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Rhodium-catalyzed reactions of arylbismuth and aryllead reagents with a chiral glyoxylate hydrate in air and water: water-promoted diastereoselectivity enhancement

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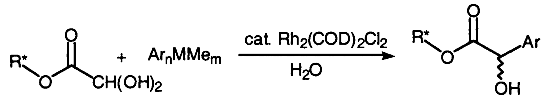
Abstract—In the presence of a rhodium catalyst, a chiral glyoxylate hydrate reacts with arylbismuth and aryllead reagents in water and under an atmosphere of air to give the corresponding addition products in high yields. The diastereoselectivities of the reactions were dramatically improved by using water as the solvent. © 2002 Elsevier Science Ltd. All rights reserved.

In recent years, organic reactions in aqueous media have received much attention.[1] One of the reasons for this interest is the fact that chemical reactions often benefit noticeably from the special properties of liquid water, i.e. its small molecular size, its three-dimensional hydrogen-bond network, and hydrophobic interactions.[2] On the other hand, while numerous asymmetric and diastereoselective reactions in organic solvents[3] have been developed, related reactions in aqueous media remain challenging but also attractive.[4] Recently, rhodium-catalyzed phenylations of aldehydes or α,β-unsaturated esters in water have been reported. It was found that arylbismuth, aryltin, aryllead, arylboron, and arylsilicon reagents could react effectively with aldehydes or α,β-unsaturated esters and ketones in water and under an atmosphere of air to give the corresponding nucleophilic addition products in the presence of a catalytic amount of a rhodium catalyst.[5]

Mandelic acid and derivatives are a class of compounds of synthetic and biological importance.[6] The Friedel–Crafts type coupling of phenols with glyoxylates catalyzed by Lewis acids is limited to highly electron-rich phenols.[7,8] It is highly desirable to have a general approach towards non-phenol based mandelic acid derivatives. Herein, we wish to report an efficient and diastereoselective coupling of arylbismuth and aryllead reagents with a glyoxylate hydrate catalyzed by rhodium in air and water to provide mandelic esters (Eq. (1)). The diastereoselectivity of the reaction was found to be dramatically enhanced by using water as the solvent.



(1)

2a-d **1a-i** **3a-g**

Since glyoxylates are often moisture sensitive and easily hydrated and polymerized, ethyl glyoxylate hydrate **2a** was used to react with triphenylbismuth **1a** in the presence of $Rh_2(COD)_2Cl_2$ (5 mol%) in water and air at 50°C overnight. However, no desired product was detected, while the starting material disappeared (as shown by TLC, Table 1, entry 1) due to hydrolysis of **2a** in water. Interestingly, when isopropyl glyoxylate hydrate **2b** was used, the desired addition product **3a** was obtained in 71% yield under the same reaction conditions (Table 1, entry 2). When the hydrate of (−)-menthyl glyoxylate **2c** was reacted with **1a**, the desired addition product was obtained in 75% yield, although the diastereomeric excess (d.e.) of **3b** was only 3% (obtained by measuring the two diastereomeric ^{13}C signals of the ester carbonyl group at 171.7 and 172.8 ppm, Table 1, entry 3). The use of tris(β-naphthyl)-bismuth **1b** improved the d.e. of the addition product **3c** slightly to 13% (entry 4). Although the diastereoselectivities were rather low, the smooth addition of arylbismuth reagents to **2c** in water encouraged us to examine the hydrate of (−)-8-phenylmenthyl gly-

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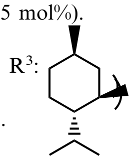
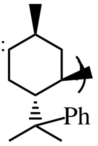
Table 1. Rh(I)-catalyzed reactions of glyoxylate hydrates **2a**–**2d** with arylmetals **1a**–**1i** in water[a]

Entry	Ar_nMR_m	Glyoxylate (R)[b]	Temp. (°C)	Product (Ar, R)	Yield (%)[c]	d.e.[d] (%)
1	**1a**, Ph_3Bi	**2a**, R^1	50	–		
2	**1a**	**2b**, R^2	50	**3a**, Ph, R^2	71	
3	**1a**	**2c**, R^3	50	**3b**, Ph, R^3	75	3
4	**1b**, $(C_{10}H_8)_3Bi$	**2c**	50	**3c**, $C_{10}H_8$, R^3	68	13
5	**1a**	**2d**, R^4	50	**3d**, Ph, R^4	70	67
6	**1b**	**2d**	50	**3e**, $C_{10}H_8$, R^4	81	85
7	**1c**, $(p\text{-}CH_3Ph)_3Bi$	**2d**	60	**3f**, p-CH_3Ph, R^4	69	51
8	**1d**, $(m\text{-}ClPh)_3Bi$	**2d**	60	**3g**, m-ClPh, R^4	80	52
9	**1e**, $(p\text{-}CH_3OPh)_3Bi$	**2d**	60	**3h**, p-CH_3OPh, R^4	66	20
10	**1f**, $PhPbMe_3$	**2d**	50	**3d**	73	77
11	**1g**, $(m\text{-}ClPh)PbMe_3$	**2d**	50	**3g**	76	67
12	**1h**, $(C_{10}H_8)PbMe_3$	**2d**	60	**3e**	77	84
13	**1i**, $PhSnMe_3$	**2d**	60	**3d**	70	33

[a] Catalyst: $Rh_2(COD)_2Cl_2$ (5 mol%).

[b] R^1: C_2H_5; R^2: $(CH_3)_2CH$; R^3:  ; R^4: .

[c] Isolated yield.

[d] Determined by ^{13}C NMR.

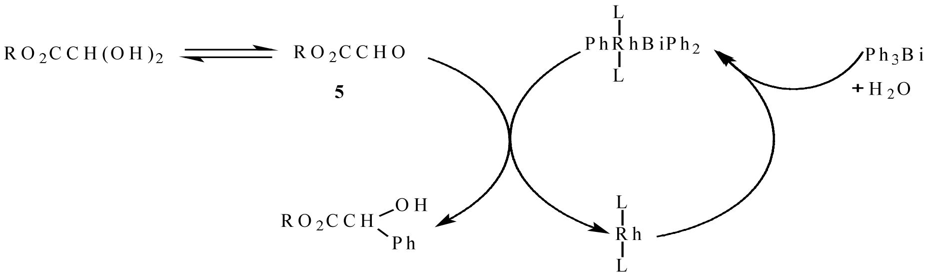
oxylate **2d**.[9] In the case of **1a**, the use of (−)-**2d** gave rise to a remarkable increase of the d.e. (to 67%) compared with (−)-**2c** (entries 5 and 3). Similarly, for **1b**, the d.e. increased markedly from 13% to 85% (entries 4 and 6). Under the same conditions, the reaction of tris(*p*-methylphenyl)bismuth **1c** with **2d** in water gave product **3d** in 51% d.e. and tris(*m*-chlorophenyl)bismuth **1d** afforded product **3g** in 52% d.e., respectively. The use of **1e** leads to the formation of **3h** in a low d.e. (20%). The reaction of phenyltrimethyllead **1f**, (*m*-chlorophenyl)-trimethyllead **1g**, and (2-naphthyl)trimethyltin **1h** with (−)-**2d** in water also exhibited good diastereoselectivities, 77, 67, and 84%, respectively (entries 10–12). However, phenyl–trimethyltin (**1i**) provided the product **3d** only in 33% d.e. (entry 13).

A marked influence on the diastereoselectivity by water was observed. The Rh(I)-catalyzed reactions of **1b** with **2d** have been performed in various organic solvents (Table 2). Although the reaction temperature is relatively low and the reaction mixture is homogeneous in organic media, the diastereoselectivity of the reaction in organic solvents is much lower than that in water (entries 1–5 and 6–9) in all cases. The absolute configuration of a newly generated stereogenic center is deduced as having the *S*-configuration through reduction to obtain the optically active (*S*)-(+)-1-phenyl-1,2-ethanediol[10,11] and by X-ray crystal analysis of **3e**. Scheme 1 outlines a tentative mechanism for the reaction of glyoxylate hydrate with an arylbismuth, in which an equilibrium exists between the glyoxylate hydrate **2b** and glyoxylate **5** in the reaction media. The glyoxylate formed in situ could react with the arylbismuth and aryllead reagents driving the equilibrium to the aldehyde to form the product.

The preference for forming the *S* product could be due to the attack of the arylbismuth–Rh(I) from the Si face of the aldehyde carbonyl group (Fig. 1) with a π-stacking interaction[12] blocking the Re face of the aldehyde. The hydrophobic effect of substrates in water can enforce the π-stacking interaction, leading to promotion of the diastereoselectivity.[13]

Table 2. Diastereoselectivity of reaction of **2d** with **1** in various solvents

Entry	Ar_nMR_m	Solvent	Temp. (°C)	Product	Yield (%)	d.e. (%)
1	**1b**, $(C_{10}H_8)_3Bi$	H_2O	50	**3e**	81	85
2	**1b**	H_2O/THF (4:1)	40	**3e**	73	46
3	**1b**	THF	40	**3e**	71	36
4	**1b**	CH_2Cl_2	35	**3e**	70	49
5	**1b**	C_2H_5OH	40	**3e**	47	75
6	**1a**, Ph_3Bi	H_2O	50	**3d**	70	67
7	**1a**	CH_2Cl_2	35	**3d**	52	52
8	**1f**, $PhPbMe_3$	H_2O	50	**3d**	73	77
9	**1f**	CH_2Cl_2	35	**3d**	75	48



Scheme 1.

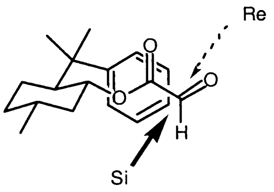


Figure 1.

A typical experimental procedure is as follows: A suspension of **1a** (100 mg, 0.327 mmol), **2d** (143 mg, 0.327 mmol) and $Rh_2(COD)_2Cl_2$ (8 mg, 0.016 mmol) in 4 mL water was stirred at 50°C. After the reaction was completed (monitored by TLC), 15 mL ether was added. The organic phase was separated and the aqueous phase was extracted with ether (3×10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by a flash chromatography on silica gel (eluent: hexane/ethyl acetate = 15:1) to give the product **3d** (83 mg, yield 70%).

Acknowledgements

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