Tetrahedron Vol. 41, No. 24, pp. 5741 to 5746, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00

CARBON–CARBON BOND FORMATION EMPLOYING ORGANOIRON REAGENTS

SYNTHESES OF LAVANDULOL AND RED SCALE PHEROMONE

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(*Received in USA* 24 *May* 1984)

Abstract—Some aspects of the chemistry of (η^1-allyl)Fp complexes [Fp = η^5-$C_5H_5Fe(CO)_2$] are briefly reviewed, especially the means available for their elaboration. The range of electrophiles which react with (η^1-allyl)Fp complexes has been enlarged to include allyl iodides. Two examples of this reaction are given, the first leading to lavandulol **9**, the second providing a short synthesis of the red scale pheromone (*R,S*-**15**).

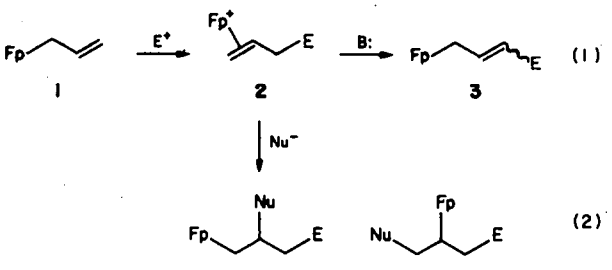
INTRODUCTION

Among η^1-allylmetal compounds with significant metal–carbon covalent character, which have found use in organic synthesis, the (η^1-allyl)Fp complexes [Fp = $C_5H_5Fe(CO)_2$] are unique in their ability to transit reversibly between monohapto and dihapto bonding modes. The latter bonding state, accessible through electrophilic attack on an allyliron complex (Scheme 1), owes its stability to the presence of high lying, nonbonding d-orbital electrons on the metal, which by backbonding to the π^* ligand orbital provide stabilization not available to the structurally related allylstannane or allylsilanes.[1] So powerful is the acidifying effect of the cationic olefin-iron center upon allylic protons in these complexes, that deprotonation, with consequent reversion to a η^1-allyliron complex, may be achieved rapidly and completely even in the presence of a base as weak as triethylamine.[2] Moreover, the cationic Fp(olefin) complexes are versatile acceptors of both heteroatom[3] and carbon nucleophiles,[4] the latter ranging from unstabilized carbanions to β-dicarbonyl enolates. These transformations provide some of the essential features of the rich and synthetically useful chemistry of Fp complexes.

While (η^1-allyl)Fp complexes are generally liquids or low melting solids, the olefin complexes, as the BF_4 or PF_6 salts, are invariably solids.[5] Both the neutral organoiron compounds and the salts may be handled in air without decomposition, but in solution, and especially during chromatography, the neutral allyliron compounds are best handled in an inert atmosphere to avoid decomposition. Because of their yellow to amber color the (η^1-allyl)Fp complexes are especially suitable subjects for chromatographic analysis and purification.

While allylsilanes[6] and stannanes[7] are commonly prepared by alkylation of the metal halide, with organolithio or Grignard reagents, the method has been less frequently used with FpX compounds. Since the alkali metal salts of the Fp anion are readily preparable[8] and the anion is relatively stable but highly nucleophilic, metallation of an organic substrate is the more common method. Since products of electron transfer[9] may complicate these metallation reactions, it is advantageous to use allyl chlorides or tosylates as substrates, rather than bromides. Tertiary allylic substrates, have not been examined, but both primary and secondary allylic chlorides and tosylates have been entered in metallation reactions, generally with little competition from elimination reactions. Allylic rearrangement is however the rule. Thus metallation of 3-chloro or 3-tosyloxyalkenes gives exclusively the thermodynamically more stable product having a 1°-metal–carbon bond.[10] These products may be formed either directly through an S_N2' process or by rearrangement of the initial product through a radical chain mechanism.[11]

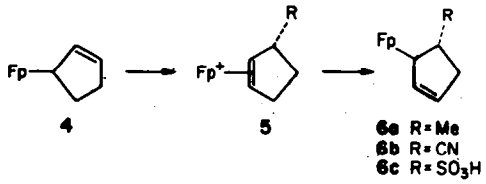
The organometallic starting material, Fp_2, is commercially available,[12] but can alternatively be prepared with comparative ease on a hundred gram scale or larger from inexpensive dicyclopentadiene and iron carbonyl.[8b] The material is readily storable for use as needed. In our own laboratory, THF solutions of NaFp are prepared by reduction of the dimer with sodium amalgam, or with sodium in the



Scheme 1.

presence of benzophenone. These solutions may be kept for several days, but are more generally used immediately.

Scheme 1 expresses the general sequences by which simple (η^1-allyl)Fp complexes may be elaborated, through electrophilic addition, followed by either deprotonation or nucleophilic addition. All of these processes occur with a high degree of stereospecificity *trans* to the activating Fp group. Thus, methylation of **4** with trimethoxonium tetrafluoroborate yields the Fp(olefin) cation **5a**, which is deprotonated by triethylamine to give **6a** exclusively. This stereoselectronic control is exerted even in the presence of the countervailing activating effect of groups such as CN or SO_3H as in **5b** and **5c**, which yield **6b** and **6c** on deprotonation.



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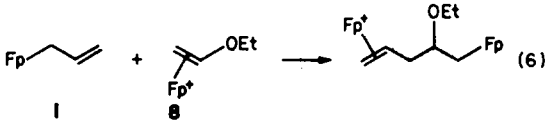
The further elaboration of **2** through nucleophilic addition finds its expression not only in intermolecular reactions, as depicted in Scheme 1, but may also be carried out intramolecularly. Thus, in the presence of a suitably chosen uncharged electrophile, complex **1** may be made to function as a C_3, 1,3-dipole equivalent. Some examples of this mode of reaction are provided by its reaction with activated isocyanates,[5] or tetracyanoethylene,[5] and with cycloalkenes[13] in the presence of aluminum bromide. These reactions give γ-lactams, tetracyanocyclopentanes and cyclopentane annulated cycloalkanones respectively (Scheme 2).

RESULTS AND DISCUSSION

The electrophiles which react with **1** and its analogs correspond closely to those which enter into similar reactions with allylsilanes[6] and allylstananes.[16] We have now sought to extend these transformations to include reaction partners not normally viewed as electrophilic reagents. The present paper describes some initial results obtained in the reactions of (η^1-allyl)Fp reagents with allyl halides. We were led to consider the possibility of effecting such condensations based on the



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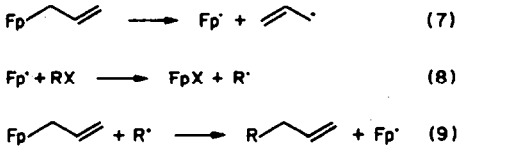
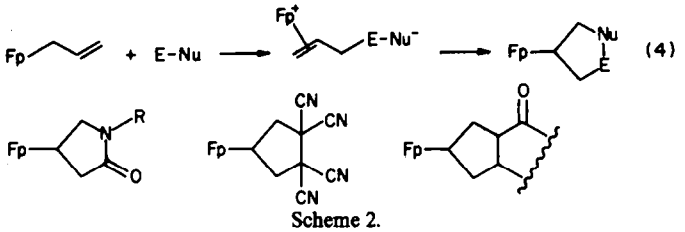
apparent high reactivity of (η^1-allyl)Fp complexes as nucleophiles. Thus, **1** condenses rapidly and cleanly with the mildly electrophilic vinyl ether complex **8**[17] ($t_{1/2}$ at 0° = 3 min), while allyltrimethylsilane is unreactive at room temperature.

An apparently related condensation of (η^1-allyl)Fp with α-haloketones and esters, and with bromotrihalomethanes has recently been reported by Lee and Giering.[18] But evidence was provided that these reactions proceed by a radical chain process initiated by Fp radicals (Eqs 7–9). This mechanism is closely related to that shown to operate in the photochemically



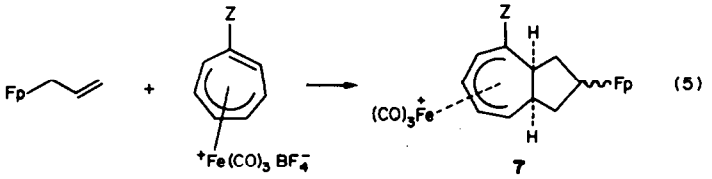
initiated substitution of CO by phosphite in (η^1-allyl)Fp complexes[19] and in the 1,3-sigmatropic rearrangements of these substances.[11]



Scheme 2.

Tropyliumiron tricarbonyl and its oxygenated derivatives also function as ambiphilic reaction partners with **1**, providing facile entry into a series of hydroazulene complexes **7**, which may be further elaborated (Eq. 5).[14] Lastly, we note that **1** and its acyclic and cyclic analogs represent only one structural form of a much larger class of Fp complexes, encompassing (η^1-propargyl)Fp and (η^1-allenyl)Fp complexes as well, all of which have similar chemistry.[15]

We chose as our initial target the relatively simple, irregular monoterpene, lavandulol **9**. While early syntheses of this substance yielded mixtures of isomeric products, more recent work has provided relatively efficient syntheses of the substance. Bertrand *et al.*[20] reported the preparation of ethyl lavandulate by conjugate addition of lithium dimethylcuprate to ethyl 2,3-butadienoate and coupling of the resulting enolate with prenyl bromide. Reduction of the product ester gave **9** in 50% overall yield. A related approach



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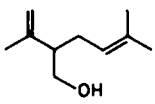
Z=H, OSiMe3, OB(n-Bu)2

involving α-alkylation of enolates derived from senecioic acid amides with prenyl bromide, followed by two step reduction of the amide has also been described



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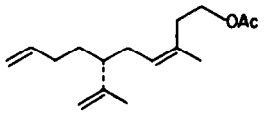
by Oakleaf *et al.*[21] Finally, Julia *et al.*[22] have examined the self condensation of prenyl acetate in the presence of lithium perchlorate, and report moderate yields of lavandulol acetate.

The present synthesis makes use of (isobutenyl)Fp **10** as starting material. This substance, readily available in high yield by NaFp metallation of isobutenyl chloride,[5] was transformed by alkylation with dioxolenium tetrafluoroborate, followed by deprotonation with triethylamine to the functionalized (η^1-allyl)Fp complex **12**. This two step sequence is conveniently carried out without isolation of the intermediate olefin complex **11**, is complete at −20° within 2 hr and gives the functionalized C_5-synthon, as a mixture of geometrical isomers, in essentially quantitative yield.

proposed for (η^1-allyl)Fp and α-halocarbonyl compounds (Eqs 7–9) does not appear to be operative here, since the coupling of **12** with prenyl bromide could not be initiated photochemically in the presence of Fp_2 or thermally in the presence of AIBN and n-Bu_3SnH. The initial product of ionic coupling **14** would be expected to suffer rapid demetallation through formation of FpI, which is a principal product of the condensation reaction.

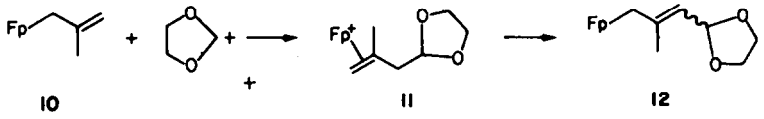
A more complex and interesting synthetic target is provided by one of the California red scale sex pheromones **15**.[24] This compound has been the subject of three earlier syntheses. In the first of these, both enantiomers were prepared from *S*- or *R*-carvone as a



15

mixture of *Z*- and *E*-isomers.[25] Bioassays of the isomers, separated by GC, showed that only the *R,Z*-isomer **15** was active.

Somewhat shorter routes to racemic mixtures of the



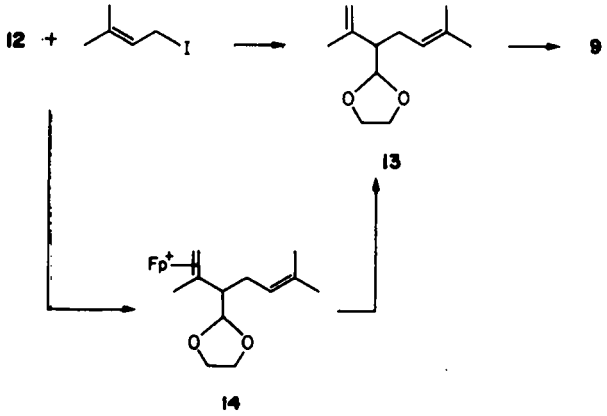
10 11 12

required *Z*-isomer have more recently been reported by Cooke and Burman[26] and by Still and Mitra.[27] The present synthesis provides a short, convergent route to the pheromone, which requires no manipulation of oxidation states or protective groups.

The starting diene **16** is commercially available, but may alternatively be prepared in good yield by the condensation of prenyl bromide and tetraallyltin in the presence of zinc chloride and a Pd(II) catalyst.[28] Conversion to the allylic chloride, with hypochlorous acid, following the procedure of Wolinsky,[29] and thence metallation with NaFp, afforded diene **18** (48%)

It is of interest to note that **11** undergoes allylic deprotonation exclusively at the methylene carbon atom, while the closely related dimethoxy acetal, derived by reaction of **10** with dimethoxycarbenium ion, gives a mixture of products resulting from deprotonation at both methyl and methylene centers.

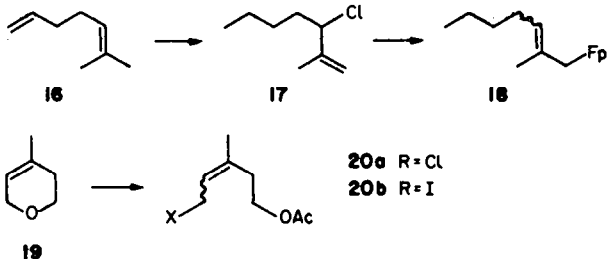
Condensation of **12** with prenyl iodide was observed to occur in acetonitrile solution over a period of several days to give lavandulal ethylene acetal **13** in 30% yield. Acid hydrolysis and reduction with sodium borohydride gave lavandulol, confirming the structure of **13**.[23]



The mechanism of the condensation reaction is, we believe, best depicted in terms of an ionic process, possibly initiated by ionization of the iodide and attack of the solvated cation on the activated acetal **12**. However, a more complex set of steps initiated by single electron transfer from **12** to prenyl iodide cannot be excluded. A radical chain process such as has been

as a mixture of *Z*- and *E*-isomers. The precise mode by which nucleophillic metallation of **17** (S_N2 or S_N2') is not consequential to the ultimate product structure, since as we have earlier noted secondary (η^1-allyl)Fp compounds rearrange spontaneously to primary isomers, if this is a structural option.[5,10]

The second component is assembled in two steps



from the commercially available dihydropyran, **19**,[30] by ring opening with acetyl chloride in the presence of $K[PtCl_3(C_2H_4)]$[31] catalyst to **20**, following a procedure recently reported by Fitch *et al.*[32] These investigators reported the opening of tetrahydrofuran and tetrahydropyrane rings using the ether in large excess, as solvent. But we find that the reaction of **19** goes well when carried out at 4° in toluene solution, and affords **20a** as a 1 : 1 mixture of *Z*- and *E*-isomers in 73% yield.

The mechanism of this reaction has not been examined, but a sequence involving cleavage of the ether ring in **19**, promoted by coordination of oxygen to Pt(II) seems likely, since the regiospecificity observed for the reaction here and by Fitch *et al.*[32] suggests substantial ionic character in the C—O bond cleavage step. Acylation of the resulting alkoxide complex could occur either directly or stepwise through oxidative addition of acid chloride to the complex, followed by reductive elimination of ester. A variant of this mechanism has been proposed for the very similar acylative opening of cyclic ethers, catalyzed by Pd(II) complexes in the presence of trialkyltin halides.[33]

Conversion of the chloro-acetate **20a** to the more reactive iodo-acetate **20b** was effected with sodium iodide in acetone. The reaction of this substance with **18**, carried out at room temperature in nitromethane solution, proceeded slowly over several days and gave racemic **15** in 42% yield. The product was shown to be identical by comparison of its ^{1}H- and ^{13}C-NMR spectra with published data.[26] Surprisingly, although **20b** is a 1 : 1 mixture of *E*- and *Z*-isomers, only the latter condenses with **18**. GC analysis of the product fails to show any detectable amount (less than 1%) of the *E*-isomer. The higher reactivity of the *Z*-isomer is probably due to anchimeric assistance to ionization provided by the acetoxy group.[34] Finally, **20b** recovered from the condensation reactions shows it to be a 1 : 1 mixture of *Z*- and *E*-isomers, suggesting that isomerization is competitive with condensation of the *Z*-isomer.

$$18 + 20b \rightarrow R,S\text{-}15$$

CONCLUSION

The scope of the observed coupling process remains to be defined. The nucleophilic character of the olefin center in (η^1-allyl)Fp complexes is certainly not great, and we are probably at the borderline of effective reactivity for such complexes in these reactions. However, enhancement in their nucleophilic reactivity could be achieved, at some cost to synthetic simplicity, by replacement of carbonyl ligands in the Fp group with phosphine or phosphite ligands.[35] Alternatively the reactivity of the electrophile partner might be increased by the use of triflates. Finally, the possibility of anionic catalysis and the effect of solvent has not as yet been examined.

EXPERIMENTAL

General

Solvents were routinely dried by standard procedures, degassed by passing dry N_2 through them and stored under N_2. All reactions and subsequent manipulations of organometallic compounds were performed under an argon atmosphere.

IR spectra were recorded on Perkin–Elmer 457 or 683 spectrophotometers in CH_2Cl_2 soln. ^{1}H-NMR spectra were obtained with a Perkin–Elmer R-32 spectrometer (NSF GU 3852), a Varian EM-390 spectrometer (NIH GM 20168), or a homebuilt 500 MHz spectrometer (NIH GM 20168). ^{13}C-NMR were determined at 22.64 MHz on a Bruker WH-90 spectrometer (NSF GU 3852, GP 37156) and were obtained with broad band decoupling. Chemical shifts were referenced to the center line of $CDCl_3$ (76.9 ppm). Mass spectra were recorded on a Hewlett–Packard GC/MS system, model 5985.

Elemental analyses were determined by Galbraith Laboratories, Knoxville, TN.

Preparation of 3-*chloro*-2-*methyl*-1,6-*heptadiene* (**17**)

To 4.41 g (31 mmol) of 6-methyl-1,5-heptadiene (purchased from Wiley Chemical Company) in a mixture of 120 ml of CH_2Cl_2 and 30 ml of water was added 12.26 g of $Ca(OCl)_2$ (70%, 60 mmol) all at once. The mixture was then vigorously stirred and small chunks of dry ice were added periodically. The flask was firmly capped with a rubber septum, using a syringe needle as a vent, and the mixture was stirred for 4 hr at ambient temp. Solids were then filtered off and washed with CH_2Cl_2. The organic soln was separated, and the aqueous layer was extracted with an additional 50 ml of CH_2Cl_2. The combined organic soln was dried over $MgSO_4$ and then stripped to dryness. The residual oil was vacuum distilled at 62°/38 mm to give 4.24 g (73%) of product as a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 6.0–5.5 (m, 1H, CH=), 5.2–4.8 (m, 4H, CH_2=), 4.35 (t, 1H, J = 6.9 Hz, CHCl), 1.86 (s, 3H, CH_3), 2.3–1.5 (m, 4H, CH_2). (Found : C, 66.24 ; H, 9.20. Calc for $C_8H_{13}Cl$: C, 66.43 ; H, 9.06%.)

Preparation of Z,E - 1 - *Fp* - 2 - *methyl* - 2,6 - *heptadiene* (**18**)

A soln of 20 mmol of NaFp in 130 ml of dimethoxyethane was prepared by reduction of Fp_2 with Na/Hg in solvent distilled from Na. The DME soln was cooled to 0° and 2.56 ml of 3-chloro-2-methyl-1,6-heptadiene was rapidly added via syringe. The cold bath was removed, and the mixture was stirred at ambient temp for 2.5 hr. Solvent was removed *in vacuo* and the residue was taken up into an argon deaerated mixture of 100 ml of water and 100 ml of ether. The organic layer was separated, and the aqueous layer was extracted with 50 ml of ether. The combined organic extracts were washed with 100 ml of water, dried over $MgSO_4$, filtered through celite and solvent was then removed *in vacuo* to give 4.6 g of crude product. Column chromatography (B III alumina, 10% ether in petroleum ether) gave, upon collection of the yellow band, 3.09 g of product as a red oil (57%). ^{1}H-NMR analysis indicates

that the product is a 3:2 mixture of geometric isomers. IR (CH_2Cl_2): 1998, 1947 cm^{-1}. ^1H-NMR (CS_2): δ 6.0–5.5 (m, 1H, CH=), 5.2–4.7 (m, 3H, vinyl), 4.67, 4.58 (2s, 5H, Cp), 2.16, 2.08 (2s, 2H, $FpCH_2$), 2.1–1.9 (m, 4H, CH_2), 1.68, 1.63 (2s, 3H, CH_3).

Preparation of 1 - *chloro* - 3 - *methyl* - 5 - *acetoxy* - 2 - *pentene* (**20a**)

To a 50 ml toluene soln of Zeise's salt (35.4 mg, 0.096 mmol) under argon at 0° was added 4.3 ml (40 mmol) of 5,6-dihydro-4-methyl-2H-pyran (Aldrich Chemical Company). Acetyl chloride (2.84 ml, 38 mmol) was then added via syringe and the mixture was then stirred in a 4° cold room for 20.5 hr, during which time the soln turned light brown in color. The reaction was quenched with 50 ml of satd $NaHCO_3$ aq and the organic phase separated and washed again with satd $NaHCO_3$ aq. The combined aqueous washings were extracted with 20 ml of toluene and the combined organic soln was dried over $MgSO_4$, filtered and stripped to dryness *in vacuo*. The crude product was then distilled in a kugelrohr at 105°/0.1 mm to give 5.18 g of product (75%) as a clear liquid. ^{13}C- and ^1H-NMR spectra indicate that **20a** is a 1:1 mixture of *Z*- and *E*-isomers. IR (CH_2Cl_2): 3058, 2973, 1738, 1666, 1450 cm^{-1}. ^1H-NMR ($CDCl_3$): δ 5.7–5.35 (m, 1H, CH=), 4.25–4.0 (m, 4H, CH_2Cl, CH_2OAc), 2.39 (dd, 2H, CH_2), 2.09 (s, 3H, CH_3CO), 1.73, 1.79 (2s, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.6, 170.2 (CO), 138.2, 137.8 (C=), 123.6, 122.6 (CH=), 62.0, 61.8 (CH_2OAc), 40.3 (CH_2Cl), 38.2 (CH_2C=, *E*-isomer), 30.9 (CH_2C=, *Z*-isomer), 23.3 (vinyl CH_3, *Z*-isomer), 15.9 (vinyl CH_3, *E*-isomer), 20.8 ($OCOCH_3$). (Found: C, 54.64; H, 7.45. Calc for $C_8H_{13}ClO_2$: C, 54.40; H, 7.42%.)

Preparation of (R,S) - Z - 3 - *methyl* - 6 - *isopropenyl* - 3,9 - *decadienyl acetate* (R,S - **15**)

The chloroacetate **20a** (468 mg, 2.65 mmol) was added to a soln of 400 mg of NaI (2.67 mmol) in 10 ml of acetone at 0°. The cold bath was removed and the clear soln became a yellow suspension after 1 hr at ambient temp. The mixture was filtered through celite to remove NaCl and solvent was removed *in vacuo*. The residue was taken up in 10 ml of nitromethane and added via cannula to a stirred soln of 656 mg (2.29 mmol) of the Fp-diene complex **18** dissolved in 10 ml of nitromethane. The soln was stirred at ambient temp for 4 days, during which time the soln became very dark green in color (FpI). Solvent was removed *in vacuo*, and the residue was extracted into petroleum ether–ether (10:1). The soln was then flash chromatographed using the same solvent system and 10 ml fractions were collected from the beginning of the yellow band (ferrocene). Fraction 8 through 12 were pure pheromone (178 mg) while fractions 13 through 20 (89 mg) were rechromatographed to give 63 mg of additional product. Total yield 241 mg (42%). IR (CH_2Cl_2): 3055, 2979, 2930, 2875, 1733, 1644, 1450, 1423 cm^{-1}. ^1H-NMR ($CDCl_3$, 500 MHz): δ 5.87–5.72 (m, 1H, H-4 or 9), 5.117 (t, 1H, J = 5.5 Hz, H-4 or 9), 4.964 (d, 1H, J = 16 Hz, *trans* H-10), 4.908 (d, 1H, J = 10.0 Hz, *cis* H-10), 4.732 (s, 1H, isopropenyl vinyl), 4.653 (s, 1H, isopropenyl vinyl), 4.099 (t, 2H, J = 7.2 Hz, H-1), 2.285 (t, 2H, J = 7.2 Hz, H-2), 2.024 (s, 3H, acetyl), 2.15–1.87 (m, 5H, H-5, 6, 8), 1.628 (br s, 3H, C-3 vinyl CH_3), 1.609 (s, 3H, isopropenyl vinyl CH_3), 1.50–1.37 (m, 2H, H-7). ^{13}C-NMR ($CDCl_3$): δ 170.7 (CO), 147.0 (isopropenyl-C=), 138.7 (C-3), 131.1 (C-9), 126.3 (C-4) 114.0 (C-10), 111.3 (isopropenyl H_2C=), 62.5 (C-1), 47.0 (C-6), 32.1, 31.9, 31.5, 31.2 (C-2, 5, 7, 8), 23.4 (C-3 Me), 20.8 (acetate Me), 18.4 (isopropenyl Me). This material showed identical retention time with that of the more mobile component from a sample of (*Z,E*)-**15** kindly provided by Dr R. Anderson of Zoecon Corp. (GE XF-1150 column, 10% on chromosorb P, column temp 150°).

When 2.2 equivalents of iodoacetate **20b** was used in this reaction, the same yield was obtained, and a proton NMR spectrum of recovered starting material showed a *Z*:*E* ratio of 1:1.

Preparation of 1 - *iodo* - 3 - *methyl* - 5 - *acetoxy* - 2 - *pentene* (**20b**)

The chloroacetate **20a** (177 mg, 1.0 mmol) was added dropwise via syringe to a soln of 150 mg (1.0 mmol) of NaI in 10 ml of acetone at 0°. The cold bath was removed and the mixture was stirred at ambient temp for 50 min. TLC analysis (cyclohexane–EtOAc, 6:1) showed that the reaction was complete. Solvent was removed *in vacuo* and the residue was taken up in nitromethane and centrifuged. The supernatant was drawn off via pipette and solvent was removed *in vacuo*. After vacuum drying, 287 mg of dark yellow oil was obtained (100%).

Preparation of 2 - *isopropenyl* - 5 - *methyl* - 4 - *hexenal ethylene glycol acetal* (**13**)

To a soln of 517 mg of NaI (3.5 mmol) in 5 ml of acetone at 0° was added dropwise 0.37 ml (1.0 equiv) of prenyl bromide. NaCl immediately precipitated. The cold bath was removed and the mixture was stirred for 10 min. The mixture was then filtered through celite and the solid cake was washed with acetone. Solvent was removed *in vacuo* and the residue was taken up in 10 ml of acetonitrile. This was added to a soln of 1.06 g of 3-Fp-1-(1,3-dioxolyl)-2-methylpropene in 15 ml of acetonitrile. The mixture was stirred at ambient temp for 4 days, during which time the mixture turned dark green, indicating the formation of FpI. Solvent was removed *in vacuo* and the residue was taken up in petroleum ether–ether (8:1) and flash chromatographed in the same solvent system. Collection of 10 ml fractions began at the beginning of the yellow, ferrocene band. Fractions 10–15 inclusive were combined to give 219 mg (30%) of product as a clear oil. ^1H-NMR ($CDCl_3$): δ 5.1–4.8 (m, 1H, CH=), 4.90 (m, 1H, CHO_2), 4.88 (s, 1H, CH_2=), 4.80 (s, 1H, CH_2=), 4.0–3.7 (m, 4H, OCH_2CH_2O), 2.4–2.0 (m, 3H, allylic CH), 1.78, 1.72, 1.65 (3s, 9H, CH_3).

Preparation of 3 - *Fp* - 1 - (1,3 - *dioxolyl*) - 2 - *methylpropene* (**12**)

Dioxolenium tetrafluoroborate (3.81 g, 23.8 mmol) was suspended in 50 ml of CH_2Cl_2 and cooled to −23°. A soln of 5.47 g of (η^1-isobutenyl)Fp (23.5 mmol) dissolved in 10 ml of CH_2Cl_2 and cooled to −23° was added to this mixture by cannula. After stirring for 1 hr at this temp, 1 equiv of Et_3N was added to the reaction, and the mixture was allowed to stir at −23° for an additional hour, then allowed to come to room temp. Ether was added to the mixture and this was filtered through celite. Solvent was removed *in vacuo* leaving the product as a yellow oil (7.0 g, 97%); ^1H-NMR (CS_2): δ 4.7–5.5 (m, 2H, CH=, OCHO), 4.65, 4.61 (2s, 5H, Cp), 3.7–4.0 (m, 4H, OCH_2), 1.98, 2.02 (2s, 2H, CH_2), 1.74 (s, 3H, CH_3).

Preparation of 2,6 - *dimethyl* - 3 - *formyl* - 1,5 - *heptadiene* - *lavandulal*

To 121 mg of ketal **13** dissolved in 25 ml of aqueous THF (10:15) was added six drops of conc HCl. The mixture was then heated at 75°, with stirring for 5.5 hr, at the end of which time starting material was completely consumed. After addition of 15 ml of satd $NaHCO_3$ aq, the soln was cooled to room temp and THF was removed *in vacuo*. The remaining aqueous phase was extracted twice with ether and the combined ether extracts were dried over $MgSO_4$, filtered through celite and solvent was removed. The residue was taken up in 10:1 low boiling petroleum ether–ether and flash chromatographed on silica gel, collecting 5 ml fractions. Fractions 3–11 gave 36 mg (39%) of lavandulal, while fractions 13–24 gave 20 mg (21%) of the isomeric 2,6-dimethyl-3-formyl-2,5-heptadiene. ^1H-NMR ($CDCl_3$) (major product): δ 9.53 (d, 1H, J = 3 Hz, CHO), 5.0–4.7 (m, 3H, vinyl), 2.96 (dt, 1H, J = 7.3 Hz, CH), 2.4–2.0 (m, 2H, CH_2), 1.76, 1.73, 1.67 (3s, 9H, CH_3); (minor product): δ 10.07 (s, 1H, CHO), 4.83 (tq, 1H, J = 6.3, 0.5 Hz, vinyl), 2.93 (d, 2H, J = 6.3 Hz, CH_2), 2.17, 1.95 (2s, 6H, CH_3), 1.68, 1.63 (2s, 6H, CH_3).

Preparation of lavandulol (**9**)

The aldehyde prepared above (36 mg) was taken up in 10 ml of EtOH and cooled to 0°. $NaBH_4$ (9 mg) in 2 ml of EtOH was added and the soln was stirred at 0° for 15 min and then at room temp for 45 min. The reaction was quenched with 20 ml of NH_4Cl. Normal workup followed by flash chromatography

of the product with low boiling petroleum ether–ether (6:1) yielded 13 mg of lavandulol. ^{1}H-NMR ($CDCl_3$): δ 5.08 (br t, 1H, J = 6 Hz, CH=), 4.91 (t, 1H, J = 1.5 Hz, CH_2=), 4.81 (m, 1H, CH_2=), 3.6–3.4 (m, 3H, CH_2OH), 2.3–1.9 (m, 3H, CH_2, CH) 1.72, 1.71, 1.61 (3s, 9H, CH_3); lit.[36] ^{1}H-NMR (CCl_4): δ 5.05 (t, 1H, J = 7 Hz, CH=), 4.86 (dq, 1H, J = 1 Hz), 4.76 (br s, 1H), 3.44 (d, 2H, CH_2OH), 2.1 (m, 3H, CH_2, CH), 1.70, 1.70, 1.62 (3s, 9H, CH_3).

Acknowledgement—This research was supported by a grant from the National Science Foundation (CHE 8117510), which is gratefully acknowledged. We thank Dr R. Anderson (Zoecon Corp.) for a sample of red scale pheromone.

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