One-pot stereoselective synthesis of trifluoromethylated penta-(2*Z*,4*E*)-dienenitriles *via* double olefination

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A novel double olefination *via* sequential transformation of diethyl (1-cyanoethyl)phosphonate and its application to the synthesis of substituted trifluoromethylated pentadienenitriles with 2*Z*,4*E*-isomers formed exclusively in 71–85% yield are described. This reaction is of broad scope since R may be alkyl, aryl or a heterocyclic group. The configuration of the products was ascertained on the basis of X-ray crystallographic analysis. The stereochemical results are rationalized by the proposed mechanism.

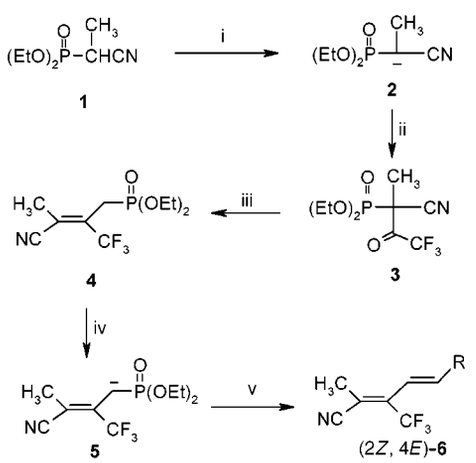
Introduction

A double olefination methodology has been reported for the one-pot synthesis of allenes in recent years.[1] This methodology is simple and convenient. However, only aldehydes bearing an α-proton were able to afford 1,3-dienes rather than allenes.[2] Sequential transformations have emerged in recent years as a powerful methodology for their operational simplicity and efficient entry to complex compounds by including two or more transformations in a single operation to increase the complexity of substrate starting from relatively simple commercially available precusors.[3] In our laboratory sequential transformations of phosphonates have been developed as a general synthetic approach for perfluoroalkylated α-fluoro-α,β-unsaturated esters,[4a] perfluoroalkylated 4-cyanoalka-1,4-dienes,[4b] perfluoroalkylated α,β-unsaturated nitriles[4c] and tetra-substituted perfluoroalkylated (*Z*)-α,β-unsaturated esters[4d] which would be difficult to prepare otherwise. Introduction of a trifluoromethyl group into organic molecules may increase the biological activity, and organofluorine compounds have been applied increasingly in pharmaceuticals, agrochemicals and other fields.[5] For example, 2′,3′-dideoxy-3-(trifluoromethyl)-pentafuranosyl nucleosides were used as antitumor and antiviral agents.[6] α,β-Unsaturated nitriles have attracted much interest since such compounds are an important structural feature of a number of naturally occurring compounds which show biological activity.[7] A comprehensive review on general methods for the introduction of the trifluoromethyl group[8a] and perfluoroalkylation with organosilicone reagents[8b] has appeared. However, to the best of our knowledge a method for the synthesis of trifluoromethylated pentadienenitriles has not appeared in the literature. Therefore it is of interest to develop a convenient method for the synthesis of title compounds since they may be expected to be useful intermediates for the synthesis of fluorine-containing biologically active compounds.

Results and discussion

In our continuing investigation of the synthetic application of seqential transformations of phosphonates in organic synthesis, herein we report a novel double olefination *via* seqential transformation of diethyl (1-cyanoethyl)phosphonates and its application to the synthesis of substituted trifluoromethylated pentadienenitriles (2*Z*,4*E* isomers exclusively) in 71–85% yield. The reaction sequence is shown in Scheme 1.

The phosphoryl-stabilized carbanion **2**, generated from the corresponding phosphonate **1** and *n*-butyllithium in THF, was acylated by the addition of TFAA to give trifluoroacylated phosphonate **3**. Without isolation, ketone, **3** was attacked by diethylphosphinoylmethyllithium and elimination of phosphonic acid anion afforded the alkene **4**. Treatment of phosphonate **4** with LDA gave phosphoryl-stabilized carbanion **5**, which in the reaction medium was treated with aldehydes to give substituted trifluoromethylated pentadienenitriles in 71–85% yield with 2*Z*,4*E*-isomers formed exclusively. The results are summarized in Table 1.



Scheme 1 *Reagents and conditions*: i, Bu^{n}Li, THF, −78 °C; ii, TFAA, −78 °C; iii, Diethylphosphinoylmethyllithium, −78 °C; iv, LDA, −78 °C; v, RCHO, −78 to 20 °C.

For the assignment of the configuration of products, we performed an X-ray crystallographic analysis of compound **6a**. The crystal structure shows that the cyano group is *cis* with respect to the trifluoromethyl group (2*Z*) and the H-atoms across the other double bond are *trans* (4*E*) (see Fig. 1). Hence the configuration of products could be ascertained on the basis of this crystal structure.

The stereochemical results may be rationalized as follows: The mechanism of first olefination for the formation of trifluoromethylated β,γ-unsaturated phosphonate is analogous to that of a bisphosphonate reported in the literature[9] and is outlined in Scheme 2.

The stereoselectivity of the reaction is determined by the condensation step. The reaction is initiated by nucleophilic attack of nucleophile on the carbon–oxygen double bond of the carbonyl group, forming intermediates **7a** and **7b** (Scheme 2).

Table 1 Preparation of substituted trifluoromethylated penta-2*Z*, 4*E*-dienenitriles

Compound	R	Yield (%)[a]
6a	C_6H_5	80
6b	4-FC_6H_4	82
6c	4-ClC_6H_4	85
6d	4-BrC_6H_4	78
6e	4-$NO_2C_6H_4$	83
6f	4-*E*-$C_6H_4CH{=}CH$	80
6g	4-$CH_3C_6H_4$	82
6h	4-$CH_3OC_6H_4$	71
6i	Furyl	73
6j	$CH_3(CH_2)_7$	75

[a] Isolated yield.

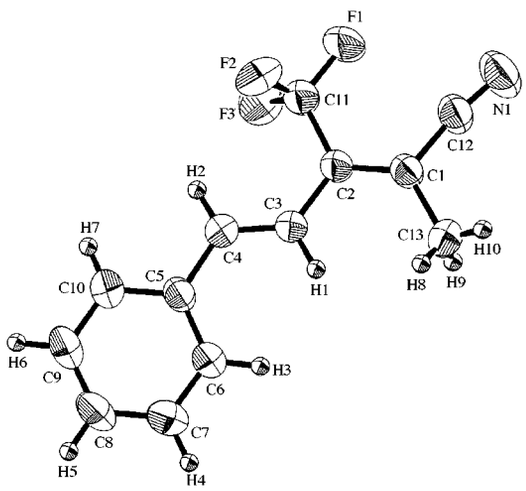
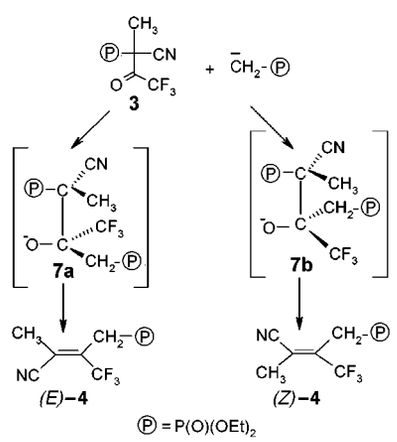


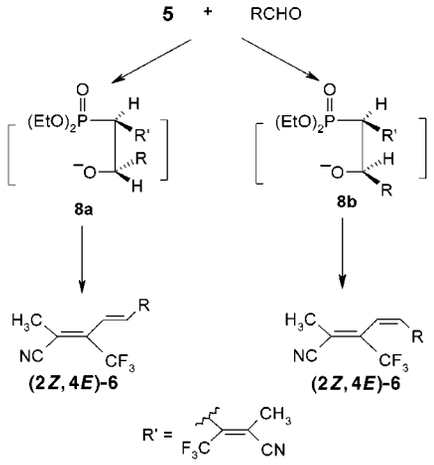
Fig. 1 The X-ray molecular structure of compound **6a**.



Scheme 2

The reactive size of groups is $CF_3 > CH_3 > CH_2PO_3Et_2$[10] > CN. Since the intermediate **7a** involves a *syn*-periplanar (eclipsed) orientation of two pairs of 'small'/'large' substituents (CH_2-PO_3Et_2/CH_3, CN/CF_3), this conformer should be favored relative to the stereoisomer **7b** which contains unfavorable 'large'/'large' (CF_3/CH_3) non-bonded interactions. Therefore the stereoselectivity of olefination in our case is a function of the conformational equilibrium of the adduct. Each of those intermediates decomposes *via* a *syn*-elimination, affording alkene **4**-(*E*) or **4**-(*Z*). In our case, formation of isomer **7a** will be favored over isomer **7b** and the *E*-isomer was obtained exclusively (the CN group is *cis* with respect to the CF_3 group).

The mechanism of the second olefination for the formation of the title compounds is analogous to that of the Horner–Wadsworth–Emmons reaction[11] and is outlined in Scheme 3.



Scheme 3

Each of those intermediates decomposes *via* a *syn*-elimination, to afford dienes **6**-(2*Z*,4*E*) or **6**-(2*Z*,4*Z*). As in the former explanation, conformer **8a** will be favored over **8b** and the *E*-isomer was obtained exclusively. The coupling constants of the vinyl Hs in products **6** are within the range 16.2–16.7 Hz, showing that the geometry of the newly formed double bond in products **6** was exclusively *E*.

In conclusion, the double olefination methodology has been applied to the synthesis of substituted tirfluoromethylated-penta-2,4-dienenitriles, giving 2*Z*,4*E*-isomers exclusively in a one-pot reaction. This reaction is of broad scope since R may be alkyl, aryl or a heterocyclic group. This methodology provides a simple and convenient synthesis of the title compounds from readily available starting materials. The title compounds would be expected to be useful intermediates for the synthesis of fluorine-containing biologically active compounds.

Experimental

Bps and mps are uncorrected. Mps were measured on a micro melting point apparatus, model ZMD-II made by Shanghai 2nd Medical University. IR spectra of solid products were obtained for KCl disks and those of liquid products for films on a Digilab FTS-20E spectrometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 (300 MHz) spectrometer (δ-values in ppm from tetramethylsilane, in $CDCl_3$; *J*-values are given in Hz). The published ^{19}F NMR spectra were taken on a Varian EM-360 (60 MHz) spectrometer and re-calculated using the standard chemical shift of reference δ(F) (CF_3CO_2H) −76.5 ppm with respect to $\delta(CFCl_3)$ 0.00 ppm. Mass spectra were measured on a Finnigan GC-MS-4021 mass spectrometer.

Lithium reagents

Bu^{n}Li and LDA were obtained from Aldrich Chemical Company. Diethylphosphinoylmethyllithium was prepared by the reaction of *n*-butyllithium (3 mmol) and diethyl methylphosphonate (3 mmol) in THF (20 cm^3) for 30 min at −78 °C.

Diethyl (1-cyanoethyl)phosphonate 1

This was prepared according to the method reported in the literature.[12]

General procedure for the preparation of trifluoromethylated 2*Z*,4*E*-dienenitriles 6

n-Butyllithium (3 mmol in 2.5 cm^3 of hexane) was added dropwise over a period of 10 min to a stirred solution of diethyl cyanoethylphosphonate **1** (3 mmol) in absolute THF (20 cm^3) at −78 °C under nitrogen. The mixture was stirred at −78 °C for 0.5 h, and TFAA (3 mmol) was added in one portion. Stirring

was continued at −78 °C for 1 h, after which diethylphosphinoylmethyllithium (3 mmol) was added dropwise to the mixture, which was then stirred for another 1 h. Then LDA (3 mmol) and an aldehyde (3 mmol) were added in turn to the mixture, which was then stirred for 1 h and allowed to warm to RT. After stirring of the mixture for 3 h and the disappearance of the aldehyde (shown by TLC), the reaction mixture was poured into water (10 cm^3) and the water layer was extracted with dichloromethane (4×20 cm^3). The combined organic layer was washed with water (2×10 cm^3) and dried over Na_2SO_4. Evaporation of the mixture gave a residue, which was purified by column chromatography with petroleum spirit (60–90 °C)–ethyl acetate (9:1) as eluent to give the product **6a**–**j**.

2-Methyl-5-phenyl-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6a. Mp 62–63 °C; ν_{max}/cm^{-1} 2220, 1620, 1580, 1390, 1350, 1120 and 690; δ_H 7.54–7.34 (m, 5H, ArH), 7.09 (d, *J* 16.6, 1H, vinyl H), 6.78 (d, *J* 16.6, 1H, vinyl H) and 2.30 (q, *J* 1.5, 3H, C=CCH$_3$); δ_F −58.8 (s, 3F); *m*/*z* 237 (M^+, 46%), 222 (39), 210 (8), 202 (100), 168 (27), 153 (27) and 77 (17) (Found: C, 66.0; H, 4.1; N, 6.0. $C_{13}H_{10}F_3N$ requires C, 65.82; H, 4.25; N, 5.90%).

5-(4-Fluorophenyl)-2-methyl-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6b. Mp 65–67 °C; ν_{max}/cm^{-1} 2210, 1620, 1590, 1420, 1350, 1160 and 830; δ_H 7.52–7.44 (m, 2H, ArH), 7.14–7.04 (m, 2H, ArH), 7.03 (d, *J* 16.3, 1H, vinyl H), 6.67 (d, *J* 16.3, 1H, vinyl H) and 2.29 (q, *J* 1.4, 3H, C=CCH$_3$); δ_F −58.8 (s, 3F) and 28.6 (s, 1F); *m*/*z* 255 (M^+, 69%), 240 (44), 220 (100), 186 (34), 171 (40), 159 (41) and 120 (12) (Found: C, 61.0; H, 3.3; N, 5.5. $C_{13}H_9F_4N$ requires C, 61.18; H, 3.55; N, 5.49%).

5-(4-Chlorophenyl)-2-methyl-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6c. Mp 122 °C; ν_{max}/cm^{-1} 2210, 1620, 1590, 1490, 1340, 1160 and 820; δ_H 7.45–7.36 (m, 2H, ArH), 7.14–7.06 (m, 2H, ArH), 7.02 (d, *J* 16.6, 1H, vinyl H), 6.74 (d, *J* 16.6, 1H, vinyl H) and 2.30 (q, *J* 1.3, 3H, C=CCH$_3$); δ_F −58.4 (s, 3F); *m*/*z* 271 (M^+, 86%), 258 (12), 256 (32), 238 (34), 236 (100), 216 (73) and 139 (34) (Found: C, 57.5; H, 3.1; N, 5.0. $C_{13}H_9ClF_3N$ requires C, 57.48; H, 3.34; N, 5.16%).

5-(4-Bromophenyl)-2-methyl-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6d. Mp 130 °C; ν_{max}/cm^{-1} 2220, 1620, 1580, 1480, 1340, 1160 and 820; δ_H 7.53 (d, *J* 6.9, 2H, ArH), 7.35 (d, *J* 6.9, 2H, ArH), 7.00 (d, *J* 16.7, 1H, vinyl H), 6.76 (d, *J* 16.7, 1H, vinyl H) and 2.29 (q, *J* 1.4, 3H, C=CCH$_3$); δ_F −58.9 (s, 3F); *m*/*z* 315 (M^+, 41%), 236 (39), 221 (94), 216 (100), 167 (99), 162 (42) and 140 (32) (Found: C, 49.2; H, 2.6; N, 4.2. $C_{13}H_9BrF_3N$ requires C, 49.39; H, 2.87; N, 4.43%).

2-Methyl-5-(4-nitrophenyl)-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6e. Mp 132–133 °C; ν_{max}/cm^{-1} 2220, 1620, 1590, 1520, 1340, 1160 and 840; δ_H 8.28 (d, *J* 6.7, 2H, ArH), 7.68 (d, *J* 6.7, 2H, ArH), 7.14 (d, *J* 16.7, 1H, vinyl H), 6.95 (d, *J* 16.7, 1H, vinyl H) and 2.37 (q, *J* 1.2, 3H, C=CCH$_3$); δ_F −58.7 (s, 3F); *m*/*z* 282 (M^+, 84%), 267 (42), 221 (82), 217 (23), 167 (100), 166 (70) and 140 (57) (Found: C, 55.3; H, 3.2; N, 9.8. $C_{13}H_9F_3N_2O_2$ requires C, 55.33; H, 3.21; N, 9.93%).

2-Methyl-7-phenyl-3-(trifluoromethyl)hepta-2*Z*,4*E*,6*E*-trienenitrile 6f. Mp 90–91 °C; ν_{max}/cm^{-1} 2210, 1680, 1610, 1490, 1340, 1170 and 750; δ_H 7.50–7.28 (m, 5H, ArH), 7.00–6.87 (m, 3H, vinyl H), 6.36 (d, *J* 16.7, 1H, vinyl H) and 2.23 (q, *J* 1.3, 3H, C=CCH$_3$); δ_F −58.3 (s, 3F); *m*/*z* 263 (M^+, 100%), 262 (70), 264 (44), 236 (38), 194 (83), 167 (59) and 77 (17) (Found: C, 68.1; H, 4.2; N, 5.0. $C_{15}H_{12}F_3N$ requires C, 68.44; H, 4.59; N, 5.32%).

2-Methyl-5-(4-methylphenyl)-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6g. Mp 78–79 °C; ν_{max}/cm^{-1} 2220, 1600, 1520, 1350, 1160 and 810; δ_H 7.39 (d, *J* 8.1, 2H, ArH), 7.21 (d, *J* 8.1, 2H, ArH), 7.04 (d, *J* 16.6, 1H, vinyl H), 6.72 (d, *J* 16.6, 1H, vinyl H), 2.38 (s, 3H, Ar-CH$_3$) and 2.28 (q, *J* 1.4, 3H, C=CCH$_3$); δ_F −58.8 (s, 3F); *m*/*z* 251 (M^+, 52%), 236 (49), 216 (100), 182 (23), 167 (43), 155 (15) and 91 (18) (Found: C, 66.6; H, 4.4; N, 5.2. $C_{14}H_{12}F_3N$ requires C, 66.93; H, 4.81; N, 5.57%).

5-(4-Methoxyphenyl)-2-methyl-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6h. Mp 72 °C; ν_{max}/cm^{-1} 2220, 1600, 1590, 1510, 1350, 1290 and 820; δ_H 7.44 (d, *J* 7.0, 2H, ArH), 7.02 (d, *J* 16.5, 1H, vinyl H), 6.92 (d, *J* 7.0, 2H, ArH), 6.64 (d, *J* 16.5, 1H, vinyl H), 3.85 (s, 3H, OCH$_3$) and 2.27 (q, *J* 1.4, 3H, C=CCH$_3$); δ_F −58.9 (s, 3F); *m*/*z* 267 (M^+, 80%), 252 (95), 233 (16), 232 (100), 198 (16), 183 (34) and 77 (9) (Found: C, 63.0; H, 4.25; N, 5.0. $C_{14}H_{12}F_3NO$ requires C, 62.92; H, 4.53; N, 5.24%).

5-Furyl-2-methyl-3-(trifluoromethyl)penta-2*Z*,4*E*-dienenitrile 6i. Mp 67–68 °C; ν_{max}/cm^{-1} 2230, 1630, 1500, 1490, 1330, 1290 and 730; δ_H 7.48 (d, *J* 1.3, 1H, Hetero-H), 6.85 (d, *J* 16.4, 1H, vinyl H), 6.73 (d, *J* 16.4, 1H, vinyl H), 6.56 (d, *J* 3.4 1H, Hetero-H), 6.49 (dd, *J* 3.4 and 1.8, 1H, Hetero-H) and 2.27 (q, *J* 1.2, 3H, C=CCH$_3$); δ_F −58.2 (s, 3F); *m*/*z* 227 (M^+, 100%), 212 (26), 158 (18), 130 (24) and 103 (16) (Found: C, 58.4; H, 3.5; N, 6.1. $C_{11}H_8F_3NO$ requires C, 58.16; H, 3.55; N, 6.17%).

2-Methyl-3-(trifluoromethyl)trideca-2*Z*,4*E*-dienenitrile 6j. Bp 128 °C/1 mmHg; ν_{max}/cm^{-1} 2220, 1630, 1340, 1200 and 970; δ_H 6.38–6.18 (m, 1H, vinyl H), 6.05 (d, *J* 16.2, 1H, vinyl H), 2.23 (dq, *J* 7.1 and 7.1, 2H, C*H*$_2$CH$_3$), 2.17 (q, *J* 1.2, 3H, CH$_3$), 1.54–1.38 (m, 2H, C*H*$_2$CH$_2$CH$_3$), 1.38–1.20 (m, 10H, [CH$_2$]$_5$) and 0.88 (t, *J* 6.6, 3H, CH$_3$); δ_F −59.2 (s, 3F); *m*/*z* 274 ($M^+ + 1$, 96%), 258 (8), 230 (11), 216 (12), 180 (100), 162 (22) and 43 (33) (Found: C, 66.1; H, 8.2; N, 5.25. $C_{15}H_{22}F_3N$ requires C, 65.91; H, 8.11; N, 5.12%).

Crystal structure determination

Crystal data for compound 6a. $C_{13}H_{10}F_3N$. M = 237.22, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.508(2)$, $b = 14.686(2)$, $c = 10.933(3)$ Å, $\beta = 106.43(2)°$, $V = 1156.3(5)$ Å^3, $Z = 4$, $D_{calc} = 1.36$ g cm^{-3}, λ(MoKα) = 0.710 69 Å, $\mu = 1.79$ cm^{-1}, $T = 293.0$ K, prismatic crystal, 0.20 × 0.20 × 0.30 mm.

Data correction and processing. Data were measured on a Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation using the ω–2θ scan technique to a maximum 2θ-value of 50.0°. Of the 2286 reflections which were collected, 2118 were unique ($R_{int} = 0.010$). The data were corrected for Lorentz and polarization factors. A correction for secondary extinction was also applied.

Structure solution and refinement. The structure was resolved by direct methods[13] and expanded using Fourier techniques.[14] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1345 observed reflections and 195 variable parameters. The final *R*- and R_w-values are 0.040 and 0.054, respectively. All calculations were performed using the TEXSAN[15] crystallographic software package from Molecular Structure Corporation.†

† Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/289.

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