Anti-Markovnikov Addition of Thiols Across Double Bonds Catalyzed by H-Rho-Zeolite

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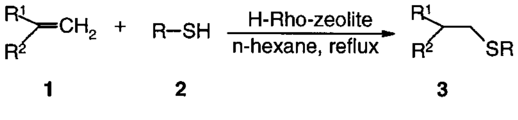
Abstract: A variety of olefins react with thiols in the presence of a catalytic amount of H-Rho-zeolite to afford the corresponding anti-Markovnikov addition products in good to excellent yields.

Key words: anti-Markovnikov addition, H-Rho-zeolite, thiols, olefins, heterogeneous catalysis

The last few years have witnessed a considerable upsurge of interest in the area of zeolite induced organic transformations.[1] In a series of publications from our group,[2] we have exploited the catalytic potential of zeolites for various organic synthetic transformations, e.g. thioacetalization of carbonyl compounds, sulfoxidation of thioethers, deketalization, tetrahydropyranylation of alcohols, oxidative cleavage of tosylhydrazones, methoxymethylation of alcohols, chemo- and stereoselective epoxidation and acetylation of aldehydes etc. In continuation, we wish to report a mild, convenient and heterogeneous catalytic methodology for the synthesis of anti-Markovnikov addition products by the reaction of thiols and olefins using Rho-zeolite.

In general, the protic acid[3] or Lewis acid[4] catalyzed addition of thiols across double bonds is known to give thioethers having structures which are in accordance with Markovnikov's rule. However, in the presence of free-radical initiator, thiols have been reported to add to double or triple bonds in anti-Markovnikov fashion by a free-radical mechanism.[5] A variety of hydroboration reagents developed for this reaction are also reported to give the anti-Markovnikov product.[6] However, the use of conventional protic or Lewis acid catalysts entails the problem of corrosivity, work-up and effluent pollution. Consequently, there is genuine need for an efficient and heterogeneous catalytic method for this reaction using inexpensive and nonpolluting reagents. Now we report that H-Rho-zeolite serves as an efficient catalyst for the thiol addition to olefins (Scheme).



Scheme

Thus, when the olefins were treated with thiols in the presence of catalytic amount of H-Rho-zeolite, the corresponding anti-Markovnikov products were obtained in good to excellent yields (Table). In a typical reaction procedure, to a stirred solution of olefin **1** (20 mmol) in n-hexane (25 ml) were added H-Rho-zeolite (0.5 equivalent by wt. of olefin) and thiol **2** (25 mmol) and the mixture was refluxed with stirring for the indicated length of time (Table). The reaction was monitored by TLC and G. C. After the completion of reaction, zeolite was filtered off and washed with n-hexane; the filtrate was then washed with 10% aq. NaOH solution to remove excess thiol and then further washed with water, brine and dried over Na_2SO_4. Removal of solvent and subsequent silica gel column chromatography afforded the pure product **3** which was analyzed by ^{1}H NMR. Much to our surprise, an anti-Markovnikov addition product was obtained which otherwise formed in the presence of peroxide. Due to steric constraints on the diffusional path of the molecules imposed by the different structural feature of the zeolite, the more bulkier Markovnikov adduct could not be retained in the zeolite pore and presumably for this reason only the anti-Markovnikov product was obtained. The mechanism of anti-Markovnikov addition could be compared with those mediated by the free-radical initiators where the main effect also seems to be steric and thus the only compound obtained is the sterically preferred anti-Markovnikov product.[5] The present procedure for thiol addition to an olefin is quite general as a wide range of olefins such as terminal, internal, cyclic, acyclic and branched olefins can be reacted with thiols easily under mild conditions. Under the reactions conditions employed, styrene reacted smoothly with a variety of thiols to afford the anti-Markovnikov products (Table**,** entries 1 & 4) and no polymerization of styrene could be observed. Similarly α-methylstyrene on reaction with thiophenol afforded the corresponding addition product in excellent yield (Table, entry 2). Mention must be made here that the reaction of thiophenol with olefin did not yield any Friedel-Crafts addition product and ethanethiol also reacted smoothly under the reaction conditions.[7]

In conclusion, we have established a facile, heterogeneous catalytic method for the anti-Markovnikov addition of thiols to a variety of olefinic compounds. The obvious advantages of heterogeneous catalysis in terms of easy separation, consistent yields and recyclability of the catalyst are noteworthy. Thus, the present catalytic method should serve as a useful addition to synthetic organic chemistry.

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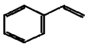
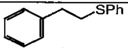
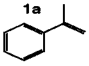
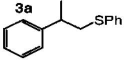
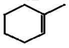
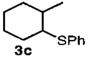
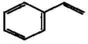
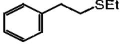
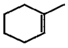
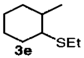
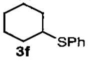
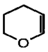
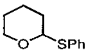
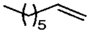
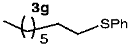
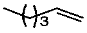
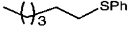
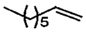
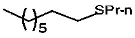
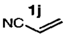
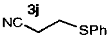
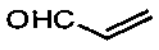
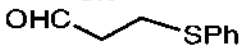
Table Addition of Thiols across Double Bonds using H-Rho–Zeolite[8]

Entry	Substrate	Thiol	Time (h)	Product[a]	Yield %[b]
1	 **1a**	PhSH	5	 **3a**	69
2	 **1b**	PhSH	6	 **3b**	98
3	 **1c**	PhSH	5	 **3c**	63
4	 **1d**	EtSH	8	 **3d**	71
5	 **1e**	EtSH	7.5	 **3e**	68
6	 **1f**	PhSH	6	 **3f**	55
7	 **1g**	PhSH	5	 **3g**	53
8	 **1h**	PhSH	10	 **3h**	54
9	 **1i**	PhSH	8	 **3i**	50
10	 **1j**	n-PrSH	10	 **3j**	69
11	 **1k**	PhSH	10	 **3k**	55
12	 **1l**	PhSH	12	 **3l**	53

(a) All products were characterized by their IR, ^{1}H-NMR and Mass spectroscopic data.[9]
(b) Yields refer to isolated pure products.

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References and Notes

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(1) (a) Davis, M. E. *Acc. Chem. Res.* **1993**, *26*, 111. (b) Holderich, W.; Hesse, M.; Naumann, F. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*,226. (c) Suib, S. L. *Chem. Rev.* **1993**, *93*, 803.
(d) Sachtler, W. M. H. *Acc. Chem. Res.***1993**, *26*, 383.
(e) Kumar, P.; Kumar, R.; Pandey, B. *J. Ind. Inst. Sci.* **1994,** *74*, 293.

(2) For an account of an oxidative transformations catalyzed by titanium and vanadium silicate molecular sieves, see :
(a) Kumar, P.; Kumar, R.; Pandey, B. *Synlett* **1995,** 289.
(b) Kumar, P.; Reddy, R. S.; Singh, A. P.; Pandey, B. *Tetrahedron Lett.* **1992,** *33*, 825. *Synthesis* **1993,** 67.
(c) Reddy, R. S.; Reddy, J. S.; Kumar, R.; Kumar, P. *J. Chem. Soc., Chem. Commun.***1992**, 84. (d) Rao, M. N.; Kumar, P.; Singh, A. P.; Reddy, R. S. *Synth. Commun.* **1992**, 1299.
(e) Kumar, P; Dinesh, C. U.; Reddy, R. S.; Pandey, B. *Synthesis* **1993**, 1069. (f) Kumar, P.; Hegde, V. R.; Pandey, B.; Ravindranathan, T. *J. Chem. Soc., Chem. Commun.***1993**, 1553. (g) Kumar, P.; Raju, S. V. N.; Reddy, R. S.; Pandey, B. *Tetrahedron Lett.* **1994**, *35*,1289. (h) Kumar, R.; Pais, G. C. G.; Pandey, B.; Kumar, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1315. (i) Kumar, P.; Hegde, V. R.; Kumar, T. P. *Tetrahedron Lett.***1995**, *36*,601.

(3) (a) Posner, T. *Ber.***1905**, *38*, 649. (b) Secrettas, C. G.; Mieha-Secrettas, M. *J. Org. Chem.*,**1979**, *44*, 713. (c) Wolf, F.; Finke, H. *Z. Chem.* **1972**, *12*, 180.

(4) (a) Mukaiyama, T.; Izawa, T.; Saigo, K; Takai, H. *Chem. Lett.***1973**, 335. (b) Belley, M. Zamboni, R. *J.Org. Chem.***1989**, *54*, 1230.

(5) For review of free-radical addition of mercaptans, see : Griesbaum, K. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 273.

(6) For a review of haloboranes, see; Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* **1982,** *239*, 23.

(7) The reaction of the thiophenol and olefin is reported to give the Friedel-Crafts product while alkylthiols failed to give any addition product see : ref. 3c.

(8) H-Rho-zeolite was procured as a gift sample from Catalysis Division, NCL, Pune. Prior to use it was calcined at 500 ^{0}C in the presence of air.

(9) Selected spectroscopic data: **3a :** colorless liquid; IR ν_{max}/ cm^{-1} (Neat) : 693, 748, 1080, 1439, 1475, 1578, 2850, 2920; ^{1}H NMR(CDCl$_3$, 200 MHz) δ : 2.9 (t, J = 6.8 Hz, 2H), 3.25 (t, J = 6.8 Hz, 2H), 7.2 – 7.55 (m,10H); MS (m/z, rel.int%) : M$^+$214 (60), 185 (5),154 (6), 123 (6), 110 (100), 109 (40), 91 (18), 77 (35), 69 (10), 65 (30). **3b :** colorless liquid; IR ν_{max}/ cm^{-1}(Neat) : 690, 749, 1080, 1439, 1478, 1579, 2849, 2920; ^{1}H NMR(CDCl$_3$, 200 MHz) δ : 1.25 (d, J = 6.8 Hz, 3H), 3.0 (m, 1H), 3.45 (m, 2H), 7.2 – 7.5 (m, 10H); MS (m/z, rel.int%) : M$^+$228 (8), 213 (12), 185 (5), 154 (5), 137 (10), 123 (95), 110 (100), 91 (50), 77 (60), 65 (45). **3h :** colorless liquid; IR ν_{max} /cm^{-1}(Neat) : 686, 732, 1021, 1083, 1371, 1464, 1577, 2851, 2919; ^{1}H NMR(CDCl$_3$, 200 MHz) δ :0.9 (t, J = 6.8 Hz, 3H), 1.2 – 1.5 (m, 8H), 1.67 (m, 4H), 2.93 (t, J = 6.8 Hz, 2H), 7.2 – 7.4 (m, 5H); MS (m/z, rel.int%) : M$^+$222 (55), 165 (2), 135 (5), 123 (56), 110 (100), 91 (9), 77 (20), 65 (13), 57 (2). **3k :** colorless liquid; IR ν_{max}/ cm^{-1}(Neat) : 667, 691, 747, 903, 1023, 1088, 1429, 1477, 1581, 2249, 2930; ^{1}H NMR(CDCl$_3$, 200 MHz) δ : 2.65 (t, J = 6.8 Hz, 2H), 3.15 (t, J = 6.8 Hz, 2H), 7.2 – 7.7 (m, 5H); MS: (m/z, rel.int%) M$^+$163 (64), 135 (3), 123 (100), 109 (36), 91 (8), 77 (42), 69 (30), 65 (49), 59 (3).

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