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Photochemical Incorporation of Diphosphorus Units into Organic Molecules**

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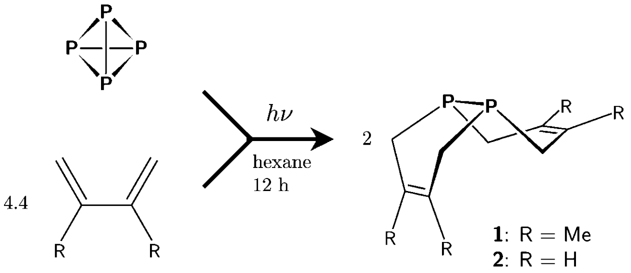
A niobium-based method for thermal transfer of P_2 to 1,3-dienes has been described previously, but this sole extant method is of limited preparative value due to the multi-step nature of the synthesis.[1] In order to make the interesting class of bi- or tetracyclic P_2R_4 molecules readily available for detailed scrutiny, we sought and have now discovered a simple one-step procedure, reported herein. The method consists of P_4 photolysis in the presence of commercially available 1,3-diene molecules to produce directly the diphosphane target molecules.

In 1937, Rathenau reported that the conversion of white phosphorus to red phosphorus under UV irradiation using a mercury lamp involves unimolecular dissociation of P_4 into P_2 molecules, followed by recombination of the latter into red phosphorus.[2] In one report on the P_4 cophotolysis with metal carbonyl complexes, Dahl et al. mention that "P_4 in solution photolyzes readily to P_2 at ambient temperatures".[3] There have been several other reports on the co-photolysis of P_4 with metal carbonyl complexes and generation of metal–phosphorus products,[4] yet we have not found any reports on using photolysis of P_4 molecules for the direct inclusion of phosphorus atoms into organic substrates.[5]

Electronic absorption features for P_4 in the gas phase at 62 °C have been reported in the UV region below 300 nm.[6] We found that upon using a mercury lamp that irradiates predominantly at 254 nm, the photolysis of P_4 in the presence of 1,3-dienes affords products consistent with double Diels–Alder additions of diene molecules to P_2 units.

Initial experiments focused on generating the previously reported[1] tetracyclic diphosphane $C_{12}H_{16}P_2$ by irradiating a mixture of P_4 and 1,3-cyclohexadiene (CHD). The appearance of the characteristic sharp singlet of the targeted diphosphane product at $\delta = -80$ ppm in ^{31}P NMR spectra of crude product mixtures was encouraging. However, upon attempting to quantify and isolate the desired diphosphane, only quantities on the order of several milligrams were obtained. Nevertheless, when 1,3-cyclohexadiene was replaced with conjugated dienes that are more transparent in the window of P_4 absorption, improved results were obtained.[7]

The photolysis of hexane solutions containing P_4 and 2,3-dimethyl-1,3-butadiene (DMB) in slight excess, led to the appearance of a singlet in the ^{31}P NMR spectra at $\delta = -53.8$ ppm, consistent with formation of the desired Diels–Alder cycloaddition product 3,4,8,9-tetramethyl-1,6-diphosphabicyclo(4.4.0)deca-3,8-diene (**1**, $C_{12}H_{20}P_2$, Scheme 1 and Figure 1). This molecule has only been prepared and reported previously as a ligand in a complex with tungsten pentacarbonyl,[1] and it is closely related to the mixed-pnictogen ligand in the complex $[(C_{12}H_{20}PAs)W(CO)_5]$.[8]



Scheme 1. One-step synthesis of diphosphanes **1** and **2** from P_4.

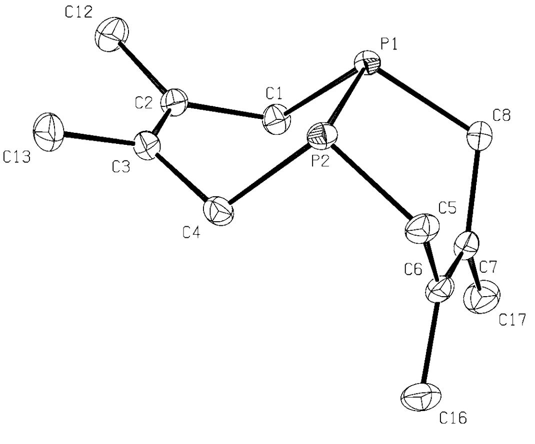


Figure 1. Molecular structure of diphosphane **1** with 50% thermal ellipsoids.[11] Selected distances [Å] and angles [°]: P1–P2 2.2218(5), P1–C1 1.8739(13), P1–C8 1.8719 (13), P2–C4 1.8745(14), P2–C5 1.8727(14); C1-P1-C8 101.33(6), C4-P2-C5 102.05(6).

The conversion of P_4 into diphosphane **1** was observed spectroscopically to proceed with good efficiency on scales up to hundreds of milligrams. Still, the product **1** is itself unstable under the harsh conditions of the 254 nm irradiation such that if the irradiation is not discontinued following the point of complete P_4 consumption, compound **1** is slowly converted

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into several new, unidentified phosphorus-containing products that give rise to ^{31}P NMR signals between $\delta = -33$ and -36 ppm.[9]

Irradiation of the homogenous starting mixture elicits formation of a colorless precipitate within 30 min. As the formed diphosphane **1** is transformed into the unidentified products, the mixture also acquires a pale yellow coloration. Interestingly, lack of any stirring during the irradiation appeared to decrease the rate and the yield of production of **1** from P_4. No red coloration was observed at any time, as would be expected to accompany the production of red phosphorus.[2] On the other hand, upon replacing DMB with a relatively unreactive diene such as furan,[10] copious amounts of a deep red precipitate were observed to form early in the photolysis, indicative of red phosphorus generation.

Diphosphane **1** was isolated from the reaction mixture by filtration through a short column of alumina, and rinsing first with pentane, and then with diethyl ether. Unconsumed P_4 was recovered from the pentane filtrate, while the desired diphosphane **1** was obtained from the diethyl ether filtrate as a pale yellow, waxy residue. After recrystallization of this residue from toluene at −35 °C, analytically pure, colorless crystals which melt at 145–146 °C were obtained. Optimization of the reaction conditions produced the best results when a hexane solution of P_4 (ca. 0.06 M) and DMB (10 % excess) in a 100 mL quartz flask was irradiated for 12 h. Isolated yields up to 15 % were attained for **1**, but when taking into account the recovery of the unconsumed P_4, corrected isolated yields in excess of 34 % were obtained. Moreover, spectroscopic quantification of the crude reaction mixtures with an internal standard indicated conversion efficiency as high as 26 % (corrected to 44 % taking unconsumed P_4 into account).[9]

A similar transformation was obtained when DMB was replaced with 1,3-butadiene. The diphosphane product 1,6-diphosphabicyclo(4.4.0)deca-3,8-diene (**2**, $C_8H_{12}P_2$, Scheme 1 and Figure 2) is characterized by a ^{31}P NMR singlet at $\delta = -70.4$ ppm, and could also be isolated pure as colorless crystals (albeit in only ca. 1 % yield, unoptimized).[9,12]

Diphosphanes **1** and **2** both were subjected to structural analysis by X-ray crystallography (Figure 1 and 2).[11] The core molecular structure and conformation of **2** is essentially identical to that of **1**, with a P−P bond distance of 2.2218(5) Å for **1**, and 2.2230(5) Å for **2**. Both molecules adopt a C_s-symmetric conformation in the solid state, but fluctuate rapidly on the NMR timescale at room temperature in solution, as the methyl environments of **1** and vinylic signals for **2** undergo fast exchange through readily accessible C_{2v}-symmetric conformations. Observations reported on the related hydrocarbon *cis*-1,4,5,8,9,10-hexahydronaphthalene (formally obtained by replacing the P atoms of **2** with CH moieties) are suggestive of similar fluxional behavior.[13] Interestingly, neither diphosphane molecule exhibits intramolecular π-stacking of double bonds as observed for the cage-constrained and tetracyclic 1,3-cyclohexadiene P_2-addition product.[1]

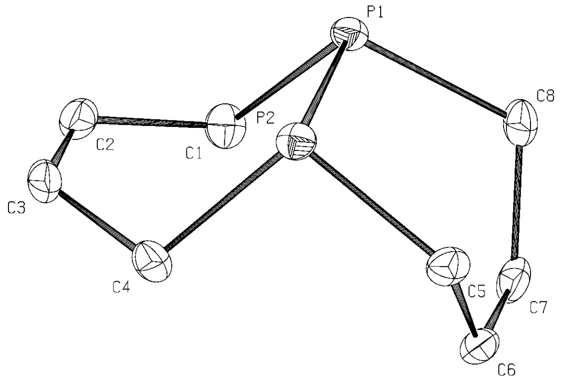

Figure 2. Molecular structure of diphosphane **2** with 50 % thermal ellipsoids.[11] Selected distances [Å] and angles [°]: P1–P2 2.2230(5), P1–C1 1.8740(14), P1–C8 1.8805(14), P2–C4 1.8840(14), P2–C5 1.8781(14); C1-P1-C8 101.57(6), C4-P2-C5 101.65(6).

A well recognized, green chemistry imperative for the industrial synthesis of phosphorus compounds is to avoid PCl_3 as an intermediate and to develop instead methods for the direct incorporation of phosphorus atoms into organic molecules from P_4.[14] While transition-metal mediated or catalyzed processes have been envisioned as a solution to this problem, P_4 activation by main-group element compounds including carbenes,[14c,15] and radicals[16] have been offered recently as potentially viable alternatives. With the present work we show that photochemical activation should be added to the aforementioned developing palette of methods, and in a way that constitutes an atom-economical and operationally simple combination of P_2 units with two equivalents of readily available, organic diene molecules.

Experimental Section

General experimental details, details on reaction optimization experiments, and the output spectrum for the photo-reactor lamps are given in the Supporting Information. Representative protocol for **1**: A 100 mL quartz round bottom flask was charged with P_4 (303.8 mg, 2.45 mmol, 1.0 equiv), 2,3-dimethylbutadiene (888.6 mg, 10.8 mmol, 4.4 equiv), hexane (40 mL), and a Teflon-coated stir bar, and the mixture was stirred until all of the P_4 was dissolved. The flask was equipped with a vacuum valve, degassed, and sealed securely before being brought outside of the glove box. The mixture was then irradiated for 12 h under stirring, as the temperature inside the photolysis chamber was maintained at ca. 55–65 °C with a cooling fan. After returning the vessel to the glove box, the yellow suspension that had been generated therein was concentrated under reduced pressure to about a quarter of the original volume, and was filtered through a column of alumina (2.5 cm long, 3.5 cm wide) inside a fritted glass filter funnel and washed with pentane (100 mL). This colorless filtrate was saved for subsequent recovery of the unreacted P_4 (182.7 mg, 60.1 %). The alumina was then washed with diethyl ether (75 mL), and the resulting pale yellow filtrate was dried to produce a yellow residue (ca. 340 mg), which afforded colorless crystals of diphosphane **1** after recrystallization from saturated toluene solutions at −35 °C in several crops (150.5 mg, 13.6 % of theoretical, or 34.1 % based on consumed P_4). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 2.04$ (dt, $^2J_{HH} = 13$ Hz, $J_{HP} = 6$ Hz, 4 H), 1.75 (dt, $^2J_{HH} = 13$ Hz, $J_{HP} = 9$ Hz, 4 H), 1.57 ppm (s, 12 H). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 125.8$ (vt, $J_{CP} = 2.5$ Hz), 27.1 (vt, $J_{CP} = 17$ Hz), 21.5 ppm (s). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6): $\delta = -53.8$ ppm (s). Elemental analysis (%) calcd. for $C_{12}H_{20}P_2$: C 63.71, H 8.91, P 27.38; found: C 63.82, H 8.88, P 27.53. GC-MS m/z: 226 (also present 144, 113, and 82).

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[1] N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* **2006**, *313*, 1276 – 1279.

[2] G. Rathenau, *Physica* **1937**, *4*, 503 – 514.

[3] M. E. Barr, B. R. Adams, R. R. Weller, L. F. Dahl, *J. Am. Chem. Soc.* **1991**, *113*, 3052 – 3060.

[4] a) O. J. Scherer, J. Vondung, *Angew. Chem.* **1989**, *101*, 1395 – 1397; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1355 – 1357; b) M. E. Barr, S. K. Smith, B. Spencer, L. F. Dahl, *Organometallics* **1991**, *10*, 3983 – 3991; c) M. E. Barr, L. F. Dahl, *Organometallics* **1991**, *10*, 3991 – 3996; d) M. Herberhold, G. Frohmader, W. Millus, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *93*, 205 – 208; e) O. J. Scherer, G. Schwarz, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1996**, *622*, 951 – 995; f) O. J. Scherer, G. Berg, G. Wolmershäuser, *Chem. Ber.* **1996**, *129*, 53 – 58; g) M. Scheer, U. Becker, *Chem. Ber.* **1996**, *129*, 1307 – 1310; h) O. J. Scherer, T. Völmecke, G. Wolmershäuser, *Eur. J. Inorg. Chem.* **1999**, 945 – 949; i) O. J. Scherer, R. Winter, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **2004**, *619*, 827 – 835.

[5] When P_4 in CCl_4 was exposed to visible light up to 100 °C, red phosphorus was found to be the main product; see: D. Perner, A. Henglein, *Z. Naturforsch. B* **1962**, *17*, 703 – 711.

[6] The molar extinction coefficient for P_4 is ca. $300\,\text{M}^{-1}\text{cm}^{-1}$ at 254 nm; see R. R. Hart, M. B. Robin, N. A. Keubler, *J. Chem. Phys.* **1965**, *42*, 3631 – 3638.

[7] The intense absorption of 1,3-cyclohexadiene at 254 nm likely acts as a filter that inhibits P_4 photolysis. The first λ_{max} for 1,3-cyclohexadiene is at 258 nm, while that for DMB is at 228 nm; for CHD see: Y. G. Dubinskii, M. I. Rozengart, B. A. Kazanskii, *Russ. Chem. Bull.* **1972**, *21*, 1193; for DMB see: R. M. Silverstein, G. C. Bassler, T. C. Morrill in *Spectrometric Identification of Organic Compounds*, 4th ed., Wiley, New York, **1981**, p. 313.

[8] H. A. Spinney, N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 16233 – 16243.

[9] See the Supporting Information for further details.

[10] A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553 – 11554.

[11] CCDC 783707 (**1**) and 783708 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] Use of isoprene (2-methyl-1,3-butadiene) as a P_2 acceptor gave a singlet signal in the ^{31}P NMR spectrum at $\delta = -57$ ppm and a set of two doublets at $\delta = -54$ and -60 ppm. While this is consistent with the production of both of the possible isomers of $C_{10}H_{16}P_2$, separation of the pure isomer mixture from other impurities has been unsuccessful so far. NMR spectra of crude samples are provided in the Supporting Information.

[13] The signal for the non-olefinic protons is reported to split into a multiplet below −75 °C; see H. J. Bestmann, H. Pfüller, *Angew. Chem.* **1972**, *84*, 528 – 530; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 508 – 510.

[14] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164 – 4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178 – 4235; c) M. Scheer, G. Balazs, A. Seitz, *Chem. Rev.* **2010**, 110, 4236 – 4256.

[15] a) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2007**, *119*, 7182 – 7185; *Angew. Chem. Int. Ed.* **2007**, *46*, 7052 – 7055; b) J. D. Masuda, W. W. Schoeller, B. Donnadieu, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 14180 – 14181; c) O. Back, G. Kuchenbeiser, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2009**, *121*, 5638 – 5641; *Angew. Chem. Int. Ed.* **2009**, *48*, 5530 – 5533.

[16] B. M. Cossairt, C. C. Cummins, *New J. Chem.* **2010**, *34*, 1533 – 1536.