hexanone both gave no oxidation under the conditions of method B. For the ester to α,β-unsaturated ester transformation, it is known that simple dialkyl ketene acetals, analogous to the alkyl trialkylsilyl ketene acetals **16** and **18**, can be oxidized to α,β-unsaturated esters with trityl salts.[10]

When the trimethylsilyl enol ethers lack a hydrogen in the allylic position β to the oxygen atom, as is the case with the enol ether **20** prepared from acetophenone, the reaction with trityl salt takes a different course. Nucleophilic attack by the electrons of the enol ether on the trityl cation is now observed and the α-tritylated ketone **21**[11] is obtained in 60% yield (entry 22). However, in all cases of silyl enol ethers having β allylic protons, this alternative pathway of nucleophilic attack is less favored than hydride abstraction, and oxidation is the predominant reaction course.

Since trialkylsilyl enol derivatives can be easily prepared regiospecifically from ketones[12] and esters[13] in high yields, this procedure should prove quite useful for the facile introduction of unsaturation into these molecules.

Experimental Section

General. All of the trialkylsilyl enol ethers were prepared by literature procedures.[12] The trimethylsilyl ketene acetals were prepared by our previously described method.[13] The procedure of Rutherford was used to prepare trityl methyl ether.[9] Trityl tetrafluoroborate was purchased from Aldrich Chemical Co. and Cationics, Inc. The triphenylpropiophenone **21** displayed physical properties identical to those reported.[11]

General Oxidation Procedure. The following are typical experimental procedures for each method.

Method A. In a 25-mL round-bottom flask, 0.497 g (1.5 mmol) of trityl tetrafluoroborate, 0.148 g (1.2 mmol) of collidine, and 0.051 g of tetralin as an internal VPC standard were dissolved with stirring in 10 mL of dichloromethane (freshly distilled from calcium hydride and stored over molecular sieves) at 25 °C under a nitrogen atmosphere. To this was added 0.170 g (1 mmol) of the trimethylsilyl enol ether of cyclohexanone **1**, and the solution was stirred. After the indicated period of time, the reaction mixture was quenched with water and analyzed by VPC (10% carbowax 20M on 60–80 mesh Chromosorb W, ⅛ in. × 6 ft column). In the case of **1**, after 2 h VPC analysis indicated a mixture of 70% cyclohexenone and 28% cyclohexanone. For 2,6-dimethylcyclohexanone, a different column was used for VPC analysis (20% carbowax 20M on 60-80 mesh Chromosorb W ⅛ in. × 11 ft column).

Method B and C. A 50-mL round-bottom flask equipped with septum inlet, mercury relief valve, and magnetic stirring was flushed with nitrogen and immersed in a water bath at 25 °C. The flask was charged with 1.37 g (5 mmol) of trityl methyl ether and 10 mL of dichloromethane (or acetonitrile). Boron trifluoride etherate, 0.94 g (6.66 mmol) was injected all at once. After 10 min of stirring, 1-trimethylsilyloxycyclohexene (**1**) 0.844 g (5 mmol) was added dropwise over a 5-min period. After an additional 30 min, the reaction mixture was quenched by addition of 3 mL of 1 M potassium carbonate in water. Pentadecane was added as internal VPC standard, and after separation and drying (anhydrous $MgSO_4$) analysis of the organic phase (20% carbowax 20 M on 60-80 mesh Chromosorb W, ¼ in. × 6 ft column) established the presence of cyclohexenone (2.3 mmol, 45%) together with recovered cyclohexanone (2.0 mmol, 40%).

Method D. In a 25-mL round-bottom flask were dissolved 0.340 g (1.5 mmol) of dichlorodicyanoquinone (DDQ) and 0.051 g of tetralin as an internal standard in 10 mL of benzene with stirring at 25 °C under a nitrogen atmosphere. To this was added in one portion 0.176 g (1 mmol) of the trimethylsilyl enol ether of cyclohexanone **1**. After 1 h, the reaction mixture was quenched with water. VPC analysis (using the same column as for method A) indicated 28% cyclohexenone and 6% cyclohexanone.

Separate experiments showed that tetralin was not oxidized to any great extent by trityl salt or DDQ within 2 h under the conditions of methods A and D.

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Registry No.—cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 2,6-dimethylcyclohexanone, 2816-57-1; cyclopentanone, 120-92-3; 2,4-dimethylpentan-3-one, 565-80-0; trityl tetrafluoroborate, 341-02-6; trityl methyl ether, 596-31-6; boron trifluoride etherate, 109-63-7; dichlorodicyanoquinone, 84-58-2.

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Reduction of Organic Compounds with the Hydroxyborohydride Ion

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The hydroxyborohydride ion, BH_3OH^-, is formed during the hydrolysis of the borohydride ion, BH_4^-.[1,2] In the reduction of esters by aqueous borohydride solutions, Kirsch and Lee[3] observed an increase in the rate of reduction when the borohydride solutions were allowed to age before adding the esters, and they proposed that the increased reducing power of the aged solutions was due to the formation of the BH_3OH^- ion. By use of a quenching flow reactor described in a previous publication,[4] it is possible to prepare alkaline solutions containing the BH_3OH^- ion in concentrations as high as 0.35 M. The half-life of BH_3OH^- in such solutions is 3.9 h at 20 °C and pH $\geq$12.5. To determine the utility of the BH_3OH^- ion as a reducing agent, we have studied the reduction of esters, nitriles, nitro compounds, ketones, and alkyl halides.

Table I. Data for reductions with BH_3OH^- at 0 °C

Substrate	Registry no.	Cosolvent	pH	Ratio BH_3OH^-/substrate[a]	Rxn time, h	% yield reduction product	Registry no.	% consumption substrate
Ethyl benzoate	93-89-0	CH_3CN	11.9	10	17	89[b]	100-51-6	97
Ethyl benzoate		None[c]	12.6	10	17	89[b]		100
Benzonitrile[d]	100-47-0	CH_3OH	12.5	10	16	89[b]	100-46-9	51
Benzonitrile		CH_3OH	12.5	10	48	89[b]		56
Nitrobenzene[e]	98-95-3	CH_3OH	11.7	10	5	78[b]	62-53-3	44
Benzophenone	119-61-9	CH_3OH	~13.5	2	0.33	84	91-01-0	>90
Cyclopentanone	120-92-3	CH_3OH	~13.5	2	0.25	86	96-41-3	~95
Cyclohexanone	108-94-1	CH_3OH	~13.5	2	0.25	74	108-93-0	~95
2-Methylcyclohexanone	583-60-8	CH_3OH	~13.5	2	0.25	74	583-59-5	~95
4-*tert*-Butylcyclohexanone	98-53-3	CH_3OH	~13.5	5	0.25	74	98-52-2	100
Camphor	464-49-3	CH_3OH	~13.5	5	0.25	73	124-76-5	~95

[a] BH_3OH^- concentration ~0.2 M in all runs. [b] Yield based on substrate consumed. [c] Sodium lauryl sulfonate added. [d] Run at 25 °C. [e] Run at 6 °C.

Table II. Data for BH_3OH^- Syntheses

BH_4^-, M	H^+, M	OH^-, M	Product temp, °C	BH_3OH^-, M	BH_3OH^-, % yield	$[BH_4^-]/[BH_3OH^-]$
0.3	0.45	0.6	6	0.091	94	<0.005
1.0	2.5	3.0	4	0.218	72	0.036
1.5	3.0	3.0	6	0.396	86	0.056
1.5	3.0	4.0	6	0.367	68	0.072
3.0	4.5	6.0	45	0.398	51	0.025

Results and Discussion

Attempts to reduce ethyl benzoate with the strongly alkaline (pH ~13.5) BH_3OH^- solutions from our quenching flow reactor yielded no benzyl alcohol; the ester was completely saponified. Therefore, the pH of the reaction mixtures was reduced to 11–13 by addition of a diethylamine–diethylammonium chloride solution (pH 8.5–9.0). The resulting solutions were not well buffered; however, the pH changed less than 0.05 unit during the course of the reactions. In some runs we added water-miscible solvents to increase the solubility of the ethyl benzoate. In other runs we added sodium lauryl sulfonate (3.4×10^{-4} M) to aid in dispersing the ethyl benzoate. Optimum conditions, in terms of yield, are reported in Table I. To determine whether hydroxyborohydride gives significantly better yields of benzyl alcohol than borohydride under similar conditions, we optimized the yield of benzyl alcohol using aqueous borohydride solutions with a BH_4^- to ethyl benzoate ratio of 10:1. The best yield (11%) was obtained at 0 °C and pH 9.8 with a reaction time of 72 h. This yield is much lower than those given in Table I.

We found that BH_3OH^- reduces benzonitrile to benzylamine and that it reduces nitrobenzene to aniline. The optimum reaction conditions are given in Table I.

We studied the reduction of ketones mainly to verify that BH_3OH^- solutions give good yields of the same products that are obtained with borohydride. The data are given in Table I. The alcohols obtained from 2-methylcyclohexanone and 4-*tert*-butylcyclohexanone had trans configurations. The camphor reduction product was mainly isoborneol, with a small amount of borneol.

We attempted the reduction of 1-chlorooctane, 1-iodooctane, and benzhydryl chloride with BH_3OH^-, but were unable to isolate any hydrocarbons.

Conclusions

The aqueous BH_3OH^- ion is potentially a valuable reducing reagent. In cold solutions it reduces esters that are reduced by $NaBH_4$ only at elevated temperatures, e.g., in refluxing methanol.[5] Benzonitrile is reduced by cold aqueous BH_3OH^-, whereas reduction of similar nitriles by $NaBH_4$ requires special conditions, such as the presence of $AlCl_3$.[6] Aqueous BH_3OH^- reduces nitrobenzene all the way to aniline rather than just to azoxybenzene as in the reduction by $NaBH_4$.[7] At 0 °C it reduces ketones as readily as $NaBH_4$ does at room temperature.[8] Thus, the hydroxyborohydride ion has a reducing power intermediate between those of the rather powerful lithium aluminum hydride and the rather mild and selective sodium borohydride.

Experimental Section

Materials and Techniques. Reagent grade $NaBH_4$ (Alfa), HCl (J. T. Baker), and NaOH (Mallinckrodt) were used to prepare the BH_3OH^- solutions. Most of the organic reagents and solvents were used as recieved from commercial suppliers; tetrahydrofuran, diglyme, octyl chloride, octyl iodide, ethyl benzoate, benzonitrile, nitrobenzene, and *d*-camphor were purified by distillation before use.

During the reduction attempts, special covered beakers, approximately 5-in. tall and 2.5 inches in diameter, were used as the reaction vessels; thus, vigorous stirring was possible without loss of solution from splashing. A Varian 1200 gas chromatograph equipped with a flame-ionizing detector was used. The yields were determined to ±5% from the GLC areas by means of calibration curves constructed with internal standards. Representative procedures for the reductions are given in some of the following paragraphs.

Preparation of BH_3OH^- Solutions. The synthesis[4] involves the mixing of streams of reactant solutions (BH_4^- and H^+) in a reaction tube, with downstream injection of a solution containing excess OH^-. The yield of BH_3OH^- is dependent upon the reaction time, i.e., the time between the initial mixing of H^+ and BH_4^- and the quenching with the OH^-. To permit accurate calculation of this time, we introduced calibrated flow meters between the reagent vessels and the reactor. The reagent solutions were precooled to 0 to −5 °C and were contained in glass-lined stainless-steel vessels. The solutions were forced into the reactor by nitrogen gas pressure; the flow rates of the three solutions were approximately equal.

By suitable adjustment of the reagent concentrations, and using a reaction time of approximately 16 ms (calculated from the flow rates), we were able to prepare BH_3OH^- solutions containing only small percentages of unreacted BH_4^-. Evidence for the BH_3OH^- ion was obtained from the boron-11 NMR spectrum, which consisted of a 1:3:3:1 quartet, upfield from a borate singlet, with a B–H coupling constant of 92 Hz. The spectrum is in excellent agreement with those recorded by previous workers.[1b,2] The ratio of BH_4^- to BH_3OH^- and other data for representative syntheses are given in Table II. The BH_3OH^- concentration of a solution was determined by measurement of the hydrogen evolved upon heating at 60 °C for 30 min or longer. The BH_4^- content was then determined from the hydrogen evolved upon addition of excess HCl. The percent yield of BH_3OH^- was calculated from the BH_3OH^- analysis and the boron analysis of a completely hydrolyzed sample. The boron-11 NMR spectrum of a 0.35 M solution of BH_3OH^- was recorded at 0 °C on a Varian HA-100 spectrometer using a carbon-13 probe and by lowering the magnetic field to resonate for boron-11 at 25.15 MHz.

Esters. An ice-cold solution (35 mL) containing 10 mmol of BH_3OH^- was adjusted to pH 11.9 by the addition of approximately 10 mL of a diethylamine–diethylammonium chloride solution. A solution of 1 mmol of ethyl benzoate in 3 mL of cold acetonitrile was added, and the mixture was stirred at 0 °C for 17 h before quenching the reaction by adding excess 1 M HCl. After quenching, 1 mmol of octyl alcohol (internal standard) was added; the mixture was extracted with three 15-mL portions of diethyl ether, and the combined extracts were analyzed by GLC. A 10-ft long, $\frac{1}{8}$ in. o.d. column, packed with 5% Carbowax 20M on acid-washed Chromosorb W support, was used.

Benzonitrile. The pH of an ice-cold solution containing 20 mmol of BH_3OH^- was adjusted to 12.5 with ice-cold diethylamine–diethylammonium chloride solution, and a solution of 1.96 mmol of benzonitrile in 5 mL of methanol was added. The reaction mixture was held at 25 °C and stirred for 16 h. The mixture was then quenched with 1 M HCl; 1 mmol of valeronitrile was added as an internal standard, and the solution was again made alkaline with NaOH before extracting with three 15-mL portions of diethyl ether. The ether extracts were washed with a known amount of acid, and the yield of benzylamine was determined by titration with standard NaOH solution. To check the titration results, the solution was made approximately 1 M in OH^-, a small excess of benzoyl chloride was added, and the precipitated benzyl benzamide was filtered, dried, and weighed. The calculated yields agreed within 2%. Unconsumed benzonitrile was determined by GLC of the ether extracts using a column of 5% FFAP on Chromosorb G.

Nitrobenzene. Two millimoles of nitrobenzenes in 5 mL of methanol was added to an ice-cold solution containing 20 mmol of BH_3OH^-. The pH of the solution was adjusted to 11.7, and the reaction mixture was stirred for 5 h at 6 °C. Then the pH was adjusted to approximately 7 by adding a solution of oxalic acid. One millimole of valeronitrile (internal standard) was added; the mixture was extracted with three 15-mL portions of diethyl ether, and the extracts were analyzed by GLC utilizing the same column used to analyze for benzylamine.

Ketones. An ice-cold solution (25 mL) containing 10 mmol of BH_3OH^- was added to an ice-cold solution of 5 mmol of benzophenone in 35 mL of methanol, and the mixture was stirred. After 15 min, a white precipitate of diphenylmethanol had formed, and the reaction was stopped by adding 1 M HCl. The product was filtered, dried, and weighed: yield, 0.924 g, 84% of theory. After recrystallization from ligroin, the melting point was 67–69 °C (lit.[9] 69 °C). Diglyme and tetrahydrofuran were used as cosolvents for some of the ketones, with no significant changes in the yields. In the case of cyclopentanone and 2-methylcyclohexanone, the products were liquids, and yields were determined by GLC using a column packed with 5% SE-30 on acid-washed Chromasorb W support.

Alkyl Halides. A solution of the halide and decane (internal standard) in ice-cold methanol was mixed with ice-cold BH_3OH^- solution. After 5 or 48 h (depending on whether the pH was ca. 11.6 or ca. 12.6, respectively), an aliquot of the reaction mixture was quenched with 1 M HCl and extracted with three 15-mL portions of diethyl ether. No octane was found in the extracts by GLC.

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A Convenient Synthesis of Methacrylates

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Previous syntheses of acrylate and methacrylate esters have generally proved tedious and have often produced the desired esters in only fair yields.[1–4] The usual methods of synthesis have utilized the reaction of methacryloyl chloride and an alcohol in the presence of triethylamine or a transesterification employing methyl methacrylate, the desired alcohol, and a trace of acid catalyst.[5,6] Competing polymerization of the reactive α,β-unsaturated esters caused by traces of free acid which are inevitably present during such reactions is often a primary cause of the low yields reported. Difficult separations of closely boiling liquids and further polymerization of the product during distillation can cause additional reductions in the overall yields. Our interest in a large variety of methacrylate esters prompted us to investigate other methods of preparing these compounds.

Molecular sieves are widely used as drying agents for organic solvents and in a few instances have been used to trap water generated during a reaction.[7–11] The ability of molecular sieves to scavenge other small molecules such as hydrogen chloride has been exploited in only a few cases.[12,13] The capacity of molecular sieves to absorb the hydrogen chloride liberated from the reaction of methacryloyl chloride and an alcohol was predicted to favor product formation as well as to prevent any polymerization. It was found that powdered 3 Å molecular sieves in refluxing carbon tetrachloride or ethylene chloride rapidly absorb the hydrogen chloride produced by the reaction of methacryloyl chloride (**1**) with a number of primary, secondary, tertiary, benzylic alcohols (**2a–d**), and phenols (**2e–j**) to form the esters **3** in good to excellent yields (Table I).

$$\underset{\mathbf{1}}{CH_2{=}C(CH_3)COCl} + \underset{\mathbf{2}}{ROH} \xrightarrow{\text{3 Å molecular sieves}} \underset{\mathbf{3}}{CH_2{=}C(CH_3)COOR}$$

The solvents of choice for these reactions are carbon tetrachloride for ordinary alcohols and ethylene chloride or acetonitrile for alcohols which are not soluble in carbon tetrachloride. Oxygen-containing solvents such as tetrahydrofuran and ethyl acetate were found to interfere with the trapping of hydrogen chloride by the molecular sieves. The capacity of the molecular sieves to prevent polymerization of the reactants allows reaction times (refluxing solvent) of at least 200 h with no evidence of polymer formation. Product isolation requires only separation of the molecular sieves by filtration of the cooled reaction mixture followed by evaporation of the solvent and any excess methacryloyl chloride under reduced pressure. Final purification of the ester is accomplished by simple vacuum distillation. Some of the higher molecular weight