led to the formation of the desired β-keto ester 8 (R = *p*-methoxylbenzyl) in 82% yield. Conversion of the *p*-methoxylbenzyl keto ester to photosubstrate **9** proceeded in 85% yield, using an excess of acetic anhydride (55 equiv) in 1:1 trifluoracetic acid/acetone (−78 °C → room temperature, 12 h). Irradiation of **9** (0.0075 M in 1:9 acetone/acetonitrile, Pyrex immersion well, 0 °C, 90 min) lead to the formation of a single photoadduct **10**[16] in 83% yield. Fragmentation of **10** (2 N potassium hydroxide, methanol, 40 °C, 4 h, 88% yield) provided keto acid **11** as a mixture of epimeric compounds, which could be interconverted as the corresponding methyl esters by using sodium methoxide in methanol. That the keto acids were epimeric at C-6 (ingenane numbering) could be demonstrated by Barton decarboxylation[17] of the separated keto acids to the same ketone **12**.[18] The chemical shift of the C-8 proton [δ 2.87 (m, 1 H)] and the infrared absorption for the carbonyl (1719 cm^{-1}) in **12** were identical with the corresponding spectral data obtained for *trans*-bicyclo[4.4.1]undecan-11-one,[19] prepared in our laboratory in a similar manner, but unambiguous proof of the inside–outside intrabridgehead stereochemical relationship in **11** follows from the single-crystal X-ray analysis of ketoamide **13**[20] [derived from the major epimer of **11** via treatment of the derived acid chloride (thionyl chloride, toluene) with aqueous ammonium hydroxide]. As indicated in Chart I, the stereochemistry of the bicyclo[4.4.1]undecane (BC rings) of **13** is trans bridged.

The exclusive formation of the inside–outside isomer can be explained by examination of the diastereomeric transition states in Chart II. The seven-membered ring can be formed in the cycloaddition in either pseudochair (A or B) or pseudoboat (C) conformations.[21] In the first two cases, the double bond can approach in either a parallel or perpendicular sense.[22] The perpendicular approach, B, presents the indicated unfavorable nonbonded interactions which are not present in A. The alternate pseudoboat conformation C suffers transannular eclipsing interactions which are not present in A or B, so that A, which leads to the desired "inside–outside" conformation, should best represent the transition state leading to photocycloaddition.

In conclusion, the results described herein represent another example of the stereochemical consequences of the conformation of the nascent ring (seven-membered in the photocycloaddition of **9**) in the intramolecular photochemical cyclization.[1,12] The viability of the intramolecular dioxolenone photocycloaddition for the establishment of the critical inside–outside intrabridgehead stereochemistry of the ingenane diterpenes has now clearly been established, and the application of this methodology to the synthesis of this fascinating class of compounds is currently under way in our laboratory.

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Supplementary Material Available: X-ray crystal stucture data, stereoview, and tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for the crystal structure of **13** (4 pages); table of crystal structure factor data of **13** (13 pages). Ordering information is given on any current masthead page.

(15) Henegar, K.; Winkler, J. *Tetrahedron Lett.*, in press. (b) For the first report of the carboxylation of ketone enolates using methyl cyanoformate, see: Mander, L.; Sethi, S. *Tetrahedron Lett.* **1979**, 5425.

(16) Spectral data for **10**: IR ($CDCl_3$) 1723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.1 (m, 13 H), 1.63 (s, 3 H), 1.75 (s, 3 H), 1.9 (m, 1 H), 2.1 (m, 2 H), 2.35 (m, 3 H), 2.62 (m, 1 H); ^{13}C NMR δ 23.6, 25.25, 30.5, 30.67, 31.3, 33.43, 35.22, 35.48, 39.77, 40.72, 41.96, 43.10, 52.72, 61.35, 93.87, 108.04, 172.49.

(17) Barton, D.; Crich, D.; Motherwell, W. *J. Chem. Soc., Chem. Commun.* **1983**, 939.

(18) Spectral data for **12**: IR ($CDCl_3$) 1719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1–2.1 (m, 21 H), 2.87 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.16, 25.96, 30.42, 30.45, 30.50, 30.59, 30.74, 34.98, 36.10, 41.07, 50.28, 54.22, 63.45, 216.90.

(19) Winkler, J.; Henegar, K., unpublished results.

(20) Data were collected on a Nicolet R3m/E crystallographic system. The structure was solved by the SHELXTL 4.1 programs. The ingenane skeleton crystallized in the centrosymmetric, monoonoclinic space group $P2_1/c$. The unit cell parameters were determined to be a = 6.723 (1) Å, b = 15.852 (6) Å, and β = 91.86 (2)°; R = 0.0461, R_w = 0.0621.

(21) Eliel, E. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 252–253.

(22) For a discussion of the stereoselectivity of the intramolecular [2 + 2] photocycloaddition, see: Shaik, S. *J. Am. Chem. Soc.* **1979**, *101*, 3184.

Reductive Cleavage of Sulfonates. Deprotection of Carbohydrate Tosylates by Photoinduced Electron Transfer

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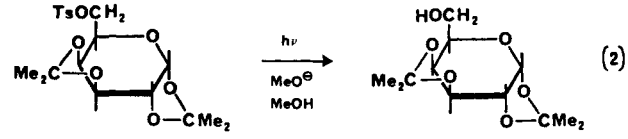
Esters of *p*-toluenesulfonic acid are used as protecting groups in carbohydrate chemistry.[1] This use is possible because tosylate displacement from carbohydrates usually requires forcing conditions; consequently, a variety of transformations can be conducted elsewhere in the molecule without altering the tosyloxy group.[2] Deprotection is accomplished with ease by photolysis in the presence of base.[3] The mechanism of this reaction has been proposed to involve homolytic cleavage of a S–O bond to form an alkoxy radical (eq 1).[4,5] Mechanistic studies have shown

$$CH_3C_6H_4SO_2OR \xrightarrow{h\nu} CH_3C_6H_4SO_2OR^1 \xrightarrow{OH^-} CH_3C_6H_4SO_2 + OR \quad (1)$$

that bases such as hydroxide quench the excited singlet state of tosylates and improve the efficiency of reaction; however, the nature of the quenching interaction has not been explained.[5]

Recent studies in our laboratories have determined the role of hydroxide in this reaction and indicated a different mechanism for the photochemical process than that previously proposed.[4,5] Photolysis of 1,2:3,4-di-*O*-isopropylidene-6-*O*-(*p*-tolylsulfonyl)-α-D-galactopyranose (**1**) (10 mM) in alkaline (25 mM NaOH) methanol under nitrogen using a Corex optical filter (240 nm cut-off) affords the alcohol **2** quantitatively after aqueous workup (eq 2).[3] Amines also promote the reaction, and the efficiency



(2)

1 2

of removal of the tosyloxy group depends upon the structure of the particular amine (Table I). No correlation is observed between the nucleophilicity of the bases and the efficiency of reaction; for example, the weakly nucleophilic diisopropylethylamine serves as one of the most effective bases. However, a qualitative correlation is found with the electron-donating ability of the amines (which is related to their ionization potentials[6]). Electron transfer

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(2) Raymond, A. L.; Schroeder, E. F. *J. Am. Chem. Soc.* **1948**, *70*, 2785.

(3) Zen, S.; Tashima, S.; Koto, S. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 3025.

(4) Izawa, Y.; Kuromiya, N. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3197.

(5) Pete, J. P.; Portella, C. *Bull. Soc. Chim. Fr.* **1980**, 275.

(6) (a) Vertical ionization potentials from: Brehon, A.; Couture, A.; Lablache-Combier, A.; Pollet, A. *Nouv. J. Chim.* **1981**, *5*, 243; Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311. (b) Foster, R. *Organic Charge Transfer Complexes*; Academic: New York, 1969.

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(8) Horner, L.; Schmitt, R.-E. *Phosphorus Sulfur* **1982**, *13*, 189. $E_{1/2}^{red}$ of $C_3H_7CH(OH)CH(C_2H_5)CH_2OTS$ in methanol (−2.22 V vs. SCE) is used as an estimate of $E_{1/2}^{red}$ of **1**.[9]

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Table I. Base-Promoted Conversion of **1** to **2**

base	IP[a]	$E_{1/2}^{ox}$[b]	$-\Delta G_{et} - C$[c]	% rctn[d]
DABCO	7.51	0.74	1.5	51
Et_3N	8.06	0.73	1.5	39
i-Pr_2NEt	7.64	0.65[e]	1.6[e]	51
t-$BuNH_2$	8.83	1.18	1.1	17
OH^-				17

[a] Vertical ionization potentials (eV) from ref 6. [b] Oxidation potentials (V vs. SCE) in aqueous methanol from ref 7. [c] Energy of electron transfer (eV) calculated according to ref 9. [d] Standard conditions: 2.0 mM **1** and 4.5 mM base in methanol were irradiated for 35 min under nitrogen using Rayonet with 16 RPR 2537-A lamps. Disappearance of **1** and formation of **2** were monitored. [e] Value for n-Pr_2NMe.

from each of the amines to singlet excited tosylate is estimated to be exergenic by more than 1 eV (cf. ΔG_{et} in Table I).[9] This suggests cleavage may be induced by an electron-transfer process as shown in Scheme I.

Scheme I

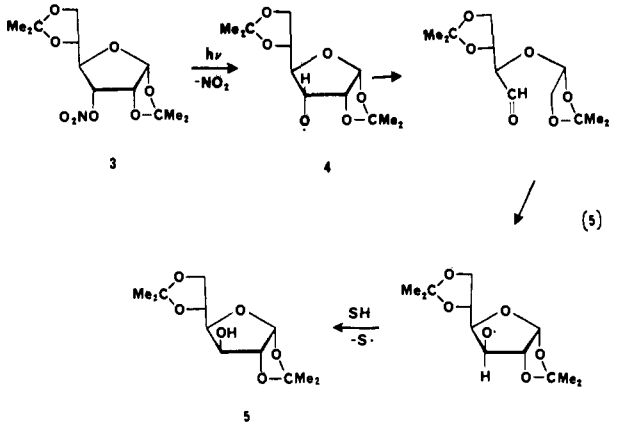
$$ArSO_2OR^1 + \text{donor} \rightarrow ArSO_2OR^{\bullet-} + \text{donor}^{\bullet+} \quad (3)$$

$$ArSO_2OR^{\bullet-} \rightarrow ArSO_2^{\bullet} + {}^-OR \quad (4)$$

We obtained direct evidence for electron transfer by examining the flash photolysis of tosylate **1** in the presence of amine donors.[10] In Figure 1a, the difference absorption spectrum observed in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) indicates two absorption bands, the first centered near 320 nm and the second near 460 nm. These absorptions are observed only in solutions containing both the tosylate **1** and DABCO.[11] The band near 460 nm is assigned to the radical cation of DABCO,[12] and the 320-nm absorption is assigned to the p-tolylsulfonyl radical.[13] The 460-nm absorption also is produced by irradiation of other acceptors such as p-dicyanobenzene (DCNB) in the presence of DABCO (▲ in Figure 1b), along with a sharp absorption near 340 nm due to the p-dicyanobenzene radical anion (λ_{max} 345 nm in DMF[14]) in this case.

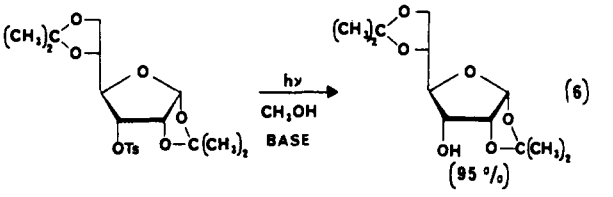
Although the (p-tolylsulfonyl)oxy group is the principal absorbing chromophore,[15] observation of the DABCO radical cation together with the p-tolylsulfonyl radical immediately following the laser pulse suggests that electron-transfer quenching of the excited tosylate (eq 3) and subsequent cleavage of the tosylate anion radical (eq 4) proceed within 200 ns.[16] A number of electron-transfer-initiated reactions driven by dissociative electron capture are known.[17-20] We confirmed the fragmentation of the tosylate radical anion on a submicrosecond time scale by pulse radiolysis.[16] The transient absorption spectrum observed upon pulse radiolysis of **1** (○, Figure 1b) has a peak near 320 nm, characteristic of the p-tolylsulfonyl radical.[13] This peak matches the 320-nm transient observed in the flash photolysis experiments and indicates that cleavage of the tosylate radical anion proceeds as shown in eq 4.[21] The alkoxide produced is optically transparent at wavelengths >300 nm and is not observed directly in these experiments.

Scheme II



3 4 5

Operation of an electron-transfer mechanism bears practical implications when applied to carbohydrate synthesis since alkoxides, rather than alkoxy radicals, are involved. The formation of alkoxy radicals can lead to reactions other than straightforward deprotection. For example, the radical **4**, produced by photolysis of 1,2:5,6-di-O-isopropylidene-3-O-nitro-α-D-allofuranose (**3**), epimerizes by fragmentation of the C_2–C_3 bond and subsequent reclosure to give a radical with inverted configuration at C_3 (Scheme II).[22] Photolysis of the corresponding tosylate **6**, however, results in deprotection *without* epimerization (eq 6). This



6 7

experiment precludes any mechanism (eq 1) in which the alkoxy radical **4** is a discrete intermediate.[23]

Preliminary results of flash photolysis of p-toluenesulfonamides with DABCO and other amines indicate the same absorbing species to be present (Figure 1a).[17] However, unlike the sulfonamides,[18] experiments involving electron-transfer sensitizers[24] have

(9) From eq 6 in: Weller, A. *The Exciplex*; Gordon, M.; Ware, W. R., Eds.; Academic: New York, 1975; Chapter 2, pp 23–28. The energy of a "pure" charge-transfer state in solution will be given by $E^{\circ}_{CT} = E_0^{ox} - E_A^{red} - C$ and the energy of electron transfer from the lowest singlet excited state (S_1) will be $-\Delta G_{et} = E_{S_1} - E^{\circ}_{CT}$ or $-\Delta G_{et} - C = E_{S_1} - (E_D^{ox} - E_A^{red})$. Values of $E_{S_1} \cong 4.5$ eV (O–O absorption of **1** is observed at 273 nm) and $E_A^{red} \cong -2.2$ V[8] are used.

(10) For a description of the flash photolysis apparatus, see: Atherton, S. J. *J. Phys. Chem.* **1984**, *88*, 2840. Foyt, D. C. *J. Comput. Chem.* **1981**, *5*, 49.

(11) The transient absorption spectrum in the absence of quencher resembles that of a triplet benzene, which exhibits bands near 240 nm ($T_1 \rightarrow T_5$), 430 nm ($T_1 \rightarrow T_4$), 700 nm ($T_1 \rightarrow T_3$), and 1500 nm ($T_1 \rightarrow T_2$). Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 283.

(12) $DABCO^{\bullet+}$ displays λ_{max} = 460 nm in acetonitrile: Halpern, A. M.; Forsyth, D. A.; Nosowitz, M. *J. Phys. Chem.* **1986**, *90*, 2677.

(13) The absorption of toluenesulfonyl has $\lambda_{max} \approx 330$ nm: Thoi, H. H.; Ito, O.; Iino, M.; Matsuda, M. *J. Phys. Chem.* **1978**, *82*, 314.

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(15) A weak electron donor–acceptor complex may be excited competitively; see: Kothandaraman, H.; Arumugasamy, N. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1115.

(16) The time scale for pulse radiolysis was limited by the pulse width of the electron beam (200 ns, ~2000 rad). Flash photolyses were performed on a similar time scale which was limited by the digitizer (a Biomation 8100 was used to average 10 channels per point, permitting a resolution of 100 ns).[10]

(17) Evidence from quenching studies indicates a similar mechanism for reaction of p-toluenesulfonamides.[18]

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(21) The isolated products include toluene and may arise from secondary photolysis of tolylsulfonyl, its dimer, or toluenesulfinic acid. See: Abad, A.; Mellier, D.; Pete, J. P.; Portella, C. *Tetrahedron Lett.* **1971**, 4555. Mullier, D.; Pete, J. P.; Portella, C. *Ibid.* **1971**, 4559, and ref 14 and 18.

(22) Binkley, R. W.; Koholic, D. J. *J. Org. Chem.* **1979**, *44*, 2048.

(23) Similar findings from electrochemical and alkali-metal reductions of optically active tosylates indicate an analogous mode of cleavage is operative under these conditions, although other processes may be occurring as well. See: (a) Schön, I. *Chem. Rev.* **1984**, *84*, 287. (b) Maia, H. L. S.; Medeiros, M. J.; Montenegro, M. I.; Court, D. I.; Pletcher, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *164*, 347. (c) Nucci, L.; Del Cima, F.; Davazza, M.; Pietra, F. *Tetrahedron Lett.* **1977**, 3099. (d) Horner, L.; Schmitt, E. *Naturwissenschaften* **1976**, *63*, 577. (e) Horner, L.; Lund, H. *Organic Electrochemistry*; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; Chapter 21, pp 751–761. (f) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970; Chapter 12, pp 395–402.

(24) Donors employed as sensitizers include triphenylamine, phenothiazine, 9,10-dimethoxyanthracene, and p-dimethoxybenzene.

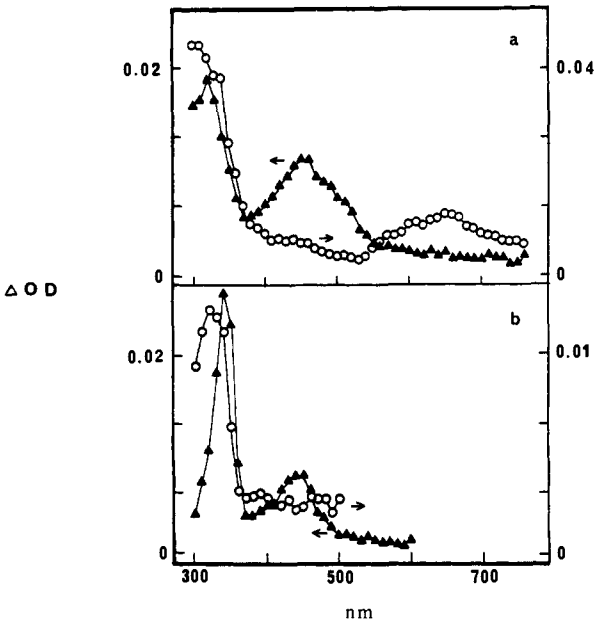

Figure 1. (a) Difference absorption spectrum of deaerated 10^{-3} M **1** in methanol 2.6 μs after 266-nm excitation alone (○) and in the presence of 0.2 M DABCO (▲). (b) Difference absorption spectrum of deaerated 2 mM **1** in 2% (vol) ethanolic 2-propanol 2 μs after a pulse radiolysis dose of ~2 krad (○) and difference absorption spectrum obtained 2.6 μs after 266-nm excitation of ~10^{-4} M DCNB in methanol containing 0.2 M DABCO (▲).

been unsuccessful in promoting electron-transfer reaction of the tosylates. The reason for the failure to sensitize the tosylate reaction may lie in the thermodynamic and steric effects of electron transfer to carbohydrate tosylates. Events on a shorter time scale will be examined to address these questions.

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Synthesis and Absolute Configuration of 4-Methyl Juvenile Hormone I (4-MeJH I) by a Biogenetic Approach: A Combination of Enzymatic Synthesis and Biotransformation

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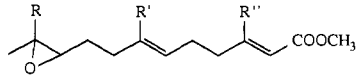
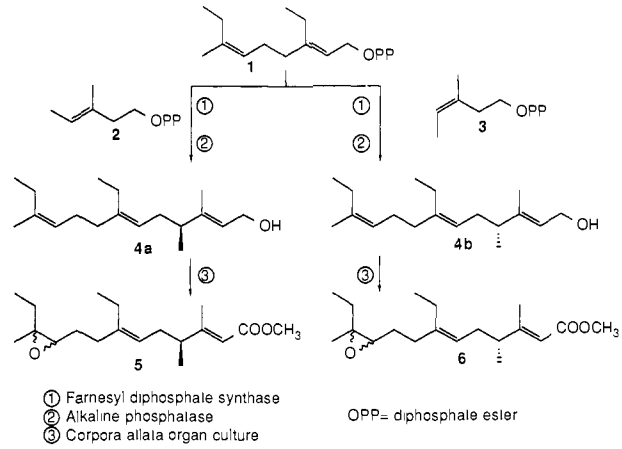
4-Methyl juvenile hormone I (4-MeJH I) (**5**) is a juvenile hormone (JH) isolated along with JH O from embryos of the tobacco hornworm, *Manduca sexta*. Bergot et al.[1] assigned its structure as a 4-methyl homologue of JH I, the first JH discovered.



R=R'=R''= Me, (10R)-JH III
R=Et, R'=R''=Me, JH II
R=R'=Et, R''=Me, (10R,11S)-JH I
R=R'=R''=Et, JH O

(1) Bergot, B. J.; Baker, F. C.; Cerf, D. C.; Jamieson, G.; Schooley, D. A. In *Juvenile Hormone Biochemistry*; Pratt, G. E., Brooks, G. T., Eds.; Elsevier: Amsterdam, 1981; pp 33-45.

Scheme I



The absolute configuration at C-4 is of particular interest as faranal,[2] the trail pheromone of the Pharaoh's ant, is a structural analogue of 4-MeJH I. We report the elucidation of the absolute configuration at C-4 of this compound by a biosynthetic approach.

The structure of 4-MeJH I led us to the following strategy for its (bio)synthesis: The farnesyl diphosphate synthase method,[2,3] which was successfully applied to the synthesis of faranal, seemed promising for the chiral synthesis of both (4*S*)-4-methyldihomofarnesol (**4a**) and (4*R*)-4-methyldihomofarnesol (**4b**), one of which should be the biosynthetic precursor of 4-MeJH I. [^{3}H]Farnesol is known[4] to be metabolized readily to [^{3}H]JH III by cultured corpora allata (the insect organ responsible for JH biosynthesis). If **4a** and **4b** are administered to corpora allata, one of them should be metabolized to a substance identical with natural 4-MeJH I.

First, tritium-labeled **4a** and **4b** were synthesized. The incubation mixture for the synthesis of **4a** contained, in a final volume of 400 mL, 8 mmol of TES [*N*-[tris(hydroxymethyl)methyl]-2-aminoethanesulfonic acid] buffer, pH 7.6, 2 mmol of $MgCl_2$, 4 mmol of 1,4-dithiothreitol, 50 mg of farnesyl diphosphate synthase purified about 50-fold from pig liver,[5] 35 μmol of (*E*)-3-methyl-3-pentenyl diphosphate (**2**),[3] and 25 μmol of [1-^{3}H]dihomogeranyl diphosphate (**1**). The latter was synthesized by phosphorylation of [1-^{3}H](2*E*,6*Z*)-3-ethyl-7-methyl-2,6-nonadien-1-ol (specific activity 1.3 Ci/mol) which had been prepared by reduction of the corresponding ester[6] with $LiAlT_4$. After incubation at 37 °C for 72 h, the mixture was treated with alkaline phosphatase to hydrolyze the diphosphate ester. The resulting alcohol was extracted with pentane and purified by TLC and HPLC to give 810 μg (12.3% yield based on **1**) of the 4*S*-(−) alcohol **4a**.[7] Similarly, the enzymatic reaction starting with **1** and (*Z*)-3-methyl-3-pentenyl diphosphate[3] (**3**) gave 590 μg (8.9% yield based on **1**) of the 4*R*-(+) alcohol **4b** (Scheme I).

The ^{3}H-labeled **4a** or **4b** (~50 μM) was incubated in 8-10 batches with 10 pairs of corpora allata from adult, female *M. sexta* (0-48-h old) in 100 μL of Medium 199 (Gibco), containing Hanks' salts and 1% bovine serum albumin. After a 5-h incubation at 28 °C, products were extracted and purified by reversed-phase HPLC (C_8 column; 70% CH_3CN). Quantification of 4-MeJH I was based on the level of ^{3}H. Thus, 1-2 μg of [5-^{3}H](4*S*)- and

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(7) MS, *m/z* 264 (M^+, $C_{18}H_{32}O$), 246 (M − 18), 233 (M − 31), 163 (M − 18 − 83), 83 (base peak, C_6H_{11}); NMR (CCl_4) δ 0.96 (t, 6 H), 0.99 (d, 3 H), 1.56 (s, 3 H), 1.66 (s, 3 H), 1.5-1.6 (m, 1 H), 1.8-2.2 (m, 10 H), 4.19 (m, 2 H), 5.06 (m, 2 H), 5.42 (t, 1 H).

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