   Bull. Chem. Soc. Jpn., 58, 2139—2140 (1985)

Reactions of Vinylphosphonates. 3.[1] One-Pot Synthesis of Dienes and Their Analogues from Vinylphosphonates, Aldehydes and Diethyl Phosphonate

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(Received January 24, 1985)

Synopsis. Functionalized dienes and tetraenes were synthesized in 26—63% yields by the one-pot reaction of the phosphoryl-stabilized carbanions, prepared from the Michael addition of diethyl lithiophosphonate to vinylphosphonates, with aromatic aldehydes. A similar reaction using phthalaldehyde gave 2-methylsulfonylnaphthalene (**7**) in 31% yield *via* an intramolecular double Horner-Wittig reaction.

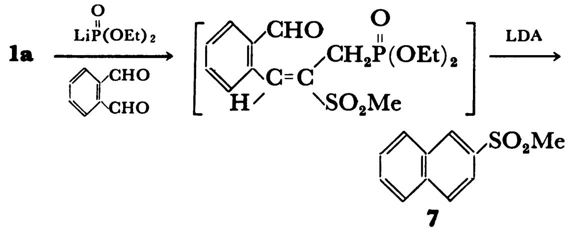
We have previously reported a new synthesis of vinylphosphonates bearing electronegative substituents such as ethoxycarbonyl and cyano groups, and their use in syntheses of functionalized heterocyclic compounds, and olefins, dienes and their analogues.[1,2] In connection with our continuing interest in the synthetic application of the vinylphosphonates, we have now developed an one-pot synthesis of unsaturated systems such as dienes and tetraenes, *etc.* having functionality.

Results and Discussion

The reaction of a phosphoryl-stabilized carbanion **2a**, generated *in-situ* from a Michael addition of diethyl lithiophosphonate to diethyl [1-(methylsulfonyl)vinyl]phosphonate (**1a**), with one equiv of benzaldehyde (**3a**) gave a mixture of 2-methylsulfonyl-1,4-diphenyl-1,3-butadiene (**4a**)(15%), diethyl (2-methylsulfonyl-3-phenyl-2-propenyl)phosphonate (**5a**)(35%), and diethyl [2-diethoxyphosphinyl-1-(methylsulfonyl)ethyl]phosphonate (**6a**)(14%). This result suggests the possibility of an one-pot synthesis of 1,3-dienes and their analogues *via* the double Horner-Wittig reaction.

Accordingly, the reaction of **2a** with an equiv of **3a**, followed by a sequential treatment with an equiv each of lithium diisopropylamide (LDA) and **3a**, afforded the expected **4a** in 63% yield. Similar reactions of **2a** with aromatic aldehydes such as *p*-chlorobenz- (**3b**), cinnam- (**3c**), and 2-thiophenecarbaldehydes (**3d**) gave the corresponding dienes and tetraenes **4b—d** in 42—53% yields. A similar treatment of [1-(ethoxycarbonyl)vinyl]phosphonate **1b** with **3a,d** produced dienes **4e,f**, albeit in low yields.

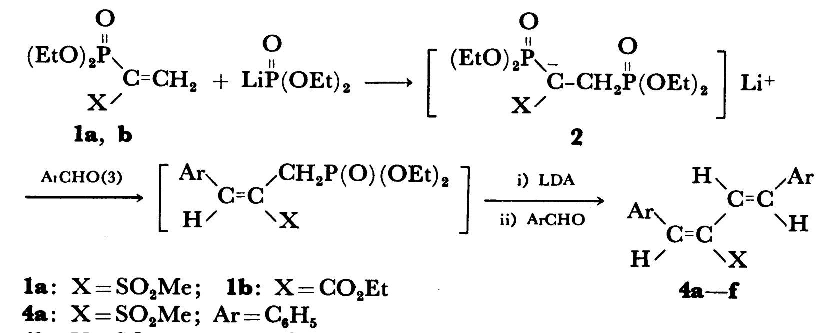
An application of similar procedures using the phosphonate **1a** to phthalaldehyde successfully gave 2-methylsulfonylnaphthalene (**7**) in 31% yield *via* an intramolecular double Horner-Wittig reaction (Eq. 1).



(1)

In contrast to aromatic aldehydes, the one-pot reaction of **1a** with butyraldehyde (**3e**) under similar conditions afforded an unexpected product, diethyl 1,3-hexadienylphosphonate (**8**) in 49% yield, whose formation can not be reasonably accounted for at present. On the other hand, a similar treatment of **1b** with **3e** produced only an 1:1 mixture of diethyl (*E*)- (**9a**) and (*Z*)-(2-ethoxycarbonyl-2-hexenyl)phosphonates (**9b**) in 40% yield.

In conclusion, vinylphosphonates serve as versatile reagents for the one-pot synthesis of dienes, tetraenes,



1a: X=SO_2Me; **1b**: X=CO_2Et
4a: X=SO_2Me; Ar=C_6H_5
4b: X=SO_2Me; Ar=p-ClC_6H_4
4c: X=SO_2Me; Ar=C_6H_5CH=CH
4d: X=SO_2Me; Ar=2-Thienyl
4e: X=CO_2Et; Ar=C_6H_5
4f: X=CO_2Et; Ar=2-Thienyl

Scheme 1.

and condensed aromatic compounds, which could be useful as synthetic precursors.

Experimental

General. ^{1}H-NMR and ^{13}C-NMR spectra were taken in a $CDCl_3$ solution on a JEOL JNM-FX-60 operating at 60 and 15.04 MHz with Me_4Si as the internal standard. IR spectra were recorded with a Shimadzu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected.

*Reaction of Diethyl [1-(Methylsulfonyl)vinyl]phosphonate (**1a**) with Benzaldehyde (**3a**) in the Presence of One Equiv. of Diethyl Lithiophosphonate.* To a cooled solution of diethyl lithiophosphonate, prepared from diethyl phosphonate (0.33 g, 2.39 mmol) and butyllithium (2.39 mmol), in THF (20 ml) at −75 °C was added **1a** (0.52 g, 2.15 mmol). The solution was stirred for 0.5 h at this temperature. Then **3a** (0.228 g, 2.15 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h. After a conventional work-up, the residue was chromatographed on a preparative TLC with ether as the eluent to give **4a** (90 mg, 0.317 mmol, 15%), **5a** (0.25 g, 0.753 mmol, 35%), and **6a** (0.11 g, 0.289 mmol, 14%), respectively.

*2-Methylsulfonyl-1,4-diphenyl-1,3-butadiene (**4a**)*: Mp 91—93 °C; IR (KBr): 1300, 1140 cm^{-1}; ^{1}H NMR δ=3.04 (3H, s, Me), 6.70—7.90 (13H, m, olefinic and phenyl H); MS Found: *m/z* 284.0868. Calcd for $C_{17}H_{16}O_2S$: 284.0871 (M^+).

Found: C, 71.74; H, 5.80. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67%.

*Diethyl (2-Methylsulfonyl-3-phenyl-2-propenyl)phosphonate (**5a**)*: Oil; IR (neat): 1300, 1250, 1130, 1020, 960 cm^{-1}; ^{1}H NMR δ=1.30 (6H, t, Me), 3.25 (3H, s, $SO_2\underline{Me}$), 3.40, 3.41 (2H, 2×d, 22.27, 22.12 Hz, P-CH_2), 3.80—4.50 (4H, m, $O\underline{CH_2}CH_3$), 7.10—8.00 (6H, m, olefinic and phenyl H); MS Found: *m/z* 333.0931. Calcd for $C_{14}H_{22}O_5SP$: 333.0926 (M^++1).

*Diethyl [2-Diethoxyphosphinyl-1-(methylsulfonyl)ethyl]phosphonate (**6a**)*: Mp 43—45 °C; IR (KBr): 1310, 1240,1135, 1010, 960 cm^{-1}; ^{1}H NMR δ=1.00—1.70 (12H, m, Me), 2.00—3.00 (3H, m, -$\underline{CH_2}$-$\underline{CH}$), 3.29 (3H, s, $SO_2\underline{Me}$), 3.70—4.60 (8H, m, $O\underline{CH_2}CH_3$); MS *m/z* 380 (M^+).

*General Procedure for the One-Pot Synthesis of 1,3-Dienes **4a**—**f**.* To a stirred solution of a phosphonate carbanion **2** (3 mmol) in THF (20 ml) at −75 °C was added an aldehyde (3 mmol). After stirring at room temperature for 4 h, the solution was cooled to −75 °C and LDA (3 mmol) in THF (5 ml) was added to the solution. After the solution was stirred at this temperature for 0.5 h, an aldehyde (3 mmol) was added to the solution. The reaction mixture was then stirred at room temperature for 10 h. After a similar work-up, a pure sample of each was obtained by preparative TLC.

*2-Methylsulfonyl-1,4-diphenyl-1,3-butadiene (**4a**)*: Yield 0.54 g (1.90 mmol, 63%).

*2-Methylsulfonyl-1,4-bis(*p*-chlorophenyl)-1,3-butadiene (**4b**)*: Yield 0.442 g (1.25 mmol, 42%); Mp 149—151 °C; IR (KBr): 1300, 1140 cm^{-1}; ^{1}H NMR δ=3.04 (3H, s, Me), 6.60—7.80 (11H, m, olefinic and phenyl H); MS *m/z* 352, 354, 356 (M^+).

Found: C, 57.83; H, 4.00. Calcd for $C_{17}H_{14}O_2SCl_2$: C, 57.80; H, 3.99%.

*4-Methylsulfonyl-1,8-diphenyl-1,3,5,7-octatetraene (**4c**)*: Yield 0.51 g (1.52 mmol, 51%); Mp 143—145 °C; IR (KBr): 1300, 1120 cm^{-1}; ^{1}H NMR δ=3.00 (3H, s, Me), 6.40—7.80 (17H, m, olefinic and phenyl H); MS *m/z* 336 (M^+).

Found: C, 74.89; H, 6.22. Calcd for $C_{21}H_{20}O_2S$: C, 74.97; H, 5.99%.

*2-Methylsulfonyl-1,4-di(2-thienyl)-1,3-butadiene (**4d**)*: Yield 0.47 g (1.59 mmol, 53%); Mp 123—125 °C; IR (KBr): 1290, 1130 cm^{-1}; ^{1}H NMR δ=3.03 (3H, s, Me), 6.70—8.00 (9H, m, olefinic and aromatic H); MS *m/z* 296 (M^+).

Found: C, 52.68; H, 4.02. Calcd for $C_{13}H_{12}O_2S_3$: C, 52.68; H, 4.08%.

*2-Ethoxycarbonyl-1,4-diphenyl-1,3-butadiene (**4e**)*: Yield 0.218 g (0.786 mmol, 26%); Oil; IR(neat) 1710 cm^{-1}; ^{1}H NMR δ=1.38 (3H, t, Me), 4.34 (2H, q, $\underline{CH_2}CH_3$), 6.50—7.80 (13H, m, olefinic and phenyl H); MS Found: *m/z* 278.1302. Calcd for $C_{19}H_{18}O_2$: 278.1302 (M^+).

*2-Ethoxycarbonyl-1,4-di(2-thienyl)-1,3-butadiene (**4f**)*: Yield 0.248 g (0.855 mmol, 29%); Oil; IR (neat) 1700 cm^{-1}; ^{1}H NMR δ=1.37 (3H, t, Me), 4.32 (2H, q, $\underline{CH_2}CH_3$), 6.50—7.80 (9H, m, olefinic and phenyl H); MS *m/z* 290 (M^+).

Found: C, 62.05; H, 4.88. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.04; H, 4.86%.

*Synthesis of 2-Methylsulfonylnaphthalene (**7**).* The similar reaction of **1a** (2 mmol) with phthalaldehyde (0.268 g, 2 mmol) gave 0.126 g (31%) yield of **7** as white solid: Mp 138—140 °C; IR (KBr) 1290, 1120 cm^{-1}; ^{1}H NMR δ=3.12 (3H, s, Me), 7.20—8.60 (7H, m, aromatic H); MS *m/z* 206 (M^+).

Found: C, 63.64; H, 4.92. Calcd for $C_{11}H_{10}O_2S$: C, 64.06; H, 4.89%.

*One-Pot Reaction of **1a,b** with Butyraldehyd (**3e**).* *The Reaction Using **1a***: The reaction of **1a** (3 mmol) with **3e** (0.433 g, 6 mmol) gave 0.323 g (49%) yield of **8**: Oil: IR (neat) 1240, 1020, 960 cm^{-1}; ^{1}H NMR δ=1.04 (3H, t, J=7.03 Hz, $CH_2\underline{CH_3}$), 1.32 (6H, t, J=7.03 Hz, $OCH_2\underline{CH_3}$), 1.80—2.50 (2H, m, $\underline{CH_2}CH_3$), 3.70—4.20 (4H, m, $O\underline{CH_2}CH_3$), 5.10—7.60 (4H, m, olefinic H); ^{13}C NMR δ=12.57, 16.12 (d, $^3J_{P\text{-}C}$=6.88 Hz), 25.49, 61.27 (d, $^2J_{P\text{-}C}$=5.16 Hz), 114.34 (d, $^1J_{P\text{-}C}$=191.70Hz), 128.20 (d, $^3J_{P\text{-}C}$=27.51 Hz), 144.77, 148.92 (d, $^2J_{P\text{-}C}$=6.02 Hz). MS Found: *m/z* 218.1075. Calcd for $C_{10}H_{19}O_3P$: 218.1072.

*The Reaction Using **1b***: The reaction of **1b** (0.70 mmol) with **3e** (0.106 g, 1.47 mmol) produced 0.082 g (0.27 mmol, 40%) of an 1:1 mixture of **9a** and **9b**: Oil; IR (neat) 1710, 1250, 1030, 970 cm^{-1}; ^{1}H NMR δ=1.29 (9H, t, J=7.03 Hz, $OCH_2\underline{CH_3}$), 0.60—1.90 (5H, m, =$CHCH_2\underline{CH_2}\underline{CH_3}$), 1.90—3.30 (4H, m, PCH_2– and =$CH\underline{CH_2}CH_2CH_3$), 3.70—4.50 (6H, m, $O\underline{CH_2}CH_3$), 5.85—6.35 (0.5H, m, vinylic H), 6.70—7.15 (0.5H, m, vinylic H); MS Found: *m/z* 292.1413. Calcd for $C_{13}H_{25}O_5P$: 292.1438.

References

1) For the preceding paper in this series, see: T. Minami, K. Nishimura, I. Hirao, H. Suganuma, and T. Agawa, *J. Org. Chem.*, **47**, 2360 (1982).

2) T. Minami, H. Suganuma, and T. Agawa, *Chem. Lett.*, **1978**, 285.