128 Hz). The IR spectrum exhibited a strong absorption at 2450 cm^{-1}, indicating the presence of nonbridged B–H species.

The following procedure is representative for the hydroboration reaction. To a solution of 1-hexene (20 mmol) in CH_2Cl_2 was added ThBHCl·SMe$_2$ (20 mmol) at 0 °C and the mixture was stirred for 1 h at 25 °C, when ^{11}B NMR showed a single resonance at δ 80, as expected for a dialkylchloroborane. Some hindered and less reactive alkenes require somewhat longer reaction times (Table I).

In conclusion, thexylchloroborane–methyl sulfide, conveniently prepared from the readily available monochloroborane–methyl sulfide, is a new reagent with exceptionally high regioselectivity. The thexylalkylchloroboranes, produced in such hydroborations, are valuable new intermediates which make possible an exceptionally general synthesis of ketones.[15]

Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; *cis*-2-pentene, 627-20-3; cyclopentene, 142-29-0; 2-methyl-1-pentene, 763-29-1; 1-methylcyclopentene, 693-89-0; 4-pentenyl acetate, 1576-85-8; styrene, 100-42-5; 2,3-dimethyl-2-butanol, 594-60-5; 2-methyl-1-butene, 563-46-2; 2-methyl-2-butene, 513-35-9; *cis*-4-methyl-2-pentene, 691-38-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 2-methyl-1-butanol, 137-32-6; 2-methyl-2-butanol, 75-85-4; 3-methyl-2-butanol, 598-75-4; 2-pentanol, 6032-29-7; 3-pentanol, 584-02-1; 4-methyl-2-pentanol, 108-11-2; 2-methyl-3-pentanol, 565-67-3; 2-phenylethanol, 60-12-8; 1-phenylethanol, 98-85-1; 2,3-dimethyl-2-butene, 563-79-1; H_2BCl·SMe$_2$, 63348-81-2; ThBHCl·SMe$_2$, 75067-06-0.

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[15] Kulkarni, S. U.; Lee, H. D.; Brown, H. C. *J. Org. Chem.*, following paper in this issue.

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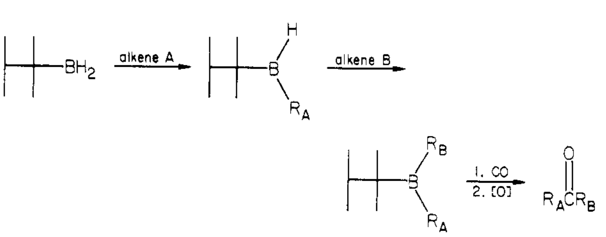
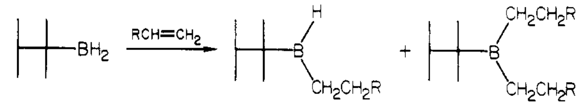
A General Synthesis of Ketones from Alkenes via Stepwise Hydroboration with Thexylchloroborane

Summary: Thexylalkylchloroboranes, reduced in the presence of a second alkene, produced mixed thexyldialkylboranes in high purity. These derivatives are readily transformed into the corresponding ketones by carbonylation or cyanidation, providing for the first time a general conversion of two different olefins into the corresponding ketone.

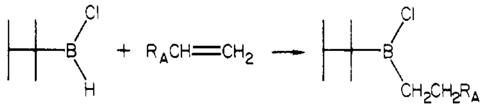
Sir: Thexylborane provides an elegant route for the conversion of two olefins into the corresponding ketone[1] (eq 1). Unfortunately, the reaction is not general. R_A must be an olefin with significant steric hindrance, one that is capable of reacting with thexylborane to give the thexylmonoalkylborane derivative.[2] Simple terminal olefins, such as $RCH{=}CH_2$, cannot be utilized[2] (eq 2). This limitation can now be circumvented by applying the new reagent, thexylchloroborane–methyl sulfide.[3] This reagent reacts cleanly with essentially all common structural types of olefins, including simple terminal alkenes (eq 3). The product, thexylalkylchloroborane, is readily reduced by the reagent potassium triisopropoxyborohydride (KIPBH)[4–6] (eq 4). The resulting thexylalkylborane readily hydroborates a second mole of olefin (eq 5). Carbonylation[1] or cyanidation[7] then provides the desired ketone (eq 6).



(1)



(2)



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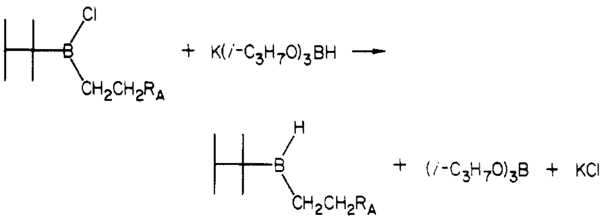

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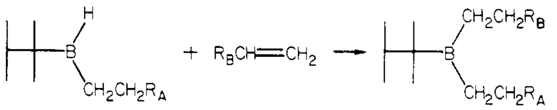

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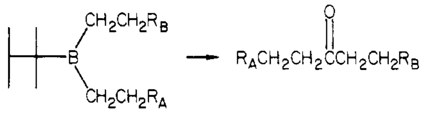

(6)

Although we have emphasized the application of this new synthetic route to the conversion of two terminal olefins into the corresponding ketone (eq 3–6), it should be noted that the synthesis appears to be general, with no limitation now known as to the nature of the two olefins which can be introduced or the order in which they need be introduced. (This contrasts with the earlier, less general synthesis where it was necessary to use a more hindered olefin for the first step (eq 1).[1])

Fortunately, KIPBH is a very gentle reducing agent, one which tolerates many functional groups.[6] Consequently, it is possible to apply this synthesis to alkenes containing many different substituents.

In order to minimize the anticipated redistribution re-

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[1] Brown, H. C.; Negishi, E. *J. Am. Chem. Soc.* **1967**, *89*, 5285.

[2] Brown, H. C.; Negishi, E.; Katz, J.-J. *J. Am. Chem. Soc.* **1975**, *97*, 2791.

[3] Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.*, preceding paper in this issue.

[4] Brown, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 4100.

[5] KIPBH is available as a 1.0 M solution in THF from the Aldrich Chemical Co.

[6] Brown, C. A.; Krishnamurthy, S.; Kim, S. C. *J. Chem. Soc., Chem. Commun.* **1973**, 391.

[7] Pelter, A.; Smith, K.; Hutchings, M. G.; Rowe, K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 129.

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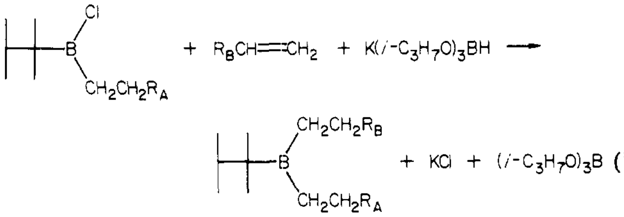
Table I. Preparation of Unsymmetrical Ketones Utilizing Thexylchloroborane as an Intermediate

alkene A	alkene B	product	% yield[a]	% purity[b]
1-heptene	1-pentene	6-tridecanone	62	95
1-octene	1-decene	9-nonadecanone	74[c]	>98
1-decene	1-octene	9-nonadecanone	72[c]	98
1-dodecene	cyclopentene	*n*-dodecyl cyclopentyl ketone	67	95
2-methyl-1-pentene	1-octene	4-methyl-6-tetradecanone	70	97
styrene	1-pentene	1-phenyl-3-octanone	59	95
styrene	4-methyl-1-pentene	1-phenyl-7-methyl-3-octanone	62	96
1-butene	4-vinylcyclohexene	1-(3-cyclohexenyl)-3-heptanone	67	97
4-pentenyl acetate	1-nonene	1-acetoxy-6-pentadecanone	75[d]	98

[a] Isolated yields; products recovered by distillation unless otherwise stated. [b] Purity of the ketones determined by GC analysis; the common impurities were the corresponding symmetrical ketones. [c] Isolated by recrystallization from pentane. [d] Liquid at room temperature which crystallized at −78 °C from pentane and was filtered and solvent removed under vacuum. Partially decomposes on distillation.

actions in the thexylmonoalkylborane intermediate (eq 4), it is recommended that the reduction of the thexylalkylchloroborane be carried out in the presence of the second olefin (eq 7).



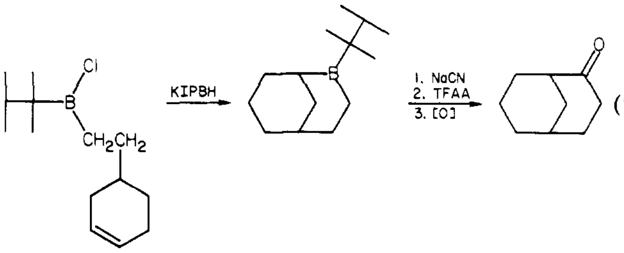
(7)

The procedure was tested with a representative set of alkenes of various structural types (Table I).

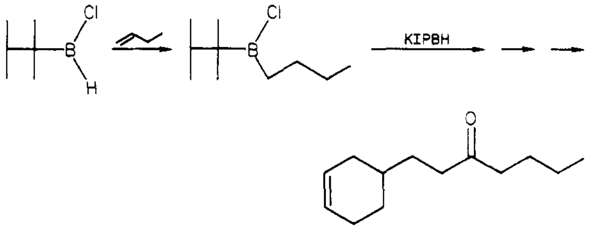
The following procedure for the conversion of 1-octene and 1-decene into 9-nonadecanone is representative. To a solution of ThBHCl·SMe$_2$ in CH$_2$Cl$_2$ (20 mmol, 2.25 M) was added 1-octene (20 mmol) at 0 °C under nitrogen. The mixture was stirred for 2 h at 25 °C and then cooled to −10 °C (ice–salt mixture). THF (20 mL) and 1-decene (20 mmol) were added, followed by the dropwise addition of KIPBH (21 mmol, 1.0 M in THF)[5] with vigorous stirring, followed by additional stirring for 2 h at 0 °C. Finely powdered, dry NaCN (40 mmol, 100% excess) was added and the mixture stirred for 2 h at 25 °C. To the thexyldialkylcyanoborate generated in this fashion was added trifluoroacetic anhydride (30 mmol) at −78 °C and the mixture was allowed to attain room temperature at which time it was stirred for an additional 1.5 h. Oxidation was carried out by adding NaOH (125mmol in 25 mL) and hydrogen peroxide (35 mL of a 30% solution) simultaneously at 0 °C. After the completion of addition, the mixture was stirred at 25 °C for 1 h and heated under reflux for 2 h. The organic materials were extracted with pentane and washed with saturated NaCl solution, and the solvent was removed. GC analysis of the residue indicated the presence of 5% 9-hexadecanone as an impurity. Recrystallization from pentane at −78 °C afforded 4.2 g (74% yield) of 9-nonadecanone (98% pure by GC), mp 47–48.5 °C.

It was pointed out earlier that there is no limitation as to the order in which the two olefins are introduced into the thexylborane moiety. This has a major advantage, in some cases, in directing the reaction along different paths. For example, treatment of thexylchloroborane with 4-vinylcyclohexene yields the corresponding thexylalkenylchloroborane (eq 8). Reduction of the intermediate in the presence of a second olefin (3,3-dimethyl-1-butene) results in preferential cyclic hydroboration. Cyanidation produced a single product, presumably bicyclo[3.3.1]nonan-2-one (eq 9). However, by utilizing the diene as the second alkene, the cyclization can be avoided (eq 10).

(8)



(9)



(10)

In summary, the new reagent, thexylchloroborane–methyl sulfide, makes possible the stepwise hydroboration of the thexylborane moiety, providing a route to thexyldialkylborane intermediates, without restriction as to the structure of the olefins used or the order in which they are introduced. This development removes a serious limitation of the earlier procedure. The mild reaction conditions and the broad generality of the procedure should make it a highly valuable one in organic synthesis.

Registry No. 1-Heptene, 592-76-7; 1-octene, 111-66-0; 1-decene, 872-05-9; 1-dodecene, 112-41-4; 2-methyl-1-pentene, 763-29-1; styrene, 100-42-5; 1-butene, 106-98-9; 4-pentenyl acetate, 1576-85-8; 1-pentene, 109-67-1; cyclopentene, 142-29-0; 4-methyl-1-pentene, 691-37-2; 4-vinyl-cyclohexene, 100-40-3; 1-nonene, 124-11-8; 6-tridecanone, 22026-12-6; 9-nonadecanone, 75030-48-7; *n*-dodecyl cyclopentyl ketone, 75030-49-8; 4-methyl-6-tetradecanone, 75030-50-1.

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(9) Postdoctoral research associate on a grant from Albany International Chemicals Division.

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