

A Highly Basic Triphenylphosphine, [2,4,6-(MeO)₃C₆H₂]₃P

Masanori Wada* and Shogo Higashizaki

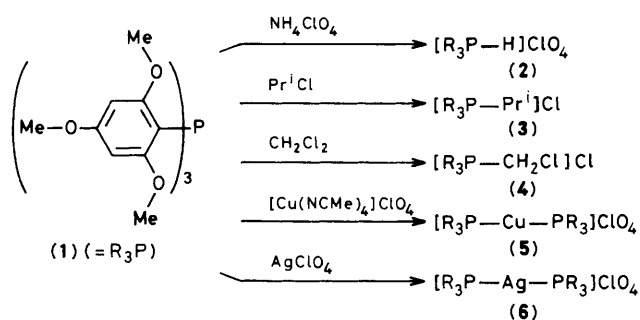
Department of Applied Chemistry, Osaka University, Suita, Osaka 565, Japan

Tris(2,4,6-trimethoxyphenyl)phosphine was found to be highly basic (pK_a , 11.2).

Triphenylphosphine is useful as a reagent or catalyst in organic chemistry and as a ligand in inorganic chemistry.¹ Its basicity is low, and *para*-substitution of the phenyl groups results in only a small increase in basicity.² Compared to these phosphines, tris(2,4,6-trimethoxyphenyl)phosphine, (**1**), is expected to show either higher basicity owing to the multi methoxy substitutions (mesomeric effect) or lower basicity owing to the bulkiness of the aryl group (B-strain). We report here that (**1**) has a very high basicity; probably the highest known for tertiary phosphines.³

Phosphine (**1**) is easily prepared from P(OPh)₃ and 2,4,6-trimethoxyphenyl-lithium in diethyl ether at 0°C to room temperature and can be recrystallized from ethanol in air as colourless crystals in 60–70% yield, † m.p. 158–160°C, ¹H n.m.r. (CDCl₃, 100 MHz) δ 3.47 (s, 2,6-MeO), 3.76 (s, 4-MeO), and 6.03 (d, *J* 3 Hz, 3,5-H).

Phosphine (**1**) reacts with perchloric acid in ethanol to give the tertiary phosphonium salt, (**2**), m.p. 186°C (decomp.), ¹H n.m.r. (CDCl₃) δ 3.69 (s, 2,6-MeO), 3.89 (s, 4-MeO), 6.17 (d, *J* 5 Hz, 3,5-H), and 8.35 (d, *J* 541 Hz, P-H). The same salt was obtained in 88% yield by treating (**1**) (1 mmol) with NH₄ClO₄ (1.5 mmol) in ethanol (50 cm³), suggesting that (**1**) has a higher basicity than NH₃ (pK_a , 9.21). Compound (**2**) can be recrystallized from ethanol containing an excess of Buⁿ₃P



(pK_a , 8.43), which is one of the most basic tertiary phosphines,³ and even from ethanol containing NEt₃ (pK_a , 10.75).

The basicity of (**1**) was studied further by examining the ¹H n.m.r. spectra of a mixture of (**2**) and a suitable amine in acetone in the region of the 2,6-MeO proton resonance. It was found to be a stronger base than Et₂NH (pK_a , 11.0), comparable to piperidine (pK_a , 11.2), but weaker than 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (pK_a , 11.5).

A series of methoxy substituted triphenylphosphines‡ was also prepared from PPhCl₂ or PPh₂Cl and 2,4,6-trimethoxyphenyl-lithium or 2,6-dimethoxyphenyl-lithium.

† The preparation of (**1**) from 1,3,5-(MeO)₃C₆H₃, PCl₃, and ZnCl₂ has been reported (ref. 4).

‡ All new compounds including (**1**) have been fully characterized by elemental (C, H, Cl) and spectral analyses.

Their basicities were compared in a similar manner as their tertiary phosphonium perchlorates.‡ The results can be summarized as follows [abbreviations: (2,4,6) = 2,4,6-(MeO)₃C₆H₂ and (2,6) = 2,6-(MeO)₂C₆H₃]: DBU (pK_a , 11.5) > (1) *ca.* = piperidine (11.2) > NEt₂H (11.0) > NEt₃ (10.75) > P(2,6)₃ > PPh(2,4,6)₂ > γ -collidine (7.4) > PPh(2,6)₂ > pyridine > PPh₂(2,4,6) > PPh₂(2,6) > PPh₃ (2.32 or 2.73³).

Apparently, the basicity of the triphenylphosphines increased as the level of methoxy substitution increased even though the bulkiness also increased. Noteworthy is the higher basicity of P(2,6)₃ than PPh(2,4,6)₂, suggesting that 2,6-methoxy groups have a greater effect than 4-methoxy groups on the increase in basicity.

Phosphine (1) reacted under mild conditions with a variety of alkyl halides including chlorides to give the quaternary phosphonium salts. In spite of the bulkiness of its aryl groups, (1) (1 mmol) reacted with isopropyl bromide (1 cm³) in less than 1 h in ethanol (20 cm³) at 65 °C, and even reacted with the chloride (2 cm³) in 15 h to give the isopropyl phosphonium salt, (3).

While triphenylphosphine is stable in dichloromethane for a prolonged period, (1) reacted rapidly at room temperature

($t_{1/2}$ < 15 min in neat CH₂Cl₂) to give the chloromethyl phosphonium salt, (4). The relative reactivity of the other methoxyphenylphosphines with dichloromethane decreased in the same order as the basicity.

While triphenylphosphine forms 4:1 complexes with Cu^I and Ag^I,⁵ (1) gave the stable 2:1 complexes, (5) and (6), in agreement with its large cone angle (184°).

Received, 30th January 1984; Com. 132

References

- 1 G. M. Kosolapoff and L. Maier, 'Organic Phosphorus Compounds,' Wiley-Interscience, New York, 1972; J. I. G. Cadogan, 'Organophosphorus Reagents in Organic Synthesis,' Academic Press, London, 1979.
- 2 H. Goetz and A. Sidhu, *Liebigs Ann. Chem.*, 1965, **682**, 71.
- 3 Wm. A. Henderson, Jr., and C. A. Streuli, *J. Am. Chem. Soc.*, 1960, **82**, 5791.
- 4 I. S. Protopopov and M. Y. Kraft, *Med. Prom. SSSR*, 1959, **13**, 5; *Chem. Abstr.*, 1960, **54**, 10914c.
- 5 F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 1960, 5267.