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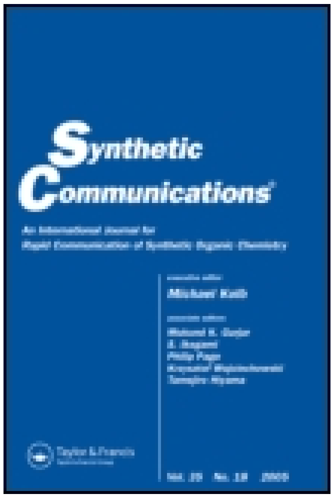

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PINACOLBORATAMETHYL- ENETRIPHENYLPHOSPHONIUM IODIDE, A NEW METHYLENE TRANSFER REAGENT

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PINACOLBORATAMETHYLENETRIPHENYLPHOSPHONIUM IODIDE, A NEW METHYLENE TRANSFER REAGENT

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ABSTRACT

The title compound is easily prepared and reacts with various aldehydes and ketone. The reagent is compatible with free hydroxy groups. Yields with various aldehydes and ketones are in 50–>99% range. Both aliphatic, aromatic and unsaturated carbonyls react.

Key Words: Methylene transfer; Boron-Wittig reagent

Several attempt to prepare Wittig-type reagents from boron-phosphorous compounds have been described in the literature, with mixed success.[1] The reaction of phosphorous ylides with chloroborates gives an intermediate, not isolated, that reacts with benzaldehyde to give a 1,3-diphenyallene,[2] a product identical to that obtained with α-zincated phosphorous

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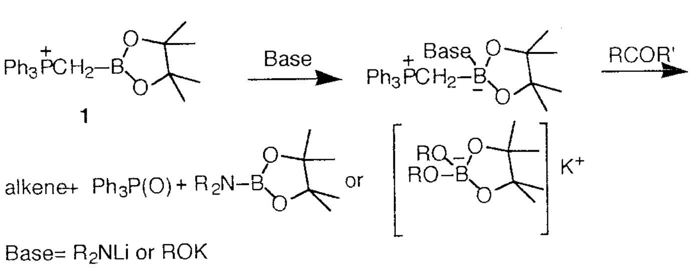
ylides.[3] A diylideborane was obtained by the reaction of a ylide with a dichloroborane.[4] These authors also prepared dialkylborylalkylidenephenylphosphoranes and showed that the latter react with polar electrophiles to give deuterated and brominated Wittig reagents.[5] Hydroboration of phosphoalkenes with either catecholborane or BH_3L gives C1 bridged phosphoboranes.[6] The reaction with aldehydes or ketones was not explored. In a series of papers, Pelter and Smith investigated the activity of hindered boranes and showed that they reacted with aldehydes to give alkenes.[7] We have recently prepared various C1 bridged phosphorous boronates.[8] In this communication we discuss the chemistry of one of the derivatives, pinacolboratamethylenetriphenylphosphonium iodide, **1**.

Compound **1** is easily prepared by the reaction of pinacolboratamethylene iodide with PPh^3. Compound **1** is stable in air and to moisture. Treatment of **1** with base and either aldehyde or ketone gave alkene (Scheme 1).

We assume that the initial step in the reaction involves coordination of the base with **1**. A free ylide-type intermediate may be formed. But we have not detected this by NMR (Scheme 1). In accordance with Scheme 1, triphenylphosphine oxide and borate were also detected by GCMS. In the case of potassium alkoxides, two equiv of base were required and borate "ate" complexes were formed. The use of lithium amides required only one equiv of base. The reason for the difference in reactivity of the lithium amides and the potassium alkoxides is not clear. But this aspect of the reaction is being investigated. The effect of base on methylene transfer was explored with benzaldehyde and 4-methoxyphenyl cyclopropyl ketone (Table 1).

Lithium hexamethyldisilazide (one equiv) and KOC_2H_5 (two equiv) gave the best results with aldehydes. Several ketones did not react with lithium hexamethydisilazide but did give satisfactory results with potassium ethoxide generated "in situ". Alkyllithium bases by themselves were not effective. Less than 5% methylene transfer was detected. Two sets



Scheme 1. Reaction of **1** with carbonyls.

Table 1. Influence of Base on the Reaction of **1** with Benzaldehyde or Cyclopropyl-4-methoxyphenyl Ketone

Base[a]	Carbonyl	Yield (%)
Hexamethyldisilazane	Benzaldehyde	>99
Tetramethylenediamine	Benzaldehyde	98
Tetramethylpiperidine	Benzaldehyde	98
Diisopropylamine	Benzaldehyde	94
Potassium methoxide	4-Methoxyphenyl cyclopropyl ketone	5[b]
Potassium ethoxide	4-Methoxyphenyl cyclopropyl ketone	90[b]
Potassium isopropoxide	4-Methoxyphenyl cyclopropyl ketone	90[b]
Potassium *t*-butoxide	4-Methoxyphenyl cyclopropyl ketone	70[b]

[a] Lithium amide was generated at 0°C with one equiv of *n*-BuLi.
[b] Two equiv of alkoxide were used. One equiv gave only 50% conversion.

of conditions were developed for methylene transfer to aldehydes and ketones. For all aldehydes lithium hexamethyldisilazide proved sufficient. For certain ketones better results were obtained with potassium tert-butoxide (Table 2). Reagent **1** reacts readily with aldehydes to transfer the methylene group. The reaction works well with both aromatic, aliphatic, and unsaturated aldehydes. Of particular interest is the fact that the reaction is compatible with a free hydroxy group, both on aldehydes and ketones, though the latter gave somewhat reduced yields (Table 2). Competition between aldehyde and ketone was tested by introducing one equiv of benzaldehyde and acetophenone to one equiv of **1**. Benzaldehyde was completely converted to styrene. The reagent was also reacted with esters and epoxides but no methylene transfer was observed. Only starting materials were recovered. The effect of solvent was also briefly explored. No reaction was observed in THF, acetonitrile, and DMF. In DMSO less than 5% reaction occurred. The solvent of choice was HMPTA. The advantage that this reagent has over the usual Wittig reagent is its compatibility with free hydroxy groups, consistently high yields and conversions for a variety of aldehydes and ketones.

EXPERIMENTAL

Preparation of pinacolboratamethylenetriphenylphosphonium iodide, 1: Triphenyl phosphine (2.62 g, 10 mL moles) was dissolved in 20 mL of dry benzene, then pinacolboratamethylene iodide (2.68, 10 mL moles) was added drop wise at 0°C. The reaction was warmed to room temperature

Table 2. Reaction of **1** with Various Aldehydes and Ketones

Aldehyde	Product	Yield (%)[a]
Benzaldehyde	$PhCH{=}CH_2$	99
2-Nitrobenzaldehyde	2-Nitro-$PhCH{=}CH_2$	99
2-Methoxybenzaldehyde	2-Methoxy-$PhCH{=}CH_2$	99
4-Methoxybenzaldehyde	4-Methoxy-$PhCH{=}CH_2$	99
Cinnamaldehyde	$PhCH{=}CHCH{=}CH_2$	99
2-Naphthaldehyde	NaphthaleneCH=CH_2	99
2,4-Dichlorobenzaldehyde	2,4-DichloroPhCH=CH_2	99
4-Dimethylaminobenzaldehyde	4-DimethylaminoPh=CH=CH_2	99
3-Hydroxy-4-methoxy-benzaldehyde	3-Hydroxy-4-methoxy-$PhCH{=}CH_2$	99
1,4-Benzodioxane-6-carboxaldehyde	$C_{10}H_{10}O_2$	90
Tetradecenal	Pentadecene	60
Citral	$C_{11}H_{18}$	99
Acetophenone	$PhC(CH_2)CH_3$	95
p-Methoxy acetophenone	*p*-$OCH_3PhC(CH_2)CH_3$	90
3,5-Dimethoxy acetophenone	$C_{11}H_{14}O_2$	85
4- Hydroxy acetophnone	4-(OH)$PhC(CH_2)CH_3$	83
4-Chlorophenyl cyclopropyl ketone	$C_{11}H_{11}$	90[b]
Cyclopropyl-4-methoxyphenyl ketone	$C_{12}H_{14}O$	90[b]
9-Fluorenone	$C_{15}H_{12}$	50[b]

[a] GCMS yield based on an internal standard. Conversion in all cases was >99.
[b] $KOCH_2CH_3$ generated "in-situ", 2 equiv was used.

and was stirred overnight. The white precipitate was filtered and washed with benzene and was dried in vacuum. Yield: 4.2 g, 78%. M.p: 162°C. ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 12 H) 3.2 (d, 2H), 3.63.8 (m, 15H); ^{31}P NMR ($CDCl_3$): δ 22.6. ^{11}B NMR ($CDCl_3$): δ 21.

Reaction of benzaldehyde is typical: 0.75 mL of 1.6 M *n*-BuLi (1.2 mmole) was added dropwise to 0.161 g (1 mmole) of hexamethyl disilazane at 0°C and the mixture was stirred for 2 h. Then 0.53 g of **1** was added (dissolved in 2 mL of HMPA) and stirred for additional 2 h. The mixture was cooled to −78°C and 0.02 g of dibromobenzene (internal standard) followed by 0.106 g (1 mmole) of benzaldehyde were added. The reaction was warmed gradually to the room temperature and was left stirring overnight at room temperature. The reaction mixture was worked up with dilute HCl. The product was extracted with ether and was analyzed by GCMS and ^{1}H NMR. All data were compared to authentic samples and found to be indentical.

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