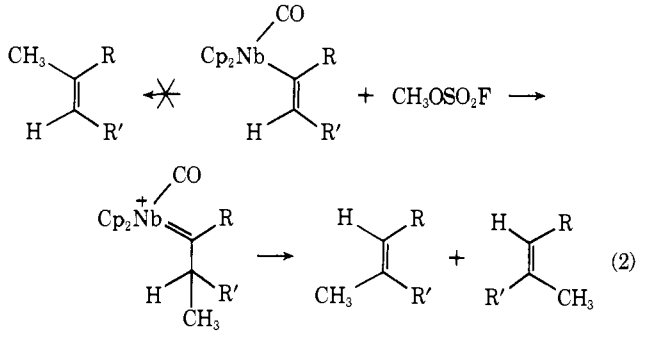
acetylene, without concomitant side reactions associated with the Nb-H group, requires that M-H insertion to give an alkenyl complex be effected prior to treatment of the organometallic species with alkylating agent. Isoelectronic hydrido(ethylene) complexes $Cp_2MH(C_2H_4)^+$ (M = Mo, W) undergo insertion to yield the ethyl complex on heating with triphenylphosphine;[8] however, prolonged treatment of **2** with excess PMe_2Ph at 110° caused no hydride insertion, and only very slow replacement of the acetylene by the phosphine was observed. In contrast, heating **2** under CO (50 psi, 75°, 15 min) caused smooth conversion to alkenyl(carbonyl) complexes **3** (Table I) which were characterized by ir (for **3a**, ν_{CO} 1900 cm^{-1}) and ^1H NMR (Table I). Apparently, the relative stability of noninserted (π-acetylene hydride) and inserted (alkenyl) forms of the Nb complexes is largely determined by the availability of electron density on Nb for back-bonding which is required to stabilize the (π-acetylene)-metal bond. Thus an electron donor ligand (PMe_2Ph) does not favor insertion whereas ligands which are electron acceptors (CO, H^+) do. For complexes of unsymmetrically substituted acetylenes, high regiospecificity for insertion is observed in which the niobium atom attaches preferentially to the vinylic carbon atom bearing the sterically smaller substituent. This insertion occurs with (C=C) cis stereochemistry.

As expected, complexes **3** react rapidly with acid to give the corresponding cis olefins. Reaction of **3c** with D_2SO_4 gives $CH_3C(D)=C(H)CH(CH_3)_2$, reinforcing the contention that protonation occurs at Nb followed by reductive elimination of olefin. Reaction of the vinylic complexes with CH_3OSO_2F is considerably slower than protonation (several hours at room temperature),[9] but methylated olefins are eventually formed. Surprisingly, however, treatment of **3c** with CH_3OSO_2F yielded none of the expected trisubstituted olefin $(CH_3)_2C=CHCH(CH_3)_2$; instead, *cis*- and *trans*-$CH_3C(H)=C(CH_3)CH(CH_3)_2$ were formed (in 75% yield based on Nb; see reaction 2). Thus alkylation proceeds



regiospecifically by attack of the electrophilic reagent on that vinylic carbon atom to which the Nb atom is *not* attached. We suggest that this unusual reaction results from an inability of the methyl group to attack at the metal center for steric reasons; instead, alkylation occurs "allylically" at the β-vinylic carbon.[10] The resulting intermediate, which may be represented as a cationic (alkylcarbene)Nb(III) complex,[11] undergoes proton migration followed by reductive elimination of the olefinic product (reaction 2).

Parallels between protonation and alkylation of low-valent transition metal complexes have previously been emphasized.[7a] As demonstrated by the contrasting results described herein, it must now be recognized that these two types of reactions may indeed proceed by *dissimilar* pathways in complexes which possess several potential sites of electrophilic attack, especially in cases where steric crowding exists at one such site.

Acknowledgments. The authors thank the National Science Foundation (GP-43026X) for generous support of this work, Hoffmann-La Roche, Inc., for providing them with elemental analysis services, and Dr. Fred N. Tebbe for helpful comments and suggestions.

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(10) In agreement with this view, $Cp_2Nb(C_2H_5)(CO)$ (prepared by carbonylation of $Cp_2NbH(C_2H_4)$[2]), which has no reactive site alternative to the metal center, is not methylated by CH_3OSO_2F.
(11) A stable (alkylcarbene)Ta(III) complex has been recently reported.[12] Furthermore, the anions formed by metalation of carbene complexes have been shown to be best represented as vinyl complexes, and these are alkylated by reagents such as CH_3OSO_2F in a reaction closely paralleling that proposed herein.[13]
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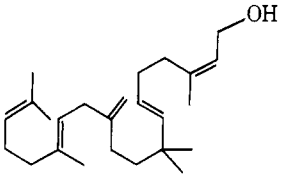
Received December 19, 1974

Sesterterpenes. I. Stereospecific Total Synthesis of Moenocinol

Sir:

The C_{25} acyclic lipid moenocinol has been obtained from the antibiotics moenomycin[1] and prasinomycin[2] by hydrolysis and shown to possess structure **1**.[2,3] This communication describes the first stereospecific synthesis of moenocinol employing nerol and geraniol as trisubstituted olefin precursors.



1

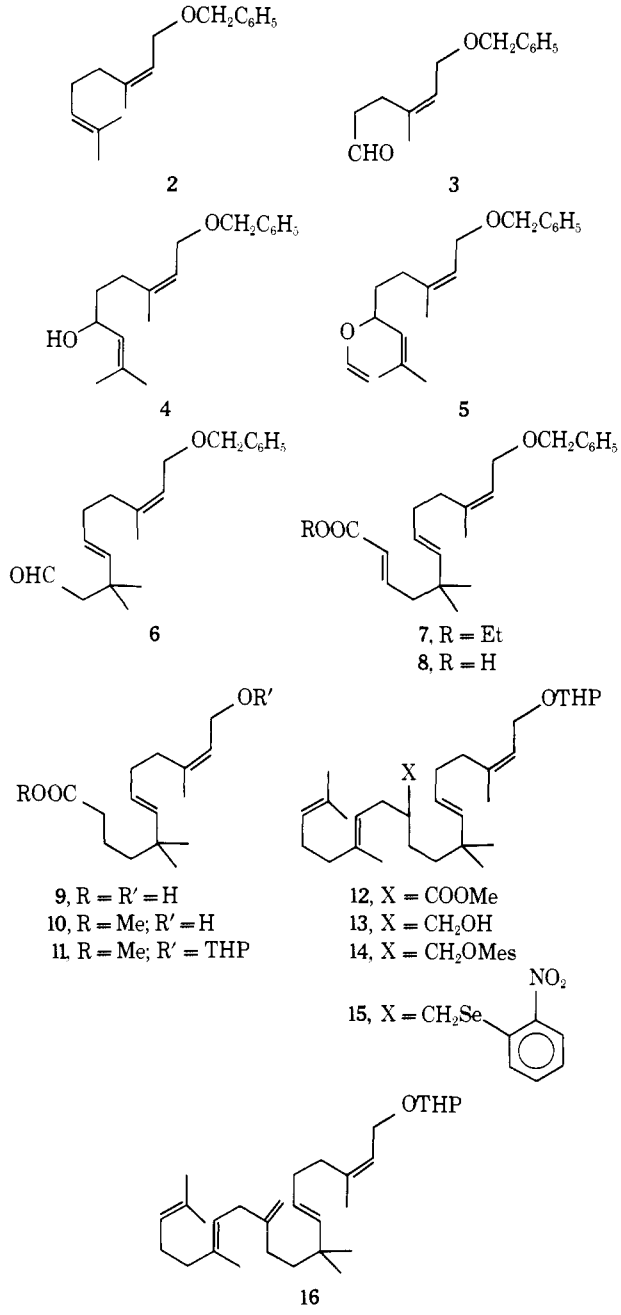
The key intermediate ester **10** was synthesized from pure nerol.[4] Ozonolysis[5] of nerol benzyl ether (**2**) (prepared from nerol (sodium hydride followed by benzyl bromide in glyme, 95%)) at −78° in methylene chloride-pyridine afforded after reduction with zinc in acetic acid, aldehyde **3** in 55% yield[6,7] (ir(neat)5.80 μ; NMR 9.65 (t, J = 1.5 Hz, 1

H)). This aldehyde was allowed to react in anhydrous ether at room temperature for 1 hr with 1-lithio-2-methyl-1-propene[8](addition at 0°). The allylic alcohol **4** was obtained in 80% yield. The NMR spectrum of **4** exhibited three singlets, each due to olefinic methyl groups at 2.58, 2.62, and 2.66 and peaks due to olefinic protons between 4.95 and 5.42 (m, 2 H). The allylic alcohol **4** was converted into vinyl ether **5** (75% yield (98% based on recovered starting material)) by equilibration[9] with ethyl vinyl ether followed by careful chromatography. When the vinyl ether was heated to reflux in xylene (3 hr) under an atmosphere of nitrogen, aldehyde **6** was generated in 99% yield and exhibited only one peak on GLC and TLC analysis. The NMR spectrum of **6** showed a singlet at 1.02 (6 H), a broad singlet at 2.66 (3 H, olefinic methyl), absorption due to olefinic protons centered at 5.36 (m, 3 H), and a triplet at 9.60 (J = 2 Hz, -CHO); the infrared spectrum exhibited peaks at 5.80 (C=O) and 10.30 (trans C=C) μ.

Elaboration of the moenocinol molecule to key intermediate **10** was completed by the following sequence: (1) Horner-Emmons reaction of aldehyde **6** with the sodio derivative of triethyl phosphonoacetate in glyme at 65° for 1.5 hr to form **7** (90% yield); (2) hydrolysis of the newly introduced ester (10% ethanolic potassium hydroxide) to the α,β-unsaturated carboxylic acid **8** (99% yield); (3) reduction (lithium-ethylamine, −78°, 1 hr) of the α,β-unsaturated acid to the saturated acid **9** (50% yield) with cleavage of the benzyl ether; and (4) esterification of **9** with ethereal diazomethane in near quantitative yield. The NMR spectrum of **10** exhibited two sharp singlets at 0.96 (6 H, C-8 methyls) and 3.58 (3 H, OMe), one broad singlet at 1.68 (3 H, olefinic methyl group), a two-proton doublet at 3.95 (J = 7.5 Hz, $-CH_2OH$), and olefinic protons centered at 5.22 (m, 3 H). The infrared spectrum of **10** showed carbonyl absorption at 5.82 μ.

Treatment of **10** with dihydropyran in methylene chloride at 0° containing tosyl acid for 1.5 hr afforded the pure tetrahydropyranyl ether **11.** Generation of the ester enolate of **11** (lithium diisopropylamide-THF, −78°) followed by addition of geranyl bromide produced a 61% yield of **12** which represents the gross skeleton of moenocinol. Conversion of the carbomethoxy function of **12** into the terminal disubstituted olefin was accomplished in the following manner: (1) reduction (lithium aluminum hydride) of ester **12** to the hydroxymethyl derivative **13** in 93% yield; (2) mesylation of **13** in pyridine at room temperature (1 hr) to afford mesylate **14** (94% crude yield); (3) displacement of the mesylate with *o*-nitrophenylselenium anion (generated from di-*o*-nitrophenyldiselenide[10] and sodium borohydride in absolute ethanol) to the selenide **15** (75% yield); and (4) elimination of the *o*-nitrophenylselenoxide[11] derived from **15** (2 equiv of 50% hydrogen peroxide in THF (3.5 hr)) with formation of the olefin **16** in 75% yield.[12] The key features of the NMR spectrum of **16** are a six proton singlet at 0.96 (C-8 methyls), a two proton doublet at 2.68 (J = 7.5 Hz, diallylic methylenes), and a broad singlet at 4.64 (terminal vinyl). Cleavage [methanol/TsOH/0° (1 hr) → rt(2 hr)] of the tetrahydropyranyl ether afforded pure moenocinol (**1**).

The NMR and infrared spectra of synthetic **1** were in complete agreement with reference spectra of natural moenocinol kindly provided by Dr. W. A. Slusarchyk. The NMR spectrum of synthetic **1** displayed a sharp singlet at 0.96 (C-8 methyls, 6 H), three singlets at 1.61 (6 H), 1.68 (3 H), and 1.73 (3 H) due to olefinic methyl groups, multiplets centered at ca. 2.1 (allylic methylene protons, 12 H) and 1.3 (methylene protons, 2 H), a two-proton broad doublet at 2.67 (J = 7 Hz, diallylic methylenes), a two-proton doublet at 4.02 (2 H, J = 7.5 Hz, $-CH_2OH$), a broad singlet due to terminal vinyl protons at 4.67 (2 H), and five olefinic protons in a complex series of peaks in the region 4.85-5.60.



2 3 4 5 6 7, R = Et 8, R = H 9, R = R' = H 10, R = Me; R' = H 11, R = Me; R' = THP 12, X = COOMe 13, X = CH_2OH 14, X = CH_2OMes 15, X = CH_2Se 16

Acknowledgment. This investigation was supported in part by a Public Health Service Research Grant (CA 13689) from the National Cancer Institute and by Eli Lilly and Company. We thank Dr. W. A. Slusarchyk (The Squibb Institute for Medical Research) for supplying us with reference spectra of natural moenocinol and Mr. F. Okuniewicz for mass spectral data. We thank Professor K. B. Sharpless for informing us of unpublished results.

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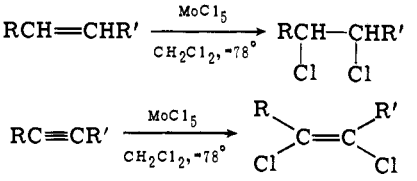
Chlorination of Alkenes and Alkynes with Molybdenum(V) Chloride[1]

Sir:

The reaction of molybdenum(V) chloride with tetrachloroethylene produces hexachloroethane in essentially quantitative yields.[2] The extension of this reaction to other olefins would, if available, constitute a potentially useful procedure for the chlorination of carbon-carbon double bonds. We wish to report that molybdenum(V) chloride reacts with vicinal disubstituted olefins and internal alkynes to produce, inter alia, dichloroalkanes and -alkenes, respectively, in fair to good yields.



In a typical experiment, a solution of cyclohexene (2.04 g, 25.0 mmol) in methylene chloride (7 ml) was added over a 15-min period to a vigorously stirred solution of molybdenum(V) chloride[3] (3.40 g, 12.0 mmol) in methylene chloride (5 ml) at −78° with the rigorous exclusions of moisture and oxygen. The resulting mixture was allowed to warm gradually to ambient temperature. After chromatography over alumina, analysis indicated the presence of *cis*-1,2-dichlorocyclohexane (68%), *trans*-1,2-dichlorocyclohexane (2%), cyclohexylcyclohexane (2%), and chlorocyclohexane (14%). Results obtained on treatment of other representative substrates are given in Table I.

This reaction sequence seems applicable to the chlorination of vicinal disubstituted olefins and internal acetylenes; in our hands, terminal, tri-, and tetrasubstituted olefins and terminal acetylenes produced poor yields of dichloro products. The use of methylene chloride or chloroform as solvents results in appreciably higher yields of dichloro products than does pentane. The principal products produced by the reaction of cyclohexene (excess) with molybdenum(V) chloride under similar conditions but in the absence of solvent are chlorocyclohexane (3%) and *cis*-1,2-dichlorocyclohexane (8%).

Table I. Reaction of $MoCl_5$ with Various Olefins and Acetylenes[a]

Olefin	Dichloride	Yield,[b] %
Cyclopentene	*cis*-1,2-Dichlorocyclopentane	66
	trans-1,2-Dichlorocyclopentane	<1
Cyclohexene	*cis*-1,2-Dichlorocyclohexane	68
	trans-1,2-Dichlorocyclohexane	<2
Bicyclo[2.2.1]heptene	*exo,cis*-2,3-Dichlorobicyclo[2.2.1]heptane	27
2-Hexene	2,3-Dichlorohexane	67
1-Hexene	1,2-Dichlorohexane	10
cis-3-Hexene	*meso*-3,4-Dichlorohexane	67
	d,l-3,4-Dichlorohexane	<1
trans-3-Hexene	*d,l*-3,4-Dichlorohexane	63
	meso-3,4-Dichlorohexane	<1
1-Methylcyclohexene	1-Methyl-1,2-dichlorocyclohexane	4
Tetramethylethylene	2,3-Dichloro-2,3-dimethylbutane	9
4-Octyne[c]	*cis*-4,5-Dichlorooct-4-ene	36
	trans-4,5-Dichlorooct-4-ene	<1
2-Pentyne[c]	*cis*-2,3-Dichloropent-2-ene	38
	trans-2,3-Dichloropent-2-ene	<1

[a] Unless otherwise indicated all additions were carried out in CH_2Cl_2 solution at −78° under an inert atmosphere of dry nitrogen. The concentration of molybdenum(V) chloride was ~1.0 *M*. [b] Yields were determined by quantitative vapor phase chromotography and are based on molybdenum(V) chloride. [c] Carried out at room temperature.

Although our understanding of the detailed course of this reaction is still incomplete, several observations permit a description of its general features. First, the products of these reactions provide convincing evidence that the resulting vicinal dichlorides do *not* arise via the ionic or free-radical pathway characteristically observed in the reaction of olefins with molecular chlorine. Specifically, the chlorination of cyclopentene and cyclohexene is essentially unaccompanied by the formation of the corresponding *trans*-1,2-dichlorocycloalkanes.[4] In addition, the treatment of norbornene yields *cis,exo*-2,3-dichloronorbornane with no evidence (<1%) of any *syn*-7-*exo*-2-dichloronorbornane, the principal dichloride obtained from the ionic chlorination of norbornene by molecular chlorine.[5] Similarly, the chlorination of *cis*- and *trans*-3-hexene proceeds stereospecifically to yield respectively *meso*- and *d,l*-3,4-dichlorohexane, again in contrast to the products produced by ionic or free-radical chlorination of these substrates.[4,6,7]

Second, other transition metal chlorides show similar reactivities as chlorinating agents. For example, the tungsten hexachloride produced moderate yields of *cis*-1,2-dichlorocyclohexane (41%) and no (<1%) *trans*-1,2-dichlorocyclohexane when treated with cyclohexene under conditions similar to those detailed above.[8,9] Such a result suggests a general reaction pathway may be common to these systems.

Finally, a similar albeit less stereoselective reaction is observed with certain transition metal bromides. Thus, for example, the addition of cyclohexene to a methylene chloride solution of what is purported to be tungsten(VI) bromide,[10] under conditions equivalent to those cited above, yields a mixture of *cis*-1,2-dibromocyclohexane (40–45%) and *trans*-1,2-dibromocyclohexane (5–10%).

Further observations relating to the mechanism of these reactions will be presented in later papers.