mmol) in anhydrous dimethoxyethane (60 ml) was allowed to reflux for 72 hr. The mixture was cooled, and water (9 ml) was added followed by 10% aqueous sodium hydroxide (7.5 ml). After stirring at room temperature for 5 hr, the mixture was filtered and the solvent was removed at reduced pressure, affording 5.0 g of viscous oil. Analysis by gas chromatography showed three components, which were identified as dihydrothujopsene (16%), unreacted epoxide **6** (47%), and tertiary alcohol **7** (37%) on the basis of vpc retention times and by comparison of the ir and nmr spectra of the isolated components with those of authentic samples.

C. From Ketone 10.—To a sample of ketone **10** (800 mg, 3.8 mmol) dissolved in ether (12 ml) was added over 20 min a solution of 2.3 *M* methyllithium in ether (10 ml, 23 mmol). After stirring at 30° for 0.5 hr, the mixture was cooled and water (10 ml) was carefully added. The mixture was extracted with ether and the organic extracts were dried over anhydrous magnesium sulfate. The solvent was removed at reduced pressure, affording 900 mg of crude solid material. Analysis by gas chromatography gave two peaks with retention times of tertiary alcohol **7** (56%) and starting ketone **10** (44%). Separation of the two peaks by preparative gas chromatography afforded a pure sample of tertiary alcohol **7**, mp 93–94°, with an ir and nmr spectra identical with those obtained from part A above.

8α-Hydroxymethyl-2α,8β,9β,10β-tetramethyl-1β-decalol (8).—Continued elution of the chromatography column employed in the separation of the hydroboration products of dihydrothujopsene (see part A above) with 25% ether in hexane afforded 4.2 g (17%) of crystalline diol **8**, mp 104–106°. Crystallization from ether at −15° afforded the analytical sample: mp 115–116°; $[\alpha]^{25}\mathrm{D}$ −24° (*c* 15%, $CHCl_3$); ir (KBr) 3200 (OH), 1182, 1049, 1025, 1001, 918 cm^{-1}; nmr ($CDCl_3$) δ 0.97, 1.04, 1.07 (s, 3 H each), 1.02 (d, 3 H, J = 5.5 Hz), 3.28, 3.32 (2 H AB pattern, J_{AB} = 6 Hz), 3.64 (d, 1 H, J = 9 Hz).

Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 75.17; H, 11.53.

8,8,9β,10β-Tetramethyl-2-decalone (10). To a mixture of freshly distilled ammonia (100 ml), anhydrous ether (40 ml), and ketone 9[3a] (4.0 g, 19.5 mmol) was added lithium wire (300 mg, 43.5 mmol) in 50-mg portions over 15 min. The resulting deep blue mixture was stirred for 1.0 hr; then a 1:1 ethanol–ether mixture (10 ml) was added. The ammonia was allowed to evaporate and the residue was extracted with ether. The ether extracts were washed with brine and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residue was crystallized from hexane (20 ml) affording 3.4 g (84%) of ketone **10**: mp 150–151°; $[\alpha]^{25}\mathrm{D}$ +10° (*c* 15, $CHCl_3$); ir (KBr) 1700 (C=O), 1296, 1270, 1111, 1018 cm^{-1}; nmr ($CDCl_3$) δ 0.81; 0.88, 1.05, 1.10 (s, 3 H each).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.60; H, 11.47.

2aβ,5aβ,8α,8bβ-Tetramethyldecahydronaphtho[1,8-*bc*]furan (11).—A solution containing diol **8** (1.5 g, 6.25 mmol) and *p*-toluenesulfonic acid (100 mg) in benzene (25 ml) was heated to reflux with a water separator for 1.5 hr. The solution was cooled and washed with sodium bicarbonate solution, and the solvent was removed at reduced pressure. Distillation of the residual oil afforded 1.34 g (97%) of ether **11**: bp 100° (bath temperature) (0.5 mm); $n^{20}\mathrm{D}$ 1.5042; $[\alpha]^{25}\mathrm{D}$ +1° (neat); ir (neat) 1075, 1026, 1000, 975 cm^{-1}; nmr ($CDCl_3$) δ 0.84, 0.97, 1.05 (s, 3 H each), 0.95 (d, 3 H, J = 5.5 Hz), 3.46, 3.49 (2 H, AB pattern, J_{AB} = 8 Hz), 3.85 (d, 1 H, J = 10.5 Hz).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.17; H, 11.76.

Attempted Oxidation of Alcohol 7.—A sample of alcohol **7** (200 mg, 0.9 mmol) was dissolved in acetone (5 ml) and cooled to 5°. Standard Jones reagent (0.25 ml, 1.1 molar equiv) was added dropwise at 5°. The mixture was stirred at 5° for 10 min and at 20° for 10 min. Isopropyl alcohol (1 ml) was then added, followed by 10 ml of water. The mixture was well extracted with hexane. The orgaic extracts were washed with water and sodium bicarbonate solution, and the solvent was removed at reduced pressure. The ir and nmr spectra of the crude crystalline residue (200 mg) were identical with those of the starting alcohol **7**.

Determination of the Product Ratios from the Hydroboration of Dihydrothujopsene (2).—The hydroboration procedure as described above was repeated employing olefin **2** (1.5 g, 7.5 mmol) and 1 *M* borane in tetrahydrofuran solution (8.5 ml) for 18 hr at 25°. The same oxidative work-up procedure afforded 1.6 g of viscous oil. This oil was treated with *p*-toluenesulfonic acid (100 mg) in benzene (20 ml) at reflux with a water separator for 2 hr. The mixture was cooled and washed with sodium bicarbonate solution and the solvent was removed under reduced pressure. The residue was distilled on a microstill head, affording 1.30 g of mobile oil, bp 80–100° (bath temperature) (0.5 mm). This mixture showed three peaks by vpc analysis identified as dihydrothujopsene (**2**, 35%), the corresponding 2,3 double bond isomer (42%), and ether **11** (23%).

Ether **11** arises solely from dehydration of diol **8** and the two olefins from dehydration of tertiary alcohol **11**. The ratio of the two hydroboration products **7** and **8** is thus shown to be 77:23, respectively.

Registry No.—**2**, 34407-70-0; **5**, 34407-71-1; **6**, 34417-83-9; **7**, 34407-72-2; **8**, 34407-73-3; **10**, 34407-74-4; **11**, 34407-75-5.

Acknowledgment.—The author wishes to thank Dr. Garry Kitchens and Dr. Gary Shaffer for their helpful discussions during the course of the above investigation.

Symmetry Considerations and the Mechanism of the Hydroboration Reaction. The Nature of π Complexes

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Consideration of the orbital symmetry of the species involved in the hydroboration of olefins shows that the four-center transition states usually proposed have significant symmetry barriers. An alternate pathway involving a complex between the olefin and the borane is discussed in terms of the three-center electron-deficient bonds implied by the π-complex formalism. It is concluded on the basis of the symmetry of these three-center molecular orbitals that the conversion of such π complexes to products can be a concerted process which does not involve significant charge separation or rearrangement to a σ complex.

Despite the great synthetic utility of the hydroboration reaction, there is surprisingly little known about its mechanism. This is certainly due in part to the great complexity of the hydroboration reaction mixtures and the concomitant difficulty of quantitative kinetic measurements in such systems. In our studies of the hydroboration of methylchlorosilylalkenes[1] we found that a consideration of the orbital symmetry of the reactants and products provides a useful insight into the

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(1) P. R. Jones, J. K. Myers, and R. C. Rains, *J. Organometal. Chem.*, **34**, C9 (1972); 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract INOR 126.

pathway of the reaction and prediction of products. The path which results from these considerations involves a π complex intermediate, a species of the type often postulated in reaction mechanisms. The symmetry and nature of the three-center molecular orbitals implied by the π complex formalism and their implications with respect to reaction paths have not heretofore been discussed.

Any mechanism for the reaction between a borane and an olefin must account for several well-known facts.

(i) The reaction results in cis,anti-Markovnikov addition of the elements B–H to an olefinic double bond.[2]

(ii) The direction of addition is strongly influenced by steric effects, giving boron substitution on the least hindered carbon of the olefin.[2] However, electronic effects can occasionally overcome the steric requirements of the addition with electron-withdrawing groups on the olefin favoring substitution α to the electronegative substituent.[1–5]

(iii) The hydroboration reaction is very facile, addition usually being complete within a few minutes.[1–4] The activation energy for the reaction of BH_3 with ethylene in the gas phase has been estimated to be 2 kcal/mol.[6] However, the rate of the reaction is solvent dependent, and its half-life increases significantly in solvents with strong Lewis base character.[7] A hydrogen–deuterium kinetic isotope effect has been reported for the reaction of chloroboranes with olefins.[8,9] Pasto and coworkers have recently observed that the hydroboration of tetramethylethylene with borane in tetrahydrofuran exhibits both a hydrogen–deuterium and a boron(10)–boron(11) kinetic isotope effect.[10]

The pathways which have been proposed for the hydroboration reaction involve species ranging from the traditional four-centered transition state[2,7] between the olefin and a dissociated molecule of borane, **1**, or between the olefin and one of the bridged B–H bonds of a dimeric borane, **2**,[11] to a triangular π complex, **3**. The π complex intermediate has been proposed[12,13] in analogy to the mechanism suggested for the addition of aluminum alkyls to olefins,[14] to explain the stereochemistry of the 1-butanol-*1-d* produced by the asymmetric hydroboration of *cis*-1-butene-*d* with diisopinocamphenylborane.[13] Although arguments against intermediate **3** have been made on the basis of other stereochemical results[15] and the kinetic isotope effects which have been observed, a consideration of the molecular orbitals implied by **3** reveals it to be a highly probable intermediate for the hydroboration reaction which satisfactorily accounts for all the known facts.

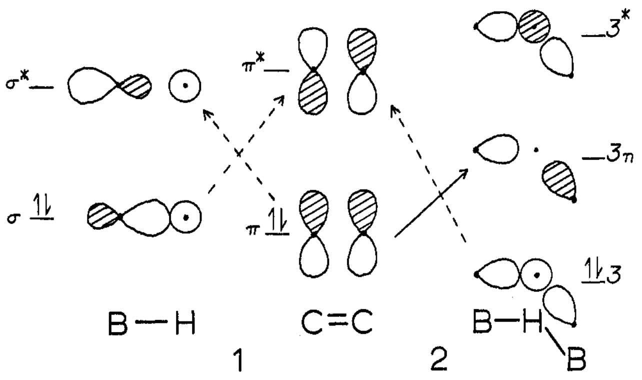
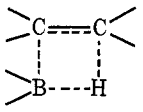


Figure 1.—Symmetry of the orbitals involved in the concerted four-center reaction of an olefin with a monomeric borane, **1**, and a bridged borane, **2**: ----, symmetry-forbidden processes; ——, symmetry-allowed process.



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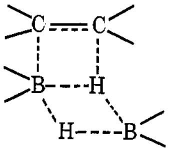

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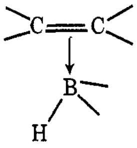

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Both transition states **1** and **2** have significant symmetry barriers which make them unlikely candidates for the extremely rapid hydroboration reaction. As is illustrated in Figure 1, transition state **1** requires concerted electron flow from the π orbital of the olefin to the σ^* orbital of the B–H bond, and from the σ B–H orbital to the π^* orbital of the olefin. The net overlap between these pairs of orbitals should be very small indeed, resulting in a symmetry restriction typical of concerted four-center additions to olefins.[16]

Similarly, transition state **2**, illustrated on the right side of Figure 1, is symmetry forbidden. It requires interaction of the three-center bonding orbital of a B–H–B bridge (3) with the π^* orbital of the olefin. There can be no net overlap of these orbitals and the concerted transition state **2** is thus ruled out.

It is useful to consider the B–H–B bridge illustrated in Figure 1 as a typical example of the molecular orbitals involved in a three-center electron-deficient bonding system. The lowest lying molecular orbital, 3, is a bonding orbital which has no nodes between the atoms and is the only occupied orbital. The 3n orbital is a nonbonding orbital with high density at the terminal atoms of the three-center system and a node at the central atom, and it is unoccupied. The highest energy orbital, 3*, is antibonding with nodes between each of the atoms, and is generally not involved in the reactions of systems containing such three-center molecular orbitals.

Nucleophilic attack on an electron-deficient three-

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(2) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962. It should be pointed out that if the polarization of the boron–hydrogen bond, $B^{\delta+}$–$H^{\delta-}$, is considered the addition is better termed Markovnikov.

(3) H. C. Brown and K. A. Keblys, *J. Amer. Chem. Soc.*, **86**, 1791 (1964); H. C. Brown and O. J. Cope, *ibid.*, **86**, 1801 (1964); H. C. Brown and R. M. Gallivan, Jr., *ibid.*, **90**, 2906 (1968); H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

(4) D. J. Pasto and Sr. R. Snyder, O. S. F., *J. Org. Chem.*, **31**, 2773, 2777 (1966); D. J. Pasto and J. Hickman, *J. Amer. Chem. Soc.*, **89**, 4445, 5608 (1967).

(5) D. Seyferth, *J. Amer. Chem. Soc.*, **81**, 1844 (1959); D. Seyferth, H. Yamazaki, and Y. Sato, *Inorg. Chem.*, **2**, 734 (1963); M. Kumada, N. Imaki, and K. Yamamoto, *J. Organometal. Chem.*, **6**, 490 (1966).

(6) T. P. Fehlner, *J. Amer. Chem. Soc.*, **93**, 6366 (1971).

(7) R. Koster, G. Griasnow, W. Larbig, and P. Binger, *Justus Liebigs Ann. Chem.*, **672**, 1 (1964).

(8) D. J. Pasto and S. Z. Kang, *J. Amer. Chem. Soc.*, **90**, 3797 (1968).

(9) G. Zweifel, *J. Organometal. Chem.*, **9**, 215 (1967).

(10) D. J. Pasto, B. Lepeska, and T. C. Cheng, *J. Amer. Chem. Soc.*, in press. Professor Pasto informed us of these very significant kinetic studies prior to the submission of his manuscript. We are indebted to him for his permission to discuss the results in this paper and for his helpful comments in this area.

(11) H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, **83**, 3417 (1961).

(12) D. Seyferth in "Progress in Inorganic Chemistry," Vol. III, F. A. Cotton, Ed., Wiley-Interscience, New York, N. Y., 1962, p 210.

(13) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, **32**, 1530 (1967).

(14) R. Robinson, *Chem. Age (London)*, **74**, 977 (1956).

(15) D. J. Pasto and F. M. Klein, *J. Org. Chem.*, **33**, 1468 (1968).

(16) R. G. Pearson, *Accounts Chem. Res.*, **4**, 152 (1971); *Chem. Eng. News*, **48**, 66 (1970).

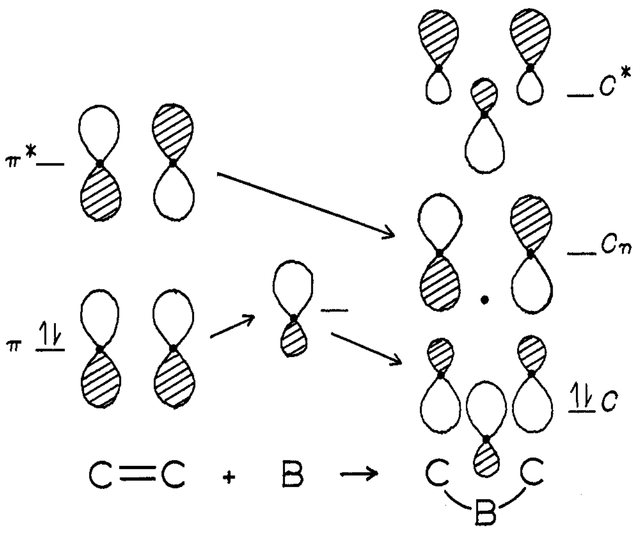
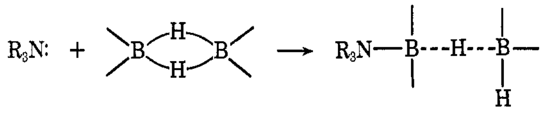


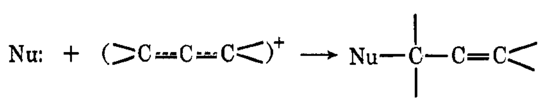
Figure 2.—Symmetry of the orbitals involved in the reaction of an olefin with a borane to form a π complex containing a C–B–C three-center bond.

center system is analagous to the process which occurs when ammonia or an amine reacts with diborane.[17] The 3n orbital is occupied by a pair of electrons from



$$R_3N{:} + {>}B\overset{H}{\underset{H}{\rangle\langle}}B{<} \longrightarrow R_3N-\overset{|}{\underset{|}{B}}\cdots H\cdots\overset{|}{\underset{|}{B}}- \quad (\text{with } H \text{ on the second } B)$$

the nucleophile, becoming a σ bond between the nucleophile and one of the terminal atoms. Orthonormalization prohibits interaction of the orbital on the attacked atom with the three-center molecular orbital. This leaves the two remaining atomic orbitals and a pair of electrons as a two-center, σ bond between the bridging atom and the other member of the three-center system. A similar description applies to nucleophilic attack on allyl cations except that in this case the three-center bond becomes a π bond between the two atoms removed from the point of attack.



$$\text{Nu:} + ({>}C\overset{\text{---}}{=}C\overset{\text{---}}{=}C{<})^+ \longrightarrow \text{Nu}-\overset{|}{\underset{|}{C}}-C=C{<}$$

For the hydroboration reaction, the symmetry of the orbitals involved in intermediate **3** is illustrated in Figure 2. The formation of this π complex may be regarded as the interaction of the olefin's π electrons with a vacant boron orbital, as is probably the case in the gas-phase reaction of borane with ethylene.[6] In solution a more reasonable path is the displacement of a solvent molecule from boron's coordination sphere by the olefin. Less likely, though possible, is a nucleophilic attack on a B–H–B bridge by the olefin similar to the process discussed above and indicated by the solid arrow in Figure 1. All of these processes are symmetry allowed. Regardless of which occurs, the result is a three-atom, two-electron bond, which is best described in terms of three-center molecular orbitals, using one p orbital from each of the carbons of the olefin and an orbital of p symmetry on boron. It is important to note that this bonding description requires *no* rehybridization of the carbon atoms of the double bond, as was suggested by Pasto's stereochemical results.[15] The lowest bonding molecular orbital (Figure 2, C) is occupied and has the same symmetry as the original π orbital of the olefin. The lowest vacant orbital of the complex, and most important in our consideration (Figure 2, Cn), has the same symmetry as the original π* orbital of the olefin, is nonbonding, and may be regarded as a "virtual" π* orbital.

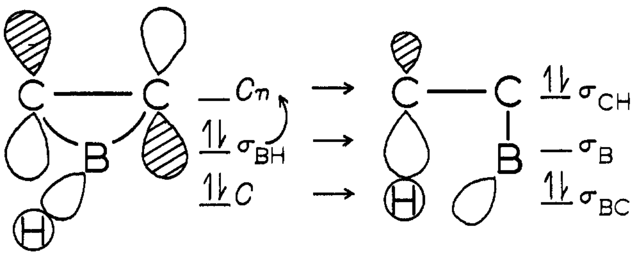
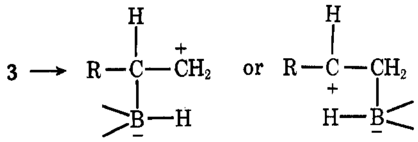


Figure 3.—Orbital symmetry and electron flow for the conversion of a C–B–C three-center system to two σ bonds.

The major arguments against the π complex intermediate, **3**, are based on the assumption that such π



$$\mathbf{3} \longrightarrow R-\overset{H}{\overset{|}{\underset{{>}\underset{-}{B}-H}{\underset{|}{C}}}}\overset{+}{-}CH_2 \quad\text{or}\quad R-\overset{H}{\overset{|}{C}}-\underset{H-\underset{-}{B}{<}}{\underset{|}{\overset{+}{C}H_2}}$$

complexes must rearrange to σ complexes in subsequent steps of the reaction. Such a rearrangement appears unlikely in view of the nearly identical internal and terminal kinetic isotope effects observed for the addition of monochloroborane to substituted styrenes;[3] the hydrogen–deuterium and boron(10)–boron(11) kinetic isotope effects;[10] and the similarity of Hammett ρ values for internal and terminal addition to styrenes.[18] Further, any significant buildup of hydridic character on the boron hydrogens would be expected to lead to reduction of groups such as chlorosilanes present in the reaction mixture. Because we observed no reduction of the silicon–chlorine bonds during the addition of borane in tetrahydrofuran to methylchlorosilylalkenes,[1] we were forced to look for a path for the hydroboration reaction consistent with the known facts about the reaction and our results.

A point which is overlooked by most chemists, but which becomes apparent when the symmetry of the orbitals involved in π complexes is considered, is that such complexes can convert to products in a symmetry-allowed *concerted* process, illustrated in Figure 3. The conversion amounts to a flow of electrons from the σ system of the moiety involved in the π complex (boron in this case) to the Cn three-center molecular orbital. As the Cn orbital is occupied and becomes a σ bond between carbon and hydrogen, the C three-center bonding orbital of the complex becomes a boron–carbon σ bond.

The concept of a three-center molecular orbital description of the bonding in a π complex applied to the hydroboration reaction accounts well for the details of this reaction. The steric requirements of the reaction are easily understood, since the complex should form

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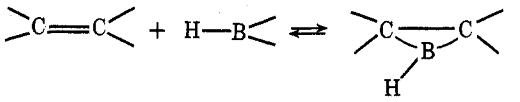
[17] R. W. Parry and S. G. Shore, *J. Amer. Chem. Soc.*, **80**, 15 (1958).

[18] J. Klein, E. Dunkelblum, and M. A. Wolff, *J. Organometal. Chem.*, **7**, 377 (1967). However, see ref 10 for a discussion of apparent discrepancies in the Hammett correlations.

on the least hindered side of the olefin. The direction of addition depends on two factors: the orientation of the remaining hydrogens on boron in the complex, and the electronic effect of other substituents on the olefin. With bulky groups on the olefin or boron one would expect the hydrogen on boron to be juxtaposed with the internal lobe of the Cn orbital of the π complex. The conversion of this intermediate to products would result in boron substitution on the least hindered carbon of the olefin. With strongly electron-withdrawing substituents on the olefin, the collapse of the complex to product should be influenced by the tendency of the electron pair in the preformed three-center bond to move toward the more electron-deficient carbon, giving boron substitution α to the electronegative group when the steric factors of the reaction permit.

In summary, we consider the hydroboration reaction as a two-step process, the first step an equilibrium resulting in the production of three-center, two-electron π complex intermediate (eq 1); the second step a rate-determining *concerted* conversion of the intermediate to products (eq 2). This mechanism satisfies the requirements of the hydroboration reaction while not involving the buildup of any significant hydridic character on the boron hydrogens. More important, the fact that olefin π complexes can convert to products by a concerted, symmetry-allowed process not involving significant charge separation in the transition state should be useful in the consideration of other reactions which involve such intermediates.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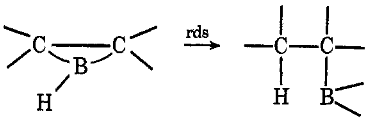

(2)

Acknowledgment.—The author expresses his thanks to the donors of the Petroleum Research Fund administered by the American Chemical Society and to the North Texas State University Faculty Research Fund for financial support of this work.

A New Synthesis of Coenzyme Q_1

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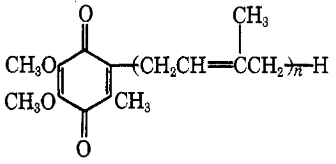
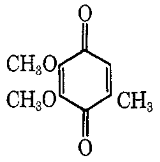
A new synthesis of coenzyme Q_1 is reported. 2,3-Dimethoxy-5-methylbenzoquinone (**2**) is converted to 6-bromo-2,3-dimethoxy-5-methylhydroquinone bis(methoxymethyl) ether (**18**), which is condensed with 1,1-dimethyl-π-allylnickel bromide (**9**) in hexamethylphosphoramide to afford 2,3-dimethoxy-5-methyl-6-(3-methyl-2-butenyl)hydroquinone bis(methoxymethyl) ether (**19**) in good yield. The hydrolysis of the condensation product **19** followed by oxidation gives coenzyme Q_1. The reaction of **9** with several other aryl halides is also reported.

Coenzyme Q_n (**1**), ubiquinone $5n$, functions in electron transfer and oxidative phosphorylation. The ten known ubiquinones, coenzyme Q_1–Q_{10}, are named according to the number of isoprene units in the side chain. Coenzymes Q_6–Q_{10} were isolated by Lester[1,2] and their structures were determined as **1**[3–5] (n = 6–10). These compounds were synthesized by Folkers, *et al.*,[3] and also by Isler and coworkers.[4,5]

In the synthesis of coenzyme Q_n there are three key steps, which include (i) a synthesis of 2,3-dimethoxy-5-methylbenzoquinone (**2**), (ii) a stereospecific synthesis of the polyprenyl alcohols **3a** or **3b**, (iii) a condensation of the aromatic nucleus **2** with the alcohols **3a** or **3b**.

All of the coenzyme Q_n synthesis reported involved the condensation of 2,3-dimethoxy-5-methylhydroquinone (**4**) with **3a** or **3b** using acid catalysts. Such condensation reactions suffer from the disadvantage that cyclization to chromanol and a cyclization of the unsaturated isoprenoid side chain often results. In order to minimize these side reactions, many kinds of catalysts ($SnCl_2$, K_2SO_4, oxalic acid, BF_3, etc.) have been used.[6] Unfortunately, these methods generally give low yields and, in addition, much labor is needed to isolate the condensation product from the complex reaction mixture. Reported here is a new method for the


1, n = 1–10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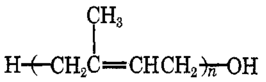
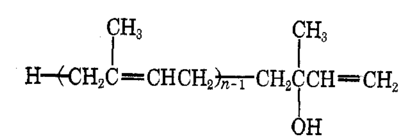

$\mathrm{H}(\mathrm{CH_2}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CHCH_2})_n\mathrm{OH}$

3a


$\mathrm{H}(\mathrm{CH_2}\overset{\mathrm{CH_3}}{\mathrm{C}}{=}\mathrm{CHCH_2})_{n-1}\mathrm{CH_2}\underset{\mathrm{OH}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH}{=}\mathrm{CH_2}$

3b

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