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Tetrahedron
Tetrahedron 60 (2004) 2187–2190

New pyrophosphate analogues: a facile access to *N*-(*O*-alkylsulfamoyl)phosphoramidic acids via a simple and quantitative reaction of *N*-(*O*-alkylsulfamoyl)trimethylphospha-λ⁵-azene with bromotrimethylsilane and water

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Received 15 October 2003; revised 12 January 2004; accepted 14 January 2004

Abstract—A new strategy to prepare pyrophosphate analogues through selective and quantitative cleavage of *N*-(*O*-alkylsulfamoyl)trialkylphospha-λ⁵-azene esters ($R-O-SO_2-N{=}P(OR')_3$) has been developed. Using pure bromotrimethylsilane, *N*-(*O*-alkyl-sulfamoyl)tris-trimethylsilylphospha-λ⁵-azenes ($R-O-SO_2-N{=}P(OSiMe_3)_3$) have been easily obtained as intermediates. *N*-(*O*-Alkyl-sulfamoyl)phosphoramidic acids ($R-O-SO_2-NH-P(O)(OH)_2$) have been formed quantitatively by hydrolysis of the silylated intermediates.

1. Introduction

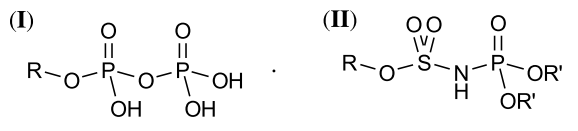
Nucleotide mono-, di-, or triphosphate analogues are of great interest for antiviral therapy.[1] They offer the possibility to bypass some of the phosphorylation steps which are essential to produce the nucleosides in their active triphosphate forms. Those products are supposed to take effect by the same mechanism: the compounds are first converted to their triphosphate analogue by cellular enzymes, followed by an inhibition of the viral DNA polymerase enzymes.[2] The antiviral potency is thought to depend on:

- The stability of phosphorylated analogues which could be hydrolyzed in the body by enzymes faster than their penetration into infected cells.
- The capacity of the analogue to penetrate the cell membrane compared to ionized species.
- The efficacy by which they are converted in infected cells into their active triphosphate form.

These problems are crucial for the antiviral potency of nucleoside analogues.[3,4] The investigations of new analogues of pyrophosphate or triphosphate groupment are of great interest.[5,6] Other molecules containing the pyrophosphate group such as isopentenyl pyrophosphate are of biological interest.[7] Isopentenyl pyrophosphate acts as an agonist of γδT cell receptors involved in the defence against viral or bacterial infections.[8,9] Isopentenyl pyrophosphate analogues represent potential activators of the immune system.

In a previous work[10] we have reported that alkylsulfamates can react with trialkylphosphite (Me, Et) in the presence of di*iso*propylazodicarboxylate (DIAD) to give *N*-(*O*-alkyl-sulfamoyl)trialkylphospha-λ⁵-azene. Under basic conditions in refluxing toluene, this derivative can loose an alkyl group to form *N*-(*O*-alkylsulfamoyl)dialkyl phosphoramidate ($R-O-SO_2-NH-P(O)(OR')_2$) (**II**). This kind of structure have only been described by Macchia and co-workers.[11] This structure (**II**) (R′=Me or Et) can be considered as a bioisostere of pyrophosphate (**I**) (Fig. 1).

Therefore, no work describing the preparation of the acidic form of (**II**) has been reported in literature. In this article, we develop in a three steps synthesis, an efficient access to



Pyrophosphate **Pyrophosphate analogue**

Figure 1. Pyrophosphate analogue.

Keywords: Alkylsulfamates; Phosphorylation; Pyrophosphate analogues.
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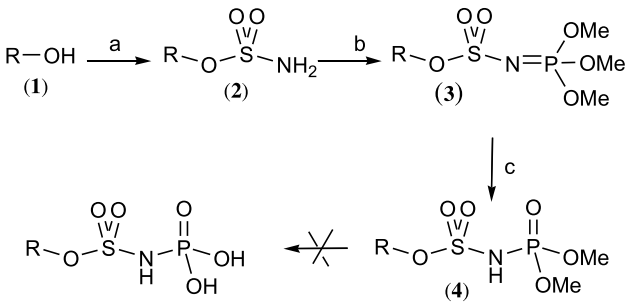
doi:10.1016/j.tet.2004.01.035

N-(*O*-alkylsulfamoyl)phosphoramidic acid starting from an alcohol.

2. Results and discussion

Sulfamates (**2**) were obtained by reacting the corresponding alcohol (**1**) with sulfamoylchloride in DMA (*N*,*N*-dimethylacetamide).[12,13] Reaction of (**2**) with trimethylphosphite (2 equiv.) and DIAD (2 equiv.) through a redox reaction afforded the *N*-(*O*-alkylsulfamoyl)trimethyl phospha-λ^5-azene (**3**). Compound (**3**) was then treated in toluene under reflux in the presence of an organic base (DABCO), to lead quantitatively to *N*-(*O*-alkylsulfamoyl)dimethylphosphoramidate (**4**) (Scheme 1). As previously mentioned[11] it was not possible to carry out successfully ester hydrolysis. Attempts with pure bromo or iodo trimethylsilane gave no results. Basic hydrolysis with bromotrimethylsilane in pyridine were inefficient. Hydrolysis under acidic conditions resulted in N–P bond cleavage, leading to phosphoric acid and sulfamate.

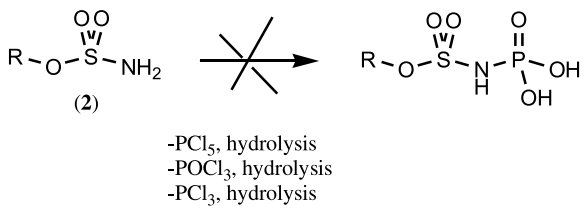


Scheme 1. Synthesis of *N*-(*O*-alkylsulfamoyl)dimethyl phosphoramidate. Reagents and conditions: (a) sulfamoyl chloride, DMA, 95%; (b) trialkyl phosphite, DIAD, THF, 70–85%; (c) DABCO, toluene, H_2O, 100%.

So, we studied different conditions for direct phosphorylation of the sulfamate (**2**):

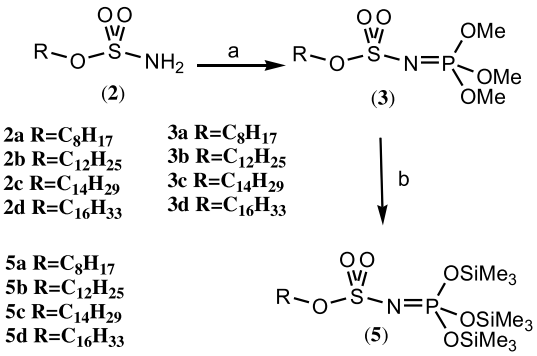
- phosphorous pentachloride with triethylamine in methylene chloride and hydrolysis.[14]
- phosphorous oxychloride and hydrolysis.[15]
- phosphorous trichloride and acidic hydrolysis.[16]

None of these methods gave satisfactory yields. Many by-products difficult to purify, were produced (Scheme 2).



Scheme 2. Different attempts of phosphorylation of sulfamates.

Despite these results, we then investigated a new approach consisting in direct hydrolysis of the phospha-λ^5-azene (**3**). Using pure bromotrimethylsilane[17,18] (3 equiv., rt, 3 h), the *N*-(*O*-alkylsulfamoyl)tristrimethylsilyl phospha-λ^5-azene (**5**), has been quantitatively obtained (Scheme 3). The phospha-λ^5-azene structure of (**5**) was confirmed by ^{1}H

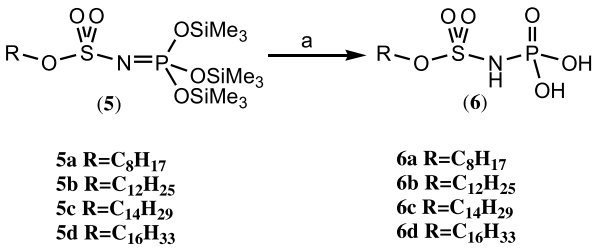


Scheme 3. Phospha-λ^5-azene approach. Reagents and conditions: (a) $P(OMe)_3$, DIAD, THF, 70–85%; (b) $BrSiMe_3$, quantitative.

NMR with the 27 protons of the silylated moiety around 0.3 ppm and by ^{29}Si NMR with a single shift at +30 ppm corresponding to the P–O–Si bond.[19]

Different methods of hydrolysis have been tested on this new silylated product (**5**): (a) MeOH, (b) MeOH/MeONa, (c) H_2O, (d) H_2O reflux, (e) H_2O/NH_4OH 1 N, (f) H_2O pH=9, (g) H_2O pH=5, (h) H_2O pH=7. The best results were obtained with H_2O pH=7 during 7 days. The corresponding hydrolysis were monitored by in situ ^{31}P NMR. The hydrolysis of the O–Si bond of the first silylated species (−25.5 ppm) were observed, whereas the hydrolysis of the second (−10.5 ppm) and third (−4.8 ppm) silylated intermediates needed 7 days to be achieved (+2.5 ppm).

Lyophilization of the reaction mixture gave quantitatively the expected *N*-(*O*-alkylsulfamoyl)phosphoramidic acid (**6**) (Scheme 4).



Scheme 4. Hydrolysis of the tristrimethylsilylphospha-λ^5-azene. Reagents and conditions: (a) H_2O, 7 days, quantitative.

3. Conclusion

Our investigations to find a novel, efficient and useful method to prepare *N*-(*O*-alkylsulfamoyl)phosphor amidic acids (**6**) have been successful. Starting from the alcohol, we have been able to form the expected product by a three steps reaction in high yield. The silylated intermediate have been isolated and characterized showing an interesting structure of phospha-λ^5-azene. We are currently evaluating the application of this method to the synthesis of nucleosides pyrophosphate analogues.

4. Experimental

4.1. General

All commercial chemicals and solvents were used as

received. Melting points were determined in open capillary tubes on a Buchi apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer S1000. ^{1}H, ^{13}C, ^{31}P and ^{29}Si spectra were, respectively, recorded in a 400 or 250 MHz Bruker spectrometers. Chemicals shifts are reported in δ units (ppm). All coupling constants J are reported in Hertz. Multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet) and combination of these signals. Electron ionization mass spectra (30 eV) were recorded in positive or negative mode on a Water MicroMass ZQ. Mass spectra were measured on a Jeol SX102 mass spectrometer and recorded in FAB positive or negative mode. All reactions were monitored by TLC on silica Merck 60 F_{254} precoated aluminium plates and were developed by spraying with molybden blue solution. Column chromatographies were performed on Merck silica gel (230–400 mesh).

4.2. General method for the synthesis of *N*-(*O*-alkylsulfamoyl)trimethylphospha-λ^5-azenes

Di*iso*propylazodicarboxylate DIAD (2 mmol, 2 equiv.) was added dropwise to a solution of alkylsulfamate (1 mmol, 1 equiv.) and trimethylphosphite (2 mmol, 2 equiv.) in THF (1 ml, 1 ml/mmol). The reaction mixture was stirred for 2 h at room temperature and then concentrated under vacuum. The residue was purified by column chromatography on silica gel (CH_2Cl_2/methanol, 98:2).

4.2.1. *N*-(*O*-Octylsulfamoyl)trimethylphospha-λ^5-azene 3a. Yield 85%; oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.87 (m, 2H, CH_2–O), 3.62 (d, 9H, J=11.7 Hz, P–O–CH_3), 1.43 (m, 2H, CH_2), 1.21 (m, 2H, CH_2), 1.09 (m, 8H, CH_2), 0.59 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 70.2 (CH_2–O), 56.5 (P–O–Me), 32.1–22.9 (CH_2), 14.4 (CH_3); ^{31}P NMR ($CDCl_3$, 250 MHz): δ (ppm) 2.5; MS (GT, FAB$^+$) 332 (M+H)$^+$; IR (KBr) cm^{-1} 2927, 2856 (CH_3, CH_2), 1375 (SO_2), 1246 (P=N), 1162 (SO_2), 1056 (P–O–C).

4.2.2. *N*-(*O*-Dodecylsulfamoyl)trimethylphospha-λ^5-azene 3b. Yield 80%; oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 3.90 (m, 2H, CH_2–O), 3.68 (d, 9H, J=11.8 Hz, P–O–CH_3), 1.46 (m, 2H, CH_2), 1.15 (m, 2H, CH_2), 1.80–1.96 (m, 16H, CH_2), 0.61 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 70.2 (CH_2–O), 56.5 (P–O–Me), 32.2–22.2 (CH_2), 14.4 (CH_3); ^{31}P NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.8; MS (ESI$^+$) 388 (M+H)$^+$, 410 (M+Na)$^+$; MS (ESI$^-$) 387 (M−H)$^-$; IR (KBr) cm^{-1} 2924, 2854 (CH_3, CH_2), 1376 (SO_2), 1241 (P=N), 1163 (SO_2), 1052 (P–O–C).

4.2.3. *N*-(*O*-Tetradecylsulfamoyl)trimethylphospha-λ^5-azene 3c. Yield 77%; oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 4.11 (m, 2H, CH_2–O), 3.86 (d J=11.7 Hz, 9H, P–O–CH_3), 1.63 (m, 2H, CH_2), 1.32 (m, 2H, CH_2), 1.27–1.13 (m, 20H, CH_2), 0.81 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 70.2 (CH_2–O), 56.5 (P–O–Me), 32.2–22.3 (CH_2), 14.4 (CH_3); ^{31}P NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.8; MS (ESI$^+$) 416 (M+H)$^+$, 438 (M+Na)$^+$; MS (ESI$^-$) 414 (M−H)$^-$; IR (KBr) cm^{-1} 2926, 2854 (CH_3, CH_2), 1375 (SO_2), 1245 (P=N), 1164 (SO_2), 1055 (P–O–C).

4.2.4. *N*-(*O*-Hexadecylsulfamoyl)trimethylphospha-λ^5-azene 3d. Yield 72%; oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 4.08 (m, 2H, CH_2–O), 3.84 (d J=11.8 Hz, 9H, P–O–CH_3), 1.63 (m, 2H, CH_2), 1.35 (m, 2H, CH_2), 1.20 (m, 24H, CH_2), 0.82 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 400 MHz): δ (ppm) 70.2 (CH_2–O), 56.5 (P–O–Me), 32.3–22.3 (CH_2), 14.4 (CH_3); ^{31}P NMR ($CDCl_3$, 400 MHz): δ (ppm) 1.8; MS (ESI$^+$) 444 (M+H)$^+$, 466 (M+Na)$^+$; MS (ESI$^-$) 442 (M−H)$^-$; IR (KBr) cm^{-1} 2926, 2854 (CH_3, CH_2), 1375 (SO_2), 1238 (P=N), 1164 (SO_2), 1056 (P–O–C).

4.3. General method for the synthesis of *N*-(*O*-alkylsulfamoyl)tristrimethylsilylphospha-λ^5-azenes

Bromotrimethylsilane (3 mmol, 3 equiv.) was added to *N*-(*O*-alkylsulfamoyl)trimethylphospha-λ^5-azene (1 mmol, 1 equiv.) under nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature, then concentrated under vacuum. The corresponding *N*-(*O*-alkylsulfamoyl)tristrimethylsilylphospha-λ^5-azene was obtained quantitatively.

4.3.1. *N*-(*O*-Octylsulfamoyl)tristrimethylsilylphospha-λ^5-azene 5a. Yield 100%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 4.19 (m, 2H, CH_2–O), 1.69 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 1.26 (m, 8H, CH_2), 0.87 (m, 3H, CH_3), 0.33 (s, 27H, $SiMe_3$); ^{31}P NMR ($CDCl_3$, 250 MHz): δ (ppm) −25.5; ^{29}Si NMR ($CDCl_3$, 250 MHz): δ (ppm) +30.3.

4.3.2. *N*-(*O*-Dodecylsulfamoyl)tristrimethylsilylphospha-λ^5-azene 5b. Yield 100%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 4.21 (m, 2H, CH_2–O), 1.68 (m, 2H, CH_2), 1.38 (m, 2H, CH_2), 1.25 (m, 16H, CH_2), 0.85 (m, 3H, CH_3), 0.31 (s, 27H, $SiMe_3$); ^{31}P NMR ($CDCl_3$, 250 MHz): δ (ppm) −25.2; ^{29}Si NMR ($CDCl_3$, 250 MHz): δ (ppm) +30.8.

4.3.3. *N*-(*O*-Tetradecylsulfamoyl)tristrimethylsilylphospha-λ^5-azene 5c. Yield 100%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 4.12 (m, 2H, CH_2–O), 1.88 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.30 (m, 20H, CH_2), 0.89 (m, 3H, CH_3), 0.31 (s, 27H, $SiMe_3$); ^{31}P NMR ($CDCl_3$, 250 MHz): δ (ppm) −25.8; ^{29}Si NMR ($CDCl_3$, 250 MHz): δ (ppm) +30.5.

4.3.4. *N*-(*O*-Hexadecylsulfamoyl)tristrimethylsilylphospha-λ^5-azene 5d. Yield 100%; oil; ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm) 4.13 (m, 2H, CH_2–O), 1.72 (m, 2H, CH_2), 1.40 (m, 2H, CH_2), 1.28 (m, 24H, CH_2), 0.90 (m, 3H, CH_3), 0.35 (s, 27H, $SiMe_3$); ^{31}P NMR ($CDCl_3$, 250 MHz): δ (ppm) −25.1; ^{29}Si NMR ($CDCl_3$, 250 MHz): δ (ppm) +30.9.

4.4. General method for the synthesis of *N*-(*O*-alkylsulfamoyl)phosphoramidic acids

The *N*-(*O*-alkylsulfamoyl)tristrimethylsilylphospha-λ^5-azene (1 mmol) was diluted in dichloromethane (5 ml) and cooled with an ice bath. Water (1 ml) was added dropwise to the mixture. The reaction was stirred at room temperature for 7 days and then concentrated under vacuum. The mixture was lyophilized to give quantitatively the *N*-(*O*-alkylsulfamoyl)phosphoramidic acid.

4.4.1. *N*-(*O*-Octylsulfamoyl)phosphoramidic acid 6a. Yield 100%; white solid; mp 58–60 °C (very hygroscopic); ^{1}H NMR (acetone d_6, 400 MHz): δ (ppm) 7.72 (s, 1H, NH), 4.13 (m, 2H, CH_2–O), 1.68 (m, 2H, CH_2), 1.41 (m, 2H, CH_2), 1.30 (m, 8H, CH_2), 0.88 (m, 3H, CH_3); ^{13}C NMR (acetone d_6, 400 MHz): δ (ppm) 70.0 (CH_2–O), 32.0–22.7 (CH_2), 13.9 (CH_3); ^{31}P NMR (acetone d_6, 250 MHz): δ (ppm) 2.9; MS (NBA, FAB$^-$) 288 (M−H)$^-$; IR (KBr) cm^{-1} 3370, 3287 (NH, OH), 2917, 2850 (CH_3, CH_2), 1398 (SO_2), 1349 (P═O), 1179 (SO_2).

4.4.2. *N*-(*O*-Dodecylsulfamoyl)phosphoramidic acid 6b. Yield 100%; white solid; mp 62–63 °C (very hygroscopic); ^{1}H NMR (acetone d_6, 400 MHz): δ (ppm) 7.75 (s, 1H, NH), 4.08 (m, 2H, CH_2–O), 1.72 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.35 (m, 16H, CH_2), 0.88 (m, 3H, CH_3); ^{13}C NMR (acetone d_6, 400 MHz): δ (ppm) 70.0 (CH_2–O), 32.1–22.8 (CH_2), 13.8 (CH_3); ^{31}P NMR (acetone d_6, 250 MHz): δ (ppm) 2.5; MS (NBA, FAB$^-$) 344 (M−H)$^-$; IR (KBr) cm^{-1} 3369, 3287 (NH, OH), 2915, 2849 (CH_3, CH_2), 1398 (SO_2), 1345 (P═O), 1181 (SO_2).

4.4.3. *N*-(*O*-Tetradecylsulfamoyl)phosphoramidic acid 6c. Yield 100%; white solid; mp 63–64 °C (very hygroscopic); ^{1}H NMR (acetone d_6, 400 MHz): δ (ppm) 7.11 (s, 1H, NH), 4.13 (m, 2H, CH_2–O), 1.82 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.30 (m, 20H, CH_2), 0.87 (m, 3H, CH_3); ^{13}C NMR (acetone d_6, 400 MHz): δ (ppm) 70.0 (CH_2–O), 32.1–21.8 (CH_2), 13.9 (CH_3); ^{31}P NMR (acetone d_6, 250 MHz): δ (ppm) 2.7; MS (NBA, FAB$^-$) 372 (M−H)$^-$; IR (KBr) cm^{-1} 3369, 3287 (NH, OH), 2916, 2849 (CH_3, CH_2), 1398 (SO_2), 1349 (P═O), 1182.1 (SO_2).

4.4.4. *N*-(*O*-Hexadecylsulfamoyl)phosphoramidic acid 6d. Yield 100%; yellow solid; mp 65–67°C (very hygroscopic); ^{1}H NMR (acetone d_6, 400 MHz): δ (ppm) 6.77 (s, 1H, NH), 4.12 (m, 2H, CH_2–O), 1.92 (m, 2H, CH_2), 1.41 (m, 2H, CH_2), 1.30 (m, 24H, CH_2), 0.86 (m, 3H, CH_3); ^{13}C NMR (acetone d_6, 400 MHz): δ (ppm) 70.0 (CH_2–O), 32.1–21.7 (CH_2), 13.9 (CH_3); ^{31}P NMR (acetone d_6, 250 MHz): δ (ppm) 2.6; MS (NBA, FAB$^-$) 400 (M−H)$^-$; IR (KBr) cm^{-1} 3369, 3287 (NH, OH), 2914, 2849 (CH_3, CH_2), 1399 (SO_2), 1349.6 (P═O), 1184 (SO_2).

Acknowledgements

Financial support of this work by La Ligue contre le Cancer (Comité de l'Aude et du Gard) (L. B PhD fellowship) is gratefully acknowledged.

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