SHORT PAPER

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Epoxidation of terminal olefins by oxygen catalysed by a mixture of manganese and cobalt salts of *p*–aminobenzoic acid supported on silica gel[†]

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A mixture of cobalt and manganese salts of *p* -aminobenzoic acid supported on silica gel catalyses the epoxidation of terminal olefins to the corresponding 1,2-epoxy compounds in the presence of oxygen.

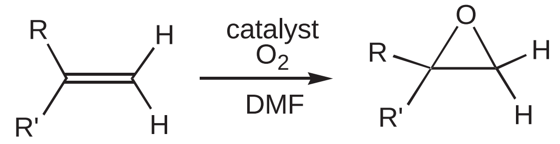
Keywords: epoxidation, olefins, manganese(II), cobalt(II), catalysis, solid support

Solid supported reagents for the organic reactions were first introduced by Merrifield[1] and Letsinger.[2] Easy access to the products via simple filtration for removing unreacted materials has rendered the method very attractive. Inorganic compounds such as silica gel have been used as solid support in many organic reactions, including catalytic oxidation of olefins.[3-5]

Epoxidation of olefins catalysed by transition metals is a subject of much investigation.[6] Many efforts have been made to develop the direct and selective epoxidation of olefins by use of molecular oxygen.[7] However this method possesses disadvantages such as: long reaction times,[8] expensive catalyst and side products,[9-11] low yields[12] and complex catalysts.[13,14] Here we report an alternative heterogeneous catalytic method for the epoxidation of terminal olefins using silica gel as solid support for synthesis of 1, 2-epoxyalkanes from linear aliphatic and aromatic olefins in presence of molecular oxygen.

The catalysts were easily prepared by the following method: silica gel was heated in a pyrolysis apparatus at 260 °C under 20 mm Hg until 5.7 % water was lost. *p*–Aminobenzoic acid was then treated with the activated silica gel. The reaction of the acid bonded to the silica gel with sodium carbonate afforded the sodium salt of the acid, which was then converted into the cobalt or manganese salts using cobalt or manganese chloride solutions.[15, 16] The catalyst is recovered quantitatively after each experiment and can be reused. The results are summarised in the Table 1.

Table 1 poxidation of aromatic and aliphatic olefins with oxygen catalysed by Co and Mn salts[a]



Entry	R	R′	Time/h	T/°C	Yield/%[b]
1	H	C_6H_5	10	Reflux	65
2	CH_3	C_6H_5	10	Reflux	69
3	H	$C_{10}H_{21}$	14	130	60
4	H	C_6H_{13}	15.5	100	51
5	H	C_5H_{11}	15	90	58

[a]All reactions were carried out in *N,N*-dimethylformamide (DMF) using 1 : 1 of Mn and Co catalyst.
[b]The yield of isolated product.

Experimental

Chemicals were purchased from Merck, Aldrich and Phillips Petroleum companies and were used after purification. IR spectra were recorded on a FT-IR Unicam Mattson 1000 Spectrophotometer. ^1H NMR spectra were recorded on Bruker DRX–500 AVANCE (500 MHz) spectrometer in $CDCl_3$ and chemical shift are indicated in δ ppm. All products are known compounds and they were identified by their IR and ^1H NMR spectroscopic properties.

Preparation of catalysts: In a pyrolysis apparatus silica gel (5g) was heated at 260 °C under reduced pressure (20 mm Hg) using phosphorus pentoxide (5g) as a desiccant. The silica gel was reduced by 0.28 g in weight after 10 h (5.7 wt %). To a mixture of ethyl acetate (70 ml) and *p*-aminobenzoic acid (2.13 g, 15 mmol) was added the activated silica gel (4.72g). The reaction mixture was then refluxed with magnetic stirring at 80 °C for 16 h and then cooled to room temperature and filtered. The solid mass was washed with ethyl acetate for 10 h (Soxhlet) in order to remove unreacted *p*-aminobenzoic acid. The solid was then dried in an oven at 100 °C to afford a pale yellow solid (6.05 g). 1.33 g (9.7 mmol) of the acid had reacted. Sodium salt of the *p*-aminobenzoic acid supported on silica gel was prepared by reaction of the supported acid (5 g) with aqueous sodium carbonate to give the sodium salt (5.25 g 11 mmol, 4.76 wt % increase). This result was verified by XRF to show a 4.47 % wt increase. A mixture of saturated cobalt(II) chloride (50 ml) and the sodium salt (5 g) of the *p*–aminobenzoic acid supported on silica gel was refluxed at 100 ° C for 2 h. The mixture was then cooled to room temperature and filtered. The solid was washed with distilled water for 10 h (Soxhlet) and then dried in an oven at 110 °C for 5h to give the cobalt salt that was verified by XRF to show a 6.10 % wt increase.

Similarly, the manganese salt of the acid was prepared using manganese chloride (II) solution to give 5.39g of a white solid (6.10 % wt increase, XRF showed 5.97 % wt increase).

Epoxidation of aromatic olefins: To a stirred solution of styrene (208 mg, 2 mmol) in solvent (DMF, 30 ml) was added the supported cobalt salt (920 mg, 1 mmol) and manganese salts (900 mg, 1 mmol). The reaction mixture was refluxed for 10 h, during which time oxygen (98 %) was bubbled at a rate of 15 ml min^{-1} into the solution. The progress of the reaction was monitored by TLC (*n*-hexane / ethyl acetate: 4.6/0.4). The reaction mixture was cooled to room temperature and then filtered to recover the solid material (Co and Mn salts). The reaction mixture was extracted with toluene(3 × 20ml) and washed with H_2O (3 × 20ml), and then the organic phase was dried over Na_2SO_4. The solvent was evaporated and the product was purified by column chromatography over silica gel, 135.2mg (65%) of styrene oxide as colourless oil was obtained.

Epoxidation of aliphatic olefins: All procedures for epoxidation of aliphatic olefins are similar to epoxidation of aromatic olefins, but the extraction and purification step are different. For 1-dodecene, after filtration to recover the solid material (Co and Mn salts), the reaction mixture was extracted with *n*-hexane 3 × 20ml) and washed with H_2O (3 × 20ml). The organic layer was dried over Na_2SO_4, and then the solvent was removed. The product was purified using vacuum distillation to give 1,2-epoxydodecane as a colourless oil.[17]

The time of reactions and yields of isolated products are shown in the Table 1.

1. *Styrene oxide*: colourless oil, (lit[18, 19]), ^1H NMR ($CDCl_3$, δ_H): 2.66 (dd, 1H, *J* = 2.6, 5.5 Hz), 3.05 (dd, 1H, *J* = 4, 5.5 Hz), 3.77

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

(dd, 1H, *J* = 2.59, 4 Hz), 7.24(m, 5H, Ph). FT-IR (neat) ν_{max}/cm^{-1}: 3030, 2923, 1600, 1473,1263, 957, 814.

2. *1, 2-Epoxy-2-phenylpropane*: colourless oil (lit[18]), ^{1}H NMR ($CDCl_3$, δ_H): 1.70 (s, 3H), 2.79 (d, 1H, *J* = 5.5 Hz), 2.95 (d, 1H, *J* = 5.5Hz), 7.24–7.50 (m, 5H, Ph). FT-IR (neat) ν_{max}/cm^{-1}: 3051, 2961, 1607, 1453, 1361, 1269, 961, 850.

3. *1, 2-Epoxydodecane*: colourless oil, (lit[18,20,21]), ^{1}H NMR ($CDCl_3$, δ_H): 0.90 (t, 3H, *J* = 6.9 Hz), 1.35–1.55 (m, 18 H), 2.47 (dd, 1H, *J* = 5.1, 2.9 Hz), 2.58 (dd, 1H, *J* = 5, 3.9 Hz), 3.3 (br, 1H). FT-IR (neat) ν_{max}/cm^{-1}: 2923, 2853, 1469, 1254, 917, 837.

4. *1, 2-Epoxyoctane*: colourless oil (lit[17, 20]), ^{1}H NMR ($CDCl_3$, δ_H): 0.88 (t, 3H, *J* = 6.9 Hz), 1.29–1.49 (m, 10H), 2.48 (dd, 1H, *J* = 2.89, 4.81 Hz), 2.57 (dd, 1H, *J* = 3.9, 4.9 Hz), 2.9 (br, 1H). FT-IR (neat) ν_{max}/cm^{-1}: 2961, 1461, 1251, 905, 830.

5. *1, 2-Epoxyheptane*: colourless oil (lit [22]), ^{1}H NMR ($CDCl_3$, δ_H): 0.9 (t, 3H, *J* = 6.8 Hz), 1.3–1.40 (m, 8H), 2.52 (dd, 1H, *J* = 2.9, 4.9 Hz), 2.58 (dd, 1H, *J* = 4, 4.9 Hz), 2.94 (br, 1H). FT-IR (neat) ν_{max}/cm^{-1}: 2923, 1451, 1376,1251, 914, 829.

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