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PREPARATION OF STABLE PHOSPHIRANES FROM PHOSPHIDE AND EPOXIDE ASSISTED BY SILICON

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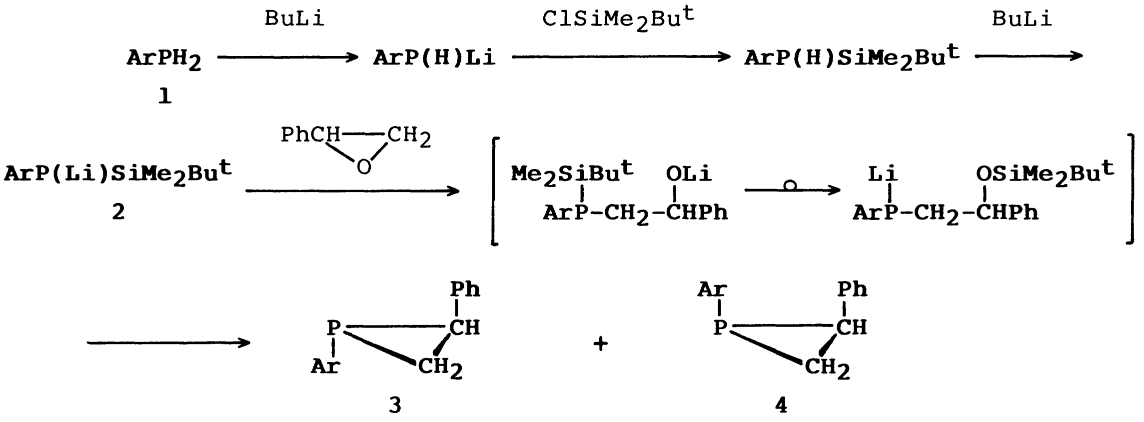
Sterically protected *E*- and *Z*-1-(2,4,6-tri-*t*-butylphenyl)-2-phenylphosphiranes were prepared from the corresponding silylphosphide and styrene oxide: the reaction might involve unusual rearrangement and elimination of a silyl group.

We have been interested in the isolation and characterization of unusual organophosphorus compounds by introducing sterically bulky groups into a molecule in order to protect sensitive moieties. We reported several new types of compounds involving -P=P-,1) -P=C<,2a) -P=C=N-,2b) -P=C=C<,2b) -P=C=P-,2c) and so on and we have demonstrated that a very bulky silylphosphide2) is an appropriate starting material for obtaining such kinds of species.

It has been of current interest to study phosphorus-containing small ring compounds.3) As for 3-membered ring compounds, it has been known that phosphiranes can be prepared from 2 equiv. of phosphides and 1,2-dihaloethanes.4a) 1-Aminophosphiranes have been prepared by Niecke et al.4b) from 1,3,4-phosphadiazolines and more recently 2-vinylphosphiranes have been prepared by Richter4c) from "magnesium butadiene" and phosphonous dichloride.

We now wish to report our preliminary results on the preparation of very stable phosphiranes obtained from a phosphine and an epoxide assisted by a silyl group. The following scheme shows the reaction sequence employed here. 2,4,6-Tri-*t*-butylphenylphosphine (**1**, 115.9 mg, 0.417 mmol) was lithiated, silylated with *t*-butyldimethylsilyl chloride, and lithiated with butyllithium and the resulting



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

silylphosphide **2** was allowed to react with styrene oxide (73.8 mg, 0.614 mmol) in THF (10 mL) at room temperature for 10 h to give a mixture of E and Z phosphiranes. The mixture was chromatographed over SiO_2 to afford **3** in 78% yield and **4** in 3% yield based on **1**. **3** (oil): $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = -173.3; ^1H NMR ($CDCl_3$) δ= 7.3-6.9 (7H, m, arom), 2.5-2.2 (1H, m, CH), 1.9-1.7 and 1.5-1.4 (1H+1H, m+m, CH_2), 1.60 (18H, d, J=7.9 Hz, o-Bu^t), and 1.30 (9H, s, p-Bu^t). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ = 32.9 (d, J=39.1 Hz, PCHPh) and 25.9 (d, J=43.3 Hz, PCH_2). Found: m/z 380.2653. Calcd for $C_{26}H_{37}P$: M, 380.2633. **4** (oil): $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = -156.2; ^1H NMR ($CDCl_3$) δ= 7.37 (2H, d, J=1.5 Hz, Ar), 6.9-6.8 and 6.1-5.9 (5H, m+m, Ph), 2.6-2.5 (1H, m, CH), 2.0-1.8 and 1.5-1.4 (1H+1H, m+m, CH_2), 1.65 (9H, s, o-Bu^t), 1.29 (9H, s, o'-Bu^t), and 1.17 (9H, s, p-Bu^t); MS m/z 380 (M^+). The phenyl protons of **4** appeared in higher field than those of **3** whereas the contrary shift was observed for the methines: the tendency is characteristic for E/Z isomers.[2a,5] Furthermore, the phosphirane **3** was oxidized with hydrogen peroxide to give the corresponding 1-oxide; an oil: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = -39.2; ^1H NMR ($CDCl_3$) δ= 7.5-7.2 (7H, m, arom), 2.4-1.3 (3H, m, CH, CH_2), 1.61 (18H, d, J=12.3 Hz, o-Bu^t), and 1.33 (9H, s, p-Bu^t);[6] IR ν(P=O) 1220 cm^{-1};[7] MS m/z 396 (M^+).

Our present method, starting from silylphosphide and oxirane, might involve 1,4-migration[8] of the silyl group from phosphorus to oxygen followed by intramolecular nucleophilic displacement to form **3** and **4**. It seems likely that this method could provide a new type of silicon-assisted methodology for the preparation of phosphorus-containing cyclic compounds.

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