Hexafluoroacetone dialkoxyphosphorylimines

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Reactions of hexafluoroacetone dialkoxyphosphorylimines with NH-, PH-, and CHnucleophiles, trimethyl phosphite, and N,N-dimethylaniline, and [2+4]-cycloaddition reaction have been studied.

Key words: hexafluoroacetone dialkoxyphosphorylimines, cyclopentadiene, NH-, PH-, CH-nucleophiles, addition to imines, [2+4]-cycloaddition, trimethyl phosphite, N,N-dimethylaniline.

Previously, 1-3 we developed convenient methods for the synthesis of hexafluoroacetone alkoxycarbonylimines and studied their transformations in reactions with nucleophiles and in cycloaddition reactions.

In a continuation of our studies of the synthesis and reactivity of N-substituted hexafluoroacetone imines containing electron-withdrawing groups at the N atom, in the present work, we report on the synthesis and reactions of hexafluoroacetone dialkoxyphosphorylimines.

O,O-Dialkyl N-hexafluoroisopropylidenephosphoramidates (2a,b) were synthesized by a method that differed from that described previously⁴ and included preparation of chloro derivatives 1a,b and subsequent dehydrochlorination (Scheme 1)



It was found that the active Cl atom in compounds **1a,b** can be replaced by an arylamino group (Scheme 2).

Compounds 22,b, which are hygroscopic liquids, react with NH- and PH-nucleophiles under mild conditions, like hexafluoroacetone alkoxycarbonylimines^{1,2} and acylimines, ^{5,6} but more vigorously, to give the products of addition at the C=N bond (Scheme 3, compounds Scheme 2

$$1 + 2 \cdot R' NH_2 \longrightarrow (RO)_2 P - NH - NHR'$$

R = Et, R' = 5-methylisoxazol-3-yl (a) $R = Pr^{i}$, R' = 4-FC₆H₄ (b)



	R	R'		R	R'
3c	Et	4,6-dimethoxy- pyrimidin-2-yl	3j 4a	Pr ⁱ Et	Bu ^s Ph
3d 3e 3f 3g	Et Et Et	2-CIC ₆ H₄CH₂ 4-MeC ₆ H₄SO₂NH PhNH PhNHC(S)NH	4b 4c 4d 5a	Et Pr ⁱ Pr ⁱ Et	Pr ⁱ O Ph EtO Me
3h 3i	Et Et	Bu ^s 4-FC₄H ₆ CH ₂	5b	Et	EtO

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3c-j, 4a-d). However, the electrophilic properties of the azomethine group are obviously insufficient for reactions with weak bases, for example, CH-nucleophiles. The addition of acetylacetone and ethyl malonate to imine 2b could be accomplished only in the presence of triethylamine; this gave C-alkylation products 5a,b in high yields (see Scheme 3).

Like hexafluoroacetone acylimines⁷ and alkoxycarbonylimines,³ compounds 2a,b proved to be active dienophiles. Their reactions with cyclopentadiene at room temperature afford stable [2+4]-cycloadducts, *N*-phosphoryl-2-azabicyclo[2.2.1]hept-5-enes (**6a,b**), in high yields (77-82%) (Scheme 4).



Substituted imines of hexafluoroacetone are known⁸ to form [1+4]-cycloadducts with trialkyl phosphites. We found that, as in the case of hexafluoroacetone ethoxycarbonylimine,⁹ imine 2b reacts with trimethyl phosphite according to an abnormal pathway resulting in the formation of N-phosphorylated enamine (7) rather than [1+4]-cycloaddition products (Scheme 5).



Unlike alkoxycarbonylimines, hexafluoroacetone diisopropoxyphosphorylimine 2b alkylates N, N-dimethylaniline on heating in the presence of TsOH into the *para*-position to give phosphoramidate (8) (Scheme 6).

Scheme 6



The structures of compounds 1-8 were confirmed by the ¹H, ¹⁹F, and ³¹P NMR spectra (Table 1). The yields, physicochemical properties, and the data of elemental analysis of the compounds obtained are presented in Table 2.

Thus, the variety of transformations of hexafluoroacetone N-dialkoxyphosphorylimines points to an increased electrophilicity of these compounds compared to that of hexafluoroacetone perfluoroacylimines.

Experimental

¹H, ¹⁹F, and ³¹P NMR spectra were recorded on a Bruker CXP-200 spectrometer (200, 188, and 81 MHz, respectively) (relative to internal tetramethylsilane and external CF₃COOH and 85% H₃PO₄) in CDCl₃ for compounds 1, 2, 3a-d, 3g, 3h, 3j, and 4-8 and in CD₃CN for 3e, 3f, and 3i. Melting points were determined in a glass capillary.

O, O-Diethyl N-[1-(trifluoromethyl)-2,2,2-trifluoro-1chloroethyl)]phosphoramidate (1a). A mixture of O, O-diethyl-N-(1-hydroxy-1-trifluoromethyl-2,2,2-trifluoroethyl)phosphoramidate⁴ (31.9 g, 0.1 mol) and SOCl₂ (16.7 g, 0.14 mol) was heated at reflux until the weight of the reaction mixture no longer changed. The excess of SOCl₂ was distilled off, and the residue was fractionated *in vacuo* to give 27.7 g of compound 1a.

Compound 1b was prepared in a similar way.

0,0-Diethyl N-(hexafluoroisopropylidene)phosphoramidate (2a). A solution of pyridine (4.74 g, 0.06 mol) in 12 mL of anhydrous ether was added dropwise with stirring at 20 °C to a solution of 1a (20.2 g, 0.06 mol) in 60 mL of anhydrous ether. The reaction mixture was stirred for 6 h, the precipitate was filtered off, the ether was evaporated, and the residue was fractionated *in vacuo* to give 14.1 g of compound 2a.

Compound 2b was prepared in a similar way.

O,O-Diethyl N-{1-{(5-methylisoxazol-3-yl)amino}-1trifluoromethyl-2,2,2-trifluoroethyl}phosphoramidate (3a). A solution of 3-amino-5-methylisoxazole (0.39 g, 4 mmol) in 12 mL of anhydrous ether was added dropwise with stirring at 20 °C to a solution of 1a (0.68 g, 2 mmol) in 20 mL of anhydrous ether. The reaction mixture was stirred for 3 h, the precipitate was filtered off, the ether was evaporated, and the residue was recrystallized from hexane to give 0.70 g of compound 3a.

Compound 3b was prepared in a similar way.

0,0-Diethyl N-{1-{(4,6-dimethoxypyrimidin-2-yl)amino]-1-trifluoromethyl-2,2,2-trifluoroethyl}phosphoramidate (3c). A solution of 2a (1.17 g, 3.9 mmol) in 10 mL of anhydrous ether was added dropwise with stirring to a cooled solution of 2-amino-4,6-dimethoxypyrimidine (0.6 g, 3.9 mmol) in 15 mL of anhydrous ether. After 4 h, the ether was evaporated and the residue was recrystallized from hexane to give 1.28 g of compound 3c.

Compounds 3d-j* were prepared in a similar way.

O,O-Diethyl N-[1-(diphenylphosphoryl)-1-trifluoromethyl-2,2,2-trifluoroethyl]phosphoramidate (4a). A solution of 2a (0.6 g, 2 mmol) in 10 mL of anhydrous ether was added with stirring to a solution of diphenylphosphinous acid in 40 mL of anhydrous ether. After 24 h, the reaction mixture was concentrated, and the residue was recrystallized from hexane to give 0.91 g of compound 4a.

Compounds 4b-d were prepared in a similar way.

0,0-Diethyl N-[2-acetyl-3-oxo-1,1-bis(trifluoromethyl)butyl]phosphoramidate (5a). A solution of acetylacetone

* Compounds 3f-i were synthesized in benzene solutions.

<u> </u>			s (1/11-)		
pour	- 	ſĤ	¹⁹ F		31p
1a	1.36 (t, 6 H, Me); 4.11 (m, 4 H, OCH ₂); 7.16 (d, 1 H, NH, J _H	p = 3.2) 0.70 (s)	(9.10 (s)
16	1.22 (d, 12 H, M	le); 4.55 (m, 2 H, OCH); 6.38 (d, 1 H, NH, J	$L_P = 3.2$) 0.96 (s)		1.70 (br.s)
2a	1.39 (t, 6 H, Me); 4.29 (m, 4 H, OCH ₂)	7.20 (s)	-:	5.70 (s)
25	1.30 (d, 6 H, Me	e); 1.36 (d, 6 H, Me); 4.81 (m, 2 H, OCH)	7.57 (s)	-7	7.62 (s)
3a	1.32 (L, 6 H, Me); 2.33 (s, 3 H, Me); 4.13 (m, 4 H, OCH ₂);	3.20 (s)	1.0	66 (br.s)
	4.50 (br.s, 1 H, 1	NH-P); 5.84 (s, 1 H, CH=); 6.03 (s, 1 H, NH)		
3b	1.27 (d, 12 H, M	le); 3.41 (br.s, 1 H, NH); 4.75 (m, 2 H, OCH)	-40.45 (br.	s, 1 F, 0.3	71 (s)
	5.52 (s, 1 H, NH	I); 6.83 (t, 2 H, C ₆ H ₄); 7.12 (m, 2 H, C ₆ H ₄)	FC ₆ H ₄); 2.	59 (s,	
			6 F, 2 CF ₃)	
3c	1.36 (t, 6 H, Me); 3.94 (s, 6 H, OMe); 4.14 (m, 4 H, OCH ₂);	1.80 (s)	0.5	51 (s)
	5.46 (s, 1 H, CH); 5.74 (br.s, 1 H, NH); 7.50 (br.s, 1 H, NH)			.,
3d	1.30 (t, 6 H, Me); 3.18 (t, 1 H, NHCH ₂ , $J_{H,H} = 6.0$);	1.50 (s)	2.4	40 (br.s)
	4.13 (m, 7 H, 2	$OCH_2 + CH_2 + NH$; 7.26 (m, 3 H, C ₆ H ₄);			
	7.54 (m. 1 H. C.	Ha)			
3e	1.38 (t. 6 H. Me): 2.44 (s. 3 H. MeC ₆ H ₄); 4.03 (g. 4 H. OCH ₂	; 3.40 (s)	2.0	65 (br.s)
	4.94 (br.s. 1 H.)	NH): 5.41 (br.s. 1 H. NH): 7.40 (d. 2 H. C.H.			()
	7.60 (brs 1 H]	$M = SO_{2}$; 7.77 (d. 2 H. C.H.)	,		
36	130 (t 6 H Me	$(4.17)(0.4 H OCH_{0})(4.96)(d.1 H NH_{-P})$	2.90 (s)	31	16 (s)
51	541 (brs 1 H 1	(4, 4, 1, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0,	2.90 (3)	5.0	10 (3)
	607 (A 2 H Ph	(11), 0.01 (0.03, 1.03, 1.03), 0.00 (0, 1.03, 0.03)			
3	1 A1 (t 6 H Ma	(1, 2, 10, 10, 10, 10) (1, 2, 10, 10, 10, 10, 10, 10, 10, 10, 10, 10	140 (c)	2 1	A (c)
56	578 (bre 1 H)	$M_{2} = P_{1} \cdot 7.28 \text{ (m} - 3.44 \text{ Ph}) \cdot 7.60 \text{ (d} - 2.44 \text{ Ph})$	1.40 (3)	2.1	14 (5)
	205 (brs 1 H 1	$M_{-}C=S(0, 2, 1)$ (m, 5 m, 1 m), 1.00 (0, 2 m, 1 g),			
շե	108 (+ 3 H CH	$-Me_{1} + 31$ (d 3 H CHMe $I_{1.1.1} = 7.0$): 1.53	16H 106 (n 3 F	- CF-) - 26	(e)
54	00 U Mai 167	$(m - 2) \mathbf{U} (CH, M_0) + 2.00 (d - 1) \mathbf{H} (H - 1.00), (1.55)$	(0) 124 (0.3 F	$C G_{3}, 2.0$	Jo (S)
	3 20 (m 1 H C	(11, 2 11, 0.12)	(\mathbf{q}, \mathbf{s}) (\mathbf{q}, \mathbf{s}) (\mathbf{q}, \mathbf{s})	, er 3,	
7:	1.30 (iii, 1 11, Ci	11, 4.11 (0.5, 1.11, 101-1), 4.52 (0., 4.11, 200)	14 -3831 (c)	10 25	26 (a)
.,		(1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1, 1	- P = F = F = 10.21 (S, 1)	ι Γ , 2.0	50 (S)
	$C_{H_2}, J_{H,H} = 0.0$); 4.10 (III, 4 II, 2 OCI 2), 4.30 (UIS, 1 II, NII II \. 7 49 (*) U O U \	$-r_{1}, r_{3}, r_{4}, r_{4}, r_{5}$	JJ (S,	
1 :		M_{4} , 7.40 (C, 2 G, C_{14}) M_{4} , 1.07 (4.2 G, C_{14}) M_{2} , 1.07 (4.2 G, C_{14}) M_{2} , 1.07 (4.2 G, C_{14})	7 6 1 1 22 (2 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2		15 (a)
ગ	0.84 (I, 3 H, CH	$2Me_{1}$; 1.07 (0, 5 H, CHMe, $J_{H,H} = 0.2$), 1.25	u, on, 1.25 (q, 5 r 86 (d. 1.52 (q, 5 r	$(, Cr_3); 0.7$	(2) (2)
	$OCHMe_2$; 1.28	$(a, 0 H, 0CHMc_2)$; 1.43 (III, 2 H, C <u>H</u> 2MC), 2.		·, Cr3,	
	$1 H, NH, J_{H,H}$	= 0.7); 3.03 (m, 1 n, Cn), 3.26 (01.5, 1 n, Nn	$-r_{F,F} = 0.3$		
4.	4.04 (m, 2 m, 2 m, 2 m		- 13.76 (c)	1.0	
43		(1, 4, 12) (11, 4 ft, $(0, 12)$, $(1, 3, 50)$ (00, 1 ft, 14ft, $(1, 3, 50)$), $(2, 50)$ (2, 7, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (00, 1 ft, 14ft, $(1, 50)$), $(2, 50)$ (1, 12ft, $(1, 50)$), $(2, 50)$ (1, 14ft, $(1, 50)$), $(1, 14ft, (1, 50)), (1, 14ft, $	H,P - 15.70 (S) DEV	i.c 2 t	(a, ir, r-inn);
	$0.0, J_{H,P} = 10.0$); 7.50—7.74 (m, 6 m, 2 m), 8.00 (m, 4 m, 2	F 11)	51	$\frac{102}{(0, 1, r, r-rn, r-rn, r)}$
41	1 20 1 45 (1	1 + 2 + 2 + 2 + 2 + 2 + 2 + 2 + 2 + 2 +	11.27 (a)	Jp J	p = 42.3
40	1.30-1.43 (m, 1-	$n_1 2 0 C n_2 Me + 2 0 C n_M e_2),$	11.57 (5)	1.2	(a, 1, P, P - (NH));
	4.10 (m, 5 H, 2	$OCH_2 + NH); 4.90 (m, 2 H, OCH)$		9.4	(a, 1 P, P-C, -14 P)
4-	1 24 74 12 11 14	L.). 4 55 (2 U CU): 5 10 (44 1 U NU	12.0 (a)	JP	p 24.0) io (a 1 p p NIU).
4C	1.24 (d, 12 H, W	(0); 4.55 (m, 2 m, Ch); 5.19 (00, 1 m, 10 m, 10, 10); 7.40 7.65 (m, 6 H, 10); 8.00 (m, 4)	L 200 (S)	0.4	(0, 1, 1, 2, 2 - (NH));
	${}^{2}J_{H,P} = 0.0, {}^{3}J_{H,P}$	p = 10.0; 7.40-7.65 (m, 6 H, Ph); 8.60 (m, 4	n, ru)	51	-32(0, 17, 7-70, -22)
	1 10 1 37 7		NU 11.26 (a)	JP	p = 23.0
40	1.18-1.36 (m,	$18 H_1 2 OCH_2 Me + 2 OCH Me_2); 3.97 (0, 1 H$	мп, 11.20 (S)	((a, 1P, P-NH);
	$J_{\rm H,P} = 14.0); 4.2$	$7 (m, 4 H, 0CH_2); 4.00 (m, 2 H, 0CH)$		11	.50 (a, 1 P, P-C.
~	1.22 1. 2.11 14		9 60 ()	JP	p = 34.2
54	1.32 (t, 6 H, Me); 2.42 (s, 6 H, Me); 4.12 (q, 4 H, OCH_2);	8.3U (S)	0.0	56 (or.s)
<i>c</i> .	4.58 (d, 1 H, CF	$J_{H,P} = 5.0, J_{H,C} = (37.7), 5.76 (00.8, 1.14, 1.14)$	7 10 (-)	0.4	(2 /)
20	1.32 (m, 12 H, M	$(m, 5 H, 2 CH_2 O - P + CH);$	7.19 (S)	U.t	53 (S)
	4.28 (m, 4 H, 2	$CH_2O=C$; 5.62 (Dr.s. 1 H, NH)			57.77
0a	1.31 (m, 6 H, M	e); 1.52 (d, 1 H, $C(7)$ H, $J = 10.0$); 2.16 (d, 1 h)	1, C(7)H, 8.31 (q, 3 f	$(Cr_3); 3.2$	50 (S)
	J = 10.0; 3.69 (or.s, $(H, U(4)H)$; 4.05 (m, 4 H, $U(H_2)$; 4.51	Dr.s, 16.25 (q, 3	r, Cr3,	
	1 H, C(1)H); 6	33 (br.s, 1 H, C(5)H); 6.69 (m, 1 H, C(6)H)	$J_{F,F} = 10.0$)	- / .
6b	1.24 (m, 12 H, 1	Me); 1.44 (d, 1 H, $C(7)$ H, $J = 8.0$); 2.05 (d, 1 H)	1, C(7)H, 8.04 (q, 3 h	$(CF_3);$ L:	5 (s)
	J = 8.0); 3.59 (b	r.s, 1 H, C(4)H; 4.38 (br.s, 1 H, C(1)H); 4.52 (m, 16.67 (q, 3	r, Cr ₃ ,	
_	2 H, OCH); 6.2	3 (d, 1 H, C(5)H); 6.63 (m, 1 H, C(6)H)	$J_{F,F} = 10.2$		•• •
7	1.25 (d, 12 H, M	(c); 2.77 (d, 3 H, Mc, $J_{H,P} = 8.8$);	-3.42 (m,	1 + C + C + 2; 3.1	13 (br.s)
	4.56 (m, 2 H, O	CH)	-1.57 (m,	$(F, CF_2);$	
			13.27 (dd,	$5 F, CF_3,$	
			${}^{4}J_{\rm F,F} = 9.5$	$J_{\rm F,F} = 22.0$	
8	1.20 (d, 6 H, M	e); 1.30 (d, 6 H, Me); 2.96 (s, 6 H, Me);	5.92 (s)	0.2	27 (s)
	4.58 (m, 2 H, O	CH); 6.70 (d, 2 H, C ₆ H ₄); 7.54 (d, 2 H, C ₆ H ₄)			

Table 1. ¹H, ¹⁹F, and ³¹P NMR spectra of compounds 1-8

Com- pound	Yield (%)	В.р./°С (р/Тогг)	n _D ²⁰	E. Ci	ound alculated	(%)	Molecular formula
		[M.p./°C]		С	Н	Р	
12	82.0	71 (1)	1.3858	<u>24.74</u> 24.90	<u>3.39</u> 3.28	<u>9.24</u> 9.17	C ₇ H ₁₁ ClF ₆ NO ₃ P
16	90.4	75 (0.7)	1.3870	<u>29.73</u> 29.57	<u>4.29</u> 4.14	<u>8,39</u> 8,47	C ₉ H ₁₅ ClF ₆ NO ₃ P
22	78.3	56—57 (1)	1.3629	<u>27.66</u> 27.92	<u>3.49</u> 3.35	<u>10.32</u> 10.28	$C_7H_{10}F_6NO_3P$
2₽	74.7	107-109 (10)	1.3694	<u>32.63</u> 32.84	<u>4.40</u> 4.29	<u>9.49</u> 9.41	C9H14F6NO3P
32	87.1	[108-109]		<u>33.27</u> 33.09	<u>3.88</u> 4.04	<u>7.86</u> 7.76	C ₁₁ H ₁₆ F ₆ N ₃ O ₄ P
3b	86.0	[85-86]	-	<u>41.10</u> 40.91	<u>4.72</u> 4.58	<u>7.11</u> 7.03	C ₁₅ H ₂₀ F ₇ N ₂ O ₃ P
3c	72.3	[48-49]	-	<u>34.00</u> 34.22	<u>4.45</u> 4.20	<u>6.71</u> 6.79	C ₁₃ H ₁₉ F ₆ N ₄ O ₅ P
3d	84.3	[54—55]		<u>38.12</u> 37.98	<u>4.13</u> 4.10	<u>6,94</u> 7.00	C ₁₄ H ₁₈ ClF ₆ N ₂ O ₃ P
3e	88.2	[94—95]		<u>34,36</u> 34.50	<u>4.30</u> 4.14	<u>6.30</u> 6.36	C ₁₄ H ₂₀ F ₆ N ₃ O ₅ PS
3f	85.3	[83-85]	~	<u>38.11</u> 38.15	<u>4.55</u> 4.43	<u>7.58</u> 7.57	$C_{13}H_{18}F_6N_3O_3P$
3g	91.0	[114-116]		<u>36.03</u> 35.90	<u>4.00</u> 4.09	<u>6.71</u> 6.61	C ₁₄ H ₁₉ F ₆ N ₄ O ₃ PS
3h	73.8	108 (1)	1.3980	<u>35.43</u> 35.30	<u>5.78</u> 5.66	<u>8.15</u> 8.28	$C_{11}H_{21}F_6N_2O_3P$
3i	83.9	[45-46]	*****	<u>39.25</u> 39.44	<u>4.20</u> 4.26	<u>7.32</u> 7.27	C ₁₄ H ₁₈ F ₇ N ₂ O ₃ P
Зј	89.4	[34-36]		<u>39.04</u> 38.81	<u>6.20</u> 6.26	<u>7.72</u> 7.70	$C_{13}H_{25}F_6N_2O_3P$
42	91.0	[122-124]		<u>45.51</u> 45.34	<u>4.12</u> 4.21	<u>12.43</u> 12.31	$C_{19}H_{21}F_6NO_4P_2$
4b	88.4	[60-61]	-	<u>33.27</u> 33.41	<u>5.23</u> 5.39	<u>13.35</u> 13.26	$C_{13}H_{25}F_6NO_6P_2$
4c	87.8	[98-100]	-	<u>47.22</u> 47.46	<u>4.89</u> 4.74	11.52 11.66	$C_{21}H_{25}F_6NO_4P_2$
4d	86.7	[59-61]		<u>33.63</u> 33.41	<u>5.52</u> 5.39	<u>13.15</u> 13.26	$C_{13}H_{25}F_6NO_6P_2$
5 a	85.6	[92—94]		<u>36.16</u> 35.92	<u>4.33</u> 4.52	<u>7.63</u> 7.72	C ₁₂ H ₁₈ F ₆ NO ₅ P
5 b*	88.2	~	1.4059	<u>36.67</u> 36.45	<u>4.99</u> 4.81	<u>6.81</u> 6.71	C ₁₄ H ₂₂ F ₆ NO ₇ P
62	81.7	93 (1)	1.4178	<u>39.00</u> 39.24	<u>4.56</u> 4.39	<u>8,30</u> 8.43	$C_{12}H_{16}F_6NO_3P$
6b	77.1	126-127 (1.5)	1.4154	<u>42,34</u> 42.54	<u>4.91</u> 5.10	<u>7.95</u> 7.84	C ₁₄ H ₂₀ F ₆ NO ₃ P
7	38.4	63-64 (1)	1.3881	<u>37.11</u> 36.93	<u>5.13</u> 5.27	<u>9.61</u> 9.52	C ₁₀ H ₁₇ F ₅ NO ₃ P
8	74.4	7677		<u>45.51</u> 45.33	<u>5.64</u> 5.60	<u>6.97</u> 6.88	$C_{17}H_{25}F_6N_2O_3P$

Table 2. Yields, physicochemical characteristics, and data of elemental analysis of compounds 1-8

* Compound 5b was isolated in a pure state without fractionation of the reaction mixture

(0.62 g, 6.2 mol) in 6 mL of anhydrous ether was added to a solution of 2a (1.88 g, 6.2 mmol) in 18 mL of anhydrous ether. After that, a catalytic quantity of triethylamine was added with stirring and cooling. After 24 h, a small amount of the precipitate was filtered off, the filtrate was concentrated, and the residue was recrystallized from hexane to give 2.14 g of compound 5a.

2-Diethoxyphosphoryl-3,3-bis(trifluoromethyl)-2azabicyclo[2.2.1]hept-5-ene (6a). A solution of 2a (4.88 g, 16.2 mmol) in 40 mL of anhydrous ether was added dropwise with stirring at 20 °C to a solution of cyclopentadiene (1.5 g, 22.7 mmol) in 30 mL of anhydrous ether. The reaction mixture was stirred for 4 h, the ether was evaporated, and the residue was fractionated to give 4.86 g of compound 6a.

Compound 5b was prepared in a similar way.

Compound 6b was prepared in a similar way.

0,0-Diisopropyl N-methyl-N-(pentafluoroisopropenyl)phosphoramidate (7). A solution of 2b (3.97 g, 12 mmol) in 15 mL of CH_2Cl_2 was added dropwise with stirring at 0 °C under argon over a period of 1 h to a solution of trimethyl phosphite (1.36 g, 11 mmol) in 10 mL of CH_2Cl_2 . The reaction mixture was warmed to room temperature with stirring and washed with water (4×10 mL). The organic layer was dried with Na₂SO₄, the solvent was evaporated, and the residue was fractionated to give 1.37 g of compound 7.

0,0-Diisopropyl N-[1-(4-dimethylaminophesyl)-1-trifluoromethyl-2,2,2-trifluoroethyl]phosphoramidate (8). A mixture of 2b (0.63 g, 1.9 mmol) and <math>N,N-dimethylaniline (0.23 g, 1.9 mmol) in 7 mL of anhydrous benzene was heated at 100 °C with a catalytic amount of TsOH in a sealed tube for 18 h. The solvent was evaporated and the residue was recrystallized from hexane to give 0.64 g of compound 8.

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