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Aromatic 3-Aza-Cope Rearrangement Over Zeolites.

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Abstract : N-Allyl-2-methyl aniline [**1a**], N-allyl and N-(2'-methyl allyl)-N-methyl anilines [**1b** & **1c**, respectively] undergo the 3-aza-Cope rearrangement in presence of HY-Zeolite, HEMT and HZeolite beta in hexane at 80° C to give Indoline derivatives as the major product. Copyright © 1996 Elsevier Science Ltd

Aza-Claisen and aza-Cope rearrangements have been extensively studied in the past over Lewis acids, Bronsted acids and thermal conditions.[1] However, no report is available in the literature in which a zeolite is employed to promote the aza-Cope rearrangement . In recent years, there has been a tremendous upsurge of interest in various chemical transformations mediated by zeolites. Their characteristic features such as shape selectivity, thermal stability and unique varying acidic and basic properties coupled with the ease of operation have made them versatile catalysts for a wide range of reactions.[2,3,4] However, their application in general organic synthesis has not been fully explored.

In this communication, the authors wish to report a mild and convenient method for aromatic 3-aza-Cope rearrangement using HY-Zeolite, HEMT and HZeolite beta. Initial attempts to bring about the 3-aza-Cope rearrangement of [**1a**] by heating a solution of it in an autoclave with a catalytic quantity of HY-Zeolite (Substrate : Catalyst weight ratio, 10 : 1) did not result in any conversion and filtration of the catalyst followed by the removal of hexane gave back the unconverted starting material. Hence in further studies large excess of zeolites were used in order to adsorb the substrate completely from the solution.

The starting materials [**1a**, **1b** & **1c**] were synthesized as reported elsewhere.[5,6] Y-Zeolite, EMT, Zeolite beta were synthesized in Professor. J. Weitkamp's Laboratory, University of Stuttgart, Germany.[7] Prior to use zeolites were calcined at 500° C for 5 h in presence of air. The reaction on HY-Zeolite was optimized with respect to temperature, reaction time and catalyst : substrate ratio.

The mixture of [**1a**] (0.1 g) and HY-Zeolite (1 g) was heated with stirring in a Teflon-lined autoclave at 80 ° C for 2 h in 150 ml dry hexane, after which it was filtered. The hexane filtrate did not contain any dissolved substance. The zeolite was extracted with methanol (3 x 50 ml), followed by removal of methanol and purification furnished **2a** and **3a** in 11% and 78% yield respectively. HEMT and HZeolite beta are large pore zeolites like HY-Zeolite. In these cases also the substrate was completely adsorbed by the zeolite from hexane solution. The results with HY-Zeolite, HEMT and HZeolite beta are listed in Table 1. This technique has been applied successfully for the 3-aza-Cope rearrangement of [**1b** & **1c**].The results are listed in Table1.

In addition the zeolite as a catalyst is advantageous with respect to their easy separation from the reaction media, high yield of Indoline derivatives[8] and regeneration of the catalyst.

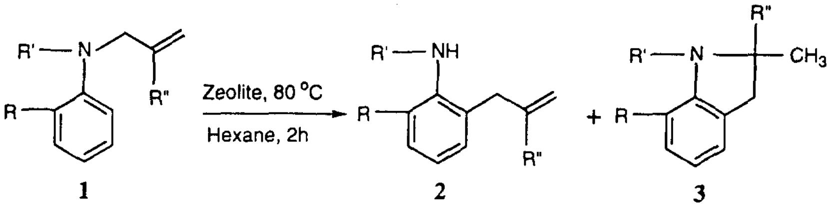

Table 1 Comparison of the yield of products over different zeolites ; T = 80° C , Reaction time = 2 h.

Substrates	Products	% Yield		
		HY-Zeolite	HEMT	HZeolite beta
1a ; R = CH_3	**2a**	11	9	18
R' = R'' = H	**3a**	78	81	58
1b ; R = R'' = H	**2b**	6	6	23
R' = CH_3	**3b**	80	80	52
1c ; R = H	**2c**	17	12	31
R' = R'' = CH_3	**3c**	64	71	48

a) Yields refer to isolated pure products.

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9. **2a** : NMR ($CDCl_3$/TMS) : δ 6.9–6.6 (m, 2H), 6.5 (t, 1H), 6.0–5.6 (m, 1H), 5.2-4.9 (m, 2H), 3.3 (b.s, NH_2), 3.1 (d, 2H) and 2.0 (s, 3H) ; MS m/z 147 (M^+). **3a** : NMR ($CDCl_3$/TMS) : δ 6.8–6.6 (m, 2H), 6.4 (t, 1H), 3.8-3.6 (m, 1H), 3.3 (b.s, NH), 3.0-2.5 (m, 2H), 1.9 (s, 3H) and 1.2 (d, 3H) MS m/z 147 (M^+).
10. **2b** : NMR ($CDCl_3$/TMS) : δ 7.3 (t, 1H), 7.0 (d, 1H), 6.8 (t, 1H), 6.6 (d, 1H), 6.2-5.9 (m, 1H), 5.2-5.0 (m, 2H), 3.7 (b.s, NH), 3.3 (d, 2H) and 2.8 (s, 3H) ; MS m/z 147 (M^+). **3b** : NMR ($CDCl_3$/TMS) : δ 7.0–6.8 (m, 2H),3.5-3.2 (m, 1H), 3.0-2.7 (m, 2H), 2.6 (s, 3H) and 1.3 (d, 3H) ; MS m/z 147 (M^+).
11. **2c** : NMR ($CDCl_3$/TMS) : δ 7.2 (t, 1H), 6.9 (d, 1H), 6.7 (t,1H), 6.5 (d, 1H),4.8-4.7 (m, 2H), 3.7 (b.s,NH), 3.2 (s, 2H),2.7 (s, 3H) and 1.7 (s, 3H) ; MS m/z 161 (M^+). **3c** : NMR ($CDCl_3$/TMS) : δ 7.0–6.7 (m, 2H), 6.5 (t, 1H), 6.2 (d, 1H), 2.8 (s, 2H), 2.6 (s, N-CH_3) and1.2 (s, 6H) ; MS m/z 161 (M^+).

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