

lution and then water and evaporated to give an oil (4.6 g). The latter was chromatographed over silica gel (100 g) and the desired product (1.3 g) was eluted with mixtures of 5–10% ethyl acetate in methylene chloride. The material showed a single peak on glc analysis [ $R_f$  14.2, 205° (10 ft  $\times$  0.25 in., 5% QF-1 on Chromosorb)] and its infrared spectrum [1660 (carbonyl) and 1605  $\text{cm}^{-1}$  (double bond)] was identical with that of a specimen prepared according to a known method.<sup>8</sup> Its mass spectrum showed a molecular ion at  $m/e$  164 and the base peak at  $m/e$  136 ( $M - 28$ ). Other significant peaks appeared at  $m/e$  122, 108, 93, 79, 41, and 39.

**Cyclization of Citronellonitrile (23).** Citronellonitrile (23, 24.4 g) and triethyloxonium fluoroborate (30.8 g) were heated together at 80° with stirring under dry nitrogen for 3 hr. Water (150 ml) containing acid (10 ml) was added and the mixture, after being stirred for a few minutes, was steam distilled. The distillate was neutralized using sodium bicarbonate and the product (6.32 g, 25%), a colorless oil with a peppermint odor, was isolated by extraction with methylene chloride. Glc analysis (5 ft  $\times$  0.25 in. column, McNair's phase, 30% on 60–80 mesh Chromosorb, 125°, He flow rate 75 ml/min) revealed the presence of six components: A ( $R_f$  5.8, 8%), B ( $R_f$  13.2, 44.6%), C ( $R_f$  15.4, 19.7%), D ( $R_f$  18.5, 4.2%), E ( $R_f$  22.2, 6.3%), and F ( $R_f$  26, 16.3%). Mass spectral data were obtained for each of these compounds. Component A showed parent ions (low-voltage study) at  $m/e$  150 and 180 and was assumed to be a mixture. It and components D and E, both of which showed  $m/e$  180 peaks for their parent ion, were not studied further. Components B and C, both with parent ions at  $m/e$  154, were identified as methone and isomenthone, respectively, by comparison of their infrared spectra and  $R_f$  values, while component F by the same criteria, proved to be pulegone (parent at  $m/e$  152, ir 1690 and 1625  $\text{cm}^{-1}$ ).

**Registry No.**—16 ( $R = R' = H$ ), 5048-19-1; 19, 2359-64-0; 20, 51004-10-5; 22, 19198-29-9; 23, 51004-11-6; 28, 51004-12-7; 29, 51004-13-8; triphenylmethylphosphonium bromide, 1779-49-3; 2-( $\beta$ -cyanoethyl)cyclohexanone, 4594-78-9; 2-( $\beta$ -cyanoethyl)cycloheptanone, 33736-92-3; 2-cyanomethylcyclopentanone, 51004-14-9; triethyloxonium fluoroborate, 368-39-8.

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### Organic Synthesis Using Borane-Methyl Sulfide. The Hydroboration-Oxidation of Alkenes

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Borane-methyl sulfide (BMS) is a stable, liquid  $\text{BH}_3$  complex, and its numerous advantages over borane-tetrahydrofuran solution as a storable reagent were discussed by Adams and coworkers.<sup>1</sup> The main advantages are that (1) BMS has a molar concentration of borane ten times that of borane-tetrahydrofuran solution, (2) BMS is soluble in and unreactive toward a wide variety of aprotic solvents, and (3) BMS is apparently stable indefinitely when refrigerated.

**Table I**  
Hydroboration-Oxidation of 1-Hexene Using BMS.  
Solvent Study<sup>a</sup>

Solvent	1-Hexanol, % <sup>b</sup>	2-Hexanol, % <sup>b</sup>	Total yield, % <sup>c</sup>
Ethyl ether	94.4	5.6	100
Tetrahydrofuran	93.6	6.4	100
Hexane <sup>d</sup>	94.1	5.9	100
Toluene <sup>d</sup>	94.2	5.8	98.1
Methylene chloride <sup>d</sup>	93.6	6.4	99.4
Ethyl acetate <sup>d</sup>	94.2	5.8	100
Acetonitrile <sup>d</sup>	93.8	6.2	80.9

<sup>a</sup> All reactions involved the addition of BMS (11 mmol) to 1-hexene (30 mmol) dissolved in 10 ml of solvent at 0–5°. After 1 hr at 20–25°, the reaction mixture was oxidized with alkaline hydrogen peroxide. <sup>b</sup> Relative amount by gc analysis. <sup>c</sup> Total yield by gc analysis using an internal standard. <sup>d</sup> Ethanol (10 ml) added as cosolvent prior to oxidation.

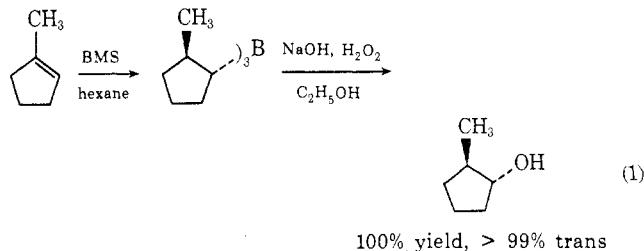
BMS is now commercially available and appears to be a useful borane reagent for organic synthesis.<sup>2</sup> However, a systematic investigation of the hydroboration of alkenes with BMS has not been reported. Such a study will now be described herein.

The miscibility of BMS with various solvents prompted an examination to determine if the solvent has any effect on the hydroboration of alkenes with BMS. 1-Hexene was chosen as a representative alkene. The standard procedure and the results of this solvent study are given in Table I.

As in the case of borane-tetrahydrofuran,<sup>2</sup> hydroboration of a monosubstituted alkene with BMS proceeds quantitatively, placing boron 94% in the terminal position and 6% in the secondary position. Surprisingly, the use of various solvents, most of which could not previously be used in hydroboration reactions, presented no problems for the hydroboration with BMS. Solvents such as ethyl ether, hexane, toluene, and methylene chloride, in which  $\text{BH}_3$  has low or negligible solubility, readily dissolve BMS to give quantitative hydroborations. Even solvents which react with diborane can be used for hydroborations with BMS; e.g., 1-hexene was hydroborated cleanly and quantitatively in ethyl acetate.

To define more fully the utility of BMS as a hydroboring agent, a series of representative alkenes were allowed to react with BMS in an appropriate solvent. Hexane was chosen as the solvent because an inexpensive grade is commercially available and is of sufficient purity to require no prior treatment.

The results of this study, as shown in Table II, indicate that the hydroboration-oxidation of alkenes with BMS in a hydrocarbon solvent is a general reaction and gives excellent yields of the corresponding alcohols. That the reaction is both regioselective and stereoselective was shown by the hydroboration-oxidation of 1-methylcyclopentene (eq 1).



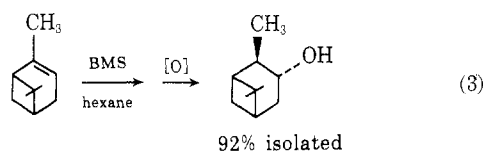
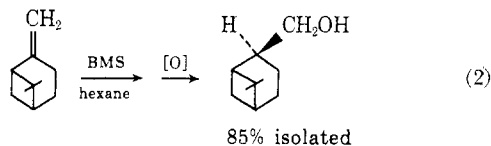
The synthetic utility of this new hydroboration-oxidation procedure was further demonstrated by treating  $\alpha$  and  $\beta$ -pinene with BMS on a molar scale in hexane. From (–)- $\beta$ -pinene an 85% isolated yield of (–)-*cis*-myrntanol

**Table II**  
Hydroboration-Oxidation of Alkenes Using BMS<sup>a</sup>

Alkene	Time, hr <sup>b</sup>	Alcohol products	Relative amounts, % <sup>c</sup>	Total yield, % <sup>d</sup>
1-Hexene	1	1-Hexanol	93.6	100
		2-Hexanol	6.4	
2-Methyl-1-pentene	1	3-Methyl-1-pentanol		99.8
		3-Hexanol		
Styrene	1	2-Phenylethanol	86.3	100
		1-Phenylethanol	13.7	
Cyclopentene	1	Cyclopentanol		96.5
Cyclohexene	1 <sup>e</sup>	Cyclohexanol		78.7
				100
Norbornene	1	<i>exo</i> -Norborneol		87
				94
1-Methyl-cyclopentene	1	<i>trans</i> -2-Methyl-cyclopentanol	>99 <sup>f</sup>	86.4

<sup>a</sup> All reactions involved the addition of BMS (11 mmol) to the alkene (30 mmol) dissolved in 10 ml of hexane at 0–5°. After an appropriate interval, ethanol (10 ml) was added and the reaction mixture was oxidized using 3 *N* aqueous NaOH (11 mmol) and 30% aqueous H<sub>2</sub>O<sub>2</sub> (33 mmol). <sup>b</sup> Time for hydroboration at 20–25°. <sup>c</sup> By gc analysis. <sup>d</sup> By gc analysis using an internal standard. <sup>e</sup> Reaction mixture was heated to reflux for 1 hr to ensure complete hydroboration. <sup>f</sup> <1% *cis* isomer.

was obtained (eq 2), while *dl*- $\alpha$ -pinene gave *dl*-isopinocampheol in 92% isolated yield (eq 3).



It is now apparent that BMS is indeed a very useful reagent for the preparation of organoboranes *via* hydroboration of alkenes. The stability, commercial availability in pure form, and solubility in a wide variety of solvents should make BMS the reagent of choice for preparative hydroborations.

### Experimental Section

All starting materials, including BMS, were used directly as obtained from the Aldrich Chemical Co. Since BMS is decomposed by atmospheric moisture, all manipulations of liquid BMS and the hydroboration reactions were carried out in dry glassware under a nitrogen atmosphere. A detailed description of the techniques necessary in handling air-sensitive solutions has been given elsewhere.<sup>3</sup>

(-)-*cis*-Myrtanol. A dry 2-l. flask equipped with a mechanical stirrer, pressure-equalizing dropping funnel, and reflux condenser was flushed with dry nitrogen and maintained under a positive nitrogen pressure. The flask was then charged with 238 ml (1.5 mol) of (-)- $\beta$ -pinene and 500 ml of hexane and cooled to 0–5° with an ice-water bath. Hydroboration was achieved by the dropwise addition of 52.5 ml (0.55 mol) of BMS. Following the addition of the hydride (0.5 hr), the cooling bath was removed and the solution was stirred for 3 hr at 20–25°. Ethanol (500 ml) was then added followed by 165 ml of 3 *N* aqueous sodium hydroxide. After cooling to 0–5° in an ice-water bath, hydrogen peroxide (185 ml of a 30% aqueous solution) was added dropwise at such a rate that the reaction mixture warmed to 25–35°. Immediately following the addition of the peroxide (1 hr), the cooling bath was removed and the reaction mixture was heated at reflux for 1 hr. The reac-

tion mixture was then poured into 6 l. of ice water. After adding 2 l. of ether and mixing thoroughly, the lower aqueous layer was removed and discarded. The upper organic layer was washed with water (2  $\times$  1 l.), washed with saturated aqueous sodium chloride, dried over anhydrous potassium carbonate, filtered, and concentrated on a rotary evaporator to give 230 g of a light yellow oil. Short-path vacuum distillation of this oil gave 196 g (85%) of (-)-*cis*-myrtanol: purity >98% by gc analysis; bp 65–67° (0.2 mm);  $n_D^{20}$  1.4911;  $[\alpha]_D^{25}$  -19.5° [lit.<sup>4</sup> bp 70–72° (1 mm);  $n_D^{20}$  1.4910;  $[\alpha]_D^{25}$  -21°].

*dl*-Isopinocampheol. Hydroboration-oxidation was carried out as described for *cis*-myrtanol using 500 ml of hexane, 160 ml (1.0 mol) of *dl*- $\alpha$ -pinene,<sup>5</sup> 52.5 ml (0.55 mol) of BMS, 500 ml of ethanol, 165 ml of 3 *N* aqueous sodium hydroxide, and 125 ml of 30% aqueous hydrogen peroxide. Isolation gave 154 g of a light yellow oil. Short-path vacuum distillation of this oil gave 141 g (92%) of *dl*-isopinocampheol, which crystallized upon cooling in the receiver, purity ~99% by gc analysis, bp 62–63° (0.25 mm), mp 39–41°. The sublimed alcohol exhibited mp 41–42° [lit.<sup>4</sup> for *l*-isopinocampheol, mp 54–56°].

**Registry No.**—Borane-methyl sulfide, 13292-87-0; 1-hexene, 592-41-6; (-)-*cis*-myrtanol, 51152-12-6; (-)- $\beta$ -pinene, 18172-67-3; *dl*-isopinocampheol, 51152-11-5; *dl*- $\alpha$ -pinene, 2437-95-8.

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### Relative Stabilities of $\alpha$ -Phenyl and $\alpha$ -Ferrocenyl Cations

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The existence of vinyl cations has now been demonstrated to the extent that these species are no longer hesitantly proposed as reaction intermediates. The first vinyl cations observed were generated in systems in which the positive charge could be delocalized as in substituted di- and triphenylethylenes. More recently, vinyl cations have been produced from a large number of compounds *via* a variety of reactions.<sup>1-7</sup>

In the course of our continued work with vinyl cations, the unusual stability of  $\alpha$ -ferrocenyl alkyl cations was noted<sup>8</sup> and it appeared that the presence of an  $\alpha$ -ferrocenyl moiety might also permit the ready generation of very stable vinyl cations. After exploratory work showed that various electrophilic additions to ethynylferrocene proceeded readily, we sought to determine the relative abilities of ferrocenyl and phenyl groups to stabilize vinyl cations, *i.e.*, the relative stabilities of  $\text{FcC}^+=\text{CR}_2$  and  $\text{PhC}^+=\text{CR}_2$ .

A qualitative answer to this question was ascertained by employing a type of intramolecular competition reaction in which either an  $\alpha$ -phenyl or  $\alpha$ -ferrocenyl vinyl cation could form as an intermediate as shown in Scheme I. When a dilute ethanolic solution of 1 was stirred at room temperature with a catalytic amount of 25% sulfuric acid, ferrocenylbenzyl ketone (3) was quantitatively produced. This result indicates that carbonium ion 2 was formed in preference to 4 and suggests that the  $\alpha$ -ferrocenyl vinyl