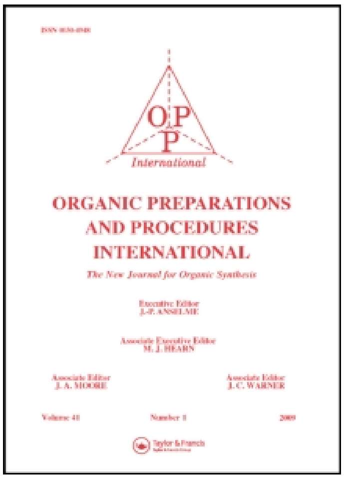

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DIATOMITE-SUPPORTED PERACETIC ACID OXIDATION OF 1,4-DIHYDROPYRIDINES

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DIATOMITE-SUPPORTED PERACETIC ACID OXIDATION OF 1,4-DIHYDROPYRIDINES

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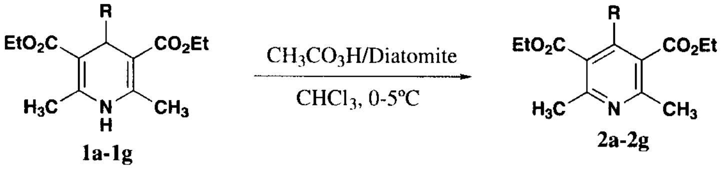
Aspects of the oxidation of 1,4-dihydropyridines (1,4-DHP) continue to be the focus point of research activity as evidenced by the appearance of a large number of publications.[1-17] We investigated diatomite-supported peracetic acid as a new oxidation reagent for 1,4-dihydropyridines (1,4-DHP).



a) R = H b) R = CH_3 c) R = n-C_3H_7 d) R = C_6H_5 e) R = p-$CH_3OC_6H_4$
f) R = p-ClC_6H_4 g) R = m-$NO_2C_6H_4$

The reaction was carried out by stirring a mixture of 1,4-DHP and diatomite-supported peracetic acid in chloroform at 0-5°C for 5-40 min and the corresponding pyridine derivatives were obtained after simple filtration and further purification by chromatography. The results and reaction conditions are summarized in *Table 1*. The products were characterized by mp., IR and ^{1}H-NMR.

To check the efficiency of the reagent, the following experiments were performed. When the oxidation of 1,4-DHP was carried out by using peracetic acid without diatomite solid-support, the yield was low with a number of side-products, which is in accordance with the previous observation that reagents and catalysts on solid supports often have modified activity as improved product selectivity.[18,19] Further studies showed that using diatomite solid-support was better than using silica gel. The effect of different solvents on the oxidation reaction was also studied. When the solvent was ethyl acetate or acetic acid, the reaction times were longer and the yields of the products were lower as compared with chloroform.

In conclusion, a novel and simple oxidation reagent for the conversion of 1,4-DHP to the corresponding pyridines has been presented. The ready availability of the reagent, its ease of manipulation and the mild reaction conditions recommend the diatomite-supported peracetic acid as a useful reagent.

Table 1. Oxidation of 1,4-Dihydropyridines by Diatomite-supported Peracetic Acid[a]

Cmpd	Yield (%)	mp. (°C)	*lit*.mp. (°C)	Temp. (°C)	Time (min)	^{1}H NMR (δ)
2a	85	72-73	72[17]	RT	40	8.67 (s, 1H), 4.34-4.41 (q, 4H, J = 7.07 Hz), 2.84 (s, 6H), 1.38-1.43 (t, 6H, J = 7.08).
2b	62	oil	oil[16]	RT	30	4.34-4.41 (q, 4H, J = 7.09 Hz), 2.49 (s, 6H), 2.24 (s, 3H), 1.34-1.38 (t, 6H, J = 7.11).
2c	49	oil	oil	0-5	35	4.33-4.40 (q, 4H, J = 7.07 Hz), 2.48-2.53 (m, 2H), 2.46 (s, 6H), 1.47-1.59 (m, 2H), 1.32-1.37 (t, 6H, J = 7.08 Hz), 0.86-0.91 (t, 3H, J = 7.35 Hz).
2d	75	63-64	62-64[16]	0-5	5	7.36-7.37 (br s, 3H), 7.25-7.27 (br s, 2H), 3.97-4.04 (q, 4H, J = 7.10 Hz), 2.62 (s, 6H), 0.88-0.93 (t, 6H, J = 7.10 Hz).
2e	80	49-50	51-53[17]	0-5	10	7.17-7.19 (b, 2H, J = 8.11 Hz), 6.87-6.90 (b, 2H, J = 8.12 Hz), 4.00-4.08 (q, 4H, J = 7.05 Hz), 3.81 (s, 3H), 2.58 (s, 6H), 0.95-1.00 (t, 6H, J = 7.06 Hz).
2f	88	72-74	68[17]	0-5	15	7.35-7.38 (b, 2H, J = 7.71 Hz), 7.20-7.22 (b, 2H, J = 7.72 Hz), 4.02-4.08 (q, 4H, J = 6.55 Hz), 2.61 (s, 6H), 0.96-1.01 (t, 6H, J = 6.78 Hz).
2g	53	50-51	63[17]	0-5	5	8.24-8.27 (m, 1H), 8.18 (m, 1H), 7.55-7.60 (m, 2H), 4.01-4.08 (q, 4H, J = 6.95 Hz), 2.62 (s, 6H), 0.96-1.01 (t, 6H, J = 6.95 Hz).

a) All reactions were carried out in chloroform using a molar ratio of 1:1.1 for DHP:PAA; Diatomite:DHP (0.75 g:1 mmol).

EXPERIMENTAL SECTION

All mps were determined on a Sanyo Gallenkamp MPD350 Melting Point apparatus and are uncorrected. IR spectra were determined on a IR-408 Infrared Spectrometer and ^{1}H-NMR spectra were recorded at 300 MHz on a R-24B Hitachi NMR Spectrometer in $CDCl_3$ using TMS as an internal standard. Diatomite may be obtained from Aldrich Chemical Co. and 1,4-dihydropyridines were prepared according to described procedures.[16]

General Procedure for the Oxidation of Hantzsch 1,4-DHP.- The reaction must be carried out in an efficient fume hood. In a 50 mL round-bottomed flask, 0.465 g (1.1 mmol) of 18.0%

peracetic acid was added dropwise to 0.75 g of diatomite and the mixture was left to stand for appropriate time (10-15 min) at room temperature. Then the resulting solid diatomite-supported PAA was added in portions over 5 min to a stirred solution of 1,4-dihydropyridine **1d** (0.329 g, 1 mmol) in chloroform (20 mL) at 0-5°C. After completion of the reaction monitored by TLC, the reaction mixture was filtered and the residue was washed with chloroform (2 x 10 mL). The combined filtrates were washed with saturated aq. $NaHSO_3$ to eliminate residual peracetic acid and then with saturated aq. Na_2CO_3, followed by drying over anhydrous Na_2SO_4. The crude product obtained on removal of the solvent at reduced pressure was then purified by column chromatography over silica gel (eluent: ethyl acetate:petroleum ether 1:3) to give the oxidized product **2d** as a colorless solid (0.245 g, 75%).

The oxidations of the other 1,4-dihydropyridines were carried out using a similar procedure.

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OXIDATION OF TOLUENES TO AROMATIC ALDEHYDES WITH MOLECULAR OXYGEN IN SUBCRITICAL WATER

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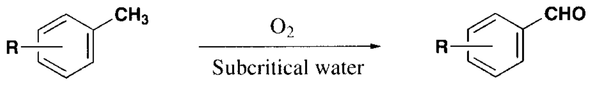
Oxidations are important transformations in organic synthesis.[1] In general, many oxidations are carried out with a large excess of chromium or manganese reagents. The metal residues are environmentally undesirable and often cause problems during work-up.[2] In addition organic oxidations in the chemical industry have traditionally been performed in either aromatic or halogenated solvents.[3] One of the most attractive oxidants is molecular oxygen,[4] since oxygen is highly soluble in subcritical water. Molecular oxygen has been used as the reagent for the oxidation of alkyl aromatic compounds in the presence of different catalysts, such as $MnBr_2$, $CoBr_2$,



R: –CN, –F, Cl, –Br, $-CH_3$, CH_3O