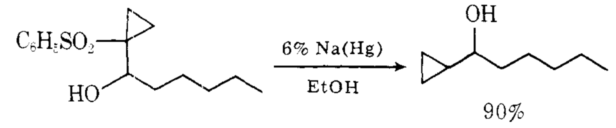
of the latter compound in the usual way gives the cyclopropylcarbinol in 90% yield (eq 11). These compounds can be



(11)

converted stereospecifically into homoallylic bromides by the elegant method developed by Julia[9a] and Johnson.[9b] In addition, cyclopropyl ketones are available by oxidation of the carbinols.

In conclusion, this method allows the synthesis of a wide variety of functionalized cyclopropanes derived from readily available $\alpha,\beta$-unsaturated aldehydes, esters, and ketones.

A typical experimental procedure for the conversion of cinnamaldehyde into phenylcyclopropane is described.

Cinnamaldehyde (26.4 g, 200 mmol) in 80 mL of 95% EtOH was added dropwise over 20 min to 0.6 g of sodium in 200 mL of 95% EtOH containing 30.8 g (280 mmol) of thiophenol at room temperature. After 20 h, 3.80 g (100 mmol) of $NaBH_4$ was added and the reaction mixture was stirred for 2 h. Workup gave 48.3 g (100%) of 3-phenyl-3-thiophenylpropanol as a thick oil which solidified upon standing: NMR ($CCl_4$) $\delta$ 2.2 (br s, 1 H), 3.6 (m, 2 H), 4.3 (t, $J$ = 7 Hz, 1 H), 7.2 (m, 10 H). This alcohol (24.2 g, 100 mmol) was dissolved in 32 mL of glacial acetic acid and 32 mL of 30% $H_2O_2$ was added dropwise over 30 min such that the temperature did not exceed 70 °C (exothermic). When the addition was complete, the reaction mixture was refluxed for 1 h, cooled, and worked up with 10% NaOH. This crude product was stirred with $K_2CO_3$ in aqueous MeOH overnight to give 24.1 g (88%) of solid sulfone. This sulfone (5.08 g, 18.5 mmol) was dissolved in 20 mL of pyridine and 3.10 g (25.9 mmol) of mesyl chloride was added dropwise over 20 min. After 5 h, the reaction mixture was poured into cold 5% HCl and extracted with $CH_2Cl_2$ to give 6.2 g (95%) of sulfone mesylate as a white solid: NMR ($CDCl_3$) $\delta$ 2.5–2.8 (m, 2 H), 2.9 (s, 3 H), 4.0–4.5 (m, 3 H), 7.1–7.6 (m, 10 H). Diisopropylamine (3.73 g, 37.0 mmol) was dissolved in 130 mL of dry THF (distilled from potassium) at 0 °C and 34 mmol of $n$-BuLi/hexane was added. After 30 min, the reaction mixture was cooled to −78 °C and 9.30 g (26.4 mmol) of the sulfone mesylate in 200 mL of THF was added dropwise over 40 min. After an additional 90 min at −78 °C, the reaction mixture was allowed to warm to room temperature and stir for 2 h more. The reaction was quenched with water and extracted with $CH_2Cl_2$ to give 6.8 g (100%) of phenyl 1-phenylcyclopropyl sulfone as a yellow solid: NMR ($CDCl_3$) $\delta$ 1.25 (dt, $J_d$ = 2 Hz, $J_t$ = 5 Hz, 2 H), 2.0 (dt, $J_d$ = 2 Hz, $J_t$ = 5 Hz, 2 H), 7.1–7.6 (m, 10 H). This sulfone (5.16 g, 20.0 mmol) was dissolved in 50 mL of absolute EtOH and refluxed with 30 g of 6% Na(Hg) for 12 h. The reaction mixture was poured into 5% HCl and extracted with ether. Careful removal of the solvent and distillation of the residue at atmospheric pressure gave phenylcyclopropane as a colorless liquid (1.95 g, 83%): bp 153–154 °C; NMR ($CCl_4$) $\delta$ 0.6–1.0 (m, 4 H), 1.7–2.1 (m, 1 H), 6.9–7.2 (m, 5 H).

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(2) (a) This is surprising since Johnson has reported[2b] without experimental detail that 3-chloropropyl phenyl sulfide yields cyclopropyl phenyl sulfide when treated with potassium amide in ether. (b) C. R. Johnson and E. R. Janiga, *J. Am. Chem. Soc.*, **95**, 7692 (1973).

(3) In fact, phenyl cyclopropyl sulfone has been prepared from the open-chain sulfone by several groups: H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960); W. E. Truce and L. B. Lindy, *J. Org. Chem.*, **26**, 1463 (1961); R. Bird and C. J. M. Stirling, *J. Chem. Soc. B*, 111 (1968).

(4) (a) A possible alternative solution to this problem is suggested by the recent work of Bryson,[4b] who has found that alkyl phenyl sulfides can be metalated with *tert*-butyllithium in the presence of hexamethylphosphoramide. This paper appeared as our study was almost complete so we did not investigate bases stronger than LDA. (b) T. M. Dolak and T. A. Bryson, *Tetrahedron Lett.*, 1961 (1977).

(5) The methine adjacent to the sulfone group (2.1–2.4 ppm, multiplet) disappears when the sulfone is treated with LDA and then quenched with $D_2O$.

(6) The required sulfones could also be prepared by Michael-type addition of a sulfinic acid. For example, 3-oxobutyl $p$-tolyl sulfone has been prepared recently from methyl vinyl ketone and sodium $p$-tolylsulfinate: J. Fayos, J. Clardy, L. J. Dolby, and T. Farnham, *J. Org. Chem.*, **42**, 1349 (1977).

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## Reduction of Aldehydes and Ketones to Alcohols and Hydrocarbons through Use of the Organosilane–Boron Trifluoride System

*Summary:* Ketones and many aldehydes are converted directly and rapidly to hydrocarbons by the action of gaseous boron trifluoride and organosilicon hydrides in dichloromethane solution.

*Sir:* Deoxygenation of aldehydes and ketones to alkanes is a step frequently encountered in organic synthesis. Of the relatively few direct methods available, none appears to be of universal applicability;[1] many require harsh reaction conditions incompatible with the requirements of high selectivity needed when dealing with polyfunctional compounds.[2] We report here a convenient alternative to previously existing methods.

Aldehydes and ketones are reduced by organosilicon hydrides[3] upon addition of Brønsted acids[4] or certain Lewis acids.[5] In general, only aryl ketones and aryl aldehydes with electron-donating ring substituents give synthetically useful yields of completely deoxygenated products.[6] Reductions of other aldehydes and ketones normally stop after 1 equiv of hydride has been transferred, to give a variety of products (e.g., alcohols, esters, silyl ethers, ethers, olefins, or Friedel-Crafts dimers) whose nature depends upon substrate and reaction conditions. Doyle and co-workers have reported similar results using boron trifluoride etherate to promote the reductions.[7]

Recently we reported the unique ability of a system consisting of an organosilicon hydride and gaseous boron trifluoride to effect rapid direct reductions of alcohols to hydrocarbons.[8] With this system, reductions of even simple secondary aliphatic alcohols to hydrocarbons take place in minutes at room temperature or below. We now report that use of this system on aldehydes and ketones results in facile reductions to alcohols and hydrocarbons in synthetically useful yields (Table I). Under the reaction conditions, the organosilicon hydride is converted into an organosilicon fluoride.

The best reaction results were obtained by a method (A) which consisted of initial formation of the carbonyl–boron

**Table I. Reduction of Aldehydes and Ketones with Triethylsilane and $BF_3$**

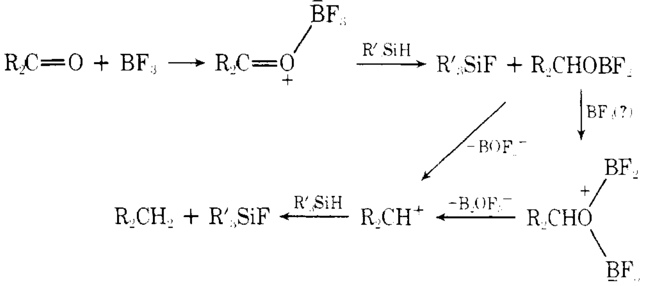
| RCOR′ | $Et_3SiH$, equiv | Method[a] | Reaction time min | Product yield, % RCH-(OH)R′ | Product yield, % $RCH_2R'$ |
|---|---|---|---|---|---|
| Undecanal | 1.5 | A | 10 | 92[b] | |
| Benzaldehyde | 18 | B | 11 | | 52[c] |
| *p*-Methylbenzaldehyde | 10 | A | 10 | | 45[c] |
| *p*-Chlorobenzaldehyde | 10 | A | 10 | | 68[c] |
| *p*-Methoxybenzaldehyde | 2 | B | 10 | | 100[d] |
| *p*-Cyanobenzaldehyde | 3 | B | 10 | 100[e] | |
| *p*-Nitrobenzaldehyde | 1.5 | B | 5 | 100[b] | |
| 2-Undecanone | 3.3 | A | 60 | | 80[b,f] |
| Cyclohexanone | 2 | B | 1.5 | 82[c] | |
| | 4 | B | 30 | | 90[d] |
| 2-Methylcyclohexanone | 2.2[g] | A[h] | 60 | | 88[c] |
| Adamantanone | 2.2 | A | 60 | | 100[b] |
| *p*-Cyanoacetophenone | 3 | B | 10 | 100[b] | |
| *p*-Nitroacetophenone | 4 | B | 3 | 100[b] | |
| | 4 | B | 30 | | 100[b] |

[a] See text. [b] Isolated yield. [c] Yield by VPC, using internal standard. [d] Yield by NMR, using internal standard. [e] Only product by NMR, VPC, and IR analyses. [f] (*E*)-2-Undecene was obtained in 16% yield. [g] Dimethylethylsilane used. [h] Reaction mixture not cooled.

trifluoride adduct by dropwise addition of a concentrated dichloromethane solution of the carbonyl compound into chilled (0 °C) dichloromethane (1–2 mL/mmol) through which a constant flow of scrubbed boron trifluoride was passed.[9] After 2–3 min, neat triethylsilane was rapidly added to the solution of complex. Slow passage of scrubbed boron trifluoride through the solution was maintained at 0 °C for the indicated period, at which time aqueous sodium chloride was added to quench the reaction prior to workup. In an earlier method (B), commercial boron trifluoride gas was passed directly without scrubbing into an uncooled dichloromethane solution of the carbonyl substrate and silane. However, when the boron trifluoride was drawn from different cylinders, this method gave variable yields of reduced product.[10] These problems were alleviated with method A.

It is significant that the present technique leads to toluene from benzaldehyde in light of the reported failure of other acid–silane systems to do so.[4,6,7] However, even with the present technique, failure to provide a large excess of silane (up to eightfold) in the reduction of benzaldehyde and several related aryl aldehydes leads to significant amounts of material of low volatility which seem to be polymers derived from Friedel–Crafts processes.[6]

Scheme I



A mechanistic rationale for the overall success of this reductive technique is offered in Scheme 1. Its basis is attributed both to the ability of gaseous boron trifluoride to rapidly coordinate with oxygen and to the formation of the extremely strong (~139 kcal/mol[11]) Si–F bond. It is known that boron trifluoride forms stable complexes with ketones and aryl aldehydes.[12] There is an early report of analogous complexes with aliphatic aldehydes.[13] We have found that the quantitative formation of these aldehyde complexes and their subsequent reduction to what are presumed to be difluoroborate esters[7] upon addition of triethylsilane may easily be observed by NMR.[14] The stepwise nature of the reductions to hydrocarbons is indicated by the isolation of alcohols from some of the carbonyl compounds. For example, when a dichloromethane solution of the boron trifluoride adduct of adamantanone was stirred with 1.1 equiv of triethylsilane at 0 °C for only 3 min without introduction of additional boron trifluoride, brine quenching yielded quantitatively a 1:1 mixture of 2-adamantanol and recovered adamantanone. These facts, taken together with the known relative ineffectiveness of boron trifluoride etherate[7] or Brønsted acids[4] at mediating complete deoxygenation, suggest that, in the case of substrates which require the intermediacy of a relatively unstable carbenium ion for passage to hydrocarbon, coordination of a second equivalent of boron trifluoride to the oxygen of the proposed difluoroborate intermediate may be beneficial in producing a better leaving group. Experiments are in progress to establish this point.

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