A Simple Preparation of Diethyl 1-Acylamino-1-ethenephosphonates

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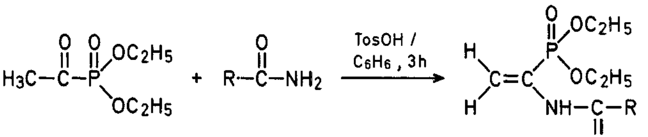
The chemistry of dialkyl 1-acylamino-1-alkenephosphonates has been little studied because of the lack of a simple synthetic method. A few members of the class, however, have been obtained[1,2].

We report a new preparation of diethyl 1-acetylamino-, 1-benzoylamino-, and 1-benzoxycarbonylamino-1-ethenephosphonates (**3a–c**) which can be obtained by condensation of crude diethyl 1-oxoethanephosphonate (**1**) with amides (**2a–c**) in dry benzene in the presence of *p*-toluenesulfonic acid.



1 **2a-c** **3a-c**

Diethyl 1-acylamino-1-ethenephosphonates (**3a–c**) were obtained in 12–20% yield. Their physicochemical and spectral data are presented in the Table. The ^{31}P-N.M.R. experiments clearly revealed that diethyl phosphite (~35%) is formed as a undesirable product of reaction of diethyl 1-oxoethanephosphonate with amides.

According to our present knowledge, the synthesis of compounds **3a–c** is the third example (after phosphonyloximes[3,4] and phosphonylhydrazine[5]) of the C—N bond formation during reactions of dialkyl 1-oxoalkanephosphonates.

I.R. spectra were recorded on a Perkin-Elmer 527 spectrophotometer. ^{1}H-N.M.R. spectra were recorded at 60 MHz with a BS 467 Tesla spectrometer using hexamethyldisiloxane as internal standard. ^{31}P-N.M.R. spectra were obtained on a Jeol JNM-C-60H1 spectrometer with H_3PO_4 as the external standard. Column chromatography was performed on the Merck silica gel, 70–230 mesh, using ethyl acetate/cyclohexane (4:1) as eluent.

Diethyl 1-Benzyloxycarbonylamino-1-ethenephosphonate (3c); Typical Procedure:

To well-stirred acetyl chloride (18.1 g, 0.23 mol), triethyl phosphite (38.2 g, 0.23 mol) is added dropwise at 0–5 °C. The mixture is kept at room temperature for 30 min and then the temperature is gradually increased to 100 °C for 1 h. The volatile components of the mixture are removed in vacuo. The residue is crude *diethyl 1-oxoethanephosphonate* (**1**); yield: 36.0 g (87%); n_D^{20}: 1.4260 (Lit.[6], n_D^{20}: 1.4231).

Crude diethyl 1-oxoethanephosphonate (**1**; 36.0 g, 0.20 mol), anhydrous *p*-toluenesulfonic acid (12.0 g), and benzyl carbamate (**2c**; 30.2 g, 0.20 mol) in benzene (200 ml) are heated under reflux with azeotropic removal of water for 3 h. The benzene solution is washed with 10% aqueous sodium hydrogen carbonate solution (50 ml) and then benzene and diethyl phosphite are distilled off in vacuo. After removal of crystallized unreacted benzyl carbamate (about 30%), the crude product is purified by column chromatography to afford pure **3c**; yield: 12.5 g (20%).

Products **3a** and **3b** are prepared in the same way as **3c** using acetamide (**2a**) and benzamide (**2b**) were employed.

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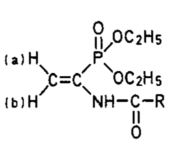
Table. Diethyl 1-Acylamino-1-ethenephosphonates **3a–c**

Product No.	R	Yield [%]	n_D^{20} or m.p. [°C]	Molecular formula[a]	I.R. (neat or KBr) ν [cm^{-1}]	^{1}H-N.M.R. (CCl_4)[b] δ [ppm]	^{31}P-N.M.R. (CCl_4)[c] δ [ppm]
3a	CH_3	12	1.4685	$C_8H_{16}NO_4P$ (221.2)	3280, 1683, 1520, 1250, 1015	5.34 [d, 1H, H(a), $J_{HP}=19$ Hz]; 6.53 [d, 1H, H(b), $J_{HP}=42$ Hz]	−12.5
3b	C_6H_5	15	1.5320	$C_{13}H_{18}NO_4P$ (283.3)	3400, 3250, 1670, 1505, 1265, 1245, 1015	5.42 [d, 1H, H(a), $J_{HP}=19$ Hz]; 6.69 [d, 1H, H(b), $J_{HP}=42$ Hz]	−12.3
3c	$C_6H_5CH_2O$	20	50–52°	$C_{14}H_{20}NO_5P$ (313.3)	3220, 1715, 1550, 1230, 1020	5.22 [d, 1H, H(a), $J_{HP}=19$ Hz]; 6.22 [d, 1H, H(b), $J_{HP}=41$ Hz]	−11.9

[a] Satisfactory microanalyses obtained: N ±0.18, P ±0.25.

[b]



[c] Signals to lower field than the standard are negative.

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