by acetylation with acetic anhydride in pyridine.

Methyl 3-*O*-Acetyl-4-*S*-acetyl-2-deoxy-4-thio-α-D-*erythro*-pentopyranoside (32). Compound 4a (3.65 g, 0.01 mol) was stirred with potassium thioacetate (3.5 g) in dry DMF (50 mL) at an oil-bath temperature of 95–100 °C under a current of dry nitrogen for 5 h. The reaction mixture was cooled to room temperature and poured with stirring into dry xylene (150 mL). The precipitated salts were filtered and washed with dry xylene. The combined filtrates were evaporated to a syrupy residue which was extracted with heptane (4 × 50 mL). The heptane solution was evaporated, and the syrupy residue was dissolved in dry pyridine (20 mL) and acetic anhydride (5 mL). After 16 h at room temperature, the reaction mixture was poured with stirring into ice–water (50 mL). The mixture was extracted with chloroform, and the extract was washed with water (2 × 10 mL), dried (Na₂SO₄), and evaporated to a syrup. Purification of this syrup by chromatography on silica gel, using solvent B as the eluant, gave **32** (52%) which was identical with an authentic sample of **32** prepared by a different procedure.[12]

Methyl 3,4-Anhydro-2-deoxy-α-D-*erythro*-pentopyranoside (5). Compound 4a (3.65 g, 0.01 mol) was dissolved in a cold (0 °C) solution of sodium methoxide (300 mg of Na) in methanol (100 mL), and the reaction mixture was kept at 4 °C for 16 h. The mixture was evaporated and the residue extracted with ether. The ether solution was filtered and evaporated. Distillation of the residue at 0.005 mmHg and 35 °C gave pure **5**.

Methyl 2,3-Anhydro-4-*O*-(*p*-toluenesulfonyl)-β-L-ribopyranoside (7). Compound **7** was prepared by tosylation of methyl 2,3-anhydro-β-L-ribopyranoside.[23,24]

Methyl 2,3-anhydro-4,6-bis[*O*-(*p*-toluenesulfonyl)]-α-D-allopyranoside (10b) was prepared according to the reported procedure.[13b]

Methyl 2,3-anhydro-4,6-bis[*O*-(*p*-chlorobenzenesulfonyl)]-α-D-allopyranoside (10a) was prepared by *p*-chlorobenzenesulfonylation of methyl 2,3-anhydro-α-D-allopyranoside.[14]

Procedure for Lithium Aluminium Hydride Reductions. To a chilled (0 °C) stirred solution of lithium aluminum hydride in dry THF was added a solution of the compound dissolved in dry ether. The reaction mixture was stirred at room temperature, and the progress of the reduction was monitored by TLC. Wet ether was added cautiously to decompose the excess hydride, and the inorganic solids were filtered and washed with THF. The residue obtained by evaporation of the combined filtrates was separated by chromatography.

Methyl 4-*O*-(*p*-chlorobenzenesulfonyl)-2,3-*O*-isopropylidene-α-L-lyxopyranoside (23) was prepared by *p*-chlorobenzenesulfonylation of methyl 2,3-*O*-isopropylidene-α-L-lyxopyranoside.[25]

Methyl 4-*O*-(*p*-Chlorobenzenesulfonyl)-α-L-lyxopyranoside (24). Compound 23 (30 g) was dissolved in 50% acetic acid (200 mL), and the solution was heated at 70 °C for 5 h. TLC of the reaction mixture showed only the presence of **24**. The solution was evaporated to a syrupy residue which was dissolved in toluene (400 mL). Evaporation of the toluene solution gave **24**.

Methyl 3,4-Anhydro-β-D-ribopyranoside (25). Compound 24 (33.9 g, 0.1 mol) was dissolved in a cold (0 °C) solution of sodium methoxide (3 g of Na) in methanol (500 mL), and the reaction mixture was kept at 4 °C for 24 h. The mixture was neutralized with methanolic HCl and evaporated, and the residue was extracted with CH₂Cl₂ (2 × 200 mL). The CH₂Cl₂ solution was filtered and evaporated to a syrup which was homogeneous by TLC.

Methyl 3,4-anhydro-2-*O*-(*p*-toluenesulfonyl)-β-D-ribopyranoside (26) was prepared by tosylation of **25**.

5,6-Anhydro-1,2-*O*-isopropylidene-3-*O*-(methylsulfonyl)-β-L-idofuranose[26] **(28)** was prepared by the reported procedure.

5,6-Anhydro-1,2-*O*-isopropylidene-3-*O*-(methylsulfonyl)-α-glucofuranose[27] **(30)** was prepared according to the published method.

Registry No. 1a, 74128-31-7; 1b, 74128-32-8; 2a, 74128-33-9; 2b, 74128-34-0; 3a, 74128-35-1; 3b, 74128-36-2; 4a, 74128-37-3; 4b, 74128-38-4; 5, 74128-39-5; 6a, 74128-40-8; 7, 74128-41-9; 8, 74128-42-0; 9, 74128-43-1; 10a, 74128-44-2; 10b, 71811-64-8; 11a, 74128-45-3; 11b, 71811-67-1; 12a, 74128-46-4; 12b, 74128-47-5; 13, 17676-18-5; 14, 74128-48-6; 15, 74128-49-7; 16, 74128-50-0; 17, 74128-51-1; 18, 66108-06-3; 19, 60134-27-2; 20, 74128-52-2; 21, 74128-53-3; 22, 74128-54-4; 23, 74128-55-5; 24, 74128-56-6; 25, 74128-57-7; 26, 74128-58-8; 27, 74128-59-9; 28, 19286-05-6; 29, 64243-86-3; 30, 16848-30-9; 31, 19235-24-6; 32, 60295-31-0; methyl 2,3-anhydro-β-L-lyxopyranoside, 6207-00-7; methyl 2,3-anhydro-β-L-ribopyranoside, 56153-83-4; methyl 2,3-anhydro-α-D-allopyranoside, 3257-61-2; methyl 2,3-*O*-isopropylidene-α-L-lyxopyranoside, 2495-99-0.

Supplementary Material Available: Physical properties and analytical data (Table I) and selected ¹H NMR spectral parameters (Table II) for the new compounds (4 pages). Ordering information is given on any current masthead page.

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Mercury in Organic Chemistry. 18. Synthesis of Symmetrical Divinyl and Diaryl Ketones via Rhodium-Catalyzed Carbonylation of Vinyl- and Arylmercurials

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Vinylmercuric chlorides readily react with rhodium(I) and rhodium(III) catalysts and carbon monoxide to give excellent yields of divinyl ketones. The best reaction conditions are 0.5 mol % [Rh(CO)₂Cl]₂ and 2 equiv of lithium chloride under 1 atm of carbon monoxide at room temperature. This rhodium catalyst also provides improved yields of diaryl ketones from arylmercurials at 70 °C under 1000–1500 psi of carbon monoxide pressure. Organorhodium compounds are presumed to be intermediates in these reactions.

Divinyl ketones are employed in organic chemistry as double[1–8] and less frequently as single[9] Michael acceptors.

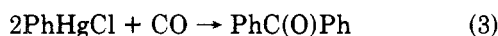Divinyl ketone equivalents have also been established as symmetrical or unsymmetrical double Michael accep-

tors.[10-12] In the Nazarov cyclization,[13] divinyl ketones are treated with acid, generating pentadienyl cations[14-19] which cyclize to cyclopentenones, in some cases stereospecifically.[20] Unfortunately, few convenient syntheses of divinyl ketones presently exist. Our own earlier work on the acylation of vinylmercurials provided a convenient new route to this class of compounds (eq 1).[21] We now
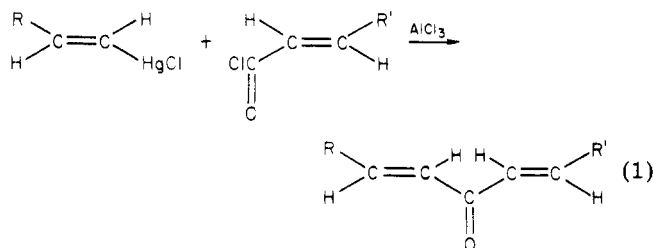
wish to report a facile, stereospecific, new synthesis of symmetrical divinyl ketones via rhodium(I)- and rhodium(III)-catalyzed carbonylation of vinylmercurials (eq 2).
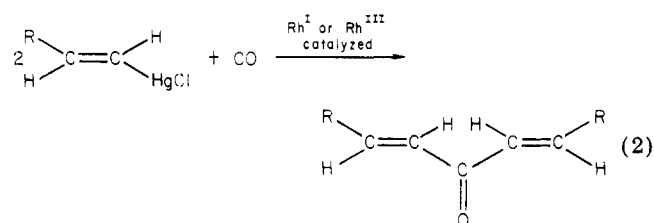
Our preferred catalyst also provides improved yields in the previously published rhodium-catalyzed carbonylation of arylmercurials to diaryl ketones (eq 3).[22]

$$2PhHgCl + CO \rightarrow PhC(O)Ph \qquad (3)$$

Table I. Effect of
Solvent and Temperature on the Formation of
trans,trans-2,2,8,8-Trimethyl-3,6-nonadien-5-one

solvent	T, °C	t, h	% yield[a]
THF	25	24	85, 94
	65	1	19
	65	24	19
Et$_2$O	25	24	68
CH$_2$Cl$_2$	25	24	58
HMPA	25	24	~60[b]
	70	1	~21[b]
	70	24	~25[b]

[a] GC analysis using an internal standard. [b] Corrected yield determined from peak heights and not peak areas, since HMPA interferes with peak-area measurement.

Although organomercurials are directly carbonylated only under high temperatures and pressures,[23,24] certain transition-metal complexes readily undergo transmetalation by organomercurials to form organo transition-metal species which are easily carbonylated. Aromatic carboxylic acids and their derivatives[25,26] as well as diaryl ketones[22,26-30] have been prepared from arylmercurials by using transition-metal complexes and carbon monoxide. We have reported that palladium-promoted carbonylation of vinylmercurials affords a convenient, stereospecific synthesis of α,β-unsaturated carboxylic acids and esters.[31] Extending our work on the synthesis of 1,3-dienes and biaryls via rhodium-catalyzed coupling of vinyl- and arylmercurials (eq 4 and 5),[32] we observed that when these

$$2PhHgCl \rightarrow Ph-Ph \qquad (5)$$
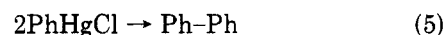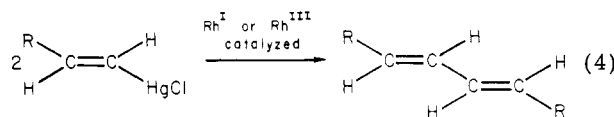
reactions are effected in the presence of carbon monoxide, divinyl and diaryl ketones are formed instead. This approach to divinyl and diaryl ketones appeared particularly promising in view of (1) the ready availability of vinylmercurials[33,34] and arylmercurials[35] from acetylenes and arenes, respectively, (2) the expectation that both transmetalation and carbonylation would proceed with complete retention of stereochemistry with respect to carbon,[36,37] and

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(3) the exceptionally mild reaction and workup conditions which were required to obtain the highly acid- and base-sensitive divinyl ketones. We now wish to report the scope of this new ketone synthesis.

Results and Discussion

Synthesis of Divinyl Ketones. Upon the observation of the formation of distyryl ketone from the reaction of *trans*-styrylmercuric chloride, carbon monoxide, and a catalytic amount of $Rh(CO)Cl[P(C_6H_5)_3]_2$ in hexamethylphosphoramide (HMPA) at 70 °C (eq 6), optimum
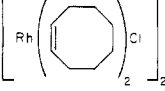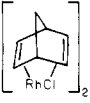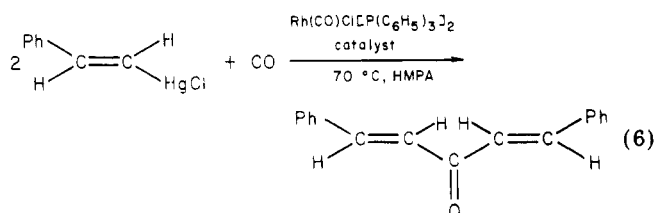

reaction conditions for divinyl ketone formation were sought. Due to the unusually low solubility of *trans*-styrylmercuric chloride in many solvents, *trans*-3,3-dimethyl-1-butenylmercuric chloride was utilized in all subsequent optimization studies. Initially the effect of solvent and temperature upon reactions catalyzed by 10 mol % of $Rh(CO)Cl[P(C_6H_5)_3]_2$ was considered (Table I). Tetrahydrofuran (THF) at room temperature produces the highest yield of divinyl ketone. In refluxing THF, the yield of divinyl ketone is substantially reduced due to preferential formation of the symmetrical diene, *trans,trans*-2,2,7,7-tetramethyl-3,5-octadiene.[32] The effect of temperature on the reaction in HMPA is similar. Although the yield in HMPA is nearly comparable to that in THF, it is not the solvent of choice due to its reported carcinogenic properties. The yield in either diethyl ether or dichloromethane at room temperature is also lower than the yield in THF. Despite the lower yield, the reaction in dichloromethane was clean.

The effect of various rhodium catalysts on the formation of divinyl ketones was considered next (Table II). The other rhodium catalysts which were nearly as effective as $Rh(CO)Cl[P(C_6H_5)_3]_2$ contained two coordinating ligands comprised of various olefins or carbon monoxide. The rhodium(I) compounds containing olefin ligands most likely undergo facile displacement of the olefin ligand by carbon monoxide to form $[Rh(CO)_2Cl]_2$ which has been found to be the most effective catalyst. A rhodium(III) compound, $RhCl_3 \cdot 3H_2O$, was also found to catalyze divinyl ketone formation. Of the various rhodium catalysts, Wilkinson's catalyst with three triphenylphosphine ligands is the least catalytic with respect to the formation of divinyl ketones. Although the initially dark red solution immediately turned yellow upon flushing the solution with carbon monoxide and the color of the reaction then resembled that of the $Rh(CO)Cl[P(C_6H_5)_3]_2$-catalyzed reactions, the yield of divinyl ketone was significantly lower. While it might be argued that the presence of three triphenylphosphines and carbon monoxide decreases the reactivity of this rhodium(I) catalyst, the competing formation of a vinylphosphonium salt similar to the recently reported reaction of Wilkinson's catalyst and α,β-unsaturated acid chlorides[38] may also be involved. While an extensive number of rhodium compounds catalyze this reaction, palladium chloride, which promotes the formation

Table II. Effect of Catalyst on the Formation of *trans,trans*-2,2,8,8-Tetramethyl-3,6-nonadien-5-one
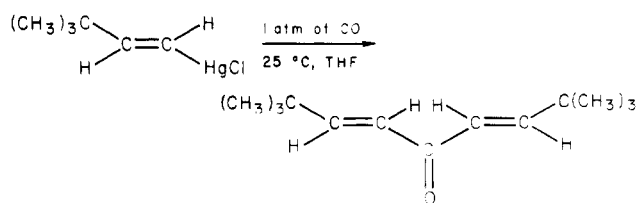
catalyst	mol % catalyst	added reagents	t, h	% yield[a]
$Rh(CO)Cl[P(C_6H_5)_3]_2$	10		24	85, 94
	1		24	69
			84	82
	0.1		24	42
			84	67
			132	64
	10	LiCl[c]	24	80
$RhCl_3 \cdot 3H_2O$			24	60
			48	68
$RhCl[P(C_6H_5)_3]_3$			24	20
			48	21
$[Rh(H_2C=CH_2)_2Cl]_2$	5		24	69
$[Rh(CO)_2Cl]_2$			24	77
		LiCl[c]	24	99
			24	52
			24	64
Li_2PdCl_4	100		6	10
			24	7
			4	33[b]
			24	18[b]
	10	$CuCl_2$[d]	6	0
			24	0

[a] GC analysis using an internal standard. [b] Reaction temperature began at -78 °C and warmed to room temperature. [c] Greater than 2 equiv of reagent added. [d] 2 equiv of reagent added.

of α,β-unsaturated esters and acids from vinylmercurials,[31] promotes the formation of divinyl ketones to a lesser extent and also appears to consume the divinyl ketone as it is formed. Since palladium(0) complexes of dibenzalacetone have been previously characterized,[39,40] the formation and further reaction or decomposition of similar palladium complexes might be proposed.

The addition of 2 equiv of lithium chloride to the reaction catalyzed by $[Rh(CO)_2Cl]_2$ established that quantitative conversion of the vinylmercurial to divinyl ketone can be effected by using 1 equiv of the vinylmercurial, 2 equiv of lithium chloride, and only 10 mol % of $[Rh(CO)_2Cl]_2$ under 1 atm of carbon monoxide in THF. In fact, as little as 0.5 mol % of the $[Rh(CO)_2Cl]_2$ catalyst was subsequently found to give nearly quantitative yields in this reaction. This set of reaction conditions also provides the smoothest isolation procedure. Analogous conditions where nitrogen replaces the carbon monoxide atmosphere have been found previously to be the best conditions for formation of 1,3-dienes from vinylmercurials.[32] Other vinylmercurials also react with carbon monoxide, lithium chloride, and 0.5 mol % $[Rh(CO)_2Cl]_2$ to afford excellent

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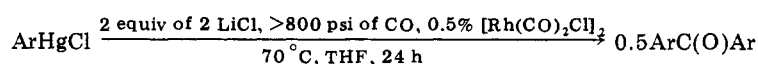
Table III. Synthesis of Symmetrical Divinyl Ketones
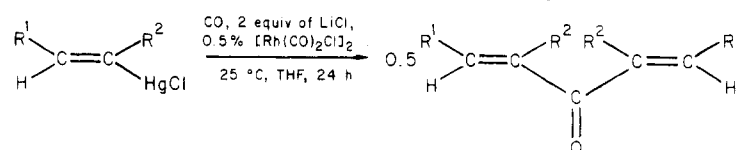
vinylmercurial	divinyl ketone	% yield[a]	vinylmercurial	divinyl ketone	% yield[a]
		96 (78)			100[c]
		94 (78)			41[c,d]
		99 (88)			89[e]
		64 (47)[b]			d

[a] Crude isolated yield (purified yield). [b] Reaction time of 4 days. [c] Attempted purification resulted in decomposition. [d] Purity of organomercurial is questionable or unknown. [e] GC yield.

Table IV. Synthesis of Symmetrical Diaryl Ketones

$$\text{ArHgCl} \xrightarrow[\text{70 °C, THF, 24 h}]{\text{2 equiv of 2 LiCl, >800 psi of CO, 0.5\% [Rh(CO)}_2\text{Cl]}_2} 0.5\text{ArC(O)Ar}$$

arylmercurial	diaryl ketone	% yield[a]	mp, °C (lit. mp, °C)	ref
PhHgCl	PhC(O)Ph	80 (66)	23–25 (26 or 48)	b
		100 (95)	159–161 (164.5)	c
		89 (78)	89–90 (90.5)	d
		60 (38)	152–153 (155–155.5)	e

[a] Crude isolated yield (recrystallized yield). [b] See ref 42. [c] See ref 43. [d] See ref 44. [e] See ref 26.

yields of the corresponding divinyl ketones (Table III). In all cases, the stereochemistry of the vinylmercurial is preserved in the resulting divinyl ketone. Vinylmercurials derived from terminal alkynes[33,34] produce nearly quantitative yields of divinyl ketones after 24 h, while diminished yields are observed with vinylmercurials derived from internal alkynes even with longer reaction times. Organomercurials derived from enynes are also transformed into the corresponding symmetrical polyenones. However, these compounds proved very difficult to purify due to their instability. Although 3-pentadienone is available by this route, it is not easily isolated due to its volatility. No yield is reported for the synthesis of *trans,trans*-1,5-dichloro-3-pentadienone due to difficulties in obtaining pure *trans*-(β-chlorovinyl)mercuric chloride[41] free from the

corresponding divinylmercurial.

Synthesis of Diaryl Ketones. Although the formation of diaryl ketones via the carbonylation of arylmercurials mediated by various transition-metal compounds is well established,[22,26–30] the yields of diaryl ketones reported by using rhodium(I) and rhodium(III) catalysts are not high.[22] Since [Rh(CO)₂Cl]₂, lithium chloride, and 1 atm of carbon monoxide transform vinylmercurials to divinyl ketones essentially quantitatively, the carbonylation of arylmercurials under these conditions deserved investigation.

The reaction of phenylmercuric chloride with 1 atm of carbon monoxide, 2 equiv of lithium chloride, and 5 mol % of [Rh(CO)₂Cl]₂ was observed to form biphenyl instead of benzophenone at room temperature. Diaryl ketones are formed only under more vigorous reaction conditions. An increase of the reaction temperature to 70 °C and the

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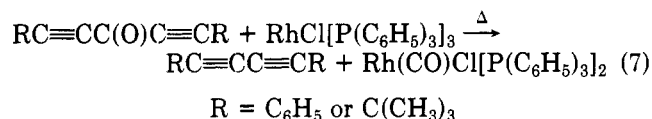(42) Zincke, T. *Justus Liebigs Ann. Chem.* 1871, *159*, 381.

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carbon monoxide pressure to 1000–1525 psi (68–104 atm) and a decrease of the catalyst concentration to 0.5 mol % of [Rh(CO)$_2$Cl]$_2$ allow good to excellent yields of diaryl ketones to be obtained in THF (Table IV). [Rh(CO)$_2$Cl]$_2$ has previously been reported by Larock et al. to catalyze the formation of biaryls from arylmercurials.[33] The optimum conditions previously established for that reaction (HMPA at 70 °C) are also more vigorous than the optimum reaction conditions for diene formation from vinylmercurials.
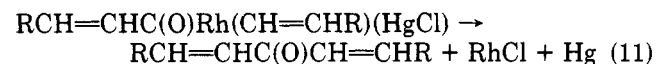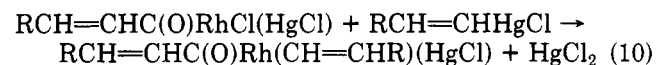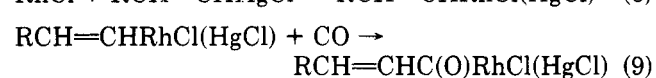
Attempted Synthesis of Dialkynyl and Dialkyl Ketones. Attempts to extend this symmetrical ketone synthesis to dialkynyl or dialkyl ketones were unsuccessful. Bis(3,3-dimethyl-1-butynyl)mercury[45] forms 2,2,7,7-tetramethyl-3,5-octadiyne when reacted with either 1 atm or 1200 psi of carbon monoxide, 2 equiv of lithium chloride, and 0.5 mol % of [Rh(CO)$_2$Cl]$_2$ in THF at room temperature. Formation of the diyne may not be too surprising considering the reported formation of diynes from the reaction of dialkynyl ketones and Wilkinson's catalyst (eq 7).[46] However, it is also possible that the organomercurial

$$RC\equiv CC(O)C\equiv CR + RhCl[P(C_6H_5)_3]_3 \xrightarrow{\Delta}$$
$$RC\equiv CC\equiv CR + Rh(CO)Cl[P(C_6H_5)_3]_2 \quad (7)$$

$$R = C_6H_5 \text{ or } C(CH_3)_3$$

itself may account for the difference. This attempted dialkynyl ketone synthesis employed a diorganomercury compound, whereas the previous divinyl and diaryl ketone syntheses began with organomercuric chlorides.

The reaction of *n*-butylmercuric chloride, 2 equiv of lithium chloride, 0.5 mol % of [Rh(CO)$_2$Cl]$_2$, and 1 atm of carbon monoxide at room temperature did not form 5-nonanone. Alkylmercurials have been shown previously by us not to couple under conditions in which rhodium(I) or rhodium(III) complexes catalyze the formation of symmetrical dienes and biaryls.[32] The failure is presumably due to facile β-hydride elimination from an intermediate alkylrhodium species, forming the corresponding alkene and a rhodium hydride.

Mechanism. Although the mechanism of divinyl ketone formation has not been rigorously investigated, the scheme shown by eq 8–11, involving (1) oxidative addition of the

$$RhCl + RCH{=}CHHgCl \rightarrow RCH{=}CHRhCl(HgCl) \quad (8)$$

$$RCH{=}CHRhCl(HgCl) + CO \rightarrow$$
$$RCH{=}CHC(O)RhCl(HgCl) \quad (9)$$

$$RCH{=}CHC(O)RhCl(HgCl) + RCH{=}CHHgCl \rightarrow$$
$$RCH{=}CHC(O)Rh(CH{=}CHR)(HgCl) + HgCl_2 \quad (10)$$

$$RCH{=}CHC(O)Rh(CH{=}CHR)(HgCl) \rightarrow$$
$$RCH{=}CHC(O)CH{=}CHR + RhCl + Hg \quad (11)$$

vinylmercurial to a rhodium(I) species, (2) insertion of carbon monoxide to form an acylrhodium derivative, (3) transmetalation of this species by another vinylmercurial, and finally (4) reductive elimination of the divinyl ketone to regenerate the rhodium(I) catalyst, seems entirely reasonable. Similar reactions have been proposed previously for reactions of organomercurials and rhodium compounds.[22,32] A number of other schemes involving alternate sequences of these same basic steps can also be envisioned. Since divinyl diketones were not observed even at carbon monoxide pressures of 1525 psi and since the insertion of

carbon monoxide into both platinum–carbon bonds of Pt(CH$_3$)$_2$[P(C$_6$H$_5$)$_3$]$_2$ is demonstrated to be facile,[47] the insertion of carbon monoxide prior to transmetalation seems reasonable. We believe oxidative addition of the vinylmercurial, carbon monoxide insertion, and reductive elimination of the ketone to be relatively easy steps, while the transmetalation step is a relatively difficult step. A similar mechanism is presumably involved in the formation of diaryl ketones from arylmercurials.

Conclusions

Excellent yields of divinyl ketones are obtained from the reaction of vinylmercurials, lithium chloride, and 0.5 mol % of [Rh(CO)$_2$Cl]$_2$ in THF under 1 atm of carbon monoxide at room temperature. The reaction is highly stereospecific. The neutral, mild conditions under which this reaction occurs permit this acid- and base-sensitive class of compounds to be isolated in high yield. Good to excellent yields of diaryl ketones are also obtained from arylmercurials if the temperature and carbon monoxide pressure are increased to 70 °C and 1000–1500 psi, respectively.

Experimental Section

Reagents. All chemicals were used directly as obtained commercially unless otherwise indicated. Ether and THF were distilled from lithium aluminum hydride. HMPA was distilled from calcium hydride at reduced pressure. Pentane was stirred over fuming sulfuric acid, washed with water, dried over anhydrous MgSO$_4$, and distilled from calcium hydride.

Vinylmercuric chloride (Orgmet) was used directly as obtained. The other vinylmercurials, except *trans*-(β-chlorovinyl)mercuric chloride, have all been previously described and were prepared by a hydroboration–mercuration sequence.[31,33,34] Preparation of *trans*-(β-chlorovinyl)mercuric chloride was attempted by following the literature procedure.[41] This compound always appeared to be contaminated by the corresponding divinylmercurial, however.

Phenylmercuric chloride (Aldrich) was used directly as obtained. 2-(Chloromercurio)naphthalene,[48] 2-(chloromercurio)thiophene,[49] and (3-nitrophenyl)mercuric chloride[50] were prepared by using literature procedures.

Although commercially available from various sources, [Rh(CO)$_2$Cl]$_2$,[51] [Rh(H$_2$C=CH$_2$)$_2$Cl]$_2$,[52] Rh(CO)Cl[P(C$_6$H$_5$)$_3$]$_2$,[53] and RhCl[P(C$_6$H$_5$)$_3$]$_3$[54] were prepared from RhCl$_3$·3H$_2$O according to literature procedures. [Rh(C$_7$H$_8$)Cl]$_2$ (Research Organic/Inorganic) was used directly as obtained commercially.

All GC yields are corrected by the use of appropriate hydrocarbon internal standards.

Effect of Solvent and Temperature on the Formation of *trans,trans*-2,2,8,8-Tetramethylnona-3,6-dien-5-one from *trans*-3,3-Dimethyl-1-butenylmercuric Chloride and Carbon Monoxide Catalyzed by 10 mol % of Rh(CO)Cl[P(C$_6$H$_5$)$_3$]$_2$. A 0.0691-g sample (0.1 mmol) of Rh(CO)Cl[P(C$_6$H$_5$)$_3$]$_2$ and 0.3192 g (1.0 mmol) of *trans*-3,3-dimethyl-1-butenylmercuric chloride were weighed into a 25-mL round-bottomed flask equipped with a septum inlet, gas-inlet tube, and magnetic stirring bar. After the system was flushed with a balloon of carbon monoxide, 0.1132 g of *n*-hexadecane and 10 mL of THF, ether, dichloromethane, or HMPA were added by syringe. The flask was flushed twice with carbon monoxide from a balloon and maintained under a carbon monoxide atmosphere by placing a balloon of carbon monoxide on the gas-inlet tube. The reaction was stirred at room temperature or in a heated oil bath at 70 °C. After being stirred

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an appropriate time, the reaction mixture was analyzed by GC ($^1/_4$ in. × 5 ft, 10% DC-550 on Chromosorb W 60/80, 160 °C). The retention time of trans,trans-2,2,8,8-tetramethylnona-3,6-dien-5-one is approximately 4 min while the retention time of n-hexadecane is approximately 7 min. The results are summarized in Table I.

Effect of Different Rhodium Catalysts on the Formation of *trans,trans*-2,2,8,8-Tetramethylnona-3,6-dien-5-one from *trans*-3,3-Dimethyl-1-butenylmercuric Chloride and Carbon Monoxide. By use of a procedure similar to the one previously described, various rhodium catalysts were reacted with 0.3192 g (1.0 mmol) of trans-3,3-dimethyl-1-butenylmercuric chloride under an atmosphere of carbon monoxide in THF at room temperature. All reactions were GC analyzed directly as previously described. Portions of 0.0691 g (0.1 mmol), 0.0069 g (0.01 mmol), or 0.0007 g (0.001 mmol) of $Rh(CO)Cl[P(C_6H_5)_3]_2$ were added, as well as 0.0263 g (0.1 mmol) of $RhCl_3 \cdot 3H_2O$, 0.0895 g (0.1 mmol) of $RhCl[P(C_6H_5)_3]_3$, 0.0194 g (0.05 mmol) of $[Rh(H_2C=CH_2)_2Cl]_2$, 0.0194 g (0.05 mmol) of $[Rh(CO)_2Cl]_2$, 0.0359 g (0.05 mmol) of $[Rh(C_8H_{14})_2Cl]_2$, and 0.0230 g (0.05 mmol) of $[Rh(C_7H_8)Cl]_2$. At least 0.0828 g (2.0 mmol) of lithium chloride was also added to reactions catalyzed by $[Rh(CO)_2Cl]_2$ and $Rh(CO)Cl[P(C_6H_5)_3]_2$. The reaction with dilithium tetrachloropalladate utilized 0.1773 g (1.0 mmol) of palladium chloride plus 0.0828 g (2.0 mmol) of lithium chloride either at room temperature or starting at -78 °C and warming slowly to room temperature. A 0.0177-g (0.1 mmol) sample of palladium chloride, 0.0083 g (0.2 mmol) of lithium chloride, and 0.1344 g (1.0 mmol) of cupric chloride were also added to the room-temperature reaction. The results are summarized in Table II.

Synthesis of Divinyl Ketones. The following procedure for the synthesis of trans,trans-trideca-5,8-dien-7-one is representative. A 1.60-g (5.0 mmol) sample of trans-1-hexenylmercuric chloride and at least 0.42 g (10.0 mmol) of lithium chloride were weighed into a 250-mL round-bottomed flask equipped with a septum inlet, a gas-inlet tube, and a magnetic stirring bar. After the apparatus was flushed with a balloon of carbon monoxide, 40 mL of THF was added by syringe. A 0.0097-g (0.025 mmol) sample of $[Rh(CO)_2Cl]_2$ (1.0 mol % of rhodium) dissolved in 10 mL of THF was added under a carbon monoxide atmosphere by using a double-ended needle. This method of catalyst addition reduces initial unwanted side reactions which occur if the rhodium catalyst and the organomercurial are both present in a very concentrated solution. The reaction was flushed twice with carbon monoxide from a balloon and maintained under a carbon monoxide atmosphere by placing a balloon of carbon monoxide on the gas-inlet tube. After being stirred at room temperature 24 h, the reaction mixture was filtered into a separatory funnel (to remove elemental mercury which forms). Pentane (80 mL) was added, and the organic layer was washed three times with saturated sodium thiosulfate and saturated sodium chloride solutions, dried over anhydrous Na_2SO_4, and concentrated to give 0.46 g (94%) of crude product which was bulb-to-bulb distilled (75–80 °C at 0.35 mm Hg) to give 0.38 g (78%) of a colorless oil: IR (CCl_4) 1675 and 1645 (C=O), 1620 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 0.7–1.1 (6, m, CH_3), 1.1–1.8 (8, m, CH_2CH_2), 2.0–2.5 (4, m, C=CCH$_2$), 6.32 (2, dt, J = 15.5, 1.0 Hz, COCH=C), 6.96 (2, dt, J = 15.5, 6.5 Hz, COC=CH); mass spectrum, m/e 194.16692 (calcd for $C_{13}H_{22}O$, 194.16707).

The following compounds were prepared similarly. trans,-trans-2,2,8,8-Tetramethylnona-3,6-dien-5-one: 0.47 g (96% crude yield); sublimed, 0.38 g (78% purified yield); white needles; mp 69–72 °C; IR (CCl_4) 1673 and 1643 (C=O), 1620 (C=C) cm^{-1}; NMR (CCl_4) δ 1.12 (18, s, $C(CH_3)_3$), 6.13 (2, d, J = 15.5 Hz, COCH=C), 6.73 (2, d, J = 15.5 Hz, COC=CH); mass spectrum, m/e 194.16713 (calcd for $C_{13}H_{22}O$, 194.16707). trans,trans-1,5-Diphenylpenta-1,4-dien-3-one: 0.58 g (99% crude yield); yellow plates (benzene); 0.52 g (88% recrystallized yield); mp 107–110 °C (lit.[55] mp 110–111 °C); IR (CCl_4) 1665 and 1630 (C=O), 1610 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 7.07 (2, d, J = 16 Hz, COCH=C), 7.1–7.6 (10, m, C_6H_5), 7.67 (2, d, J = 16 Hz, COC=CH). trans,trans-2,2,4,6,8,8-Hexamethylnona-3,6-dien-5-one: colorless oil; 0.35 g (64% crude yield); bulb-to-bulb distilled at 105–110

°C (0.35 mm Hg); 0.26 g (47% distilled yield); IR (CCl_4) 1718 (C=O), 1665 (C=C) cm^{-1}; NMR (CCl_4) δ 1.18 (18, s, $C(CH_3)_3$), 1.95 (6, d, J = 1.0 Hz, CH_3), 6.08 (2, d, J = 1.0 Hz, COC=CH); mass spectrum, m/e 222.19786 (calcd for $C_{15}H_{26}O$, 222.19837). trans,trans-1,5-Bis(1-cyclohexenyl)penta-1,4-dien-3-one: yellow solid; 0.61 g (100% crude yield); recrystallized as fine yellow needles (pentane, -78 °C, partial decomposition during recrystallization), mp 138–142 °C dec; IR (CCl_4) 1673 and 1657 (C=O), 1625 and 1608 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.5–2.0 (8, m, CH_2CH_2), 2.0–2.4 (8, m, $CH_2C=C$), 6.25 (2, m, CH=CC=CCO), 6.35 (2, d, J = 15.8 Hz, CCH=CO), 7.38 (2, d, J = 15.8 Hz, CH=CCO); mass spectrum, m/e 242.16671 (calcd for $C_{17}H_{22}O$, 242.16707). trans,trans-2,8-Dimethylnona-1,3,6,8-tetraen-5-one: yellow oil; 0.17 g (47% crude yield, decomposed prior to bulb-to-bulb distillation); IR (CCl_4) 1740 and 1720 (C=O), 1670, 1655, and 1620 (C=C) cm^{-1}; NMR (CCl_4) δ 1.90 (6, s, CH_3), 5.35 (4, d, J = 6 Hz, C=CH$_2$), 6.30 (2, d, J = 15.5 Hz, C=CHCO), 7.25 (2, d, J = 15.5 Hz, CH=CCO). 1,4-Pentadien-3-one (not isolated pure from THF due to its low boiling point and obnoxious properties): NMR (THF/CCl_4) δ 5.85 (2, dd, J = 9.5, 3.0 Hz, trans-CH=CCO), 6.25 (2, dd, J = 17.5, 3.0 Hz, cis-CH=CCO), 6.65 (2, dd, J = 17.5, 9.5 Hz, C=CHCO). A small sample was purified by preparative gas chromatography for a correction factor, and the yield was determined by GC using n-octane as the internal standard. trans,trans-1,5-Dichloropenta-1,4-dien-3-one: yellow oil; 0.18 g (crude yield); IR (neat) 1670 and 1660 (C=O), 1610 (C=C) cm^{-1} (the intensities of the neat IR do not exactly match those previously reported[56]); NMR (CCl_4) δ 6.75 (2, d, J = 13.5 Hz, COCH=C), 7.45 (2, d, J = 13.5 Hz, COC=CHCl).

Synthesis of Diaryl Ketones. The following procedure for the synthesis of benzophenone is representative. A 1.57-g (5.0 mmol) sample of phenylmercuric chloride and at least 0.42 g (10.0 mmol) of lithium chloride were weighed into a glass-lined Parr pressure reactor equipped with a magnetic stirring bar. THF (50 mL) was added and, finally, 0.0097 g (0.025 mmol) of $[Rh(CO)_2Cl]_2$ was added without stirring. The top of the reactor was put in place and the reactor sealed and charged with carbon monoxide from 950 to 1250 psi (tank pressures). The reactor was placed in a 70 °C oil bath and stirred for 24 h. The reactor was then cooled, vented, and opened, and the reaction mixture was filtered into a separatory funnel. Ether (80 mL) was added and the organic layer washed successively three times each with saturated sodium thiosulfate, 5% sodium bicarbonate, and saturated ammonium chloride solutions. (The sodium bicarbonate wash was added because it removes acidic, THF-related side products.) The ether layer was dried over anhydrous Na_2SO_4 and concentrated, giving 0.36 g (80% crude yield) of benzophenone, which was recrystallized from ether to give 0.30 g (66% yield) of product, mp 23–25 °C (lit.[42] mp 26 or 48 °C).

The following diaryl ketones were prepared in a similar manner: 2,2'-dinaphthyl ketone [100% crude yield, 95% recrystallized yield (ether/chloroform), mp 159–161 °C (lit.[43] mp 164.5 °C)], 2,2'-dithienyl ketone [89% crude yield, 78% recrystallized yield (ether), mp 89–90 °C (lit.[44] mp 90.5 °C)]; 3,3'-dinitrobenzophenone [60% crude yield, mp 150–151 °C; 38% recrystallized yield (ethyl acetate), mp 152–153 °C (lit.[26] mp 155–155.5 °C)].

Attempted Synthesis of a Dialkynyl Ketone. The reaction with bis(3,3-dimethyl-1-butynyl)mercury[45] was performed in a manner similar to the synthesis of divinyl ketones with 1 atm of carbon monoxide or in a manner similar to the synthesis of diaryl ketones with 1100 psi of carbon monoxide at room temperature. Following sublimation, white needles were obtained. The spectra and melting point indicated that 2,2,8,8-tetramethyl-3,5-octadiyne was formed; mp 130–130.5 °C (lit.[57] mp 130–131 °C).

Attempted Synthesis of a Dialkyl Ketone. The reaction with n-butylmercuric chloride was performed in a manner similar to the divinyl ketone synthesis with 1 atm of carbon monoxide at room temperature. GC analysis indicated that 5-nonanone was not formed.

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Registry No. *trans,trans*-2,2,8,8-tetramethylnona-3,6-dien-5-one, 73838-78-5; *trans,trans*-trideca-5,8-dien-7-one, 73838-79-6; *trans,-trans*-1,5-diphenylpenta-1,4-dien-3-one, 35225-79-7; *trans,trans*-2,2,4,6,8,8-hexamethylnona-3,6-dien-5-one, 73838-80-9; *trans,trans*-1,5-bis(1-cyclohexenyl)penta-1,4-dien-3-one, 73838-81-0; *trans,-trans*-2,8-dimethylnona-1,3,6,8-tetraen-5-one, 73838-82-1; 1,4-pentadien-3-one, 1890-28-4; *trans,trans*-1,5-dichloropenta-1,4-dien-3-one, 73838-83-2; benzophenone, 119-61-9; 2,2'-dinaphthyl ketone, 613-

56-9; 2,2'-dithienyl ketone, 704-38-1; 3,3'-dinitrobenzophenone, 21222-05-9; *trans*-3,3-dimethyl-1-butenylmercuric chloride, 36525-02-7; *trans*-1-hexenylmercuric chloride, 50874-36-7; *trans*-2-phenylethenylmercuric chloride, 36525-03-8; *trans*-1,3,3-trimethyl-1-butenylmercuric chloride, 38010-69-4; *trans*-2-(1-cyclohexenyl)ethenylmercuric chloride, 56453-89-5; *trans*-3-methyl-1,3-butadienylmercuric chloride, 56453-81-7; ethenylmercuric chloride, 762-55-0; *trans*-2-chloroethenylmercuric chloride, 1190-78-9; phenylmercuric chloride, 100-56-1; 2-naphthylmercuric chloride, 39966-41-1; 2-thienylmercuric chloride, 5857-39-6; 3-nitrophenylmercuric chloride, 2865-17-0; CO, 630-08-0; bis(3,3-dimethyl-1-butynyl)mercury, 73838-84-3; 2,2,7,7-tetramethyl-3,5-octadiyne, 6130-98-9.

Acyclic Stereoselection. 9. Stereochemistry of the Addition of Lithium Enolates to α-Alkoxy Aldehydes[1]

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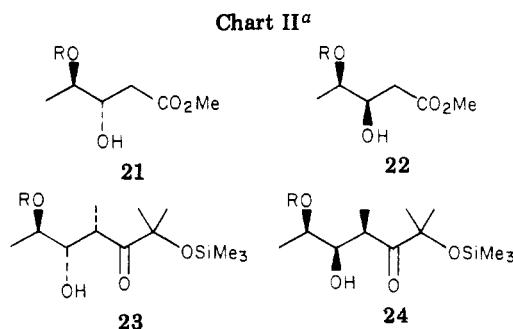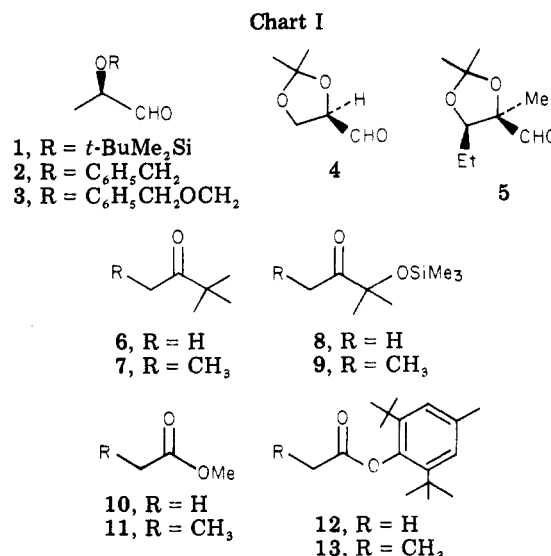
The stereochemistry of addition of lithium enolates derived from esters and ketones to the α-alkoxy aldehydes 1–5 has been investigated. In all cases, the predominant product is that predicted by application of Felkin's model for asymmetric induction and by assuming the alkoxy group to be the "large" group. The Cram cyclic model for asymmetric induction is *not* followed. Stereostructures have been assigned by a combination of conversion to products of known stereostructure, ^{13}C and ^{1}H NMR correlations, and single-crystal X-ray analysis.

Any program aimed at the total synthesis of macrolide antibiotics or polyether ionophores using stereoselective aldol condensations[1] must confront the problem of diastereoface selectivity in additions to chiral α-alkoxy aldehydes (relative asymmetric induction).[2] To examine this question, we have studied the additions of several lithium enolates to the α-alkoxy aldehydes 1–5. The carbonyl compounds which have been utilized are ketones 6–9 and esters 10–13 (Chart I).

The preparation of α-alkoxy aldehydes was accomplished as follows. Aldehydes 1–3 were prepared in racemic form by ozonolysis of ethers 14–16. The *R* enan-
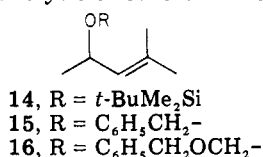
14, R = *t*-BuMe₂Si
15, R = C₆H₅CH₂-
16, R = C₆H₅CH₂OCH₂-

tiomer of 4 was prepared from D-mannitol by the method of Baer and Fischer.[3] Aldehyde 5[4] was prepared in racemic form by the route outlined in Scheme I. Condensation of the known[5] dioxolanone 17 with propionaldehyde affords adduct 18 as a 70:30 mixture of diastereomers. After hydrolytic removal of the isopropylidene group, the major erythro[6] dihydroxy acid may be obtained by crys-

Chart I

1, R = *t*-BuMe₂Si
2, R = C₆H₅CH₂
3, R = C₆H₅CH₂OCH₂

4

5

6, R = H
7, R = CH₃

8, R = H
9, R = CH₃

10, R = H
11, R = CH₃

12, R = H
13, R = CH₃

Chart II[a]

21

22

23

24

a **a,** R = *t*-BuMe₂Si; **b,** R = C₆H₅CH₂; **c,** R = C₆H₅CH₂OCH₂.

tallization. The overall yield of crystalline 19[7] is 30% from dioxolanone 17. Although this synthesis of Bergel'son's

(1) For paper 8, see: C. H. Heathcock and M. C. Pirrung, *J. Org. Chem.*, **45**, 1727 (1980).

(2) P. A. Bartlett, *Tetrahedron*, **36**, 2 (1980).

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(4) J. Inananga, A. Takeda, N. Okukado, and M. Yamaquchi, *Mem. Fac. Sci., Kyushi Univ., Ser. C*, **9**(2), 295 (1975).

(5) M. Farines and J. Soulier, *Bull. Soc. Chim. Fr.*, 332 (1970).

(6) It has been convenient for us to have a stereostructural nomenclature which is invariant of the nature of R and R' (eq 2). We prefer the prefixes erythro and threo and use them in the following sense: when the backbone of the aldol is written in an extended (zigzag) manner and the α-alkyl and β-hydroxy substituents both extend toward the viewer or away from the viewer, this is the erythro diastereomer.