THE SYNTHESIS AND REACTIONS OF 2,4-DITERTIARYBUTYLYL-3-CHLORO-1,3-DIAZA-3-PHOSPHETIDINE-1,1-DIOXIDE, A HETEROCYCLE CONTAINING NITROGEN, SULFUR, AND TRICOORDINATE PHOSPHORUS

**Authors:**
Alan H. Cowley, Sushil K. Mehrotra, and Herbert W. Roesky

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**Abstract:**
A new four-membered nitrogen-sulfur-phosphorus ring of composition $O_2S(t-BuN)_2PCl$ has been prepared by the action of PCl$_3$ on the sulfamide, $(t-BuNH)_2SO_2$ in the presence of $Et_3N$ and characterized by elemental analysis, and NMR, IR, and mass spectroscopy. Reaction of the title...
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\lambda^{5}-THIA-2,4-DIAZA-3-PHOSPHETIDINE-1,1-DIOXIDE, A HETEROCYCLE
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Department of Chemistry
University of Texas at Austin
Austin, Texas 78712

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CONTAINING NITROGEN, SULFUR, AND TRICOORDINATE PHOSPHORUS

ALAN H. COWLEY\(^1\), SUSHIL K. MEHROTRA\(^1\), and HERBERT W. ROESKY\(^2\)

Received

A new four-membered nitrogen-sulfur-phosphorus ring
of composition \( O_2S(t\text{-BuN})_2PCl \) has been prepared by the
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presence of \( Et_3^\text{N} \) and characterized by elemental analysis,
and NMR, IR, and mass spectroscopy. Reaction of the
title compound with \( SbF_3^\text{III} \) and \( Me_3^\text{Si}Me_2^\text{I} \) afforded the 3-
fluoro and 3-dimethylamino derivatives, \( O_2S(t\text{-BuN})_2PF \)
and \( O_2S(t\text{-BuN})_2PNMe_2 \), respectively, and treatment with
sodium in \( n\text{-octane} \) produced the diphosphine,
\( (O_2S(t\text{-BuN})_2P)_2 \). Treatment of the thiadiazaphosphetidine
ring with \( Fe_2(CO)_9 \) afforded the phosphorus-iron bonded
complex, \( O_2S(t\text{-BuN})_2P(\text{Cl})Fe(CO)_4 \).
INTRODUCTION

Following the discovery of the diazadiphosphetidines 1A\textsuperscript{3,4} and 1B\textsuperscript{5}, numerous publications have appeared concerning the stereochemistry,\textsuperscript{6} ligative behavior,\textsuperscript{7} and cognate chemistry\textsuperscript{8} of this class of compound. The present paper is concerned with the synthesis of a four-membered nitrogen-sulfur-phosphorus ring system, which is related to the dihalodiphosphetidines by replacing a PX by an SO\textsubscript{2} moiety. This particular four-membered (thiadiazaphosphetidine) ring system has, in fact, been known for a number of years. For example, Becke-Goehring and co-workers\textsuperscript{9} prepared the pentacoordinate phosphorus compounds 2-5.

\[ \text{X=F, Cl} \]
\[ \text{R=Me, Ph} \]
More recently, it has been shown that the reaction of $N,N' \text{-dimethyl-}$ or $N,N' \text{-diethylsulfamide}$ with $\text{PCl}_3$ in the presence of tertiary amines leads to apparently polymeric materials of composition $[O_2S(N\text{Me})_2\text{PCl}]_n$ and to ring-opened products, respectively.\textsuperscript{10}

Since it is known from e.g. diazadiphosphetidine chemistry that sterically bulky nitrogen substituents stabilize the four-membered ring, we decided to investigate the reaction of $N,N' \text{-ditertiarybutylsulfamide}$ with $\text{PCl}_3$ in an effort to prepare 6.
RESULTS AND DISCUSSION

2,4-diteriarybutyl-3-chloro-1-\(\lambda^6\)-thia-2,4-diaza-3-phosphetidine-1,1-dioxide, \(\mathbf{6}\), can be prepared by the action of \(\text{PCl}_3\) on the sulfamide, \((t-\text{BuNH})_2\text{SO}_2\) in the presence of \(\text{Et}_3\text{N}\).

\[
\begin{array}{c}
\text{t-Bu} \\
H \\
N \\
\text{t-Bu} \\
O_2S \\
N \\
H \\
\text{t-Bu}
\end{array}
\quad + \quad \text{PCl}_3 \quad \xrightarrow{\text{Et}_3\text{N}} \quad \begin{array}{c}
\text{t-Bu} \\
H \\
N \\
\text{t-Bu} \\
O_2S \\
N \\
\text{PCl} + 2[\text{Et}_3\text{NH}]\text{Cl}
\end{array}
\]

The monomeric nature of \(\mathbf{6}\) is indicated by the mass spectrum which exhibits a parent peak at \(m/e\) 273. There was no evidence for species possessing higher mass.

The significance of \(\mathbf{6}\) is that it represents the first example of a four-membered nitrogen-sulfur-phosphorus (III) ring. As pointed out in the Introduction, only pentacoordinate phosphorus compounds featuring this ring system had been described previously.\(^9\) The successful synthesis of \(\mathbf{6}\) can be attributed to the steric demands of the \(t\)-butyl groups since the attempted syntheses of the methyl or ethyl analogues of \(\mathbf{6}\) resulted in production of apparently polymeric substances of composition, \([O_2S(\text{NMe})_2\text{PCl}]_n\), or to ring-opened products.\(^{10}\) Replacement of \(\text{PCl}_3\) by the phosphinous chlorides, \(\text{MePCl}_2\) of \(\text{PCl}_3\), resulted in the production of eight-membered ring compounds, \(\mathbf{7}\).\(^{10}\)
The geometry of 6, by analogy with that of the diazadiphosphetidine, 1A6, is expected to feature a slightly puckered four-membered ring with both nitrogens possessing essentially trigonal planar geometries. Moreover, since the SO2 moiety of 7 is arranged with the O-S-O planes perpendicular to the N-S-N planes,10 a similar structural feature may be assumed for 6. With these assumptions it is obvious that 6 can exist in only one conformation. Accordingly, only one peak was detectable in the 31P NMR (Table I).

Treatment of 6 with SbF3 and a catalytic amount of SbF5 affords 8 in ~69% yield. Conventional elemental analysis (Table II) of 8
proved to be very difficult due to the moisture sensitivity of the compound. Accordingly, the characterization of 8 was based on NMR and mass spectroscopy. For example, a parent peak is apparent in the mass spectrum of 8 at m/e 256. Moreover, the presence of a PF (rather than e.g. a PF₃) moiety is established by the ³¹P and ¹⁹F NMR spectra of 8, both of which consist of doublet at anticipated chemical shift values (Table I).

The metathetical reaction of 6 with Me₃SiNMe₂ affords 9 in virtually quantitative yield.

\[
\text{\begin{tikzpicture}
\node (1) at (0,0) {\text{t-Bu}};
\node (2) at (0,-1) {\text{t-Bu}};
\node (3) at (0.5,0.5) {\text{N}};
\node (4) at (1,0) {\text{N}};
\node (5) at (1,-0.5) {\text{PNMe}_2};
\node (6) at (0,-1.5) {\text{O}_2\text{S}};
\end{tikzpicture}}
\]

Compound 9 is a fluxional molecule. Below -40°C two N-methyl signals are apparent in the ¹H NMR spectrum (Figure 1). Coalescence occurs -40°C, and above this temperature averaging of the two methyl environments becomes rapid on the NMR time scale. The foregoing observations can be accommodated by postulating 10 as the ground state structure. In this conformation one of the exocyclic N-methyl groups (Me') is situated syn to the phosphorus lone pair while the other (Me) lies across the PN₂S ring.
Assignment of the larger PNCH coupling to Me' (Table I) is consistent with previous observations on aminophosphines$^{11}$ and with more general trends concerning the influence of a syn lone pair of electrons on coupling constants.$^{12}$ A parallel may be drawn between 10 and the ground state structure which has been suggested$^{13}$ for R$_2$N-substituted diazaphospholanes. We note that other suggestions have been made$^{14}$ for the geometry of the exocyclic R$_2$N moiety in diazaphospholanes. However, we favor 10 because it corresponds to the "bisected" geometry of acyclic aminophosphines$^{15}$ in which the nitrogen and phosphorus lone pairs are mutually orthogonal.

Lappert, Goldwhite, and co-workers$^{16}$ have shown that the treatment of phosphinous chlorides with sodium or electron-rich-olefins leads to the production of stable radicals, R$_2$P, provided the bulk of the R groups is sufficient to impart kinetic stabilization. We were therefore prompted to treat 6 with sodium in n-octane in an attempt to generate 11. However, 11 is not sufficiently long-lived to permit its isolation or spectroscopic identification and the reaction results in the production of the diphosphine 12 which is the dimer of 11.
The conformational behavior of diphosphines is a matter of current interest. On one hand, it has been found that the gauche ground state preference of tetraalkyldiphosphines increases as the steric bulk of the alkyl group is increased from Me to t-Bu. On the other hand, we have found recently that bulky aryl groups, such as mesityl, favor the adoption of the anti conformation. In the case of 12, the $^1$H NMR signal for the t-Bu groups remains a singlet down to -90°C. In all likelihood, P-P rotation is still rapid on the NMR time scale at this temperature; however, our observations are also consistent with an anti ground state geometry.

The treatment of haloaminophosphines with halide ion abstractors has been shown to result in amino-substituted phosphenium ions, $R_2P^+$. We therefore attempted to prepare 13 via
the following routes: (1) the reaction of $\text{6}$ with $\text{Al}_2\text{Cl}_6$, (2) the reaction of $\text{6}$ with $\text{NaBPh}_4$, (3) the reaction of $\text{6}$ with $\text{AgBF}_4$, and (4) the reaction of $\text{8}$ with $\text{SbF}_5$. Reactions 1 and 2 do not proceed, reaction 3 affords $\text{O}_2\text{S}(\text{t-BuN})_2\text{PF}$ (8) and unidentified products, while reaction 4 produces the phosphonium cation 14,

![Chemical structure](image)

14

together with unidentified products. Reaction 4 implies the net transfer of $\text{F}^+$ from $\text{SbF}_5$ to 8.\textsuperscript{20} While the mechanism of this reaction is unknown, it can be speculated that two steps are involved. Presumably, the first step involves oxidative fluorination of 8 to the trifluorophosphorane, and the second step is fluoride ion abstraction from the latter.

From the reaction of $\text{6}$ with $\text{Fe}_2(\text{CO})_9$ it is possible to isolate 15 in almost quantitative yield.
This compound is formulated as the P-bonded complex for the following reasons: (i) there is a significant change in the $^{31}\text{P}$ NMR chemical shift upon coordination (Table II); (ii) coupling between $^{31}\text{P}$ and the carbonyl carbons is detectable and of appropriate magnitude for $^{2}J_{\text{PFeC}}$; and (iii) $^{13}\text{C}$ NMR spectroscopy indicates that the t-Bu groups are isochronous.

It is interesting to contrast the behavior of 1A and 6 toward $\text{Fe}_{2}(\text{CO})_{9}$. The diazadiphosphetidine, 1A, can act in a chelating (16) or bridging (17) capacity. $^{7a,c}$
Finally, we note that although the phosphorus atom of 6 can behave as a donor toward an Fe(CO)$_4$ moiety, it is not sufficiently active to react with elemental sulfur or MeI.

**Experimental Section**

**Materials and General Procedures.** N,N'-ditertiarybutylsulfamide, $O_2S(t$-BuNH)$_2$ was prepared according to the method of Bernann and Van Wazer.$^{21}$ The physical properties of $O_2S(t$-BuNH)$_2$ corresponded to those reported by Stowell.$^{22}$ Dimethylamino-trimethylsilane was synthesized by the literature method$^{23}$, and Fe$_2$(CO)$_9$ was prepared by UV irradiation of Fe(CO)$_5$ in n-pentane. All other reagents were procured commercially and used without subsequent purification. All solvents were carefully dried prior to use.

Virtually all the materials described herein are moisture sensitive. Accordingly, it was necessary to perform all operations in vacuo or under an inert atmosphere.

Elemental analyses were carried out by Canadian Microanalytical Service, Ltd., Vancouver, B.C., Canada. The analytical data are summarized in Table II.

**Spectroscopic Measurements.** The $^1$H and $^{19}$F NMR spectra were recorded on Varian A-60 and EM-390 instruments operating at spectrometer frequencies of 60 and 84.96 MHz, respectively. The variable temperature $^1$H NMR experiments were conducted on a Varian HA 100 spectrometer. Except where indicated in Table I,
the $^1$H and $^{19}$F chemical shifts were measured with respect to internal CH$_2$Cl$_2$ (δ, 5.28 ppm) relative to Me$_4$Si and external CCl$_3$F, respectively. The $^{13}$C and $^{31}$P NMR spectra were measured in the FT mode on a Bruker WH-90 instrument operating at spectrometer frequencies of 22.6 and 30.6 MHz, respectively. Dichloromethane (54.2 ppm relative to Me$_4$Si) was employed as the internal reference for the $^{13}$C spectra, and 85% H$_3$PO$_4$ was used as the external reference for the $^{31}$P spectra. The NMR data are summarized in Table I.

IR spectra of nujol mulls were recorded on a Perkin-Elmer 137 spectrophotometer using NaCl plates. Selected IR data are summarized in Table I. The mass spectra were determined on a CEC 21-491 spectrometer at an ionizing voltage of 70 eV.

**Preparation of O$_2$S(t-Bu)$_2$PCL (5).** A 20% excess of the required amount of Et$_3$N was added to a solution of 6.0g (28.8 mmol) of O$_2$S(t-BuNH)$_2$ in 60 mL diethyl ether. To this solution, a solution of 3.8g (27.7 mmol) of PCl$_3$ in 15 mL of Et$_2$O was added slowly with constant stirring. An exothermic reaction was observed. After the addition was complete, the mixture was refluxed for approximately 4h. Filtration, removal of solvent, and subsequent vacuum distillation (bp 86-91°C @ 0.5 torr) gave an oil which solidified immediately upon cooling. The yield of the product after distillation was 5.0g (18.3 mmol, 64.7% yield). The white solid, mp 61-4°C, can also be purified by sublimation in vacuo or by recrystallization from a mixture of dichloromethane and n-pentane at low temperatures.
Preparation of $\text{O}_2\text{S}$(t-BuN)$_2$PF (8). A mixture of 6.44 g (24.4 mmol) of $\text{O}_2\text{S}$(t-BuN)$_2$PCl, a 20% excess of SbF$_3$, and a catalytic amount of SbF$_5$ in ~60 mL of dichloromethane was refluxed for approximately 6 h. Filtration and removal of solvent gave a white, solid product which contained some impurities. Purification was achieved by vacuum distillation at 81°C (0.5 torr). A white crystalline solid, mp 53-5°C, was formed on cooling. The yield was 69% (4.3 g, 16.78 mmol).

Preparation of $\text{O}_2\text{S}$(t-BuN)$_2$PNMe$_2$ (9). A solution of 2.0 g (7.33 mmol) of $\text{O}_2\text{S}$(t-BuN)$_2$PCl (6) and 0.94 g (8.02 mmol) of Me$_3$SiNMe$_2$ in ~40 mL of CH$_2$Cl$_2$ was stirred at -20°C for 2 h. The temperature of the reaction mixture was raised slowly, initially to room temperature and then to reflux. The refluxing was continued for 2 h. Removal of solvent and subsequent vacuum distillation (86-87°C at 0.5 torr) gave the pure white, waxy solid product in 96% yield (1.98 g, 7.04 mmol).

Preparation of $\text{O}_2\text{S}$(t-BuN)$_2$P$_2$ (12). A mixture of 3.48 g (12.8 mmol) of $\text{O}_2\text{S}$(t-BuN)$_2$PCl (6) and 0.43 g (18.7 mmol) of Na in 40 mL of n-octane was heated under reflux for 3 h. A black solid separated out from the reaction mixture as the sodium reacted. Filtration and removal of the solvent gave 2.34 g (4.95 mmol) of yellowish solid 12.
ATTEMPTED PREPARATION OF \([O_2S(t\text{-}BuN)_2P]^+\) (13)

**ATTEMPTED REACTION OF \(O_2S(t\text{-}BuN)_2P\)\(\text{Cl}\) (6) WITH \(\text{Al}_2\text{Cl}_6\).**

Aluminum trichloride (1.5g, 1.13 mmol) was added to a stirred solution of 3.1g (1.14 mmol) of \(O_2S(t\text{-}BuN)_2\text{P}\)\(\text{Cl}\) (6) at \(-80^\circ\text{C}\). The suspended solid dissolved slowly; however, \(^{31}\text{P}\) NMR spectroscopic assay of the solution revealed only the presence of unreacted 6.

**ATTEMPTED REACTION OF \(O_2S(t\text{-}BuN)_2\text{P}\)\(\text{Cl}\) (6) WITH \(\text{NaB}_{4}\text{F}_4\).**

Sodium tetraphenylborate (2.495g, 7.29 mmol) was added to a solution of 6 (1.99g, 7.30 mmol) in -30 mL of \(\text{CH}_2\text{Cl}_2\) at \(-80^\circ\text{C}\). The mixture was stirred for 2h at this temperature, allowed to warm to room temperature, and stirred an additional 4h. \(^{31}\text{P}\) NMR spectroscopic assay of the solution indicated that no reaction had occurred.

**REACTION OF \(O_2S(t\text{-}BuN)_2\text{P}\)\(\text{Cl}\) (6) WITH \(\text{AgBF}_4\).**

Silver tetrafluoroborate (2.31g, 1.19 mmol) was added to a stirred solution of 2.3g (0.84 mmol) of \(O_2S(t\text{-}BuN)_2\text{P}\)\(\text{Cl}\) (6) in -20 mL of \(\text{CH}_2\text{Cl}_2\) at \(-80^\circ\text{C}\). An evolution of gas was observed at low temperatures. The \(^{31}\text{P}\) NMR spectrum of the solution at room temperature revealed the presence of \(O_2S(t\text{-}BuN)_2\text{PF}\) (8) together with some unidentified signals.

**REACTION OF \(O_2S(t\text{-}BuN)_2\text{PF}\) (8) WITH \(\text{SbF}_5\).**

Antimony pentafluoride (3.6g, 1.66 mmol) was added to a vigorously stirred
solution of 4.23g (1.65 mmol) of \( \text{O}_2\text{S(t-Bu)N}_2\text{PF} \) (8) in \( 20 \text{ mL} \) of \( \text{CH}_2\text{Cl}_2 \) at \(-80^\circ\text{C}\). The \( ^{31}\text{P} \) spectrum of the solution was measured after approximately 3h of stirring, and found to consist of several peaks. The color of the solution changed from colorless to black during this time. After 2 days, the \( ^{31}\text{P} \) spectrum of the reaction mixture exhibited a triplet at \( 31.98 \text{ ppm} \) with \( J_{\text{PF}} = 1187.4 \text{ Hz} \), which is attributed to the difluorophosphonium cation, \( \left[\text{O}_2\text{S(t-Bu)N} \right]_2\text{PF}_2^+ \).

**PREPARATION OF \( \text{O}_2\text{S(t-Bu)N}_2\text{P(Cl)Fe(CO)}_4 \) (15).** A mixture of 1.95g (7.15 mmol) of \( \text{O}_2\text{S(t-Bu)N}_2\text{PCl} \) and 2.2g (6.05 mmol) of \( \text{Fe}_2\text{CO}_9 \) in \( 30 \text{ mL} \) of \( \text{n-pentane} \) was heated under reflux for 4-5h. The suspended solid went into solution slowly accompanied by the evolution of gas and change of color of the reaction mixture from yellow to brown. After stripping the solvent, the product was evacuated for 4h, then recrystallized from \( \text{n-pentane} \) at low temperatures. Yellow needles of 15 (mp \( 123-4^\circ\text{C} \)) were obtained in virtually quantitative yield.

**ATTEMPTED REACTION OF \( \text{O}_2\text{S(t-Bu)N}_2\text{PCl} \) (6) WITH MeI.** A solution of 1.2g (0.44 mmol) of \( \text{O}_2\text{S(t-Bu)N}_2\text{PCl} \) (6) and \( 15 \text{ mL} \) of \( \text{MeI} \) was heated under reflux for approximately 5h. The solution remained clear during this period. \( ^{31}\text{P} \) NMR spectroscopy indicated the presence of only unchanged starting material.
**Attempted Reaction of \( \text{O}_2\text{S}(\text{t-BuN})_2\text{PCl} \) (6) with Elemental Sulfur.** A mixture of 2.63 g (0.96 mmol) of \( \text{O}_2\text{S}(\text{t-BuN})_2\text{PCl} \) (6) and an excess of elemental sulfur was refluxed in benzene for approximately 5 h. Upon standing overnight, yellow crystals of elemental sulfur deposited from the solution. NMR spectroscopic examination of the filtrate revealed only the presence of unchanged starting material.

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REFERENCES AND NOTES

1. University of Texas at Austin.

2. Universität Frankfurt


18. Baxter, S. G.; Cowley, A. H.; Davis, R. E.; Riley, P. E. to be published.

20. We have observed this type of reaction previously when certain fluorophosphines are treated with AsF$_5$. Cowley, A. H.; Pagel, D. J.; Wilburn, J. C. to be published.


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<th>compd</th>
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$^a$ See Experimental Section for statement of references used.

$^b$ Chemical shift measured relative to internal C$_6$H$_6$ ($\delta$, 7.24 ppm).

$^c$ Chemical shift measured relative to internal $n$-pentane (13.70 ppm for Me groups).
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<sup>a</sup> In cm⁻¹.  
<sup>b</sup> Assigned by analogy to the sulfamide, (t-BuNH)₂SO₂, which exhibits these vibrations at 531, 1140, and 1306 cm⁻¹.  
<sup>c</sup> Analysis impossible due to rapid hydrolysis. See text.
FIGURE CAPTIONS

FIGURE 1. $^1H$ NMR spectra of $O_2S(t$-BuN)$_2$PNMe$_2$ (9) at various temperatures.