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ORGANOLITHIUM DISPLACEMENT OF ARYL ANIONS FROM TERTIARY PHOSPHINE DERIVATIVES OF DIPHENYL ETHER[1,2]

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Abstract Methyllithium displaces a phenyl anion from 10-phenyl-10H-phenoxaphosphine to produce a 70:30 mixture of 10-methyl-10H-phenoxaphosphine and starting phosphine. Butyllithium gives 50% conversion to 10-butyl-10H-phenoxaphosphine. These reactions could take place either by a one-step nucleophilic displacement or by ring cleavage followed by recyclization. To show the feasibility of the two-step process, non-heterocyclic lithiated tertiary phosphines were generated and shown to cyclize to phenoxaphosphines. For example, reaction of 2-phenoxyphenyldiphenylphosphine with phenyllithium produced 10-phenyl-10H-phenoxaphosphine (by lithiation ortho to oxygen followed by cyclization) along with triphenylphosphine (by direct displacement of 2-lithiodiphenyl ether). Other compounds prepared in this work: 2,2'-bis(diphenylphosphino)-diphenyl ether, bis(2-phenoxyphenyl)phenylphosphine, tris(2-phenoxyphenyl)phosphine, 4-carboxy-10-phenyl-10H-phenoxaphosphine, and the oxides and sulfides of the phosphines.

Key Words: nucleophilic displacement, 10-phenyl-10H-phenoxaphosphine, methyllithium, butyllithium, phenyllithium.

INTRODUCTION

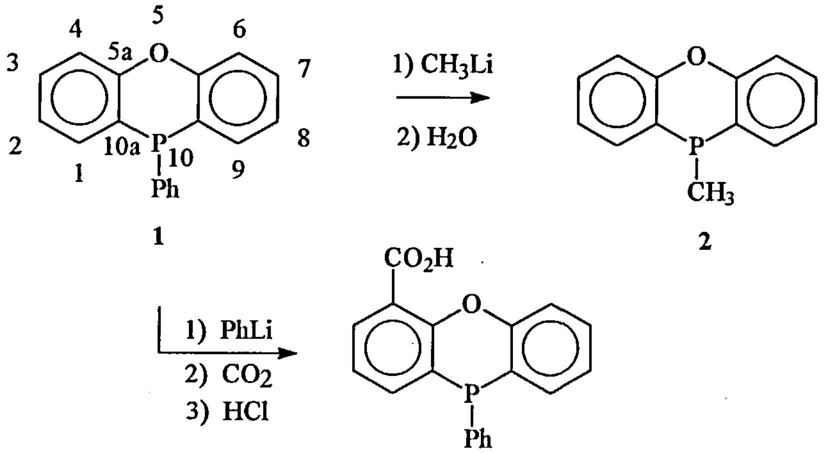
Nucleophilic displacement of good leaving groups from phosphines is well known, an example being the reaction of 2,2'-dilithiodiphenyl ether with phenylphosphonous dichloride to form 10-phenyl-10H-phenoxaphosphine (1).[3-7] In contrast, we have found only three previous reports of nucleophilic displacements of aryl anions from tertiary phosphines by alkyl anions of organolithium reagents and no previous reports of one aryl anion displacing another. Mathey[8] reported displacement of a phenyl anion of a phosphole by *t*-butyllithium; Kyba and Hudson[9] observed substitution of a phenyl of methyldiphenylphosphine by either an n-butyl or a *t*-butyl group; and Kyba[10] also determined that displacement of a benzyl group from optically active benzylmethylphenylphosphine by either n-butyl or *t*-butyl occurred with inversion of configuration.

RESULTS AND DISCUSSION

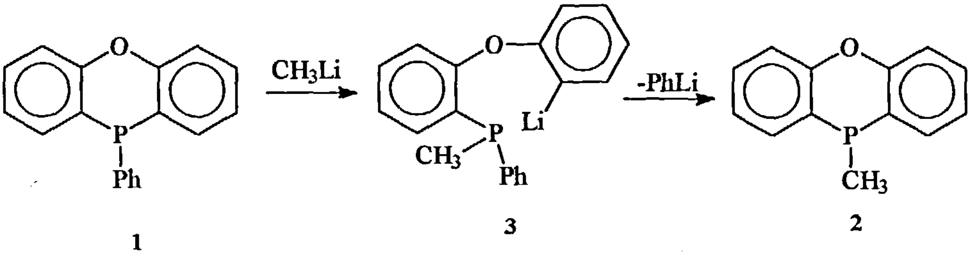
Reaction of 10-Phenyl-10H-phenoxaphosphine(1) with Lithium Reagents

Reaction of 10-phenyl-10H-phenoxaphosphine (**1**) with methyllithium cleanly produced after hydrolysis a 70:30 mixture of 10-methyl-10H-phenoxaphosphine (**2**) and the starting phosphine. 10-Methyl-10H-phenoxaphosphine[11] was identified by its ^{1}H, ^{13}C, and ^{31}P NMR spectra and by its mass spectrum. Reaction of **1** with butyllithium instead of methyllithium gave a 50% conversion to 10-butyl-10H-phenoxaphosphine.

In these reactions any lithiation of **1** at the 4-position of the phenoxaphosphine ring system (abstraction of a proton ortho to the oxygen) or lithiation of the 10-alkyl group was reversed by hydrolysis in the workup. That deprotonation of the phenoxaphosphines had occurred was confirmed by hydrolysis of an aliquot of the reaction mixture with deuterium oxide and then examination of the mass spectrum of the product. Reaction of **1** with phenyllithium in the presence of tetramethylethylenediamine followed by carbonation gave after acidification 4-carboxy-10-phenyl-10H-phenoxaphosphine in 65% yield. When phenyllithium was employed for proton abstraction, any competing nucleophilic substitution simply replaced one phenyl group by another.



It was at first surprising that cleavage of the exocyclic C-P bond had occurred in the reaction of **1** with alkyllithiums, since alternative ring cleavage would have produced an *o*-lithiated diphenyl ether derivative (**3**) in which the negative carbon would have been stabilized by the nearby oxygen. Ring cleavage is known to take place both in the reaction of hydroxide ion with 10-methyl-10-phenyl-10H-phenoxaphosphonium iodide, which formed methyl-2-phenoxyphenylphenylphosphine oxide, and in the reaction of hydroxide ion with 10,10-dimethyl-10H-phenoxaphosphonium iodide, which formed dimethyl-2-phenoxyphenylphosphine oxide.[11] In these reactions, in which ring cleavage occurred upon attack by hydroxide ion, protonation of the negative carbon of the ring-opened species by a hydroxyl-containing species probably occurred rapidly. In the reaction of **1** with methyllithium, however, there would not have been a sufficiently acidic group present to rapidly protonate **3**. Therefore, we propose that **3** could have been generated in our reaction of **1** with methyllithium but, if so, it then cyclized by an internal nucleophilic substitution reaction to form **2** plus phenyllithium.



Synthesis of Tertiary Phosphines

We decided to test the two-step mechanism by synthesizing species similar to the proposed intermediate **3** in order to observe whether or not cyclization would occur spontaneously forming phenoxaphosphines. The phosphines needed were prepared by reaction of the appropriate chlorophosphines with 2-lithiodiphenyl ether. The yields were low because reaction of diphenyl ether with an equimolar amount of butyllithium gave a 7:3 ratio of monolithiated to dilithiated diphenyl ether, as determined both by hydrolysis with D_2O followed by mass spectral analysis and by reaction with diphenylphosphinous chloride followed by ^{31}P NMR analysis of the product mixture. Reaction of diphenyl ether with two moles of butyllithium as in the synthesis of **1** gave a good yield (58% after recrystallization) of 2,2'-bis(diphenylphosphino)diphenyl ether upon reaction with diphenylphosphinous chloride.

Reactions of 2-Phenoxyphenyldiphenylphosphine or Bis(2-phenoxyphenyl)phenylphosphine with Phenyllithium or Methyllithium

The reaction of 2-phenoxyphenyldiphenylphosphine with phenyllithium followed by hydrolysis was carried out to see if 10-phenyl-10H-phenoxaphosphine (**1**) would be produced as a result of abstraction of a proton ortho to the oxygen followed by cyclization through nucleophilic displacement of a phenyl anion. Indeed **1** was formed along with an approximately equal amount of triphenylphosphine, and both products support the feasibility of the two-step mechanism, **1** to **3** to **2**. The formation of triphenylphosphine in this reaction, which may represent the first example of nucleophilic displacement of an aryl anion from a phosphine by another aryl anion, is very similar to the displacement proposed as the first step of the two-step mechanism, and the conversion of 2-lithio-2'-diphenylphosphinodiphenyl ether to **1** is analogous to the second step of the two-step mechanism. Reaction of 2-phenoxyphenyldiphenylphosphine with methyllithium followed by hydrolysis gave the following relative amounts of products: **2** > **1** > triphenylphosphine > methyldiphenylphosphine. Reaction of bis(2-phenoxyphenyl)-phenylphosphine with phenyllithium or methyllithium gave mechanistically similar results and indicated that a diphenyl ether anion was displaced ten times more readily than a phenyl anion.

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