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A VERY CROWDED MOLECULE:
FORMATION OF BIS(2,4,6-TRI-t-BUTYLPHENYL)PHOSPHINIC CHLORIDE

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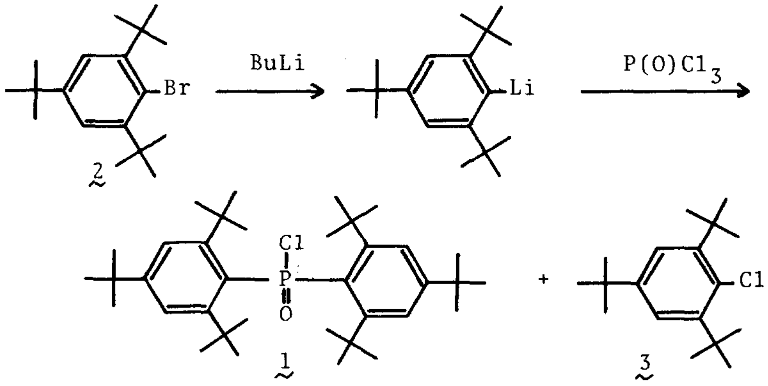
SUMMARY: Reaction of 2,4,6-tri-t-butylphenyllithium with phosphoryl trichloride gave a very crowded compound, bis(2,4,6-tri-t-butylphenyl)phosphinic chloride (1), and 2,4,6-tri-t-butylchlorobenzene (3), while the reaction with thiophosphoryl trichloride afforded 3.

Sterically hindered compounds have been of interest in view of their protecting nature of reactive sites or molecules.[1-4] During the course of our study on reactions of 1,3,5-tri-t-butylbenzene, we have unexpectedly found that 2,4,6-tri-t-butylphenyllithium reacts with phosphoryl trichloride to give a very crowded compound, bis(2,4,6-tri-t-butylphenyl)phosphinic chloride (1). This is, as far as we know, the first successful preparation of a compound carrying two and very bulky 2,4,6-tri-t-butylphenyl groups attached geminally on one element.

Into a solution of 2,4,6-tri-t-butylbromobenzene (2)[5] (5.00 mmol) in tetrahydrofuran (20 ml) was added butyllithium (5.64 mmol) in hexane at - 78 °C and the mixture was stirred for 1.5 h. Then phosphoryl trichloride (10.9 mmol) was added and the mixture was stirred overnight allowing the mixture to warm up to room temperature gradually. After removal of the solvent and the excess of phosphoryl trichloride in vacuo, the residue was chromatographed on silica gel to give 1 (1.21 mmol; 49 % yield based on 2), 2,4,6-tri-t-butylchlorobenzene (3)[6] (1.44 mmol; 29 % yield), and 1,3,5-tri-t-butylbenzene (0.46 mmol; 9 % recovery). The chloride (1) was insensitive to moisture and recrystallized from hexane (mp 210 - 210.5 °C). The elemental analysis of 1 gave satisfactory results.



The spectral data of **1** are as follows: ^{1}H-NMR ($CDCl_3$) at 60 and 90 MHz: δ 0.75 (s, 9H, o-Bu^t), 0.78 (s, 9H, o-Bu^t), 1.32 (s, 18H, p-Bu^t), 1.61 (s, 9H, o-Bu^t), 1.66 (s, 9H, o-Bu^t), and 7.20 - 7.70 (m, 4H, aromatic protons); IR (KBr): 1240 cm^{-1} ($\nu_{P=O}$); MS: m/e 572.3891 (M^{+}, calcd for $C_{36}H_{58}POCl$: 572.3911); Mol. wt. (vapor phase osmometric method): 579.3 (calcd: 573.3); ^{13}C-NMR at 15.04 and 25.16 MHz: δ 30.96 (p-($\underline{C}H_3)_3C$), 32.67, 33.48, 34.09, and 34.41 (o-($\underline{C}H_3)_3C$), 41.84 - 43.06 (m, $Me_3\underline{C}$), 123.45 - 127.38 (4 sets of doublets, m-C), 128.52 (d, J_{PC}= 134.28 Hz, ipso-C), 132.19 (d, J_{PC}= 126.34 Hz, ipso-C), 151.51 and 151.67 (2 sets of doublets, p-C), 153.60 - 156.32 (2 sets of doublets, o-C), and 160.01 - 162.94 (2 sets of doublets, o-C). The ^{1}H and ^{13}C NMR spectra indicated that the two bulky phenyl rings in **1** are nonequivalent because of its large steric hindrance.

As expected, the chlorine atom of **1** considerably resists toward the further nucleophilic attack because of the steric congestion around the phosphorus atom.

Under similar conditions 2,4,6-tri-t-butylphenyllithium was allowed to react with thiophosphoryl trichloride to give mainly **3** (59 % yield based on **2**) and tri-t-butylbenzene (16 % recovery), suggesting that highly hindered phenyllithium attacks one of the chlorine atoms of thiophosphoryl trichloride instead of the phosphorus atom, and the analogous bis(2,4,6-tri-t-butylphenyl)phosphinothioic chloride or 2,4,6-tri-t-butylphenylphosphonothioic dichloride could not be detected.

$$\mathbf{2} \xrightarrow[\text{2) } P(S)Cl_3]{\text{1) BuLi}} \mathbf{3}$$

Further investigations are under way.

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