Synthesis of Ketones and Tertiary Alcohols from Trialkylboranes. Use of Lithium Tris(phenylthio)methanide

By Andrew Pelter* and J. Madhusudhana Rao

(*Department of Chemistry, University College of Swansea, Singleton Park, Swansea* SA2 8PP)

Summary The interaction of lithium tris(phenylthio)-methanide with trialkylboranes followed by oxidation allows the production of ketones or tertiary alcohols in good yields under mild conditions.

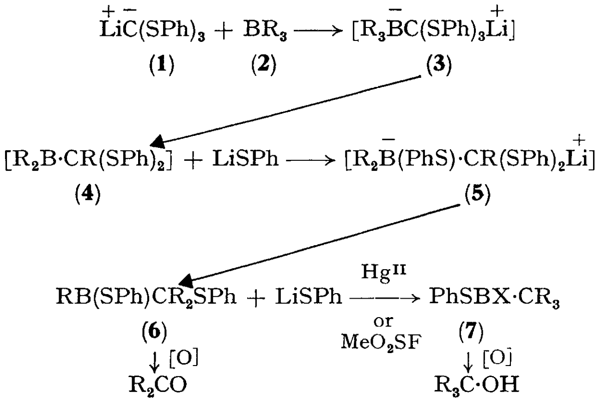
Trialkylboranes have been converted into ketones and tertiary alcohols by a variety of methods[1] including interaction with carbon monoxide, with sodium cyanide followed by trifluoroacetic anhydride or with the anion derived from α,α-dichloromethyl methyl ether followed by treatment with lithium 1,1-diethylpropoxide. We now report that the anion[2] derived from readily available[3] tris(phenylthio)-methane reacts under mild conditions with trialkylboranes so that two migrations of alkyl groups from boron to carbon occur spontaneously and the third may be induced under mild conditions (Scheme). The reactions are 'one-pot' and do not involve the use of pressure or any hazardous reagents.

When anion (**1**) is mixed with (**2**) reaction proceeds spontaneously at room temperature as far as (**6**), which on oxidation ($NaOH,H_2O_2$) yields the corresponding ketone. We believe that initially the complex (**3**) is produced which undergoes one migration of an alkyl group to yield the organoborane (**4**) and lithium benzenethiolate. These two products interact to yield the organoborate (**5**) which breaks down to yield the dialkylphenylthioborane (**6**). There is precedent for the production of such an intermediate in the

TABLE 1. Ketone synthesis[a] as in the Scheme.[b]

Expt.	Trialkylborane ($R^1R^2R^3B$) R^1	R^2	R^3	Product	Yield (%)[c]
i	Hexyl	Hexyl	Hexyl	R^1COR^2	82
ii	Heptyl	Heptyl	Heptyl	R^1COR^2	80
iii	c-Pentyl[d]	c-Pentyl	c-Pentyl	R^1COR^2	81
iv	c-Hexyl[d]	c-Hexyl	c-Hexyl	R^1COR^2	80
v	c-Hexyl	Pentyl	Pentyl	R^1COR^2	76 { 46[e]
				R^1COR^3	54
vi	2-Methyl-c-hexyl	2-Methyl-c-hexyl	Hexyl	—	
vii	Thexyl[f]	Hexyl	Hexyl	R^1COR^2	72 { 85[e]
				R^2COR^3	15

[a] All products have been characterised either by direct comparison with authentic samples or by analysis and physical data. [b] For brevity R_3B is used in the Scheme; in practise some mixed alkylboranes were used as shown here. [c] Yields are of isolated, purified ketonic product. [d] c-Pentyl and c-hexyl are cyclopentyl and cyclohexyl. [e] Ratio determined by g.l.c. of crude ketonic product before separation into components. [f] Thexyl = 1,1,2-trimethylpropyl.



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spontaneous *single* migrations induced in trialkylboranes by the anions of bis(phenylthio)methane[4] and 2-alkyl-1,3-benzodithioles.[5] Results are presented in Table 1.

The reaction is somewhat sensitive to steric factors. Thus whereas tricyclohexyl- and dicyclohexylpentyl-borane give good yields of ketone, no ketone at all was isolated using bis-(2-methylcyclohexyl)hexylborane (expt. vi). This is presumably due to difficulty in formation of the primary adduct (**3**). The process is unique in that in at least one of the first two migrations there is preferential migration of the tertiary thexyl (1,1,2-trimethylpropyl) group compared with the primary hexyl group (expt. vii). The ratio of the products remains the same in the presence of a radical inhibitor (galvinoxyl), while radical initiators inhibit the process. Thus the preferential migration would not seem to be due to migration of the groups as radicals and may be due to a conformational factor.

In general the third migration to species such as (**7**) is carried out by reaction with mercury(II) chloride in tetrahydrofuran at room temperature. In one case (expt. xi), in which the phenylthio-group at the potential migration terminus is heavily hindered, this method failed and a less bulky electrophile, methylfluorosulphonate, was used. However it is particularly noteworthy from the viewpoint of potential synthetic application that the bulky thexyl group migrates at room temperature without the need for any modification in the usual gentle conditions. As all these groups are utilised there is no ambiguity with regard to product structure. The results are presented in Table 2.

TABLE 2. Synthesis of tertiary alcohols (Scheme).[a,b]

Expt.	Trialkylborane R^1	R^2	R^3	Yield (%)[g]
viii	Hexyl	Hexyl	Hexyl	91
ix	Heptyl	Heptyl	Heptyl	79
x	c-Pentyl[d]	c-Pentyl	c-Pentyl	82
xi	c-Hexyl[d]	c-Hexyl	c-Hexyl	43[h]
xii	c-Hexyl	c-Hexyl	c-Hexyl	83
xiii	Thexyl[f]	Hexyl	Hexyl	71

[a,b,d,f] As in Table 1. [g] Yields are of isolated, purified tertiary alcohol. [h] MeO_2SF in glyme was used for the third migration.

The availability of trialkylboranes and tris(phenylthio)-methane together with the gentle, neutral conditions of the reactions makes the reported reactions simple, efficient, and general syntheses of ketones and tertiary alcohols and presents new two- and three-connective processes to the synthetic organic chemist.

We thank the University of Wales for support during the period of this research.

(*Received*, 19*th August* 1981; *Com.* 1016.)

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