Table 3. Bond lengths (Å) in phosphaalkynes P≡C—X calculated in the 6-31** basis

X	R(P≡C)	R(C—X)
H	1.515	1.063
NH_2	1.538	1.316
OH	1.527	1.289

that p(N)—π*(P≡C) interaction is stronger than p(O)—π*(P≡C) interaction. The endothermic character of the **3** → **4** rearrangement in the gas phase is also indicative of the fact that the oxaderivative is less stabilized by p—π*-interaction.

Thus, no matter which basis is used, the calculations predict a smaller tendency to rearrange into a compound with a one-coordinated phosphorus atom for 1-oxa-3-phosphaallene compared to 1-aza-3-phosphaallene. Unlike the rearrangement of 1-aza-3-phosphaallene, rearrangement **3** → **4** by a [1,3]-*H*-shift does not proceed through the formation of intermediates, because two consequent [1,2]-*H*-shifts can lead only to phosphinidene **5**.

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Polyfluorinated enol acetates

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The synthesis of polyfluorinated enol acetates has been performed by reductive dechlorination of chloropolyfluoroketones with zinc in Ac_2O. Under these conditions, hexafluoroacetone is preferably reduced at the carbonyl group.

Key words: polychlorofluoroketones; reductive dehalogenation; polyfluorinated enol acetates; synthesis; reactivity.

It is known that the reactions of hexafluoroacetone (HFA) with metals occur in multiple ways and result both in dimerization of the ketone into perfluoropinacol and in its reductive defluorination to give pentafluoro-2-propenolates of the respective metals or products of their condensation with the carbonyl precursor.[1] The ratio of the dimerization and defluorination processes depends markedly on the nature of the metal and solvent. In particular, the reaction of HFA with Zn in THF results only in defluorination of the ketone.[1]

It was shown in this study that the reaction of HFA with Zn in Ac_2O also results in reductive defluorination of HFA to Zn enolate, which then undergoes acylation to give pentafluoroisopropenyl acetate (**1**) (for the acylation of other polyfluorinated enolates, *cf.* Refs. 2—4). However, this direction of the reaction is only realized to a small extent, and the yield of compound **1** does not exceed 5 %. The predominant process is reduction of the carbonyl group in HFA resulting in $AcOCH(CF_3)_2$. Perfluoropinacol is not formed in this reaction.

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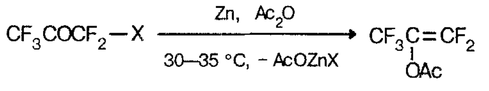
Chlorine is abstracted much more readily than fluorine in the reductive dehalogenation,[5] so one could expect that reductive dehalogenation would predominate over reduction of the C=O group on going from HFA to chloropentafluoroacetone. In fact, it turned out that when this ketone reacts with Zn in Ac_2O, reduction of the C=O group does not occur, and enol acetate **1** is formed in a high yield. The reaction of fluorosulfonyloxypentafluoroacetone with Zn in Ac_2O occurs equally unambiguously.



$$CF_3COCF_2{-}X \xrightarrow[30\text{—}35\ ^\circ C,\ -AcOZnX]{Zn,\ Ac_2O} CF_3\underset{OAc}{C}{=}CF_2$$

1

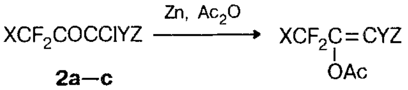
$X = F, Cl, OSO_2F$

Similarly, enol acetates **3a—c** are formed from polychlorofluoroacetones (**2**) (Scheme 1).

Polychlorofluoroacetones also smoothly undergo oxidative dechlorination with zinc in $(CF_3CO)_2O$. Under these conditions, for example, ketone **2a** is transformed to tetrafluorochloroisopropenyl trifluoroacetate (**4**), which was isolated as dibromide **5** (Scheme 2).

Enol acetates **1** and **3** undergo deacylation in conc. H_2SO_4 under mild conditions to give high yields of enols **6a—c** (Scheme 3).

Scheme 1



$$XCF_2COCClYZ \xrightarrow{Zn,\ Ac_2O} XCF_2\underset{OAc}{C}{=}CYZ$$

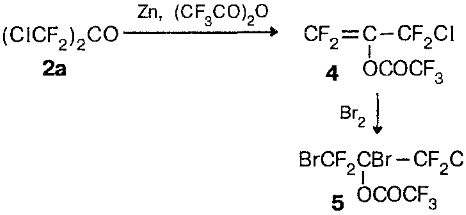
2a—c **3a—c**

a: X = Cl, Y = Z = F

b: X = Z = Cl, Y = F

c: X = F, Y = Z = Cl

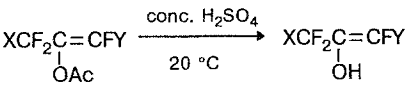
Scheme 2



$$(ClCF_2)_2CO \xrightarrow{Zn,\ (CF_3CO)_2O} CF_2{=}\underset{OCOCF_3}{C}{-}CF_2Cl \xrightarrow{Br_2} BrCF_2\underset{OCOCF_3}{C}Br{-}CF_2Cl$$

2a **4** **5**

Scheme 3



$$XCF_2\underset{OAc}{C}{=}CFY \xrightarrow[20\ ^\circ C]{conc.\ H_2SO_4} XCF_2\underset{OH}{C}{=}CFY$$

6a—c

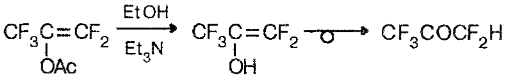
a: X = Y = F

b: X = Cl, Y = F

c: X = Y = Cl

Thus, the $Zn—Ac_2O$ system is a convenient reagent for the one-step synthesis of polyfluorinated enol acetates which can be smoothly transformed to the respective enols.* This reaction sequence is particularly convenient for synthesizing enol **6b** since when the alternative procedure[5] based on the reaction of ketones **2** with metallic Al in the THF—ether medium is carried out starting from ketone **2a**, it undergoes partial isomerization to $CF_3COCFCl_2$, and the process finally results in a mixture of enols **6b** and $CF_3C(OH){=}CFCl$.

Deacylation also takes place in nucleophilic reactions of polyfluorinated enol acetates. For example, the reaction of enol acetate **1** with ethanol in the presence of Et_3N results in enol **6a**, which isomerizes to pentafluoroacetone (**7**) under the reaction conditions (*cf.* Ref. 6).



$$CF_3\underset{OAc}{C}{=}CF_2 \xrightarrow[Et_3N]{EtOH} CF_3\underset{OH}{C}{=}CF_2 \longrightarrow CF_3COCF_2H$$

1 **6a** **7**

Experimental

^{19}F NMR spectra were recorded on a Bruker-200 SY spectrometer (188.3 MHz, CCl_4, CF_3COOH as the external standard). IR spectra were obtained on a UR-20 spectrophotometer.

Pentafluoroisopropenyl acetate (1). Chloropentafluoroacetone (22.5 g) was passed through a mixture of activated Zn dust (10 g) and Ac_2O (100 mL) for 0.5 h at ≤30 °C. After the exothermic reaction ceased (~2 h), the mixture was poured into water (300 mL) and stirred until hydrolysis of the Ac_2O was completed. Then a product (20 mL) was distilled off. The lower layer of the distillate was dried with $MgSO_4$ and distilled to give 20.6 g (87 %) of enol acetate **1**, b.p. 74—75 °C, n_D^{20} 1.3151 (*cf.* Ref. 6). A similar procedure starting from $CF_3COCF_2OSO_2F$ gave compound **1** (yield 83 %), and that starting from ketones **2** resulted in enol acetates **3** (Table 1).

3-Chlorotetrafluoroisopropenyl trifluoroacetate (4). A mixture of Zn dust (5.7 g), $(CF_3CO)_2O$ (45 mL), and 1,3-dichlorotetrafluoroacetone (10 g) was refluxed with stirring for 10 h, then the excess $(CF_3CO)_2O$ and enol acetate **4** were distilled off *in vacuo* (10 Torr), and Br_2 (2 mL) was added with UV irradiation. After complete transformation of enol acetate **4** (^{19}F NMR monitoring), dibromide **5** was isolated by fractionation. A solution of dibromide **5** (10.3 g) in Ac_2O (15 mL) was added with stirring to a suspension of Zn dust (3.6 g) in Ac_2O (20 mL), the mixture was stirred for 0.5 h at 40 °C, and enol acetate **4** was isolated by distillation.

3-Chloro-2-hydroxytetrafluoro-1-propene (6b). Enol acetate **3a** (5 g) was added dropwise with cooling and stirring to conc. H_2SO_4 (15 mL), and the mixture was heated to 20 °C. Distillation *in vacuo* (15 Torr) gave 3.3 g (83 %) of enol **6b**, b.p. 78—79 °C, which was similar to the compound reported before (^{19}F NMR, *cf.* Ref. 6). Enol **6a** (yield 78 %, *cf.* Ref. 6) and enol **6c** (yield 77 %, *cf.* Ref. 5) were obtained in a similar way.

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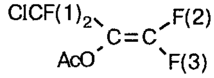
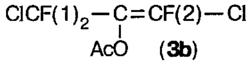
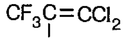
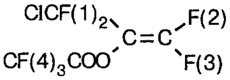
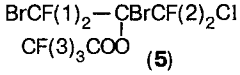
* Enol acetate **1** has been obtained previously[6] by the opposite reaction, acetylation of enol **6a**.

Table 1. Parameters of compounds obtained

Compound	Yield (%)	B.p./°C (p/Torr)	n_D^{20}	IR, ν/cm^{-1}	^{19}F NMR, δ, J/Hz	Found / Calculated (%)			Molecular formula
						C	H	F	
 (**3a**)	81	99—100	1.3580	1765; 1805	−22.7 (dd, F(1)); 9.6 (dt, F(3)); 15.9 (dt, F(2)); $J_{1-2} = J_{2-3} = 29$; $J_{1-3} = 6.5$	29.08 29.06	1.47 1.45	36.75 36.80	$C_5H_3ClF_4O_2$
 $ClCF(1)_2-C(OAc)=CF(2)-Cl$ (**3b**) *Z*/*E* = 80/20	77.5	134—136	1.3960	1695; 1800	*Z*-**3b**: −23.9 (d, F(1)); 11.8 (t, F(2)); $J = 26$ *E*-**3b**: −24.2 (d, F(1)); 2.7 (t, F(2)); $J = 8$	26.98 26.91	1.40 1.35	25.78 25.56	$C_5H_3Cl_2F_3O_2$
 $CF_3C(OAc)=CCl_2$ (**3c**)	86	134—135	1.3960	1632; 1796	−12.58 s	27.02 26.91	1.61 1.35	25.85 25.56	$C_5H_3Cl_2F_3O_2$
 (**4**)	67.4	67—68.5	1.3100	1785; 1840	−21.7 (dd, F(1)); −1.5 (s, F(4)); 7.0 (dt, F(3)); 13.2 (dt, F(2)); $J_{1-2} = J_{2-3} = 29$; $J_{1-3} = 6$	23.04 23.03	—	51.06 51.09	$C_5ClF_7O_2$
 $BrCF(1)_2-CBr(OCOCF(3)_3)CF(2)_2Cl$ (**5**)	53	48—49 (25)	1.3865	—	−26.2 (m, F(1)); −22.1 (m, F(2)); −1.4 (s, F(3))	14.43 14.27	—	32.16 31.63	$C_5ClBr_2F_7O_2$

Pentafluoroacetone (7). A solution of enol acetate **1** (5.7 g) in EtOH (8 mL) and Et_3N (1 mL) was kept for 4 days at ~20 °C and mixed with cooling with conc. H_2SO_4 (20 mL). Distillation gave 2.3 g (40 %) of ketone **7**, b.p. 14—16 °C, which was similar to the compound reported before (^{19}F NMR, *cf.* Ref. 7).

Reaction of hexafluoroacetone with Zn in Ac_2O. A stirred suspension of Zn dust in Ac_2O (50 mL) at ≤35 °C was treated with HFA (13 g). After 2 h the mixture was poured into water. Distillation gave 7.5 g of a fraction with b.p. 70—74 °C containing (GLC, ^{19}F NMR) 12 % $(CF_3)_2CHOH$, 8 % enol acetate **1**, and 80 % $AcOCH(CF_3)_2$ (*cf.* Ref. 8).

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