Ethyl heptyl ether (XIII): ^{13}C NMR 70.6, 65.8, 31.7, 29.7, 29.0, 26.0, 22.4, 15.0, 13.8; bp 159–161 °C (lit.[16e] bp 166 °C); 90% yield.

(*R*,*S*/*S*,*R*)-Bis[3,3-dimethyl-2-butyl] ether (XVIII): ^{13}C NMR 75.4, 26.2, 25.3, 17.7.

(*R*,*R*/*S*,*S*)-Bis[3-methyl-2-butyl] ether (IXX): ^{13}C NMR 78.2, 77.0, 33.4, 32.9, 18.7, 18.5, 17.8, 17.5, 16.8, 16.2.

Ethyl 3-pentoxy-2,3-dimethylbutanoate (diastereomeric mixture) (XIV): ^{13}C NMR 173.4, 173.1, 76.1, 75.8, 68.4, 68.2, 59.1, 59.0, 45.3, 44.8, 29.5, 28.2, 22.1, 16.0, 15.7, 13.7, 13.4, 11.8, 11.5.

2-(3,3-Dimethyl-2-butoxy)pentane (diastereomeric mixture) (XV): ^{13}C NMR 81.0, 79.3, 74.4, 72.2, 39.9, 39.4, 35.3, 34.7, 26.3, 26.0, 25.8, 20.9, 19.5, 18.9, 18.8, 16.0, 14.3, 14.2.

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Ruthenium-Catalyzed Oxidative Transformation of Alcohols and Aldehydes to Esters and Lactones

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Primary alcohols undergo oxidative condensation upon treatment with $RuH_2(PPh_3)_4$ catalyst to give esters and molecular hydrogen. Similarly, 1,4- and 1,5-diols can be converted into the corresponding γ- and δ-lactones, respectively. The lactonization is greatly enhanced by accepting hydrogen with an appropriate hydrogen acceptor such as acetone. Primary alcohols are oxidized chemoselectively in the presence of secondary alcohols to give the corresponding lactones. These reactions are operationally simple and highly efficient for synthesis of esters and lactones from alcohols. The principle of the oxidative condensation of alcohols can be extended to ester formation from aldehydes and alcohols. The ruthenium-catalyzed reaction of aldehydes with water gives esters, while the same reaction in the presence of a hydrogen acceptor gives carboxylic acids. The key step of these reactions is the oxidative addition of ruthenium into the OH bonds of alcohols and subsequent β-elimination of (RuH) species to give the corresponding carbonyl compounds.

The development of a novel catalytic process that simulates the enzymatic function of alcohol dehydrogenase[1] is of synthetic and biological interest. The reported methods for such an oxidation of alcohols by dehydrogenation with homogeneous catalysts are limited to few reactions that involve formation of aldehydes along with molecular hydrogen evolution,[2] alkylation of amines with alcohols,[3] and condensation of phenylacetonitriles[4] with alcohols, although hydrogen-transfer reactions of alcohols to ketones are well documented.[5]

During the course of our study on the simulation of the function of alcohol dehydrogenase[1] with metal catalysts, we found an efficient method for the oxidative condensations of alcohols to give esters and lactones catalyzed by dihydridotetrakis(triphenylphosphine)ruthenium ($RuH_2(PPh_3)_4$, **1**) as shown in eq 1.[6]

$$2RCH_2OH \xrightarrow{RuH_2(PPh_3)_4\ (1)} RCO_2CH_2R + 2H_2 \qquad (1)$$

Many methods for the preparation of esters[7] and lactones[8] by the oxidative condensation of alcohols have been performed by using various stoichiometric oxidants. Heterogeneous metal-catalyzed transformations of alcohols to esters and lactones have been reported; however, these reactions require extremely high temperature and proceed nonselectively.[9] Homogeneous catalysts such as $Pd(OAc)_2$ and $Ru_3(CO)_{12}$ catalyze oxidative condensation of alcohols in the presence of a stoichiometric amount of bromobenzene[10] and diphenylacetylene,[11] respectively. Our

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(5) (a) Review: Brieger, G.; Nestrick, T. J. *Chem. Rev.* **1974**, *74*, 567. Kolomnikov, I. S.; Kukolev, V. P.; Vol'pin, M. E. *Russ. Chem. Rev., Engl. Transl.* **1974**, *43*, 399. (b) Ru catalyst: Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887. Speier, G.; Marko, L. *J. Organomet. Chem.* **1981**, *210*, 253. Imai, H.; Nishiguchi, T.; Fukuzumi, K. *J. Org. Chem.* **1976**, *41*, 665. Smith, T. A.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *289*, 385. Farnetti, E.; Vinzi, F.; Mestroni, G. *J. Mol. Catal.* **1984**, *24*, 147. Visintin, M.; Spogliarich, R.; Kasper, J.; Graziani, M. *Ibid.* **1984**, *24*, 277.

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(8) (a) CrO_3: Stenberg, V. I.; Perkins, R. J. *J. Org. Chem.* **1963**, *28*, 323. (b) MnO_2: Marshall, J. A.; Cohen, N.; Hochstetler, A. R. *J. Am. Chem. Soc.* **1966**, *88*, 3408. (c) Ag_2CO_3–Celite: Fetizon, M.; Golfier, M.; Louis, J.-M. *Tetrahedron* **1975**, *31*, 171. Boeckman, R. K., Jr.; Thomas, E. W. *J. Am. Chem. Soc.* **1977**, *99*, 2805. Chakraborty, T. K.; Chandrasekaran, S. *Tetrahedron Lett.* **1984**, *25*, 2891. (d) $NiBr_2$–Bz_2O_2: Doyle, M. P.; Dow, R. L.; Bagheri, V.; Patrie, W. J. *Tetrahedron Lett.* **1980**, *21*, 2795. (e) $Ni(OOCR)_2$–Br_2: Doyle, M. P.; Dow, R. L.; Bagheri, V.; Patrie, W. J. *J. Org. Chem.* **1983**, *48*, 476. (f) Pt–O_2: Lansbury, P. T.; Hangauer, D. G., Jr.; Vacca, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3964. (g) Oxoammonium salt: Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492. Miyazawa, T.; Endo, T. *J. Org. Chem.* **1985**, *50*, 3930.

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Table I. Catalytic Activity of Various Metal Complexes for the Reaction of 1-Hexanol[a]

entry	catalyst	convn (%)	yield[b] (%) $C_5H_{11}CO_2C_6H_{13}$ (2)	yield[b] (%) $C_5H_{11}CH(OC_6H_{13})_2$ (3)	yield[b] (%) $(C_6H_{13})_2O$ (4)
1	$RuH_2(PPh_3)_4$	24	89	3	1
2	$RuH_2(CO)(PPh_3)_3$	24	75	5	5
3	$RuCl_2(PPh_3)_3$	35	19	69	5
4	$RuCl_3 \cdot nH_2O$	10	3	58	10
5	$Ru_3(CO)_{12}$	30	0	10	21
6	$Ru(OCOCF_3)_2(CO)(PPh_3)_2$	22	55	0	35
7	$PdCl_2$	4	23	58	3
8	$RhH(PPh_3)_4$	22	35	40	10
9	$RhCl_3 \cdot nH_2O$	7	4	54	20
10	$RhCl(PPh_3)_3$	15	1	67	3

[a] A mixture of 1-hexanol (2.0 mmol) and catalyst (0.02 mmol) was heated at 180 °C for 4 h in a sealed tube under argon. [b] Determined by GLC analysis based on converted 1-hexanol.

Table II. Ruthenium-Catalyzed Reaction of Primary Alcohols

entry	alcohol	condtn[a]	convn (%)	ester	yield[b] (%)
1	C_4H_9OH	A	96	$C_3H_7CO_2C_4H_9$	97
2	$C_6H_{13}OH$	A	95	$C_5H_{11}CO_2C_6H_{13}$ (2)	95
3	$C_6H_{13}OH$	B	75	$C_5H_{11}CO_2C_6H_{13}$ (2)	98
4	$C_8H_{17}OH$	A	100	$C_7H_{15}CO_2C_8H_{17}$ (5)	95[c]
5	$C_{14}H_{29}OH$	A	100	$C_{13}H_{27}CO_2C_{14}H_{29}$ (6)	82[c]
6	$PhCH_2OH$	A	100	$PhCO_2CH_2Ph$	60
7	$PhCH_2OH$	B	88	$PhCO_2CH_2Ph$	97
8	$C_2H_5CH(CH_3)CH_2OH$	A	60	$C_2H_5CH(CH_3)CO_2CH_2CH(CH_3)C_2H_5$ (7)	32
9	$C_2H_5CH(CH_3)CH_2OH$	B	52	$C_2H_5CH(CH_3)CO_2CH_2CH(CH_3)C_2H_5$ (7)	78
10	$C_3H_7CH(CH_3)CH_2OH$	B		$C_3H_7CH(CH_3)CO_2CH_2CH(CH_3)C_3H_7$ (8)	51[c]
11	$(CH_3)_2CHCH_2CH_2OH$	B		$(CH_3)_2CHCH_2CO_2CH_2CH_2CH(CH_3)_2$ (9)	60[c]
12	$PhCH_2CH_2OH$	B		$PhCH_2CO_2CH_2CH_2Ph$ (10)	79[c]
13	$C_6H_{11}CH_2OH$	B	89	$C_6H_{11}CO_2CH_2C_6H_{11}$ (11)	93[d]
14	$(CH_3)_2NCH_2CH_2OH$	B	54	$(CH_3)_2NCH_2CO_2CH_2CH_2N(CH_3)_2$ (12)	55

[a] Method A: a mixture of alcohol (2.5 mmol) and 1 (0.05 mmol) in dry mesitylene (0.5 mL) was refluxed at 180 °C for 24 h udner argon. Method B: a mixture of alcohol (2.5 mmol) and 1 (0.05 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 24 h in a sealed tube under argon. [b] Determined by GLC analysis based on alcohols. [c] Isolated yield. [d] Diphenylacetylene (2.5 mmol) was added.

method has advantages over previous methods with respect to high efficiency, freedom from the need for stoichiometric amount of oxidants, and facile isolation of desired products. Recently, Shvo demonstrated that when (η^4-tetracyclone)$RuH_2(CO)_2$ is used as catalyst, the oxidative condensation of alcohols proceeds without hydrogen acceptors.[12]

Application of the present reaction provides novel catalytic reactions that involve the oxidative condensation of aldehydes with alcohols to give esters and with water to give acids or esters. We describe full details of these catalytic transformations of alcohols with respect to scope, synthetic applications, and mechanism.

Results and Discussion

Catalytic Transformation of Alcohols to Esters. Treatment of a variety of primary alcohols with a suitable group 8 transition-metal catalyst gives the corresponding esters along with evolution of molecular hydrogen. The catalytic activity of various metal complexes was examined with respect to the reaction of 1-hexanol. Representative results are shown in Table I. The products detected during the reaction are hexyl hexanoate (2), 1,1-bis(hexyloxy)hexane (3), and dihexyl ether (4). Ruthenium dihydride complexes such as $RuH_2(PPh_3)_4$ and $RuH_2(CO)(PPh_3)_3$ gave the best results. Chloride complexes such as $PdCl_2$, $RuCl_3 \cdot nH_2O$, $RuCl_2(PPh_3)_3$, $RhCl_3 \cdot nH_2O$, and $RhCl(PPh_3)_3$ produced either 3 or 4 predominantly. When a nonpolar solvent such as hexane, toluene, and mesitylene was used or in the absence of a solvent, satisfactory results were obtained; however, chloroform, carbon tetrachloride, THF, and diglyme retarded the reaction. A reaction temperature higher than 140 °C was required.

Representative results of the oxidative condensation of primary alcohols are shown in Table II. Alkyl and benzyl alcohols are readily converted into the corresponding esters with evolution of molecular hydrogen. The reaction proceeds efficiently at 180 °C either in mesitylene (method A) or in toluene in a sealed tube (method B). Generally, higher conversion of alcohols is obtained in method A than in method B, because the open system promotes the dissociation of molecular hydrogen. In method A, the reaction of the alcohols bearing a substituent at the β position, such as benzyl alcohol and 2-methyl-1-butanol, gives a considerable amount of the hydrocarbons (20–30%), which are derived from the decarbonylation of the corresponding intermediate aldehydes. The closed system (method B) retards the dissociation of carbon monoxide. Amino alcohols also undergo the esterification efficiently. Since the dehydrogenation step in the present esterification is reversible,[13] the reaction can be enhanced by accepting hydrogen with an appropriate hydrogen acceptor. When the reaction was carried out in the presence of 1–2 equiv of diphenylacetylene, the conversion of alcohols increased; however, the yields of esters often decreased. Particularly, the reaction of less reactive, sterically hindered alcohols is enhanced remarkably by using a hydrogen acceptor. Thus, the reaction of cyclohexanemethanol in the presence of diphenylacetylene gave cyclohexylmethyl cyclohexanecarboxylate (11) in 93% yield (89% conversion of alcohol)

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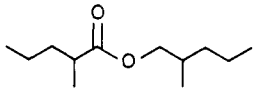
Table III. Effect of Hydrogen Acceptor for the Lactonization of 1,4-Butanediol[a]

entry	hydrogen acceptor	convn (%)	yield[b] (%) of γ-butyrolactone
1	none	74	63
2	$PhNO_2$	93	53
3	*p*-benzoquinone	86	0
4	PhC≡CPh	81	75
5	CH_2=$CHCOCH_3$	100	99
6	PhCH=CHCOCH$_3$	100	98
7	CH_3COCH_3	90	99
8	$CH_3CH_2COCH_3$	79	84

[a] A mixture of 1,4-butanediol (2.5 mmol), hydrogen acceptor (2.5 mmol), and 1 (0.05 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 3 h in a sealed tube under argon. [b] Determined by GLC analysis based on converted diols.

(entry 13), while without the hydrogen acceptor the conversion was only 30%. Naturally, diphenylacetylene was converted into *trans*-stilbene quantitatively. Recently, ruthenium-catalyzed oxidations of alcohols have been performed by using various oxidants, such as $NaIO_4$,[14] $NaBrO_3$,[15] *N*-methylmorpholine *N*-oxide,[16] iodosylbenzene,[17] *t*-BuOOH,[18] $Me_3SiOOSiMe_3$,[19] O_2,[20] and allyl methyl carbonate.[21] With use of these oxidants the oxidation reactions give aldehydes and do not give the corresponding esters.

The usefulness of the present reaction is illustrated by the preparation of perfume esters[22] from readily available industrial materials. The reaction of 2-methyl-1-pentanol with $RuH_2(PPh_3)_4$ catalyst gave 2-methylpentyl 2-methylpentanoate (**8**, 60%), which is the fragrance component of perfume esters.[23] Similar treatments of 3-methyl-1-butanol and 2-phenylethanol gave 3-methylbutyl 3-methylbutanoate (**9**, apple-like fragrance) and 2-phenylethyl 2-phenylacetate (**10**, hyacinth-like fragrance) in 51% and 79% isolated yields, respectively.



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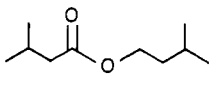

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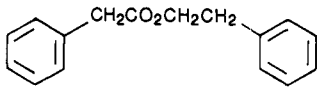

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The cross reactions of two different alcohols have also been studied. The reaction of benzyl alcohol with 2-butanol gave benzyl benzoate (65%) without formation of 1-methylpropyl benzoate. The reaction of 1-octanol with benzyl alcohol gave scrambled esters, octyl octanoate (**5**, 13%), benzyl benzoate (14%), octyl benzoate (**13**, 11%), and benzyl octanoate (**14**, 11%). It is noteworthy that the reaction of 1-hexanol with phenol gave **2** (60%) along with a trace amount of phenyl hexanoate.

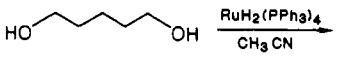
Lactone Synthesis from Diols. The oxidative condensation reaction can be applied to lactone synthesis from diols (eq 2). The addition of a hydrogen acceptor en-

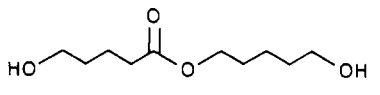
(2)

hances the rate of the lactonization remarkably. Table III summarizes the results of the oxidative condensation of 1,4-butanediol with various hydrogen acceptors. Without a hydrogen acceptor, 1,4-butanediol was converted into γ-butyrolactone in 63% yield. Diphenylacetylene promotes the reaction considerably. The reaction is greatly enhanced by the use of methyl vinyl ketone or benzalacetone; however, these hydrogen acceptors are expensive and difficult to remove from the reaction mixture. We have found that acetone is an excellent hydrogen acceptor for the lactonization because of its cheapness and easy separation from the reaction mixture, although aliphatic ketones are generally less effective hydrogen acceptors in comparison with alkynes and α,β-unsaturated ketones.[5b]

Table IV summarizes the representative results of the ruthenium-catalyzed lactonization of diols. 1,4- and 1,5-diols can be converted into five- and six-membered lactones in excellent yields. Allylic alcohols such as *cis*-2-butene-1,4-diol undergo the lactonization along with hydrogenation of the carbon–carbon double bonds. Phenols also undergo lactonization slowly. Benzylic alcohols are oxidized to give preferentially lactones of benzoic acid. Diethanolamines are also cyclized efficiently, giving morpholine skeletons. α,ω-Diols except 1,4- and 1,5-diols undergo intermolecular condensation to give the corresponding polyesters.[24]

Interestingly, the addition of 1 equiv of acetonitrile retards the intramolecular reaction of diols. Thus, the ruthenium-catalyzed reaction of 1,5-pentanediol in the presence of acetone gave δ-valerolactone in 82% yield, while the reaction in the presence of 1 equiv of acetonitrile gave intermolecular esterification product, 5-hydroxypentyl 5-hydroxypentanoate (**22**) in 41% yield. δ-Valerolactone was not detected among the reaction products. This is probably due to the strong coordination of acetonitrile to the ruthenium complex in comparison with alcohols. In this case bidentate chelation of diols and subsequent ring closure seems to be inhibited.





22

Since electronic stabilization resulting from hydrogen abstraction favors oxidation at the secondary position,[25] selective oxidation of primary alcohols continues to rep-

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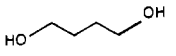
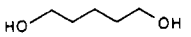
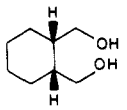
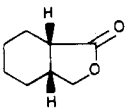
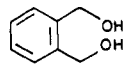
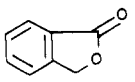
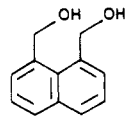
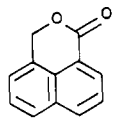
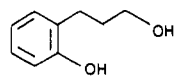
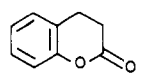
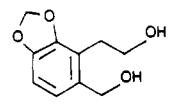
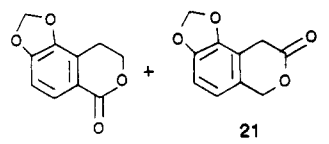
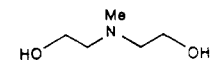
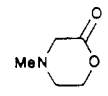
Table IV. Ruthenium-Catalyzed Lactonization of Diols[a]

entry	diol	time (h)	acetone[b]	conv (%)	lactone	yield[c] (%)
1		3	1	90		99
2		2	3	86		95
3		3	3	100		88
4		15	0	100	 **15**	83[d]
5		12	0	100	 **16**	82[d]
6		6	3	100	 **17**	95[d]
7		10	3	89	 **18**	90
8		3	3		 **20** + **21** 2 : 1	60[d]
9		3	3	100	 **19**	95[d]

[a] A mixture of diol (2.5 mmol), acetone, and 1 (0.05 mmol) in dry toluene (0.5 mL) was heated at 180 °C in a sealed tube under argon. [b] The molar ratio of acetone/diol. [c] Determined by GLC analysis based on diol. [d] Isolated yield.

Table V. Ruthenium-Catalyzed Reaction of Aldehydes with Alcohols[a]

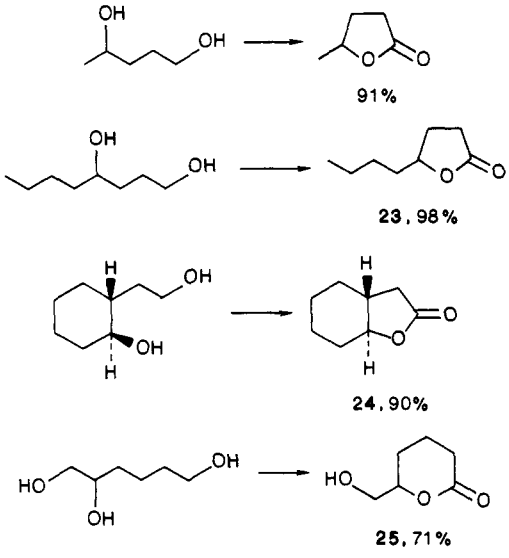
entry	aldehyde	alcohol	convn (%) of aldehyde	product	yield[b] (%)
1	C_3H_7CHO	C_4H_9OH	100	$C_3H_7CO_2C_4H_9$	96
2	$C_7H_{15}CHO$	$C_8H_{17}CHO$	98	$C_7H_{15}CO_2C_8H_{17}$ (**5**)	80
3	PhCHO	$PhCH_2OH$	93	$PhCO_2CH_2Ph$	85
4	PhCHO	$C_8H_{17}OH$		$C_7H_{15}CO_2C_8H_{17}$ (**5**)	21[c]
				$PhCO_2C_8H_{17}$ (**13**)	15[c]
				$C_7H_{15}CO_2CH_2Ph$ (**14**)	24[c]
				$PhCO_2CH_2Ph$	19[c]

[a] A mixture of aldehyde (2.0 mmol), alcohol (2.0 mmol), and 1 (0.1 mmol) in dry toluene (1.0 mL) was heated at 180 °C for 24 h in a sealed tube under argon. [b] Determined by GLC analysis based on aldehydes. [c] Isolated yield.

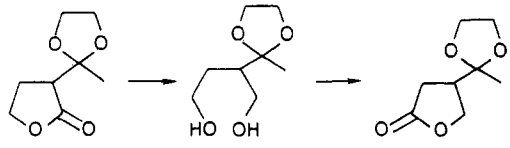
resent a notable synthetic challenge. With use of the present reaction, primary alcohols are oxidized chemoselectively in the presence of secondary alcohols. It is reported that primary alcohols are oxidized with a stoichiometric amount of $RuCl_2(PPh_3)_3$ 50 times faster than secondary alcohols.[26] The reaction of 1,4-pentanediol with $RuH_2(PPh_3)_4$ as catalyzed in the presence of 3 equiv of acetone at 180 °C for 3 h gave γ-valerolactone in 91% yield. Similar treatment of 1,4-octanediol gave γ-octanolactone (**23**) in 98% yield. The reaction of *trans*-2-(2-hydroxyethyl)cyclohexanol gave *trans*-hexahydro-2-benzofuranone (**24**) in 90% yield. 1,2,6-Hexanetriol undergoes oxidative condensation to afford 6-hydroxy-5-hexanolide (**25**) chemoselectively in 71% yield. The favored reactivity of primary hydroxyl groups over secondary hydroxyl groups is ascribed to the difference in the stereochemical congestion between primary and secondary hydroxyls.

As already pointed out, lactone formation from unsym-

(26) Tomioka, H.; Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1605.



metrical diols proceeds regioselectively.[6] The unsymmetrical primary,primary diols bearing bulky substituents are oxidized at the sterically less hindered position. The formation of **25** is an example of such a reaction. The reaction of α-substituted diol **27**, derived from lactone **26**, with $RuH_2(PPh_3)_4$ catalyst gave lactone **28** in 95% yield.



The regioselectivity of the lactonization is up to 97:3. Since the starting unsymmetrical diols can be readily prepared by the α-substitution of lactones[27] followed by reduction, the present reaction provides an efficient method for the preparation of β-substituted-γ-butyrolactones from α-substituted-γ-butyrolactones. Similar regioselective oxidations using ruthenium phosphine complexes[28] and $NiBr_2/Bz_2O_2$[8d] have been reported.

Ruthenium-Promoted Oxidative Condensation of Aldehydes. The oxidative condensation of alcohols can be rationalized simply by assuming the reactions shown in Scheme I.[6] The activation of alcohols by means of ruthenium complex gives carbonyl compounds and ruthenium dihydride complex. The condensation of the intermediate aldehydes with alcohols gives hemiacetals which undergoes further dehydrogenation to afford esters.

This principle can be extended to a novel catalytic condensation of aldehydes. With assumption of the formation of hemiacetals as shown in Scheme I, the oxidative condensation of aldehydes with alcohols can be performed to afford esters as depicted in eq 3.[11] Since oxidative

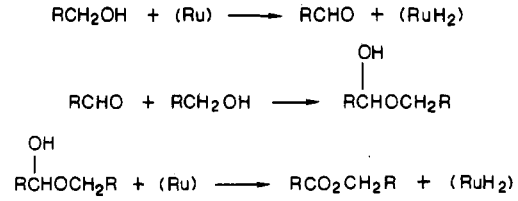
$$RCHO + RCH_2OH \xrightarrow{RuH_2(PPh_3)_4} RCO_2CH_2R + H_2 \quad (3)$$

transformations of aldehydes to esters are important, much effort has been devoted to find efficient methods for this type of oxidation, and indirect methods[29] have been explored. The reaction of aldehydes with an equimolar amount of alcohols at 180 °C in the presence of $RuH_2(PPh_3)_4$ catalyst gave the corresponding esters directly in high yields. The results are shown in Table V. Typically, the ruthenium-catalyzed reaction of butanal with 1-butanol gave butyl butanoate in 96% yield. The cross condensation of aldehyde (R^1CHO) with alcohol (R^2CH_2OH) proceed nonselectively. Thus, the reaction of benzaldehyde with 1-octanol at 180 °C gave a mixture of octyl octanoate (**5**) (21%), benzyl benzoate (19%), octyl benzoate (**13**) (15%), and benzyl octanoate (**14**) (24%). The scrambling of the product distribution is due to the formation of alcohol (R^1CH_2OH) by the hydrogen transfer to the starting aldehyde (R^1CHO). Therefore, when a hydrogen acceptor is used, the hydrogen transfer is completely retarded and the unsymmetrical esters are obtained selectively. Typically, the reaction of octanal with methanol in the presence of mesityl oxide at 140 °C gave methyl octanoate (**29**, 66%) without any formation of **5** and octyl formate.

$$C_7H_{15}CHO + CH_3OH \xrightarrow[(CH_3)_2C{=}CHCOCH_3]{RuH_2(PPh_3)_4} C_7H_{15}CO_2CH_3$$
29

By analogy to the reaction of aldehydes with alcohols, we next investigated the reaction of aldehydes with water. Treatment of aldehydes with water in the presence of a

Scheme I



Scheme II

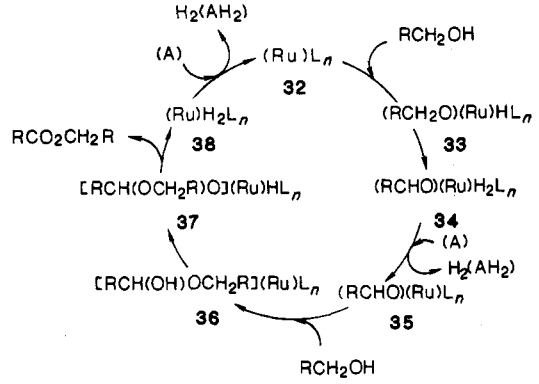


Table VI. Ruthenium-Catalyzed Reaction of Aldehydes with Water[a]

entry	aldehyde	convn (%)	product	yield[b] (%)
1	C_3H_7CHO	99	$C_3H_7CO_2H$ (**30**)	91
2	$C_5H_{11}CHO$	99	$C_5H_{11}CO_2H$	67
3	$C_7H_{15}CHO$	99	$C_7H_{15}CO_2H$	70
4	PhCHO	93	$PhCO_2H$	75

[a] A mixture of aldehyde (3.0 mmol), water (6.0 mmol), benzalacetone (3.0 mmol), and 1 (0.09 mmol) in 1,2-dimethoxyethane (0.5 mL) was heated at 180 °C for 24 h in a sealed tube under argon. [b] Determined by GLC analysis based on converted aldehydes.

(27) Grieco, P. A. *Synthesis* **1975**, 67. Gammill, R. B.; Wilson, C. A.; Bryson, T. A. *Synth. Commun.* **1975**, *5*, 245. Newaz, S. S. *Aldrichimica Acta* **1977**, *10*, 64.

(28) Ishii, Y.; Osakada, K.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *J. Org. Chem.* **1986**, *51*, 2034. Ishii, Y.; Ikariya, T.; Saburi, M.; Yoshikawa, S. *Tetrahedron Lett.* **1986**, *27*, 365.

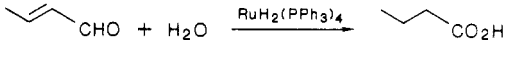
(29) Corey, E. J.; Gilman, N. W.; Ganem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616. Sundararaman, P.; Walker, E. C.; Djerassi, C. *Tetrahedron Lett.* **1978**, 1627. Wilson, S. R.; Tofigh, S.; Misra, R. N. *J. Org. Chem.* **1982**, *47*, 1360. Chiba, T.; Okimoto, M.; Nagai, H.; Takata, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 335. Shono, T.; Matsumura, Y.; Hayashi, J.; Inoue, K.; Iwasaki, F.; Itoh, T. *Ibid.* **1985**, *50*, 4967.

hydrogen acceptor gave the corresponding carboxylic acid as depicted in eq 4. The results are listed in Table VI. Typically, the $RuH_2(PPh_3)_4$-catalyzed reaction of butanal with water (2.0 equiv) in 1,2-dimethoxyethane in the presence of benzalacetone (1.0 equiv) at 180 °C gave butyric acid (**30**) (91%) and trace amounts of 1-butanol and butyl butanoate (**31**). In the absence of a hydrogen acceptor, the reaction of aldehydes with water gave the corresponding ester preferentially (eq 5). The ruthenium-catalyzed reaction of butanal with water at 180 °C afforded ester **31** (65%) along with carboxylic acid **30** (15%) and 1-butanol (3%). Similar treatment of octanal gave ester **5** (58%) along with octanoic acid (7%) and 1-octanol (3%). Maitlis reported that transition-metal-promoted disproportionations of acetaldehyde give acetic acid and ethanol.[30]

$$RCHO + H_2O \xrightarrow[\text{hydrogen acceptor}]{RuH_2(PPh_3)_4} RCO_2H + (H_2) \quad (4)$$

$$RCHO + H_2O \xrightarrow{RuH_2(PPh_3)_4} RCO_2CH_2R \quad (5)$$

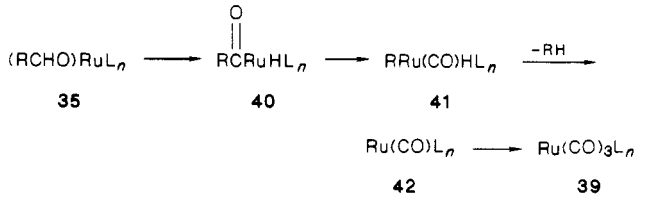
In contrast, α,β-unsaturated aldehydes undergo the condensation reaction with water in the absence of a hydrogen acceptor, giving saturated carboxylic acids via intramolecular hydrogen transfer. Typically, the reaction of crotonaldehyde with water in the presence of $RuH_2(PPh_3)_4$ catalyst gave acid **30** in 68% yield (91% conversion).



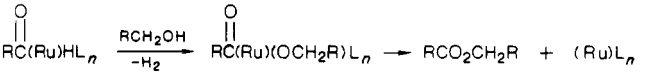
30

Reaction Mechanism. The ruthenium-catalyzed transformation of primary alcohols to esters can be rationalized by assuming the formation of the hemiacetal intermediate as shown in Scheme II. The catalytically active species seems to be the coordinatively unsaturated ruthenium complex, $(Ru)L_n$ (**32**), which is formed by reductive elimination of hydrogen from hydrido-ruthenium complex $(Ru)H_2L_n$. When the reaction is carried out in the presence of a hydrogen acceptor, zerovalent complex **32** is formed by hydrogen transfer from $RuH_2(PPh_3)_4$[31] to the hydrogen acceptor. It is also suggested that the active intermediate for the $RuH_2(PPh_3)_4$-catalyzed hydrogen transfer from 2-propanol to olefins[32] is not a Ru(II) species but coordinatively unsaturated $Ru(PPh_3)_3$. Oxidative addition of **32** to the O–H bond of primary alcohols gives hydridoalkoxyruthenium complex **33**. The presence of alkoxyruthenium intermediates has been postulated from kinetic experiments.[5b] β-Elimination of **33** leads to complex **34**.[33,34] The evidence supporting β-elimination mechanism for the ruthenium-catalyzed oxidation of alcohols has been obtained from both H–D exchange reactions and racemization reactions of optically active alcohols.[13] Such a pathway has been also suggested in the hydrogen-transfer reaction of alcohols[5b] and alkylation of amines with alcohols.[3] Dissociation of molecular hydrogen from **34** and subsequent reaction with an alcohol at the coordinated carbonyl carbon of **35** gives hemiacetal complex **36**. Further, oxidative addition of the ruthenium into the O–H bond of the coordinated hemiacetal gives alkoxyruthenium complex **37**. β-Elimination of **37** gives ester and dihydridoruthenium complex **38**, which undergoes elimination of molecular hydrogen to complete the catalytic cycle. In the presence of hydrogen acceptors (A) such as acetone and α,β-unsaturated ketones, transfer hydrogenations[31,32] from both complexes **34** and **38** proceed efficiently to enhance the condensation reaction. $Ru_3(CO)_{12}$-catalyzed esterification of alcohols needs a stoichiometric amount of a hydrogen acceptor such as diphenylacetylene.[11] Esters could not be obtained without a hydrogen acceptor (entry 5 in Table I), indicating that reductive elimination of molecular hydrogen from mononuclear complexes **34** and **38** proceeds more readily in comparison with that from hydridoruthenium clusters. A nonredox process has been proposed for the dehydrogenation of alcohols catalyzed by ruthenium(II) carboxylate complexes $Ru(OCOR^1)_2L_n$.[2b,c] Solvolysis with alcohols R^2CH_2OH gives acids R^1CO_2H and alkoxides $Ru^{II}(OCOR^1)(OCH_2R^2)L_n$ that undergo β-elimination to give aldehydes and $Ru^{II}H(OCOR^1)L_n$. Subsequent reaction of the hydrido complex with the acid R^1CO_2H liberates molecular hydrogen and regenerates the catalyst. However, the nonredox process seems not to be operative in the present reaction, because the obsered acceleration caused by hydrogen acceptors cannot be explained by this mechanism. $Ru(OCOCF_3)_2(CO)(PPh_3)_2$ catalyst[2b] shows lower catalytic activity for the esterification in comparison with the hydridoruthenium catalyst (entry 6 in Table I).

Scheme III

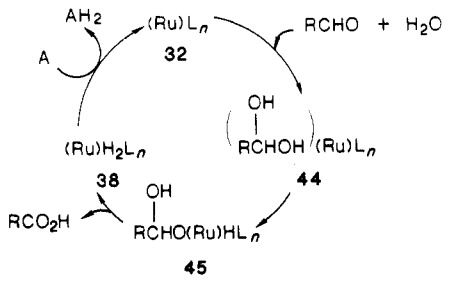


On working up the system after completion of the reaction, $Ru(CO)_3(PPh_3)_2$ (**39**) was isolated as the sole characterizable ruthenium complex. The formation of **39** can be accounted for by the pathway shown in Scheme III. Thus, the aldehyde in complex **35** oxidatively adds to the ruthenium to give hydridoacylruthenium complex **40**. Such oxidative addition of metal into the C–H bond of aldehydes has been postulated in various metal-catalyzed decarbonylations of aldehydes,[35] and some hydridoacyl complexes have been isolated.[36] Acyl–alkyl rearrangement gives alkylcarbonylruthenium complex **41**, which undergoes reductive elimination of hydrocarbons to give carbonylruthenium complex **42**. Repetition of the oxidative addition and decarbonylation would give tricarbonylruthenium complex **39**. The formation of hydrocarbons by such a dehydrogenation–decarbonylation sequence of alcohols has been suggested.[2b,33,34] Eventually, GC–MS analysis showed that a small amount of the dehydrogenation–decarbonylation product, heptane, was formed from the reaction of 1-octanol with $RuH_2(PPh_3)_4$ catalyst. These facts suggest the possibility of the alternative Tishchenko-type mechanism. That is, the reaction of **40** with alcohols gives acylalkoxyruthenium complex **43**, which un-



(30) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2342.
(31) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2553.
(32) Imai, H.; Nishiguchi, T.; Kobayashi, M.; Fukuzumi, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1585.
(33) Chatt, J.; Shaw, B. L.; Field, A. E. *J. Chem. Soc.* **1964**, 3466.
(34) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 1546.
(35) Tsuji, J. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, pp 595.
(36) Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640. Rauchfuss, T. B. *Ibid.* **1979**, *101*, 1045.

Scheme IV



dergoes reductive coupling to give esters. Recently, the ruthenium-catalyzed Tishchenko-type dimerization of aldehydes to esters in vacuo without a solvent has been reported.[37] However, this mechanism seems unlikely in the present reaction, because the initial step is not operative under the reaction conditions. In fact, the reaction of benzaldehyde with benzyl alcohol in the presence of known decarbonylation catalyst $RhCl(PPh_3)_3$, which reacts smoothly with aldehydes to give $RCORhHL_n$,[36] gave benzene and a trace amount of the corresponding ester. The following experiment also eliminates the Tishchenko-type mechanism. The treatment of hexanal with $RuH_2(PPh_3)_4$ (1 mol %) at 180 °C gave hexyl hexanoate in only 6% yield (conversion 52%).

The ruthenium-catalyzed reaction of aldehydes with water is rationalized by assuming the similar pathway shown in Scheme IV. Aldehydes react with water in the presence of **32** to give *gem*-diol complex **44**. Oxidative addition of ruthenium into the O–H bond gives complex **45**. β-Elimination gives carboxylic acid and hydridoruthenium complex **38**, which reacts with hydrogen acceptor (A) to complete the catalytic cycle. A similar pathway has been postulated for the metal-catalyzed Cannizzaro reaction of acetaldehyde.[30] Furthermore, it has been reported that the reaction of $RuH_2(PPh_3)_4$ with aldehydes in the presence of water gives carboxylato–carbonyl complex, $Ru(O_2CR)_2(CO)(PPh_3)_2$.[37]

In the absence of a hydrogen acceptor, the starting aldehyde is hydrogenated with ruthenium hydride **38** to give the alcohol. Esters are then formed by three pathways: the condensation of carboxylic acids with alcohols (eq 6), the catalytic reaction of aldehydes with alcohols (eq 7), and the catalytic oxidative condensation of alcohols (eq 8).

$$RCO_2H + RCH_2OH \rightarrow RCO_2CH_2R + H_2O \quad (6)$$

$$RCHO + RCH_2OH \xrightarrow{Ru} RCO_2CH_2R + H_2 \quad (7)$$

$$2RCH_2OH \xrightarrow{Ru} RCO_2CH_2R + 2H_2 \quad (8)$$

In summary, the ruthenium-catalyzed reaction of primary alcohols gives the corresponding esters efficiently. Similar treatment of 1,4- and 1,5-diols affords the corresponding lactones chemo- and regioselectively. The principle of the reactions can be extended to the oxidative condensation of aldehydes with alcohols to give esters. The reaction of aldehydes with water gives esters preferentially, while the reaction in the presence of a hydrogen acceptor gives carboxylic acids.

Experimental Section

All melting points were determined in capillary tubes and are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. ^1H NMR spectra were obtained on a 60 MHz JNM-PMX-60 SI (JEOL) and a 100 MHz JNM-FX-100 (JEOL) spectrometer; chemical shifts (δ) were expressed in parts per million downfield from Me_4Si. Analytical GLC evaluations of product mixtures were performed on JEOL Model JGC-20-KFP flame ionization chromatograph by using a 1-m analytical column packed with PEG 20 M on Celite. Preparative GLC was carried out on a JEOL Model JGC-20-KT thermal conductive chromatograph by using a 1-m column packed with PEG 20 M on Celite. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer and on a Shimadzu GCMS QP-1000 by using a 1.1-m analytical column packed with silicone OV-17 on Chromosorb W. Elemental analyses were performed on a Yanagimoto MT-2 CHN corder.

Caution: When using sealed tubes, sealed tubes are thick enough and of sufficient capacity to withstand the pressure developed by hydrogen. For opening the sealed tubes a small hole should be made carefully by heating with strong focused flame.

Materials. Benzene and toluene were distilled over benzophenone ketyl and stored under argon atmosphere. Mesitylene was distilled over calcium hydride. Acetone was distilled over potassium permanganate. Methanol was distilled over magnesium and stored under an argon atmosphere. Commercially available γ-butyrolactone, γ-valerolactone, δ-valerolactone, benzyl benzoate, alcohols, and aldehydes were purified by distillation. Diols were prepared by the $LiAlH_4$ reductions of the corresponding lactones and anhydrides. 2-(2-(Hydroxymethyl)-4,5-(methylenedioxy)-phenyl)ethanol was prepared by ortho-lithiation of piperonyl alcohol followed by the treatment with ethylene oxide in THF. The complexes $RuH_2(CO)(PPh_3)_3$,[38] $RhCl_2(PPh_3)_3$,[39] $Ru(OCOCF_3)_2(CO)(PPh_3)_2$,[40] $RhH(PPh_3)_4$,[41] and $RuCl(PPh_3)_3$[42] were prepared according to the reported methods. $RuH_2(PPh_3)_4$ (**1**) was prepared from $RuCl_3 \cdot nH_2O$ according to the literature procedure[43] with slight modification.

Catalytic Activity of Various Metal Complexes. A mixture of 1-hexanol (2.0 mmol) and a catalyst (0.02 mmol) was heated at 180 °C for 4 h in a sealed Pyrex tube (180 × 18 mm) under argon. The conversion of 1-hexanol and the yields of hexyl hexanoate (**2**), 1,1-bis(hexyloxy)hexane (**3**), and dihexyl ether (**4**) were determined by the GLC analysis of the reaction mixture using an internal standard (undecane). The results with various catalysts are shown in Table I. The products, **2**, **3**, and **4**, were purified by preparative GLC (10% PEG 20 M on Celite) after Kugelrohr distillation, and their structures were established by comparison of their spectral data with those of the authentic samples. **2**: IR (neat) 2970, 2940, 2880, 2870, 1740 (C=O), 1475, 1250, 1175, 1100 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.70–1.10 (m, 6 H), 1.10–1.87 (m, 14 H), 2.20 (t, J = 7 Hz, 2 H), 3.97 (t, J = 6 Hz, 2 H). **3**: IR (neat) 2925, 2875, 1470, 1380, 1350, 1120, 1070, 720 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.62–1.05 (m, 9 H), 1.05–1.88 (m, 24 H), 3.32 (t, J = 6 Hz, 4 H), 4.28 (t, J = 5 Hz, 1 H). **4**: IR (neat) 2930, 2860, 1470, 1380, 1120 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.67–1.07 (m, 6 H), 1.07–1.80 (m, 16 H), 3.27 (t, J = 6 Hz, 4 H).

Ruthenium-Catalyzed Reaction of Alcohols (General Procedure). Method A. In a test tube (195 × 20 mm) equipped with a magnetic stirring bar and a reflux condenser connected to an argon inlet were placed alcohol (2.5 mmol), $RuH_2(PPh_3)_4$ (0.058 g, 0.050 mmol), and dry mesitylene (0.5 mL). The mixture was heated with stirring at 180 °C for 24 h under argon atmosphere. Column chromatography (SiO_2, elution with a mixture of ether/hexane) gave the esters. The conversion of the starting alcohol and the yield of the ester were determined by GLC analysis using an appropriate internal standard (see Table II).

Method B. A mixture of alcohol (2.5 mmol) and $RuH_2(PPh_3)_4$ (0.05 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 24 h in a sealed Pyrex tube (180 × 18 mm) under argon. After the

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reaction, the sealed tube was carefully opened (evolution of molecular hydrogen). The resulting wine-red mixture was distilled or subjected to column chromatography (SiO_2, elution with a mixture of ether/hexane) to give ester.

2-Methylpentyl 2-Methylpentanoate (8). The reaction was carried out at 200 °C: bp 101–103 °C/40 mm (Kugelrohr); IR (neat) 2970, 2930, 2880, 1740 (C=O), 1475, 1385, 1250, 1180, 1150, 1090, 980, 925, 740 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.83–1.93 (m, 21 H), 2.27–2.60 (m, 1 H), 3.87 (d, J = 6.0 Hz, 2 H). Anal. Calcd for $C_{12}H_{14}O_2$: C, 71.95; H, 12.08. Found: C, 71.85; H, 12.09.

3-Methylbutyl 3-Methylbutanoate (9). The reaction was carried out at 200 °C: bp 85–87 °C/155 mm (Kugelrohr); IR (neat) 1950, 1880, 1740 (C=O), 1475, 1375, 1300, 1195, 1175, 1125 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.92 (d, J = 6.4 Hz, 6 H), 0.93 (d, J = 6.4 Hz, 6 H), 1.58 (dt, J = 2.0, 6.0 Hz, 2 H), 2.17 (d, J = 2.0 Hz, 2 H), 4.07 (t, J = 6.0 Hz, 2 H). Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.75; H, 11.71. Found: C, 69.49; H, 11.67.

2-Phenylethyl Phenylacetate (10). The reaction was carried out at 200 °C: bp 120–150 °C/1 mm (Kugelrohr); IR (neat) 3075, 3040, 2970, 1740 (C=O), 1610, 1500, 1455, 1245, 1150, 1000, 695 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 2.83 (t, J = 7 Hz, 2 H), 3.50 (s, 2 H), 4.20 (t, J = 7 Hz, 2 H), 6.88–7.27 (m, 10 H); mass spectrum, m/e (relative intensity) 105 (18), 104 (100), 91 (42), 65 (10). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.00; H, 6.74.

Cyclohexylmethyl Cyclohexanecarboxylate (11). A mixture of cyclohexanemethanol (0.236 g, 2.08 mmol), diphenylacetylene (0.362 g, 2.03 mmol), and $RuH_2(PPh_3)_4$ (0.054 g, 0.047 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 24 h in a sealed tube under argon. After evaporation of the solvent the residue was subjected to column chromatography to give **11** (0.185 g, 80 %): bp 130–150 °C/6 mm (Kugelrohr); IR (neat) 2930, 2860, 1740 (C=O), 1455, 1170 cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.56–2.49 (m, 22 H), 3.81 (d, J = 6 Hz, 2 H); mass spectrum, m/e (relative intensity) 129 (11), 128 (8), 111 (18), 97 (26), 96 (100), 83 (60), 82 (9), 81 (85), 68 (18), 67 (32), 56 (9), 55 (100), 54 (13). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.77; H, 10.79.

2-(Dimethylamino)ethyl 2-(dimethylamino)acetate (12): bp 125–160 °C/24 mm (Kugelrohr); IR (neat) 2930, 2770, 1740 (C=O), 1450, 1270, 1150, 1035, cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.30 (s, 6 H), 2.38 (s, 6 H), 2.60 (t, J = 6 Hz, 2 H), 3.22 (s, 2 H), 4.27 (t, J = 6 Hz, 2 H).

Ruthenium-Catalyzed Reaction of Benzyl Alcohol with 1-Octanol. A mixture of benzyl alcohol (0.135 g, 1.25 mmol), 1-octanol (0.163 g, 1.25 mmol), and $RuH_2(PPh_3)_4$ (0.058 g, 0.05 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 24 h in a sealed tube under argon. After removal of the solvent the residual yellow oil was purified by preparative TLC (SiO_2, ether/hexane = 1/5) to afford **5** (0.021 g, 13%), benzyl benzoate (0.019 g, 14%), octyl benzoate (**13**) (0.031 g, 11%), and benzyl octanoate (**14**) (0.032 g, 11%). **13**: IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.80–1.83 (m, 15 H), 4.22 (t, J = 9.0 Hz, 2 H), 7.20–7.47 (m, 3 H), 7.80–8.00 (m, 2 H); mass spectrum, m/e (relative intensity) 234 (M^+, 1), 208 (6), 207 (31), 145 (6), 123 (100), 112 (15), 106 (7), 105 ($M^+ - C_8H_{17}O$, 81), 84 (16), 83 (20), 82 (7), 79 (8), 77 (41), 71 (8), 70 (26), 69 (17). **14**: IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR (CCl_4, 60 MHz) δ 0.77–1.70 (m, 13 H), 2.23 (t, J = 9.0 Hz, 2 H), 5.00 (s, 2 H), 7.22 (s, 5 H); mass spectrum, m/e (relative intensity) 235 (M^+ + 1, 1), 234 (M^+, 6), 207 (13), 143 ($M^+ - CH_2Ph$, 12), 127 ($M^+ - OCH_2Ph$, 11), 125 (16), 109 (9), 108 (79), 107 ($M^+ - C_7H_{15}CO$, 9), 97 (11), 91 ($M^+ - C_7H_{15}CO_2$, 100), 90 (10), 83 (14), 65 (12).

General Procedure for the Ruthenium-Catalyzed Reaction of Diols. A mixture of diol (2.5 mmol), acetone (7.5 mmol), and $RuH_2(PPh_3)_4$ (0.05 mmol) in dry toluene (0.5 mL) was heated at 180 °C for an appropriate time (see Table IV) in a sealed Pyrex tube (180 × 18 mm) under argon. After the reaction the resulting wine-red solution was subjected to distillation or column chromatography (SiO_2, elution with ether/hexane) to give lactones. The conversion of the starting diol and the yield of lactone were determined by GLC analysis of the reaction mixture using an appropriate internal standard.

***cis*-Hexahydrophthalide (15):** bp 110–130 °C/5 mm (Kugelrohr); IR (neat) 2935, 2880, 1780 (C=O), 1450, 1380, 1220, 1190, 1160, 1130, 1070, 1040, 990, 940, 915, 845, 670 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.67–2.28 (m, 8 H), 2.28–2.87 (m, 2 H), 3.93 (d, J = 10 Hz, 1 H), 4.22 (dd, J = 4.5, 8.5 Hz, 1 H); mass spectrum, m/e (relative intensity) 141 (M^+ + 1, 2), 140 (M^+, 11), 95 (6), 85 (16), 82 (12), 81 (100), 79 (9), 68 (41), 67 (72), 55 (41), 54 (55), 53 (18). Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.04; H, 8.59.

1,8-Naphthalide (17): mp 154.5–156.0 °C; IR (Nujol) 1710 (C=O), 1350, 1250, 1090, 1050, 780 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 5.84 (s, 2 H), 7.53 (dd, J_{56} = 8 Hz, J_{67} = 8 Hz, H^6), 7.59 (dd, J_{23} = 7 Hz, J_{34} = 7 Hz, H^3), 7.86 (d, J_{34} = J_{56} = 9 Hz, H^4, H^5), 8.15 (d, J_{67} = 8 Hz, H^7), 8.45 (d, J_{23} = 7 Hz, H^2); mass spectrum, m/e (relative intensity) 185 (M^+ + 1, 11), 184 (M^+, 85), 183 (M^+ – 1, 25), 156 (28), 155 (100), 128 (15), 127 (82), 126 (17). Anal. Calcd for $C_{12}H_8O_2$: C, 78.25; H, 4.38. Found: C, 78.26; H, 4.43.

4-Methylmorpholin-2-one (19): bp 143–163 °C/19 mm (Kugelrohr); IR (neat) 2950, 2800, 1750 (C=O), 1460, 1410, 1345, 1230, 1190, 1140, 1060 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.37 (s, 3 H, CH_3N), 2.68 (t, J = 5.5 Hz, 2 H, NCH_2C), 3.28 (s, 2 H, NCH_2CO), 4.47 (t, J = 5.5 Hz, 2 H, $-CH_2O-$).

Ruthenium-Catalyzed Reaction of 2-(2-(Hydroxymethyl)-4,5-(methylenedioxy)phenyl)ethanol. Preparative TLC (SiO_2, benzene/ether = 5/1) gave the lactone in 60% yield. ^1H NMR spectrum indicated that the product is a mixture of 3,4-dihydro-5,6-(methylenedioxy)isocoumarin (**20**) and 5,6-(methylenedioxy)-isochroman-3-one (**21**) in a ratio of 2:1: ^1H NMR ($CDCl_3$, 60 MHz) δ 2.99 (t, J = 6 Hz, 2 H × 2), 3.61 (s, 2 H), 4.53 (t, J = 6 Hz, 2 H × 2), 5.19 (s, 2 H), 5.94 (s, 2 H), 6.13 (s, 2 H × 2), 6.65 (s, 2 H), 6.88 (d, J = 8 Hz, 1 H × 2), 7.83 (d, J = 8 Hz, 1 H × 2). Four singlets at δ 3.61, 5.19, 5.94, and 6.65 were consistent with those of an authentic sample of **21** prepared by Battersby's method.[44] **21**: IR (Nujol) 1720 (C=O), 1300, 1245, 1160, 1060, 1040, 1020, 965, 920, 830, 800, 790 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.61 (s, 2 H), 5.19 (s, 2 H), 5.94 (s, 2 H), 6.65 (s, 2 H).

Ruthenium-Catalyzed Reaction of *cis*-2-Butene-1,4-diol. A mixture of *cis*-2-butene-1,4-diol (0.231 g, 2.62 mmol), acetone (0.465 g, 8.01 mmol), and $RuH_2(PPh_3)_4$ (0.061 g, 0.053 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 3 h in a sealed tube under argon. Kugelrohr distillation gave colorless γ-butyrolactone (0.192 g, 85%): bp 53–60 °C/7 mm (GLC yield 88%, conversion 100%).

Ruthenium-Catalyzed Reaction of 1,5-Pentanediol in the Presence of Acetonitrile. A mixture of 1,5-pentanediol (0.364 g, 3.49 mmol), acetonitrile (0.156 g, 3.80 mmol), and $RuH_2(PPh_3)_4$ (0.068 g, 0.059 mmol) in dry toluene (0.5 mL) was heated at 180 °C for 5 h in a sealed tube under argon. After evaporation of the solvent the residue was diluted with $CHCl_3$ (2 mL) and extracted with water (1 mL × 10). Combined aqueous layers were evaporated to dryness (2 mmHg), affording 5-hydroxypentyl 5-hydroxypentanoate (**22**) (0.145 g, 41%) as a colorless oil: IR (neat) 3325 (OH), 2940, 2875, 1725 (C=O), 1070 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.87–2.00 (m, 10 H), 2.35 (t, J = 7.0 Hz, 2 H), 2.93 (br s, 2 H, OH), 3.62 (t, J = 6.5 Hz, 4 H), 4.08 (t, J = 6.5 Hz, 2 H).

***trans*-Hexahydro-2-benzofuranone (24):** bp 100–135 °C/6 mm (Kugelrohr); IR (neat) 2940, 2870, 1785 (C=O), 1450, 1430, 1300, 1220, 1195, 1175, 1080, 1035, 935, 880, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.83–2.93 (m, 11 H), 3.84–4.10 (m, 1 H); mass spectrum, m/e (relative intensity) 140 (M^+, 1), 139 (M^+ – 1, 2), 97 (8), 96 ($M^+ - CO_2$, 10), 84 (5), 83 (6), 81 (26), 79 (15), 71 (4), 70 (9), 69 (10), 68 (54), 67 (100). Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.37; H, 8.63.

6-Hydroxy-5-hexanolide (25). Preparative TLC (SiO_2, ethyl acetate/hexane = 1/1) gave **25** (R_f 0.1, 0.240 g, 71%): IR (neat) 3300 (OH), 2940, 1730 (C=O), 1250, 1170, 1050 cm^{-1}; ^1H NMR (CD_3COCD_3, 60 MHz) δ 1.24–1.98 (m, 4 H), 2.11–2.60 (m, 2 H, $-CH_2CO_2-$), 3.52 (s, 1 H, OH), 3.78 (m, 2 H, $-OCH_2-$), 4.12 (t, J = 5 Hz, 1 H, -CHOCO-).

3-Acetyl-γ-butyrolactone Ethylene Acetal (28). Kugelrohr distillation gave the lactone (0.162 g, 95%) as a colorless liquid. GLC analysis of the distillate showed that the ratio of **28**:2-acetyl-γ-butyrolactone (**26**) is up to 97:3. The product was purified by preparative GLC: bp 150–170 °C/2 mm; IR (neat) 2980, 2900, 1780 (C=O), 1485, 1420, 1380, 1160, 1030, 950, 880, 845, 680 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 1.30 (s, 3 H), 2.52 (d, J = 7 Hz, 2

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H), 2.88 (tt, J = 7, 7 Hz, 1 H), 3.98 (s, 4 H), 4.28 (d, J = 7 Hz, 2 H); mass spectrum, m/e (relative intensity) 157 (10), 100 (4), 99 (21), 88 (5), 87 (100), 85 (3), 71 (4), 55 (15), 53 (4). Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.72; H, 7.04.

Ruthenium-Catalyzed Reaction of Aldehydes with Alcohols (General Procedure). A mixture of aldehyde (2.0 mmol), alcohol (2.0 mmol), and $RuH_2(PPh_3)_4$ (0.1 mmol) in dry toluene (1.0 mL) was heated at 180 °C for 24 h in a sealed Pyrex tube (180 × 18 mm) under argon. Short column chromatography (SiO_2, elution with ether–hexane) gave ester. The product was identified by comparison of the spectral data with that of the ester prepared by the catalytic esterification of alcohols described above. GLC analysis of the reaction mixture using an appropriate internal standard gave the conversion of aldehyde and the yield of ester (see Table V).

Ruthenium-Catalyzed Reaction of Benzaldehyde with 1-Octanol. Preparative TLC (SiO_2, ether/hexane = 1/5) afforded **5** (0.054 g, 21%) (R_f 0.76), **10** (0.036 g, 15%) (R_f 0.68), **11** (0.055 g, 24%) (R_f 0.62), and benzyl benzoate (0.041 g, 19%) (R_f 0.53).

Methyl Octanoate (29). A mixture of octanal (0.128 g, 1.00 mmol), methanol (0.638 g, 19.9 mmol), mesityl oxide (0.498 g, 5.07 mmol), and $RuH_2(PPh_3)_4$ (0.115 g, 0.10 mmol) in dry toluene (0.5 mL) was heated at 140 °C for 4 days under argon. Column chromatography (5 g of SiO_2, elution with pentane) afforded yellow oil **29** (0.104 g, 66%): IR (neat) 1740 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 0.87 (t, J = 5.0 Hz, 3 H), 1.10–1.87 (m, 10 H), 2.30 (t, J = 7.0 Hz, 2 H), 3.63 (s, 3 H); mass spectrum, m/e (relative intensity) 127 ($M^+ - OCH_3$, 3), 115 (4), 101 (4), 87 (32), 74 (100), 69 (5), 59 (14), 57 (18), 55 (19). Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.51; H, 11.51.

General Procedure for the Ruthenium-Catalyzed Reaction of Aldehydes with Water. The reaction of butanal with water is representative. **(A) In the Presence of a Hydrogen Acceptor.** A mixture of butanal (0.216 g, 3.00 mmol), water (0.108 g, 5.99 mmol), benzalacetone (0.439 g, 3.00 mmol), and $RuH_2(PPh_3)_4$ (0.104 g, 0.09 mmol) in 1,2-dimethoxyethane (0.5 mL) was heated at 180 °C for 24 h in a sealed Pyrex tube (180 × 18 mm) under argon. Short column chromatography (SiO_2) of the reaction mixture gave butyric acid (**30**) (0.224 g, 85%) along with the trace amount of butyl butanoate (**31**). **(B) In the Absence of a Hydrogen Acceptor.** The same reaction was carried out in the absence of benzalacetone. Short column chromatography (SiO_2) gave ester **31** (0.132 g, 59%) along with carboxylic acid **30** (0.027 g, 10%).

Reaction of Crotonaldehyde with Water. A mixture of crotonaldehyde (0.216 g, 3.08 mmol), water (0.113 g, 6.27 mmol), and $RuH_2(PPh_3)_4$ (0.104 g, 0.09 mmol) in 1,2-dimethoxyethane (0.5 mL) was heated at 180 °C for 48 h in a sealed Pyrex tube (180 × 18 mm) under argon. Short column chromatography (SiO_2) of the reaction mixture gave **30** (0.163 g, 60%). GLC analysis of the reaction mixture showed that acid **30**, 1-butanol, and ester **31** were obtained in 68%, 2%, and 8% yields, respectively (conversion of aldehyde 91%).

Registry No. **2**, 6378-65-0; **3**, 33673-65-3; **4**, 112-58-3; **5**, 2306-88-9; **6**, 3234-85-3; **7**, 2445-78-5; **8**, 90397-38-9; **9**, 659-70-1; **10**, 102-20-5; **11**, 2611-02-1; **12**, 64945-70-6; **13**, 94-50-8; **14**, 10276-85-4; **15**, 6939-71-5; **16**, 87-41-2; **17**, 518-86-5; **18**, 119-84-6; **19**, 20721-78-2; **20**, 74786-83-7; **21**, 81683-97-8; **22**, 80880-36-0; **23**, 104-50-7; **24**, 27345-71-7; **25**, 81683-96-7; **27**, 109908-74-9; **28**, 109908-75-0; **29**, 111-11-5; **30**, 107-92-6; **31**, 109-21-7; $RuH_2(PPh_3)_4$, 19529-00-1; $RuH_2(CO)(PPh_3)_3$, 25360-32-1; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuCl_3$, 10049-08-8; $Ru_3(CO)_{12}$, 15243-33-1; $Ru(OCOF_3)_2(CO)(PPh_3)_2$, 65912-34-7; $PdCl_2$, 7647-10-1; $RhH(PPh_3)_4$, 18284-36-1; $RhCl_3$, 10049-07-7; $RhCl(PPh_3)_3$, 14694-95-2; C_4H_3OH, 71-36-3; $C_6H_{13}OH$, 111-27-3; $C_8H_{17}OH$, 111-87-5; $C_{14}H_{29}OH$, 112-72-1; $PhCH_2OH$, 100-51-6; $C_2H_5CH(CH_3)CH_2OH$, 137-32-6; $C_3H_7CH(CH_3)CH_2OH$, 105-30-6; $(CH_3)_2CHCH_2CH_2OH$, 123-51-3; $PhCH_2CH_2OH$, 60-12-8; $C_6H_{11}CH_2OH$, 100-49-2; $(CH_3)_2NCH_2OH$, 108-01-0; $PhCO_2CH$[2Ph, 120-51-4; $PhNO_2$, 98-95-3; CH_2=CH-$COCH_3$, 78-94-4; $CH_3CH_2COCH_3$, 78-93-3; HO-$CH_{24}OH$, 110-63-4; $HOCH_2$-o-$C_6H_4CH_2OH$, 612-14-6; HO-o-$C_6H_4(CH_2)_3OH$, 1481-92-1; $HOCH_2CH_2NMeCH_2CH_2OH$, 105-59-9; $C_5H_{11}CHO$, 66-25-1; $C_7H_{15}CHO$, 124-13-0; PhCHO, 100-52-7; $C_2H_{11}CO_2H$, 142-62-1; $C_7H_{15}CO_2H$, 124-07-2; $PhCO_2H$, 65-85-0; 1,4-octanediol, 51916-47-3; *trans*-2-(2-hydroxyethyl)cyclohexanol, 27345-72-8; 1,2,6-hexanetriol, 106-69-4; diphenylacetylene, 501-65-5; γ-butyrolactone, 96-48-0; *cis*-2-butene-1,4-diol, 6117-80-2; acetonitrile, 75-05-8; methanol, 67-56-1; mesityl oxide, 141-79-7; acetone, 67-64-1; benzalacetone, 122-57-6; 1,5-pentanediol, 111-29-5; butanal, 123-72-8; tetrahydropyran-2-one, 542-28-9; *cis*-1,2-bis(hydroxymethyl)cyclohexane, 15753-50-1; 1,8-bis(hydroxymethyl)-naphthalene, 2026-08-6; 4-(2-hydroxymethyl)-5-(hydroxymethyl)benzodioxole, 81683-95-6; crotonaldehyde, 4170-30-3; *p*-benzoquinone, 106-51-4.

Supplementary Material Available: Spectral data of compounds **5–7** (Table II), **16**, **18** (Table IV), and **23** (2 pages). Ordering information is given on any current masthead page.

Cycloaddition Reactions of a Bisisobenzofuran Leading to Linear Polyacenequinones and a Quadruply Bridged Cyclophane

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The bisisobenzofuran 1,3,7,9-tetrakis(4-*tert*-butylphenyl)anthra[2,3-*c*:6,7-*c*']difuran-5,11 dione (**3**) was reacted with dienophiles. Maleic anhydride and *N*-methylmaleimide produced bis adducts that were the syn and anti isomers resulting from endo additions. The relative rates of the first and second additions were measured by time-resolved NMR for the reaction of **3** with *N*-methylmaleimide. Reaction of **3** with the longer dienophile *N*-(4-*tert*-butylphenyl)maleimide gave only the anti-bis-endo adduct. All three bis adducts were cleanly aromatized by dehydration to form soluble pentacenequinone derivatives. Reaction of **3** with the bis dienophile 1,4-*N*,*N*'-dimaleimidobenzene gave a 1:1 adduct, which is an unusual quadruply bridged cyclophane.

We have become interested in the synthesis of long, rigid molecules with delocalized π-systems, and recently we have reported the preparation of polyacenequinones **1** and **2**.[1,2] Although the length of the undecacenepentaquinone (**1**) suggests that it should have unusual properties, it is extremely insoluble, making it difficult to purify or to study. For this reason Dr. W. Christopfel, in this laboratory, has developed a scheme to prepare soluble compounds of this type.[2] His synthesis hinges on the bisisobenzofuran **3**, which has *p*-*tert*-butylphenyl groups attached for solubility. Compound **3** should be useful for elongation

(1) Miller, L. L.; Thomas, A. D. *J. Org. Chem.* **1986**, *51*, 4160.
(2) Christopfel, W. C.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4169.

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