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Oxidation of Primary Alcohols over Hydrous Zirconium(IV) Oxide

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Synopsis. The oxidation of primary alcohols with quinone or benzophenone was carried out by catalysis with hydrous zirconium(IV) oxide in both batch and flow reaction systems. As a result, it was elucidated that a lot of primary alcohols can be efficiently oxidized over hydrous zirconium(IV) oxide.

In the oxidation of alcohols with carbonyl compounds by catalysis with metal alkoxide, which is known as an Oppenauer-type oxidation, it has been difficult to apply primary alcohols as the reactants. This is because an aldol condensation easily occurs between an aldehyde of the product and a carbonyl compound of the hydrogen acceptor. Recently, the oxidation of some primary alcohols was reported to proceed efficiently using bis(cyclopentadienyl)zirconium(IV) dihydride as a complex catalyst.[1] However, the oxidation of the primary alcohol over a solid catalyst has never been achieved.

In a previous paper,[2] we reported that the Oppenauer-type oxidation of secondary alcohols with ketones proceeded efficiently over hydrous zirconium(IV) oxide. Several ketones, for example, acetone, diethyl ketone, and cyclohexanone, could be used as a hydrogen acceptor. However, primary alcohols were not efficiently converted to the corresponding aldehydes. As reported in our previous paper,[3] the ability of primary alcohols to provide a hydrogen donor is less than that of secondary alcohols. Further, the aldehydes produced from primary alcohols were easily condensed with ketones when the ketones which have a hydrogen atom at the α-position of the carbonyl group were used as the hydrogen acceptor. Thus, compounds which could not undergo the aldol condensation were used as the hydrogen acceptor for the oxidation.

In this paper we report that the Oppenauer oxidation of primary alcohols proceeds efficiently using *p*-benzoquinone or benzophenone as the hydrogen acceptor over hydrous zirconium(IV) oxide. The Oppenauer oxidation is the best method for the preparation of aldehydes from primary alcohols, since further oxidation of the aldehydes does not theoretically occur. Furthermore, the following advantages are expected in our method; (1) easy product isolation, (2) a lack of the need to maintain water-free conditions, (3) reusability of the catalyst, and (4) durability of the catalytic activity. These oxidations could be carried out in both batch and flow reaction systems.

Experimental

Catalyst and Materials. Hydrous zirconium(IV) oxide was prepared in the manner described in a previous paper.[3] The calcination of the catalyst was performed at 300 °C for 5 h. Comercial reagents were used for the reaction without any further purification.

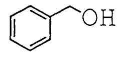
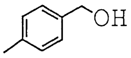
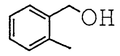
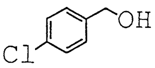
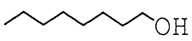
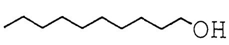
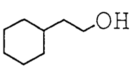
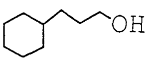
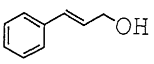
General Procedure in the Batch Reaction System. The following were placed in a 20 cm^3 round-bottomed flask equipped with a reflux condenser: hydrous zirconium oxide (24—60 mesh; 0.1 or 0.3 g), an alcohol (0.1 or 0.25 mmol), a ketone (20 mmol) or *p*-benzoquinone (1.5 mmol), and a hydrocarbon as an internal standard. The contents were then heated under gentle reflux. The reaction mixture was collected at an appropriate time after refluxing, and the products were analyzed by GLC (a capillary column PEG 20 M 30 m or OV101 30 m) and GC-MS (Shimadzu QP1000).

General Procedure in the Flow Reaction System. Catalytic oxidation was carried out in a glass-flow reactor (6.5 mm in diameter) with a fixed-bed catalyst: flow rate of nitrogen=60 cm^3 min^{-1}; catalyst=1.5—2.0 g, 24—60 mesh; reaction temperature=200 °C; A xylene solution (10 mmol cm^{-3}) of an alcohol, a ketone (2 mol cm^{-3}), and a hydrocarbon as an internal standard was fed into the reactor (5 cm^3 h^{-1}) by means of a microfeeder. The yields of the products were analyzed in a similar manner to that described above after a steady state condition had been reached.

Results and Discussion

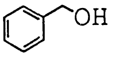
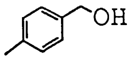
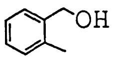
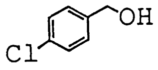
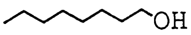
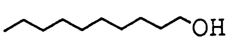
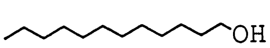
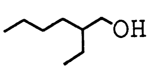
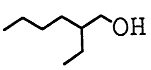
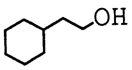
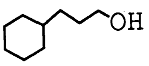
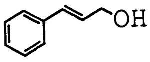
Oxidation of Alcohols with *p*-Benzoquinone. By using *p*-benzoquinone as the hydrogen acceptor, oxida-

Table 1. Oxidation of Primary Alcohols with *p*-Benzoquinone in the Batch Reaction System[a)]

Reactant	Time/h	Yield/%
	4.0	85.8
	4.0	31.4
	4.0	35.9
	4.0	47.8
	4.0	29.7
	4.0	9.8
	8.0	46.2
	8.0	27.9
	4.0	46.8

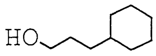
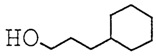
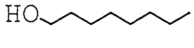
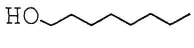
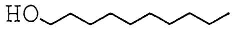
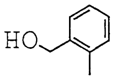
a) Catalyst: 0.3 g, alcohol: 0.25 mmol, *p*-benzoquinone: 1.5 mmol, xylene: 10 cm^3, reflux temperature.

Table 2. Oxidation of Primary Alcohols with Benzophenone in the Batch Reaction System[a)]

Reactant	Time/h	Yield/%
	2.0	81.0
	4.0	65.4
	4.0	63.3
	4.0	45.8
	2.0	35.4
	2.0	10.3
	2.0	6.4
	2.0	25.5
	8.0	50.9
	8.0	46.2
	8.0	27.9
	4.0	46.8

a) Catalyst: 0.1 g, alcohol: 0.1 mmol, benzophenone: 20 mmol, xylene: 10 cm^3, reflux temperature.

Table 3. Oxidation of Primary Alcohols with Benzophenone in the Flow Reaction System[a)]

Reactant	Catalyst/g	Yield/%
	1.5	63.3
	2.0	48.7
	1.5	62.4
	2.0	74.3
	1.5	50.0
	2.0	69.0

Alcohol: 0.05 mmol h^{-1}, benzophenone: 10 mmol h^{-1}, xylene: 5 cm^3 h^{-1}, temperature: 200 °C.

tion of the alcohols was carried out in the batch reaction system. The results are listed in Table 1. Benzyl alcohol was efficiently oxidized to give benzaldehyde in high yield; most of the alcohols were converted to the corresponding aldehydes without aldol condensations, even though the yields were relatively low. The low reactivity in these systems can be explained as being due to the catalyst being inactivated by the strong adsorption of *p*-benzoquinone.

Oxidation of Alcohols with Several Ketones. The oxidation of benzyl alcohol and 1-octanol with several ketones was carried out in the batch reaction system. In the case of acetone, both benzyl alcohol and 1-octanol could not be converted to the corresponding aldehyde. The aldol condensation of the compound produced from the primary alcohol occured with acetone. Since the oxidizing ability of diisopropyl ketone is much smaller than that of acetone,[2)] the oxidation of the primary alcohol does not occur. Compared with these ketones, benzophenone has a high ability for oxidizing the alcohols and resisting aldol condensation. Accordingly, it was elucidated that benzophenone is the best hydrogen acceptor for the oxidation of the primary alcohol among these ketones.

Oxidation of Alcohols with Benzophenone in the Batch Reaction System. All of the alcohols could be oxidized in this system, as shown in Table 2. These yields were almost the same as those when using *p*-benzoquinone as the hydrogen acceptor. Compared with benzyl alcohol and its derivative, the other alcohols were never efficiently convereted to the corresponding aldehydes. The Oppenauer oxidation was believed to proceed via a hydride transfer from the alcohol to ketone, and the reactivity of alcohol was affected by the electron density of the hydrogen on the α-carbon of the hydroxyl group. Compared with aliphatic alcohols, the derivertives of benzyl alcohol had a high ability to provide a hydrogen donor, because of a π-electron donation from the phenyl group.

Oxidation of Alcohols with Benzophenone in the Flow Reaction System. The results of the oxidation of primary alcohols in the flow reaction system are listed in Table 3. Most of the alcohols were efficiently converted to the corresonding aldehydes. In particular, it was noteworthy that the aliphatic alcohols were efficiently oxidized in comparison with the batch reaction system.

In conclusion, it was elucidated that the oxidation of primary alcohols with benzophenone in a flow reaction system proceeds efficiently by catalysis with hydrous zirconium(IV) oxide.

References

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2) H. Kuno, K. Takahashi, M. Shibagaki, and H. Matsushita, *Bull. Chem. Soc. Jpn.*, **63**, 1943 (1990).

3) M. Shibagaki, K. Takahashi, and H. Matsushita, *Bull. Chem. Soc. Jpn.*, **61**, 3283 (1988).