

PREPARATION OF 1,2-DIHYDRO-1,2-DIPHENYL-1^λ,2^λ-DIPHOSPHORIN
1,2-DISULFIDE

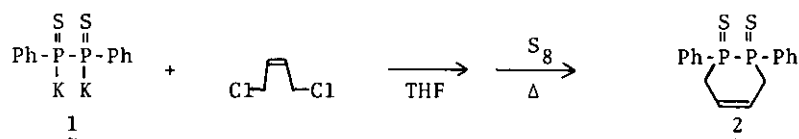
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Abstract: 1,2-Dihydro-1,2-diphenyl-1^λ,2^λ-diphosphorin 1,2-disulfide was synthesized from the corresponding 1,2,3,6-tetrahydro derivative by lithiation, bromination with bromotrichloromethane and dehydrobromination successively. Direct bromination of 1,2,3,6-tetrahydro derivative resulted in the P-P bond cleavage.

There is no report on 1,2-dihydrophosphorin or 1H-phosphorin derivative containing a hetero atom at α-position except 2-mesityl-1,2^λ-oxaphosphorin 2-oxide¹ which was employed for study on generation and reactivity of mesitylmetaphosphonate. In this paper, we would like to report a novel synthesis of the titled compound which could be derived to a precursor of phenylphosphinothioylidene dimer postulated as a reaction intermediate in our laboratory.²

1,2-Diphenyl-1,2-dipotassiodiphosphane (1)³ was allowed to react with *cis*-1,4-dichloro-2-butene⁴ in tetrahydrofuran (THF) under nitrogen atmosphere, followed by sulfurization to afford 1,2,3,6-tetrahydro-1,2-diphenyl-1^λ,2^λ-diphosphorin 1,2-disulfide (2) in 53.2% yield.

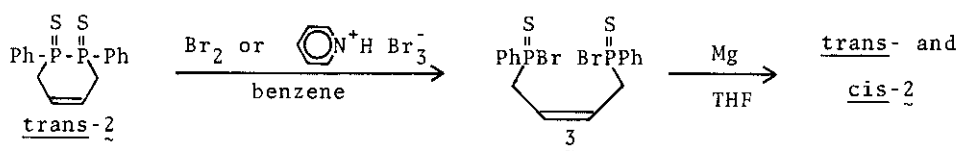


Trans and *cis* isomers were separated by dry column chromatography on silica gel in a ratio of 8:1. Their structure determinations were done by their behavior on silica gel and spectral analyses,⁵ especially ¹H-NMR.

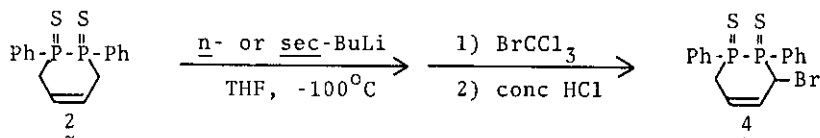
Trans-2 (less polar isomer): mp 198.2-199.5°C (acetone); IR (KBr disc): $\nu_{C=C}$ 1650 cm^{-1} ; $^1\text{H-NMR}$ (CD_2Cl_2): δ 2.69-3.45 (m,2H), 3.70-4.50 (m,2H), 5.95-6.34 (m,2H), 7.16-7.73 (m,6H), and 7.73-8.23 (m,4H); $^{31}\text{P-NMR}$ (using 85% H_3PO_4 as an external standard) (CDCl_3): δ_{P} 25.31 ppm; High resolution MS (70 eV) Found: m/e 334.0171. Calcd for $\text{C}_{16}\text{H}_{16}\text{P}_2\text{S}_2$: 334.0169. Anal. Found: C, 57.76; H, 5.05; S, 18.77%. Calcd for $\text{C}_{16}\text{H}_{16}\text{P}_2\text{S}_2$: C, 57.47; H, 4.82; S, 19.18%.

Cis-2 (more polar one): mp 183-185°C (decomp)(acetone); IR (KBr disc): $\nu_{C=C}$ 1650 cm^{-1} ; $^1\text{H-NMR}$ (CD_2Cl_2): δ 3.02-3.71 (m,4H), 5.80-6.40 (m,2H), and 7.00-8.79 (m,10H); $^{31}\text{P-NMR}$ (CDCl_3): δ_{P} 28.41 ppm; High resolution MS (70 eV) Found: m/e 334.0170. Calcd: 334.0169. Anal. Found: C, 57.42; H, 4.92; S, 19.07%.

Reaction of trans-2 with bromine or pyridinium tribromide in benzene gave no corresponding 4,5-dibromide in contrast to 1,2 λ -oxaphosphorin system,¹ but afforded bisphosphinothiaryl dibromide (3), which was recycled with magnesium to give a 1:1 mixture of trans- and cis-2 in 31% yield.



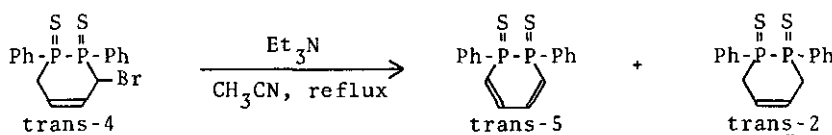
Trans-2 was treated with *n*-butyllithium or *sec*-butyllithium at -100°C in THF and the resulting lithio derivative was allowed to react with bromotrichloromethane and then the reaction mixture was quenched by conc HCl at -100°C. After rapid silica-gel chromatography with benzene, recrystallization from acetone gave the corresponding 3-bromide (4)⁶ in 24.4% yield, along with unchanged 2 in 11% recovery.



Trans-4: mp 165-166°C (acetone); IR (KBr disc): $\nu_{C=C}$ 1640 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 2.72-3.31 (m,2H), 3.92-4.15 (m,1H), 5.40-5.72 (m,1H), 5.80-7.30 (m,2H), and 7.35-8.10 (m,10H); $^{31}\text{P-NMR}$ (CDCl_3): δ_{P} 16.39 (d, P_1) and 17.56 (d, P_2), $J_{\text{P}_1, \text{P}_2} = 36.62$ Hz; High resolution MS Found: m/e 411.9275. Calcd for $\text{C}_{16}\text{H}_{15}\text{BrP}_2\text{S}_2$: 411.9275. Anal. Found: C, 46.75; H, 3.65; Br, 19.78%. Calcd for $\text{C}_{16}\text{H}_{15}\text{BrP}_2\text{S}_2$: C, 46.50; H, 3.67; Br, 19.34%.

From cis-2 was obtained cis-4 similarly in 4.8% yield; High resolution MS Found: m/e 411.9259. Cis-4 was more polar than trans-4.

Dehydrobromination of trans-4 by triethylamine in refluxing acetonitrile afforded 1,2-dihydro-1,2-diphenyl-1 λ ,2 λ -diphosphorin 1,2-disulfide (5) in 46.8% yield as yellow crystals. Reduction reaction also occurred competitively to give trans-2 in 14% yield. This undesirable reaction was predominant when the bulky 1,8-diazabicyclo[5.4.0]undec-7-ene instead of triethylamine was used.



Trans-5: mp 168-170°C (acetone); IR (KBr disc): $\nu_{\text{C}=\text{C}}$ 1639 cm^{-1} ; ^1H -NMR (CDCl_3): δ 6.38-7.37 (m, 4H), 7.37-7.72 (m, 6H), and 7.72-8.11 (m, 4H); ^{31}P -NMR (CDCl_3): δ_{P} 17.16 ppm; High resolution MS Found: m/e 331.9975. Calcd for $\text{C}_{16}\text{H}_{14}\text{P}_2\text{S}_2$: 332.0010.

Analytically pure sample has not been obtained yet.

Reaction of trans-5 with tetracyanoethylene afforded elemental sulfur in 50% yield. Reactions of 5 with other dienophiles are being investigated now, and the results will be reported in a future.

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REFERENCES AND NOTES

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3. K. Issleib and K. Krech, *Chem. Ber.*, 1966, **99**, 1310. Tetraphenylcyclotetraphosphane was prepared as described in the following paper: M. Eppstein and F. S. Seichter, *J. Am. Chem. Soc.*, 1963, **85**, 2462.
4. J. M. Bobbitt, L. H. Amundsen, and R. I. Steiner, *J. Org. Chem.*, 1959, **25**, 2230.
5. ^1H -NMR and ^1H noise-decoupled ^{31}P -NMR spectra were measured with Varian EM 390 and JEOL FX 90Q spectrometers, respectively. High resolution mass spectra

were obtained with a JEOL D 300 mass spectrometer.

The half-chair conformation is more favored than the boat one for this tetrahydrodiphosphorin system, because all substituents on phosphorus atoms in the latter must be eclipsed about the P-P bond. In the case of trans-2, the half-chair conformation with phenyl groups at the equatorial positions and sulfur atoms at the axial positions seems more stable than the other one, since phenyl group is bulkier than sulfur atom. On the other hand, if phenyl group on P₁ atom would occupy the equatorial position in the cis-2, phenyl group on P₂ atom must take the axial position, so that two half-chair conformations are energetically equivalent each other. Therefore, the ring inversion results in some average for signals assignable to unequivalent protons of methylene groups adjacent to phosphorus atoms for cis-2, but does not for trans-2.

6. The ³¹P-NMR spectrum of 4 shows to be a single compound. Similarity of signals of methylene and methine protons attached to phosphorus atoms to those of trans-2 and the result that undesirable reduction reaction of 4 gave only trans-2 indicate that stereochemistry of diphosphane moiety is the same as that of trans-2. Since lithiation and bromination are expected to occur from the less hindered side, the bromo atom in 4 seems to be in trans configuration to phenyl group, but the actual stereochemistry of bromo atom could not be determined from the spectral data for lack of the data in analogous compounds.

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