)_2$ with 1,3-dienes.

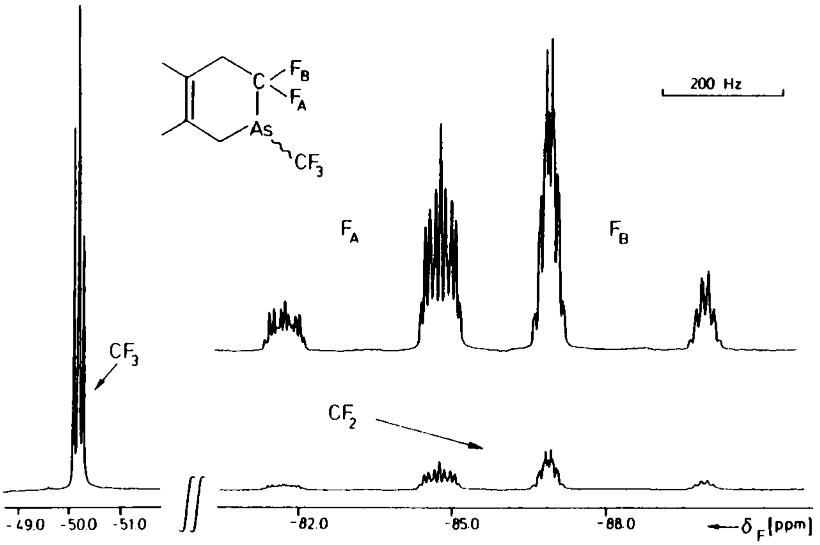


FIGURE 8 ^{19}F-NMR spectrum of the product of **21** formed from 2,3-dimethylbutadiene and $Me_3SnAs(CF_3)_2$.

20a, **20b**, **20a*** and **20b*** in the ratio 22 : 13 : 25 : 40. A thorough study showed **20a** to be the first product formed, slowly transforming to **20b** as the thermodynamically more stable isomer, both later rearranging to **20a*** and **20b*** with a different position of the methyl substituent. The formation of the latter can only be explained by a retrodiene cleavage of **20a** and **20b** occurring even at 70°C. This assumption proved to be correct in a separate experiment: On heating a mixture of **20** and 2,3-dimethyl-1,3-butadiene to 70°C a quantitative reaction takes place yielding **16** and 2-methylfurane.

Figure 8 shows as one example of the reactions of $Me_3SnAs(CF_3)_2$ the cycloaddition product **21** of 2,3-dimethylbutadiene with $CF_3As{=}CF_2$ and its ^{19}F-NMR spectrum. A doublet of doublets is observed for the CF_3 group, giving the pattern of a pseudo-triplet, and a typical AB spectrum for the CF_2 group with a large F_AF_B coupling in addition to FF and FH interactions.

Retrodiene Reactions of Diels-Alder Adducts

For three of the [2 + 4] cycloadducts (Figure 9) the thermal retrodiene cleavage has been studied. **13** was found to be the best source of the reproduction of **1**. This can be deduced from the temperatures and the first cycle yields of the pyrolysis experiments. Only three cycles are necessary for a complete cleavage. Of special interest is the side reaction occurring together with the retrodiene cleavage of the cyclohexadiene adduct **14** at 600°C. It leads to the new phosphetane **22** in about 30% yield in addition to the known dimers of the formally expected cyclobutadiene: Tricyclooctadiene and cyclooctatetraene **22** were characterized by mass- and NMR spectroscopic studies. The typical fragmentation pattern and ^{31}P-NMR spectrum confirm the identity of the ring system (Figure 10).

A detailed investigation of the retrodiene thermolysis of **13** in the inlet system of a quadrupole mass spectrometer allowed us to calculate the enthalpy of the cleavage reaction by measuring the appearance potentials of $C_5H_6^+$ as arising from the

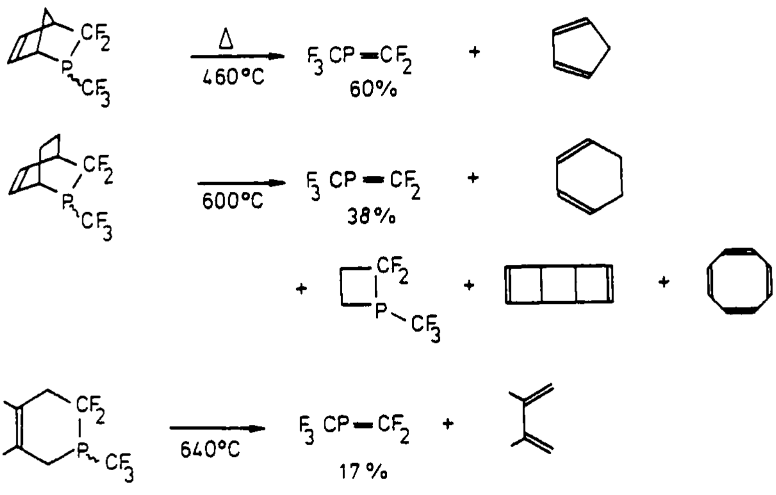


FIGURE 9 Retrodiene cleavage of **13**, **14** and **16**.

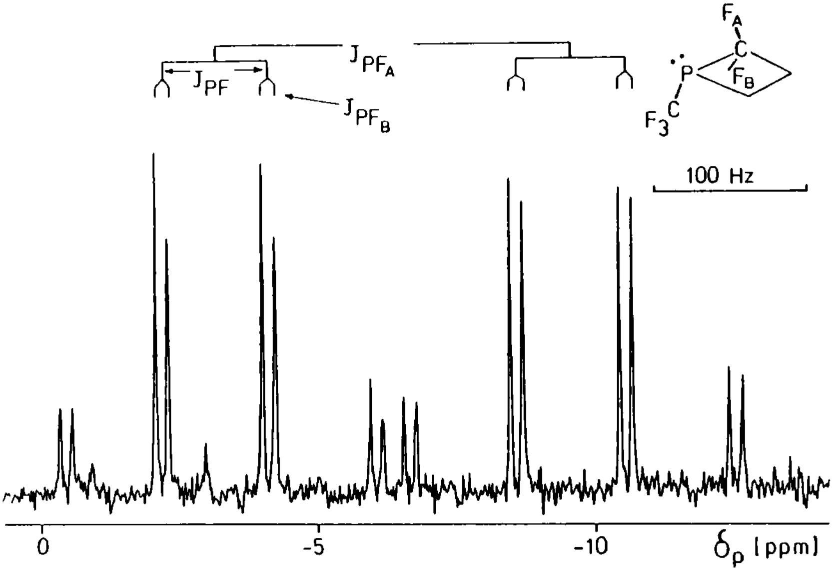


FIGURE 10 $^{31}P\{^1H\}$-NMR spectrum of the phosphetane **22**.

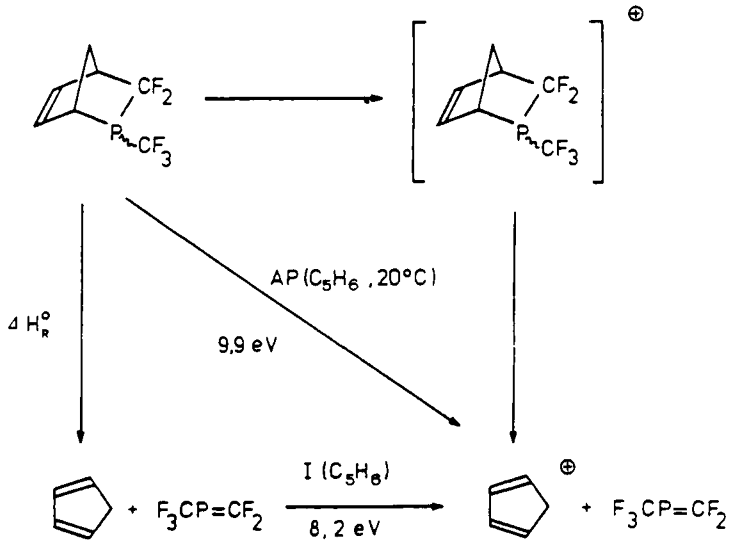


FIGURE 11 Thermochemical cycle for the calculation of the enthalpy of the cleavage reaction of **13** to C_5H_6 and $F_3CP{=}CF_2$ (**1**).

cycloadduct or from free C_5H_6 formed by the retrodiene reaction. The thermochemical cycle used for this calculation is given in Figure 11.

With a value of 164 kJ/mol for ΔH°_R and literature data for the bond energies $E_\sigma(CC)$, $E_\pi(CC)$, and the resonance energy $E_R(C_5H_6)$, reasonable values for the PC σ- and PC π-bond energies of 330 and 157 kJ/mol, respectively, have been estimated. The E_σ value obtained is about 20% higher than tabulated data, indicating a stabilization of the σ-framework of **1** by the so-called perfluoro effect.[5]

RECENT DEVELOPMENTS

In view of the surprising stability of **1** it was very tempting to extend our work to other perfluoroalkyl derivatives. Up to now, we successfully studied the thermolysis of $Me_3SnP(C_2F_5)_2$, affording the new phosphaalkene $C_2F_5P{=}C(F)CF_3$ (**3**), and the one-pot Diels-Alder procedure for this compound. The cycloaddition reactions occur in a similar way as for **1** giving the expected products in high yields. Since in this case the cycloadducts contain several chiral centers, a complicated mixture of diastereomers is obtained. The isolated phosphaalkene $C_2F_5P{=}C(F)CF_3$ is less stable than **1** and has been used up to now for investigating HX addition and [2 + 4] cycloaddition reactions. The result, that HX addition (X = Br, OMe, NMe_2) generally leads to the PX derivatives in contrast to the reactions of **1**, is particularly noteworthy.

Having been so successful in the field of (2p–3p)π (P=C) and (2p–4p)π systems (As=C), we tried to produce the (3p–3p)π compound $F_3CP{=}PCF_3$ (**23**) and to study its reactions as dienophile. Figure 12 shows the results of a one-pot procedure, in which **23** is formed from CF_3PI_2 and $SnCl_2$ as a reactive intermediate and trapped by the dienes applied. The Diels-Alder products **24**–**27** are generated in a stereospecific reaction; ^{31}P-NMR spectra establish the exclusive formation of the isomers with trans positions of the CF_3 groups. Only in the case of **26** two isomers (4 : 1) are obtained due to the two possible orientations of the CHMe bridge. The observed stereoselectivity suggests a concerted mechanism for the [2 + 4] cycloaddition of **23**.

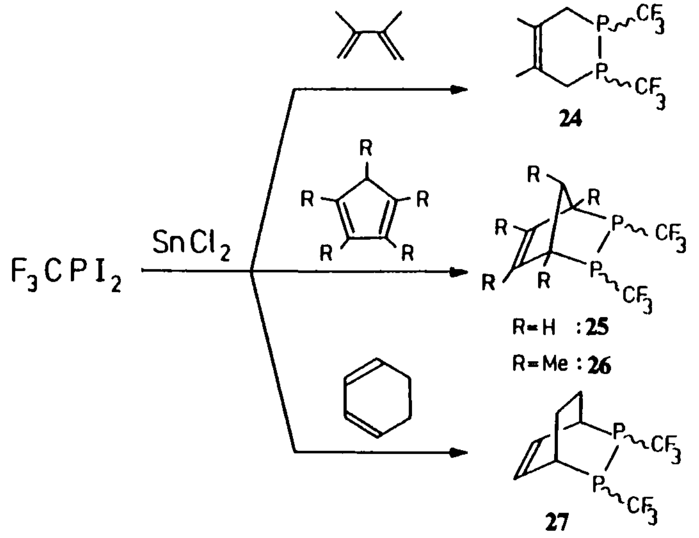


FIGURE 12 Diels-Alder adducts **24–27** produced by the reaction of $CF_3P{=}PCF_3$ (**23**) with dienes.

The diphosphene intermediate is ascertained by the following facts and arguments:

(a) Compounds **24** to **27** are formed at room temperature within less than 12 hours, independent of the amount of the diene component (variation between 1 : 1 and 1 : 10).

(b) In the incomplete reactions of **23** with C_5R_5H (R = H, Me) the only by-product is the cyclotetraphosphane $(PCF_3)_4$ which can be plausibly explained by [2 + 2] cycloaddition.

(c) The retrodiene cleavage of **27** at 70°C in the presence of 2,3-dimethylbutadiene gives **24** and cyclohexadiene in quantitative yield within 2 days.

(d) The methanolysis of **25** at 70°C leading to equimolar amounts of CF_3H, CF_3PH_2 and $P(OMe)_3$ can be rationalized in terms of **23** as the reactive intermediate.

The formation of the new heterocycles **24**–**27** in a one-pot process not only proves the existence of the diphosphene **23**, but also opens pathways for a systematic study of its properties. The results support earlier investigations about the dienophilic character of PP double-bond systems.[25]

OUTLOOK

Thermolysis of organotin derivatives of the type $Me_3SnE(CF_3)_2$, $Me_3SnE'CF_3$ and $Me_3SnE(R)R_F$ (E=P, As; E'=S, Se) proved to be a versatile method for the production of new E=C or E'=C (p–p)π compounds in preparative amounts and high purity. For Diels-Alder type reactions, the procedure can even be reduced to a one-pot process starting with the trimethyltin compound and the diene, thus enabling the synthesis of cycloadducts of E(p = C) intermediates too reactive for a two-step reaction, e.g. $CF_3As(p = CF_2)$. Furthermore, heterosubstituted P=C systems are accessible via HX addition to $F_3CP{=}CF_2$ and subsequent 1,2-HF elimination with NMe_3.

The fluorine containing EC (p–p)π compounds described in this report will be of particular value for the development of heteroalkene chemistry, because they combine a fairly high stability with a pronounced reactivity unrestricted by steric hindrance, which is otherwise a limiting factor in reactivity studies of phosphaalkenes. Therefore, further investigations including the preparation of heteroallene and heterodiene compounds as well as the use of heteroalkenes as ligands in transition-metal complexes will be a very promising task.

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