PERFLUOROCARBOXYLIC ACID ANHYDRIDES AND HALIDES IN THE WITTIG REACTION

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Carboxylic acid anhydrides and halides react with phosphorus ylides as acylating agents [1] or as sources of ketenes [2]. Only cyclic anhydrides undergo the Wittig reaction with stable phosphorus ylides (for example, see [3, 4]); direct participation in the Wittig reaction with retention of the C—Hal bond has not been described for acid halides.* On the other hand, the stable hexafluoroisopropylidenetriethoxyphosphorane (I) has not yet undergone the Wittig reaction even with typical carbonyl components such as benzaldehyde, trifluoroacetophenone, and hexafluoroacetone [7, 8].

However, we have found that perfluorocarboxylic acid anhydrides and halides react under mild conditions with ylide I to give Wittig reaction products II:

$$(CF_3)_2C{=}P(OEt)_3 + R_FCOX \rightarrow (CF_3)_2C{=}CXR_F + (EtO)_3PO$$

(I) (II)

$R_F = CF_3$, $X = CF_3CO_2$ (a); F (b); Cl (c); Br (d); $R_F = n\text{-}C_3F_7$, $X = n\text{-}C_3F_7CO_2$ (e); F (f).

This reaction can be used for the synthesis of fluorine-containing unsaturated compounds; however, it is complicated by side processes in many cases. In addition to "normal" products of the Wittig reaction, the reaction often gives significant amounts of other unsaturated compounds of the II type in which the X residue does not correspond to the starting acid anhydride or halide but is replaced by fluorine or a perfluoroacyloxy or ethoxy group to give, respectively, olefins IIb, f, IIa, e, and IIa, b; in addition, diethyl pentafluoroisopropenylphosphonate (IV), diethyl fluorophosphate (V), and EtX (ethyl perfluoroacylate or ethyl halide) are detected in the mixtures.† The formation of the products can be represented in terms of transformation of intermediate phosphobetaine VI via the following pathways (scheme 1): 1) the normal Wittig reaction; 2) rearrangement with migration of an ethyl group (see [7]), which leads to ethoxy-substituted phosphonate VII; 3) O-acylation by another mole of R_FCOX (see [9]), which is accompanied by splitting out of EtX to give acyloxy-substituted phosphonate VIII; 4) splitting out of EtX to give C-acylated phosphonate IX. Intermediates VII and VIII undergo cleavage (see [7]) to $(EtO)_2P(O)X$ (X) and, respectively, ethoxy olefins III or acyloxy olefins IIa, e. Like hexafluoroacetone [7], intermediate IX can split out an F^- ion from phosphorus ylide I to generate an α-fluoro alkoxide ion (XI) and phosphonium cation XII. Anion XI, which is an intermediate in the Wittig—Horner reaction, undergoes cleavage to give a fluoro-substituted olefin (IIb, f) and the $(EtO)_2PO_2^-$ ion, which is alkylated to give triethyl phosphate by cation XII, during which the latter is converted to unsaturated phosphonate IV. Another similar reaction of phosphorus ylide I — dealkylfluorination under the influence of $(EtO)_2P(O)X$, which undergoes conversion to fluorophosphate V in the process — probably also serves as a source of phosphonate IV.

*A paper [6] dealing with the olefination of perfluorocarboxylic acid fluorides by the substituted fluoromethylenephosphorane $Bu_3P{=}CF{-}\overset{+}{P}Bu_3\overline{X}$ (where X = Cl, Br) appeared after publication of our preliminary communication [5].

†Other products are also formed in very small amounts.

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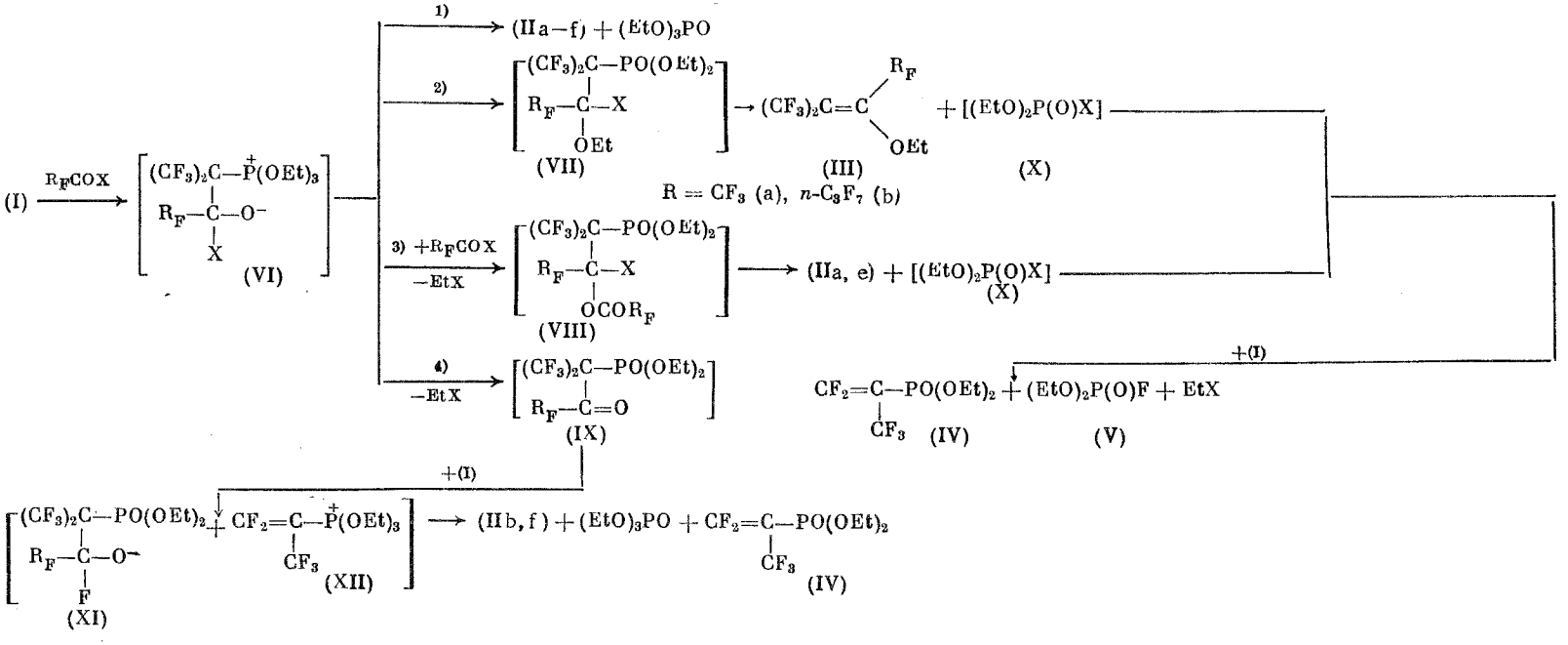
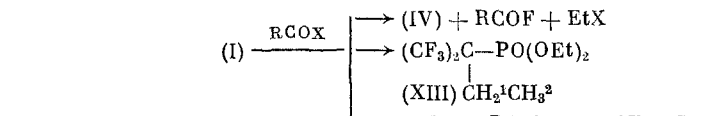
Scheme 1

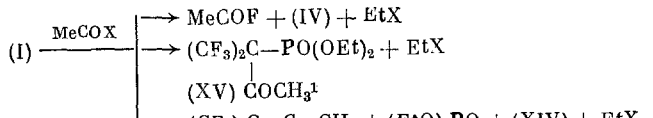

(I)
R_FCOX
$[(CF_3)_2C-\overset{+}{P}(OEt)_3\ R_F-\underset{X}{\underset{|}{C}}-O^-]$
(VI)
1)
(IIa–f) + $(EtO)_3PO$
2)
$[(CF_3)_2C-PO(OEt)_2\ R_F-\underset{OEt}{\underset{|}{C}}-X]$
(VII)
$(CF_3)_2C=C(R_F)(OEt)$
(III)
$+[(EtO)_2P(O)X]$
(X)
R = CF_3 (a), n-C_3F_7 (b)
3) $+R_FCOX$
$-EtX$
$[(CF_3)_2C-PO(OEt)_2\ R_F-\underset{OCOR_F}{\underset{|}{C}}-X]$
(VIII)
(IIa, e) + $[(EtO)_2P(O)X]$
(X)
4)
$-EtX$
$[(CF_3)_2C-PO(OEt)_2\ R_F-C=O]$
(IX)
+(I)
$CF_2=\underset{CF_3}{\underset{|}{C}}-PO(OEt)_2$ (IV)
$+(EtO)_2P(O)F + EtX$
(V)
+(I)
$[(CF_3)_2C-PO(OEt)_2\ R_F-\underset{F}{\underset{|}{C}}-O^-]$
(XI)
$+\ CF_2=\underset{CF_3}{\underset{|}{C}}-\overset{+}{P}(OEt)_3$
(XII)
(IIb, f) + $(EtO)_3PO$ + $CF_2=\underset{CF_3}{\underset{|}{C}}-PO(OEt)_2$
(IV)

In contrast to R_FCOX, unfluorinated carboxylic acid anhydrides and halides do not undergo the Wittig reaction with ylide I. Chiefly dealkylfluorination, rearrangement (see [10]), and, to a slight extent, dealkylation of ylide I are observed upon heating with benzoic or acetic anhydride, benzoyl halides, and acetyl fluoride, as a result of which unsaturated ester IV, α-ethyl phosphonate XIII, and α-hydro phosphonate XIV, as well as an acyl fluoride, EtX, and ethylene, are formed.*



R = Ph, X = $PhCO_2$, F, Cl, Br; R = Me, X = $MeCO_2$, F.

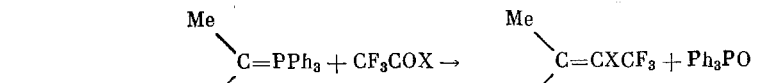
α-Acetyl phosphonate XV, 1,1-bis(trifluoromethyl)allene (XVI), and triethyl phosphate are formed in addition to acetyl fluoride, an ethyl halide, and phosphonates IV and XIV in the reaction with acetyl chloride and acetyl bromide:



X = Cl, Br.

Thus ylide I behaves like other phosphorus ylides [1, 2]; here, it is acylated and gives a product of olefination of ketene (in addition to undergoing dealkylfluorination, which is most characteristic for it).

We found that the properties displayed by ylide I in reactions with perfluorocarboxylic acid anhydrides and halides also are not unique — other disubstituted phosphorus ylides are also capable of undergoing the Wittig reaction with these unusual carbonyl components. This was demonstrated in the case of α-carbethoxyethylidenetriphenylphosphorane (XVII), which readily forms the corresponding unsaturated compounds (XVIII) upon reaction with trifluoroacetic anhydride, trifluoroacetyl fluoride, and trifluoroacetyl chloride:†



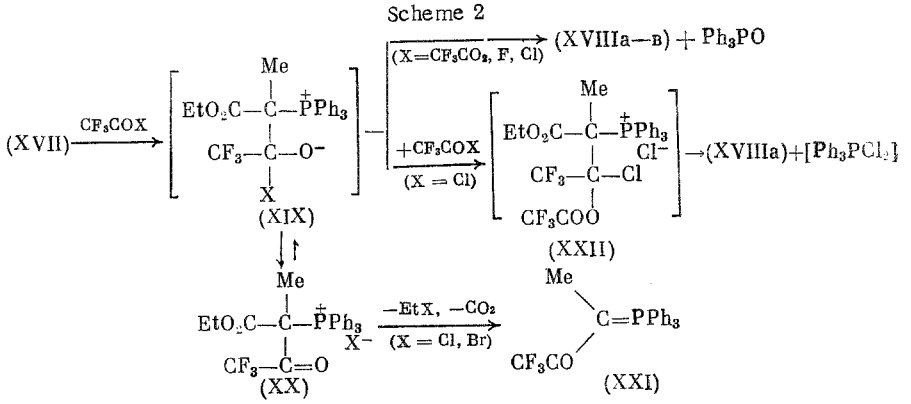
X = CF_3CO_2 (a), F (b), Cl (c).

It should be noted that in the reaction of ylide XVII with trifluoroacetic anhydride, trifluoroacetyl chloride, and trifluoroacetyl bromide the intermediately formed phosphonium betaines XIX are evidently capable of irreversibly splitting out a trifluoroacetate or halide ion to give products of C-alkylation of the ylide, viz., phosphonium salts XX [4] (demonstrated from the NMR spectra). In the case of the relatively "hard" CF_3COO^- gegenion, which readily adds reversibly to the carbonyl group, the thermodynamic reaction product is trifluoroacetoxy-substituted unsaturated ester XVIIIa, which is formed in good yield as a result of the Wittig reaction. The "soft" bromide ion preferentially cleaves the R—O bond in the carbethoxy group, so that trifluoroacetyl-substituted phosphorus ylide XXI is formed as a result of dealkylation and decarboxylation [11]. The chloride ion, which occupies an intermediate position, reacts via both pathways at comparable rates. In addition phosphobetaine XIXc can be acylated by a second molecule of trifluoroacetyl chloride, and trifluoroacetoxy-substituted unsaturated ester XVIIIa is formed after cleavage of acyloxy-substituted phosphonium ion XXII (a second unidentified reaction product is probably triphenyldichlorophosphorane) (scheme 2):

*The presence of very small amounts of diethyl fluorophosphate (V) in the reaction products probably constitutes evidence for cleavage of the phosphonates.

†In contrast to carbethoxy ylide XVII, α-acyl-substituted phosphorus ylides RCOC(Me)=PPh_3 (R = Me, Ph, CF_3) react with trifluoroacetic anhydride, trifluoroacetyl chloride, and trifluoroacetyl bromide to give O-acylation products (according to NMR spectroscopy) [9], prolonged heating of which at 50°C leads to mixtures of unidentified substances.

Scheme 2



X = CF_3CO_2 (a), F (b), Cl (c), Br (d).

It follows from the results presented above that perfluorocarboxylic acid anhydrides and halides can undergo the Wittig reaction with stable phosphorus ylides that do not contain an α-H atom. This is probably explained by the significant electrophilicity of the carbonyl C atom and "strengthening" of the C—O or C—Hal bond in the intermediate phosphobetaines of the VI or XIX type under the influence of the negative inductive effect of the perfluoroalkyl groups. Such phosphobetaines, on the one hand, are readily formed, and, on the other, can be stabilized not only by ejection of an acylate or halide ion (which occurs in the case of unfluorinated acid anhydrides and halides) but via other pathways, one of which is the Wittig reaction.*

EXPERIMENTAL

The NMR spectra were recorded with Perkin-Elmer R-12 (^1H, 60 MHz), Perkin-Elmer R-32 (^1H, 90 MHz; ^{19}F, 84.6 MHz), Hitachi (^{19}F, 56.4 MHz), and Bruker HX-90 (^{31}P, 36.4 MHz) spectrometers with tetramethylsilane (^1H, δ scale), CF_3COOH (^{19}F), and 85% H_3PO_4 (^{31}P, δ scale) as the external standards. The IR spectra were recorded with a UR-20 spectrometer. The Raman spectra were obtained with a Ramanor HG-2S spectrometer. The mass spectra were recorded with a Varian MAT CH-8 mass spectrometer at 70 eV; the m/z values, intensities in percent, and tentative assignments are presented (data only for the ^{35}Cl and ^{79}Br isotopes are presented for the Cl- and Br-containing ions). Preparative gas–liquid chromatography (PGLC) was carried out with Carlo-Erba G W-221 and Perkin-Elmer F-21 chromatographs and the following columns: column A (with a length of 4 m and a diameter of 25 mm) was packed with QF-1 on Chromosorb, and column B (with a length of 3.6 m and a diameter of 25 mm) was packed with Krytox on Chromosorb. The starting substances and CH_2Cl_2 were dried by standard methods, and the experiments were carried out in an atmosphere of dry Ar. The characteristics of the compounds obtained are presented in Tables 1-5. The molar ratios of the principal components in the mixtures are presented in all cases.

Reaction of Perfluorocarboxylic Acid Anhydrides and Halides with Hexafluoroisopropylidenetriethoxyphosphorane (I). A mixture of R_FCOX and ylide I was maintained in a sealed flask or sealed ampul at ~20°C, during which the volatile components were removed by distillation in vacuo (1-10 mm, ≈ 20°C) into a trap (—78°C). The mixtures were analyzed by means of ^1H and ^{19}F NMR spectroscopy and GLC, and the products were isolated by distillation or PGLC.

a) The reaction of 6.39 g (20.2 mmole) of I and 4.59 g (21.9 mmole) of $(CF_3CO)_2O$ for 9 days gave 4.61 g (66%) of perfluoro-2-methyl-3-acetoxy-2-butene (IIa) and 2.69 g (73%) of triethyl phosphate with bp 84-87°C (7 mm).

b) The reaction of 9.32 g (29.5 mmole) of I and 4.67 g (40.3 mmole) of CF_3COF for 3 days gave a mixture of IIb, IIIa, V, $(EtO)_3PO$, CF_3COF, and phosphonate IV (1.0:1.1:0.8:0.8:0.9:0.2). Fractionation gave 1.75 g (23.7%) of perfluoro-2-methyl-2-butene (IIb), with bp 28-30°C [13] (NMR, Raman, and mass spectra), and 2.84 g (34.9%) of 3-ethoxyperfluoro-2-methyl-2-butene (IIIa).

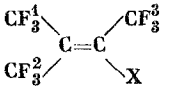
*A similar effect of fluoroalkyl groups on the direction of the reaction of carboxylic acid esters with phosphorus ylides was previously demonstrated in [12].

TABLE 1. Characteristics of the Synthesized Compounds

Compound	bp, (p, mm Hg)	IR (Raman) spectrum, ν, cm^{-1}		Found/calculated, %			Empirical formula
		C=C	C=O	C	H	F	
(IIa)	73–75	1685 m	1839 s	24,2 / 24,4	–	65,2 / 66,3	$C_7F_{12}O_2$
(IIc)	56–57	1635 m	–	22,4 / 22,5	–	65,1 / 64,2	C_5F_9Cl
(IId) *	72,5–73,5	1630 m (1630)	–	19,5 / 19,3	–	54,5 / 55,0	C_5F_9Br
(IIe)	52–53 (21)	1670 m	1835 s	24,3 / 24,3	–	68,6 / 69,8	$C_9F_{16}O_2$
(IIf)	73–74	1690 m	–	24,1 / 24,0	–	76,1 / 76,0	C_7F_{14}
(IIIa)	96–98	1645 m, 1660 sh	–	30,3 / 30,5	1,90 / 1,82	61,6 / 61,9	$C_7H_5F_9O$
(IIIb)	127–128	1635 m, 1643 sh	–	28,4 / 28,7	1,45 / 1,33	64,0 / 65,7	$C_9H_5F_{13}O$
(XVIIIa)	63–65 (17)	1675 sh (1672) (*Z*) 1690 w (1690) (*E*)	1740 s (1735) 1820 s (1820)	36,1 / 36,8	2,67 / 2,75	38,8 / 38,8	$C_9H_8F_6O_4$
(XVIIIb)	128–130 (*Z*) 123–125 (*E*)	1691 w (1687) (*Z*) 1711 sh (1708) (*E*)	1725 s (1730) (*Z*) 1740 s (1739) (*E*)	41,7 / 42,0	4,04 / 4,03	38,0 / 38,0	$C_7H_8F_4O_2$
(XVIIIc)	52–54 (11–12)	1640 sh (1635) (*Z*) 1652 m (1654) (*E*)	1740 s (1741) 1730 sh	38,9 / 38,8	3,74 / 3,72	26,4 / 26,3	$C_7H_8ClF_3O_2$
(XXI) †	mp 194–196	1570 s, 1580 s		68,6 / 68,4	4,74 / 4,70	14,6 / 14,8	$C_{22}H_{18}F_3OP$

*Found: Br 25.0%. Calculated: 25.7%.
†Found: P 8.26%. Calculated: 8.02%.

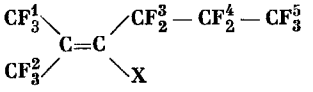
TABLE 2. NMR and Mass Spectra of 2-Substituted Perfluoroisopentenes



Compound	X	^{19}F NMR spectrum					Mass spectrum
		chemical shift, ppm			J, Hz		
		F^1 (qq)	F^2 (q)	F^3 (q)	F^1-F^2	F^1-F^3	
(IIa)	CF_3CO_2 *	−16,9	−15,8	−12,0	9,3	13,8	325, 0,04, $(M-F)^+$; 316, 1,0, $(M-CO)^+$; 297, 1,6, $(M-COF)^+$; 231, 1,6, $(M-CF_3COO)^+$; 209, 14,4, $C_5F_7O^+$; 159, 26,9, $C_4F_5O^+$; 97, 35,6, CF_3CO^+; 69, 100, CF_3^+.
(IIc)	Cl	−18,1	−15,6 †	−14,9 †	10,9	15,2	266, 10,3, M^+; 247, 14,6, $(M-F)^+$; 197, 36,5, $(M-CF_3)^+$; 109, 16,7, $C_3F_2Cl^+$; 93, 21,9, $C_3F_3^+$; 69, 100, CF_3^+.
(IId)	Br	−18,6	−16,0	−17,6	10,5	15,0	310, 42,3, M^+; 291, 23,0, $(M-F)^+$; 241, 22,6, $(M-CF_3)^+$; 231, 29,1, $(M-Br)^+$; 181, 35,2, $(M-CF_2Br)^+$; 143, 23,5, $C_4F_5^+$; 93, 28,2, $C_3F_3^+$; 69, 100, CF_3^+.
(IIIa)	EtO ‡	−18,9	−17,7	−12,5	9,8	14,0	276, 0,3, M^+; 261, 0,3, $(M-Me)^+$; 229, 4,1, $(M-C_2H_4F)^+$; 209, 7,0, $C_5H_7O^+$; 159, 8,9, $C_4F_5O^+$; 69, 15,2, CF_3^+; 29, 100, $C_2H_5^+$; 27, 27,8, $C_2H_3^+$.

*CF_3CO_2: −1.3 s.
†F^2 and F^3 qq, $J_{2-3} \approx 1$ Hz.
‡PMR spectrum: 1.0 br. t (CH_3) and 3.8 br. q (CH_2); ($J_{CH_3-CH_2}$ = 7.2 Hz).

TABLE 3. NMR and Mass Spectra of 3-Substituted Perfluoroisoheptenes



Compound	X	^{19}F NMR spectrum									Mass spectrum
		chemical shift, ppm					J, Hz				
		F^1	F^2	F^3	F^4	F^5	F^1-F^2	F^1-F^3	F^1-F^4	F^3-F^5	
(IIe)	$CF_3{}^8CF_2{}^7CF_2{}^6CO_2$ *	−19,4 t.t.q	−16,0 br.q	+34,7 br.q.q	+47,0 br.q	+4,7 t	10,5	20,6	9,9	10,3	525, 0,4, $(M-F)^+$; 497, 0,1, $(M-COF)^+$; 425, 0,1, $(M-C_2F_5)^+$; 375, 0,2, $(M-C_3F_7)^+$; 331, 1,4, $(M-C_3F_7COO)^+$; 309, 2,6, $C_7F_{11}O^+$; 197, 21,7, $C_3F_7CO^+$; 169, 100, $C_3F_7^+$; 100, 10,3, $C_2F_4^+$; 69, 88,4, CF_3^+.
(IIf)	F^6 †	−19,6 d.d.t.q	−16,7 d.q	+37,9 br.d.q.q.	+49,2 br.dq	+5,1 d.t	9,8	~20	7,5	9,6	350, 0,4, M^+; 331, 32,7, $(M-F)^+$; 231, 46,9, $(M-C_2F_5)^+$; 181, 82,7, $C_4F_7^+$; 119, 32,7, $C_2F_5^+$; 93, 18,4, $C_3F_3^+$; 69, 100, CF_3^+.
(IIIb)	EtO ‡	−20,6 t.t.q	−17,3 q	+34,0 br.q.q	+46,0 m	+4,4 t	10,1	20,2	6,5	10,0	376, 0,2, M^+; 361, 0,2, $(M-Me)^+$; 329, 2,3, $(M-C_2H_4F)^+$; 309, 6,7, $(M-C_2H_5F_2)^+$; 159, 6,2, $C_4F_5O^+$; 69, 11,4, CF_3^+; 29, 100, $C_2H_5^+$; 27, 22,0, $C_2H_3^+$.

*+47.4 br. q (F^6), +49.9 br. s (F^7), +4.6 t (F^8), J_{6-8} = 8.5 Hz.
†+19.7 m (F^6), J_{2-6} = 32.0, J_{4-6} = 10.9, J_{5-6} = 2.3, $J_{1-6} \approx 10$ Hz.
‡ PMR spectrum: 1.1 br. t (CH_3), 4.0 br. q (CH_2), $J_{CH_3-CH_2}$ = 6.5 Hz.

TABLE 4. NMR and Mass Spectra of Ethyl Esters of β-Substituted α-Methyl-γ,γ,γ-trifluorocrotonic Acids

CF_3^1 \ $C{=}C(CH_3^2)COOCH_2^3CH_3^4$ / X

Compound	X	Isomer	^1H and ^{19} NMR spectra							Mass spectrum
			Chemical shift, ppm					J, Hz		
			F^1	F^5	H^2	H^3 (q)	H^4 (t)	F^1-H^2	H^3-H^4	
(XVIIIa)	$CF_3{}^5CO_2$	*Z*	−12,9 q	−2,4 s	1,85 q	3,94	0,93	2,1	7,2	294, 2,0, M^+; 266, 1,8 $(M-C_2H_4)^+$; 249, 21,9, $(M-OEt)^+$; 221, 9,7, $(M-CO_2Et)^+$; 152, 52,2, $(M-CF_3CO_2Et)^+$; 83, 100, $C_4H_3O_2^+$; 69, 75,6, CF_3^+; 29, 80,6, $C_2H_5^+$; 27, 32,8, $C_2H_3^+$.
		E	−10,9 q	−2,4 s	1,62 q	3,98	0,97	1,9	7,2	
(XVIIIb)	F^5	*Z* *	−10,3 dq	+42,2 br.q.q	1,9 dq	4,2	1,2	2,5	7,0	200, 0,1, M^+; 185, 0,6, $(M-Me)^+$; 173, 0,7, $(M-C_2H_3)^+$; 155, 22,1, $(M-OEt)^+$; 77, 27,7, $C_3F_2H_3^+$; 57, 19,6, $C_3H_2F^+$; 45, 19,6, $C_2H_5O^+$; 29, 100, $C_2H_5^+$; 27, 41,9, $C_2H_3^+$.
		E †	−8,7 dq	+50,8 qq	1,8 qdq	4,1	1,1	1,9	7,2	200, 1,8, M^+; 185, 3,6, $(M-Me)^+$; 172, 4,7, $(M-C_2H_4)^+$; 155, 100, $(M-OEt)^+$; 136, 11,0, $(M-C_2H_2F_2)^+$; 132, 14,2, $(M-C_2H_6F_2)^+$; 131, 18,6, $(M-CF_3)^+$; 77, 53,8, $C_3H_3F_2^+$; 57, 23,8, $C_3H_2F^+$; 45, 24,4, $C_2H_5O^+$; 29, 63,1, $C_2H_5^+$; 27, 30,2, $C_2H_3^+$.
(XVIIIc)	Cl	*Z*	−15,7 q	−	2,13 q	4,28 and 4,24	1,29 and 1,26	2,4	7,1	216, 3,6, M^+; 201, 1,7, $(M-Me)^+$; 196, 2,5, $(M-HF)^+$; 188, 5,3, $(M-C_2H_4)^+$; 181, 6,4, $(M-Cl)^+$; 171, 75, $(M-OEt)^+$; 148, 15,6, $(M-C_2H_6F_2)^+$; 143, 18,6, $(M-COOEt)^+$; 93, 23,0, $C_3H_3ClF^+$; 57, 12,1, $C_3H_2F^+$; 45, 17,1, $C_2H_5O^+$; 39, 23,6, $C_3H_3^+$; 29, 100, $C_2H_5^+$; 27, 32,7, $C_2H_3^+$.
		E	−12,7 q	−	2,09 q			1,7	7,1	

*J_{1-5} = 7.0, J_{2-5} = 4 Hz.
†J_{1-5} = 8.8, J_{2-5} = 4 Hz.

TABLE 5. NMR and Mass Spectra of Diethyl Esters of α-Ethyl-(XIII) and α-Acetylhexafluoroisopropylphosphonic Acid (XV) and 1,1-Bis(trifluoromethyl)allene (XVI)

Compound	^{19}F NMR		PMR		Mass spectrum*	
	ppm	J, Hz	δH^1, ppm	J, Hz	m/z, tentative assignment	metastable ions; tentative fragmentation
(XIII)	−14,7 d	5,5(F−P)	1,9 dq	14,4(H^1−P) 7,3(H^1−H^2)	317, $(M+H)^+$; 315, $(M-H)^+$; 301, $(M-Me)^+$; 289, $(M-C_2H_3)^+$; 288, $(M-C_2H_4)^+$; 261, $(M-C_4H_7)^+$; 243, $(M-C_4H_9O)^+$; 241, $(M-C_4H_8F)^+$; 233, $(M-C_6H_{11})^+$; 232, $(M-C_6H_{12})^+$; 215, $(M-C_6H_{13}O)^+$; 212, $(M-C_6H_{13}F)^+$; 195, $C_3HF_5O_2P^+$; 145, $C_4H_2F_5^+$; 141, $C_5H_5F_4^+$; 138; 137, $(EtO)_2PO^+$; 111; 109, $EtOPOOH^+$; 101; 93, $C_3F_3^+$; 91, $C_2H_4O_2P^+$; 82, $(HO)_3P^+$; 81, $(HO)_2PO^+$; 69, CF_3^+; 65, $(HO)_2P^+$; 47, $C_2H_4F^+$; 45, $C_2H_5O^+$; 43, $C_2H_3O^+$; 29, $C_2H_5^+$; 27, $C_2H_3^+$.	236,5; 288 $\xrightarrow{-C_2H_3}$ 261 208,0; 261 $\xrightarrow{-C_2H_4}$ 233 193,8; 232 $\xrightarrow{-HF}$ 212 177,0; 215 $\xrightarrow{-HF}$ 195 76,0; 109 $\xrightarrow{-H_2O}$ 91
(XV)	−18,3 d	5,2(F−P)	2,4 br.s	–	330, M^+; 303, $(M-C_2H_3)^+$; 288, $(M-CH_2CO)^+$; 285, $(M-EtO)^+$; 261, $(M-C_4H_5O)^+$; 257, $(M-C_4H_9O)^+$; 233, $(M-C_6H_9O)^+$; 232, $(M-C_6H_{10}O)^+$; 213, $(M-C_6H_{10}FO)^+$; 212, $C_3H_2F_5O_3P^+$; 137, $(EtO)_2PO^+$; 109, $EtOPOOH^+$; 93, $C_3F_3^+$; 81, $(HO)_2PO^+$; 65, $(HO)_2P^+$; 43, $MeCO^+$; 29, $C_2H_5^+$.	236,5; 288 $\xrightarrow{-C_2H_3}$ 261 208,0; 261 $\xrightarrow{-C_2H_4}$ 233 193,7; 232 $\xrightarrow{-HF}$ 212
(XVI)	−16,3 t	3,0(F−H)	5,95 h	3,1(H−F)	176, M^+; 157, $(M-F)^+$; 137, $(M-HF_2)^+$; 112, $C_3F_4^+$; 107, $(M-CF_3)^+$; 106, $(M-CHF_3)^+$; 88, $C_4H_2F_2^+$; 75, $C_3HF_2^+$; 69, CF_3^+; 64, $C_2H_2F_2^+$; 57, $C_3H_2F^+$; 38, $C_3H_2^+$.	119,5; 157 $\xrightarrow{-HF}$ 137

*Only the intense peaks are presented. We were unable to select satisfactory empirical formulas for some of the ions.

TABLE 6. Reaction of Acid Anhydrides and Halides RCOX with Hexafluoroisopropylidenetriethoxyphosphorane (I)

R	X	Reaction time, h	Principal final products, molar ratios											
			RCOF	RCOX	EtF	EtX	C_2H_4*	(IV)	(V)	(XIII)	(XIV)	(XV)	(XVI)	$(EtO)_3PO$
Me †	$MeCO_2$	18	1,0	–	Traces	0,7	Traces	–	0,3	0,2	0,4	–	–	–
Me	F	11	1,0	–	0,9	–	Traces	1,0	–	0,15	0,05	–	–	–
Me	Cl	7	1,0	0,5	–	2,2	–	0,9	Traces	–	1,3	0,15	0,7	1,0
Me	Br	4 days, 20°	1,0	0,1	–	1,6	–	1,0	Traces	–	0,4	0,4	0,1	0,5
Ph	$PhCO_2$	39	1,0	1,9	Traces	1,2	Traces	1,3	0,2	0,7	0,2	–	–	–
Ph	F	42	1,0	–	0,7	–	Traces	0,8	–	0,4	Traces	–	–	–
Ph	Cl	11	1,0	8,3	3,3	1,0	0,7	4,3	Traces	5,0	1,0	–	–	–
Ph	Br	11	1,0	0,5	0,4	1,0	Traces	1,9	Traces	0,4	Traces	–	–	–

*Identified only from the PMR spectrum (∿5 ppm, s).
†Small amounts of $(CF_3)_2CH_2$, $CF_3CH{=}CF_2$, and MeCOOH are formed in addition to the indicated products; the ^{19}F NMR spectrum contains unidentified signals at —16.3 (m), —13.6 (m), —5.1 (d) (J_{P-F} = 710 Hz), and +8.1 ppm (d) (J_{P-F} = 990 Hz).

c) The reaction of 6.93 g (21.9 mmole) of I and 3.87 g (29.2 mmole) of CF_3COCl for 49 days gave a mixture of IIc, IIa, IIIa, CF_3COCl, IV, V, $(EtO)_3PO$, and EtCl (1.0:0.4:0.2:0.3:0.2:0.2:1.3:0.7). Preparative GLC (column B, 50°C) gave 1.94 g (33.2%) of perfluoro-2-methyl-3-chloro-2-butene (IIc).

d) The reaction of 8.46 g (26.8 mmole) of I and 4.62 g (26.1 mmole) of CF_3COBr for 6 days gave a mixture of IId, IIa, I, IV, V. $(EtO)_3PO$, and EtBr (1.0:0.5:0.2:0.7:0.5:0.8:1.2). Preparative GLC (column A, 30°C) gave 2.82 g (34.7%) of perfluoro-2-methyl-3-bromo-2-butene (IId).

e) The reaction of 8.00 g (25.3 mmole) of I and 8.07 g (19.7 mmole) of $(n\text{-}C_3F_7CO)_2O$ for 60 days gave, after distillation, 10.70 g of a mixture of IIe, IIf, and $n\text{-}C_3F_7COOEt$ (1.0:0.7:2.1). Preparative GLC (column B, 130°C) gave 2.95 g (27.5%) of perfluoro-2-methyl-3-butyryloxy-2-hexene (IIe); the residue consisted of triethyl phosphate, unsaturated phosphonate IV, and diethyl fluorophosphate (V) (1.5:2.0:1.0).

f) The reaction of 10.97 g (34.7 mmole) of I and 8.01 g (37.1 mmole) of $n\text{-}C_3F_7COF$ for 40 days gave a mixture of IIf, IIIb, $n\text{-}C_3F_7COF$, $(EtO)_3PO$, V, and IV (1.0:0.8:0.3:0.9:0.7:0.3). Fractionation gave 4.94 g (40.7%) of perfluoro-2-methyl-2-hexene (IIf). Preparative GLC (column A, 70°C) of the residue from the fractionation gave 3.39 g (26.0%) of 3-ethoxyperfluoro-2-methyl-2-hexene (IIIb).

Reaction of Acetic and Benzoic Acid Anhydrides and Halides with Hexafluoroisopropylidenetriethoxyphosphorane (I). A mixture of RCOX (≈1 mmole) and ylide I (2-16% excess) was heated in a sealed ampul at 90-100°C until the starting ylide vanished, after which the mixture was analyzed by means of ^1H and ^{19}F NMR spectroscopy, GLC, and chromatographic mass spectrometry. Data on the reaction times and the compositions of the resulting mixtures are presented in Table 6.

Reaction of Trifluoroacetic Acid Anhydride and Halides with α-Carbethoxyethylidenetriphenylphosphorane (XVII). A sample of CF_3COX and ylide XVII were dissolved in CH_2Cl_2 in a sealed ampul, the NMR spectra were recorded, and the solution was heated. The volatile products were distilled in vacuo (1 mm) at 20-50°C into a trap (—78°C). Fractionation or preparative GLC gave Wittig reaction products (XVIIIa-c) in the form of mixtures of the Z and E isomers (the Z/E ratios were determined by NMR spectroscopy and GLC).

a) The reaction of 4.47 g (12.3 mmole) of XVII and 2.79 g (13.3 mmole) of $(CF_3CO)_2O$ in 9.12 g of CH_2Cl_2 at 20°C for 10 min gave a solution of phosphonium salt XXa (^{19}F NMR spectrum, ppm: —6.9 s and —3.7 s). After 11 h at 50°C the mixture yielded 2.61 g (72.1%) of ethyl α-methyl-β-trifluoroacetoxy-γ,γ,γ-trifluorocrotonate (XVIIIa) (Z/E =5).

b) The reaction of 35.47 g (97.87 mmole) of XVII and 20.56 g (177.2 mmole) of CF_3COF in 57.71 g of CH_2Cl_2 at 20°C for 15 min gave 18.05 g (92.2%) of ethyl α-methyl-β,γ,γ,γ-tetrafluorocrotonate (XVIIIb) (Z/E = 0.2) with bp 124-133°C (preparative GLC with column A at 80°C yielded the Z and E isomers). Workup of the residue yielded Ph_3PO with mp 152-157°C (from ethyl acetate).

c) The reaction of 21.89 g (60.4 mmole) of XVII and 13.51 g (102.0 mmole) of CF_3COCl in 35.67 g of CH_2Cl_2 at 50°C for 8 h gave 2.24 g (17.1%) of ethyl α-methyl-β-chloro-γ,γ,γ-trifluorocrotonate (XVIIIc) (Z/E = 1) and 7.51 g (42.3%) of trifluoroacetoxy-substituted ester XVIIIa (Z/E = 1) (isolated by means of preparative GLC with column B at 100°C). The reaction of 194.5 mg (0.536 mmole) of XVII and 123.5 mg (0.932 mmole) of CF_3COCl in 302.1 mg of CH_2Cl_2 at 20°C for 10 min gave a solution of phosphonium salt XXc [^{19}F NMR spectrum, ppm: —6.5 s and —2.7 s (excess CF_3COCl)]. After 2 h at 50°C, the mixture contained XVIIIc, XVIIIa, and EtCl (1.0:2.4:1.0) but did not contain starting ylide XVII (according to NMR spectroscopy and GLC).

d) The reaction of 2.3613 g (6.5155 mmole) of XVII and 1.1525 g (6.5142 mmole) of CF_3COBr in 4.4837 g of CH_2Cl_2 at 20°C for 10 min gave a solution of phosphonium salt XXd. ^{19}F NMR spectrum, ppm: —7.0 s. PMR spectrum, ppm: 7.4-7.8 m (≈20H), 5.28 s (CH_2Cl_2), 3.87 q (2H, J =7.3 Hz), 2.05 d (3H, J = 17.5 Hz), and 0.78 t (3H, J = 7.2 Hz). After 28 h at 50°C, the ampul was cooled, opened (pressure!), and distilled to give a mixture containing EtCl and EtBr (~1:1), CH_2Cl_2, and, probably, CH_2ClBr (PMR spectrum, ppm: 5.14 s). Extraction of the residue with hot ethyl acetate gave 1.97 g of a light-beige solid, recrystallization of which from heptane gave 1.82 g (72.3%) of α-trifluoroacetylethylidenetriphenylphosphorane (XXI) in the form of colorless crystals. NMR spectra (in CH_2Cl_2), ppm: ^1H 7.4-7.9 m (19H), 1.77 dq (3H), J_{H-P} = 16.5, J_{H-F} = 2.0 Hz; ^{19}F —8.0 m; $^{31}P-\{^1H\}$: +22.2 q, J_{P-F} = 3.1 Hz. Mass

spectrum: 386 (27.4), M^+; 317 (100), $(M - CF_3)^+$; 262 (6.2), PH_3P^+; 201 (7.3), Ph_2PO^+; 183 (30.7), $(C_6H_4)_2P^+$; 108 (12.4), PhP^+ or $C_4H_3F_3^+$; 77 (8.8), Ph^+; 51 (8.0), $C_4H_3^+$.

CONCLUSIONS

1. Perfluorocarboxylic acid anhydrides and halides undergo the Wittig reaction with stable phosphorus ylides that do not contain an α-hydrogen atom.

2. In contrast to other carbonyl compounds, perfluorocarboxylic acid anhydrides and halides undergo the Wittig reaction with hexafluoroisopropylidenetriethoxyphosphorane.

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ISOMERIZATION OF A PERFLUORO α-LACTAM TO A SUBSTITUTED CARBAMOYL FLUORIDE

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It is known [1] that α-lactams of the I type, which contain an H atom in the β position relative to the carbonyl group, undergo isomerization to amides of α,β-unsaturated acids with cleavage of the C—N bond and migration of β-H to N. This sort of transformation is unlikely for the perfluorinated analog (II) of the α-lactam. In fact, 1-perfluoro-tert-butyl-3,3-bis(trifluoromethyl)aziridin-2-one (II) remains unchanged when it is heated under more severe conditions than in the case of I [2], but it undergoes a different transformation, viz., isomerization to hexafluoroacetone perfluoropivalylimine (III) with cleavage of the C—C bond and migration of the perfluoro-tert-butyl group from N to the carbonyl C atom, under the influence of equimolar amounts to CsF [3].

We have found that α-lactam II is converted almost quantitatively to acid fluoride IV under the influence of catalytic amounts of tertiary amines. This new isomerization can be conceived of as the nucleophilic analog of isomerization of unfluorinated lactams: F^- is split out instead of H^+, characteristic (for α-lactam II) cleavage of the C—C bond occurs instead of cleavage of the C—N bond [3, 4], and the fluoride ion migrates to the carbonyl group (the rate of isomerization increases as the basicity of the amine increases)

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