(2 mL) was added, the total mixture was extracted with CH_2Cl_2, and the extract (73 mg) was chromatographed (silica gel; benzene/ether, 9:1) to give a colorless mixture of **7** and **8** (ratio 1:3) in 71% yield. Mixture of **7** and **8**: ^1H NMR δ 1.67, 1.75, 1.90 (br s each), 2.0–3.5 (a broad spectrum of m), 4.83 (br s), 5.65, 5.85 (m each), 6.35 (2 d, J = 5, 2 Hz), 9.5 (br s); IR (CCl_4) 3300–2400 (m), 1700 (s), 1410 (m), 890 (w) cm^{-1}. The relative intensities of the NMR signals at δ 5.65, 4.83, and 1.90 were 1:2:3 and those of the signals at δ 6.35, 5.83, 1.67, and 1.75 were 1:1:3:3. Irradiation at δ 3.13 caused the change of the signals at δ 5.85 and 6.35 into a doublet for each.

Thermal Treatment of 3. When **3** was heated without additives at 110 °C for 4 h in a sealed tube under N_2, it melted and gradually formed a yellow liquid which consisted of **3**, **2**, and **1** in a ratio 7:1:1, but no evidence for the production of **4** was obtained by NMR analysis.

Ring Cleavage of 9. Preparation of 1-(Carboxymethyl)-2-isopropylidenecyclopent-3-ene (10). A mixed solution of *t*-BuOK (2.16 g, 97% grade, 18.7 mmol) and water (0.130 mL, 7.2 mmol) in 20 mL of dry dimethyl sulfoxide (Me_2SO) was added to a solution of **9** (0.515 g, 3.5 mmol) in 10 mL of dry Me_2SO under an N_2 atmosphere at room temperature. The solution changed from yellow-brown to dark green. After 1 h, the reaction mixture was worked up with cold water and methylene chloride. The aqueous layer was acidified with hydrochloric acid and extracted with ether which was then washed with saturated brine and dried (Na_2SO_4). A brown liquid of **10** was obtained; 0.56 g (97%). Because of the instability of **10**, it was treated with diazomethane to afford the corresponding methyl ester. Methyl ester of **10**: ^1H NMR 1.74 (6 H, s, CH_3), 1.85–3.40 (5 H, m, CH and CH_2), 3.65 (3 H, s, OCH_3), 5.80 (1 H, m, olefinic), 6.25 (1 H, 2 t, J = 5.5, 2 Hz, olefinic).

Oxidation of 10. Preparation of 1-(2-Hydroxy-2-propyl)-2-oxa-3-oxobicyclo[3.3.0]oct-7-ene (13). Peroxyformic acid was prepared according to a reported procedure. As soon as the carboxylic acid **10** (551 mg, purity <90%) was dissolved in cooled formic acid (10 mL), a solution of peroxyformic acid was added dropwise to it at 0 °C. After 1 h, the reaction was quenched with aqueous $NaHSO_3$ (357 mg, 3.4 mmol). Formic acid was removed under reduced pressure, and the residue was worked up with water and methylene chloride. The organic extract was washed with aqueous 1% NaOH and dried. A 177 mg of **13** was obtained. On the other hand, the combined aqueous layer was acidified with hydrochloric acid and extracted with methylene chloride to give **12** (305 mg). This was dissolved in methanol (4 mL), 2 mL of 3% HCl was added, and the mixture was stirred for 2 days at room temperature. The solution was made alkaline with 1% NaOH and extracted with methylene chloride to give 246 mg of **13**. The combined yield of **13** was 423 mg (67% from **9**). **13**: mp 66–68 °C; ^1H NMR δ 1.16 and 1.33 (3 H each, s, CH_3), 2.9–3.4 (6 H, m, CH, CH_2, and OH), 5.74 and 6.01 (1 H each, 2 t, J = 5.5, 2 Hz, CH=CH); IR (KBr) 3490 (s, OH), 3000 (m), 1750 (s, C=O, five-membered lactone ring), 1420 (m), 1270 (m), 1210 (m), 1120 (m), 1030 (m), 1000 (m), 970 (m), 850 (m), 780 (m), 740 (m) cm^{-1}; mass spectrum, m/e 164 ($M^+ - H_2O$, 3.3), 105 (100), 96 (71.9), 82 (60.9), 70 (40.2), 59 (72.7). Anal. Calcd for $C_{10}H_{14}O$: C, 65.92; H, 7.74. Found: C, 65.66; H, 7.87.

Reduction of 13. Preparation of 1-(1-Hydroxy-1-methylethyl)-2-(2-hydroxyethyl)-4-cyclopenten-1-ol (14). Lactone **13** (437 mg, 2.4 mmol) was dissolved in dry ether (5 mL) to which was added lithium aluminum hydride (169 mg, 3.3 mmol) at 0 °C. After 40 min, the mixture was warmed to 25 °C and stirred for 1.5 h. The reaction was quenched by a small amount of ethanol and subsequently by water, and the mixture was extracted with benzene and ether. A colorless solid of **14** (352 mg, 79%) was obtained. **14**: mp 89–91 °C; ^1H NMR δ 1.23 (6 H, s, CH_3), 1.5–2.8 (5 H, m, CH and CH_2), 2.95 (3 H, s, 3 OH), 3.70 (2 H, br t, J = 6 Hz, OCH_2), 5.66 and 5.96 (1 H each, m, olefinic); IR (KBr) 3470, 3360, and 3250 (s, OH for each), 3050 (m), 2980 (m), 1120 (m), 1070 (m), 1050 (m), 1030 (m), 1000 (m), 940 (m), 730 (m) cm^{-1}; mass spectrum, m/e 150 ($M^+ - 2H_2O$, 7.1), 135 (24.5), 110 (28.6), 109 (100), 82 (40.1), 81 (47.6).

Oxidation of 14. Preparation of 5-(2-Hydroxyethyl)-2-cyclopenten-1-one (15). Triol **14** (93 mg, 0.50 mmol) was dissolved in dry benzene (3 mL) to which was added, under stirring, powdered lead tetraacetate (251 mg, 0.57 mmol), which was recrystallized from acetic acid. After 2.5 h, the solution was filtered, and water was added to give a brown solution. Aqueous $NaHSO_3$ was added until the brown color disappeared. After addition of a small amount of $NaHCO_3$ and NaCl, the solution was extracted with ether. By removal of the solvents under a nitrogen stream a colorless liquid of **15** (46 mg, 73%) was obtained. **15**: ^1H NMR δ 1.5–3.4 (5 H, m, CH and CH_2), 3.80 (2 H, t, J = 6 Hz, OCH_2), 4.27 (1 H, s, OH), 6.20 (1 H, 2 t, J = 5.5, 2 Hz, olefinic), 7.73 (1 H, 2 t, J = 5.5, 2.5 Hz, olefinic); IR (neat) 3400 (br s, OH), 2940 (m), 1690 (s, C=O), 1595 (m), 1440 (m), 1360 (m), 1060 (m), 780 (m) cm^{-1}; mass spectrum, m/e 126 (M^+, 9), 108 (10), 97 (33.5), 95 (15), 82 (100), 81 (19), 79 (28.5), 67 (22); high-resolution mass spectrum, m/e 126.0655 (calcd for $C_7H_{10}O_2$ 126.0681).

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Registry No. 1, 2175-91-9; 2, 3061-65-2; 3a, 87371-52-6; 3b, 87371-53-7; 4 (isomer 1), 87371-54-8; 4 (isomer 2), 87371-55-9; 5, 87371-56-0; 7, 87371-57-1; 8, 87371-58-2; 9, 37939-82-5; 10, 87371-59-3; 12, 87371-60-6; 13, 87393-25-7; 14, 87371-61-7; 15, 87371-62-8.

Mercury in Organic Chemistry. 25.[1] Rhodium(I)-Catalyzed Alkenylation of Arylmercurials

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Arylmercurials and vinyl halides are catalytically cross-coupled to aryl olefins in fair to good yields by 10% $ClRh(PPh_3)_3$. This reaction appears to proceed through an arylvinylrhodium(III) intermediate.

Organomercurials are attractive synthetic intermediates due to their ready availability, stability, and ability to accommodate almost all important organic functional groups. A number of important synthetic applications of these compounds are now known.[2] Until recently, however, there have been few methods available for the direct alkylation of organomercurials. Lately, procedures based

(1) For part 24 see: Larock, R. C.; Liu, C. L. *J. Org. Chem.* **1983**, *48*, 2151.

(2) Larock, R. C. *Tetrahedron* **1982**, *38*, 1713.

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Table I. Reaction Conditions

solvent[a]	% $ClRh(PPh_3)_3$	temp, °C	time, h	% yield
THF	10	reflux	6	0
benzene	10	reflux	6	0
Me_2SO	10	70	6	45
DMF	10	70	6	67
HMPA	10	70	6	82
HMPA	10	70	12	81
HMPA	10	70	24	67
HMPA	5	70	24	43
HMPA	1	70	24	23
HMPA	10	70	24	10

[a] LiCl was an additional reagent in the first nine cases.

on organopalladium intermediates,[3] free radicals,[4] and organocopper cross-coupling reactions[5] have helped to fill this void.

We previously reported that alkenyl-, alkynyl-, and arylmercurials could be methylated in excellent yield upon treatment with stoichiometric amounts of $CH_3RhI_2(PPh_3)_2$ (eq 1).[6] Although this same cross-coupling reaction could

$$RHgX + CH_3RhI_2(PPh_3)_2 \rightarrow RCH_3 \quad (1)$$

be effected by using methyl iodide and catalytic amounts of Wilkinson's catalyst, $ClRh(PPh_3)_3$, the catalyst turnover was very low (eq 2). The major difficulty appeared to be

$$RHgX + CH_3I \xrightarrow{ClRh(PPh_3)_3\ (catal)} RCH_3 \quad (2)$$

dimerization of the organomercurial by the rhodium catalyst (eq 3), a reaction reported previously by us.[7] To

$$2RHgX \xrightarrow{Rh(I)\ or\ Rh(III)\ (catal)} R\text{–}R + HgX_2 + Hg \quad (3)$$

improve the catalytic cross-coupling reaction, we reasoned that we must employ organomercurials which neither contain a β-hydrogen (in order to avoid β-hydride elimination) nor undergo facile rhodium-catalyzed dimerization. Since arylmercurials are dimerized by rhodium catalysts much less readily than vinylmercurials[7] and contain no β-hydrogens which can be readily eliminate, they appeared to be the organomercurials of choice. It was also evident that the organic halide employed must undergo rapid oxidative addition to the rhodium(I) catalyst. Since β-bromostyrene is reported to oxidatively add to PdL_n and PtL_n complexes 100 times faster than methyl iodide,[8] vinyl halides appeared most suitable as the organic halide in our cross-coupling reaction. We now report the results of our study of the rhodium(I)-catalyzed cross-coupling of arylmercurials and vinyl halides.

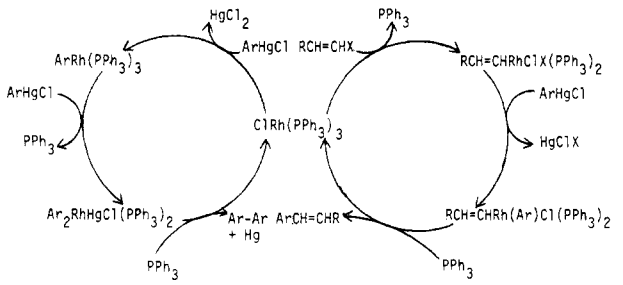
Results and Discussion

We first studied the reaction of phenylmercuric chloride and excess vinyl bromide in the presence of $ClRh(PPh_3)_3$ in order to optimize the reaction conditions (eq 4). The

$$PhHgCl + H_2C{=}CHBr \xrightarrow{ClRh(PPh_3)_3} PhCH{=}CH_2 \quad (4)$$

results are summarized in Table I. The best conditions for cross-coupling proved to be 10% $ClRh(PPh_3)_3$ as the catalyst, dry hexamethylphosphoramide (HMPA) as the solvent, the addition of excess LiCl, and a reaction temperature of 70 °C for 6–12 h. Under these conditions an 82% yield of styrene can be obtained. Attempts to significantly reduce the amount of the rhodium catalyst unfortunately resulted in sharply reduced yields of cross-coupled product.

Scheme I



We next examined the cross-coupling of a variety of arylmercurials and vinyl halides. The results are reported in Table II. Diarylmercurials, arylmercuric chlorides bearing electron-donating and -withdrawing groups, and heterocyclic mercurials can all be satisfactorily employed in this reaction (entries 2–5). As expected, vinyl iodides give higher yields than vinyl bromides (compare entry 6 with 7 and 8) and need not be used in large excess. While *trans*-1-hexenyl iodide gave the anticipated trans coupling product (entry 7), the corresponding *cis*-vinyl iodide (entry 8) gave a cis–trans mixture, with the trans product predominating. Better results appear to be obtained when one uses vinyl iodides bearing electron-withdrawing groups as seen in entry 9. The only significant side reaction observed is dimerization of the arylmercurial.

The following mechanistic scheme (Scheme I) appears to best account for the products in these cross-coupling reactions. The dimerization side reaction may actually proceed by an oxidative addition–transmetalation sequence instead of that shown.[7] Vinyl halides such as *trans*-1-iodo-1-octen-3-one (entry 9), which undergo particularly facile oxidative addition to the rhodium catalyst, give only a trace of dimerization product, consistent with the competition shown in Scheme I.

Conclusion

Arylmercurials and vinyl halides can be cross-coupled to yield aryl olefins in fair to good yield by using 10% $ClRh(PPh_3)_3$. The reaction appears to involve initial oxidative addition of the vinyl halide to the rhodium(I) catalyst to yield a vinylrhodium(III) species and subsequent arylation by the organomercurial to generate an arylvinylrhodium(III) intermediate which reductively eliminates the olefin and regenerates the catalyst. Alternatively, arylation followed by oxidative addition may be occurring to afford the same key rhodium(III) intermediate.

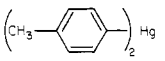
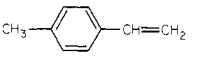
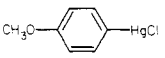
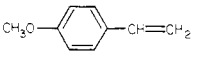
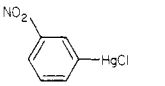
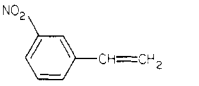
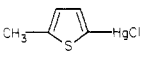
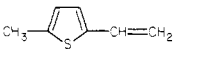
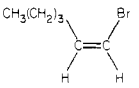
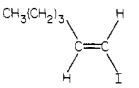
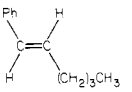
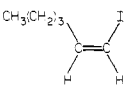
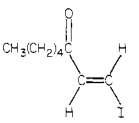
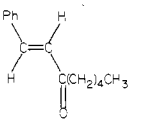
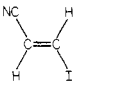
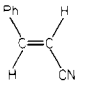
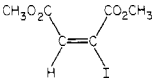
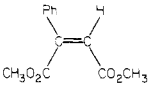
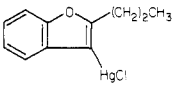
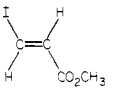
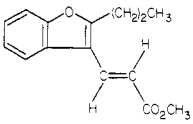
Experimental Section

Reagents. All reagents were used as obtained commercially unless otherwise noted. Tetrahydrofuran (THF) was distilled from calcium hydride. HMPA was distilled from calcium hydride at reduced pressure.

Phenylmercuric chloride (Aldrich) and di-*p*-tolylmercury (Eastman) were used directly as obtained commercially. *p*-Anisylmercuric chloride,[9] 2-(chloromercuri)-5-methylthiophene,[10] and (*m*-nitrophenyl)mercuric chloride[11] were prepared by using

(3) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518; **1969**, *91*, 6707; **1971**, *93*, 6896.
(4) (a) Giese, B.; Heuck, K. *Tetrahedron Lett.* **1980**, *21*, 1829. (b) Giese, B.; Zwick, W. *Ibid.* **1980**, *21*, 3569. (c) Giese, B.; Kretzchmar, G.; Meixner, J. *Chem. Ber.* **1980**, *113*, 2787.
(5) Larock, R. C.; Leach, D. R. *Organometallics* **1982**, *1*, 74.
(6) Larock, R. C.; Hershberger, S. S. *J. Organomet. Chem.* **1982**, *225*, 31.
(7) Larock, R. C.; Bernhardt, J. C. *J. Org. Chem.* **1977**, *42*, 1680.
(8) Rajaram, J.; Pearson, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 2103.
(9) Dimroth, O. *Chem. Ber.* **1902**, *35*, 2853.
(10) Steinkopf, W.; Bauermeister, M. *Justus Liebigs Ann. Chem.* **1914**, *403*, 50.

Table II. Alkenylation of Arylmercurials

entry	arylmercurial	vinyl halide (equiv)	product(s)	% yield[a]
1	PhHgCl	H_2C=CHBr (10)	$PhCH=CH_2$	82
2		H_2C=CHBr (10)		75[b]
3		H_2C=CHBr (10)		80
4		H_2C=CHBr (10)		64
5		H_2C=CHBr (10)		(40)
6	PhHgCl		$PhCH=CH(CH_2)_3CH_3$	trace
7	PhHgCl			72
8	PhHgCl		$PhCH=CH(CH_2)_3CH_3$ (1:3 cis/trans)	65
9	PhHgCl			(70)
10	PhHgCl			(31)[c]
11	PhHgCl			trace
12				(50)

[a] Yields were determined by gas–liquid chromatography by using an internal standard an an appropriate corrections factor (isolated yields in parentheses). [b] Based on utilization of only one aryl group. [c] 1.2 equiv of phenylmercuric chloride was employed.

literature procedures. 3-(Chloromercuri)-2-*n*-propylbenzofuran was kindly provided by L. W. Harrison of Iowa State University. Wilkinson's catalyst, $ClRh(PPh_3)_3$, was prepared from $RhCl_3 \cdot 3H_2O$ according to the literature procedure.[12]

The following vinyl halides were prepared according to the literature procedures: *cis*-1-iodo-1-hexene,[13] *trans*-1-iodo-1-hexene,[14] *trans*-1-iodooctene-3-one,[15] *trans*-3-iodoacrylonitrile,[16] dimethyl iodomaleate,[17] *cis*-1-bromo-1-hexene.[18] Vinyl bromide was obtained from Aldrich and used directly.

Equipment. Gas chromatographic analyses were carried out on a Varian Model 3700 gas chromatograph with a flame-ionization detector. The retention times of authentic samples were used to identify products. In addition, a Finnigan 4023 gas chromatograph–mass spectrometer was employed to verify the identity of the products. All gas chromatographic yields were determined by using hydrocarbon internal standards and appropriate correction factors. ^1H NMR spectra were obtained on Varian A-60 or EM-360 instruments with tetramethylsilane as an internal standard.

Alkenylation of Arylmercurials. The following procedure for the reaction of phenylmercuric chloride with vinyl bromide is representative. Approximately 0.25 g of lithium chloride was placed in a 25-mL round-bottomed flask equipped with a septum inlet, gas inlet tube, and magnetic stirring bar. The lithium chloride was dried by using a hot-air gun under vacuum, and 0.023 g (0.025 mmol) of $ClRh(PPh_3)_3$ and 0.0785 g (0.25 mmol) of phenylmercuric chloride were added while back-flushing with nitrogen. A condenser was placed on the flask, approximately 1.5 mL (10 equiv) of vinyl bromide was added, and the gas inlet tube was reattached to the top of the condenser. *n*-Decane (0.0355 g, 0.25 mmol; internal standard) and 2.5 mL of dry, freshly distilled HMPA were added by syringe. After the mixture stirred the appropriate time at 70 °C, 5 mL of water and 2 mL of benzene were added, and the benzene layer was analyzed by gas chromatography.

Synthesis of *trans*-1-Phenyl-1-octen-3-one. Lithium chloride (3.36 g, 80 mmol) was placed in a 250-mL round-bottomed flask with a side-arm gas inlet tube and a magnetic stirring bar. The LiCl was dried by using a hot-air gun under vacuum. Phenylmercuric chloride (2.507 g, 8 mmol) and $ClRh(PPh_3)_3$ (0.747 g, 0.8 mmol) were added while back-flushing with nitrogen. The *trans*-1-iodo-1-octen-3-one (2.016 g, 8 mmol) was then added, followed by 80 mL of HMPA. The reaction mixture was heated at 70 °C for 6 h and then poured into ice. Pentane was added,

(11) Klapproth, W. J.; Westheimer, F. H. *J. Am. Chem. Soc.* **1950**, *72*, 4461.
(12) Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.
(13) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086.
(14) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.
(15) Price, C. G.; Pappalarado, J. A. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 186.
(16) Coe, P. C.; Milner, N. E.; Smith, J. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 654.
(17) Jones, G., II; Fantina, M. E.; Pachtman, A. H. *J. Org. Chem.* **1976**, *41*, 329.
(18) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 6456.

and the suspension formed was filtered off. The residue was washed with pentane. The organic layer was separated, and the aqueous layer was extracted twice with pentane. The pentane layer was washed with water, dilute HCl, water, and dilute NaOH in that order and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. Purification by flash column chromatography with 9:1 hexane/ethyl acetate (R_f 0.38) gave the product: 1.10 g (70% yield); ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 6 Hz, CH_3), 1.0–1.75 (m, 6 H, CH_2's), 2.48 (br t, 2 H, J = 5 Hz, CH_2CO), 6.55 (d, 1 H, J = 18 Hz, =CHCO), 7.0–7.6 (m, 6 H, C_6H_5CH); IR (Nujol) 3100, 3065, 3020, 1695, 1670, 1615, 980, 740, 680 cm^{-1}; mass spectrum, m/z 202 (M^+).

Some other compounds that were prepared by using this basic procedure are as follows.

Cinnamonitrile: 31% yield; ^{1}H NMR ($CDCl_3$) δ 5.70 (d, 1 H, J = 18 Hz, =CHCN), 7.0–7.45 (m, 6 H, C_6H_5CH); IR (neat) 3070, 3030, 2210, 1620, 965, 745, 680 cm^{-1}; mass spectrum, m/z 129 (M^+).

2-Methyl-5-vinylthiophene: 40% yield; ^{1}H NMR ($CDCl_3$) δ 2.66 (s, 3 H, CH_3), 4.73–5.36 (m, 3 H, vinyl), 6.40–6.86 (m, 2 H, thiophene); IR (neat) 3100, 3080, 2970, 2920, 2880, 1620, 1450 cm^{-1}; mass spectrum, m/z 124 (M^+).

Methyl *trans*-3-(2-*n*-propyl-3-benzofuryl)acrylate: 50% yield; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H, J = 6 Hz, CH_3), 1.67 (m, 2 H, CH_2CH_3), 2.78 (t, 2 H, J = 7 Hz, CH_2), 3.69 (s, 3 H, OCH_3), 6.45 (d, 1 H, J = 18 Hz, vinyl), 7.1–7.84 (m, 6 H, aryl and vinyl); IR (neat) 3020, 2970, 2880, 1720, 1635, 1580, 1455, 1435, 1300, 1270, 1170, 965, 850, 750 cm^{-1}; mass spectrum, m/z calc for $C_{15}H_{16}O_3$ 244.109 95, obsd 244.109 74.

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Registry No. $ClRh(PPh_3)_2$, 14694-95-2; $PhCH{=}CH_2$, 100-42-5; *cis*-$PhCH{=}CH(CH_2)_3CH_3$, 15325-54-9; *trans*-$PhCH{=}CH(CH_2)_3CH_3$, 6111-82-6; PhHgCl, 100-56-1; $H_2C{=}CHBr$, 593-60-2; LiCl, 7447-41-8; Me_2SO, 67-68-5; HMPA, 680-31-9; DMF, 68-12-2; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4; *m*-nitrostyrene, 586-39-0; 2-methyl-5-vinylthiophene, 62485-03-4; *trans*-1-phenyl-1-octen-3-one, 29478-39-5; cinnamonitrile, 1885-38-7; dimethyl phenylmaleate, 29576-99-6; methyl *trans*-3-(2-*n*-propyl-3-benzofuryl)acrylate, 87226-83-3; di-*p*-tolylmercury, 537-64-4; *p*-anisylmercuric chloride, 3009-79-8; (*m*-nitrophenyl)mercuric chloride, 2865-17-0; 2-(chloromercuri)-5-methylthiophene, 87226-84-4; 3-(chloromercuri)-2-*n*-propylbenzofuran, 87226-85-5; *cis*-1-bromo-1-hexene, 13154-12-6; *trans*-1-iodo-1-hexene, 16644-98-7; *cis*-1-iodo-1-hexene, 16538-47-9; *trans*-1-iodoocten-3-one, 39178-64-8; *trans*-3-iodoacrylonitrile, 56017-69-7; dimethyl iodomaleate, 1600-35-7; methyl *trans*-3-iodoacrylate, 6213-88-3.

Stereospecific Synthesis of Selectively C-7-Acetalized Substituted 4aβ-Methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-diones. A Short Total Synthesis of (±)-β-Eudesmol, (±)-β-Selinene, and (±)-β-Dictyopterol

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An efficient general method has been developed for the synthesis of 4aβ,8α-dimethyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-ethylene acetals **1** and 4aβ-methyl-3,4,4a,5,6,8aα-hexahydronaphthalene-1(2*H*),7(8*H*)-dione 7-dimethyl acetals **2**, which are important intermediates in the total synthesis of eudesmanes and other sesquiterpenes. With (substituted) 4aβ-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2-(3*H*)-ones **3** as the starting compounds, the 8-positions were hydroxylated by *m*-chloroperbenzoic acid oxidation of the corresponding dienol ethers **4** or dienol acetates **5**. The 8-hydroxy unsaturated ketones **6** and **7** were oxidized to enediones **11**. Reductions of **11** to the diones **12**, **13**, and **14** were accomplished by using titanium(III) chloride or hydrogen iodide. Isomerization of the C-1-unsubstituted 8-hydroxy enones **6** and **7** with hydrogen bromide gave the diones **12** and **14** directly. Selective acetalization using 2-butanone dioxolane or trimethyl orthoformate gave **1** and **2**, respectively. Compounds **2a** and **2e** were converted into the methylene ketones **18a** and **18e**. Peterson olefination of the carbonyl functions with methoxy(phenylthio)(trimethylsilyl)methyllithium (**19**) was used for the preparation of intermediate ketene *O,S*-acetals which were methanolized directly to a stereoisomeric mixture of the methyl esters **21a,e** and **22a,e**. Finally, these esters were converted into (±)-β-eudesmol, (±)-β-selinene, and (±)-β-dictyopterol.

In the last decade several different approaches have been applied to the synthesis of eudesmanes[1] and/or eudesmanolides.[1a,b,2] Most of the reported syntheses of this class of sesquiterpenes have started from the Wieland–Miescher ketone or its derivatives, which are readily available from Robinson annelations of 2-methylcyclohexanone or 2-methyl-1,3-cyclohexanedione. Further elaboration of the Wieland–Miescher ketone or its analogues to intermediates with structure **1** has been demonstrated not only in the synthesis of several eudesmanes[3] or eudesmanolides[4] but also in the synthesis of guaiazulenic ses-

(1) For an extensive review of the total synthesis of eudesmane sesquiterpenes through the middle of 1970 see: (a) Heathcock, C. H. In "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley: New York, 1973, Vol. II, Chapter 2. For the period 1970–1978 see: (b) *Terpenoids Steroids* **1971–1979**, *1–9*. (Chemical Society Specialists Periodical Reports). Recent reports on the synthesis of eudesmanes: (c) Cooper, J. L.; Harding, K. E. *Tetrahedron Lett.* **1977**, 3321. (d) Mackenzie, B. D.; Angelo, M. M.; Wolinsky J. *J. Org. Chem.* **1979**, *44*, 4042. (e) Wilson, S. R.; Mao, D. T. *J. Am. Chem. Soc.* **1978**, *100*, 6289. (f) Torii, S.; Inokuchi, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2642. (g) Miller, R. B.; Frincke, J. M. *J. Org. Chem.* **1981**, *46*, 2972.

(2) Schultz, A. G.; Godfrey, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 2414 and references herein.

(3) (a) Marshall, J. A.; Pike, M. T.; Carroll, R. D. *J. Org. Chem.* **1966**, *31*, 2933. (b) Posner, G. H.; Loomis, G. L.; Sawaya, H. S. *Tetrahedron Lett.* **1975**, 1373. (c) Vig, O. P.; Sharma, M. L.; Anand, R.; Sharma, S. D. *J. Indian Chem. Soc.* **1976**, *53*, 81. (d), Vig, O. P.; Kumar, S. D.; Vig, R.; Sharma, S. D. *Indian J. Chem.* **1980**, *19B*, 871.

(4) (a) Minato, H.; Nagasaki, T. *J. Chem. Soc. C* **1968**, 621. (b) Grieco, P. A.; Nishizawa, M. *J. Chem. Soc., Chem. Commun.* **1976**, 582. (c) Nishizawa, M.; Grieco, P. A.; Burke, S. D.; Metz, W. *Ibid.* **1978**, 76.

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