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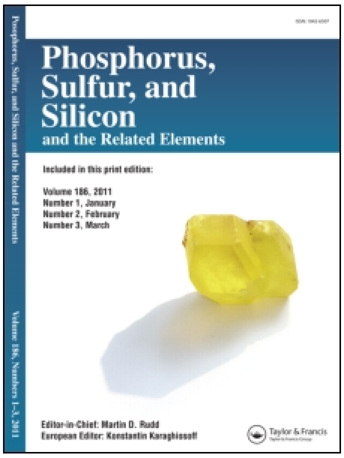

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Reactions of 1-Hydro-5-carbaphosphatrane: Tautomerization between Five-Coordinate and Three-Coordinate Species

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REACTIONS OF 1-HYDRO-5-CARBAPHOSPHATRANE: TAUTOMERIZATION BETWEEN FIVE-COORDINATE AND THREE-COORDINATE SPECIES

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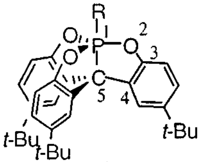
Oxidation, sulfurization, and selenation of a 1-hydro-5-carbaphosphatrane afforded the corresponding cyclic phosphonate, cyclic phosphonothioate, and cyclic phosphonoselenoate, respectively. These results indicate the existence of the tautomerization between the five-coordinate 5-carbaphosphatrane and the three-coordinate cyclic phosphonite.

Keywords: Chalcogenation; hypervalent phosphorus compounds; oxidation; phosphatrane; tautomerization

While various main-group atranes have been reported so far,[1] there has been no example of an atrane bearing a carbon atom at the 5-position instead of a group 15 element such as nitrogen or phosphorus. Recently, we have reported the synthesis and structure of 5-carbaphosphatranes **1**, the first example of 5-carbon analogues of phosphatranes[2] (Scheme 1). It was found that the structural and spectroscopic properties of 5-carbaphosphatranes **1** are similar to those of



1 a: R = H
b: R = Me

SCHEME 1

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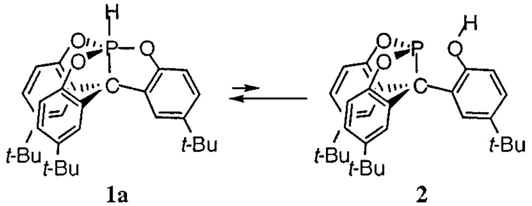


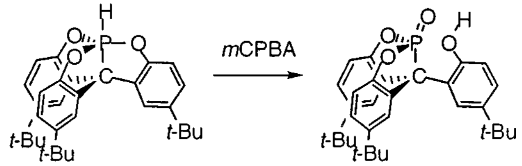
1a **2**

SCHEME 2

usual phosphatranes having the isoelectronic structure. On the other hand, the reactivities of 5-carbaphosphatranes are expected to be different from those of phosphatranes, reflecting the difference in the bonding properties; the P—N bond of phosphatranes is a dative bond, while the P—C bond of 5-carbaphosphatranes is covalent. We have previously reported the reactivity of 1-hydro-5-carbaphosphatrane **1a** based on the tautomerization between the five-coordinate phosphatrane **1a** and the three-coordinate cyclic phosphonite **2** in the reaction with deuterium oxide[2] (Scheme 2). Here we report oxidations and chalcogenations of 5-carbaphosphatrane **1a** that corroborate the existence of the tautomerization more strongly.

RESULTS AND DISCUSSION

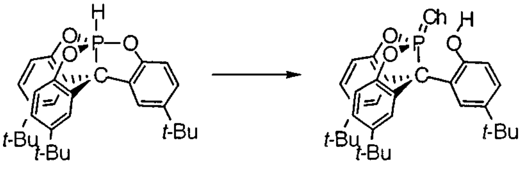
m-CPBA is known to oxidize trivalent phosphines to the corresponding phosphine oxides. Treatment of **1a** with an equimolar amount of *m*-CPBA in $CDCl_3$ afforded the cyclic phosphonate **3**, which showed a ^{31}P-NMR signal at 63 ppm (Scheme 3). The cyclic phosphonate **3** is considered to be formed by oxidation of the tautomer **2**.



1a **3** (52%)

SCHEME 3

Sulfurization of **1a** has proceeded in a similar way to the oxidation. The toluene-d_8 solution of **1a** was heated in the presence of elemental sulfur and the reaction was monitored by ^{31}P-NMR. After heating for 6 d at 140°C, the formation of phosphonothioate **4** (δ_P 124) was observed (Scheme 4). This reaction was completed more rapidly in xylene-d_{10} at



1a

4 (Ch = S) 100%
5 (Ch = Se) 90%

SCHEME 4

160°C (16.5 h). Moreover, this reaction was accelerated by the addition of 3.8 equivalents of benzoic acid (2 d at 140°C in toluene-d_8). Such remarkable acceleration by acid is consistent with the acceleration of the H–D exchange by DCl/D_2O.[2] Selenation of **1a** also proceeded by heating of **1a** in the presence of elemental selenium at 160°C to give phosphonoselenoate **5**.

These oxidation and chalcogenation reactions are considered to proceed via the cyclic phosphonite **2**, and strongly support the existence of the tautomerization between **1a** and **2**, although **2** could not be observed by ^{31}P-NMR. Such reactivities based on the tautomerization have not been reported for phosphatranes, and the difference in reactivities between phosphatranes and 5-carbaphosphatrane described here is attributed to the difference in the properties of the transannular bonds.

In summary, we have presented the oxidation and chalcogenations of 1-hydro-5-carbaphosphatrane **1a** indicating the existence of the tautomerization between 1-hydro-5-carbaphosphatrane **1a** and the cyclic phosphonate **2**. Considering the fact that such tautomerization is one of the typical reactivities of alkoxy substituted hydrophosphoranes,[3] 1-hydro-5-carbaphosphatrane **1a** should be regarded as a hydrophosphorane rather than as a phosphatrane derivative in view of reactivities, although **1a** is quite similar to usual phosphatranes in spectroscopic and structural aspects, as we previously reported.

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