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SYNTHESIS OF BUTADIENYLPHOSPHONATES CONTAINING ELECTRONEGATIVE SUBSTITUENTS AND THEIR SYNTHETIC APPLICATIONS TO FUNCTIONALIZED CYCLOPENTENYLPHOSPHONATES

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Treatment of 1,3-butadienylphosphonates bearing electronegative substituents with oxosulfonium and phosphonium ylides leads to functionalized 2-cyclopenten-1-ylphosphonates.

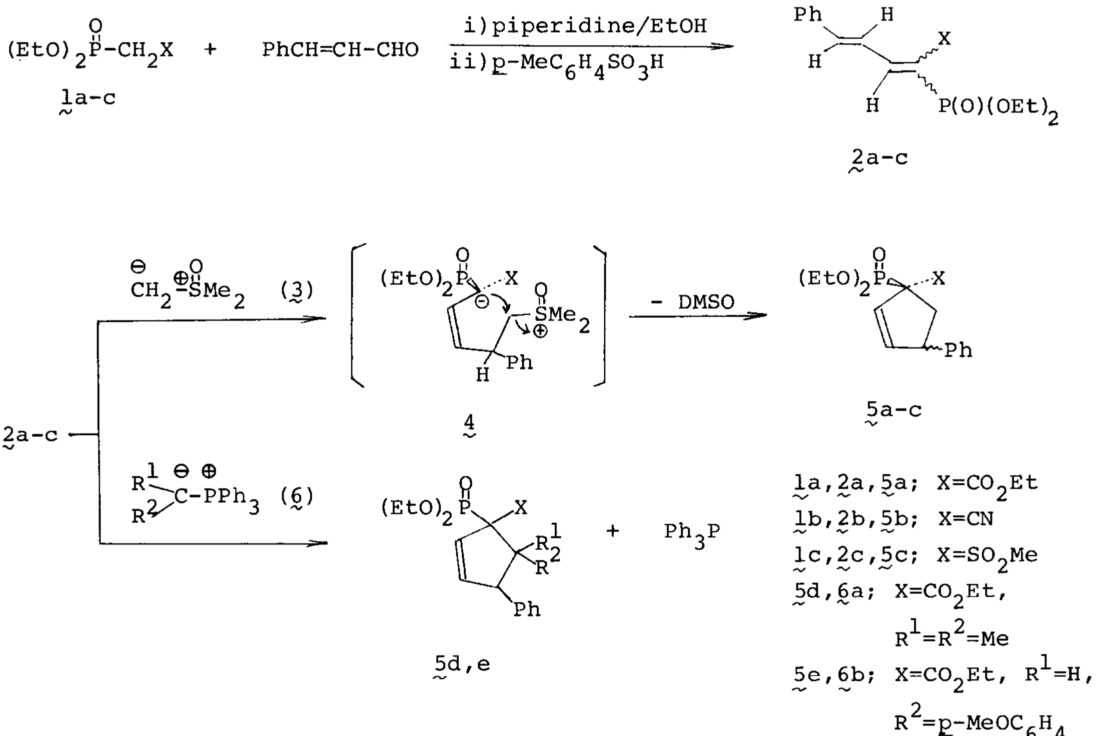
In the previous papers[1,2], we reported the synthesis of vinylphosphonates and their use in syntheses of various kinds of heterocyclic compounds, and of unsaturated systems such as trienes, dienynes, etc. bearing functionality which permitted production of regioselectively substituted aromatic compounds. In connection with continuing interest in the synthetic application of vinylphosphonates and their related organophosphorus reagents, we report here the synthesis of butadienylphosphonates containing electronegative substituents and their synthetic applications to functionalized cyclopentenylphosphonates.

Diethyl 1-ethoxycarbonyl-(**2a**), 1-cyano-(**2b**) and 1-methanesulfonylbutadienylphosphonates (**2c**) were synthesized in good yields by the condensations of diethyl ethoxycarbonylmethyl-(**1a**), cyanomethyl-(**1b**) and (methanesulfonyl)methylphosphonates (**1c**) with cinnamaldehyde.

While 2,4-dienoic acid esters reacted with sulfonium[3] and oxosulfonium ylides[4] to give exclusively cyclopropanation products, treatment of the 1,3-butadienylphosphonates **2** with dimethyloxosulfonium methylide (**3**) led to none of the expected cyclopropanation products but to only diethyl 1-substituted-4-phenyl-2-cyclopenten-1-yl phosphonates **5** in very good yields (Table 1).

This interesting finding could be explained by the Michael addition of the oxosulfonium ylide **3** to the δ carbon of the butadienylphosphonates **2** giving the intermediate betains **4** stabilized by both phosphoryl and electron-withdrawing groups, followed by elimination of dimethylsulfoxide into the 2-cyclopentenylphosphonates **5**. Such preference of the attack of nucleophiles to the δ carbon of butadienylphosphonate derivatives has been similarly observed in the reactions using nucleophiles such as anions[5,6].

This result prompts us to investigate whether or not use of phosphonium ylides, instead of the oxosulfonium ylide **3**, produces similar results. The reaction of **2a** with isopropylidene-(**6a**) and *p*-methoxybenzylidenetriphenylphosphoranes (**6b**) afforded the hoped-for 5,5-dimethyl-2-pentenyl-(**5d**) and 5-(*p*-methoxyphenyl)-



Scheme 1

2-pentenylphosphonate derivatives (5e) in 58 % and 45 % yields accompanying elimination of comparable yield of triphenylphosphine.

Thus, butadienylphosphonates bearing electronegative substituents are versatile reagents for the synthesis of functionalized cyclopentenylphosphonates, which could be useful as potential synthetic precursors to highly functionalized cyclopenten systems.

Experimental procedures for synthesis and reactions of the butadienylphosphonates were demonstrated in a representative example as follows:

Synthesis of the butadienylphosphonate 2a. A solution of 1a (11.2 g, 0.05 mol) and cinnamaldehyde (6.61 g, 0.05 mol) in ethanol (100 ml) containing catalytic amounts of piperidine was refluxed for ca. 30 hrs until disappearance of the carbonyl absorption at 1675 cm^{-1} in the ir spectrum. After removal of solvent ethanol, the residue was dissolved in dry benzene (100 ml) containing catalytic amounts of p-toluenesulfonic acid and the solution was refluxed for 3 hrs. After usual work-up, bulb-to-bulb distillation of the residue gave 13.9 g (82 %) yield of pure 2a having the following physical properties: bp 178°C (1 mm); ir (neat) 1695 (C=O) and 1230 cm^{-1} (P=O); ^1H nmr ($CDCl_3$) δ 1.35 and 1.38 (9H, t, CH_3), 3.91-4.51 (6H, m,

Table 1.[a] Physical Properties and Yields of Butadienylphosphonates 2 and Cyclopentenylphosphonates 5

Compd.	X	R^1	R^2	Bp[°C(mmHg)] Mp[°C]	Yield[b] (%)	^{1}H-NMR($CDCl_3$) (δ)
2a	$CO_2C_2H_5$	—	—	178(1)	82	1.35 and 1.38(t, 9H), 3.91-4.51(m, 6H), 6.90-8.50(m, 8H)
2b	CN	—	—	168(2)	78	1.38(t, J=7.05Hz, 6H), 3.90-4.50(dq, 4H), 7.05-8.05(m, 8H)
2c	SO_2CH_3	—	—	114	93	1.31(t, J=7.10Hz, 6H), 3.13(s, 3H), 3.85-4.45(dq, 4H), 6.90-8.40(m, 8H)
5a	$CO_2C_2H_5$	—	—	190(2)	91	1.0-1.55(m, 9H), 1.60-2.10 (m, 2H), 2.20-3.05(m, 1H), 3.80-4.50(m, 6H), 5.70-6.20(dd, 1H), 6.45-6.85 (m, 1H), 7.26(s, 5H)
5b	CN	—	—	175(2)	87	1.38(t, J=7.14Hz, 6H), 1.55-2.20(m, 2H), 2.30-3.0(m, 1H), 3.90-4.50(dq, 4H), 5.65-6.15(dd, 1H), 6.62-6.89(d, 1H), 7.30 (s, 5H)
5c	SO_2CH_3	—	—	77	40	1.10-1.55(m, 6H), 1.60-2.20(m, 2H), 2.50-3.10(m, 1H), 3.15(s, 3H), 3.85-4.55(dq, 4H), 6.0-7.10(m, 2H), 7.39(s, 5H)
5d	$CO_2C_2H_5$	CH_3	CH_3	oil	58	1.10-1.60(t, J=6.93Hz, 9H), 1.35(s, 6H), 2.39-2.96(m, 1H), 4.02-4.50 (m, 6H), 6.42-6.95(m, 2H), 7.23-7.55(m, 5H)
5e	$CO_2C_2H_5$	H	p-$CH_3OC_6H_4$	oil	45	1.27(t, J=6.96Hz, 9H), 1.50-2.50(m, 2H), 3.71(s, 3H), 3.84-4.32(m, 6H), 6.08-6.81(m, 2H), 7.11-7.41(m, 9H)

a. Satisfactory elemental analyses and spectroscopic data were obtained in all compounds 2 and 5 listed in the table.

b. Yields were not optimized and correspond to isolated yields.

OCH_2), and 6.90-8.50(8H, m, phenyl and olefinic H).

Synthesis of the 2-cyclopentenylphosphonate 5a. To a solution of dimethyloxosulfonium methylide(3)(5 mmol) in 15 mL of dry DMSO was added 2a(1.67 g, 5 mmol) in 5 mL of dry DMSO and then the reaction mixture was stirred at 50°C for 5hrs. After conventional work-up, distillation of the residue produced 1.60 g(91 %) yield of pure 5a having the following physical properties: bp 190°C(2 mm); ir (neat) 1705(C=O) and 1240 cm^{-1}(P=O); ^{1}H nmr($CDCl_3$)δ 1.0-1.55(9H, m, CH_3), 1.60-2.10(2H, m, $-CH_2-$), 2.20-3.05(1H, m, -CH<), 3.80-4.50(6H, m, OCH_2), 5.70-6.20(1H, dd, J=8.70, 15.10Hz, =CH-), 6.45-6.85(1H, m, =C$\underline{\text{H}}$-CHPh-), and 7.26(5H, s, phenyl H); ^{13}C nmr(CDCl$_3$)δ 14.0, 16.63(d, $J_{^{31}P-^{13}C}$=6.01Hz, P-OCH$_2\underline{\text{C}}$H$_3$), 20.98, 24.52(d, $J_{^{31}P-^{13}C}$=161.61Hz, P-$\underline{\text{C}}$-CO$_2$C$_2$H$_5$), 33.44, 61.96(d, $J_{^{31}P-^{13}C}$=13.75Hz, P-O$\underline{\text{C}}$H$_2$CH$_3$), 62.18, 124.48, 125.97, 127.23, 128.37, 133.57(d, $J_{^{31}P-^{13}C}$=6.88Hz, P-C-CH=$\underline{\text{C}}$H-), 136.54, 169.41(d, $J_{^{31}P-^{13}C}$=6.9Hz, P-C-$\underline{\text{C}}$O$_2$C$_2$H$_5$).

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