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PHOSPHORUS CONTAINING SPIROAZIRIDINES

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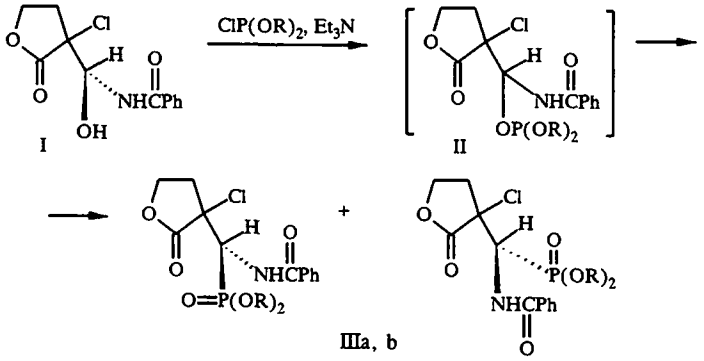
2-[Benzoylamino(dialkoxyphosphoryl)methyl]-2-chloro-4-butanolides are readily prepared by treating the corresponding half amidal of α-chloro-α-formyl-γ-butyrolactone with chlorophosphites. They undergo intramolecular nucleophilic substitution using sodium hydride to give previously unknown phosphorus containing aziridines.

Acylamino organophosphorus compounds are available reagents and are widely used in the synthesis of five- and six-membered nitrogen- and phosphorus-containing heterocyclic systems [1-3]. However, there is no evidence for the use of these reagents for the preparation of small heterocycles, in particular aziridines. We report a convenient preparative method for synthesis of functionally substituted α-aminophosphonates IIIa, b which is of interest since these compounds can react with bases to give polyfunctional aziridines.

The synthesis of α-chloro-α-formyl-γ-butyrolactone (I) has previously been reported by us [4]. It reacts with chlorophosphites in dioxane solvent with triethylamine to give the phosphonates IIIa, b in 70-75% yield. Evidently the intermediate phosphites II are unstable adducts which readily undergo phosphite–phosphonate rearrangement under the experimental conditions, as is seen in similar types of compounds [5-7].



I II IIIa, b

III a R = Et, b R = Pr-*i*

The IR spectra of butanolides IIIa, b show characteristic, intense bands for the phosphoryl group at 1230 cm^{-1}, amide and lactone carbonyl bands at 1670 and 1790 cm^{-1} respectively, and a broad NH stretching absorption band at 3300-3320 cm^{-1}. From the ^1H and ^{31}P NMR data, compounds IIIa, b are formed as a mixture of diastereomers. Thus in the PMR spectra of lactones IIIa, b the methine proton appears as two doublets at 5.33-5.40 ppm. The phosphorus chemical shifts occur at 15.8-17.8 ppm as two singlets which confirms the phosphonate structure and the presence of diastereomers.

Functionally substituted aziridines are formed from the phosphonates III by treatment with sodium hydride. The proposed mechanism of formation of the substituted aziridines Va, b includes a stage of generation of the N-anion IV and its intramolecular nucleophilic cyclization.

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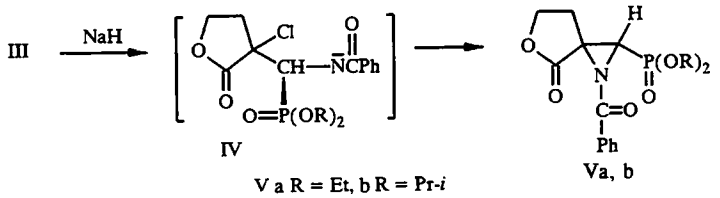
TABLE 1. Parameters for Compounds Synthesized

Compound	Empirical formula	Found, %/ Calculated, %			mp, °C	Yield, %
		Cl	N	P		
IIIa	$C_{16}H_{21}ClNO_6P$	9,25 / 9,11	3,47 / 3,59	7,91 / 7,95	121	70
IIIb	$C_{18}H_{25}ClNO_6P$	8,25 / 8,48	3,48 / 3,35	7,35 / 7,41	126	75
Va	$C_{16}H_{20}NO_6P$		3,95 / 3,96	8,81 / 8,78	165	60
Vb	$C_{18}H_{24}NO_6P$		3,70 / 3,67	8,07 / 8,13	153	55

Compound	IR spectrum, cm^{-1}	PMR spectrum, ppm, J, Hz, (DMSO-D_6)	^{31}P NMR spectrum, ppm
IIIa	1020 (P—O—C), 1230 (P=O), 1675 (N—C=O), 1790 (OC=O), 3300 (NH)	1,10 (6H, m, CH_3); 2,50, 3,18 (2H, m.m, CH_2); 4,00 (2H, m, OCH_2); 4,50 (2H, m, OCH_2); 5,33 (1H, d.d, J = 20, 11,2, CH); 7,50 (3H, m, Ph), 7,9 (2H, m, Ph), 8,9 (1H, d, J = 11,25, NH)	16,0, 17,8
IIIb	1020 (P—O—C), 1230 (P=O), 1675 (N—C=O), 1785 (OC=O), 3320 (NH)	1,15 (12H, d, CH_3); 2,60, 3,15 (2H, m.m, CH_2); 4,3 (2H, m, OCH_2); 4,75 (2H, m, OCH); 5,40 (1H, d. d J = 20, 11,25, CH); 6,85 (1H, d, J = 11,25, NH); 7,50 (3H, m, Ph); 7,90 (2H, m, Ph)	15,80, 15,83
Va	1030 (P—O—C), 1250 (P=O), 1675 (NC=O), 1790 (OC=O)	1,30 (6H, m, CH_3); 2,30 (2H, m, CH_2); 4,15 (6H, m, OCH_2); 4,75 (1H, d, J = 17,5, CH); 7,50 (3H, m Ph); 7,90 (2H, m, Ph)	16,0
Vb	1020 (P—O—C), 1250 (P=O), 1670 (NC=O), 1785 (OC=O)	1,15 (12H, t, CH_3); 2,75, 3,15 (2H, m, CH_2); 4,50 (4H, m, OCH_2, OCH); 5,15 (1H, d, J = 20,2, CH); 7,50 (3H, m, Ph); 7,90 (2H, m, Ph)	15,3

*^{13}C NMR Spectrum, ppm: 25.7 (CH_3); 56.1 (CH_2); 67.7 (OCH_2); 71.1, 71.8 (OCH_2); 79.7, 81.2 (PCH); 98.9 (C—N); 137.4, 137.6, 137.8, 140.8 (Ph); 173.5 (Ph—C=O); 183.1 (OC=O).



V a R = Et, b R = Pr-*i*

The spiro compounds Va, b are white crystalline materials existing as a single diastereomer. Their structure was proved using IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy and confirmed using elemental analysis (see Table 1). It should be noted that the ^1H and ^{13}C NMR data do not lead to an absolute steric structure for Va, b.

EXPERIMENTAL

IR Spectra were recorded on a UR-20 instrument for Vaseline mulls and ^1H and ^{13}C NMR spectra on a Tesla BW-567 spectrometer at 100 MHz. ^{31}P NMR Spectra were recorded on a Bruker WP-80.

Parameters for the compounds obtained are given in Table 1.

2-[Benzoylamino(dialkoxyphosphoryl)methyl]-2-chloro-4-butanolide (IIIa, b). Triethylamine (0.03 mole) was added with stirring to a mixture of the half amidal I (0.03 mole) and dialkylchlorophosphite (0.03 mole) in dry dioxane (50 ml) at 10-15°C. The product was held for 2 h at room temperature. The precipitate was filtered and, after removal of solvent, the precipitated crystals of IIIa, b were filtered and dried *in vacuo*.

1-Benzoyl-2-dialkoxyphosphoryl-4-oxo-1-aza-5-oxaspiro[2,4]heptane (Va, b). Sodium hydride (0.02 mole) was added with stirring to a solution of the phosphonate IIIa, b (0.01 mole) in dry dimethoxyethane (40 ml) at −10°C. The mixture was held with cooling for 1 h and at room temperature for 3 h. Water (2 ml) was added to the reaction mixture, the solvent removed, and the product extracted with chloroform (3 × 15 ml) and then dried ($MgSO_4$). After removal of solvent, the precipitated crystals of Va, b were filtered and recrystallized from acetone (see Table 1).

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