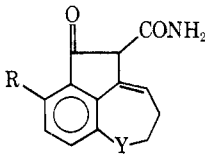
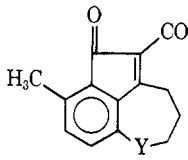
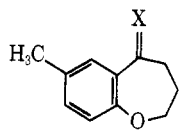
Application of this procedure to the ylidenemalononitrile derivatives of benzosuberone and 2,3,4,5-tetrahydrobenzo[*b*]thiepin[1] has yielded compounds **1** and **2**. This reaction has now been successfully applied to the 3,4-dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitrile (**3**).



1, Y = CH_2; R = H
5, Y = O; R = CH_3

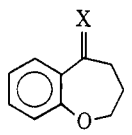


2, Y = S
6, Y = O

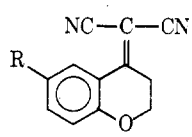


3, X = $C(CN)_2$
4, X = O

Compound **3**, which was readily available[1] from **4**,[3] immediately produced a wine-red solution, similar to the formation of **1**, when placed in polyphosphoric acid at 85°. Quenching the reaction yielded **5** as the only product with no indication of isomer **6**. In contrast to the sulfur series,[1] use of sulfuric acid as the cyclizing media produced only small amounts of **5**. On the other hand, no isolable material resulted when the 7-demethylated ylidenemalononitrile (**7**) was subjected to either polyphosphoric acid or sulfuric acid. This result parallels that in the sulfur series[1,4] in which the position para to the heteroatom is susceptible to electrophilic substitution.



7, X = $C(CN)_2$
8, X = O



9, R = H, CH_3

The structure of **5** was based on several lines of evidence: (a) white color analogous to that of **1**[5] and in contrast to the indenone **2**[1] which is red; (b) infrared bands at 5.82 (ketone carbonyl) and 6.08 μ (amide carbonyl) which are in exact agreement with those recorded in our laboratory for **1**; (c) ultraviolet absorptions at 245 and 268–278 nm similar to those of **1**;[5] and (d) an nmr spectrum analogous to that of **1**[6] possessing a vinylic proton absorption at τ 3.91.

The formation of **5** was unexpected in view of the formation of noncyclized ring-sulfonated products when **9**[7] was subjected to similar conditions. The fact that the reaction of **3** gives **5**, analogous to the carbocyclic system, rather than **6**, which would parallel the sulfur series, may be due simply to the similarity in size of O and CH_2. The larger sulfur atom in the sulfur analog may cause greater puckering in the thiepin ring, favoring the exo double bond.

Experimental Section[8]

3,4-Dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitriles. A 400-ml xylene solution containing 190 mmol of either **4**[4] or **8**,[9] 33 g (500 mmol) of malononitrile, 12 g of ammonium acetate, and 36 ml of glacial acetic acid was refluxed with the aid of a Dean-Stark trap until the collection of water ceased. The xylene solution was cooled and decanted from a polymeric mass of malononitrile in the reaction vessel. After this mass was washed with xylene, the xylene fractions were combined and washed with water (3 × 100 ml). After drying over anhydrous $MgSO_4$, the xylene solution was concentrated *in vacuo* and the residue crystallized upon ice cooling.

3,4-Dihydro-1-benzoxepin-5(2*H*)-ylidenemalononitrile (7) was obtained in 65% yield as white needles from aqueous ethanol: mp 98–100°; ir (KBr) 4.50 μ (CN); nmr ($CDCl_3$) τ 2.36–3.10 (m, 4 H, aromatic), 5.89 (t, J = 6 Hz, 2 H, α to oxygen), 7.0 (t, J = 6 Hz, 2 H, γ to oxygen), 7.74 (pentet, J = 6 Hz, 2 H, β to oxygen).

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.28; H, 4.77. Found: C, 74.30; H, 4.90.

3,4-Dihydro-7-methyl-1-benzoxepin-5(2*H*)-ylidenemalononitrile (3) was obtained in 75% yield as yellow needles from cold aqueous ethanol: mp 60–62°; ir (KBr) 4.50 μ (CN); nmr ($CDCl_3$) τ 2.7 (m, 1 H, aromatic), 2.88–3.15 (m, 2 H, aromatic), 5.91 (t, J = 6 Hz, 2 H, α to oxygen), 7.0 (t, J = 6 Hz, 2 H, γ to oxygen), 7.72 (s, 3 H, methyl), 7.75 (br, 2 H, β to oxygen).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 75.00; H, 5.35. Found: C, 74.73; H, 5.50.

2,3,5,6-Tetrahydro-7-methyl-6-oxoindeno[7,1-*bc*]oxepin-5-carboxamide (5). Three grams (13.4 mmol) of **3** was slowly added to 40 g of mechanically stirred polyphosphoric acid at 85°. The resulting solution became wine red almost immediately and stirring was continued at 85° for 1 hr. The resultant solution was poured in 1.8 l. of ice water and the insoluble material which resulted was filtered, washed with water, and air dried. Several recrystallizations from 95% ethanol yielded 47% of **5** as white prisms: mp 186–188°; nmr (DMSO-d_6) τ 2.9–3.15 (br, 2 H, aromatic), 3.91 (br, 1 H, vinyl), 5.75 (t, J = 4 Hz, 2 H, α to oxygen), 5.95 (broad s, 1 H, methine), 7.57–7.88 (5 H, methyl singlet superimposed on multiplet of $-CH_2-$ β to oxygen); mass spectrum *m/e* (rel intensity) 243 (72), 226 (62), 200 (79), 198 (47), 185 (50), 141 (47), 128 (48), 115 (94), 44 (100), and 18 (68).

Anal. Calcd for $C_{14}H_{13}NO_3$: C, 69.13; H, 5.35. Found: C, 68.97; H, 5.28.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to Dr. T. R. Bosin of the Department of Pharmacology at Indiana University for his assistance in obtaining the mass spectrum for compound **5**.

Registry No.—**3**, 50790-48-2; **4**, 41177-66-6; **5**, 50790-49-3; **7**, 50790-50-6; **8**, 6786-30-7.

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(6) The nmr spectrum of **1**, which has previously not been reported in the literature, was found to be (DMSO-d_6) τ 2.32–2.96 (m, 3 H, aromatic), 3.92 (t, J = 5 Hz, 1 H, vinyl), 5.90 (broad s, 1 H, methine), 6.91 (t, J = 5 Hz, 2 H, CH_2), 7.36 (br, 2 H, CH_2), and 8.02 (br, 2 H, CH_2).
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(8) Melting points were taken on a Mel-Temp capillary melting point apparatus and are uncorrected. The nmr spectra were obtained on a Varian A-60 spectrometer using TMS as an internal standard. The ultraviolet absorption spectrum was determined with a Cary Model 14 recording spectrophotometer using 1-cm sample cells. Ir spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer. The mass spectrum was determined on a Varian MAT CH-7 at Indiana University, Bloomington, Ind. The microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.
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Cyclization of δ- and γ-Alkenenitriles by Triethyloxonium Fluoroborate

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The acid-catalyzed cyclization of δ- and γ-unsaturated nitriles has received little study in the past. In the course of investigating the abnormal Beckmann rearrangement,

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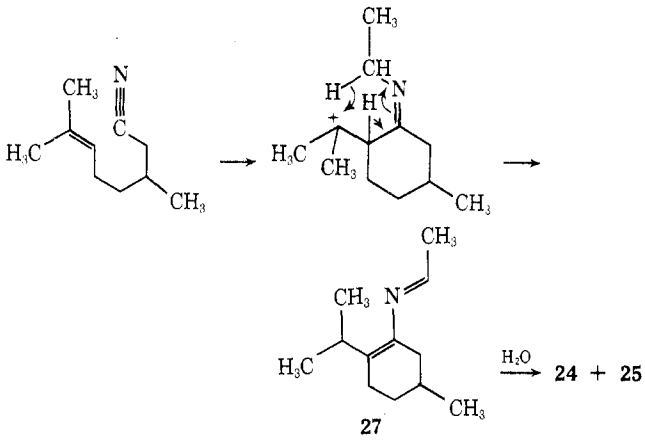
Hill and Conley[1] showed that the isomeric nitriles **1** and **2** both give rise to the octalone **3**. Under the same conditions they found that **4** afforded **5** and in an extension of the work Conley and Nowak[2] were able to show that **6** afforded **7**. Other reactions studied[2,3] involved the general system **8**. In the methylenecyclopentane case **8** [R, R = $(CH_2)_4^-$] a single product **9** was obtained, whereas **8** (R = CH_3) afforded a mixture of **10** and **11**. On the other hand, **8** (R = Ph) led to the imine **12** (isolated as the hydrochloride). More recently, Black and Gill[4] have suggested that the conversion[5] of adamantanone (**13**) to **15** by sodium azide in methanesulfonic acid proceeds *via* the intermediate **14**, thus aligning it with the cyclications noted above.

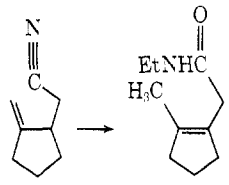
In our work we were interested in finding a method for accomplishing this reaction under conditions milder than hot polyphophoric acid. We decided therefore to examine the use of triethyloxonium fluoroborate as the cyclizing agent, since it seemed likely that the intermediate N-alkylated nitrile[6] (**17**) ought to undergo spontaneous cyclization with proton elimination to give the imine **18**. Hydrolysis of the latter then could be expected to give the desired α,β-unsaturated ketone. In practice we found that little or no reaction could be induced by heating the unsaturated nitrile with triethyloxonium fluoroborate in methylene chloride or nitromethane. Under Meerwein's conditions[6] (heating the components together without solvent), however, reaction proceeded at a reasonable rate and at 80° almost all of the ether expected had been evolved after 30 min. In all cases the reaction product was hydrolyzed with aqueous acid and for the most part the desired products were isolated by steam distillation. The yields, however, were discouraging. In the case of 5-hexencarbonitrile (**16**, R = R′ = H) 2-cyclohexenone was obtained in only 10–12% yields, whereas the 2-cyanoethyl methylenecycloalkanes **19** and **20** afforded the corresponding bicycloalkenones **21** and **22** in 58 and 29% yields, respectively. The product from **19** was a mixture of **21a** and **21b** in the ratio 1:1.8, which is to be contrasted with the enamine synthesis[7] of **21**, which affords these components in the ratio of 1:6.7 (72% yield). On the other hand, **20** gave **22** as the sole isomer, a result in accord with a recent Robinson–Mannich-style synthesis[8] of the latter compound.

More interesting was the cyclization of citronellonitrile (**23**). This afforded a steam distillate consisting principally of three components, menthone (**24**), isomenthone (**25**), and pulegone (**26**), in the percentages noted. It appears that in this case the principal pathway followed involves an internal redox reaction, a possible mechanism for which is shown below. The final intermediate, **27**, would give on hydrolysis **24**, **25**, and probably ammonia and acetaldehyde. No attempt was made to identify the latter compounds, however.

Attempts to extend this cyclization process to the synthesis of a five-membered ring did not succeed. The action of triethyloxonium fluoroborate on **28** did not afford



any steam-volatile product after hydrolysis of the reaction mixture. In fact, the only product that could be isolated was the *N*-ethylcarboxamide **29**, in which the double bond had migrated into the ring.



28 **29**

It should be mentioned also that attempts to effect some of these cyclizations with stannic chloride or boron trifluoride in benzene were unsuccessful. Finally, phenyldiazonium fluoroborate, which is known[6] to form *N*-phenyl salts with nitriles, was heated with **23**, but there was obtained only an 8% yield of a steam-volatile oil containing five components no one of which was pulegone. This was not investigated further.

In general, it may be concluded that triethyloxonium fluoroborate causes cyclization of δ-unsaturated nitriles to give, after hydrolysis of the intermediates, α,β-unsaturated ketones. However, the rather poor yields of product limit the usefulness of the reaction.

Experimental Section

The nmr spectra were obtained using a Varian A56-60 spectrometer while infrared spectra were taken on a Baird spectrophotometer, No. 4-55. Glc data were recorded by a Hewlett-Packard 5750 chromatograph with a helium flow rate of 100 ml/min unless stated otherwise.

2-(β-Cyanoethyl)-1-methylenecyclohexane (19). Sodium hydride dispersion (5.99 g, 56.1% NaH) was washed free of oil with dry petroleum ether (bp 30–60°) and then treated with dry dimethyl sulfoxide (50 ml). The mixture was held at 70° with stirring under nitrogen until homogeneous (1 hr) and then cooled in an ice bath. To this was added in one portion a solution of triphenylmethylphosphonium bromide (48 g) in dimethyl sulfoxide (125 ml). After stirring for 20 min, 2-(β-cyanoethyl)cyclohexanone (20 g) was added dropwise over 20 min. The mixture was heated to 65° for 30 min and then stirred at room temperature overnight. Water (150 ml) was then added and the total liquid was extracted with petroleum ether (4 × 100 ml). The combined extracts were washed with water and dried ($MgSO_4$). Removal of the solvent afforded a thick oil (17.34 g), which was dissolved in methylene chloride and percolated through a column of silica gel (100 g) to remove triphenylphosphine oxide. The oil (16 g) obtained from the eluate was distilled to give the desired material (12.1 g): bp 95.5–96° (3.8 mm); glc R_f 5.0 (min), 205° (10 ft × 0.25 in. column, 5% QF-1 on Chromosorb), $n^{25}D$ 1.4770; ir (film) 2280 (CN), 1755 and 900 cm^{-1} (=CH_2).

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.50; H, 10.11; N, 9.41.

2-(β-Cyanoethyl)-1-methylenecycloheptane (20). This compound was prepared in the same way as its lower homolog 19 using 10.5 g of sodium hydride dispersion (51% NaH), 72 g of triphenylmethylphosphonium bromide, and 32 g of 2-(β-cyanoethyl)-cycloheptanone. The crude product (30 g) was distilled to give the desired compound (17 g) as a colorless liquid: bp 96° (2.5 mm); ir (film) 2250 (CN), 1670 and 885 cm^{-1} (=CH_2).

Anal. Calcd for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.71; H, 10.64; N, 8.70.

2-Cyanomethyl-1-methylenecyclopentane (28). This compound was prepared according to the method described above using sodium hydride (56.1% NaH, 4.85 g) in dimethyl sulfoxide (40 ml), a solution of triphenylmethylphosphonium bromide (43 g) in dimethyl sulfoxide (100 ml), and 2-cyanomethylcyclopentanone (14.16 g). This afforded a pale yellow oil (6.74 g) which was distilled at 89–92° (13 mm) to give the pure desired product (4.7 g): $n^{25}D$ 1.4685; ir (film) 2275, 1660, 893 cm^{-1}; nmr (neat) 4.97 ppm (sextet, =CH_2, J = 4.5 Hz).

Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.5; H, 9.4; N, 11.4.

Cyclization of 5-Hexene-1-carbonitrile (16, R = R′ = H). Triethyloxonium fluoroborate (8 g) was added to 5-hexene-1-carbonitrile[9] (2 g) under dry nitrogen. The mixture was warmed to 72° with stirring and rapidly became homogeneous and dark brown in color. After 65 min the resulting liquid was added to 6% aqueous acetic acid (50 ml) and the total mixture was steam distilled. The volatile oil (0.4 g) by glc showed two peaks in addition to that due to a small quantity of starting material (R_f 3.2, 80°, QF-1). Of these, by far the major peak could be identified as 2-cyclohexenone by comparison of the R_f (2.2 min, 80°, QF-1) with that of an authentic sample. Comparative glc also showed the yield to be 12%. A sample of the oil (96 mg) was treated with 2,4-dinitrophenylhydrazone reagent (0.4 ml). This gave an orange-red solid (29.7 mg) which was dissolved in benzene and percolated through a column of silica gel (10 g). Elution with benzene afforded the derivative as orange-red needles, mp 167–169°, which did not depress the melting point of an authentic specimen. Their infrared spectra were identical also.

The other component (~20%) of the product was separated by analytical glc (R_f 1.8, 80°, QF-1 on Chromosorb, column 12 ft × 0.25 in.). It showed a sharp band at 1635 cm^{-1} and a broad, very intense band at 1120 cm^{-1} in the infrared spectrum suggesting the presence of fluorine. It was not investigated further.

Attempted Cyclization of 2-Cyanomethyl-1-methylenecyclopentane. The olefinic nitrile **28** (1 g) was heated with triethyloxonium fluoroborate (3.14 g) at 80°. Initially the mixture rapidly liquified, became yellow, and evolved gas. After 3 hr, the red liquid was diluted with a mixture of water (10 ml) and acetic acid (1 ml). Extraction of the resulting solution with ether led to an orange oil (0.38 g). This was dissolved in benzene and chromatographed over silica gel (20 g). Elution with 10% ether in benzene (v/v) afforded a white solid (218 mg), which after repeated crystallization from ethyl acetate gave pure *N*-ethyl 2-[1′-(2′-methylcyclopent-1′-ene)]acetamide (**29**): mp 76–77°; nmr (CCl_4) 1.10 (t, $NHCH_2CH_3$, J = 7 Hz), 1.66 (s, CH_3 on double bond), 1.73 (m, CH_2), 2.30 (m, 2, CH_2), 2.91 (s, =CCH_2CO), 3.19 (p, -$NHCH_2CH_3$, J = 7 Hz), and 7.90 ppm (t, NH, J = 7 Hz); ir (Nujol) 330 (NH) and 1660 cm^{-1} (amide). The mass spectrum showed a fairly intense parent ion at m/e 167 and a base peak at m/e 81 corresponding to loss of the *N*-ethylacetamide group.

Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.38. Found: C, 71.80; H, 10.40; N, 8.40.

Bicyclo[4.4.0]-1-octen-3-one (21b) and Bicyclo[4.4.0]-1(6)-octen-3-one (21a). 2-[β-Cyanoethyl]methylenecyclohexane (**19**, 1.5 g) and triethyloxonium fluoroborate were heated together at 80° for 3.3 hr. Water (100 ml) containing acetic acid (3 ml) was then added and the mixture was steam distilled until no more oil came over. A little sodium bicarbonate was added to neutralize the distillate and the mixture was extracted with methylene chloride. This extract yielded a sweet-smelling oil (1.0 g) whose glc showed basically only two peaks (R_f 7.2 and 8.2, 205°, 5% QF-1 on Chromosorb on a 10 ft × 0.25 in. column) in the ratio of 1:1.8, in addition to a trace amount of starting material. The retention times were identical with those observed for an authentic specimen of these two substances prepared by the method of Stork, *et al.*,[7] except that the ratio of the components in the latter case was 1:6.7. Preparation of a 2,4-DNP according to Fieser[10] using the mixture of components from our procedure gave a brick-red crystalline compound, mp 172–174° (lit.[7] mp 168–170°).

Bicyclo[5.4.0]-7-undecen-9-one (22). 2-(β-Cyanoethyl)methylenecycloheptane (**20**, 4.5 g) and triethyloxonium fluoroborate (18 g) were heated together at 85° for 2 hr. Water (100 ml) containing concentrated hydrochloric acid (6 ml) was added and the mixture was boiled for 1 hr. The mixture was extracted with methylene chloride and the extract was washed with sodium bicarbonate so-

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 × 0.25 in., 5% QF-1 on Chromosorb)] and its infrared spectrum [1660 (carbonyl) and 1605 cm^{-1} (double bond)] was identical with that of a specimen prepared according to a known method.[8] 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 × 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 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-(β-cyanoethyl)cyclohexanone, 4594-78-9; 2-(β-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 BH_3 complex, and its numerous advantages over borane–tetrahydrofuran solution as a storable reagent were discussed by Adams and coworkers.[1] 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[a]

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

[a] 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. [b] Relative amount by gc analysis. [c] Total yield by gc analysis using an internal standard. [d] Ethanol (10 ml) added as cosolvent prior to oxidation.

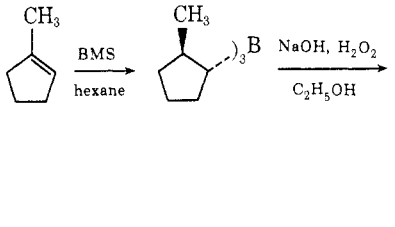
BMS is now commercially available and appears to be a useful borane reagent for organic synthesis.[2] However, a systematic investigation of the hydroboration of alkenes with BMS has not been reported. Such a study will now be described herein.

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,[2] 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 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 hydroborating 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).



(1)

100% yield, > 99% trans

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