

Note

Rare earth exchanged HY zeolite, an efficient catalyst for the synthesis of N-monosubstituted amides

A R A S Deshmukh*, V K Gumaste & B M Bhawal

Division of Organic Chemistry (Synthesis)
National Chemical Laboratory, Pune 411 008, India

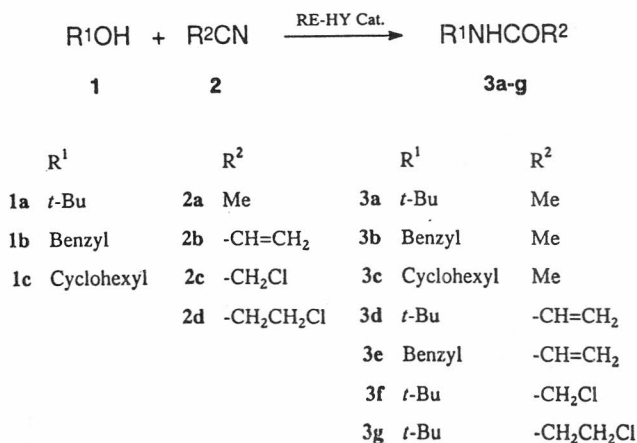
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The use of rare earth exchanged HY (RE HY) zeolite catalyst for the synthesis of N-monosubstituted amides **3a-g** starting from alcohols **1** and nitriles **2** in good yields is described

During the last decade zeolites have not only been used in the petrochemical industry but also in the synthesis of fine chemicals and important organic intermediates. The Bronsted and Lewis acid properties along with shape selectivity have been exploited for many organic transformations.¹ Recently, we have been engaged in exploring applications of zeolite catalysts in organic transformations². As a part of this programme we now report a mild and simple method for the synthesis of N-alkylamides starting from aliphatic nitriles and alcohols using zeolite catalyst.

The strong acid, such as sulfuric acid which catalyses the reaction of nitriles with alcohols or alkenes to form N-alkylamides is a normal Ritter reaction³. This reaction involves the generation of carbocation from alcohols or alkenes in the presence of strong acid, which reacts with nitrile to give nitrilium ion. This nitrilium ion further reacts with water to give amide⁴.

The reaction of *t*-butanol with acetonitrile (see Scheme I) was carried out at different temperatures ranging from 60-160 °C in the presence of RE-HY catalyst⁵ for 24 hr (Table I). A maximum yield of (43%) of N-*t*-butylacetamide was obtained when the reaction was carried out at 100 °C for 24 hr (entry 3). The drop in the yield at higher temperatures may be due to thermal decomposition of the product. The increase in the reaction period did not improve the yield of the product. This reaction was also studied using various zeolite catalysts at 100 °C. But the best results were obtained with rare earth exchanged HY (RE-HY)



Scheme I

Table I — Synthesis of N-*t*-butylacetamide starting from *t*-BuOH and acetonitrile in the presence of zeolite catalysts

Entry No.	Catalyst ^a used	Reaction Temp. (°C)	Yield ^{b,c} (%)
1.	RE-HY	50	10
2.	RE-HY	80	28
3.	RE-HY	100	43
4.	RE-HY	120	30
5.	RE-HY	140	25
6.	RE-HY	160	18
7.	H-ZSM-5	100	6
8.	RE-NaY	100	22
9.	H-Mordenite	100	5
10.	H-Y	100	5
11.	Ts-1	100	13

^a The catalyst was calcinated at 400 °C for 3 hr prior to use.

^b The reactions were carried out in a Parr reactor under autogenous pressure for 24 hr.

^c Isolated yields

catalyst, as this catalyst possesses both Lewis and Bronsted acidic sites for the reaction.

The generality of this reaction was tested by heating different alcohols **1** with excess of nitrile **2** in the presence of RE-HY catalyst in a Parr reactor under autogenous pressure at 100 °C for 24 hr which gave amides **3a-g** in good yields (Table II). The catalyst was recovered after the reaction by filtration and the product was isolated from the filtrate after removing the unreacted alcohol and nitrile. The product obtained was purified by crystallization. The reaction of acetonitrile with benzyl alcohol gave N-benzylacetamide **3b** in 63% yield (entry 2) along with a small amount (6%) of N,N-dibenzylacetamide. The primary alcohols such as methanol and ethanol did not give amides under

Table II — Synthesis of various N-substituted amides starting from alcohols and nitriles in the presence of RE-HY^a

Entry No.	R ¹	R ²	Product ^b	Yield ^c (%)	m.p. °C	Lit. m.p. °C
1.	<i>t</i> -Bu	Me	3a	43	98-99	97-98 ^{4a}
2.	Benzyl	Me	3b	63d	62-63	61 ⁶
3.	Cyclohexyl	Me	3c	20	105-6	105-6 ⁷
4.	<i>t</i> -Bu	-CH=CH ₂	3d	56	128-30	126-29 ^{4a}
5.	Benzyl	-CH=CH ₂	3e	61	69-71	70-72 ⁸
6.	<i>t</i> -Bu	-CH ₂ Cl	3f	58	81-82	82-83 ⁹
7.	<i>t</i> -Bu	-CH ₂ CH ₂ Cl	3g	45	92-93	93-94 ¹⁰

^a The catalyst was calcinated at 400 °C for 3 hr prior to use.

^b The reactions were carried out at 100 °C in a Parr reactor under autogenous pressure for 24 hr.

^c Isolated yields.

^d A small amount (6%) of N,N-dibenzylacetamide was isolated along with the product.

^e Use of cyclohexene in place of cyclohexanol gave the same product in 19% yield.

these conditions, while secondary alcohol gave a very low yield of the corresponding N-alkylamide (entry 3). It is clear from the above observations that better yields are obtained with the alcohols which can generate stable carbocation.

It is interesting to note that acrylonitrile on reaction with *t*-butanol and benzyl alcohol gave N-*t*-butylacrylamide **3d** an N-benzyl-acrylamide **3e** respectively in good yields. These acrylamides are important monomers for polyamides. The reaction of cyclohexene instead of cyclohexanol with acetonitrile also gave N-cyclohexylacetamide **3c** in a comparable yield.

Experimental Section

General. All melting points were determined on a Thermo-nik Campbell melting point apparatus and are uncorrected. ¹H NMR spectra were recorded in CDCl₃ solution on a Varian FT-80 (80 MHz), Bruker WH-90 (90 MHz) or Bruker AC 200 (200 MHz) spectrometer (chemical shifts are in δ, ppm downfield from tetramethylsilane). IR spectra were recorded on a Perkin-Elmer Infracord spectrophotometer Model 599-B using sodium optics. Mass spectra were recorded on a Finnigan Mat-1020 spectrometer.

A general procedure for the preparation of N-substituted amides 3. A mixture of alcohol (5g) and nitrile (50 mL) was taken in a Parr reactor and freshly activated zeolite RE-HY (5g) added to it slowly. It was then heated to 100 °C under autogenous pressure for 24 hr. The reactor was

cooled to room temperature and the catalyst filtered and washed with chloroform (2×10 mL). The unreacted starting materials and solvents were removed by distillation under reduced pressure. The solid residue was recrystallized from suitable solvents to give N-substituted amide (**3a-g**).

N-*t*-Butylacetamide 3a : IR (Nujol) : 3300, 1655 cm⁻¹; ¹H NMR : 1.37 (s, 9H), 1.93 (s, 3H), 5.50 (bs, 1H); MS : m/z 115 (M⁺, 100%).

N-Benzylacetamide 3b : IR (Nujol) : 3420, 1655, 1380, 1220 cm⁻¹; ¹H NMR : 0.94 (s, 3H), 4.32 (d, *J* = 6.4 Hz, 2H), 6.00 (bs, 1H), 7.22 (s, 5H).

N-Cyclohexylacetamide 3c : IR (Nujol) : 3300, 1655 cm⁻¹; ¹H NMR 1.00-2.00 (m, 10H), 2.05 (s, 3H), 3.55-4.00 (m, 1H), 5.80 (bs, 1H); MS : m/z 141 (M⁺, 100%).

N-*t*-Butylacrylamide 3d : IR (Nujol) : 3260, 1660, 1630 cm⁻¹; ¹H NMR : 1.37 (s, 9H), 5.37 (bs, 1H), 5.56 (dd, *J* = 3.5 and 10 Hz, 1H), 5.87 (dd, *J* = 10 and 16 Hz), 6.18 (dd, *J* = 3.5 and 16 Hz); MS : m/z 127 (M⁺, 10%), 72 (100%).

N-Benzylacrylamide 3e : IR (Nujol) : 3185, 1645, 1625, 1450 cm⁻¹; ¹H NMR : 4.50 (d, *J* = 4.8 Hz, 2H), 5.65 (dd, *J* = 2.5 and 14.6 Hz, 1H), 6.15 (dd, *J* = 9.7 and 14.6 Hz, 1H), 6.35 (dd, 2.4 and 14.6 Hz, 1H), 7.35 (m, 5H).

N-*t*-Butyl-2-chloroacetamide 3f : IR (Nujol) : 3230, 1665 cm⁻¹; ¹H NMR : 1.35 (s, 9H), 3.88 (s, 2H), 6.28 (bs, 1H); MS : m/z 149 (M⁺, 33%), 134 (100%).

N-t-Butyl-3-chloropropanamide 3g : IR (Nujol) : 3230, 1670, cm^{-1} ; $^1\text{H NMR}$: 1.40 (s, 9H), 2.51 (t, $J = 2\text{H}$), 3.80 (t, $J = 2\text{H}$), 5.45 (bs, 1H).

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