## RING OPENING OF DIPHOSPHIRANES LEADING TO 1,3-DIPHOSPHAALLENE

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Abstract: The 3,3-dihalogeno-1,2-diphosphiranes 1(a-b) and its photochemical isomers, the 2,3-dihalogeno-diphosphapropenes 8(a-b) lead to the 1,3-diphosphaallene 4 by action the methyllithium. The anionic ring opening mechanism appears most likely.

We describe the ring opening reactions of halogeno-diphosphiranes, prepared by action of halogeno-carbenes on the corresponding diphosphene (1). The presence of leaving groups on the intracyclic carbone and the weakness of the P-P bond promote the ring opening reactions.

As with the analogous gem-dihalocyclopropanes (2), the diphosphiranes 1(a-b) react with methyllithium at 0 °C in diethyl ether, and lead quantitatively to the 1,3-diphosphaallene 4, already obtained by other methods (3)

We have not detected the formation of the corresponding carbene intermediate 5. By analogy to the cyclopropanes (4,5), the carbene 5 should give the dimer 6 or the spiranic product 7 in the presence of olefins. Although the spiranic structure is quite stable (6,7), we have not obtained the corresponding spiran 7 by trapping 5 in diethyl ether at 0 °C by an excess of cyclohexene (6 eq.) or tetramethylethylene (20 eq.).

As, we have not detected the dimer 6, the reaction path (A) seems not to take place. On the other hand, we have shown that the anionic ring opening of monohalogenated diphosphiranes by action of BuLi occurs by cleavage of the P-P bond and formation of allylic intermediate (8). For the dihalogenodiphosphiranes 1(a-b), by using methyllithium in the same conditions, we have not detected at -70 °C, the intermediates 2 and 3. In spite of these results, the reaction path (B) appears most likely.

The 1,3-diphosphapropenes 8(a-b) obtained by photolysis of 1(a-b) give quantitatively 4 by action of methyllithium on at low temperature in diethyl ether.

1(a-b) 
$$Ar - P = \begin{bmatrix} X \\ 1 \\ X \end{bmatrix}$$
 
$$MeLi$$
 
$$Ether/0^{\circ}C$$
 4

In conclusion, the P-P bond cleavage of the halogeno-diphosphirane, by action of organo alkali metal compounds, is an efficient method for obtaining 1,3-diphosphapropene (8) or 1.3-diphosphaallene.

## References

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$$Ar_p = P_{Ar} + C_{SPh_2} - Ar_{N,p} = C_{SPh_2}$$

m.p. 160 °C; m/e (FD) = 593;  $^{1}$ H nmr (300 MHz), CDC1<sub>3</sub>)  $\delta$  -0.18 (m, 2H, CH<sub>2</sub>), 0.52 (m, 2H, CH<sub>2</sub>), 1.24 (s, 18H, p-tBu), 1.54 (s, 32H, o-tBu), 7.12 (m, 4H, Ar).  $^{13}$ C nmr (CDC1<sub>3</sub>) 136.30 (t,  $^{1}$ J<sub>CP</sub> = 38.5Hz,  $^{2}$ J<sub>CP</sub> = 36Hz, 2C<sub>1</sub>), 155.24 (t,  $^{2}$ J<sub>CP</sub> = 3.25Hz, 4C<sub>2</sub>), 121.6 (s, 4C<sub>3</sub>), 146.90 (s, 2C<sub>4</sub>), 38.36 (s, 4C<sub>5</sub>), 37.59 (s, 2C<sub>6</sub>), 34.17 (t,  $^{4}$ J<sub>CP</sub> = 7Hz, 12C<sub>7</sub>), 31.02 (s, 6C<sub>8</sub>),33.69 (t, J<sub>CP</sub> = 58Hz, C<sub>9</sub>), 8.59 (t, J<sub>CP</sub> = 9Hz, C<sub>10</sub> and C<sub>11</sub>). (7) a) B.M. Trost, Acc. Chem. Res., 7, 85 (1974).

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