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A convenient lactonization of diols to γ- and δ-lactones catalyzed by transition metal polyhydrides

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Abstract

Transition metal polyhydrides-catalyzed oxidative condensation of diols to 5 and 6-ring lactones was studied. The regioselective dehydrogenation of unsymmetrically substituted 1,4-diols gave β- or γ-substituted γ-lactones in high yields. The mechanism of dehydrogenation under neutral and mild conditions was discussed.

Introduction

There has been great interest in selective synthesis of lactones because of their occurrence in natural products and biologically active compounds and because they are versatile synthetic intermediates in organic synthesis [1]. Thus, considerable efforts have been devoted to developing effective methods of lactone synthesis [2] in which the Ru dihydride complex-catalyzed oxidative condensation method has advantages with respect to high efficiency, facile isolation and mild reaction conditions over the stoichiometric use of oxidants [3]. Here we present a new kind of catalyst for convenient lactonization of diols to γ- and δ-lactones, namely transition metal polyhydrides acting under neutral and mild conditions.

Results and discussion

We have reported the catalytic dehydrogenation under mild conditions of saturated secondary alcohols to saturated ketones in the absence of a hydrogen acceptor by the $IrH_5(^iPr_3P)_2$ complex [4a]. Oxidative dehydrogenation from primary alcohol to aldehyde was not observed, probably because of the rapid decarbonylation of the aldehyde formed in the dehydrogenation of the primary alcohol. However, when a primary diol, 1,4-butanediol, was used as the substrate

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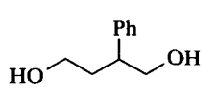
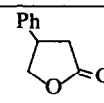
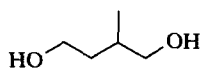
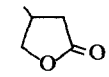
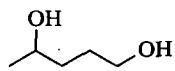
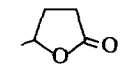
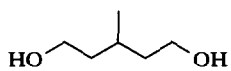
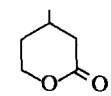
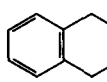
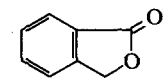
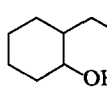
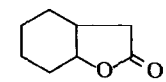
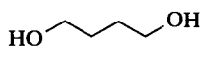
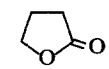
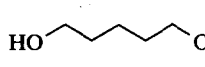
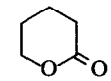
Table 1

Selective oxidative condensations of diols catalyzed by transition metal polyhydrides [a]

Entry	Diols	Cat. [b]	(mole%)	Time (h)	Yield [c] (%)	Products
1		A	(2.0)	24	77	
		B	(2.5)	24	81	
		C	(4.8)	29	82	
2		A	(1.9)	48	80	
		B	(2.0)	24	77	
3		A	(2.2)	48	93	
		B	(1.6)	24	86	
4		A	(1.9)	48	91	
		B	(1.5)	24	75	
5		A	(1.8)	48	96	
		B	(2.0)	22	94	
6		A	(2.3)	48	61	
		B	(1.9)	24	66	
7		A	(2.0)	48	91 [d]	
		B	(2.0)	24	85	
8		A	(2.0)	48	88 [d]	
		B	(2.0)	24	70 [e]	

[a] 2.5 mmol diol, [acetone]/[diol] = 3. [b] A = $IrH_5(^iPr_3P)_2$, reacted at 75°C in benzene. B = $RuH_4(PPh_3)_3$, reacted at 48°C in benzene. C = $RuH_2(^iPr_3P)_2$, reacted at 65°C in benzene. [c] The products were separated by distillation or column chromatography (silica gel, petroleum ether/ethyl acetate eluent). [d] GLC yield based on diol. [e] ^1H NMR yield based on diol.

in the presence of 1.0 mole% of $IrH_5(^iPr_3P)_2$ in benzene at 75°C, the γ-butyrolactone was obtained in 54% yield without a hydrogen acceptor.

The rate of dehydrogenation of diols was increased remarkably by the addition of benzalacetone or acetone as hydrogen acceptor and 95% conversion was deduced from ^1H NMR spectra. A variety of 1,4- and 1,5-diols can be converted respectively into 5- and 6-membered lactones in excellent yields. The results are shown in Table 1. In general, lactone formation becomes relatively slow in step with a progression from common to large-sized rings, with a minimum yield from 7–12 membered rings [6]. Over the past decade, there has been intense interest in the develoging of methods for formation of macrocyclic and medium ring lactones, since a number of these substances possess important and useful biological properties [7]. Using transition metal polyhydrides, the medium-ring and macro-

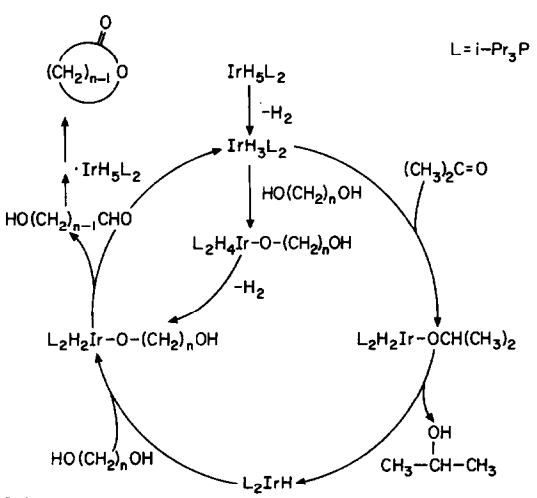
cyclic lactones from 1,6-hexanediol and 1,10-decanediol can also be formed in moderate yields under mild condition (eq. 1).

$$HO(CH_2)_nOH \xrightarrow[(CH_3)_2C{=}O,\ 40°C,\ 24\ h]{RuH_4(Ph_3P)_3,\ 2\ mole\%} O{=}\overline{C(CH_2)_{n-2}O} \qquad (1)$$

($n = 6, 10$) (yield: 34%, 42%)

The dehydrogenation of substituted diols was generally achieved with higher yield and regioselectivity than that of unsubstituted diols. In the case of an asymmetrical primary diol, the primary hydroxyl group having less hindered substituents was regioselectively oxidized to give β-substituted γ-butyrolactones (entries 1 and 2). In our previous publication [4a], the pentan-2-ol can be completely converted to pentan-2-on in the absence of hydrogen acceptor using 1.0 mole% of iridium pentahydride as catalyst, but 1,4-pentanediol with both a primary and a secondary hydroxyl group gives γ-valerolactone in 93% yield exclusively (entry 3). This indicates that the primary hydroxyl group was dehydrogenated in preference to the secondary hydroxyl group. In other words, primary alcohol was oxidized chemoselectively in the presence of secondary alcohol.

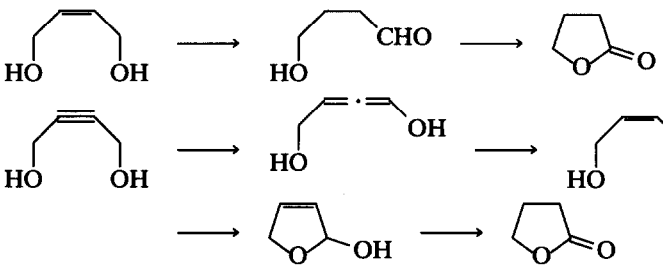
The oxidative condensation of diols catalyzed by Ru, Re, Ir-polyhydrides can be carried out under neutral and mild conditions (see entry 1 in Table 1). Especially for the Ru molecular hydrogen complex, the reaction can be carried out at 25–40°C. It was reported [4d] that the Ru-complex possess excellent reactivity in the hydrogen transfer reaction between ketones and isopropanol at room temperature. This is because the dihydrogen ligand in Ru molecular hydrogen complex dissociated readily under very mild conditions to afford an unsaturated intermediate. In the presence of hydrogen acceptor, it may form a 14e intermediate of highly unsaturated coordination which favours for the oxidative addition of O–H bond and thus leads to a remarkable increase in the rate of dehydrogenation. Thus, acetone is an excellent hydrogen acceptor even reacting at room temperature



Scheme 1.

under our experimental conditions. In contrast to the reported methods, the present reaction has advantages in its high efficiency and great convenience.

The mechanism of this reaction may be similar to that of the dehydrogenation of saturated secondary alcohol in the absence of hydrogen acceptor or the hydrogen transfer reaction in the presence of hydrogen acceptor. The catalytic cycle is proposed as Scheme 1. The intramolecular condensation of the intermediate aldehydes with alcohols gives hemiacetals which undergo further dehydrogenation to afford lactones. We have reported that unsaturated secondary alcohols can be completely isomerized to the saturated ketones with a catalytic amount of iridium polyhydride [4b,c], but conversion from unsaturated primary alcohol to saturated aldehyde was not detected under the same conditions. However, both 2-butene-1,4-diol and 2-butyne-1,4-diol can easily be converted to γ-butyrolactone using the Ir or Ru complex. These imply that the rate of condensation between aldehyde and alcohol was considerably facilitated by the same catalytic system. These reactions may proceed via the isomerization of the unsaturated C=C bond [4b,c] followed by condensation to form a hemiacetal [5] as shown as eqs. 2 and 3.



(2)

(3)

Experimental

All reactions were carried out under prepurified dinitrogen or argon. Benzene was distilled from sodium and benzophenone under dinitrogen. ^{1}H NMR spectra were recorded on an EM-360 or Varian XL-200 spectrometer. Chemical shifts (δ) were expressed in parts per million with Me_4Si as an internal standard. Infrared spectra were taken as liquid films with an IR-440 instrument. Mass spectral data were obtained with electron ionization on a Finnigan 4021 spectrometer. GLC analyses were performed on a 102G instrument using a PEG 20000 column(3m) at 180°C.

Materials

The complexes $IrH_5(^iPr_3P)_2$ [8], $ReH_7(^iPr_3P)_2$ [9], and $RuH_4(Ph_3P)_3$ [10] were prepared according to the reported methods. 2-Phenyl-1,4-butanediol, 2-methyl-1,4-butanediol, 2-methyl-1,5-pentanediol, and 1,2-benzenedimethanol were prepared by the $LiAlH_4$ reduction [11] of phenylsuccinic acid, methyl-succinic acid, levulinic acid methyl ester, and phthalic acid, respectively. 2-(2-hydroxyethyl)cyclohexanol was prepared from the $LiAlH_4$ reduction of ethyl 2-cyclohexanoneacetate [12]. 3-Methyl-1,5-pentanediol and other chemicals were purchased (Tokyo Kasei) and purified by recrystallization or distillation if necessary.

General procedure for Ir- or Ru-catalyzed reaction of diols. A mixture of diol (2.5 mmol), catalyst (0.05 mmol), and acetone (1.0 ml) in benzene (2.0 ml) was

heated at 25–75°C for 24–48 h. After cooling and removal of the solvent, the residue was distilled under reduced pressure or isolated by column chromatography (silica gel, elution with petroleum/ethyl acetate) to give lactones. The conversion of the starting diol and the yield of lactone were determined by GLC analyses or ^{1}H NMR spectroscopy.

Dihydro-4-methyl-2(3H)-furanone. ^{1}H NMR (60 MHz): 1.15 (d, 3H), 1.85–2.80 (m, 3H), 3.75 (dd, 1H), 4.25 (dd, 1H). IR (neat): 1760 cm^{-1} (C=O). MS: *m/e* 100 (M^+), 70, 56, 42.

Dihydro-4-phenyl-2(3H)-furanone. ^{1}H NMR: 2.55–2.85 (m, 2H), 3.65 (m, 1H), 4.16 (t, 1H), 4.55 (t, 1H), 7.25 (s, br, 5H). IR: 1760 cm^{-1} (C=O). MS: *m/e* 162 (M^+), 117, 104, 91.

γ-Valerolactone. ^{1}H NMR: 1.35 (d, 3H), 1.55–2.60 (m, 4H), 4.50 (q, 1H). IR: 1760 cm^{-1} (C=O). MS: *m/e* 100 (M^+), 85, 56.

Tetrahydro-4-methyl-2(2H)-pyranone. ^{1}H NMR: 1.05 (d, 3H), 1.35–2.65 (m, 5H), 4.20 (m, 2H). IR: 1720 cm^{-1} (C=O). MS: *m/e* 114 (M^+), 70, 55, 42.

Benzofuranone. ^{1}H NMR: 5.35 (s, 2H), 7.3–8.1 (m, 4H). IR: 1720 cm^{-1} (C=O) MS: *m/e* 134 (M^+), 106, 89, 77.

Hexahydro-2-benzofuranone. ^{1}H NMR: 1.50–2.20 (m, 9H), 3.80 (m, 2H), 4.50 (m, 1H). IR: 1720 cm^{-1} (C=O). MS: *m/e* 141 (M^+), 123, 111, 96. 67. Anal. Found: C, 68.48; H, 8.60. $C_8H_{12}O_2$ calc.: C, 68.57; H, 8.57%.

γ-Butyrolactone. ^{1}H NMR: 2.4 (m, 4H), 4.30 (t, 2H). IR: 1760 cm^{-1} (C=O). MS: *m/e* 86 (M^+), 71, 56, 42.

Tetrahydro-2(2H)-pyranone. ^{1}H NMR: 1.90 (m, 4H), 2.3–2.8 (m, 2H), 4.35 (t, 2H). IR: 1730 cm^{-1} (C=O). MS: *m/e* 100 (M^+), 56, 42.

6-Hexanolide. ^{1}H NMR: 1.80 (m, 6H), 2.55 (m, 2H), 4.20 (m, 2H). IR: 1730 cm^{-1} (C=O).

10-Decanolide. ^{1}H NMR: 1.25 (m), 2.25 (m), 4.0 (t). IR: 1725 cm^{-1} (C=O).

Acknowledgements

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