Table I. ^{31}P and Selected ^{1}H NMR Chemical Shifts of the Palladium Complexes Presented in Scheme I[a]

	^{31}P, δ (J)[b]		^{1}H, δ			
			R,R[c]		S,S[c]	
complex	R,R[c]	S,S[c]	NMe	CMe[d]	NMe	CMe[d]
7a	33.6 (s)[e]	33.7 (s)[e]	2.70[f]	1.80	2.73	1.75
7b	44.7 (25)	47.6 (26)	2.63, 2.88[g]	1.53	2.70	1.48
	29.3 (25)	31.0 (26)				
7c	48.4 (27)	45.3 (25)	2.83	1.63	2.71	1.70
	32.1 (27)	32.8 (25)				
7d	48.4[e,h]	46.7 (5)[e]		1.85		1.89
		44.6 (5)				
7e	42.6 (7)[e]	45.5 (8)[e]		1.93		1.96
	42.0 (7)	44.2 (8)				

[a] Spectra determined on ca. 0.1 M solutions in $CDCl_3$. The ^{31}P chemical shifts are defined as positive when downfield from external 85% H_3PO_4. [b] The absorptions for **7b-e** are pairs of doublets with coupling constants in hertz in parentheses. [c] Configurations of the chiral centers in the *free* diphosphine ligand. [d] All signals are doublets, J = 6 Hz. [e] It is important to use a 1:1 ratio of 1 to diphosphine to obtain this spectrum. [f] The most pronounced chemical shift differences are due to the acetonide methyl resonances: *R,R*, 1.20; *S,S*, 1.10. [g] The two NMe groups are magnetically different in this complex. [h] Narrow, unresolved multiplet.

titative as observed by ^{31}P NMR spectroscopy. On the other hand, reaction of (−)-**3** with **7c** (five-membered chelate) is much slower (at least a factor of 30), and the conversion to **7b** and (+)-**4** proceeds to an equilibrium mixture slightly favoring **7b** + (+)-**4** (ratio **7b**/**7c** = 70:30). Apparently the religation process to form a five-membered chelate is so much more favored entropically than for a seven-membered chelate, that a species such as **8** is not formed in the former case, thus making site–site exchange slow or even nonexistent for the two phosphines.

In spite of the very small ^{31}P NMR chemical shift difference between the diastereomeric complexes of **7a**, we were able to optimize the conditions for determining the spectrum so that we were able to detect the presence of less than 3% of the minor isomer in a synthetic mixture. We also quantitated two synthetic mixtures of **2**: (a) (+)-**2**/(−)-**2**, 88.1:11.9 (prepared), 88.3:11.7 (measured); (b) 59.6:40.4 (prepared), 59.0:41.0 (measured). We observed similar accuracy in determining the composition of synthetic mixtures of (+)- and (−)-**3** by the above-described method. We have noted also that in most of the ^{1}H NMR spectra there are absorptions in each diastereomeric pair of **7** that may be used to quantitate enantiomeric ratios, although generally not with the accuracy of the ^{31}P NMR method.

Finally, this technique has the advantage that the diphosphine can be recovered essentially quantitatively from **7**, using a method described previously.[4] Thus, valuable ligands need not be lost in the evaluation of optical purity, as is the case with a technique for determining optical purities of chiral monophosphines.[8]

Experimental Section

General Procedures. Proton-decoupled ^{31}P NMR spectra were determined on either a Varian FT-80[9] or Bruker WH-90 instrument at 32.4 and 36.4 MHz, respectively. ^{1}H NMR spectra were taken on either a Varian EM-390 or FT-80 instrument.

The following compounds were prepared by procedures described in the literature: (+)-bis(μ-chloro)bis[(*S*)-dimethyl(α-methylbenzyl)aminato-C^2,*N*]dipalladium(II) (**1**),[5,10] (−)-(*S,S*)-1,2-bis(methylphenylphosphino)benzene,[4] (−)-(*R,R*)-5-*exo*-6-*endo*-bis(diphenylphosphino)bicyclo[2.2.1]heptane (**6**).[3i] The ligands (+)-(*R,R*)-2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)dioxolane (diop, **2**) and its enantiomer are commercially available (Alfa); (+)-(*S,S*)-1,2-bis(2-anisylphenylphosphino)ethane (dipamp, **4**) and its racemate were obtained as a gift.[6]

Preparation of [(*S*,*S*)-1,2-Bis(2-anisylphenylphosphino)ethane]-[(*S*)-dimethyl(α-methylbenzyl)aminato-C^2,*N*]palladium(II) Chloride (7c). The diphosphine **4** (185 mg, 0.404 mmol) was added in one portion to the palladium dimer **1** (119 mg, 0.202 mmol) in $CDCl_3$ (4 mL) to give a clear straw-yellow solution, upon which the spectra reported in Table I were determined.

All solutions of other complexes were prepared as above, although generally only on half the scale, since only ca. 2 mL of solution is necessary for the ^{31}P NMR spectral determination.

Acknowledgment. Financial support from the National Science Foundation (Grant CHE 81-13090), the Air Force Office of Scientific Research (Grant No. AFOSR-79-0090), and the Robert A. Welch Foundation (Grant No. F573) is gratefully acknowledged.

Registry No. **1**, 34424-15-2; **7a**, 83248-39-9; **7b**, 83290-87-3; **7c**, 83248-40-2; **7d**, 83248-41-3; **7e**, 83248-42-4.

(8) (a) Casey, J. P.; Lewis, R. A.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 2790. (b) Lewis, R. A.; Mislow, K. *Ibid.* **1969**, *91*, 7009.

(9) We are grateful for an NSF matching grant to E.P.K. and A. H. Cowley of this department, which enabled the purchase of this instrument.

(10) In our hands this preparation gave the complex **1** contaminated with a small amount of black solid that we suspect to be Pd(0). Dissolution of the complex in dichloromethane (ca. 1:10, w/v) followed by filtration and evaporation of the solvent gave **1** as a yellow powder.

A Facile Stereoselective Route to the Sex Pheromone of the Codling Moth via Thermolysis of an Allylic Sulfoxide

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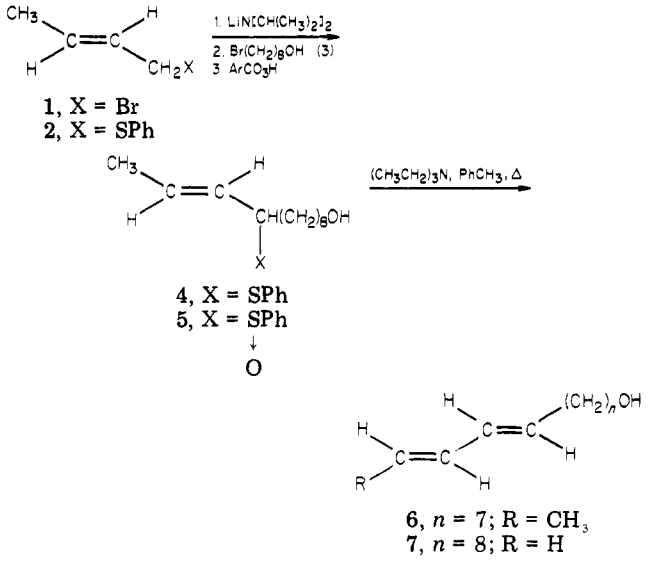
In recent years considerable attention has been focused on the possibility of minimizing use of pesticides in insect control programs. One particular development in this area has been the examination of the use of insect sex pheromones[1] as a means of controlling insect behavior. Among the insect pests for which a sex pheromone has been identified is the codling moth, *Laspeyresia Pomonella* L., a major worldwide pest of apple orchards. The sex pheromone produced by the virgin female of this species was first isolated in 1969,[2] but the structure remained

(1) Jacobson, M. "Insect Sex Pheromones"; Academic Press: New York, 1972.

(2) McDonough, L. M.; George, D. A.; Butt, B. A.; Jacobson, M.; Johnson, G. R. *J. Econ. Entomol.* **1969** *62*, 62.

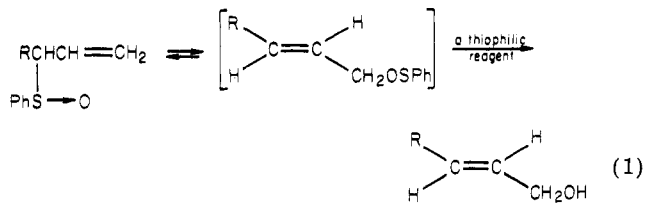
0022-3263/82/1947-4801$01.25/0

Scheme I



unknown until 1971 when Roelofs and co-workers[3] identified it as 8(*E*),10(*E*)-dodecadien-1-ol (**6**). The latter compound has subsequently been shown to be one of the most promising lepidoptera sex pheromones for use in a confusion technique as a method of controlling codling moth populations in apple orchards.[4] As a result there has been considerable interest in developing synthetic routes to dienol **6**, and to date at least eight approaches have been reported.[5] In this note we report a different methodology that is both highly stereoselective and convenient for small-scale preparation of this pheromone (**6**).

In planning the route to **6**, allylic sulfoxide **5** (Scheme I) seemed to be an attractive intermediate. Although thermal interconversion of allylic sulfoxides and sulfenates followed by subsequent nucleophilic decomposition of the latter to alcohols (eq 1) has found wide application in



(1)

organic synthesis,[6] until recently elimination of sulfenic acid[7] from allylic sulfoxides (or sulfenates) to afford 1,3-dienes was not extensively utilized by synthetic chemists. A recent study in this area demonstrated that thermolysis of allylic sulfoxides can indeed be a useful methodology for the synthesis of functionalized dienes.[8] The dienes reported in this latter paper, however, were thought to have been formed by allylic rearrangement of the initial sulfoxides followed by thermal elimination of sulfenic acid from the corresponding sulfenates. A similar transformation involving sulfoxide **5** would afford dienol **7**, the acetate derivative of which is the sex pheromone of the red bollworm moth,[9] instead of the desired **6**. In order to clarify the outcome of this thermolysis, a facile three-step route to allylic sulfoxide **5** was developed.

Allylic sulfide **4** was obtained in 68% yield by alkylation of crotyl phenyl sulfide (**2**)[10] with 8-bromo-1-octanol (**3**)[11] in the presence of 2 equiv of lithium diisopropylamide. The latter bromide (**3**) was in turn readily obtained in >90% yield by continuous extraction with cyclohexane of a solution of 1,8-octanediol[12] in aqueous hydrobromic acid at 75 °C. Subsequent treatment of sulfide **4** with 1 molar equiv of *m*-chloroperbenzoic acid[12] proceeded smoothly to afford the corresponding sulfoxide (**5**) in quantitative yield. As we had anticipated, thermolysis of the latter compound (**5**) in the presence of triethylamine afforded, after purification via column chromatography, the desired conjugated diene **6**[13] in approximately 30% overall yield from 1,8-octanediol. Although our synthetic pheromone was homogeneous by TLC and VPC analysis, ^{13}C NMR analysis[14] revealed the presence of a small amount (<10%) of stereoisomeric impurities. One recrystallization of this material, however, effectively removed all impurities and afforded a stereochemically homogeneous sample of dienol **6**, whose melting point and spectral properties were identical with those previously reported[15] for this same compound. In view of the stereoselectivity of this process and the few steps required overall, the method reported in this note represents a convenient one for synthesis of small quantities of the sex pheromone of the codling moth.

Experimental Section

General Procedures. Reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran (THF) was purified prior to use by distillation from lithium aluminum hydride. The isolation of reaction products was accomplished by extracting them with the specified solvent. Unless indicated otherwise, the combined extracts were washed in successive order with 2 M aqueous hydrochloric acid, water, saturated aqueous sodium bicarbonate, and saturated brine. After the extracts were dried over anhydrous magnesium sulfate, the solvent was removed by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. Melting points were determined on a Fisher-Johns block and are uncorrected. ^1H NMR spectra were recorded with a Varian EM-360 spectrometer and ^{13}C NMR spectra were obtained with a Varian FT80 spectrometer. All infrared spectra were recorded with a Beckman Acculab 1 spectrophotometer and TLC analyses were conducted on precoated silica gel sheets (E. M. Merck, catalog no. 5775). Vapor-phase chromatography (VPC) was performed on a Hewlett-Packard 5750 chromatograph using a 6 ft × 0.125 in. column packed with 5% OV-17 on 100–120-mesh Gas Chrom. Q. Where indicated, percentages refer to peak areas without correction for response factors relative to an internal standard. Microanalyses were performed by Micro-Tech Laboratories, Skokie, IL.

Crotyl Phenyl Sulfide (2). To a solution of 13.0 g (96.3 mmol) of crotyl bromide (**1**)[12] in 250 mL of anhydrous ether at 0 °C (bath temperature) was added triethylamine (16.7 mL, 120 mmol), followed by dropwise addition over 5 min of thiophenol (12.3 mL, 120 mmol). This mixture was subsequently stirred at 0 °C for 15 min, after which the ice–water bath was removed and the mixture was stirred at room temperature for an additional 2.5 h. The product was isolated by washing the ether layer thoroughly

(3) Roelofs, W.; Comeau, A.; Hill, A.; Milicevic, G. *Science* **1971**, *174*, 297.
(4) Samain, D.; Descoins, C.; Commercon, A. *Synthesis* **1978**, 388 and references cited therein.
(5) Trost, B. M.; Fortunak, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 2841 and references cited therein.
(6) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.
(7) For a review on the thermolysis of sulfoxides, see Trost, B. M. *Chem. Rev.* **1978**, *78*, 363.
(8) deGroot, Ae,; Jansen, B. J. M.; Reuvers, J. T. A.; Tedjo, E. M. *Tetrahedron Lett.* **1981**, *22*, 4137.
(9) Nesbitt, B. F.; Beevor, P. S.; Cole, R. A.; Lester, R.; Poppi, R. G. *Nature (London), New Biol.* **1973**, *244*, 208.
(10) Cope, A. C.; Morrison, D. E.; Field, L. *J. Am. Chem. Soc.* **1950**, *72*, 59.
(11) For the experimental details involved in the preparation of monobromide **3**, see Babler, J. H.; Invergo, B. J. *J. Org. Chem.* **1979**, *44*, 3723.
(12) Available from Aldrich Chemical Co., Milwaukee, WI.
(13) None of the isomeric dienol **7** could be detected by NMR analysis. For the spectral properties of **7**, see ref 11.
(14) For a recent paper that discusses the ^{13}C NMR spectra of various insect pheromones (including dienol **6**), see Rossi, R.; Carpita, A.; Quirici, M. G.; Veracini, C. A. *Tetrahedron* **1982**, *38*, 639.
(15) Descoins, C.; Henrick, C. A. *Tetrahedron Lett.* **1972**, 2999.

with water and 1 M aqueous sodium hydroxide solution, followed by the aqueous washes described above in the general experimental section, affording 13.5 g (85%) of sulfide **2**, the physical and IR spectral properties of which were identical with those previously reported[10] for this same compound: bp 90 °C (bath temperature; 1.5 mm); NMR (CCl_4, Me_4Si) δ 7.19 (5 aromatic H's), 5.55 (m, 2 vinyl H's), 3.44 (complex m, CH_2S), 1.67 (br d, J = 5 Hz, vinyl CH_3). VPC analysis (oven temperature 170 °C, flow 15 mL/min) indicated the distilled product (retention time, 2.1 min) to be >98% pure.

(*E*)-9-(Phenylthio)-10-dodecen-1-ol (4). To a solution of 2.0 g (12.2 mmol) of crotyl phenyl sulfide (**2**), 2.0 g (9.6 mmol) of 8-bromo-1-octanol (**3**),[11] and approximately 50 mg of sodium iodide in 80 mL of anhydrous THF cooled to −70 °C (bath temperature) was added dropwise via syringe a solution of 24 mmol of lithium diisopropylamide[16] in 40 mL of 1:1 (v/v) anhydrous ether THF. This mixture was allowed to warm up to 5 °C over a period of 4 h, after which the reaction was quenched by addition of water. After removal of most of the solvent using a rotary evaporator under reduced pressure, the residue was diluted with 50 mL of solvent ether and washed in successive order with the aqueous solutions cited in the general experimental procedure. Since the crude product (3.37 g, >100% yield based on bromide **3**) could not be distilled without decomposition, it was chromatographed[17] on silica gel (150 mL, gradient elution using hexane–ether) to afford allylic sulfide **4** in 68% yield on the basis of bromo alcohol **3**: IR, ν_{max} (film) 3360 (OH), 1665, 1585, 1480, 1440, 1050, 1020, 955, 735, 685 cm^{-1}; NMR (CCl_4, Me_4Si) δ 7.28 (5 aromatic H's), 5.31 (m, 2 vinyl H's), 3.56 [3 H's, overlapping triplet (J = 6.5 Hz, CH_2OH) and multiplet (CHS)], 3.00 (s, OH), 1.61 (br d, J = 5 Hz, vinyl CH_3). Anal. Calcd. for $C_{18}H_{28}OS$: C, 73.92; H, 9.65; S, 10.96. Found: C, 73.92; H, 9.30; S, 10.79.

(*E*)-9-(Phenylsulfinyl)-10-dodecen-1-ol (5). To a solution of allylic sulfide **4** (11.5 mmol) in dichloromethane (100 mL) at 0 °C (bath temperature) was added in small portions over a period of several minutes 2.6 g of 85% *m*-chloroperbenzoic acid.[12] This mixture was subsequently stirred at 0 °C for 2 h, after which it was washed with 10% aqueous sodium carbonate and saturated brine. Removal of the organic solvent in the usual manner, followed by chromatography[17] on silica gel, afforded allylic sulfoxide **5** in quantitative yield: IR ν_{max} (film) 3440 (OH), 1665, 1585, 1445, 1375, 1305, 1145, 1080, 1035, 960, 775, 745, 685 cm^{-1}; NMR (CCl_4, Me_4Si) δ 7.53 (5 aromatic H's), 5.03–5.67 (complex pattern, 2 vinyl H's), 3.75 (s, OH), 3.3–3.7 (overlapping triplet and multiplet, CH_2OH and CHS), 1.1–1.8 (complex, 17 H). Anal. Calcd for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15; S, 10.39. Found: C, 70.23; H, 8.93; S, 10.02.

8(*E*),10(*E*)-Dodecadien-1-ol (6). A solution of allylic sulfoxide **5** (3.6 g, 11.7 mmol) and triethylamine (3.5 mL, 25 mmol) in 100 mL of toluene was heated at 80 °C (bath temperature) for 18 h. After this mixture was cooled to room temperature, it was washed in successive order with 5% aqueous hydrochloric acid, water, 5% aqueous sodium hydroxide, and saturated brine. Removal of the solvent in the usual manner, followed by chromatography on silica gel (50 mL, gradient elution using hexane–ether) and evaporative distillation [bp 135 °C (bath temperature), 3.0 mm], afforded 1.27 g (60%)[17] of dienol **6**, the IR and ^1H NMR spectral properties[13] of which were identical with those previously reported[15] for this pheromone. The chromatographed and distilled product was a low-melting solid (mp 25–30 °C) and was shown to be homogeneous by TLC and VPC analysis (oven temperature 150 °C; flow 15 mL/min; retention time, 5.3 min). ^{13}C NMR analysis,[14] however, revealed the presence of a small amount (<10%) of stereoisomeric impurities. The latter could be effectively removed after one recrystallization of this material from hexane at −5 °C, affording a stereochemically homogeneous sample of dienol **6**: mp 29–29.5 °C (lit.[15] mp 29–30 °C). The ^{13}C NMR spectrum exhibited by this material was fully consistent with the data recently reported[14] for an authentic sample of 8(*E*),10-(*E*)-dodecadien-1-ol (**6**).

Acknowledgment. We thank Dr. David S. Crumrine of Loyola University of Chicago for his assistance in determining the ^{13}C NMR spectrum of our synthetic pheromone.

Registry No. (*E*)-**1**, 29576-14-5; (*E*)-**2**, 36195-56-9; **3**, 50816-19-8; (*E*)-**4**, 83248-81-1; (*E*)-**5**, 83248-82-2; (*E*,*E*)-**6**, 33956-49-9; thiophenol, 108-98-5.

(16) This base was prepared by dropwise addition of a 1.2 M solution of methyllithium in ether (20 mL) to a solution of diisopropylamine (4.2 mL, 30 mmol) in 20 mL of anhydrous THF at −10 °C.

(17) Purification of intermediates **4** and **5** is not essential for the success of the overall synthetic sequence. 8-Bromo-1-octanol could be converted into dienol **6** in 33% overall yield (after chromatographic purification of the latter compound) with use of the crude product mixtures obtained in the preparation of **4** and **5**.

Synthesis of 4-Arylpyridines

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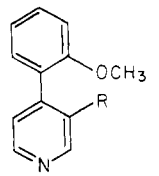
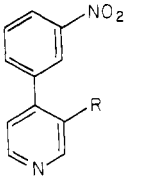
During the course of an investigation into intramolecular nucleophilic additions to pyridinium salts we required the 4-arylpyridines **1a** and **1b**.[1] We hoped to prepare these materials from the aromatic aldehydes and became attracted to the recent report of a preparation of **2a** and **2b** by modification of the Weiss procedure for pyridine synthesis.[2] The important feature of this new method is the



1a, R = H
b, R = CH_3



2a, R = H
b, R = CH_3

use of acylfurans **4** as the methylenic components in the condensation reaction with chalcones, leading to the isolation of the 2,6-difuryl-4-(3-nitrophenyl)pyridines. The furan moieties may be selectively oxidized to the diacids, which are readily decarboxylated to **2**. Furthermore, the preparation of the unsymmetrical pyridine **2b** is a distinct improvement over the original Chichibabin pyridine synthesis since α,β-unsaturated ketones were subject to reverse aldol reactions leading to product mixtures.[3] The principal drawback inherent in the Weiss procedure is the low yield of pyridine obtained since the intermediate dihydropyridine, formed in the initial stages of this reaction, aromatizes by the transfer of hydrogen to the chalcone.[4] This inefficient utilization of the aldehyde precursor prohibits the use of expensive or difficult to obtain aldehydes. In order to provide a satisfactory synthesis of 4-arylpyridines from the corresponding aldehydes, we investigated the simple and classical alternative to this procedure, which involves the preparation of 3-aryl-1,5-difuryl-1,5-pentanediones **5** and their reaction with hy-

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(2) Carbateas, P. M.; Williams, G. L. *J. Heterocycl. Chem.* **1974**, *11*, 819.
(3) Frank, R. L.; Seven, R. P. *J. Am. Chem. Soc.* **1949**, *71*, 2629.
(4) Weiss, M. *J. Am. Chem. Soc.* **1952**, *74*, 200.

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