Communications to the Editor

Facile Synthesis of a Pentacoordinated Diphosphorane

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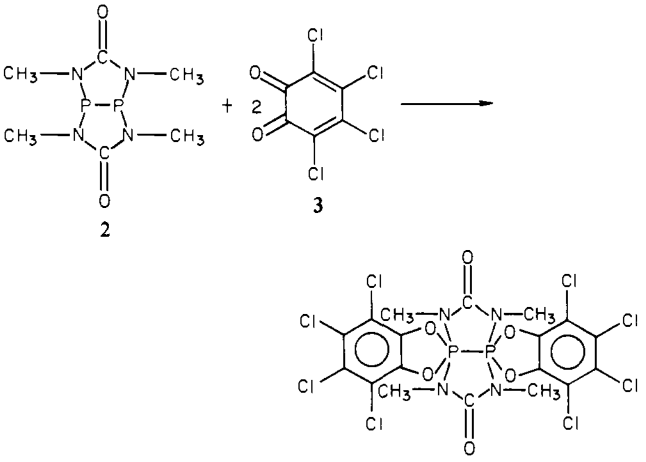
Richman et al.[1] have recently reported the synthesis and X-ray structural analysis of the first diphosphorane to contain a λ^5P–λ^5P bond. In this dicyclene–phosphorane (**1**) the phosphorus atoms are surrounded by tetrakis(substituted amino) groups. A 33% distortion[2] of the trigonal bipyramid at phosphorus toward a rectangular pyramidal geometry was observed. It could be assumed that only electron-rich substituents can stabilize such P–P bonds.

We report herein the oxidation of 2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^3,5λ^3-diphosphabicyclo[3.3.0]octane-3,7-dione[3] (**2**) with tetrachloro-*o*-benzoquinone (**3**), which leads to the formation of the corresponding diphosphorane (**4**) without breaking of the P–P bond. (**4** is prepared in toluene at room temperature and with stirring for 4 days.) In contrast to **1**, which displays an equatorial λ^5P–λ^5P bond, **4** is the first compound known to contain an axial λ^5P–λ^5P bond.



2 **3** **4**

4 forms colorless crystals, which were purified by recrystallization from CH_2Cl_2 in a yield of 76%, mp 183–185 °C. The ^{31}P NMR chemical shift of δ −44.0 (upfield, 85% H_3PO_4 (−)) (ext 85% H_3PO_4) lies in the characteristic range for pentacoordinate phosphorus. The molecular structure of **4** was confirmed by X-ray structural analysis.

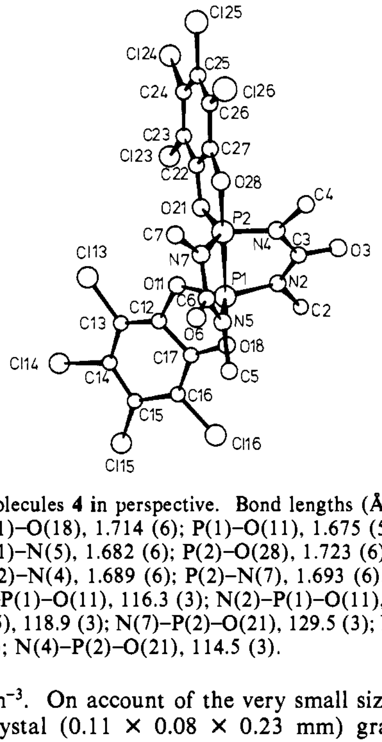


Figure 1. Molecules **4** in perspective. Bond lengths (Å): P(1)–P(2), 2.256 (3); P(1)–O(18), 1.714 (6); P(1)–O(11), 1.675 (5); P(1)–N(2), 1.689 (6); P(1)–N(5), 1.682 (6); P(2)–O(28), 1.723 (6); P(2)–O(21), 1.669 (5); P(2)–N(4), 1.689 (6); P(2)–N(7), 1.693 (6). Bond angles (deg): N(5)–P(1)–O(11), 116.3 (3); N(2)–P(1)–O(11), 124.9 (3); N(2)–P(1)–N(5), 118.9 (3); N(7)–P(2)–O(21), 129.5 (3); N(7)–P(2)–N(4), 116.0 (3); N(4)–P(2)–O(21), 114.5 (3).

Crystal Data: $C_{18}H_{12}N_4O_6P_2Cl_8 \cdot CH_2Cl_2$, triclinic, space group $P\bar{1}$, with a = 12.429 (4) Å, b = 15.954 (7) Å, c = 8.145 (3) Å, α = 100.46 (3)°, β = 100.77 (3)°, γ = 75.07 (3)°, Z = 2, D_x = 1.77 g cm^{-3}. On account of the very small size of the best available crystal (0.11 × 0.08 × 0.23 mm) graphite-monochromated Cu Kα radiation was used for the data collection. A total of 3833 independent reflections were measured on a Syntex P2$_1$ diffractometer ($2\theta_{\max}$ = 105°). An empirical absorption correction was applied (μ = 9.5 mm^{-1}). The structure was solved by direct methods (SHELX) and refined by full-matrix least-squares to an R value of 0.061, with a weighted index R_w $(=\sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o|)$ of 0.051 for 2472 reflections with $F_o^2 \geq 2.0\sigma(F_o^2)$. Both P atoms in **4** display a basically trigonal-bipyramidal geometry as evidenced by the axial P–P–O bond angles of respectively 178.7 (2) and 177.9 (2)°. As would be expected on the basis of the relative electronegativities of the substituents at phosphorus, the five-membered ring of the tetrachloro-*o*-benzoquinone system adopts the preferred axial–equatorial placement. This forces the bicyclus to take up the less favorable facial arrangement with an axial P–P bridgehead and equatorial N substituents. A similar placement of the bicyclus has been found for two tricyclic phosphoranes with analogous electronegativity differences between the ligands.[4] It has been observed that the P–P bond distance, independent of the oxidation state and nature of the substituents, normally falls within a narrow range (2.18–2.25 Å).[5] Recently a few notable exceptions have been observed to this rule, e.g., 2.122 (1) Å in the complex of a four-electron P$^+$ cation[6] and 2.36 Å in α-P_4S_4.[7] The λ^5P–λ^5P distances in **1** and **4** lie just above the above range and are not significantly different from one another. Indeed the axial P–P distance of 2.256 (3) Å in **4** is somewhat shorter than the equatorial P–P distance of 2.264 (2) Å in **1**. It should, however, be remembered in this context that this latter bond has a significant degree of apical character (in a rectangular pyramid).

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Registry No. 2, 77507-69-8; **3**, 2435-53-2; **4**, 81255-54-1.

Supplementary Material Available: Observed and calculated structure factor amplitudes, atomic coordinates (Table I), and anisotropic temperature factors (Table II) (19 pages). Ordering information is given on any current masthead page.

Models for Asymmetric [2 + 2] Cycloadditions

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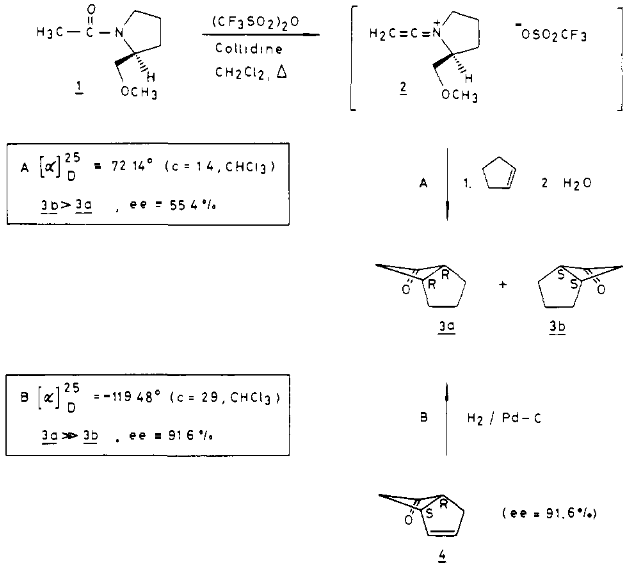
Strained molecules have become valuable and often used intermediates in organic synthesis.[1] Thus, in the vicinal alkylation of olefins,[2] the key step involves the formation of a cyclobutanone by [2 + 2] cycloaddition of an olefin to a ketene or a ketene iminium salt. Then, the energy-rich four-membered ring is cleaved to give a product that is the net result of the regio- and stereoselective attachment of two carbon-chains to an olefinic double bond. Obviously, the availability of asymmetric [2 + 2] cycloadditions would considerably enhance the usefulness of this methodology. Here we report our preliminary studies on models for asymmetric [2 + 2] cycloadditions to olefins.

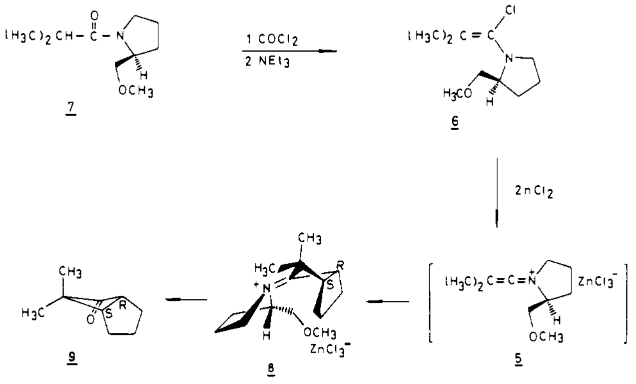
We have examined a ketene equivalent bearing the chiral inductor on the carbon atom where bonding is expected to be the most advanced in the transition state of the cycloaddition. In principle, keteneiminium salts derived from chiral amines meet the above stated structural specifications.

1-Acetyl-2-(methoxymethyl)pyrrolidine[3] (**1**) ($[\alpha]^{25}_D$ −82.15°, *c* 2.0, CH_2Cl_2) was converted into the corresponding ketene iminium triflate **2** by treatment with an equivalent amount of triflic anhydride (added over a period of 6 h, CH_2Cl_2, reflux) in the presence of collidine (1.2 equiv) according to our recently described procedure for the preparation of aldoketene iminium salts.[4] **2** was trapped in situ by cyclopentene (~5 equiv) to give, after hydrolysis (H_2O, overnight), a 30% yield of adduct **3**: ν ($CHCl_3$) 1765 cm^{-1}, $[\alpha]^{25}_D$ +72.14°, *c* 1.4, $CHCl_3$, (Scheme I). The use of a chiral shift reagent, Eu(hfc)$_3$, at various concentrations gave complex spectra even at 200 MHz. The enantiomeric excess was determined by comparing the optical rotation of adduct **3** with that of an authentic sample of (1*R*,5*R*)-bicyclo[3.2.0]heptan-6-one prepared by hydrogenation of **4** (ee = 91.6%).[5] The enantiomeric excess in the adduct **3** was 55.4% in favor of the (1*S*,5*S*) isomer **3b**.

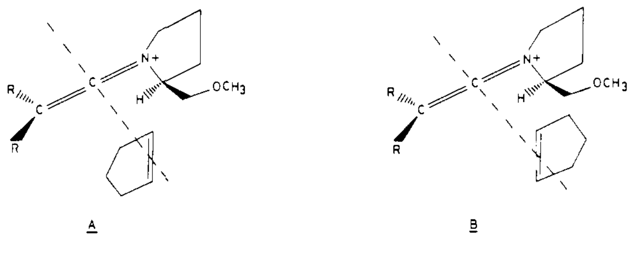
Scheme I



Scheme II



Scheme III



The diastereoselectivity was even higher for the reaction of cyclopentene with the β-disubstituted ketene iminium salt **5** (Scheme II). The precursor, α-chlorenamine **6**, was obtained from amide **7**[3] according to the standard procedure.[6] Compound **6** (~8 mM) was dissolved in dichloromethane (15 mL) and reacted with zinc chloride (14 mM) and cyclopentene (22 mM) for 16 h at 20 °C. Hydrolysis (3 N NaOH, 3 h) of the crude iminium salt **8** yielded **9** [bulb-to-bulb 145 °C (20 torr); 70% from **7**; $[\alpha]^{20}_D$ −170.3°, *c* 2.1, $CHCl_3$; $\nu_{C=O}$ 1760 cm^{-1} in CH_2Cl_2]. Cyclobutanone **9** showed a single set of NMR signals (200 MHz) in the presence of Eu(hfc)$_3$, thus indicating *almost* (>*97%*) *complete asymmetric induction*. The nonequivalence of the two diastereoisomeric complexes with the chiral shift reagent would

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(5) We thank Dr. A. H. Wadsworth and Dr. S. M. Roberts (Glaxo) for a generous gift of chiral **4**.

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