Supplementary Material

Phosphonate-amidophosphate rearrangements in phosphorylated enamides and imines

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General procedure for the preparation of compounds 1a-c. A solution of corresponding trichloroacetimidoylchloride (0.03 mol) and trialkylphosphite (0.06 mol) in toluene (50 ml) was stirred at 120°C for 2-3 h. Solvent was evaporated in vacuo, the residue was distilled.

Diethyl (2,2-dichloro-1-(diethoxyphosphoryl)vinyl)(methyl)phosphoroamidate (1a).[16] Obtained from 2,2,2-trichloro-N-methyl-acetimidoyl chloride (5.85 g, 0.03 mol) and triethylphosphite (9.96 g, 0.06 mol). Yield 6.33 g (53%), bp 118-120°C (0.08 Torr) [lit.[16] bp 132-135°C (0.01 Torr)]. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.28-1.40 m (12H, $OCH_2\underline{CH_3}$), 2.83 d (3H, NMe, J ~ 9.3Hz), 4.2 m (8H, OCH_2). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ 10.0 (CP), 3.4 (NP).

Diethyl (2,2-dichloro-1-(diethoxyphosphoryl)vinyl)(ethyl)phosphoroamidate (1b).[16] Obtained from 2,2,2-trichloro-N-ethyl-acetimidoyl chloride (6.27 g, 0.03 mol) and triethylphosphite (9.96 g, 0.06 mol).Yield 8.65 g (70%) bp 143-145°C (0.07 Torr) [lit.[16] bp 130-132°C (0.01 Torr)]. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.16 t (3H, $NCH_2\underline{CH_3}$), 1.28-1.40 m (12H, $OCH_2\underline{CH_3}$), 3.32 m (2H, NCH_2), 4.22 m (8H, OCH_2). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ 10.5 (CP), 3.3 (NP).

Dipropyl (2,2-dichloro-1-(dipropoxyphosphoryl)vinyl)(methyl)phosphoroamidate (1c).[16] Obtained from 2,2,2-trichloro-N-methyl-acetimidoyl chloride (6.21 g, 0.03 mol) and tripropylphosphite (12.48 g, 0.06 mol).Yield 8.99 g (66%), bp 151-152°C (0.08 Torr) [lit. [16] bp 148-149°C (0.01 Torr)]. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 0.98 m (12H, $OCH_2CH_2\underline{CH_3}$), 1.72 m (8H, $OCH_2\underline{CH_2}CH_3$), 2.84 d (3H, NMe, J ~ 7.8Hz), 4.1 m (8H, OCH_2). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ 10.3 (CP), 3.3 (NP).

Diethyl (1-(diethoxyphosphoryl)-2,2-bis(diethylamino)vinyl)(methyl)phosphoroamidate (2a).[16] A solution of (1a) (2.99 g, 7.5 mmol) and diethylamine (3.29 g, 45 mmol) in benzene (in 25 mL) в was stirred at 90°C for 13 h. The obtained precipitate was filtered off, the filtrate was concentrated and distilled. Yield 2.58 g (73%), bp 148°C (0.15 Torr) [lit.[16] bp 140°C (0.01 Torr)], n_D^{20} 1.4822. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.12 m (12H, $\underline{Me}CH_2N$), 1.30 m (12H, $\underline{Me}CH_2O$), 2.88 d (3H, MeN, $^{3}J_{HP}$ 8.1Hz), 2.9-4.3 m (8H, CH_2N), 4.04 m (8H, OCH_2). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ 9.8 (NP), 25.4 (CP).

