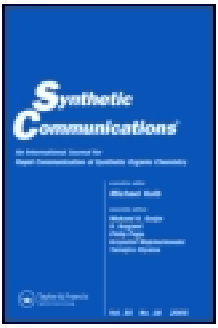

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Knoevenagel Condensation Catalyzed by USY Zeolite

Q. L. Wang [a] , YuDao Ma [a] & BoJun Zuo [a]

[a] Department of Chemistry, Shandong University, Jinan, 250100, China

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KNOEVENAGEL CONDENSATION CATALYZED BY USY ZEOLITE

Q. L. Wang*, YuDao Ma and BoJun Zuo
Department of Chemistry, Shandong University, Jinan, 250100, China

ABSTRACT The Knoevenagel condensation of substituted benzaldehydes with active methylene compounds was performed very efficiently by using a USY (ultrastable Y) zeolite as heterogeneous catalyst.

Knoevenagel condensation is one of the elemental reactions in organic chemistry. Traditionally, it was carried out in the presence of a base catalyst[1], e.g., ammonia, amine and their salts. For its importance in organic synthesis, several new procedures have been found during the last two decades[2-8]. Noteworthy are the results reported by Attanasi et al[6], Shanthan Rao et al[7]. and Bao et al.[8] who used Lewis acids, $CuCl_2$, $ZnCl_2$ and SmI_3, respectively, as catalysts for performing the Knoevenagel condensation reactions. On the other hand, because of the developments of catalysis science, many heterogeneous catalysts become commercially available and/or easy to be prepared today. In fact, the use of heterogeneous catalyst in organic synthesis began 30 years ago[9]. Nowadays the application of an important sort of heterogeneous catalysts, solid acids[10], especially zeolites[11], as catalysts for organic synthesis is increasing rapidly[12]. Besides the general advantages associated with heterogeneous catalysts (easy separation, convenient to use, little production of contaminant wastes, inexpensive, ···), zeolites can be prepared with different porosity, hydrophobicity, strength of acid sites and their distribution, which make them to suit particular reactions. Being inspired by the works[6-8] using Lewis acids as homogeneous catalysts, we have found a new procedure for performing the Knoevenagel condensation reaction, by using a so-called USY (Ultra Stable Y) zeolite catalyst which contains Bronsted and predominantly Lewis acid sites in its pore system[10] and has wide applications in petrochemical processes. The results are listed in Table.

Table. Knoevenagel condensation over USY zeolite*

$$ArCHO+R^1\text{-}CH_2\text{-}R^2 \xrightarrow[\Delta]{USY} ArCH{=}CR^1R^2+H_2O$$

Entry	Ar	R^1	R^2	Reaction time (h)	Yield %
1	C_6H_5	-COOH	-COOH	6	82
2	C_6H_5	MeCO-	MeCO-	6	89
3	C_6H_5	-COOMe	-COOMe	8	89
4	C_6H_5	-CN	-CN	12	92
5	2-ClC_6H_4	-COOH	-COOH	5	84
6	4-ClC_6H_4	-COOH	-COOH	5	92
7	4-ClC_6H_4	MeCO-	MeCO-	5	81
8	4-ClC_6H_4	-CN	-CN	5	95
9	3-$O_2NC_6H_4$	-COOH	-COOH	4. 5	91
10	4-$O_2NC_6H_4$	-COOH	-COOH	6	83
11	4-$MeOC_6H_4$	-COOMe	-COOMe	8	89
12	4-$MeOC_6H_4$	MeCO-	MeCO-	2. 3	89
13	4-HOC_6H_4	-CN	-$CONH_2$	5	90
14	4-HOC_6H_4	-COOMe	-COOMe	8	83

* For Entry 13, the product was mainly (~90%) *E* -isomer.
For Entry 1,5,6,9,10, the product was *E* -$ArCH{=}CHCO_2H$.

The USY zeolite was very active heterogeneous catalyst for the reactions of substituted benzaldehydes with active methylene compounds. The condensation products could be generally obtained with high yield (>80%). Several hours were sufficient for the completion of the reactions. The polymerization of the condensation product was practically insignificant.

Experimental To a mixture of 0. 05mol benzaldehyde, 0. 05mol active methylene compound and 5cm^3 benzene (as water-carrying agent), was suspended 4g USY zeolite (framework Si/Al = 10, total Si/Al = 2. 5, obtained from the Petrochemical Corporation of Qilu, China, calcined at 500℃ for 5h and conserved in a desiccator for use). The resulted suspension was stirred with gentle reflux till the completion of the reaction, as shown by the rate of the segregation of water. The catalyst was then filtered and washed with 10cm^3 solvent (ether, chloroform or ethanol, according to the polarity of the product). The organic solution was evaporated under reduced pressure, or treated by chromatograthy on a silica gel column (eluted by a mixture of cyclohexane and ethyl acetate), leading to the product with satisfactory purity. The structure of which was confirmed by m. p. data and NMR evidence.

Structural data of typical reaction products:

Entry 2. bp: 168—171℃/13mmHg ^{1}HNMR(90MHz, $CDCl_3$): 2. 26(s, 3H), 2. 40 (s, 3H), 7. 46(s, 1H), 7. 20—7. 42(m, 5H)

Entry 14. mp: 163—165℃ ^{1}HNMR(90MHz, $CDCl_3$): 3. 80(s, 3H), 3. 84(s, 3H), 5. 80—6. 00(br, 1H), 6. 76—6. 86, 7. 26—7. 36(m, 4H), 7. 70(s, 1H)

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