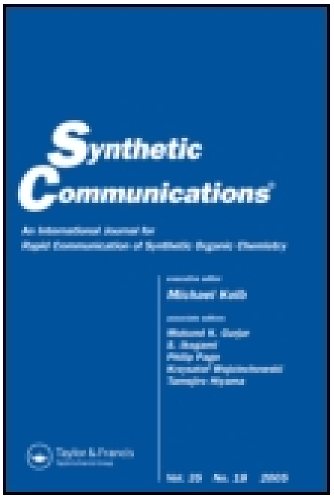

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Oxidation of Aldehydes and Ketones into Carboxylic Acids and Esters Using 4-Amino-2-Chloroperbenzoic Acid Supported on Silica Gel

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Abstract: 4-Amino-2-chloroperbenzoic acid supported on silica gel was found to be a versatile and efficient oxidant for the oxidation of aldehydes and ketones to the corresponding carboxylic acids and esters.

Keywords: Oxidation, 4-amino-2-chloroperbenzoic acid, aldehydes, ketones

Traditionally, solids, especially chromatographic adsorbents, have been used in reactions to provide a surface on which a reagent spread out. Empirically,

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such procedures were often found to provide high yields under mild conditions. The ease of setup and workup was often matched only by the cleanliness of the reactions.[1,2] However, little thought appeared to go into the choice of the solid, except to make sure that it offered ample active surface.

Progress in surface science,[3] the improved understanding of heterogenous catalysis, and the availability of numerous new solids provide opportunities for better design of catalysts as well as supported reagents, which can lead to enhanced performance in these processes. Microporous solids such as silica gel offer a wide range of active sites for supporting reagents and most can often be regenerated if deactivated during a reaction. Silica gel as an inorganic support has been used in various chemical reactions.[1–6] However, there are few examples of chemical reactions for supporting organic molecules on silica gel as oxidizing agents.

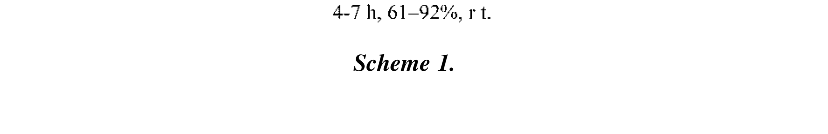
The oxidation of aldehydes to corresponding carboxylic acid and Baeyer–Villiger oxidation of ketones has been widely investigated and numerous procedures are known.[7]

In course of our systematic study on the development of supported reagents and catalysts for the oxidation of organic compounds,[8–18] we herein report a novel heterogeneous oxidant based on 4-amino-2-chloroperbenzoic acid supported on silica gel through Si-N bonding as an efficient and convenient oxidant for the oxidation of aldehydes and ketones to the corresponding carboxylic acids and esters in good yields (Scheme 1). Silica-gel-supported 4-amino-2-chloroperbenzoic acid can be prepared in the reaction of 4-amino-2-chlorobenzoic acid with activated silica gel (by Si-N bond formation), which is then oxidized to 4-amino-2-chloroperbenzoic acid using hydrogen peroxide as an oxidant.

The oxidation of aldehydes and ketones is performed in dichloromethane as solvent and workup is a simple extraction and separation of the heterogeneous supported oxidant by filtration. Removal of the solvent, followed by purification of products by column chromatography, gives carboxylic acids and esters in good yields. Representative reaction times and yields are given in Table 1.

Table 2 shows reusability of this heterogeneous supported-oxidant system after we replicated oxidation of benzaldehyde to benzoic acid three times. In each experiment, the supported 4-amino-2-chlorobenzoic acid was recovered quantitatively.

In summary, mild reaction conditions, good yields, ease of workup, and reusability of supported reagent are the most significant benefits of this method.



Scheme 1.

Table 1. Oxidation of aldehydes and ketones with silica-gel-supported 4-amino-2-chloroperbenzoic acid

Substrate	Time (h)	Product[a]	Yield (%)[b]	Mp or Bp °C Found	Mp or Bp °C Reported[19]
C_6H_5CHO	4	$C_6H_5CO_2H$	90	121	122.4
$2\text{-}(NO_2)C_6H_4CHO$	6	$2\text{-}(NO_2)C_6H_4CO_2H$	72	145	146
$4\text{-}(NO_2)C_6H_4CHO$	6	$4\text{-}(NO_2)C_6H_4CO_2H$	75	239	241
$4\text{-}(CH_3O)C_6H_4CHO$	4	$4\text{-}(CH_3O)C_6H_4CO_2H$	92	183	184–186
$C_6H_5CH_2CHO$	4	$C_6H_5CH_2CO_2H$	78	75	76
C_2H_5CHO	4.5	$C_2H_5CO_2H$	78	140	141
$C_2H_5CH_2CHO$	4.5	$C_2H_5CH_2CO_2H$	77	161	162.5
$CH_3COC_6H_5$	5	$CH_3CO_2C_6H_5$	70	194.5	196.7
$C_6H_5COC_6H_5$	5	$C_6H_5CO_2C_6H_5$	82	70	69
$CH_3COC_2H_5$	7	$CH_3CO_2C_2H_5$	61	76	77

[a]All compounds were fully characterized by their mp or bp, and IR and ^{1}H-NMR spectra.

[b]Yields refer to pure isolated products.

EXPERIMENTAL

Activation of Silica Gel

Chromatographic-grade silica gel (10 g, 70–230 mesh) was heated in an electric furnace at 680°C for 3 h. Then, it was cooled to room temperature to obtain 9.3 g of activated silica gel.

Support of 4-Amino-2-Chlorobenzoic Acid on Activated Silica Gel

To a stirring solution of 4-amino-2-chloro benzoic acid (3.43 g, 20 mmol) in 100 mL of ethyl acetate, activated silica gel (9.3 g) was added, and the

Table 2. Reusability of silica-gel-supported 4-amino-2-chloroperbenzoic acid[a]

Entry	Substrate	Product	Yield (%)
1	C_6H_5CHO	$C_6H_5CO_2H$	90
2	C_6H_5CHO	$C_6H_5CO_2H$	85
3	C_6H_5CHO	$C_6H_5CO_2H$	83

[a]All reactions were carried out under the typical procedure.

mixture was refluxed with stirring for 20 h. Then, the mixture was cooled to room temperature and filtered. The solid material was continously extracted with ethyl acetate in a Soxhlet apparatus for 14 h to extract the probable unreacted 4-amino-2-chlorobenzoic acid. Then, it was filtered and dried in an oven at 80°C for 5 h to yield 11.34 g silica-gel-supported 4-amino-2-chlorobenzoic acid. 4-Amino-2-chlorobenzoic acid (2.04 g, 11.2 mmol) was supported on 9.30 g of activated silica gel.

Oxidation of Silica-Gel-Supported 4-Amino-2-Chlorobenzoic Acid to the Corresponding Peracid

Silica-gel-supported 4-amino-2-chloro benzoic acid (8.33 g) that contained 1.50 g of 4-amino-2-chlorobenzoic acid was added to a stirring solution of commercial 30% hydrogen peroxide at room temperature and the reaction mixture was stirred for 9 h. Then, it was filtered through a sintered-glass funnel. The residue was washed with 5 × 20 mL of distilled water and the solid material was dried at room temperature in vacuum (40 torr) to obtain 8.46 g of silica-gel-supported 4-amino-2-chloroperbenzoic acid. In the IR spectrum of this supported reagent, signals at 890 cm^{-1} and 1560 cm^{-1} correspond to Si-N stretching bond energy.

Oxidation of Benzaldehyde to Benzoic Acid, Typical Procedure

Benzaldehyde (0.53 g, 5.0 mmol) was disolved in 60 mL of dichloromethane and one drop of hydrochloric acid (0.1 N) was added to this solution. Then, silica-gel-supported 4-amino-2-chloroperbenzoic acid (6.20 g containing 6.3 mmol of 4-amino-2-chloroperbenzoic acid) was added, and the mixture was stirred at room temperature for 4 h. The progress of the reaction was monitored by TLC. Then, the reaction mixture was filtered and the residue was washed with 2 × 10 mL of dichloromethane. The filtrate was evaporated to give the crude solid product, which was purified by column chromatography on silica gel (methanol-dichloromethane, 4:1, v/v) to obtain 0.55 g (4.5 mmol, 90% yield) of pure benzoic acid.

Reusability of Silica-Gel-Supported 4-Amino-2-Chloroperbenzoic Acid

After using silica-gel-supported 4-amino-2-chloroperbenzoic acid as an oxidant for the oxidation of aldehydes and ketones, it can be reconverted to corresponding peracid derivative by treatment with hydrogen peroxide. In a typical procedure, silica-gel-supported 4-amino-2-chloroperbenzoic acid was reoxidized after the first use for the oxidation of benzaldehyde to benzoic acid with hydrogen peroxide according to the mentioned procedure and was used again for the oxidation of benzaldehyde to benzoic acid. The second and third use of this procedure for the oxidation of benzaldehyde to benzoic acid showed little decrease in the reaction yields, (see Table 2).

The silica-gel-supported 4-amino-2-chlorobenzoic acid was retrieved quantitatively after each experiment.

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