Reactions of buta-1,2-dienylphosphonate with thiols

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Addition of propane-1-thiol and ethane-1,2-dithiol to 3,3-dimethylallenylphosphonate occurs at the 1,2-double bond of the cumulene system.

Key words: allenylphosphonates, propane-1-thiol, ethane-1,2-dithiol, nucleophilic addition.

Allenes activated by a phosphoryl group are known[1] to be highly reactive in different types of reactions; for instance, nucleophilic reagents easily add to the 1,2-double bond of their cumulene system. Earlier,[2] we showed that allenylphosphonates bearing no substituents at the terminal C atom undergo base-catalyzed isomerization into the corresponding alkynes; as a result, it is alkynes that are attacked by nucleophilic reagents. The introduction of two methyl groups at the terminal C atom of allenylphosphonates prevents their isomerization.[3,4] It was of interest to estimate the possibility of adding thiols to 3,3-disubstituted allenylphosphonates using reactions of propane-1-thiol and ethane-1,2-dithiol with 3-methylbuta-1,2-dienylphosphonate as examples. Note that reactions of allenylphosphonates with dithiols have not been studied previously.

The reaction of diethyl 3-methylbuta-1,2-dienylphosphonate (**1**) with an equimolar amount of PrSH in the presence of PrSNa affords adduct **2** (Scheme 1). The addition of the thiol to the 1,2-double bond of the cumulene was deduced from spectroscopic data. The IR spectrum of adduct **2** contains no absorption band at 1955 cm^{-1} for the allene triad, and its ^1H NMR spectrum shows a doublet for the methylene protons at δ 3.00 ($^2J_{P,H}$ = 21.6 Hz) and signals for the protons of two methyl groups bound to the sp^2-C atom.

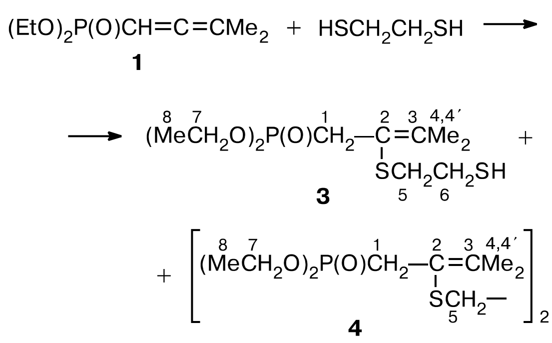
Scheme 1

$$\underset{\mathbf{1}}{(EtO)_2P(O)CH{=}C{=}CMe_2} + PrSH \longrightarrow$$

$$\longrightarrow \underset{\mathbf{2}}{(EtO)_2P(O)CH_2{-}C(SPr){=}CMe_2}$$

Phosphonate **1** reacts with an equimolar amount of ethane-1,2-dithiol in the presence of EtONa to give 1 : 1 and 2 : 1 adducts (**3** and **4**) in 41 and 26% yields, respectively. Compound **3** contains a free HS group; in its ^1H NMR spectrum, a triplet for the HS-proton appears at δ 1.96 ($^3J_{H,H}$ = 8.1 Hz) (*cf.* for C_3H_7SH: ^1H NMR, δ: 1.97 (t, 1 H, SH, $^3J_{H,H}$ = 7.9 Hz)). The ^1H NMR spectrum of adduct **4** exhibits no signal for the HS-proton. The structures of compounds **3** and **4** were confirmed by the parameters of their ^1H and ^{13}C NMR spectra, integral intensity ratios, and the data from elemental analysis and mass spectrometry (Scheme 2).

Scheme 2



$$\underset{\mathbf{1}}{(EtO)_2P(O)CH{=}C{=}CMe_2} + HSCH_2CH_2SH \longrightarrow$$

$$\longrightarrow \underset{\mathbf{3}}{(\overset{8}{Me}\overset{7}{C}H_2O)_2P(O)\overset{1}{C}H_2{-}\underset{\underset{5}{S}\overset{}{C}H_2\underset{6}{C}H_2SH}{\overset{2}{C}}{=}\overset{3}{C}\overset{4,4'}{Me_2}} +$$

$$+ \underset{\mathbf{4}}{\left[(\overset{8}{Me}\overset{7}{C}H_2O)_2P(O)\overset{1}{C}H_2{-}\underset{\underset{5}{S}CH_2{-}}{\overset{2}{C}}{=}\overset{3}{C}\overset{4,4'}{Me_2}\right]_2}$$

With a double excess of butadienylphosphonate (**1**) with respect to dithiol, the yield of compound **4** is increased to 50—60%.

Thus, the above reaction is a simple and convenient method for the synthesis of new polyfunctional alkenes containing heteroatomic groups.

Experimental

IR spectra were recorded on a UR-20 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian Unity-300 spectrometer (300, 75.43, and 121.42 MHz, respectively). ^1H and ^{13}C chemical shifts were referenced to Me_4Si, ^{31}P chemi-

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cal shifts, to 85% H_3PO_4 as the external standard. Mass spectra were recorded on a MAT-212 mass spectrometer.

Diethyl 3-methyl-2-propylthiobut-2-enylphosphonate (2). A saturated solutions of PrSNa in PrSH (5—6 drops) was added to a mixture of buta-1,2-dienylphosphonate[3] **1** (2.88 g, 0.014 mol) and PrSH (1.07 g, 0.014 mol); the addition was accompanied by a temperature rise to 70 °C. The reaction mixture was kept at 80—100 °C until the absorption band at 1955 cm^{-1} disappeared from its IR spectrum and distilled to give compound **2** (2.45 g, 62%), b.p. 104—106 °C (0.02 Torr), n_D^{20} 1.4810. Found (%): C, 52.23; H, 8.78. $C_{12}H_{25}O_3PS$. Calculated (%): C, 51.79; H, 8.93. ^1H NMR ($CDCl_3$), δ: 1.04 (t, 3 H, $C\underline{H}_3CH_2CH_2S$, $^3J_{H,H} = 7.3$ Hz); 1.38 (t, 6 H, $C\underline{H}_3CH_2OP$, $^3J_{H,H} = 7.1$ Hz); 1.58 (tq, 2 H, $C\underline{H}_2CH_2S$, $^3J_{H,H} = 7.3$ Hz); 1.93 (d, 3 H, $=CCH_3$, $^5J_{P,H}^{cis} = 4.7$ Hz); 2.08 (d, 3 H, $=CCH_3$, $^5J_{P,H}^{trans} = 6.4$ Hz); 2.67 (t, 2 H, $CH_2C\underline{H}_2S$, $^3J_{H,H} = 7.3$ Hz); 3.00 (d, 2 H, CH_2P, $^2J_{P,H} = 21.6$ Hz); 4.18 (dq, 4 H, $CH_3C\underline{H}_2OP$, $^3J_{P,H} = {}^3J_{H,H} = 7.1$ Hz). ^{31}P-{^1H} NMR (CCl_4), δ: 25.6.

The reaction of buta-1,2-dienylphosphonate (1) with ethane-1,2-dithiol. A saturated ethanolic solution of EtONa (4—5 drops) was added to a mixture of phosphonate **1** [3] (3.35 g, 0.016 mol) and dithiol (1.89 g, 0.020 mol). A temperature rise to 110 °C was observed. The mixture was kept at 70—100 °C for 1.5 h (monitored by IR spectroscopy). Distillation gave **diethyl [2-(2-mercaptoethyl)thio-3-methylbut-2-enyl]phosphonate (3)** and **2,2´-(ethylenedithio)di(diethyl 3-methylbut-2-enylphosphonate) (4)**. Compound 3. Yield 2.15 g (41%), b.p. 131—132 °C (0.1 Torr), n_D^{20} 1.5061. Found (%): C, 45.08; H, 7.99; S, 21.52. $C_{11}H_{23}O_3PS_2$. Calculated (%): C, 44.29; H, 7.72; S, 21.48. ^1H NMR ($CDCl_3$), δ: 1.57 (t, 6 H, $C\underline{H}_3CH_2OP$, $^3J_{H,H} = 7.0$ Hz); 1.96 (t, 1 H, HS, $^3J_{H,H} = 8.1$ Hz); 2.13 (d, 3 H, $=CCH_3$, $^5J_{P,H}^{cis} = 4.5$ Hz); 2.27 (d, 3 H, $=CCH_3$, $^5J_{P,H}^{trans} = 5.9$ Hz); 2.86 (dt, 2 H, $CH_2C\underline{H}_2SH$, $^3J_{H,H} = 8.1$ Hz, $^3J_{H,H} = 7.5$ Hz); 3.10 (d, 2 H, CH_2P, $^2J_{P,H} = 21.0$ Hz); 3.14 (t, 2 H, $CH_2SC=$, $^3J_{H,H} = 7.5$ Hz); 4.30 (dq, 4 H, $MeC\underline{H}_2OP$, $^3J_{H,H} = {}^3J_{P,H} = 7.0$ Hz). ^{13}C-{^1H} NMR ($CDCl_3$), δ, $J_{P,C}$: 16.03 (d, C(8), $^3J = 4.8$ Hz); 21.65 (d, C(4´), $^4J = 2.6$ Hz); 23.30 (d, C(4), $^4J = 2.6$ Hz); 24.22 (s, C(6)); 31.88 (d, C(1), $^1J = 140.3$ Hz); 36.43 (s, C(5)); 61.28 (d, C(7), $^2J = 6.6$ Hz); 114.91 (d, C(3), $^3J = 11.5$ Hz); 142.5 (s, C(2)).

Compound **4**. Yield 1.35 g (26%), b.p. 199—201 °C (0.1 Torr), n_D^{20} 1.5145. Found (%): C, 48.21; H, 7.83; P, 12.35; S, 13.43. $C_{20}H_{40}O_6P_2S_2$. Calculated (%): C, 47.81; H, 7.97; P, 12.35; S, 12.75. ^1H NMR ($CDCl_3$), δ: 1.47 (t, 12 H, $C\underline{H}_3CH_2OP$, $^3J_{H,H} = 7.0$ Hz); 2.02 (d, 6 H, $=CCH_3$, $^5J_{P,H}^{cis} = 4.8$ Hz); 2.17 (d, 6 H, $=CCH_3$, $^5J_{P,H}^{trans} = 6.0$ Hz); 2.93 (s, 4 H, $SC\underline{H}_2C\underline{H}_2S$); 3.07 (d, 4 H, CH_2P, $^2J_{P,H} = 20.5$ Hz); 4.23 (dq, 8 H, $MeC\underline{H}_2OP$, $^3J_{P,H} = {}^3J_{H,H} = 7.0$ Hz). ^{13}C-{^1H} NMR ($CDCl_3$), δ, $J_{P,C}$: 15.87 (d, C(8), $^3J = 5.1$ Hz); 21.35 (d, C(4´), $^4J = 1.2$ Hz); 23.03 (d, C(4), $^4J = 1.2$ Hz); 31.46 (d, C(1), $^1J = 139.7$ Hz); 32.16 (s, C(5)); 61.16 (d, C(7), $^2J = 5.3$ Hz); 115.1 (d, C(3), $^3J = 13.2$ Hz); 142.1 (s, C(2)). MS (EI, 60 eV), *m/z* (I_{rel} (%)): 502 $[M]^+$ (50), 238 (100), 205 (62), 149 (61), 67(66).

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