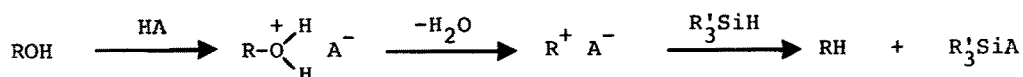


A CONVENIENT ONE-STEP SYNTHESIS OF HYDROCARBONS FROM ALCOHOLS
THROUGH USE OF THE ORGANOSILANE-BORON TRIFLUORIDE REDUCING SYSTEM

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The ability of organosilanes to transfer hydride selectively to a variety of carbocations has been utilized in the development of numerous useful synthetic techniques.¹ One such application is found in the direct conversion of alcohols to hydrocarbons.² Such transformations depend upon the capture by organosilanes of intermediate carbenium ions formed through interaction of alcohols with protic acids. They thus occur in high synthetic yields only under reaction conditions in which significant concentrations of the carbenium ions are formed.

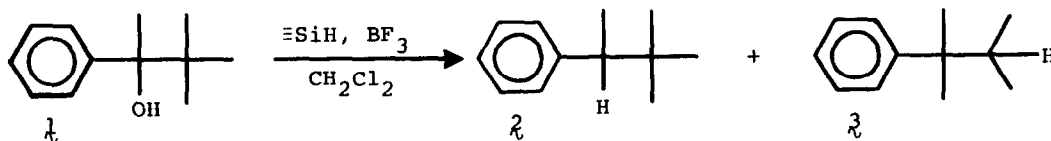


These reductions commonly proceed at 0 to 25°C in homogeneous solutions of dichloromethane containing alcohol and a silane such as triethylsilane in the presence of trifluoroacetic acid. The use of stronger protic acids or higher reaction temperatures may lead to extensive protonolysis and destruction of the organosilane.³

During the course of our continuing studies of asymmetric syntheses resulting from the capture of prochiral carbenium ions by chiral organosilanes,⁴ we have discovered at least two general sets of conditions under which the use of protic acids to generate the required carbenium ions from alcohol precursors is unsatisfactory. These include cases in which the starting alcohol suffers rapid skeletal rearrangement and elimination upon contact with the protic acid and cases in which the alcohol, by virtue of having strongly electron-withdrawing substituents within its structure, does not readily yield a sufficient concentration of carbenium ions when treated with protic acids which do not themselves destroy the organosilane.

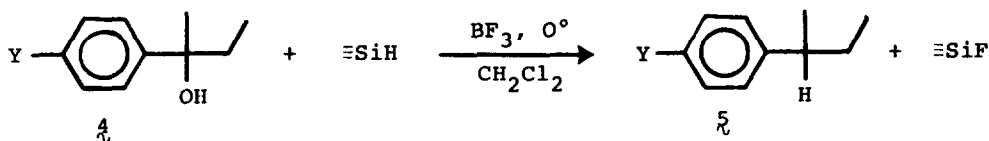
In marked contrast to their behavior in the presence of protic acids, we have found that dichloromethane solutions of a number of alcohols and silanes undergo facile reaction to form the corresponding hydrocarbons and fluorosilanes when boron trifluoride is passed into the solution.⁵ Several examples will serve to illustrate the relative efficacy and ease of this method.

For example, a solution consisting of 3,3-dimethyl-2-phenyl-2-butanol, **1**, (6.0 mmol) and 1-naphthylphenylmethylsilane⁶ (6.6 mmol) in 50 ml of anhydrous dichloromethane was cooled to -60° and boron trifluoride was slowly bubbled in through a capillary tube extending below the liquid surface. After six minutes the flow of boron trifluoride gas was stopped and the reaction mixture was quenched by addition of solid potassium carbonate followed by water. Nmr and glpc analysis of the organic portion showed that the alcohol had reacted cleanly to give 86.5% of the desired structurally intact hydrocarbon 3,3-dimethyl-2-phenylbutane, **2**, together with 13.5% of the methyl-shifted hydrocarbon 2,3-dimethyl-2-phenylbutane, **3**.⁷ The only silicon-containing product observed was



1-naphthylphenylmethylfluorosilane.⁶ In contrast to this, attempted reduction of this alcohol under a variety of conditions using either trifluoroacetic or methanesulfonic acid resulted in the formation of little or no hydrocarbon **2** and predominant or exclusive production of a mixture of the two olefins 3,3-dimethyl-2-phenyl-1-butene and 2,3-dimethyl-3-phenyl-1-butene. Use of a 1:1 molar ratio mixture of trifluoromethanesulfonic acid-trifluoromethanesulfonic anhydride with a 50 mole % excess of silane gave good yields of **2**, but also caused extensive protonolysis of the silane as evidenced by the formation of large quantities of naphthalene,⁸ even at short reaction times.

A variety of para-substituted 2-phenyl-2-butanols, **4**, when dissolved in dichloromethane and treated with boron trifluoride in the presence of a slight excess (2-10 mole%) of phenylneopentylmethylsilane⁹ gave, after very short reaction times at 0° and work-up (K_2CO_3 then water), excellent yields of



hydrocarbon products, $\mathfrak{5}$. In each case, phenylneopentylmethylfluorosilane⁹ was formed and the substituent Y was not affected. In the case of Y = CF₃, $\mathfrak{5}$ was formed in 80% yield after only two minutes of treatment with boron trifluoride. When trifluoroacetic acid was used, no product $\mathfrak{5}$ was obtained, even after two hours reaction time. With Y = CH₃O, both boron trifluoride and trifluoroacetic acid gave $\mathfrak{5}$ quantitatively within two minutes. Of particular note is the behavior of 2-(p-nitrophenyl)-2-butanol ($\mathfrak{4}$, Y = NO₂). Use of boron trifluoride produced 2-(p-nitrophenyl)butane quantitatively within ten minutes. Attempted reductions using trifluoroacetic acid or methanesulfonic acid under otherwise similar conditions led to recovery of starting alcohol and no hydrocarbon formation even after reaction times as long as eight hours.

Use of boron trifluoride permits reduction even of simple secondary aliphatic alcohols by organosilanes. Thus, slow passage of boron trifluoride through a dichloromethane (15 ml) solution of 2-octanol (3.3 mmol) and triethylsilane (10.9 mmol) for one-half hour at room temperature followed by work-up gave a 50% yield of n-octane¹⁰ together with triethylfluorosilane. Similar reduction of 2-adamantanol gave an 86% isolated yield of pure adamantane. Such transformations of simple secondary alcohols to saturated hydrocarbons, which would have to proceed through relatively unstable secondary aliphatic carbenium ions, do not appear to take place even under extreme reaction conditions when protic acids are used instead of boron trifluoride.^{2,11}

In summary, the organosilane-boron trifluoride reducing system offers a convenient direct route for conversion of many alcohols to their respective hydrocarbons, even in the case of alcohols which are structurally labile or those which possess easily reducible functionalities such as the nitro group. We are continuing our studies of this system in order to define its scope and limitations.¹²

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12. This work was supported in part by a grant from The University of Toledo Faculty Research Fund.