Reaction of Cycloalkylphosphorane with Perfluoroalkylnitrile: A New Synthesis of Some Fluorine-Containing Cyclic 1,3-Diketones and Oxo Esters

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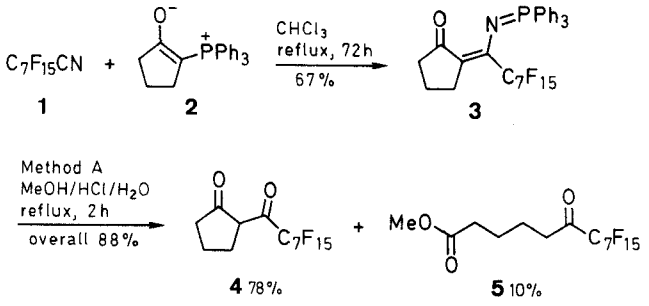
The preparation of some new perfluoroalkyl 1,3-dicarbonyl compounds is reported. The alcoholysis reaction of these 2-perfluoroalkanoylcycloalkanones in the presence or in the absence of base catalysis occurs, involving ring cleavage to yield fluorinated oxo esters.

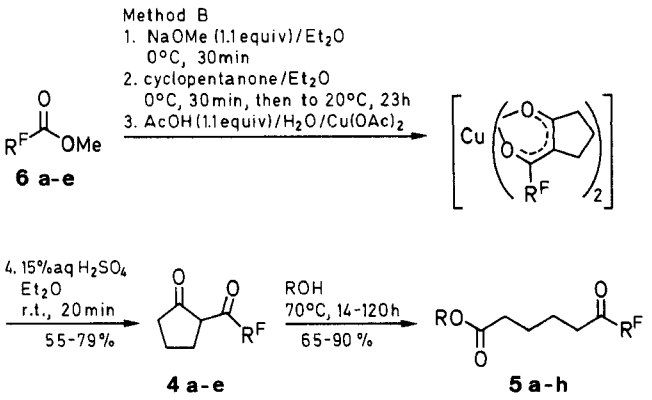
Various reports concerning the reactions of phosphorus ylides with nitriles have been published. While "non-stabilized" trialkyl- or triarylphosphoranes have been found to react in the presence of aliphatic or aromatic nitriles to yield ketones after hydrolysis,[1,2] in the presence of cyanogen or trifluoroacetonitrile only resins have been obtained; the use of trinitriles in the condensation with phosphonium ylides and subsequent hydrolysis of the adducts affords an iminopyrrolidine.[3] On the other hand, resonance-stabilized ylides do not react with aliphatic nitriles but reaction occurs in the presence of cyanogen or trifluoroacetonitrile. The isolated adducts seem to be stable and hydrolysis-resistant.[4] We have recently reported that the iminophosphoranes resulting from reactions between stabilized ylides and highly fluorinated nitriles were easily hydrolyzed leading to 1,3-dicarbonyl compounds.[5-8] Further studies on the reactions of phosphorus ylides with perfluoronitriles for the synthesis of 1,3-diarbonyl compounds enable us to report on a new method for preparing cyclic 1,3-dicarbonyl compounds[9-14] by condensing perfluoronitrile with an α-oxo phosphonium ylide[15,16] (Scheme 1).



Scheme 1

2-Pentadecafluorooctanoylcyclopentanone **4** and oxo ester **5** were obtained on reaction of iminophosphorane **3** with methanolic hydrochloric acid. Yields were of 78% and 10%, respectively. With a view to accounting for the formation of oxo ester **5**, cyclic 1,3-diketones were prepared using the Claisen reaction[9] (Scheme 2).

Compounds **4a–e** were treated with alcoholic hydrochloric acid, alcoholic orthophosphoric acid, pure orthophosphoric acid and pure alcohol. They were found to remain unchanged after heating (40°C) in pure orthophosphoric acid, but ring cleavage occurred with primary and secondary alcohols to give a mixture including



4, 6	R^F	5	R	R^F	5	R	R^F
a	C_3F_7	**a**	Me	C_3F_7	**e**	Me	C_7F_{15}
b	C_5F_{11}	**b**	Me	C_5F_{11}	**f**	Et	C_7F_{15}
c	C_6F_{13}	**c**	$C_4F_9(CH_2)_2$	C_5F_{11}	**g**	*i*-Pr	C_7F_{15}
d	C_7F_{15}	**d**	Me	C_6F_{13}	**h**	Me	C_8F_{17}
e	C_8F_{17}						

Scheme 2

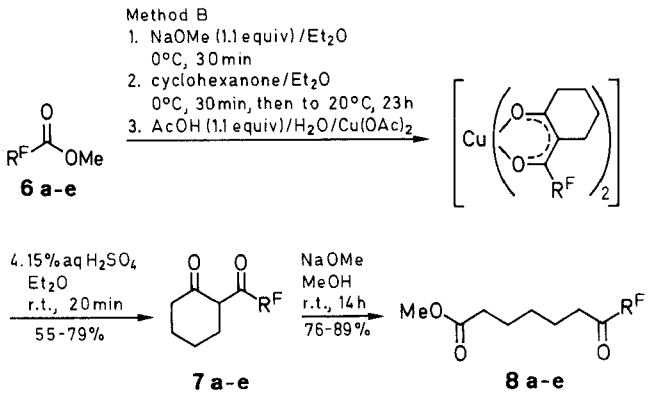
Table 1. 1,3-Diketones **4a–e** and **7a–e** Prepared

Product	Reaction Method	Yield (%)[a]	bp (°C)/ Torr	Molecular[b] Formula	MS (70 eV) *m/z* (M^+)
4a	B	57	45/30	$C_9H_7F_7O_2$ (280.1)	280
4b	B	70	48/0.8	$C_{11}H_7F_{11}O_2$ (380.1)	380
4c	B	74	63/0.8	$C_{12}H_7F_{13}O_2$ (430.1)	430
4d	A	78	75/0.8	$C_{13}H_7F_{15}O_2$ (480.1)	480
	B	79			
4e	B	68	81/0.7	$C_{14}H_7F_{17}O_2$ (530.2)	530
7a	B	56	76/30	$C_{10}H_9F_7O_2$ (294.2)	294
7b	B	64	63/0.6	$C_{12}H_9F_{11}O_2$ (394.2)	394
7c	B	64	71/0.6	$C_{13}H_9F_{13}O_2$ (444.2)	444
7d	B	64	83/0.6	$C_{14}H_9F_{15}O_2$ (494.2)	494
7e	B	65	103/0.6	$C_{15}H_9F_{17}O_2$ (544.2)	544

[a] Yield of isolated products.
[b] Satisfactory microanalyses obtained: C ±1.04, H ±0.10, F ±1.01.

essentially compounds **5a–h** in 65–90% and starting materials (cyclic ketone and perfluoroalkyl carboxylic acid ester) in small amounts (Scheme 2).

It is interesting to note that the alcoholysis yielding oxo esters **5a–h** is not affected by acidic catalysis. However, basic catalysts play a role in the reaction of perfluoroalkyl carboxylic acid ester with cyclohexanone, and the formation of both cyclic 1,3-diketones **7a–e** and accompanying oxo esters **8a–e** (in low yield, < 5%) is observed. This yield increases whenever the reaction is carried out at room temperature. Thus, sodium methoxide/methanol alcoholysis of 1,3-diketones **7a–e** at room temperature is completed after a reaction time of 14 hours and affords products **8a–e** (Scheme 3, Table 2).



6–8	a	b	c	d	e
R^F	C_3F_7	C_5F_{11}	C_6F_{13}	C_7F_{15}	C_8F_{17}

Scheme 3

Thus, oxo ester **5e** (or **5**) formed during the hydrolysis reaction of iminophosphorane **3** (Scheme 1) is due to the alcoholysis reaction of 2-pentadecafluorooctanoylcyclopentanone **(4d)** (or **4**) with methanol. The alcoholysis reaction of analogous compounds is reported.[17–20] The structures of the synthesized compounds were determined from the spectroscopic (Tables 1–4) and elemental analysis data: The ^1H NMR and ^{19}F NMR show that, for the most part, such compounds can be found as enol forms, and that while endocyclic double bonds are favored in cyclopentanone enols, exocyclic double bonds are favored in cyclohexanone enols. Moreover, the formation of a small amount of cyclohexanone enol exhibiting endocyclic double bonds was observed when the ^{19}F NMR spectra of products **7a–e** in $CDCl_3$ were recorded in the presence of a trace of sodium methoxide.

The ring-opening process for products **4a–e** and **7a–e** may be accounted for as follows: when mixed with alcohol, the alcohol molecule binds to the endocyclic enol form to give unstable hemiketals which undergo retro ene reaction to yield oxo esters **5a–h** and **8a–e** (Scheme 4).

Table 2. Oxo Esters **5a–h** and **8a–e** Prepared

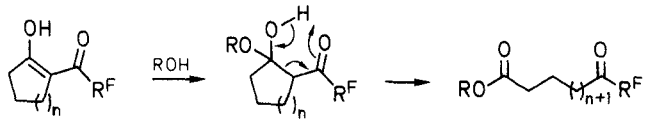
Product	Reaction Conditions		Yield (%)[a]	bp (°C)/ Torr	n_D^{20}	Molecular[b] Formula	MS (70 eV) *m/z* (%)
	Time (h)	Temp. (°C)					
5a	14	70	93	57/0.8	1.3622	$C_{10}H_{11}F_7O_3$ (312.2)	313 (MH^+, < 1), 312 (M^+, < 1), 281 ($M^+ - 31$,3), 143 (16), 111 (50), 55 (100)
5b	14	70	92	75/0.8	1.3512	$C_{12}H_{11}F_{11}O_3$ (412.2)	412 (M^+, 1), 381 ($M^+ - 31$,3), 143 (18), 111 (52), 55 (100)
5c	120	70	65	101/0.4	1.3406	$C_{17}H_{12}F_{20}O_3$ (644.2)	644 (M^+, < 1), 375 (3), 111 (88), 55 (100)
5d	14	70	90	81/0.8	1.3510	$C_{13}H_{11}F_{13}O_3$ (462.2)	462 (M^+, < 1), 431 ($M^+ - 31$,3), 143 (35), 111 (55), 55 (100)
5e	14	70	90	85/0.8	1.3520	$C_{14}H_{11}F_{15}O_3$ (512.2)	512 (M^+, 1), 481 ($M^+ - 31$,4), 143 (23), 111 (58), 55 (100)
5f	14	70	88	72/0.5	1.3488	$C_{15}H_{13}F_{15}O_3$ (526.2)	526 (M^+, 2), 481 ($M^+ - 45$,7), 157 (24), 111 (94), 55 (100)
5g[c]	60	70	90	78/0.2	1.3520	$C_{16}H_{15}F_{15}O_3$ (540.2)	540 (M^+, < 1), 481 ($M^+ - 59$,4), 129 (26), 111 (16), 43 (100)
5h[c]	14	70	90	79/0.2	1.3468	$C_{15}H_{11}F_{17}O_3$ (562.2)	562 (M^+, < 1), 531 ($M^+ - 31$,3), 143 (53), 111 (77), 55 (100)
8a	10	25	84	58/0.3	1.3690	$C_{11}H_{13}F_7O_3$ (326.2)	327 (MH^+, < 1), 295 ($M^+ - 31$,4), 157 (19), 125 (23), 69 (97), 55 (100)
8b	10	25	85	84/0.3	1.3551	$C_{13}H_{13}F_{11}O_3$ (426.2)	426 (M^+, < 1), 395 ($M^+ - 31$,3), 394 (7), 157 (22), 125 (24), 69 (100)
8c	10	25	80	69/0.2	1.3576	$C_{14}H_{13}F_{13}O_3$ (476.2)	476 (M^+, < 1), 445 ($M^+ - 31$,3), 444 (11), 157 (24), 125 (25), 69 (100)
8d	10	25	76	78/0.2	1.3530	$C_{15}H_{13}F_{15}O_3$ (562.2)	527 (MH^+, < 1), 526 (M^+, < 1), 495 $M^+ - 31$,3), 494 (3), 157 (28), 125 (31), 69 (100)
8e[c]	10	25	89	87/0.2	1.3490	$C_{16}H_{13}F_{17}O_3$ (576.2)	576 (M^+, < 1), 545 ($M^+ - 31$,3), 157 (27), 125 (26), 69 (100)

[a] Yield of isolated products.
[b] Satisfactory microanalyses obtained: C ±0.35, H ±0.06, F ±0.34.
[c] The products **5g**, **5h** and **8e** crystallized at r.t.

Table 3. Spectral Data of 1,3-Diketones **4a–e** and **7a–e**

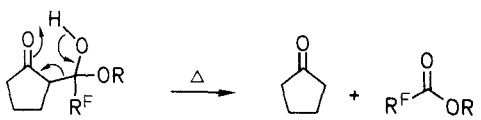
Product	IR[a] ν (cm^{-1})	^{19}F NMR ($CDCl_3/CCl_3F$) δ[b]	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)
4a	1686, 1628, 1300–1100	81.3 (3F, CF_3), 119.1 (q, 2F, 1-CF_2), 122.5 (s, 2F, 2-CF_2)	2.01 (m, 2H, CH_2), 2.53 (t, 2H, J = 7.9, CH_2), 2.80 (m, 2H), CH_2, 13.47 (br s, OH)
4b	1686, 1628, 1300, 1100	81.4 (3F, CF_3), 119.1 (m, 2F, 1-CF_2), 123.4 (m, 4F, 2-3-CF_2), 126.8 (m, 2F, 4-CF_2)	2.05 (m, 2H, CH_2), 2.54 (t, 2H, J = 7.9, CH_2), 2.81 (m, 2H, CH_2), 13.5 (br s, 3H, OH)
4c	1686, 1628, 1300, 1100	81.3 (3F, CF_3), 119.1 (t, 2F, 1-CF_2), 122.5 (m, 2F, 1-CF_2)	2.05 (m, 2H, CH_2), 2.54 (t, 2H, J = 7.9, CH_2), 2.81 (m, 2H, CH_2), 13.5 (br s, OH)
4d	1686, 1628, 1300–1100	81.3 (3F, CF_3), 118.9 (t, 2F, 1-CF_2), 122.3 (m, 4F, 2-3-CF_2), 123.2 (m, 4F, 4-5-CF_2), 126.6 (m, 2F, 6-CF_2)	2.05 (m, 2H, CH_2), 2.53 (t, 2H, J = 7.9, CH_2), 2.81 (m, 2H, CH_2), 13.5 (br s, OH)
4e	1686, 1628, 1300–1100	81.3 (3F, CF_3), 119.1 (m, 2F, 1-CF_2), 122.3 (m, 6F, 2-4-CF_2), 123.2 (m, 4F, 5-6-CF_2), 126.6 (m, 2F, 7-CF_2)	2.01 (m, 2H, CH_2), 2.54 (t, 2H, J = 7.9, CH_2), 2.82 (m, 2H, CH_2), 13.5 (br s, OH)
7a	1628–1570, 1300–1100	80.8 (3F, CF_3), 116.4 (q, 2F, 1-CF_2), 127.2 (s, 2F, 2-CF_2)	1.73 (m, 4H, CH_2), 2.53 (m, 4H, CH_2), 15.75 (br s, OH)
7b	1628–1570, 1300–1100	81.3 (3F, CF_3), 115.5 (m, 2F, 1-CF_2), 122.2 (m, 2F, 2-CF_2), 122.8 (m, 2F, 3-CF_2), 126.8 (m, 2F, 4-CF_2)	1.73 (m, 4H, CH_2), 2.54 (m, 4H, CH_2), 15.74 (br s, OH)
7c	1628–1570, 1300–1100	81.3 (3F, CF_3), 115 (t, 2F, 1-CF_2), 121.9 (m, 4F, 2-3-CF_2), 123.3 (m, 2F, 4-CF_2), 126.6 (m, 2F, 5-CF_2	1.74 (m, 4H, CH_2), 2.53 (m, 4H, CH_2), 15.74 (br s, OH)
7d	1628–1570, 1300–1100	81.3 (3F, CF_3), 115.5 (m, 2F, 1-CF_2), 121.6–123.3 (m, 8F, 2-5-CF_2), 126.6 (m, 2F, 6-CF_2)	1.73 (m, 4H, CH_2), 2.53 (m, 4H, CH_2), 15.75 (br s, OH)
7e	1628–1570, 1300–1100	81.3 (3F, CF_3), 115.6 (t, 2F, 1-CF_2), 122.2 (m, 2-5-CF_2), 123.3 (m, 2F, 6-CF_2), 126.7 (m, 2F, 7-CF_2)	1.71 (m, 4H, CH_2), 2.53 (m, 4H, CH_2), 15.8 (br s, OH)

[a] Only the most characteristic absorption bands are given.
[b] δ from CCl_3F, as an internal reference, taken negatively with increasing fields.



Scheme 4

However, in neutral alcoholysis, the mechanism of the formation of starting materials (cyclic ketone and perfluoroalkyl carboxylic acid ester) may be established by decomposing in boiling alcohols hemiketals formed by addition of alcohol to the more electrophilic carbonyl group (Scheme 5).



Scheme 5

This result appears to offer a means of differentiating between two carbonyl groups of different reactivity and shows the formation of oxo esters along the pathway (nucleophilic attack of alcohol on less reactive carbonyl) probably to be impossible.

Perfluorooctanenitrile (**1**)[21–23] and perfluoroalkyl carboxylic acid esters **6a–e**[22] were prepared following the literature procedures. The 2-oxocyclopentylidenetriphenylphosphorane **(2)** was prepared according to the literature procedure.[15] Et_2O was distilled over sodium metal prior to use. Other reagents and solvents were purchased from Aldrich Chemical Co. and used as received. Melting points were determined with Büchi apparatus and are not corrected. Spectroscopic data were recorded on the following instruments: MS: Nermag Ribermag R 10-10C Spectrometer; IR: Bruker IFS 45 Spectrometer; ^{19}F NMR: Bruker 200 MHz Spectrometer at 188.3 Hz; ^1H NMR: Bruker 200 MHz Spectrometer.

2-[1-(Triphenylphosphorylideneamino)perfluorooctylidene]cyclopentanone (3)

A mixture of perfluorooctanenitrile (**1**; 8.69 g, 0.022 mol), 2-oxocyclopentylidenetriphenylphosphorane (**2**; 6.88 g, 0.02 mol) and $CHCl_3$ (20 mL) was stirred and refluxed for 72 h. The solvent was removed under reduced pressure and the crude product was purified by chromatography on silica gel (50 g, Merck 60, 70–230 mesh) using Et_2O as eluent, yield: 10 g (67%) as a yellow solid, mp 66 °C.

$C_{31}H_{21}F_{15}NOP$	calc.	C 50.35	H 2.86	F 38.54	P 4.19
(739.4)	found	50.16	2.82	38.66	4.11

MS (70 eV): m/z (%) = 739 (M^+, 15), 262 (100).

IR (KBr): ν = 1666 (CO), 1528 (C=C), 1300–1100 cm^{-1} (C_7F_{15}).

^1H NMR (200 MHz, $CDCl_3$/TMS): δ = 1.54 (m, 2H, CH_2), 1.80 (t, 2H, J = 7.5 Hz, CH_2), 2.72 (m, 2H, CH_2), 7.37–7.74 (m, 15 H_{arom}).

^{19}F NMR ($CDCl_3/CCl_3F$): δ = 81.2 (3F, CF_3), −110.5 (2F, 1-CF_2), −120.6 (2F, 2-CF_2), −122.1 (4F, 3-4-CF_2), −123.1 (2F, 5-CF_2), −126.5 (2F, 6-CF_2).

Cyclic 1,3-Diketones 4a–e and 7a–e:

Method A (for **4d** from **3**): To a solution of iminophosphorane **3** (9 g, 0.012 mol) in MeOH (20 mL) was added conc. HCl (20 mL) and H_2O (20 mL) and the mixture was refluxed for 2 h. After decantation the residue obtained was purified by distillation under vacuum in the presence of a small amount of $CaCl_2$ (Table 1).

Method B (for **4a–e, 7a–e**): Perfluoroalkyl carboxylic acid ester **6a–e** (0.1 mol) was added dropwise, over 30 min, to a suspension of NaOMe (5.94 g, 0.11 mol) vigorously stirred and cooled at 0 °C by an ice-bath, in dry Et_2O (100 mL) under N_2. To this mixture maintained at 0 °C was then added dropwise, over 30 min, a solution of cyclopentanone or cyclohexanone (0.1 mol) in dry Et_2O (20 mL). Stirring was continued for 23 h, thus the mixture was slowly allowed to reach 20 °C. The mixture was then treated with a solution of glacial AcOH (6.6 mL, 0.11 mol) in H_2O (30 mL), followed by the addition of $Cu(OAc)_2$ (10 g) dissolved in H_2O (150 mL). The

Table 4. Spectral Data of Oxo Esters **5a–h** and **8a–e**

Product	IR[a] ν (cm^{-1})	^{19}F NMR ($CDCl_3/CCl_3F$) δ[b]	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)
5a	2959, 2870, 1757, 1740, 1300–1100	81 (t, 3F, CF_3), 121.7 (q, 2F, 1-CF_2), 127.1 (s, 2F, 2-CF_2)	1.69 (m, 4H, $(CH_2)_2$), 2.36 (t, 2H, J = 6.9, CH_2), 2.78 (t, 2H, J = 6, CH_2), 3.68 (s, 3H, OCH_3)
5b	2964, 2872, 1757, 1745, 1300–1100	81.3 (t, 3F, CF_3), 120.8 (m, 2F, 1-CF_2), 122.9 (m, 4F, 2-3-CF_2), 126.8 (m, 2F, 4-CF_2)	1.69 (m, 4H, $(CH_2)_2$), 2.36 (t, 3H, J = 6.9, CH_2), 2.78 (t, 2H, J = 6, CH_2), 3.68 (s, 3H, OCH_3)
5c	2959, 2870, 1757, 1747, 1300–1100	81.3 (t, 3F, CF_3), 81.6 (t, 3F, CF_3), 114.5 (m, 2F, 1-CF_2), 120.8 (m, 2F, 1-CF_2), 122.9 (m, 4F, 2-3-CF_2), 125 (m, 2F, 2-CF_2), 126.5 (m, 4F, 4-CF_2, 3-CF_2)	1.71 (m, 4H, $(CH_2)_2$), 2.38 (t, 2H, J = 6.9, $C_5F_{11}C(O)-C\underline{H}_2$), 2.5 (m, 2H, $C_4F_9C\underline{H}_2CH_2-$), 2.78 (t, 2H, J = 6, CH_2), 4.40 (t, 2H, J = 6.4, $C_4F_9CH_2C\underline{H}_2-$)
5d	2954, 2870, 1757, 1745, 1300–1100	81.3 (t, 3F, CF_3), 120.8 (m, 2F, 1-CF_2), 122 (m, 2F, 2-CF_2), 122.7 (m, 2F, 3-CF_2), 123.3 (m, 2F, 4-CF_2), 126.6 (m, 2F, 5-CF_2)	1.69 (m, 4H, $(CH_2)_2$), 2.36 (t, 2H, J = 6.9, CH_2), 2.78 (t, 2H, J = 6, CH_2), 3.68 (s, 3H, OCH_3)
5e	2956, 2872, 1760, 1745, 1300–1100	81.3 (t, 3F, CF_3), 120.8 (m, 2F, 1-CF_2), 121.9 (m, 2F, 2-CF_2), 122.6 (m, 4F, 3-4-CF_2), 123.2 (m, 2F, 5-CF_2), 126.6 (m, 2F, 6-CF_2)	1.69 (m, 4H, $(CH_2)_2$), 2.36 (t, 2H, J = 6.9, CH_2), 2.78 (t, 2H, J = 6, CH_2), 3.68 (s, 3H, OCH_3
5f	2954, 2872, 1759, 1636, 1300–1100	81.3 (t, 3F, CF_3), 120.8 (m, 2F, 1-CF_2), 121.9 (m, 2F, 2-CF_2), 122.6 (m, 4F, 3-4-CF_2), 123.2 (m, 2F, 5-CF_2), 126.7 (m, 2F, 6-CF_2)	1.26 (t, 3H, J = 7.2, CH_3), 1.68 (m, 4H, $(CH_2)_2$), 2.35 (t, 2H, J = 6.8, CH_2), 2.79 (t, 2H, J = 6.4, CH_2), 4.14 (q, 2H, J = 7.2, $OC\underline{H}_2CH_3$)
5g	2954, 2872, 1759, 1745, 1300–1100	81.2 (t, 3F, CF_3), 120.8 (t, 2F, 1-CF_2), 121.9 (m, 2F, 2-CF_2), 122.6 (m, 4F, 3-4-CF_2), 123.2 (m, 2F, 5-CF_2), 126.6 (m, 2F, 6-CF_2)	1.24 (d, 6H, J = 6.3, $(CH_3)_2CH$), 1.69 (m, 4H, $(CH_2)_2$), 2.32 (t, 2H, J = 6.8, CH_2), 2.79 (t, 2H, J = 6.2, CH_2), 5.02 (m, 1H, $(CH_3)_2C\underline{H}$)
5h	2959, 2870, 1757, 1742, 1300–1100	81.3 (t, 3F, CF_3), 120.8 (m, 2F, 1-CF_2), 121.8 (m, 2F, 2-CF_2), 122.4 (m, 6F, 3-5-CF_2), 123.2 (m, 2F, 6-CF_2), 126.6 (m, 2F, 7-CF_2)	1.69 (m, 4H, $(CH_2)_2$), 2.36 (t, 2H, J = 6.9, CH_2), 2.79 (t, 2H, J = 6.9, CH_2), 2.79 (t, 2H, J = 6.2, CH_3), 3.68 (s, 3H, OCH_3)
8a	2955, 2872, 1760, 1744, 1300–1100	81 (t, 3F, CF_3), 121.6 (q, 2F, 1-CF_2), 127.1 (s, 2F, 2-CF_2)	1.37 (m, 2H, CH_2), 1.70 (m, 4H, $(CH_2)_2$), 2.33 (t, 2H, J = 7.2, CH_2), 2.76 (t, 2H, J = 7, CH_2), 3.67 (s, 3H, OCH_3)
8b	2955, 2872, 1757, 1742, 1300–1100	81.2 (t, 3F, CF_3), 120.8 (t, 2F, 1-CF_2), 122.8 (m, 4F, 2-3-CF_2), 126.6 (m, 2F, 4-CF_2)	1.37 (m, 2H, CH_2), 1.70 (m, 4H, $(CH_2)_2$), 2.33 (t, 2H, J = 7.2, CH_2), 2.76 (t, 2H, J = 7, CH_2), 3.67 (s, 3H, OCH_3)
8c	2955, 2872, 1757, 1744, 1300–1100	81.2 (t, 3F, CF_3), 120.8 (t, 2F, 1-CF_2), 122 (m, 2F, 2-CF_2), 122.7 (m, 2F, 3-CF_2), 123.3 (m, 2F, 4-CF_2), 126.6 (m, 2F, 5-CF_2)	1.37 (m, 2H, CH_2), 1.70 (m, 4H, $(CH_2)_2$), 2.33 (t, 2H, J = 7.2, CH_2), 2.76 (t, 2H, J = 7, CH_2), 3.67 (s, 3H, OCH_3)
8d	2955, 2872, 1757, 1742, 1300–1100	81.2 (t, 3F, CF_3), 120.8 (t, 2F, 1-CF_2), 121.9 (m, 2F, 2-CF_2), 122.6 (m, 4F, 3-4-CF_2), 123.2 (m, 2F, 5-CF_2), 126.6 (m, 2F, 6-CF_2	1.37 (m, 2H, CH_2), 1.70 (m, 4H, $(CH_2)_2$), 2.33 (t, 2H, J = 7.2, CH_2), 2.76 (t, 2H, J = 7, CH_2), 3.67 (s, 3H, OCH_3)
8e	2955, 2872, 1757, 1744, 1300–1100	81.2 (t, 3F, CF_3), 120.8 (t, 2F, 1-CF_2), 121.9 (m, 2F, 2-CF_2), 122.4 (m, 6F, 3-5-CF_2), 123.2 (m, 2F, 6-CF_2), 126.6 (m, 2F, 7-CF_2)	1.37 (m, 2H, CH_2), 1.70 (m, 4H, $(CH_2)_2$), 2.33 (t, 2H, J = 7.2, CH_2), 2.76 (t, 2H, J = 7, CH_2), 3.67 (s, 3H, OCH_3)

[a] Only the most characteristic absorption bands are given.
[b] ^{19}F NMR data for $(CF_2)_nCF_3$ in products **5a–h** and **8a–e**, δ form CCl_3F, as an internal reference, taken negatively with increasing fields. Broad signals were observed for CF_2 groups at C-3 to C-5.

organic layer was separated, then washed with H_2O (3 × 20 mL) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was dried under vacuum. The copper chelate obtained was dissolved in Et_2O (100 mL), treated with 15% aq H_2SO_4 (100 mL), and stirred at r.t. for 20 min. The organic layer was separated, washed with H_2O (20 mL) and dried ($CaCl_2$). The Et_2O layer was then concentrated under reduced pressure and the resulting oil was purified by distillation (Table 1).

Oxo Esters 5a–h; General Procedure:
A solution of 1,3-diketone **4a–e** (0.01 mol) and the appropriate alcohol (5 mL) was heated and stirred for 14–120 h. Excess alcohol was then evaporated and the crude product distilled under vacuum in the presence of a small amount of $CaCl_2$ to yield products **5a–h** according to Table 2.

Oxo Esters 8a–e; General Procedure:
To a solution of 1,3-diketone **7a–e** (0.01 mol) in abs. MeOH (5 mL) was added NaOMe (0.2 g, 3.7 mmol). The mixture was stirred at r.t. for 14 h, then diluted with H_2O (10 mL) and conc. HCl (0.1 mL) and finally extracted with $CHCl_3$ (3 × 20 mL). The $CHCl_3$ layer was washed with H_2O (10 mL), then dried (Na_2SO_4). After evaporation, the residue was distilled under vacuum (Table 2).

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