The First Preparation of an Unsymmetrical 1,3-Diphospha-allene carrying 2,4,6-Tri-t-butylphenyl and 2,4,6-Tri-t-pentylphenyl as Protecting Groups

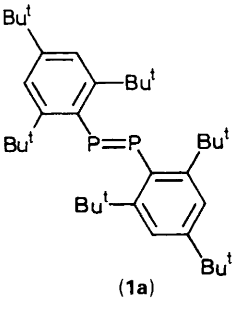
Masaaki Yoshifuji,*[a] Shigeru Sasaki,[b] and Naoki Inamoto[b]

[a] *Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980, Japan*
[b] *Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan*

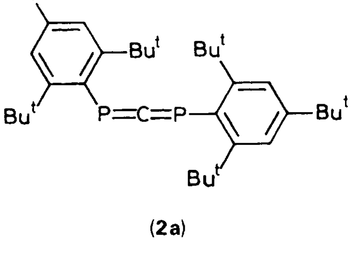
1-(2,4,6-Tri-t-butylphenyl)-3-(2,4,6-tri-t-pentylphenyl)-1,3-diphospha-allene was prepared from the corresponding unsymmetrical diphosphene and the NMR coupling constant $^2J_{P=C=P}$ was observed for the first time.

Sterically hindered groups are of current interest because they are used as a strategic tool for kinetically stabilising highly reactive molecules, unless otherwise unstable. For example, the 2,4,6-tri-t-butylphenyl group (hereafter abbreviated to Ar) is one of the most useful protective groups for the purpose of stabilisation of unusual compounds involving heavier main group elements. Using this Ar group, we have been successful in preparing diphosphene (**1a**)[1] and 1,3-diphospha-allene (**2a**)[2] as stable compounds, which are the new type of phosphorus compounds with isolated and cumulative double bonding.

We now report the first preparation of an unsymmetrical 1,3-diphospha-allene bearing Ar and another new protective group, 2,4,6-tri-t-pentylphenyl (hereafter abbreviated to Aa).[3] As a starting material, 2,4,6-tri-t-pentylbromobenzene AaBr (**3**) was prepared by a similar method to that employed for ArBr[4,5].



(**1a**)



(**2a**)

The bromide (**3**)† was lithiated with butyl-lithium in tetrahydrofuran (THF) and was allowed to react with phosphorus trichloride (Scheme 1). After the usual workup, (**4b**) was obtained as an oily material in 92% yield, ^{31}P NMR (pentane) δ_P 149.3 p.p.m. (from external 85% H_3PO_4). In order to demonstrate the utility of Aa as a protective group in low co-ordination organophosphorus chemistry, attempts were made to prepare the diphosphene (**1b**) from (**4b**) by the method described for the preparation of (**1a**).[1] [Compound (**1b**): m.p. 115—118.5 °C, orange needles, 16% yield based on (**4b**).] Furthermore, the diphosphene (**1b**) was allowed to react with a large excess of dichlorocarbene[6,7] generated from

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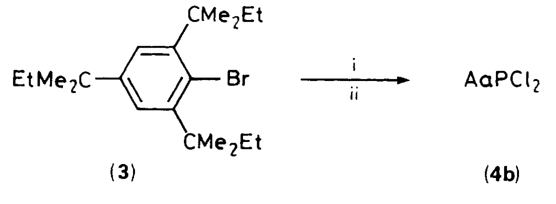
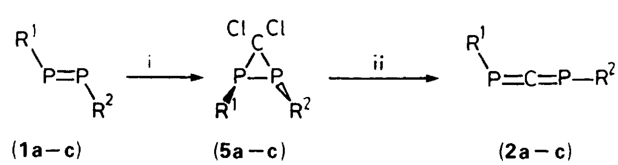
† Benzene (24.7 g, 0.316 mol) was allowed to react with t-pentyl chloride (308 g, 2.89 mol) in the presence of anhydrous aluminium chloride (14.2 g, 0.107 mol) with stirring at −60 °C for 15 min and then at −20 °C for 1 h. The reaction product was fractionally distilled to give pure 1,3,5-tri-t-pentylbenzene (25.9 g, 89.8 mmol, 28% yield): b.p. 113—119 °C/0.52 mmHg. Into a solution of the benzene (16.3 g, 56.6 mmol) in trimethyl phosphate (110 g, 793 mmol) was added bromine (17.2 g, 108 mmol) in trimethyl phosphate (23.9 g, 171 mmol) at 75—80 °C and the mixture was stirred for 3 days at 90—110 °C. The resulting oil after the usual workup was chromatographed over silica gel (pentane as an eluent) to give 14.8 g (40.3 mmol) of colourless oil of 2,4,6-tri-t-pentylbromobenzene (**3**) in 71% yield. Compound (**3**): ^{1}H NMR ($CDCl_3$) δ 7.23 (2H, s, aromatic), 2.11 (4H, *o*-CH_2, q, J 7.48 Hz), 1.60 (2H, *p*-CH_2, q, J 7.43 Hz), 1.52 (12H, s, *o*-CH_3), 1.27 (6H, s, *p*-CH_3), 0.65 (6H, t, J 7.44 Hz, *o*-CH_2CH_3), 0.61 (3H, t, J 7.55 Hz, *p*-CH_2CH_3). Found: m/z 366.1900 and 368.1915. Calcd. for $C_{21}H_{35}{}^{79}Br$ and $C_{21}H_{35}{}^{81}Br$: M, 366.1921 and 368.1903.

Table 1. ^{31}P NMR data for diphosphenes (**1**), diphosphiranes (**5**), and 1,3-diphospha-allenes (**2**) in [$^2H_1$]chloroform.

	(1)			(5)			(2)		
	a	**b**	**c**	**a**	**b**	**c**	**a**	**b**	**c**
δ_P/p.p.m.	490.3	490.8	491.2 489.9	−69.3	−69.0	−67.8 −68.4	141.7	142.2	142.5 142.4
J_{PP}/Hz			582.9			137.7			18.5



Scheme 1. *Reagents*: i, BuLi; ii, PCl_3.



a; $R^1 = R^2 = Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2$
b; $R^1 = R^2 = Aa = 2,4,6\text{-}t(C_5H_{11})_3C_6H_2$
c; $R^1 = Ar$, $R^2 = Aa$

Scheme 2. *Reagents*: i, CCl_4, BuLi; ii, MeLi.

$$ArPCl_2 + AaPCl_2 + 2Mg \longrightarrow (\mathbf{1a}) + (\mathbf{1b}) + (\mathbf{1c})$$

Scheme 3

carbon tetrachloride and butyl-lithium to give the corresponding diphosphirane (**5b**) (m.p. 115.2—126.1 °C, 42% yield). The diphosphirane (**5b**) was allowed to react with methyl-lithium to give 1,3-diphospha-allene (**2b**) in 31% yield after chromatography, m.p. 64.5—78.0 °C (Scheme 2). Relatively low yields of (**1b**), (**5b**), and (**2b**) even under more severe reaction conditions indicate that the group Aa is much more sterically hindered than Ar.

On the other hand, a mixture of (**4b**) (525 mg, 1.34 mmol) and (**4a**) (57.3 mg, 2.6 mmol) in THF (8 ml) was allowed to react with magnesium metal (322 mg, 0.926 mg-atom) at 0 °C for 15 min and then at room temperature for 30 min (Scheme 3). The usual workup procedure including column chromatography gave an unsymmetrical diphosphene (**1c**) [112 mg, 0.188 mmol, 41% yield based on (**4a**)] together with symmetrical diphosphenes (**1b**) [86.9 mg, 0.136 mmol, 20% yield based on (**4b**)] and (**1a**) [36.6 mg, 0.0709 mmol, 15% yield based on (**4a**)]. (**1c**): m.p. 132.5—138.0 °C; ^{31}P NMR ($CDCl_3$) δ_P 491.2 and 489.9 p.p.m. (AB, $^1J_{PP}$ 582.9 Hz).

The unsymmetrical diphosphene (**1c**) (37.4 mg, 0.0629 mmol) thus obtained and 20.0 mg of carbon tetrachloride (0.13 mmol) were mixed in THF (4.0 ml). Butyl-lithium (0.126 mmol) was then added at −78 °C and was warmed up to room temperature. After the usual workup through column chromatography on silica gel (pentane as an eluent), the unsymmetrical diphosphirane (**5c**) (14.5 mg, 0.0214 mmol, 34% yield) was isolated as a colourless solid together with the starting diphosphene (**1c**) (10% recovery). [Compound (**5c**): m.p. 152.0—156.7 °C, ^{31}P NMR ($CDCl_3$) δ_P −67.8 and −68.4 p.p.m. (AB, $^1J_{PP}$ 137.7 Hz).] The unsymmetrical diphosphirane (**5c**) thus isolated (19.4 mg, 0.0286 mmol) was dissolved in ether (1.0 ml), cooled at −78 °C, and 0.0458 mmol of methyl-lithium was added. The mixture was immediately warmed up to room temperature. The solvent was removed and the resulting oil was chromatographed over silica gel (pentane) to give 6.3 mg of (**2c**) (0.0104 mmol) in 36% yield as a colourless solid. [Compound (**2c**): m.p. 126.9—132 °C, ^{31}P NMR ($CDCl_3$) δ_P 142.5 and 142.4 p.p.m. (AB, $^2J_{PP}$ 18.5 Hz).]

This is the first example of an unsymmetrical 1,3-diphospha-allene and is stable with two extremely bulky substituents. The coupling constant $^2J_{P=C=P}$ was rather small. Table 1 shows some ^{31}P NMR data observed during this study on diphosphenes, diphosphiranes, and diphospha-allenes. It should be noted here that the reaction of dichlorocarbene with 1-(2,4-di-t-butyl-6-methylphenyl)-2-(2,4,6-tri-t-butylphenyl)diphosphene[8] gave the corresponding dichlorodiphosphirane (δ_P −71.8 and −74.9 p.p.m., $^1J_{PP}$ 125.7 Hz), but that further attempts to obtain the unsymmetrical diphospha-allene by methyl-lithium failed under various conditions. Furthermore, Koenig *et al.* have recently reported[9] that the dichlorodiphosphirane with Ar and tris(trimethylsilyl)methyl is not stable enough to permit purification by silica gel column chromatography. Therefore, the 2,4,6-tri-t-pentylphenyl (Aa) group is an alternative and promising protective moiety especially for studies on multiple bonding involving heavier main group elements.

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