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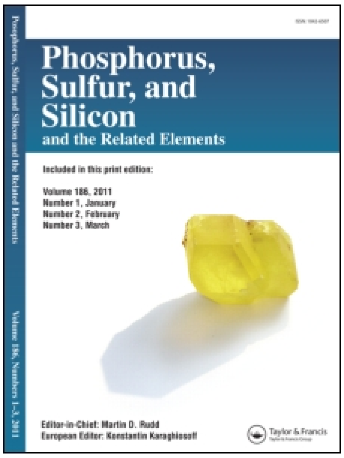

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THE HYDROBORATION OF P-PHENYL-CTERT-BUTYL-C-TRIMETHY LSILOXYMETHYLENE PHOSPHINE

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THE HYDROBORATION OF P-PHENYL-C-TERT-BUTYL-C-TRIMETHYLSILOXYMETHYLENE PHOSPHINE

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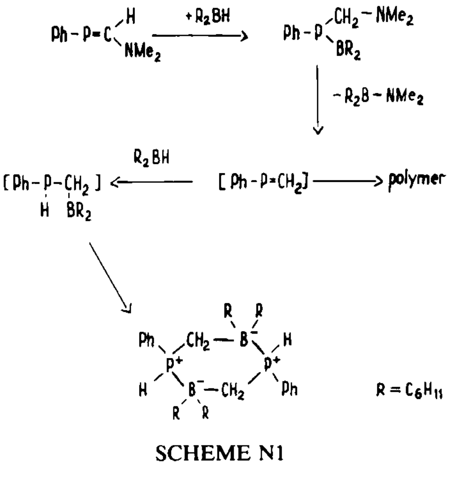
P-Phenyl-C-tert.-butyl-C-trimethylsiloxymethylene phosphine (1) has been shown to add catecholboran $C_6H_4O_2BH$ or dicyclohexylboran $(C_6H_{11})_2BH$ to give 1:1-adducts with P—B bond which undergo spontaneous β-elimination of trimethylsiloxycatecholboran (4) or trimethylsiloxydicyclohexylboran (8) respectively. The mechanism of reactions is discussed.

Key words: P-Phenyl-C-tert.-butyl-C-trimethylsiloxymethylene phosphine hydroboration; catecholborane; dicyclohexylborane; β-elimination; dicyclohexyl(2,2-dimethyl-1-phenylphosphinylprop-1-yl)borane; dicyclohexyl(2,2-dimethyl-1-phenylphosphinyl-1-trimethylsiloxyprop-1-yl)borane.

INTRODUCTION

The heterosubstituted olefins C=C—X (X = O, S, Cl, N) are known to add various hydroboranes, with the regiochemistry of adducts being strongly affected by the heterosubstituent X, determining usually the β-position for the boron atom. The hydroboration products, however, tend to undergo β-elimination, the rate of which is dependend mainly on the nature of the heterosubstituent X, reaching a maximum with X = Cl or OR.[1,2]



SCHEME N1

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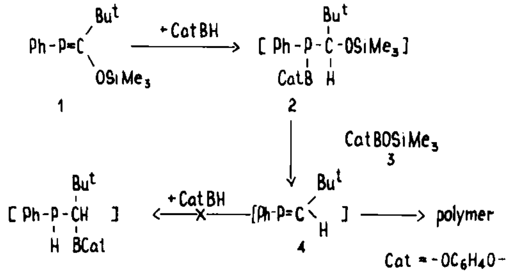
In the series of C-heterosubstituted phosphaalkenes the hydroboration was carried out only with C-N,N-dialkylaminophosphaalkenes. The adducts obtained were shown to undergo the uncatalyzed β-elimination with the formation of the "nacked" phosphaalkene which could be trapped with excess dialkylborane.[3,4]

It was of interest to study the hydroboration of C-trimethylsiloxyphosphaalkenes with the previously used[3,4] catecholborane and dicyclohexylborane.

RESULTS AND DISCUSSION

Reaction of P-phenyl-C-tert.-butyl-C-trimethylsiloxymethylene phosphine (1) with catecholborane was found to take place at room temperature. It should be noted, however, that heating up to 50–60°C for 1–2 hours is needed for its completion (control by ^{31}P NMR spectroscopy), while the hydroboration of siloxyethers of enols occurs at 0°C within 1 hour and that of the nucleophilic C-N,N-dialkylaminophosphaalkenes even at −40°C within several minutes. The observed decrease in the rate of hydroboration of C-trimethylsiloxyphosphaalkene seems to be caused by the decrease in the nucleophilicity of its phosphorus atom.



SCHEME N2

The intermediate adduct (2) could not be observed in the ^{31}P NMR spectrum presumably because of easy β-elimination of trimethylsiloxycatecholborane (3)† and transformation into P-phenyl-C-tert.-butyl-methylene phosphine (4), which in turn, being sterically underloaded, appears to be unstable and tends to polymerize. In fact, in the ^{31}P NMR spectrum of the reaction mixture there were observed signals at δ_P −10, −15 and −17 ppm of its polymer. Though attempts to trap (3) by excess of catecholborane failed, the more active dicyclohexylborane proved to be useful for this purpose.

Trimethylsiloxycatecholborane (4) was isolated by distillation, with its structure being confirmed by analytical and spectral (NMR, MS) data. In its electron impact (EI) mass spectrum, in particular, along with peak of the molecular ion (M/e 208) there are peaks of fragment ions: $C_6H_4O_2BOSiMe_2^+$, $C_6H_4O_2BOSi(H)Me^+$, $C_6H_4O_2BOSiH_3^+$, $C_6H_4O_2BO^+$, $C_6H_4O_2B^+$.

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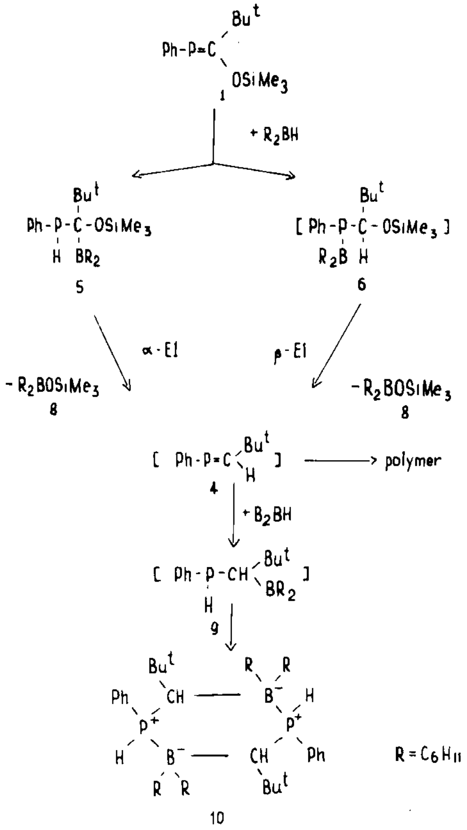
† The products of hydroboration of acyclic trimethylsiloxyethers of enols could also not be isolated, owing to the spontaneous β-elimination.[5]

Reaction of (1) with dicyclohexylborane most likely proceeds with the intermediate participation of 1:1-adducts both with P-H bond (5) and with P—B bond (6).



SCHEME N3

However, like (2) the adduct (6) with P—B bond could not be observed in ^{31}P NMR spectrum. Being unstable, (6) easily undergoes β-elimination to afford P-phenyl-C-tert.-butylmethylene phosphine (V) and trimethylsiloxy (dicyclohexyl)borane (8). The latter was identified after distillation by its EI mass-spectrum, displaying besides molecular ion (*M*/*e* 266) fragments ions: $C_6H_{11}BOSiM_3^+$, $C_6H_{11}(H)BOSiMe_3^+$, $C_6H_{11}(H)B\text{-}O^+$, (H)B-OSiMe$_3$, as well as by its hydrolysis to the known dicyclohexylhydroxyborane $(C_6H_{11})_2BOH$.[6]

Unlike catecholborane dicyclohexylborane was shown to add to phosphaalkene (4) with the formation, of a compound with a P—H bond—dicyclohexyl(2,2-dimethyl-1-phenylphosphinylprop-1-yl)borane (9). The structure of this distillable compound (9) corresponding to a polarization of the P=C bond in (4) is supported by ν_{P-H} absorption bond at 2390 cm^{-1} in IR spectrum as well as by singlet resonance at −66.40 ppm with $^1J_{PH}$204.9 Hz in its ^{31}P NMR spectrum. The EI mass-spectrum of (9) contains in addition to peak of the molecular ion (*M*/*e* 356) peaks of fragment ions: PhPH$^+$, $C_6H_{11}BH^+$, $C_6H_{11}{}^+$, $C_6H_{10}{}^+$. Like the other compounds with geminal boron and phosphorus atoms[7,8] compound (9) tends to dimerize completely within two weeks. The ^{31}P NMR spectrum of its dimer (10) shows only one signal at δ 17.82 ppm with $^1J_{PH}$ 457.4 Hz corresponding to a tetracoordinated phosphorus compound with P—H bond. This is consistent with the absorption band at 2420 cm^{-1} ($\nu_{P—H}$- in the IR spectrum of (10). The fact that similar(dicyclohexylboryl-methyl)(phenyl)phosphine (HPPh)$CH_2B(C_6H_{11})_2$ exists exclusively as bisphosphonium dimer,[4] allows to suggest that there are substantial steric hindrances caused by tert.-butyl and cyclohexyl groups in the molecule of (9) which impede its dimerization and make possible its existence, though for a short time, as a compound with the two coordinated phosphorus atom.

Unlike (6) the adduct with a P—H bond (5) is observable in the ^{31}P NMR spectrum of the reaction mixture, displaying a signal at δ_P −87.04 ppm and $^1J_{PH}$ 224.5 Hz. The compound (6) should be stable at room temperature since α-elimination occurs usually under more drastic conditions than β-elimination does,—on distillation, for example.[9] As matter of fact the suggested dicyclohexyl(2,2-dimethyl-1-phenylphosphinyl-1-trimethylsiloxyprop-1-yl)borane (5) is decomposed on distillation probably with α-elimination and the concerted 1,2-(PC)-hydride shift (compare with [10]). The phosphaalkene (4) formed is capable to interact then with excess dicyclohexylborane affording (9) or to turn into a polymer. Therefore, comparison of the relative intensity of ^{31}P NMR signal of (5) δ_P −87.04 ppm.) with those of (9) δ_P −66.40 ppm) and of polymeric product (δ_P −10+ −17 ppm) makes possible to estimate indirectly the ratio of the intermediate adducts (5) and (6) approximately as 9:33.

CONCLUSION

The above said allows to deduce that the regiochemistry of the hydroboration of C-trimethylsiloxyphosphaalkene (1) is strongly affected by the trimethylsiloxy-group, determining the β-position for the boron atom either exclusively as in reaction of (1) with catecholborane or predominantly as in reaction of (1) with the more active dicyclohexylborane.

EXPERIMENTAL

PMR spectra were recorded on a Varian T-60 spectrometer at 34.6°C with TMS as internal standard. ^{31}P NMR spectra were recorded on a Bruker M-250 spectrometer with 85% H_3PO_4 as external standard. IR spectra were measured on a spectrophotometer UR-20. Electron impact mass spectra were recorded on a MX-1310 spectrometer at 60 V. All experiments were carried out under dry argon in anhydrous THF.

The hydroboration of P-phenyl-C-tert.-butyl-C-trimethylsiloxymethylene phosphine (1) *with catecholborane.* A solution of catecholborane (4.2 g; 35.00 mmol) in THF (10 ml) was added with stirring at room temperature to (1) (3.76 g; 14.13 mmol). The reaction mixture, after being heated at 50–60°C for 1–2 hours (till complete consumption of (1) according to ^{31}P NMR spectra), was distilled to give trimethylsiloxycatecholborane (4) as a hydrolyzable liquid (2.1 g; 71%), b.p. 54°C/10^{-3} mm. (Found: C 52.9; H 6.4. $C_9H_{13}BO_3Si$ requires C 51.9; H 6,2).

The hydroboration of (1) *with dicyclohexylborane.* To a stirred solution of (1) (4.12 g; 15.47 mmol) in THF (10 ml) was added at room temperature a solution of dicyclohexylborane (6.9 g; 38.76 mmol) in THF (15 ml). The reaction mixture, after being heated at 50–60°C for 3 hours, was subjected to a molecular distillation at 50°C/10^{-3} mm to afford trimethylsiloxydicyclohexylborane (8) an easily hydrolyzable liquid (3.6 g; 87%). PMR δ: 0.97 (s, 9H, $SiMe_3$), 1.96 – 2.67 (m, 22H, $C_6H_{11}B$). (8) was hydrolyzed to give dicyclohexylhydroxyborane, m.p. 54°C (lit.[6]; 54°C). The remainder being distilled separately gave dicyclohexyl(2,2-dimethyl-1-phenylphosphinylprop-1-yl)borane (9) as a viscous oil (1.21 g; 22%), b.p. 81–82°C/10^{-3} mm, (Found: P 7.9. $C_{23}H_{38}BP$ requires P 8.7). IR; ν_{max} 2390 cm^{-1} (P—H).

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