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Zeolite-Hy : A Selective And Efficient Catalyst For The Alcoholyses Of Various Alcohols

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SYNTHETIC COMMUNICATIONS, 29(11), 1921-1927 (1999)

ZEOLITE-HY : A SELECTIVE AND EFFICIENT CATALYST FOR THE ALCOHOLYSES OF VARIOUS ALCOHOLS

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Abstract: An efficient and selective method for the conversion of various alcohols into their corresponding ethers in the presence of zeolite under solvolytic condition is described. The reaction proceeds efficiently at ambient pressure in high yields.

Direct conversion of alkyl halides into ethers is an important synthetic process for which a number of literature reports are available. Many excellent procedures can be used for the preparation of alkyl aryl ethers while the Williamson synthesis which has been extensively investigated and modified since its introduction in the early part of this century, remains the most useful and general procedure for the preparation of structurally simple dialkyl ethers. Other common methods for this conversion are based on the reaction of metal salts of alcohols with different alkylating agents[1]. Condensation of alcohols or their salts with aldehydes[2],

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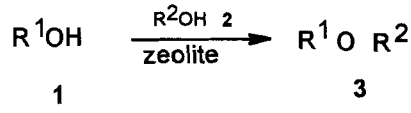
olefins[3], alkyl oxides[4] and dialkyl phosphites[5] are also reported to be useful methods for this transformation. But careful scrutiny of the reaction procedure reveals some shortcomings in most of the procedures. therefore, there is still merit in developing a catalytic procedure for the preparation of ethers using efficient and inexpensive reagents. Moreover, in recent years considerable resurgence of interest in the area of zeolite induced organic transformations[6] have figured prominantly for their remarkable catalytic properties. Several methods using this catalyst e.g. thioacetalization of carbonyl compounds, sulphoxidation of thioethers, deketalisation and oxidative cleavage of tosylhydrazones have been investigated[7]. Herein we wish to report that zeolite-HY effects the formation of various ethers in excellent yields and with an extremely simple work-up, which makes it a reagent of practical synthetic value. The reaction is fairly general, facile and efficient and is devoid of any side products emanating from functional groups present.



In a typical case, zeolite-HY was treated with a solution of 3-phenyl-2-propen-1-ol in isopropyl alcohol. The resulting mixture was stirred magnetically under reflux condition for 30 min. After completion, the reaction mixture was allowed to reach room temperature and the solvent was removed under vacuum on a rotary evaporator using water bath temperature lower than 40°C. The residue on purification by column chromatography on silica gel gave the corresponding cinnamyl ether (entry 1) in 90% yield. Similar treatment of other substrates gave the corresponding ethers 3 in 75-93% yields. Compared to typical benzylation conditions such as BnBr, NaH in DMF and benzyl triflate[8], benzylation by zeolite proceeds under mild conditions in high yields. Treatment of cinnamyl alcohol and benzyl alcohol in (1:1) molar ratio at 80°C for 30 mins gives the corresponding

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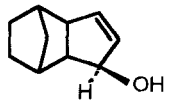
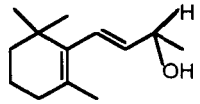
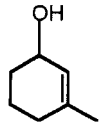
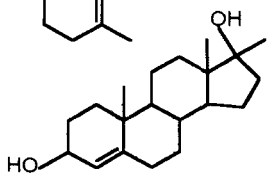
Table: Zeolite-HY catalysed formation of ethers 3

Entry	Substrate 1	Alcohols 2	Products	Yields[a] (%)	Yields reported[9]	Time (min)	Time reported[9] hr.
1	Ph CH=CH CH_2OH	i-PrOH	3a	90	78	30	8
2	Ph CH=CH CH_2OH	t-BuOH	3b	82	80	45	4
3	Ph CH=CH CH_2OH	BnOH	3c	80	-	35	-
4	Ph CH=CH CH(OH)CH_3	i-PrOH	3d	90	96	40	1
5	4-MeO Ar CH=CH CH(OH)CH_3	i-PrOH	3e	93	96	45	5
6	4-MeO Ar CH=CH CH(OH)CH_3	t-BuOH	3f	88	96	45	7.5
7	Ph CH=CH CH(OH)CH_3	t-BuOH	3g	76	96	45	7.5
8	Ph C(CH_3)(C_2H_5)OH	i-PrOH	3h	80	14	45	48
9		i-PrOH	3i	83	85	50	5
10		i-PrOH	3j	80	60	45	1.5
11		i-PrOH	3k	75	96	40	0.5
12		i-PrOH	3l	75	95	45	2.5

[a]Yields refer to isolated products.

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benzylated derivative in 80% yield without any by-product formation. Also selective alcoholysis of allylic hydroxyl group in the presence of tertiary group was observed in 75% yield when carried out with steroidal alcohol (entry 12). Therefore in contrast to Williamson and related synthesis, the present method provides a simple and efficient route, for the preparation of a wide variety of ethers in which due to the reaction medium employed there is no necessacity for use of strictly anhydrous reagents or conditions. All the compounds obtained were characterised by comparing the infrared and ^1H NMR spectroscopic data with authentic samples.

In conclusion, the results described herein demonstrate the novelty of zeolite catalyst which exercises unique selectivity. The main advantages of this new method are mild reaction conditions, devoid of side products, ease of work-up procedure, low cost of the reagent and excellent yields.

Experimental

Mps were determined by using a buchi melting point apparatus and are uncorrected. The IR spectra were obtained on a Perkin-Elmer 237B IR spectrophotometer. All reagents were of commercial quality from freshly opened containers and were purchased from Aldrich Chemical Company and used without further purification.

General Procedure for the Alcoholyses of Various Alcohols :- Zeolite-HY (0.6g) was added to a solution of 3-phenyl-2-propen-1-ol (0.27g, 2mmol) in isopropyl alcohol (15mL). The mixture was stirred magnetically under reflux condition for 30 min (monitored vide tlc). After completion, the reaction mixture

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was allowed to reach room temperature and the solvent was removed under vacuum on a rotary evaporator using water bath temperature lower than 40°C. The residue on purification by column chromatography on silica gel afforded the corresponding cinnamyl ether **3a** as a colourless oil in 90% yield, ^{1}H NMR 7.10-7.20 (m, 5H, ArH), 6.25 (d, 1H), 5.82 (dd, 1H), 4.25 (d, 2H), 3.90 (m, 1H), 1.06 (d, 6H,). MS m/e; 176 (M^+). Anal. Calcd. (found) for $C_{12}H_{16}O$; C, 81.81 (81.66); H, 9.09 (9.15). Similar treatment of other substrates gave the corresponding ethers **3** in 75-93% yields. Several examples illustrating this novel and rapid procedure are given in the table and their characteristics are recorded here. 3b. oil, ^{1}H NMR 7.10-7.21 (m, 5H, ArH), 6.21 (d, 1H), 5.76 (dd, 1H), 4.31 (d, 2H), 1.02 (m, 9H). MS m/e; 190 (M^+). Anal. Calcd. (found) for $C_{13}H_{18}O$; C, 82.10 (82.25); H, 9.47 (9.54). 3c. oil, ^{1}H NMR 7.08-7.20 (m, 10H, ArH), 6.20 (d, 1H), 5.80 (dd, 1H), 4.20 (m, 4H). MS m/e; 224 (M^+). Anal. Calcd. (found) for $C_{16}H_{16}O$; C, 85.71 (85.79); H, 7.14 (7.26). 3d. oil, ^{1}H NMR 7.08-7.15 (m, 5H, ArH), 6.30 (d, 1H), 5.76 (dd, 1H), 3.91 (m, 1H), 3.52 (m, 1H), 1.30 (d, 3H), 1.02 (d, 6H). MS m/e; 190 (M^+). Anal. Calcd. (found) for $C_{13}H_{18}O$; C, 82.10 (82.02); H, 9.47 (9.57). 3e. oil, ^{1}H NMR 7.06-7.16 (m, 4H, ArH), 6.18 (d, 1H), 5.78 (dd, 1H), 3.90 (m, 1H), 3.52 (m, 1H), 3.76 (s, 3H), 1.32 (d, 3H), 1.02-1.12 (m, 6H). MS m/e; 220 (M^+). Anal. Calcd. (found) for $C_{14}H_{20}O_2$; C, 76.36 (76.50); H, 9.09, (9.18). 3f. oil, ^{1}H-NMR 7.08-7.19 (m, 4H, ArH), 6.22 (d, 1H), 5.82 (dd, 1H), 3.88 (m, 1H), 3.80 (s, 3H), 1.30 (d, 3H), 1.00-1.16 (m, 9H). MS m/e; 234 (M^+). Anal. Calcd. (found) for $C_{15}H_{22}O_2$; C, 76.92 (76.83); H, 9.40 (9.45). 3g. oil, ^{1}H-NMR 7.08-7.16 (m, 5H, ArH), 6.32 (d, 1H), 5.78 (dd, 1H), 3.88 (m, 1H), 1.28 (d, 3H), 1.02 (m, 9H). MS m/e; 204 (M^+). Anal. Calcd. (found) for; $C_{14}H_{20}O$;C, 82.35, (82.31), H, 9.80, (9.88). 3h. oil. ^{1}H-NMR 7.02-7.12 (m, 5H, ArH), 4.22 (q, 2H), 3.90 (m, 1H), 1.30 (d, 3H), 0.8-1.16 (m, 9H). MS m/e 192 (M^+). Anal. Calcd. (found) for, $C_{13}H_{20}O$;C, 81.25, (81.36); H, 10.41, (10.52). 3i.

oil, ^{1}H-NMR 5.82 (bs, 2H), 3.70 (m, 1H), 4.25 (unresolved, 1H), 0.90-2.20 (complex, 16H). MS m/e 192 (M^+). Anal. Calcd. (found) for, $C_{13}H_{20}O$; C, 81.25, (81.20), H, 10.41, (10.49). 3j. oil. ^{1}H-NMR 5.90 (d, 1H), 5.22 (dd, 1H), 3.56 (m, 1H), 0.90-2.32 (complex, 25H). MS m/e 236 (M^+). Anal. Calcd. (found) for $C_{16}H_{28}O$; C, 81.35, (81.26); H, 11.86, (11.75). 3k. Oil. ^{1}H-NMR 5.42 (s, unresolved, 1H), 3.90 (m, unresolved, 1H), 3.52 (m, 1H), 1.02-2.2 (m, 15H). MS m/e 154 (M^+). Anal. Calcd. (found) for $C_{10}H_{18}O$; C, 77.92, (77.85); H, 11.68, (11.76). 3l. MS m/e 330 (M^+) Anal. Calcd. (found) for $C_{23}H_{38}O$; C, 83.63, (83.59); H, 11.51, (11.43).

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