Synthesis of highly electrophilic fluorinated alkenyl phosphonates as new precursors of heterocyclic compounds

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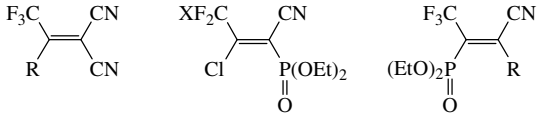
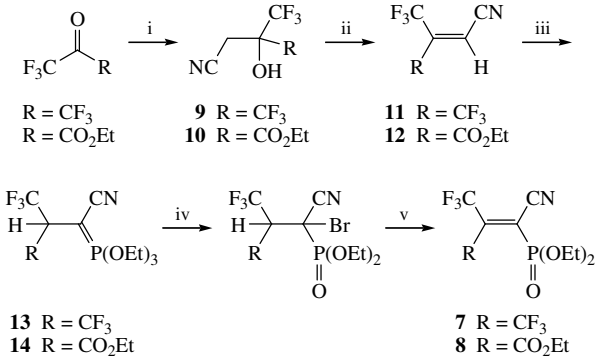
New approaches to the synthesis of highly electrophilic fluorinated alkenyl phosphonates as convenient precursors of fluorine-containing heterocyclic phosphonates have been developed.

Trifluoromethyl-substituted cyanoethylenes are convenient precursors for the synthesis of heterocyclic compounds.[1–7] For instance, 4-trifluoromethyl-substituted 1,4-dihydropyridines and 1,4-dihydropyrimidines exhibiting high insecticidal activity have been obtained from 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene **1** and its analogue, ethyl 3,3-dicyano-2-(trifluoromethyl)acrylate **2**.[5–7] The use of difluoromethyl- and difluorochloromethyl-substituted cyanoethylenes made it possible to synthesise heterocycles modified with corresponding fluorinated groups.[8] We have recently shown that 1-diethoxyphosphoryl-1-cyano-2-trifluoromethyl-2-chloroethylene **3** and its difluorochloromethyl analogue **4** can be used for the synthesis of fluorinated heterocyclic phosphonates.[9] Thus, fluorinated vinyl phosphonates[10,11] form an important class of synthons, which open new opportunities for studying the biological activity of fluorinated heterocycles[7,12,13] and searching for new biologically active phosphonates.[14–19] This work is devoted to the synthesis of highly electrophilic fluorinated vinyl phosphonates related to trifluoromethyl-substituted cyanoethylenes **1** and **2**.



1 R = CF_3
2 R = CO_2Me
3 X = F
4 X = Cl
5 R = CN
6 R = CO_2Me

The preparation of 1,1-dicyano-2-diethoxyphosphoryl-2-(trifluoromethyl)ethene **5** and methyl 2-cyano-3-diethoxyphosphoryl-4,4,4-trifluorocrotonate **6** by heating of corresponding vinyl chlorides with triethylphosphites has been reported.[20] Isomeric alkenes **7** and **8** containing a diethoxyphosphoryl group in the α-position with respect to the nitrile group have not been known. The first attempts to synthesise alkenes **7** and **8** failed. Condensation of either ethyl trifluoropyruvate or hexafluoroacetone with diethoxyphosphorylacetonitrile leads to elimination of the diethoxyphosphoryl group to give products of the Horner–Wittig reaction. The attempts to obtain alkene **7** similarly to alkenes **5** and **6**, *i.e.*, by heating of either the corresponding vinyl bromides or vinyl fluorides with triethylphosphite, also failed.



R = CF_3
R = CO_2Et
9 R = CF_3
10 R = CO_2Et
11 R = CF_3
12 R = CO_2Et
13 R = CF_3
14 R = CO_2Et
7 R = CF_3
8 R = CO_2Et

Scheme 1 *Reagents and conditions*: i, HO_2CCH_2CN, Py, 20 °C, 24 h; ii, $SOCl_2$, NEt_3, 20 °C, 24 h; iii, $P(OEt)_3$, –20 → 20 °C, 24 h; iv, Br_2, $CHCl_3$, –5 → 20 °C, 24 h; v, NEt_3, 0 → 20 °C, 24 h.

We managed to obtain desired compounds **7** and **8**† using a new synthesis (Scheme 1). Alkenes **11**[21,22] and **12**‡ were prepared from cyanoacetic acid and either hexafluoroacetone or ethyl trifluoropyruvate by a two-step synthesis, respectively. The above compounds react with triethylphosphite to form ylides **13** and **14**§ in almost quantitative yields.[23,24] Bromination of ylides[25] is accompanied by the intramolecular Arbuzov reaction to give bromoalkyl phosphonates, which underwent dehydrobromination (without isolation) with triethylamine to afford

† ^1H and $^{13}C\{^1H\}$ NMR spectra were taken with TMS as an internal standard. ^{19}F and ^{31}P NMR spectra were taken with CF_3CO_2H or 85% H_3PO_4 as an external standard, respectively.

7: 41% yield; bp 60–62 °C (1 Torr), n_D^{20} 1.3930. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 1.44 (t, 6H, $2OCH_2\mathit{Me}$, ^3J_H 7.2 Hz), 4.36 (m, 4H, $2OC\mathit{H}_2Me$). ^{13}C NMR (100.61 MHz, $CDCl_3$) δ: 12.0 (d, $OCH_2\mathit{Me}$, $^3J_{C,P}$ 7 Hz), 62.0 (d, OCH_2Me, $^2J_{C,P}$ 6 Hz), 107.0 (s, CN), 114.9 (m, $2CF_3$), 118.3 [d, $\mathit{C}(CN)P(O)(OEt)_2$, $^1J_{C,P}$ 178 Hz], 138.7 [m, $\mathit{C}(CF_3)_2$]. ^{19}F NMR (376.47 MHz, $CDCl_3$) δ: 18.56 (br. q, 3F, CF_3, $^4J_{F,F}$ 8.6 Hz), 16.27 (q, 3F, CF_3, $^4J_{F,F}$ 8.6 Hz). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: 0.19 [q, 1P, $P(O)(OEt)_2$, $^4J_{F,P}$ 2.0 Hz].

8 (*Z*-isomer): 36% yield; bp 110–114 °C (1 Torr), n_D^{20} 1.4150. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 1.35 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.2 Hz), 1.39 (m, 6H, $2OCH_2\mathit{Me}$), 4.25 (m, 4H, $2OC\mathit{H}_2Me$), 4.39 (q, 2H, $OC\mathit{H}_2Me$, ^3J_H 7.2 Hz). ^{13}C NMR (100.61 MHz, $CDCl_3$), 13.9 (s, $OCH_2\mathit{Me}$), 16.3 (d, $OCH_2\mathit{Me}$, $^3J_{C,P}$ 6 Hz), 64.3 (s, OCH_2Me), 65.4 (d, OCH_2Me, $^2J_{C,P}$ 6 Hz), 111.0 (d, CN, $^3J_{C,P}$ 5 Hz), 114.1 [d, $\mathit{C}(CN)P(O)(OEt)_2$, $^1J_{C,P}$ 185 Hz], 119.2 (qd, CF_3, $^1J_{C,F}$ 278 Hz, $^3J_{C,P}$ 22 Hz), 149.6 [qd, $\mathit{C}(CF_3)(CO_2Et)$, $^2J_{C,F}$ 34 Hz, $^2J_{C,P}$ 8 Hz], 159.9 (d, $\mathit{C}O_2Et$, $^3J_{C,P}$ 8 Hz). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 15.42 (s, 3F, CF_3). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: 2.77 [s, 1P, $P(O)(OEt)_2$].

‡ **9**:[26] 57% yield; bp 116–120 °C (60 Torr), n_D^{20} 1.3440. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 3.07 (s, 2H, CH_2), 4.31 (br. s, 1H, OH). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 0.41 (s, 3F, CF_3).

10: 60% yield; bp 85–90 °C (3 Torr), n_D^{20} 1.3905. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 1.38 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.2 Hz), 3.02 (AB-system, 2H, CH_2, ^2J_H –16.5 Hz), 4.25 (br. s, 1H, OH), 4.44 (m, 2H, $OC\mathit{H}_2Me$). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: –1.23 (s, 3F, CF_3).

11: 43% yield; bp 85–90 °C (740 Torr), n_D^{20} 1.3260. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 6.53 (q, 1H, CH, $^4J_{F,H}$ 1.5 Hz). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 12.13 (br. q, 3F, CF_3, $^4J_{F,F}$ 6.4 Hz), 15.03 (q, 3F, CF_3, $^4J_{F,F}$ 6.4 Hz).

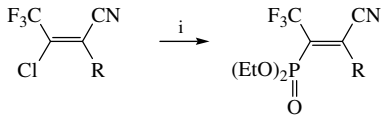
12 (mixture of *Z*- and *E*-isomers): 81% yield; bp 40–45 °C (1 Torr), n_D^{20} 1.4010. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 0.84 and 0.94 [t, 3H (*Z* + *E*), $OCH_2\mathit{Me}$, ^3J_H 7.2 Hz], 3.79 and 3.87 [q, 2H (*Z* + *E*), $OC\mathit{H}_2CH_3$, ^3J_H 7.2 Hz], 5.18 and 5.50 (br. s, 1H, CH). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 12.49 and 15.41 [br. s, 3F (*Z* + *E*), CF_3].

§ **13**: 80% yield; mp 80 °C. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 1.40 (t, 9H, $3OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 3.11 (m, 1H, CH), 4.27 (m, 6H, $3OC\mathit{H}_2Me$). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 10.06 (d, 6F, $2CF_3$, $^3J_{F,H}$ 7.7 Hz). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: 51.71 [s, 1P, $P(OEt)_3$].

14: 100% yield. ^1H NMR (400.13 MHz, $CDCl_3$) δ: 1.29 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.2 Hz), 1.37 (t, 9H, $3OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 3.31 (m, 1H, CH), 4.22 (m, 8H, $4OC\mathit{H}_2Me$). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 7.90 (d, 3F, CF_3, $^3J_{F,H}$ 8.5 Hz). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: 52.10 [s, 1P, $P(OEt)_3$].

desired alkenes **7** and **8**. Note that alkene **8** is obtained in the form of a *Z*-isomer only.

In addition, we optimised the procedure for obtaining alkenes **5** and **6**.¶ The use of CCl_4 as a solvent in the reactions of the corresponding vinyl chlorides with triethyl phosphite (Scheme 2) increased the yields of the desired products up to 80%, as compared to 40–60% in the original procedure.[20] Alkene **6** was obtained as a mixture of geometry isomers in a ratio of 3 : 1.

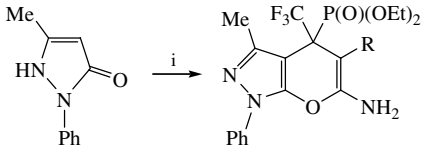


5 R = CN
6 R = CO_2Me

Scheme 2 *Reaction conditions*: i, $P(OEt)_3$, CCl_4, reflux, 1 h.

We studied the use of alkenes **5**–**8** as precursors of heterocyclic compounds modified both with trifluoromethyl and diethoxyphosphoryl group by the example of their reaction with 3-methyl-1-phenyl-2-pyrazolin-5-one. It is well known that alkenes **1** and **2** react with the latter compound to give 1,4-dihydropyrano[2,3-*c*]pyrazole derivatives.[4] We found that alkene **5** reacts with 3-methyl-1-phenyl-2-pyrazolin-5-one to form compound **15**†† in 90% yield. The reaction occurs at room temperature and is complete within several hours (Scheme 3).

Alkene **6** also reacts with 3-methyl-1-phenyl-2-pyrazolin-5-one to give 1,4-dihydropyrano[2,3-*c*]pyrazole derivative **16**‡‡ in high yield. However, in this case, the reaction is much slower and completed only after the reaction mixture was kept for a long time (up to 14 days) at 20 °C (Scheme 3). Note that intramolecular cyclization occurs at the nitrile group rather than the methoxycarbonyl group.



15 R = CN
16 R = CO_2Me

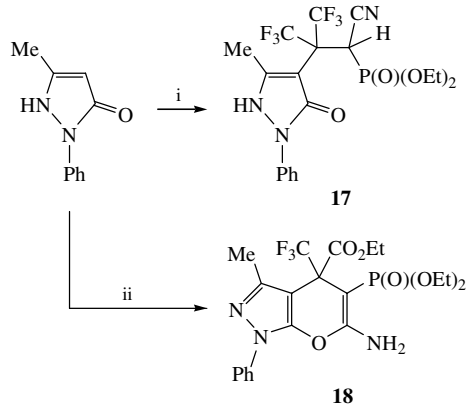
Scheme 3 *Reaction conditions*: i, $CHCl_3$, alkene **5** or **6**, 20 °C.

¶ **5**: 80% yield; bp 91–93 °C (1 Torr). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 1.60 (t, 6H, $2OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 4.45 (m, 4H, $2OCH_2Me$). ^{19}F NMR (188.31 MHz, $CDCl_3$), 18.57 (d, 3F, CF_3, $^3J_{F,P}$ 2.1 Hz). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: –1.78 [q, 1P, $P(O)(OEt)_2$, $^3J_{F,P}$ 2.1 Hz].

6 (mixture of *Z*- and *E*-isomers): 73% yield; bp 110–115 °C (1 Torr). ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 1.42 and 1.47 [t, 6H ($Z + E$), $2OCH_2\mathit{Me}$, ^3J_H 7.1 Hz], 4.00 and 4.02 [s, 3H ($Z + E$), OMe], 4.35 [m, 4H ($Z + E$), $2OCH_2Me$]. ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 18.27 (d, 3F, CF_3, $^3J_{F,P}$ 2.5 Hz), 19.05 (d, 3F, CF_3, $^3J_{F,P}$ 3.8 Hz). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: 0.83 [q, 1P, $P(O)(OEt)_2$, $^3J_{F,P}$ 2.5 Hz], 0.27 [q, 1P, $P(O)(OEt)_2$, $^3J_{F,P}$ 3.8 Hz].

†† **15**: 90% yield; mp 212 °C. ^{1}H NMR (400.13 MHz, [$^2H_6$]DMSO) δ: 1.07 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 1.29 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 2.38 (q, 3H, Me, $^6J_{F,H}$ 1.6 Hz), 3.91 (m, 1H, OCH_2Me), 4.01 (m, 1H, OCH_2Me), 4.16 (m, 2H, OCH_2Me), 7.39 (t, 1H, Ar, *J* 7.5 Hz), 7.52 (dd, 2H, Ar, *J* 7.8 and 7.5 Hz), 7.74 (d, 2H, Ar, *J* 7.8 Hz), 7.79 (br. s, 2H, NH_2). ^{19}F NMR (188.31 MHz, [$^2H_6$]DMSO) δ: 13.47 (br. s, 3F, CF_3). ^{31}P NMR (160.62 MHz, [$^2H_6$]DMSO) δ: 16.92 [q, 1P, $P(O)(OEt)_2$, $^3J_{F,P}$ 2.1 Hz]. MS, *m*/*z* (%): 456 $[M]^+$ (1.2), 319 $[M - P(O)(OEt)_2]^+$ (56.9), 76 $[Ph]^+$ (100), 69 $[CF_3]^+$ (1.5).

‡‡ **16**: 84% yield; mp 129 °C. ^{1}H NMR (400.13 MHz, [$^2H_6$]DMSO) δ: 1.07 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 1.18 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 2.38 (q, 3H, Me, $^6J_{F,H}$ 2.1 Hz), 3.67 (s, 3H, CO_2Me), 3.93 (m, 4H, $2OCH_2Me$), 7.36 (t, 1H, Ar, *J* 7.5 Hz), 7.51 (dd, 2H, Ar, *J* 7.8 and 7.5 Hz), 7.77 (d, 2H, Ar, *J* 7.8 Hz), 8.22 (br. s, 2H, NH_2). ^{19}F NMR (282.38 MHz, [$^2H_6$]DMSO) δ: 18.45 (dq, 3F, CF_3, $^3J_{F,P}$ 3.8 Hz, $^6J_{F,H}$ 2.1 Hz). ^{31}P NMR (160.62 MHz, [$^2H_6$]DMSO) δ: 20.12 [q, 1P, $P(O)(OEt)_2$, $^3J_{F,P}$ 3.8 Hz]. MS, *m*/*z* (%): 489 $[M]^+$ (1.4), 352 $[M - P(O)(OEt)_2]^+$ (100), 76 $[Ph]^+$ (35.5), 69 $[CF_3]^+$ (0.9).



Scheme 4 *Reaction conditions*: i, $CHCl_3$, alkene **7**, 20 °C; ii, $CHCl_3$, alkene **8**, 20 °C.

Compounds **7** and **8** also react with 3-methyl-1-phenyl-2-pyrazolin-5-one much slower than alkene **5** does. In the case of alkene **7**, we managed to isolate C4-alkylation product **17**.§§ In the case of compound **8**, the similar intermediate product was converted to 1,4-dihydropyrano[2,3-*c*]pyrazole **18**¶¶ (Scheme 4) as a result of intramolecular cyclization.

The decreased reactivity of alkenes **6**–**8** compared to that of compound **5** can be explained, on the one hand, by lowering electrophilicity of the double bond as a result of replacing the nitrile group by the diethoxyphosphoryl and especially by the methoxycarbonyl group and, on the other hand, by increasing the stability of C4-alkylation intermediates as a result of the formation of hydrogen bonds between the hydrogen of the hydroxy group in the oxy form of pyrazolone and the phosphonate or methoxycarbonyl oxygen. Previously, we have shown that it is the oxy form in which pyrazolones undergo C4 alkylation with unsaturated compounds.

Therefore, we have developed a basically new procedure for the synthesis of alkenes **7** and **8**, which were not described earlier, optimised the synthesis of alkenes **5** and **6** and found that compounds **5**–**8** can be used as precursors of 1,4-dihydropyrano[2,3-*c*]pyrazoles modified with trifluoromethyl and diethoxyphosphoryl groups.

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§§ **17**: 53% yield. ^{1}H NMR (400.13 MHz, $CDCl_3$) δ: 1.44 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 1.49 (t, 3H, $OCH_2\mathit{Me}$, ^3J_H 7.1 Hz), 2.17 (s, 3H, Me), 4.41 (m, 4H, OCH_2Me), 7.18 (m, 1H, Ar), 7.24 (m, 2H, Ar), 7.42 (m, 2H, Ar), 7.77 (d, CH, $^2J_{P,H}$ 29.7 Hz), 11.21 (br. s, 1H, NH). ^{19}F NMR (188.31 MHz, $CDCl_3$) δ: 15.02 (br. s, 3F, CF_3), 9.12 (q, 3F, CF_3, $^4J_{F,F}$ 4.8 Hz). ^{31}P NMR (160.62 MHz, $CDCl_3$) δ: 9.88 [s, 1P, $P(O)(OEt)_2$].

¶¶ **18**: 55% yield; mp 189 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ: 1.38 (m, 9H, $3OCH_2\mathit{Me}$), 2.25 (s, 3H, Me), 4.18 (m, 4H, $2OCH_2Me$), 4.35 (m, 2H, OCH_2Me), 5.75 (br. s, 2H, NH_2), 7.38 (t, 1H, Ar, *J* 7.3 Hz), 7.52 (dd, 2H, Ar, *J* 7.8 and 7.3 Hz), 7.71 (d, 2H, Ar, *J* 7.8 Hz). ^{19}F NMR (282.38 MHz, $CDCl_3$) δ: 5.52 (s, 3F, CF_3). ^{31}P NMR (121.49 MHz, $CDCl_3$) δ: 21.22 [s, 1P, $P(O)(OEt)_2$]. MS, *m*/*z* (*I*, %): 503 $[M]^+$ (1.4), 430 $[M - CO_2Et]^+$ (100), 76 $[Ph]^+$ (87.3), 69 $[CF_3]^+$ (7.7).

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