Reaction of Disubstituted Ylides with Perfluoronitriles. A New Synthesis of 2-Substituted 3-Perfluoroalkyl-1,3-Dicarbonyl Compounds

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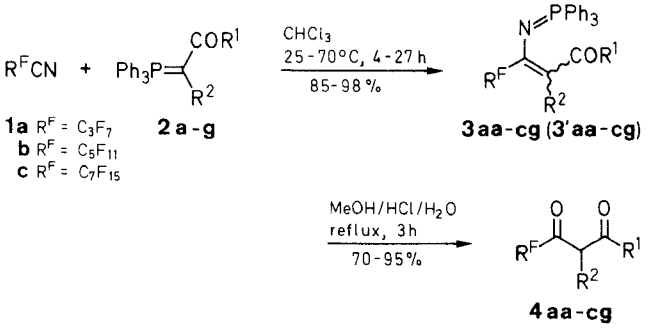
A new synthesis of some 2-substituted 3-perfluoroalkyl 1,3-dicarbonyl compounds by the reaction of stabilized phosphonium ylides with perfluoronitriles is reported. The ^{19}F-NMR data of these compounds are discussed.

Due to the easy formation of their enol forms,[1-6] fluoroalkylated 1,3-diketones [containing fluorinated groups: CF_3, CH_2F, HCF_2CF_2, C_3F_7, $H(CF_2)_4$] readily react with halogens,[7-9] amines,[10,11] thionyl chloride,[12] nitrogen dioxide,[13] and alkyl halides.[2,14,15] However, the yields of reactions with alkyl halides are generally low. Moreover, it should be mentioned that alkylation of 1,3-diketones containing long chain perfluoroalkyl groups, e.g. C_5F_{11} or C_7F_{15} proved to be unsuccessful under basic conditions.[16] Recently we have shown that the synthesis of 1,3-diketones possessing perfluoroalkyl groups is possible by Claisen's reaction[17-24] or by the reaction[25-27] between stabilized phosphonium ylides and perfluoronitriles.

We have now investigated the preparation of 2-substituted 3-perfluoroalkyl 1,3-diketones **4**. It is possible to consider the preparation of such derivatives **4**, by replacing one hydrogen atom at C-2 of unsubstitued iminophosphoranes by an alkyl chain via alkylation or by



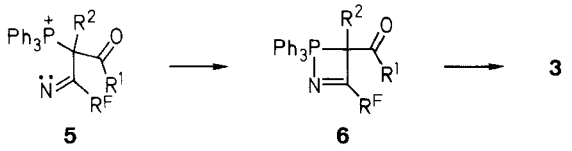
3, 4	R^1	R^2	R_F
aa	OMe	Me	C_3F_7
ba	OMe	Me	C_5F_{11}
ca	OMe	Me	C_7F_{15}
bb	OEt	Me	C_5F_{11}
cb	OEt	Me	C_7F_{15}
cc	OEt	Et	C_7F_{15}
cd	OEt	Pr	C_7F_{15}
ce	OEt	Bu	C_7F_{15}
cf	OEt	CH_2=$CHCH_2$	C_7F_{15}
cg	Me	Me	C_7F_{15}

Scheme A

starting directly from disubstituted phosphonium ylides.[28-31] The direct alkylation of iminophophoranes by an alkyl halide failed, however, the condensation of disubstituted phosphonium ylides with perfluoronitriles afforded iminophosphoranes **3** in good yields (85–98%).

Hydrolysis of **3** with methanolic hydrochloric acid furnished **4** (Scheme **A**).

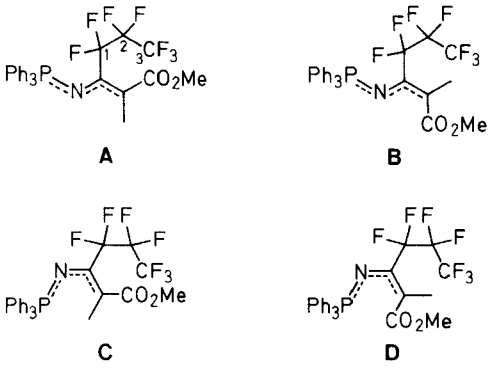
The study of the mechanism of addition of perfluoronitriles to ylides certainly requires further investigation.[32] In agreement with Ciganek[27] it is suggested that the products of the reaction between the nitrile and ylide can be accounted for by the stepwise formation of a betaine and a four-membered compound (intermediates **5** and **6**). (Scheme **B**).



Scheme **B**

The condensation reaction of disubstituted phosphonium ylides with perfluoronitriles was not stereospecific (Table 1). A mixture of products was obtained. Isomer ratios were estimated by the integrated intensities of peaks of 1-CF_2 (see Scheme **C**) in the ^{19}F-NMR spectra. The stereochemistry of the isomers **3** and **3'** was determined with the help of chemical shifts of 1-CF_2 group in the R^F chain. Indeed ^{19}F-NMR spectroscopic data of the mixture of isomers obtained show that signals for CF_3, and 3-CF_2...6-CF_2 groups are very close; the 1-CF_2 and 2-CF_2 groups show noteworthy variations related to the structure of each isomer. To elucidate the structure of compounds **3**, we used the iminophosphorane **3aa** with a short perfluoroalkyl chain (C_3F_7) as a model structure. As a matter of fact, the number of couplings in a long chain ($R_F > C_3F_7$) makes the measurement difficult, as each CF_2 or CF_3 group gives one multiplet that cannot be identified by a first order treatment.

Rotation around the N–C bond provides four different conformations for iminophosphorane **3aa** as shown in Scheme **C**. The probable structural assignments for the structural isomers were based on ^{19}F- and ^{31}P-NMR data.



Scheme **C**

The ^{31}P-NMR spectroscopic data of compound **3aa** show two isomers characterized by the $^5J_{PH}$ coupling 4.08 Hz and 4.85 Hz in a 56:44 molar ratio, respectively (Table 1). This result allowed us to attribute the structure **A** or **B** to the major product, the *trans* $^5J_{PH}$ coupling being always smaller than *cis* coupling.[33] Moreover, for this isomer there exists a $^4J_{PF}$ coupling 1.2 Hz indicating that the R^F chain and the phosphorus atom are *cis*; this $^4J_{PF}$ coupling does not exist for the minor product [structure **C** or **D**]. The structure of **3aa** was further supported by the ^{19}F-NMR spectrum. The signals corresponding to 1-CF_2 group were observed at $\delta = -107$ and -107.7, respectively. The shielding of the signal to $\delta = -107.7$ corresponding to 1-CF_2 group of the major product [structure **A** or **B**] may be attributed to the magnetic anisotropy effect of aromatic rings. The ^{1}H-NMR spectrum shows that the major isomer has a greater chemical shift than the

Table 1. Compounds **3** Prepared

Product	Reaction Conditions		Yield[a] (%)	Ratio[b] of **3**:**3'**	mp[c] (°C)	Molecular Formula[d]	MS (70 eV) *m/z* (M^+)
	Time (h)	Temp. (°C)					
3aa	24	25	85	44:56	viscous liquid	$C_{26}H_{21}F_7NO_2P$ (543.4)	543
3ba	4	40	98	40:60	61	$C_{28}H_{21}F_{11}NO_2P$ (643.4)	643
3ca	4	40	94	40:60	viscous liquid	$C_{30}H_{21}F_{15}NO_2P$ (743.5)	743
3bb	4	40	91	45:55	65	$C_{29}H_{23}F_{11}NO_2P$ (657.5)	657
3cb	4	40	97	37:63	64	$C_{31}H_{23}F_{15}NO_2P$ (757.5)	757
3cc	27	70	96	25:75	65	$C_{32}H_{25}F_{15}NO_2P$ (771.5)	771
3cd	27	70	85	47:53	viscous liquid	$C_{33}H_{27}F_{15}NO_2P$ (785.5)	785
3ce	27	70	95	44:66	viscous liquid	$C_{34}H_{29}F_{15}NO_2P$ (799.6)	799
3cf	27	70	90	39:61	56	$C_{33}H_{25}F_{15}NO_2P$ (783.5)	783
3cg	27	70	87	25:75	viscous liquid	$C_{30}H_{21}F_{15}NOP$ (727.5)	727

[a] The yield corresponds to mixture of isomers **3** and **3'** (*s-cis* + *s-trans*).
[b] Estimated from ^{19}F-NMR spectra.
[c] Melting points are uncorrected.
[d] Satisfactory microanalyses obtained: C ±0.30, H ±0.07, F ±0.35, P ±0.14.

minor isomer for methoxy groups. The chemical shift difference between methoxy groups in *s-trans* and *s-cis* isomers is probably due to shielding by phenyl groups. So the structure of the minor isomer must be **D**. This conformation (R^F chain and CH_3 group in *cis* position) explains a $^5J_{HF}$ homoallylic coupling of 4 Hz. In the case of the major isomer this $^5J_{FH}$ coupling is only of 1.5 Hz; such a difference can only be explained on the basis of a strong structural difference between the two isomers (R^F chain and CH_3 group in *trans* position). So we conclude that the structure of this *s-trans* isomer is **A**. On the basis of this structural study, we can attribute the *s-cis* structure to the isomer of compounds **3** whose 1-CF_2 group resonates at a lower field. The other isomer is the *s-trans* (Table 2).

During iminophosphorane hydrolysis, the subsequent formation of β-keto acids and a mixture of β-dicarbonyl compounds (keto and enol form) were observed. The β-

Table 2. Spectral Data of compounds **3**

Product	IR (KBr/film) $\nu(cm^{-1})$	^{19}F-NMR ($CDCl_3/CCl_3F$)[a] δ	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
3aa	1723, 1612, 1300–1100	**3aa:** 81 (t, 3F, CF_3), 107 (m, 2F, 1-CF_2), 125.4 (s, 2F, 2-CF_2) **3'aa:** 81.4 (t, 3F, CF_3), 107.7 (m, 2F, 1-CF_2), 122.9 (s, 2F, 2-CF_2)	**3aa:** 1.92 (m, CH_3), 3.26 (s, OCH_3) **3'aa:** 1.68 (m, CH_3), 3.77 (s, OCH_3), 7.6–7.4 (m, H_{arom})
3ba	1723, 1612, 1300–1100	**3ba:** 106.3 (m, 2F, 1-CF_2), 121.2 (m, 2F, 2-CF_2) **3'ba:** 81.3 (3F, CF_3), 107.2 (m, 2F, 1-CF_2), 118.8 (m, 2F, 2-CF_2), 123.9 (m, 2F, 3-CF_2), 126.7 (m, 2F, 4-CF_2)	**3ba:** 1.88 (m, CH_3), 3.24 (s, OCH_3) **3'ba:** 1.66 (m, CH_3), 3.56 (s, OCH_3), 7.63–7.38 (m, H_{arom})
3ca	1721, 1612, 1300–1100	**3ca:** 106.3 (m, 2F, 1-CF_2), 121 (m, 2F, 2-CF_2) **3'ca:** 81.4 (3F, CF_3), 107.1 (m, 2F, 1-CF_2), 118.6 (m, 2F, 2-CF_2), 122.6–123.2 (m, 6F, 3-5-CF_2), 126.7 (m, 2F, 6-CF_2)	**3ca:** 1.88 (m, CH_3), 3.25 (s, OCH_3) **3'ca:** 1.66 (m, CH_3), 3.62 (s, OCH_3), 7.63–7.38 (m, H_{arom})
3bb	1716, 1611, 1300–1100	**3bb:** 106.4 (m, 2F, 1-CF_2), 121.4 (m, 2F, 2-CF_2) **3'bb:** 81.4 (3F, CF_3), 107.4 (m, 2F, 1-CF_2), 119.2 (m, 2F, 2-CF_2), 123.4 (m, 2F, 3-CF_2), 126.8 (m, 2F, 4-CF_2)	**3bb:** 0.96 (t, $OCH_2C\underline{H}_3$, J = 7.1), 1.88 (m, CH_3), 3.76 (q, $OC\underline{H}_2CH_3$, J = 7.1) **3'bb:** 1.12 (t, $OCH_2C\underline{H}_3$, J = 7.1), 1.64 (m, CH_3), 4.08 (q, $OC\underline{H}_2CH_3$, J = 7.1), 7.63–7.38 (m, H_{arom})
3cb	1716, 1611, 1300–1100	**3cb:** 106 (m, 2F, 1-CF_2), 120.9 (m, 2F, 2CF_2) **3'cb:** 81.1 (3F, CF_3), 107 (m, 2F, 1-CF_2), 118.7 (m, 2F, 2-CF_2), 122.3–123.0 (m, 6F, 3-5-CF_2), 126.4 (m, 2F, 6-CF_2)	**3cb:** 0.97 (t, $OCH_2C\underline{H}_3$, J = 7.2), 1.89 (m, CH_3), 3.78 (q, $OC\underline{H}_2CH_3$, J = 7.2) **3'cb:** 1.18 (t, $OCH_2C\underline{H}_3$, J = 7.2), 1.64 (m, CH_3), 4.07 (q, $OC\underline{H}_2CH_3$, J = 7.2), 7.63–7.38 (m, H_{arom})
3cc	1716, 1611, 1300–1100	**3cc:** 106 (m, 2F, 1-CF_2), 121.1 (m, 2F, 2-CF_2) **3'cc:** 81 (3F, CF_3), 107.3 (m, 2F, 1-CF_2), 118.7 (m, 2F, 2-CF_2), 122.1–123.0 (m, 6F, 3-5-CF_2), 126.4 (m, 2F, 6-CF_2)	**3cc:** 0.91 (t, $CH_2C\underline{H}_3$, J = 7), 0.97 (t, $OCH_2C\underline{H}_3$, J = 7.1), 2.31 (m, $C\underline{H}_2CH_3$), 3.76 (q, $OC\underline{H}_2CH_3$, J = 7.1) **3'cc:** 0.71 (t, $CH_2C\underline{H}_3$, J = 7), 1.19 (t, $OCH_2C\underline{H}_3$, J = 7.1), 2.16 (m, $C\underline{H}_2CH_3$), 4.09 (q, $OC\underline{H}_2CH_3$, J = 7.1), 7.60–7.38 (m, H_{arom})
3cd	1716, 1608, 1300–1100	**3cd:** 106.5 (m, 2F, 1-CF_2), 121.1 (m, 2F, 2-CF_2) **3'cd:** 81 (3F, CF_3), 107.3 (m, 2F, 1-CF_2), 118.7 (m, 2F, 2-CF_2), 122.1–122.9 (m, 6F, 3-5-CF_2), 126.4 (m, 2F, 6-CF_2)	**3cd:** 0.79 (t, $CH_2CH_2C\underline{H}_3$, J = 7), 0.97 (t, $OCH_2C\underline{H}_3$, J = 7.1), 2.22 (m, $C\underline{H}_2CH_2CH_3$), 3.78 (q, $OC\underline{H}_2CH_3$, J = 7.1) **3'cd:** 0.7 (t, $CH_2CH_2C\underline{H}_3$, J = 7), 1.19 (t, $OCH_2C\underline{H}_3$, J = 7.1), 1.26 (m, $CH_2C\underline{H}_2CH_3$), 2.12 (m, $C\underline{H}_2CH_2CH_3$), 4.09 (q, $OC\underline{H}_2CH_3$, J = 7.1), 7.62–7.39 (m, H_{arom})
3ce	1716, 1607, 1300–1100	**3ce:** 106 (m, 2F, 1-CF_2), 121.0 (m, 2F, 2-CF_2) **3'ce:** 81.4 (3F, CF_3), 107.6 (m, 2F, 1-CF_2), 119.3 (m, 2F, 2-CF_2), 122.5–123.2 (m, 6F, 3-5-CF_2), 126.7 (m, 2F, 6-CF_3)	**3ce:** 0.78 (t, $CH_2CH_2CH_2C\underline{H}_3$, J = 7), 1.06 (t, $OCH_2C\underline{H}_3$, J = 7.2), 2.30 (m, $C\underline{H}_2CH_2CH_2CH_3$), 3.78 (q, $OC\underline{H}_2CH_3$, J = 7.2) **3'ce:** 0.72 (t, $CH_2CH_2CH_2C\underline{H}_3$, J = 7), 1–1.5 (m, $CH_2C\underline{H}_2CH_2CH_3$), 1.17 (t, $OCH_2C\underline{H}_3$, J = 7.2), 2.13 (m, $C\underline{H}_2CH_2CH_2CH_3$), 4.10 (q, $OC\underline{H}_2CH_3$, J = 7.2), 7.62–7.38 (m, H_{arom})
3cf	1707, 1635, 1604, 1300–1100	**3cf:** 106 (m, 2F, 1-CF_2), 121.1 (m, 2F, 2-CF_2) **3'cf:** 81.4 (3F, CF_3), 107.3 (m, 2F, 1-CF_2), 118.8 (m, 2F, 2-CF_2), 122.6–123.3 (m, 6F, 3-5-CF_2), 126.7 (m, 2F, 6-CF_2)	**3cf:** 0.99 (t, $OCH_2C\underline{H}_3$, J = 7.1), 3.17 (m, $C\underline{H}_2CH{=}CH_2$), 3.76 (q, $OC\underline{H}_2CH_3$, J = 7.1) **3'cf:** 1.18 (t, $OCH_2C\underline{H}_3$, J = 7.1), 2.96 (m, $C\underline{H}_2CH{=}CH_2$), 4.08 (q, $OC\underline{H}_2CH_3$, J = 7.1), 4.98 (m, $CH_2CH{=}C\underline{H}_2$), 5.5 (m, $CH_2C\underline{H}{=}CH_2$), 7.69–7.45 (m, H_{arom})
3cg	1697, 1608, 1300–1100	**3cg:** 105.7 (m, 2F, 1-CF_2), 121.2 (m, 2F, 2-CF_2) **3'cg:** 81.4 (3F, CF_3), 106.7 (m, 2F, 1-CF_2), 119.3 (m, 2F, 2-CF_2), 122.5–123.2 (m, 6F, 3-5-CF_2), 126.7 (m, 2F, 6-CF_2)	**3cg:** 1.81 (m, CH_3), 2.08 (s, $COCH_3$) **3'cg:** 1.50 (m, CH_3), 2.09 (s, $COCH_3$), 7.66–7.39 (m, H_{arom})

[a] ^{19}F-NMR data for $CF_2CF_2CF_2CF_2CF_2CF_2CF_3$ in products **3a–j**, δ from CCl_3F as an internal reference, taken negatively with increasing fields. Broad signals were observed for CF_2 groups at C-2 to C-5.

Table 3. Compounds **4** Prepared

Product	Yield (%)	Ratio[a] of Ketone : Enol	bp (°C)/Torr	n_D^{20}	Molecular Formula[b]	MS (70 eV) *m/z* (%)
4aa	70	81 : 19	40/580	1.3451	$C_8H_7F_7O_3$ (284.1)	285 (MH^+, 2.8), 59 (100)
4ba	92	95 : 5	57/30	1.3407	$C_{10}H_7F_{11}O_3$ (384.1)	385 (MH^+, < 1), 59 (100)
4ca	92	87 : 13	95/20	1.3376	$C_{12}H_7F_{15}O_3$ (484.2)	485 (MH^+, < 1), 115 (100)
4bb	91	85 : 15	52/20	1.3445	$C_{11}H_9F_{11}O_3$ (398.2)	399 (MH^+, 12.4), 129 (100)
4cb	86	90 : 10	104/15	1.3471	$C_{13}H_9F_{15}O_3$ (498.2)	499 (MH^+, 3.1), 129 (100)
4cc	95	91 : 9	117/15	1.3430	$C_{14}H_{11}F_{15}O_3$ (512.2)	513 (MH^+, 3.1), 43 (100)
4cd	92	97 : 3	91/1.5	1.3480	$C_{15}H_{13}F_{15}O_3$ (526.2)	527 (MH^+, 4.9), 157 (100)
4ce	94	98 : 2	81/2	1.3530	$C_{16}H_{15}F_{15}O_3$ (540.2)	541 (MH^+, 4.1), 171 (100)
4cf	93	87 : 13	90/1.5	1.3515	$C_{15}H_{11}F_{15}O_3$ (524.2)	525 (MH^+, 1.5), 109 (100)
4cg	87	70 : 30	102/13	1.3406	$C_{12}H_7F_{15}O_2$ (468.2)	469 (MH^+, 2), 99 (100)

[a] Estimated from ^{1}H-NMR spectra.
[b] Satisfactory microanalyses obtained: C ±0.32, H ±0.15, F ±0.33.

Table 4. Spectral Data of Compounds **4**

Product	IR (film) ν (cm^{-1})	^{19}F-NMR ($CDCl_3/CCl_3F$)[a] δ, J (Hz)	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
4aa	1769–1747, 1670, 1639, 1300–1100	81 (3F, CF_3), 120.2 (m, 2F, 2-CF_2, J = 293.8), 127 (s, 2F, 2-CF_2), 127.4 (2-CF_2 enol form)	keto ester: 1.48 (d, 3H, $CHC\underline{H}_3$, J = 7.1), 3.77 (s, 3H, OCH_3), 3.98 (q, 1H, CH, J = 6.9) *enol:* 1.91 (t, =CCH_3, J_{HF} = 2.87), 3.87 (s, OCH_3), 12.9 (t, OH, J_{HF} = 2.7)
4ba	1767, 1746, 1669, 1626, 1300–1100	81.7 (3F, CF_3), 120 (m, 2F, 1-CF_2, J = 289.9), 123.2–123.5 (m, 4F, 2,3-CF_2), 127 (m, 2F, 4-CF_2)	*keto ester:* 1.42 (d, 3H, $CHC\underline{H}_3$, J = 7.1), 3.72 (s, 3H, OCH_3), 3.94 (q, 1H, CH, J = 7) *enol:* 1.86 (t, =CCH_3, J_{HF} = 2.92), 3.83 (s, OCH_3), 12.9 (t, OH, J_{HF} = 2.8)
4ca	1766, 1746, 1669–1622, 1300–1100	82 (3F, CF_3), 120.4 (m, 2F, 1-CF_2, J = 288.5), 122.5–123.7 (m, 8F, 2-5-CF_2), 127.2 (m, 2F, 6-CF_2)	*keto ester:* 1.44 (d, 3H, $CHCH_3$, J = 7.1), 3.72 (s, 3H, OCH_3), 3.94 (q, 1H, CH, J = 7.1) *enol:* 1.88 (t, =CCH_3, J_{HF} = 3), 3.83 (s, OCH_3), 12.9 (t, OH, J_{HF} = 2.7)
4bb	1764, 1743, 1664, 1622, 1300–1100	81.2 (3F, CF_3), 119.4 (m, 2F, 1-CF_2, J = 288.6), 122.7 (m, 4F, 2,3-CF_2), 126.7 (m, 2F, 4-CF_2)	*keto ester:* 1.25 (t, 3H, $OCH_2C\underline{H}_3$, J = 7), 1.45 (d, 3H, $CHC\underline{H}_3$, J = 7), 3.92 (q, 1H, CH, J = 7), 4.2 (m, 2H, $OC\underline{H}_2CH_3$) *enol:* 1.3 (t, $OCH_2C\underline{H}_3$, J = 7), 1.9 (t, =CCH_3, J = 3), 4.27 (q, $OC\underline{H}_2CH_3$, J = 7), 13 (t, OH, J_{HF} = 2.7)
4cb	1764, 1746, 1664, 1620, 1300–1100	81.5 (3F, CF_3), 119.4 (m, 2F, 1-CF_2, J = 287.6), 122.6 (m, 8F, 2-5-CF_2), 126.7 (m, 2F, 6-CF_2)	*keto ester:* 1.25 (t, 3H, $OCH_2C\underline{H}_3$, J = 7), 1.47 (d, 3H, $CHC\underline{H}_3$, J = 7), 3.97 (q, 1H, CH, J = 7), 4.2 (m, 2H, $OC\underline{H}_2CH_3$) *enol:* 1.3 (t, $OCH_2C\underline{H}_3$, J = 7), 1.9 (t, =CCH_3, J = 3), 4.3 (q, $OC\underline{H}_2CH_3$, J = 7), 12.9 (t, OH, J_{HF} = 2.7)
4cc	1764, 1742, 1662, 1620, 1300–1100	81 (3F, CF_3), 119.4 (m, 2F, 1-CF_2, J = 292.5), 121.8–123.2 (m, 8F, 2-5-CF_2), 126.7 (m, 2F, 6-CF_2)	*keto ester:* 0.99 (t, 3H, $CHCH_2C\underline{H}_3$, J = 7), 1.23 (t, 3H, $OCH_2C\underline{H}_3$, J = 7), 2.02 (m, 2H, $CHC\underline{H}_2CH_3$), 3.8 (t, 1H, CH, J = 7), 4.19 (m, 2H, $OC\underline{H}_2CH_3$) *enol:* 13.04 (t, OH, J_{HF} = 2.6)
4cd	1764, 1742, 1661, 1620, 1300–1100	81.4 (3F, CF_3), 119.4 (m, 2F, 1-CF_2, J = 287.7), 121.8–123.3 (m, 8F, 2-5-CF_2), 126.7 (m, 2F, 6-CF_2)	*keto ester:* 0.90 (t, 3H, $CH_2CH_2C\underline{H}_3$, J = 7), 1.20 (t, 3H, $OCH_2C\underline{H}_3$, J = 7.2), 1.3 (m, 2H, $CH_2C\underline{H}_2CH_3$), 1.88 (m, 2H, $CH_2CH_2CH_3$), 3.83 (t, 1H, CH, J = 7), 4.16 (m, 2H, $OC\underline{H}_2CH_3$) *enol:* 13.08 (t, OH, J_{HF} = 2.6)
4ce	1764, 1742, 1661, 1620, 1300–1100	81.4 (3F, CF_3), 119.4 (m, 2F, 1-CF_2, J = 289.1), 121.8–123.8 (m, 8F, 2-5-CF_2), 126.7 (m, 2F, 6-CF_2)	*keto ester:* 0.92 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, J = 7), 1.24 (t, 3H, $OCH_2C\underline{H}_3$, J = 7), 1–1.95 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.95 (m, 2H, $C\underline{H}_2CH_2CH_2CH_3$), 3.85 (t, 1H, CH, J = 7), 4.2 (m, 2H, $OC\underline{H}_2CH_3$) *enol:* 13.06 (t, OH, J_{HF} = 2.6)
4cf	1764, 1743, 1671, 1640–1620, 1300–1100	81.4 (3F, CF_3), 119.4 (m, 2F, 1-CF_2, J = 288.2), 122.4–123.2 (m, 8F, 2-5-CF_2), 126.7 (m, 2F, 6-CF_2)	*keto ester:* 1.26 (t, 3H, $OCH_2C\underline{H}_3$, J = 7), 2.7 (m, 2H, $C\underline{H}_2CH{=}CH_2$), 3.95 (t, 1H, CH, J = 7), 4.2 (m, 2H, $OC\underline{H}_2CH_3$), 5.15 (m, 2H, $CH_2CH{=}C\underline{H}_2$), 5.7 (m, 1H, $CH_2C\underline{H}{=}CH_2$) *enol:* 13.23 (t, OH, J_{HF} = 2.7)
4cg	1762, 1716, 1674, 1591, 1300, 1100	81.4 (3F, CF_3), 114.8 (m, 1-CF_2, enol form), 120 (m, 2F, 1-CF_2, J = 289.8), 122–123 (m, 8F, 2-5-CF_2), 126.8 (m, 2F, 6-CF_2)	*ketone:* 1.37 (d, 3H, $CHC\underline{H}_3$, J = 7.1), 2.2 (1s, 3H, CH_3CO), 4.09 (q, 1H, CH, J = 7.1) *enol:* 1.93 (t, 3H, =CCH_3, J = 2.51), 2.23 (s, CH_3CO), 16.17 (s, OH)

[a] Recorded from CCl_3F as an internal reference, taken negatively with increasing fields. For numbering of CF_2 groups, see Table 1. The two fluorine atoms of 1-CF_2 group are diastereotropic. Broad two fluorine atoms of 1-CF_2 group are signals were observed for CF_2 groups at C-2 to C-5.

keto acids were formed by acid hydrolysis of the corresponding β-keto esters in small quantity (~ 5%). These products were identified by mass spectrometry. In β-keto esters the amount of enol form is low (Table 3). The ratio was determined by high resolution ^{1}H-NMR spectrometry. The enol form can be detected by infrared spectroscopy. Infrared spectra of the mixture of keto and enol forms in a β-keto ester showed some characteristic absorptions in the range of $\nu = 1767$ to $1620\,cm^{-1}$. The band seen at $\nu = 1767-1764\,cm^{-1}$, and the one of slightly higher intensity at $\nu = 1746-1742\,cm^{-1}$, are respectively ascribed to the ketone and ester groups of the keto ester. The enol form shows the C=O band at $\nu = 1671-1661\,cm^{-1}$ and C=C band at $\nu = 1640-1620\,cm^{-1}$, the shift of each band to lower frequencies being due to conjugation.

The experimental procedure is quite simple, and the structures of all compounds prepared are ascertained by MS, IR, ^{19}F and ^{1}H-NMR spectra (Tables 1–4).

Melting points were determined with Büchi apparatus and are not corrected. Spectroscopic data were recorded on the following instruments: MS: Nemag Ribermag R 10-10C Spectrometer; IR: Perkin-Elmer model 983 G Spectrometrer; ^{19}F-NMR: Bruker WH 90 Spectrometrer at 84.67 MHz; ^{1}H-NMR: Bruker 300 MHz Spectrometrer; ^{31}P-NMR: Bruker 200 MHz Spectrometer at 81 MHz.

Methyl 3-[(Triphenylphosphoranylidene)amino]-3-heptafluoropropylmethacrylate (3aa):

To an autoclave equiped with magnetic stirrer and charged with a solution of methyl 2-(triphenylphosphoranylidene)propionate (**2a**;[30,31,34] 6.97 g, 0.02 mol) in $CHCl_3$ (20 mL) at liquid N_2 temperature under vacuum is transferred heptafluoropropyl nitrile[35–38] (**1a**; 4.29 g, 0.022 mol). The autoclave is closed and allowed to come to r.t. After stirring for 24 h at r.t., the autoclave is opened and rinsed out with Et_2O (20 mL). The residue obtained after removal of the solvent is purified by column chromatography on silica gel (50 g, Merck 60, 70–230 mesh) using Et_2O as eluent; yield: 9.24 g (85%); viscous liquid (Tables 1 and 2).

Iminophosphoranes 3ba–cg; General Procedure:

A mixture of the appropriate ylide **2a–g**[30,31] (0.02 mol), perfluoronitrile **1a–c** (0.022 mol) and $CHCl_3$ (20 mL) is heated with stirring at 40 °C for 4 h for **3ba–cb**, and at 70 °C for **3cc–cg**. The solvent is removed under reduced pressure and the crude product is chromatographed on silica gel as described above for **3aa** (Tables 1 and 2).

Methyl 2-Methyl-3-oxo-3-pentadecafluoroheptylpropanoate (4ca); Typical Procedure:

To a solution of **3ca** (11.15 g, 0.015 mol) in MeOH (20 mL) are added conc. HCl (20 mL) and water (20 mL) and the mixture is refluxed for 3 h. After decantation **4ca** is obtained as a liquid pure enough to be directly used further in synthesis;[39] yield: 6.7 g (92%); bp 95 °C/20 Torr; $n_D^{20} = 1.3407$ (Tables 3 and 4).

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