A New Type of Silicon–Tin Rearrangement Involving Neighbouring Group Participation of an α-Phosphoryl Group

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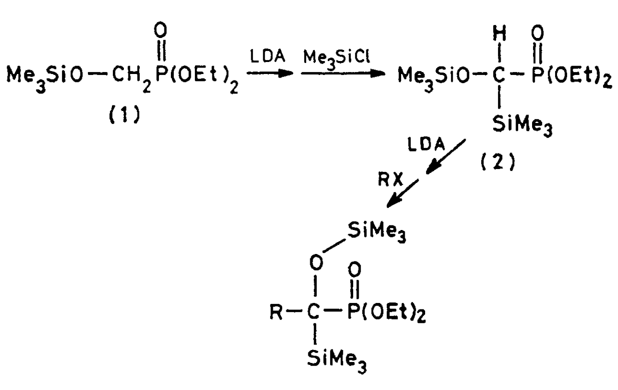
Summary Diethyl 1-hydroxy-3-phenyl-1-trimethylsilylpropylphosphonate (**5**) underwent silicon–tin rearrangement with tributyltin alkoxides to afford the 1-silyloxy-1-stannylpropylphosphonate (**6**) in high yield; the 1-hydroxypropylphosphonate (**8**) was converted by treatment with a stannylating agent into the ketone (**9**).

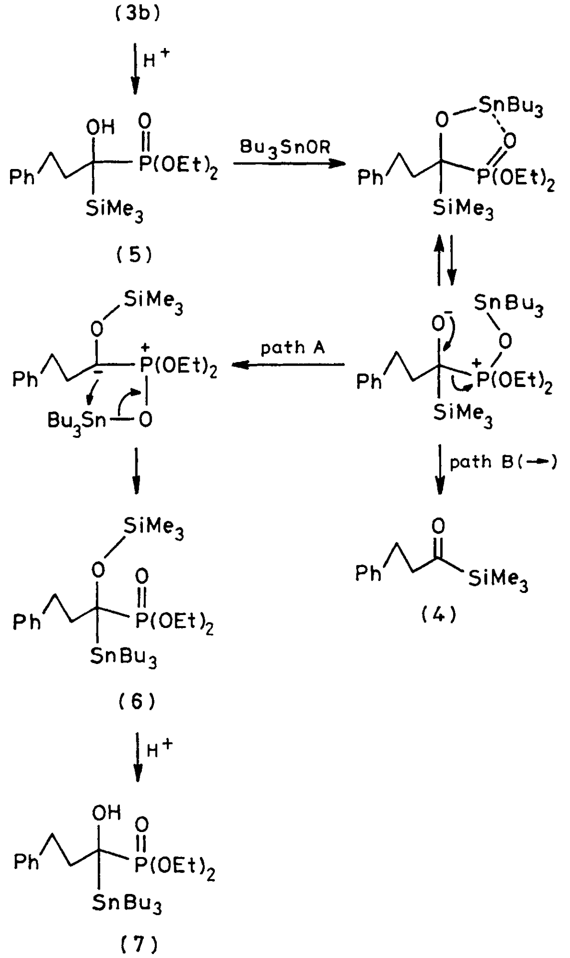
In connection with our studies of the synthesis of unsymmetrical ketones,[1-3] we have found a new type of silicon–tin intramolecular rearrangement reaction of 1-tributylstannyloxy-1-trimethylsilylalkylphosphonates. Treatment of diethyl trimethylsilyloxymethylphosphonate (**1**) with lithium di-isopropylamide (LDA) (1·1 equiv.) in tetrahydrofuran (THF) at −78 °C for 30 min followed by silylation with trimethylsilyl chloride (1·1 equiv.) at −78 °C to room temperature (2 h) afforded the phosphonate (**2**) in 95% yield. The α-carbanion species from (**2**) was readily generated by treatment with LDA (1·1 equiv.) in THF at −78 °C



(3a) R = PhCH$_2$
(3b) R = PhCH$_2$CH$_2$

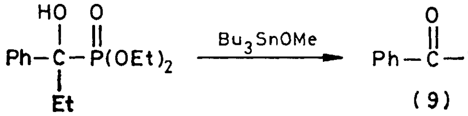
for 1 h. Alkylation of the carbanion with benzyl bromide (1·1 equiv.) or benzyl iodide (1·8 equiv.) at −78 °C (30 min) to room temperature (2—2·5 h) gave the alkylated product (**3a**) in 82 or 90% yield. Similarly, alkylation using phenethyl bromide (1·2 equiv.) or phenethyl iodide (1·1 equiv.) afforded the alkylated product (**3b**) in 55 or 67% yields.

In attempts to obtain the acylsilane (**4**) from (**3b**) by a similar procedure to that used for the synthesis of unsymmetrical ketones,[1–3] (**3b**) was treated under various basic conditions, but (**4**) was not obtained and considerable amounts of the aldol product were formed. We have very recently reported that the stannylation of 2-halogeno-1-hydroxy phosphonates led to the formation of enol phosphates.[4] This reaction seems to proceed as a result of the strong co-ordination of the stannyl group to the phosphoryl oxygen (P=O) of the α-phosphoryl group.[4] Therefore, the conversion of (**3b**) into (**4**) by a process involving stannylation was examined. Treatment of (**3b**) with a catalytic amount of toluene-*p*-sulphonic acid in methanol under reflux for 15 min gave diethyl 1-hydroxy-3-phenyl-1-trimethylsilylpropylphosphonate (**5**) in 92% yield. When (**5**) was treated with tributyltin methoxide (1·0 equiv.) in toluene under reflux for 24 h, phenethyl trimethylsilyl ketone (**4**) was first eluted and obtained in 30% yield by silica gel column chromatography; the oily product (**6**), possessing both a tributylstannyl and a trimethylsilyl group, was then eluted and obtained in 57% yield. The structure of (**6**) was assigned from its elemental analysis and n.m.r. and i.r. spectra: $\delta(\mathrm{CDCl_3})$ 0·24 (s, 9H, $\mathrm{Me_3Si}$), 0·84—1·64 (m, 33H, $\mathrm{Bu_3Sn}$ and 2 × $Me\mathrm{CH_2O}$), 2·64—3·04 (m, 4H, CH_2CH_2-Ph), 4·09 (m, 4H, $\mathrm{Me}CH_2\mathrm{O}$), and 7·19 (s, 5H, Ph); ν_{max} (NaCl) 1035, 1055, 1105, and 1250 ($\nu_{P=O}$) cm^{-1}. The yield of (**6**) could be increased to 82% by using tributyltin t-butoxide as the stannylating agent under similar conditions (in toluene, reflux, 35 min). Treatment of (**6**) with a catalytic amount of toluene *p*-sulphonic acid in methanol under reflux for 10 min gave the phosphonate (**7**) in 20% yield.



SCHEME

This reaction might proceed *via* path A as shown in the Scheme. The driving force of this reaction seems to result from the co-ordination of the stannyl group to the α-phosphoryl oxygen and the strong affinity of the silyl group for the resulting oxide ion (the Brook rearrangement[5]). On the basis of these observations, we have found a new route from α-hydroxy phosphonates to ketones under mild conditions: when the phosphonate (**8**) was refluxed with tributyltin methoxide (1 equiv.) in toluene for 30 min, ethyl phenyl ketone (**9**) was obtained in 84% yield. This reaction also suggests that the co-ordination between the stannyl group and the α-phosphoryl group leads to facile cleavage of the P-C bond.



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