

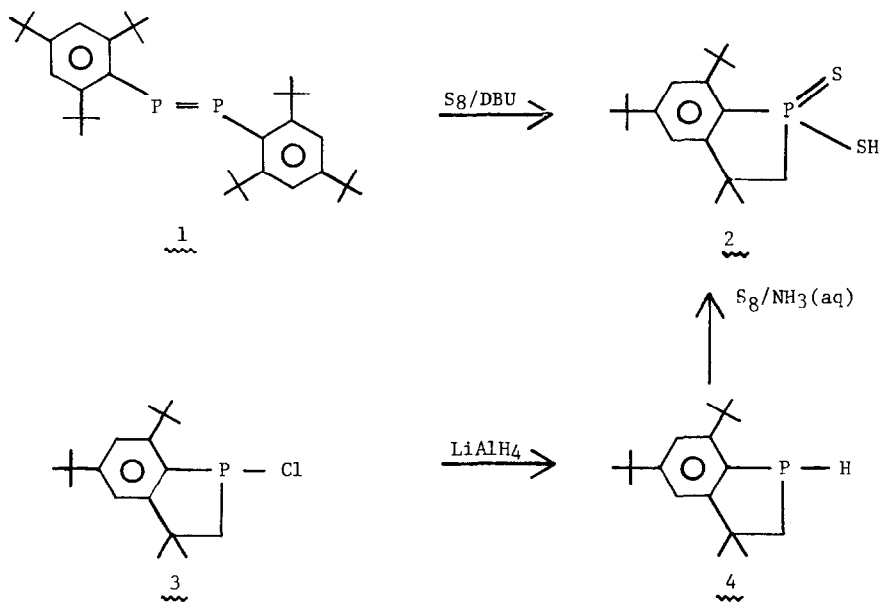
SULFUR CLEAVAGE OF A PHOSPHORUS-PHOSPHORUS DOUBLE BOND

Alan H. Cowley* and Marek Pakulski

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

Cleavage of the phosphorus-phosphorus double bond takes place when the diphosphene, (2,4,6-(*t*-Bu)₃C₆H₂P)₂, is treated with excess sulfur in the presence of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene).

Now that means have been found for stabilizing diphosphenes (RP=PR) and their heavier congeners [1], attention has turned to examination of the reactivity patterns of these intriguing molecules. The reactions of diphosphenes, diarsenes, and phospharsenes with elemental sulfur have attracted recent attention because the sulfur can bind in an η¹[2] or η³[3] fashion. We have now discovered a different type of reaction, namely cleavage of the phosphorus-phosphorus double bond. Thus, refluxing a toluene solution of the diphosphene, (2,4,6-(*t*-Bu)₃C₆H₂P)₂ (**1**) [4] with excess S₈ in the presence of an equimolar quantity of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) resulted in the dithiophosphinic acid, **2**. HRMS for **2**: (M⁺ calcd, 340.14482; found, 340.14408).



The above structure for **2** follows from e.g. ¹H NMR (90 MHz)(CH₂Cl₂): δ 1.30(s, 9H, *p-t*-Bu), 1.45(s, 6H, 3-CH₃), 1.55(s, 9H, *o-t*-Bu), 2.30(m, 2H, 2-CH₂), 7.35(m, 2H, aromatic), and ³¹P NMR (32.384 MHz)(CH₂Cl₂): δ 75.0(d, ²J_{PCH} = 8 Hz). Confirmation of this structure

assignment follows from an independent synthesis of 2. Thus, reduction of 3[5] with LiAlH_4 affords the new phosphine, 4, which can be converted to 2 by treatment with elemental sulfur in aqueous ammonia. HRMS for 4: (M^+ calcd, 276.2007; found, 276.1994). ^{31}P { ^1H } NMR (32.384 MHz)(CH_2Cl_2) for 4: δ -77.0(s).

The mechanism of formation of 2 is not yet clear. However, it is possible that this compound arises via intramolecular C-H oxidative addition of an o-t-Bu group of 5 or 6, followed in the case of 6 by reaction with sulfur.



This work was supported by the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation.

References

1. A. H. Cowley, *Polyhedron*, in press.
2. M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Chem. Soc. Chem. Commun.*, 862 (1983).
3. (a) E. Niecke and R. Rüger, *Angew. Chem. Int. Ed. Engl.*, 22, 155 (1983); (b) J. Escudié, C. Couret, H. Ranaivonjatovo and J.-G. Wolf, *Tetrahedron Lett.*, 24, 3625 (1983); (c) C. Couret, J. Escudié, Y. Madaule, H. Ranaivonjatovo, and J.-G. Wolf, *Tetrahedron Lett.*, 24, 2769 (1983).
4. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Am. Chem. Soc.*, 103, 4587 (1981).
5. M. Yoshifuji, I. Shima, K. Ando, and N. Inamoto, *Tetrahedron Lett.*, 24, 933 (1983).

(Received in USA 27 February 1984)