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REDUCTION OF DIPHOSPHENE: FORMATION OF dl- AND meso-DIPHOSPHANES

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Bis(2,4,6-tri-*tert*-butylphenyl)diphosphene was reduced with aluminum hydrides to give dl- and meso-bis(2,4,6-tri-*tert*-butylphenyl)diphosphanes as stable compounds.

By introducing an extremely bulky group into a molecule, we have been successful in preparation and characterization of diphosphene, *E*-bis(2,4,6-tri-*tert*-butylphenyl)diphosphene (**1**)[1] as a stable compound. The molecule is of current interest[2-4] because of its unusual phosphorus-phosphorus double bond which is sterically protected. During the course of the studies on reactivities of **1**, we have found that **1** reacts with aluminum hydrides such as sodium bis(methoxyethoxy)aluminum hydride (Vitride) and lithium aluminum hydride to give stable diphosphanes (**2a**,**b**).

(**1**) (**2a**,**b**)

(Ar = 2,4,6-$Bu^t{}_3C_6H_2$-)

Into the diphosphene **1** in ether was added slightly excess Vitride (70 % in toluene) at 0 °C to give a dark purple solution immediately. It was quenched with water after 10-min stirring at room temperature, treated with 15 % aqueous sodium hydroxide, washed with water, and extracted with benzene. After removal of the solvent, the residue was washed with methanol or acetone to give white solid (**2**) in 84 % yield, mp 144 - 147 °C, where the isomer ratio of **2a** and **2b** was about 5 : 1 according to the $^{31}P\{^1H\}$ NMR. Although we have succeeded in isolation of the

TABLE 1. ^{31}P NMR of 1,2-Bis(2,4,6-tri-tert-butylphenyl)diphosphanes (**2**)

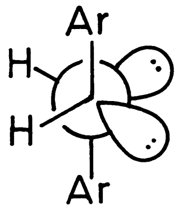
Compound	δ_P/ppm^a	$^1J_{PP}$/Hz	$^1J_{PH}$/Hz	$^2J_{PH}$/Hz	$^3J_{HH}$/Hz
2a	-64.4	191.8	220.1	15.9	0
(major)		(192.4	221.0	16.0	1.0)^b
2b (minor)	-65.0	190.6	210.8	7.2	1.5

a) 85 % H_3PO_4 as external standard (THF).

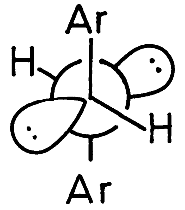
b) Data taken from Ref. 3.

predominant isomer **2a** in the pure form (mp 147 - 148.5 °C), the purification of the minor **2b** has not been successful so far. (The diphosphanes **2** were also formed as minor reaction products in the preparation of **1** when excess amount of magnesium was employed.)$^{1)}$

Table 1 shows the results of ^{31}P NMR of the diphosphanes **2** in THF at 36.3 MHz (room temperature) analyzed as AA'XX' pattern.$^{5)}$ Very recently Cowley reported the formation of a diphosphane in the oxidative coupling reaction of the corresponding phosphide, however, neither the formation of the other isomer has been reported nor the configuration of the obtained isomer has been discussed.$^{3)}$ The diphosphane obtained by Cowley seems to be identical with **2a**. By comparing two sets of the ^{31}P NMR signals (non-decoupled) we have tried the determination of the configuration of diphosphanes **2**.$^{6)}$ The major diphosphane is supposed to be dl-**2a** because of the small or negligible $^3J_{HH}$ value and the minor to the meso isomer.



2a (dl)



2b (meso)

By considering the Newman's projection around the P - P bond (Figure), the stable conformation of the dl isomer is trans causing the lone pairs in gauche,$^{7,8)}$

TABLE 2. ESR Spectra of Reaction Intermediates for **2**

Species	$g_{av.}$	a(P)/mT	a'(other)/mT
2a· (major)	2.008_6	9.91	3.94
2b· (minor)	2.008_6	9.91	1.21

whereas the stable form of the meso isomer is also supposed to be trans, however, causing the lone pairs in trans. Similar relationships have been discussed in the case of 1,2-diphenyldiphosphanes,[9-11] however, in the present diphosphanes **2**, due to the extremely bulky vicinal aryl groups, the most important conformation seems to be trans aryl form in both isomers. Attempts to resolve the ^{31}P NMR signal of the dl isomer in a chiral solvent, D(+)-α-phenylethylamine,[11] failed, probably due to its unusual bulkiness in **2**.

On the other hand, the preparation reaction was monitored by means of ESR and two sets of double doublets were observed in about 5 : 1 ratio. Table 2 shows the results of hyperfine splitting constants (mT) and $g_{av.}$-factors for the intermediates at the temperature range of -23.5 to 30 °C in ether. Hyperfine splitting constant with the vicinal phosphorus nuclei, a'(other), is related to a degree of mixing of orbital of unpaired electron with lone paired electron orbital of the vicinal phosphorus, and shows the angular dependence.[12,13] The overlap of both orbitals is more effective when they are in trans than in gauche. The larger splitting of a' observed in the set of the stronger signals is reasonably assignable to that for **2a·**, which leads to the major diphosphane **2a**, where in **2a·** the unpaired electron and the vicinal phosphorus lone pair are in the trans form. The other set of the weaker signals (**2b·**) was supposed to lead to the minor **2b**, where in **2b·** the robe of the radical and the lone pair of the vicinal phosphorus atom are in gauche.

An attempt to deprotonate from **2** with butyllithium failed, however, monophosphide anion was observed in the $^{31}P\{^1H\}$ NMR spectrum of a reaction mixture of **1** with a mixture of potassium hydride and Vitride at -41.5 ($\underline{P}$H, d) and -70.7 ppm ($\underline{P}^-$, d) with $^1J_{PP}$=367.4 Hz. It was quenched with methyl iodide to give methylated diphosphane, ArP(H)P(Me)Ar, δ_P -34.2 ($\underline{P}$Me) and -52.2 ppm ($\underline{P}$H) with $^1J_{PP}$=244.1 Hz. Attempts to isolate the diphosphane failed giving hydrolyzed products, 2,4,6-tri-*tert*-butylphenylphosphine oxide,[14] δ_P -10.0 ppm, and methy(2,4,6-tri-*tert*-

butylphenyl)phosphine (1 : 1) almost quantitatively. The latter methylphosphine was stable, mp 76 - 78 °C; IR (KBr) ν_{PH} 2400 cm^{-1}; $^{31}P\{^1H\}$ NMR δ_P -91.7 ppm; ^1H NMR ($CDCl_3$) 7.39 (d, arom, $^4J_{PH} = 2.2$ Hz), 5.06 (dq, P<u>H</u>, $^1J_{PH} = 225.6$ Hz, $^3J = 6.8$ Hz), 1.58 (s, 18H, o-Bu^t), 1.30 (s, 9H, p-Bu^t), and 1.08 (dq, p-<u>Me</u>, $^2J_{PH} = 5.1$Hz, $^3J = 6.8$ Hz) ; MS m/e 292 (M^+, 100 %).

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