CHEMISTRY LETTERS, pp. 1401-1404, 1979.

ALDOL CONDENSATIONS WITH Co(II)-POLYMER COMPLEX CATALYSTS

Kazuo IRIE, Atsushi IMAZAWA, and Ken-ichi WATANABE*
Department of Chemistry, Faculty of Science, Tokyo
Metropolitan University, Fukazawa, Setagayaku, Tokyo 158

Aldol condensation of aldehydes with ketones catalyzed by complex of cobalt(II) acetate and 4-vinylpyridine-styrene-divinylbenzene copolymer gave α,β-unsaturated ketones in high yields without containing self-condensation product of ketone, and the catalyst was able to be re-used.

A number of polymer catalysts have been utilized in organic reactions.[1)] They have advantages that the catalysts are easily removed by filtration from the reaction mixture and can be used repeatedly. It has been known that aldol condensation reactions are catalyzed by ion exchange resin but product yields of the reactions are somewhat inferior to those obtained with strong acid or base as homogeneous catalyst.[2)]

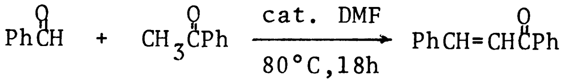
Recently, we have found that cobalt(II) complex of 4-vinylpyridine-styrene-divinylbenzene copolymer was good catalyst for aldol condensations of aldehydes with ketones. The reactions with this complex catalyst gave α,β-unsaturated ketones in high yields without containing self-condensation product of ketone. The results of studies on the aldol condensations with this polymer complex and some related complex catalysts will be described in this paper.

Polymers used for the catalysts were poly(4-vinylpyridine)(PVP), crosslinked 4-vinylpyridine copolymer(VP), and crosslinked 4-vinylpyridine-styrene-copolymer(VP_x-St_y:molar ratio=x:y), and they were prepared according to the conventional methods.[3)] A solution of cobalt(II) acetate($Co(OAc)_2\cdot 2H_2O$, 0.75g) in DMF(21ml) was added to swelled copolymer($VP_{1.0}$-$St_{3.2}$,1.0g) in DMF and was stirred at room temperature for 24h. Cobalt(II) complex of the copolymer formed was filtered and washed with DMF and ether successively. It was reddish purple and the content of cobalt(II) ion in the complex was determined by atomic absorption spectrophotometry.[4)] In the presence of the catalyst(51mg), a solution of benzaldehyde(63mg) and excess acetophenone(2.5ml) in DMF(0.5ml) was stirred at

80°C for 18h. The polymer complex catalyst was easily removed from the reaction mixture by filtration. The solvent and excess acetophenone used were evaporated in vacuo to give 1,3-diphenyl-2-propen-1-one(chalcone) as a yellow oil and the yield was determined by GLC. Similarly, the aldol condensation of benzaldehyde with acetophenone with some other catalysts were carried out for comparison. The results are summarized in Table 1.

The reaction did not occur without catalyst, and PVP or VP$_{1.0}$-St$_{3.2}$ had no catalytic activity at all, while Co(OAc)$_2$ itself showed some activity. The condensation reactions catalyzed by Co(II)-complexes of PVP(**1**),VP(**2**),and VP(**3**) (Table 1) gave chalcone in moderate yield. However, when Co(II)-complexes of VP-St(**4**) and (**5**) were used, the product yields were quantitatively. The condensation reaction, without accompanying the self-condensation product, was well catalyzed also by Co(II)-py complex, which was analogous to our previous studies on Cu(II)-amine complex catalyst for the aldol condensation.[5] In this case, removal of the homogeneous Co(II)-py catalyst from the reaction mixture was troublesome after the reaction. In the reaction with Co(II)-VP-St complex(**4**), the yield of the product reached 100% in 18h. On the other hand, in the reaction with Co(II)-py, the yield was 80% in 18h and was 94% in 40h even. The reaction with ion exchange resin, Am.IR-120, gave chalcone in low yield(36%) accompanying 1,3-diphenyl-2-butene-1-one as self-condensation product of acetophenone. For further investigation of aldol condensations with the polymer complex catalyst, we examined the reactions between several kinds of

Table 1. Aldol condensation with various polymer complex catalysts



$$\mathrm{Ph\overset{O}{\overset{\|}{C}}H} + \mathrm{CH_3\overset{O}{\overset{\|}{C}}Ph} \xrightarrow[80^\circ\mathrm{C,18h}]{\text{cat. DMF}} \mathrm{PhCH{=}CH\overset{O}{\overset{\|}{C}}Ph}$$

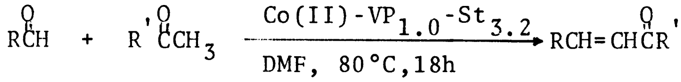
Catalyst[a)]*	Yield(%)[b)]
none	0
PVP	0
VP$_{1.0}$-St$_{3.2}$	0
Co(OAc)$_2$·2H$_2$O	31
Co(II)-PVP(**1**)[c)]	41
Co(II)-VP(**2**)[d)]	53
Co(II)-VP(**3**)[e)]	54
Co(II)-VP$_{1.0}$-St$_{3.2}$(**4**)[d,f)]	100(84)[g)]
Co(II)-VP$_{1.0}$-St$_{6.5}$(**5**)[d,f)]	100
Co(II)-py[c)]	80
Am.IR-120	36

* PVP:poly(4-vinylpyridine),VP:crosslinked 4-vinylpyridine copolymer,VP-St:crosslinked 4-vinylpyridine-styrene copolymer, py:pyridine.

a) The amount of catalyst was based on Co(II) ion and was 16mol% for benzaldehyde. b) GLC yield. c) Molar ratio of Co(II) to pyridine unit=2:3. d) Divinylbenzene(DVB)(1mol%) was used as a crosslinking agent. e) DVB (10mol%) was used. f) VP$_{1.0}$-St$_{3.2}$: molar ratio =1.0:3.2, VP$_{1.0}$-St$_{6.5}$: molar ratio=1.0:6.5 g) Isolated yield.

ketones and aldehydes with complex catalyst (4). The reaction method was similar to that of Table 1, but the reaction products were isolated and identified. The results are summarized in Table 2.

Table 2. Aldol condensations of various aldehydes with ketones in the presence of catalyst (4)



$$\mathrm{R\overset{O}{\overset{\|}{C}}H} + \mathrm{R'\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow[\text{DMF, 80°C,18h}]{\mathrm{Co(II)\text{-}VP_{1.0}\text{-}St_{3.2}}} \mathrm{RCH{=}CH\overset{O}{\overset{\|}{C}}R'}$$

R	R'	Yield(%)[a]	Mp(°C)(lit[2])
p-CN-C_6H_4	C_6H_5	98	162[b]
p-NO_2-C_6H_4	C_6H_5	93	164-165(158-160)
p-Cl-C_6H_4	C_6H_5	81	118-119(114)
C_6H_5	C_6H_5	84(100)[c]	55-58(57-58)
p-MeO-C_6H_4	C_6H_5	55	76-77(72-74)
p-Me-C_6H_4	C_6H_5	37	97-98(96)
$C_6H_5CH{=}CH$	C_6H_5	50	103-106(102-103)
$(CH_3)_2CH$	C_6H_5	29	oil[d]
C_6H_5	CH_3	20	oil[e]
C_6H_5	CH_3CH_2	0	——

a) Isolated yield. b) Identified by elemental analysis, MS, NMR, and IR. c) GLC yield d) Identified by MS,NMR, and IR. e) Identified by NMR and IR.

The reactions of acetophenone with substituted benzaldehydes gave the corresponding chalcones. In these reactions, product yields were remarkably affected by substituent groups of aldehydes. The resulting yields were high in the case of aldehydes with electron attractive groups(NO_2,CN) and were low with electron donative groups(Me,MeO). It was found that the reactions with aliphatic aldehydes or aliphatic ketones did not proceed successfully.

In addition, the polymer complex catalyst was used repeatedly in the reactions in order to examine the catalytic ability. The Co(II)-$VP_{1.0}$-$St_{3.2}$ catalyst was used for the reaction of 4-nitrobenzaldehyde with acetophenone. The reaction conditions were similar to those of Table 1 and the catalyst was washed with DMF and ether successively for the re-use. As the result,4-nitrochalcone was obtained(isolated) in 92%(1st.), 90%(2nd.), and 92%(3rd.) yields, respectively.

References and Notes

1) D.C.Neckers, Chem. Technol. 108 (1978); J.Rebek, Tetrahedron, **35**, 723 (1979).

2) A.T.Nielsen and W.J.Houlihan, Org. React., Vol. 16, (1968).

3) Polymer Handbook, 2nd ed, ed by J.Brandrup and E.H.Immergut (1975); In a typical example, a solution of 4-vinylpyridine(10mmol), styrene(40mmol) divinylbenzene(0.5mmol), and azobisisobutyronitrile(82mg) in benzene(10ml) was poured in polymerization tube, and was sealed off under vacuum, heated at 70°C for 40h. The crosslinked polymer was purified by washing with benzene in a Soxhlet extractor for 8 h. The molar ratio of vinylpyridine and styrene in the polymer was determined by elemental analysis and was 1.0:3.2($VP_{1.0}$-$St_{3.2}$).

4) Cobalt(II) contents(mmol/g) in polymer complexes were calculated from the difference of initial amount to untrapped amount of Co(II) ion;(**2**),3.0mmol/g; (**3**),0.63mmol/g;(**4**),2.0mmol/g;(**5**),1.2mmol/g.

5) K.Irie and K.Watanabe, Chem. Lett., 539 (1978).

(Received August 1. 1979)