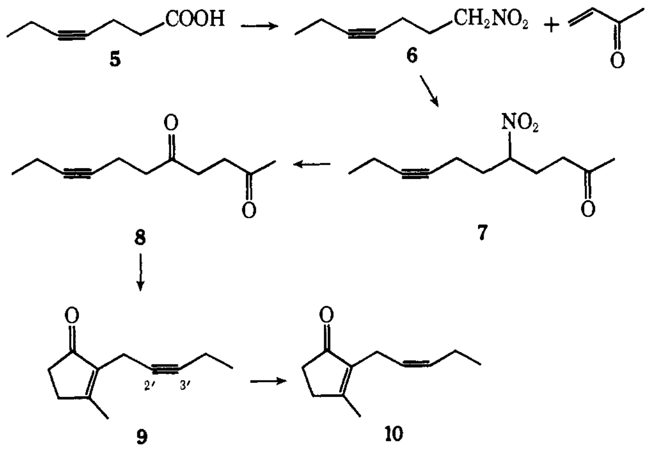
which was cyclized with 5% aqueous NaOH to the known 2′,3′-dehydrojasmone (**9**; 62% from **7**; 2,4-DNP, mp 165°; lit.[10e] 166°). Hydrogenation over Lindlar catalyst[13] gave pure *cis*-jasmone (**10**; 95%; 2,4-DNP, mp 116°; lit.[10a] 117.5°) identified by comparison (ir, nmr, uv, vpc, mass spectrum) with an authentic sample.[10h]

Scheme II



The Ti^{III} reduction of nitro compounds to ketones thus appears to be a mild, high-yield procedure which should significantly improve the usefulness of the nitro function in organic synthesis. We are continuing our investigation.

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(13) The Lindlar catalyst was purchased from Fluka, A.G.

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Stereospecific Synthesis of 2,7-Dimethyl-*trans,trans*-2,6-octadiene-1,8-dial, a Tail-to-Tail All-Trans Bifunctional Isoprenoid Synthetic Unit. A Convenient Synthesis of Squalene

Sir:

We have reported[1-3] that selenium dioxide oxidation of a *gem*-dimethyl olefin leads stereospecifically to a trans aldehyde. More recently[4] we have shown that with selenium dioxide *gem*-dimethyl olefins are oxidized stereospecifically to trans allylic alcohols and have provided an interpretation for this phenomenon. Now we report the oxidation of 2,7-dimethyl-2,6-octadiene (**2**) to 2,7-dimethyl-*trans,trans*-2,6-octadiene-1,8-dial (**3**) a bifunctionalized tail-to-tail linked isoprenoid, and the specificity involved in oxidation of allylic alcohols to α,β-unsaturated aldehydes. Also, the application of **3** to symmetrical coupling, affording a facile synthesis of all-trans squalene, and to unsymmetrical coupling is reported.

Among the methods available for the synthesis of allylic alcohols of type **5a** are a complex stereospecific procedure[5] and a stereoselective method involving an aldehyde and sodio diethyl 1-ethoxycarbonyl-1-ethanephosphonate[6-8] followed by reduction; the latter, although resulting in an undesirable mixture (cis–trans, 12:88),[8] is widely used. Our procedure gives all-trans diallylic alcohols.

The diphosphonium salt **1**[9] with butyllithium in dimethyl sulfoxide followed by acetone gave diene **2** (bp 137°) which was oxidized with selenium dioxide[1,3] to dialdehyde **3**[10] (bp 99° (0.2 mm); R_t = 9 min 45 sec) in 48% yield. The nmr of **3** showed only one singlet at δ 9.23 for the aldehydic proton,[11] establishing the dialdehyde as all trans. Reduction of dialdehyde **3** with sodium borohydride in ethanol at 0° gave diol **5a** in 85% yield and gc (homogeneous) and nmr[4,11] showed that it was all trans. Also, its ^{13}C nmr, with absorption for carbon bearing the alcoholic function only at 59.20 ppm from benzene, confirmed[4] the all-trans assignment for **5a** (diacetate, bp 105° (0.2 mm), R_t = 15 min 10 sec).

Synthesis of **5a** in a nonstereospecific fashion from phosphonium salt **1** using butyllithium in tetrahydrofuran and hydroxyacetone (as its tetrahydropyranyl ether, bp 50° (1 mm)), 6 hr at room temperature and 2 hr at reflux, gave cis enriched **5d** (62%). Ether cleavage was achieved with *p*-toluenesulfonic acid in methanol for 2.5 hr and both *cis,cis*- (δ 1.70, $C{=}CCH_3$; 3.90, CH_2OH) and *trans,trans*- (δ 1.60, $C{=}CCH_3$; 3.81, CH_2OH) **5a** were easily discernible by gc (cis,cis, R_t = 7 min 6 sec; trans,trans, R_t = 9 min 48 sec; cis,trans, broad peak in between.

The cis enriched **5a** obtained above on oxidation with MnO_2–C[12] in methylene chloride gave bis-α,β-unsaturated aldehyde **3** as a mixture of 73% cis and 27% trans aldehydes based on the nmr absorption for the aldehydic protons (δ 10.01, 9.23, respectively). However, oxidation of cis enriched **5a** with selenium dioxide gave all-trans aldehyde **3** in 66% yield. This result was confirmed by reduction of this aldehyde with sodium borohydride in ethanol at 0° to *all-trans*-**5a** in 80% yield. The stability of the aldehyde groups of **3** in the cis configuration (MnO_2–C reaction product) to the selenium dioxide reaction conditions was demonstrated by gc and nmr analysis which showed that

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(10) Satisfactory elemental analysis and mass spectral data were obtained for all new compounds. Structures assigned are consistent with ir and nmr data, the latter being obtained in carbon tetrachloride or deuteriochloroform with internal TMS (δ 0). ^{13}C nmr were obtained in deuteriochloroform and are referred to benzene.[4] Gc analyses were on 10% SE-20 (10 ft × 1/4 in.) at 150° and 60 ml/min flow rate; retention times are designated as R_t.

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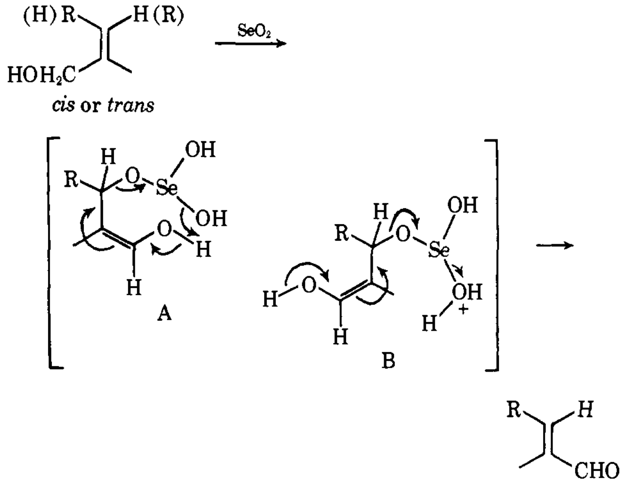
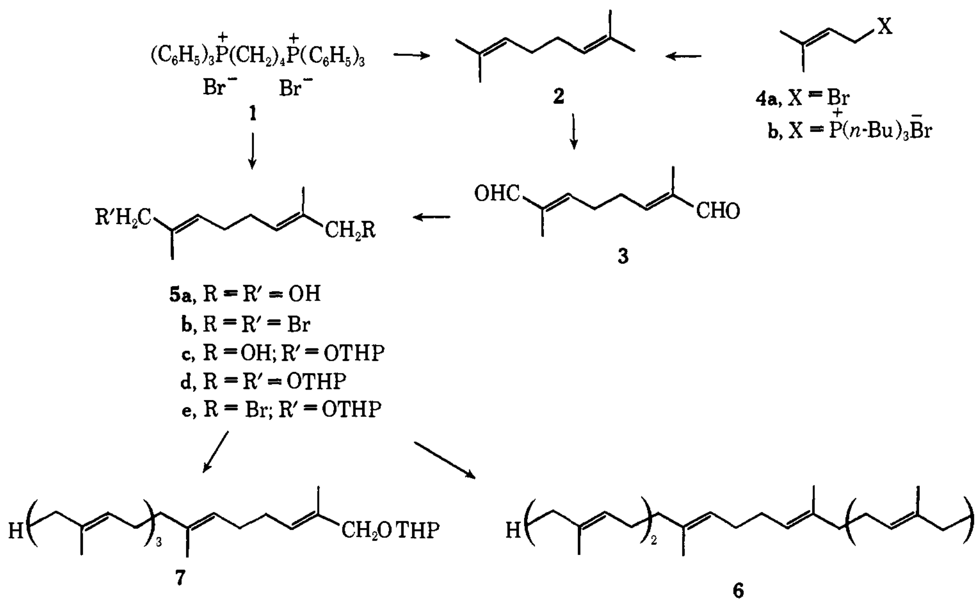
the cis groups of **3** remained unchanged.[13] This result, establishing that such cis allylic alcohols (as well as trans) are specifically oxidized to trans α,β-unsaturated aldehydes, can be explained by considering elimination of the intermediate allylic selenite ester *via* a cyclic transition state, analogous to SNi′-(rather than SN2′[14]) type solvolyses.





Elimination *via* conformers A and B, both of which should contribute if only steric factors are considered, would lead to trans and cis aldehydes, respectively. Exclusive production of trans aldehyde indicates only A is involved, probably because of ready cyclic transition-state formation. This conversion of an unacceptable cis–trans mixture of allylic alcohols to all-trans allylic alcohol *via* the trans α,β-unsaturated aldehyde in 53% yield is of considerable synthetic value.

As an example, we have applied the synthon **5a** to the synthesis of squalene (**6**). Numerous syntheses of squalene have been reported, including those employing Wittig reactions giving substantial cis–trans mixtures,[15–17] *via* the iodohydrin with trans preference,[18] the highly stereoselective chloro ketal Claisen method,[19] and by coupling of farnesyl bromide.[20–23]

Utilizing the bifunctional C_{10} unit **5a**, our approach to squalene ($C_{10} + C_{10} + C_{10}$) required a convenient coupling procedure. Those considered were alkylation of sulfonium[21] or phosphonium[22] salts followed by ethylamine–lithium reduction and use of nickel carbonyl.[24] Since the latter was reported recently[23] to give tertiary–primary as well as primary–primary coupled products, alkylation of phosphonium salts was chosen. As a further test of unidirectional coupling, the olefin **2** was prepared by this method. Phosphonium salt **4b** (mp 85°) was alkylated with 1-bromo-3-methyl-2-butene (**4a**) in tetrahydrofuran at −78° using phenyllithium as the base, and the resulting salt was reduced with lithium in methylamine and tetrahydrofuran at −78° for 1 hr and 4 hr at −23° to give **2** in 68% yield from **4a**. Gc and nmr and mass spectra showed that the product was exclusively primary–primary coupled, identical with **2** prepared previously.

Therefore, this procedure was applied to **5a**. Treatment with carbon tetrabromide and triphenylphosphine in acetonitrile gave dibromide **5b** which was used to alkylate the ylide from 2 mol of *trans*-geranyltributylphosphonium bromide, generated with phenyllithium in tetrahydrofuran at −78°. Reduction with lithium, methylamine, and tetrahydrofuran at −78° for 1.5

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[13] In 30 min, the time needed for oxidation of cis allylic alcohols of **5a** to trans aldehyde **3**, the cis aldehyde form of **3** was stable, but 30% isomerization to trans aldehyde was observed after 4 hr.

[14] In acyclic compounds, the SN2′ mechanism predicts a mixture of cis and trans compounds whose proportions will depend on conformational preference [G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4604, 4609 (1956), and references therein].

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hr and −23° for 16 hr gave a 46% yield from **5a** of all-trans squalene **6**.[25]

As an example of the use of synthon **5a** in an unsymmetrical fashion, it was treated with 1 mol of dihydropyran in the presence of *p*-toluenesulfonic acid to give **5c** (45%), together with **5d** and recovered **5a** (separated on silica gel using benzene with increasing amounts of ethyl acetate). Treatment of **5c** with carbon tetrabromide–triphenylphosphine led to **5e**. *trans,trans*-Farnesyltributylphosphonium bormide[22] was alkylated with **5e** and the product was reduced with lithium in methylamine and tetrahydrofuran (−78°, 4 hr) to give a 40% yield of **7** from **5e**. Synthesis of **7** enables unsymmetrical coupling and introduction of specific labeled fragments. It is clear that suitable manipulation also allows differential substitution of the two methylene groups of the C_{10} unit.

(25) A quantitative yield of thiourea clathrate was obtained from 6 which was identical [ir, nmr, and gc (20% FFAP, 6 ft × 1/4 in.)] with an authentic sample of *all-trans*-squalene. The cis–trans ratio of allylic methyl groups was 3:1.

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An Unusual Five-Coordinate Complex of Copper(II)

Sir:

It is well known that the nitrite anion (NO_2^-) is capable of bonding to transition metals in several different ways. It may bond through the nitrogen to give the well-known nitro complexes or through one of the oxygens to give the less common nitrito complexes. The anion may also function as a bridging ligand coordinating through the nitrogen and one of the oxygens.[1,2] Recently the nitrite anion has been shown to also be capable of acting as a bidentate ligand, coordinating through the two oxygens.[3] This last mode of coordination is by far the least common. There are, however, no reports of the nitrite anion coordinating in two different ways in the same monomeric complex. It is the purpose of this communication to report such a complex.

We have previously shown that the ligand *N,N′*-ethylenedimorpholine (EDM) ($C_{10}H_{20}N_2O_2$) has extreme steric requirements.[4-6] During the course of our investigation of the coordination chemistry of this ligand, we prepared the Co(II), Ni(II), and Cu(II) nitrite complexes of EDM. It was anticipated that all three complexes would have an octahedral coordination geometry obtained from two bidentate nitrite groups and one bidentate EDM ligand, as has been found with other sterically demanding nitrogen ligands, tetramethylethylenediamine, quinoline, and α-picoline.[3]

All three complexes were prepared according to the general method of Goodgame and Hitchman and had the stoichiometry $M(NO_2)_2(EDM)$.[3,7] The cobalt and nickel complexes were shown to be isomorphous through their X-ray powder patterns. Both of the complexes are nonelectrolytes in methylene chloride solution. The electronic spectra of both complexes can be readily interpreted on the basis of an octahedral model. The nickel complex has absorption bands at 9250 cm^{-1} (ϵ 7.5), 15,150 (ϵ 14), and 25,000 (ϵ 42). The cobalt complex has absorptions at 8350 cm^{-1} (ϵ 16), 18250 (ϵ 81), and 20,200 (ϵ 65). The magnetic moments of the complexes, determined by the method of Evans, are also consistent with an octahedral coordination geometry.[8] That of the nickel complex is 3.26 BM while that of the cobalt complex is 4.67 BM. This latter value is somewhat lower than is normally found for octahedral cobalt(II) complexes, but several authors have reported magnetic moments in this range.[9] The infrared spectra of the two complexes show nitrite absorptions at 850, 1175, and 1300 cm^{-1}. These infrared absorptions are compatible only with nitrite acting as a bidentate ligand bonding through the two oxygens.[3,10] Thus, cobalt and nickel nitrite complexes of EDM have been assigned the anticipated octahedral coordination geometry.

The copper complex, however, is not isomorphous with the cobalt and nickel complexes. It is a nonconducting monomer in methylene chloride and chloroform solutions. The magnetic moment of 1.95 BM at 305°K is in the range that is normally found for Cu(II) complexes, where there are no magnetic interactions between neighboring ions. The electronic spectrum consists of one band in the near-infrared and visible regions at 14,100 cm^{-1} (ϵ 197). This band is asymmetric to lower energies. It is very probable that there is more than one absorption band within this envelope, but it is not possible to resolve them. The infrared spectrum of the complex has nitrite absorptions at 1375, 1350, 1290, and 1175 cm^{-1}. There are also shoulders at about 860 and 830 cm^{-1} which are probably due to nitrite absorptions, but they cannot be assigned with certainty because they appear as shoulders on more intense ligand bands. The bands at 1290, 1175, and 860 cm^{-1} are the same as those found for nitrite in a bidentate environment. The appearance of NO_2^- absorptions at 1375, 1350, and 830 cm^{-1} indicates that nitrite is also functioning in a manner other than as a bidentate ligand in the complex. The positions of these "extra bands" is most compatible with nitrite behaving as a monodentate ligand coordinating through nitrogen.[10]

Thus, with one bidentate nitrite and one monodentate nitrite as well as one EDM molecule in the coordina-

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(6) A picture of the ligand may be found in either ref 4 or 5.

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