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Oxidation of Benzylic Methylene Compounds to Ketones with 4-Aminoperoxybenzoic Acid Supported on Silica Gel in Presence of Oxygen or Air

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Summary. 4-Aminoperoxybenzoic acid supported on silica gel in presence of oxygen or air was found to be a convenient and selective oxidant for the oxidation of benzylic methylene compounds to the corresponding ketones.

Keywords. Oxidation; Benzylic methylene; 4-Aminoperoxybenzoic acid; Silica gel.

Introduction

Solid phase synthesis for preparation of various organic compounds has provided an attractive option for organic synthesis [1, 2]. Solids such as silica gel offer a wide range of actives reactions. However there are few examples of supported organic molecules on silica gel as oxidizing agents [3–6]. Peroxyacids are used for oxidation of organic compounds occasionally [7–11]. A supported peroxyacid is described in the present report.

Results and Discussions

During the course of our systematic study on the development of supported reagents and catalysts for the oxidation of organic compounds [12–22] we report a novel heterogeneous oxidant based on 4-aminoperoxybenzoic acid supported on silica

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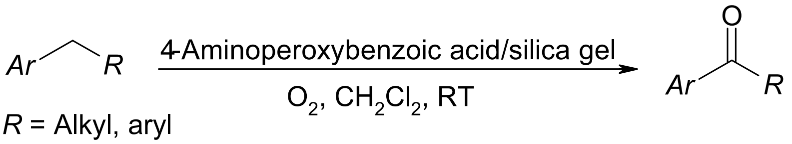

Scheme 1

gel in presence of oxygen or air as a convenient and selective oxidant for the oxidation of benzylic methylene compounds to the corresponding ketones in good yields (Scheme 1). Other methylene groups cannot be oxidized under these conditions.

4-Aminoperoxybenzoic acid is easily prepared by the reaction of 4-aminobenzoic acid with activated silica gel. This is then oxidized to the supported 4-aminoperoxybenzoic acid using hydrogen peroxide. The oxidation of benzylic methylene compounds is performed in dichloromethane as the solvent in presence of oxygen or air. Work up is accomplished simply by extraction and separation of the supported oxidant by filtration. In this method benzylic alcohols were not detected and the ketones are formed in high yields. The reactions cannot be carried out with the unsupported reagent. The results are summarized in Table 1.

The supported reagent is recovered in each experiment and can be reused. Table 2 demonstrates the reusability of this supported reagent after three times

Table 1. Oxidation of benzylic methylene compounds with 4-aminoperoxybenzoic acid supported on silica gel in presence of oxygen or air

Entry	Substrate	Product	Oxygen		Air	
			Time/h	Yield/%[a]	Time/h	Yield/%[a]
1	$C_6H_5CH_2C_6H_5$	$C_6H_5COC_6H_5$	9	98	16	95
2	$C_6H_5CH_2CH_2C_6H_5$	$C_6H_5COCOC_6H_5$	9	98	16	94
3	$C_6H_5CH_2CH_3$	$C_6H_5COCH_3$	12	93	18	88
4	$2\text{-}ClC_6H_4CH_2CH_3$	$2\text{-}ClC_6H_4COCH_3$	12	76	20	76
5	$4\text{-}ClC_6H_4CH_2CH_3$	$4\text{-}ClC_6H_4COCH_3$	12	80	20	77
6	$2\text{-}BrC_6H_4CH_2CH_3$	$2\text{-}BrC_6H_4COCH_3$	12	73	20	72
7	$4\text{-}BrC_6H_4CH_2CH_3$	$4\text{-}BrC_6H_4COCH_3$	12	74	20	71

[a] Isolated yields

Table 2. Reusability of 4-aminoperoxybenzoic acid supported on silica gel for oxidation of diphenylmethane to benzophenone

Experiment	Yield/%	
	Oxygen	Air
1st	98	95
2nd	89	87
3rd	87	87

of oxidation of diphenylmethane to benzophenone. In each experiment the supported 4-aminobenzoic acid was recovered quantitatively.

In summary, mild reaction conditions, selectivity, good yields, ease of work up, and reusability of the supported reagent are the most significant aspects of this method.

Experimental

Chemicals were purchased form Merck, Aldrich, and Riedel de Haen AG and were used without further purification. IR and NMR spectra were recorded on FT-IR Unicam Mattson 1000 and Bruker AC-80 (80 MHz). All products are known compounds and they were characterized by comparison of their physical and spectral data with those of authentic samples. All yields refer to pure isolated products.

Activation of Silica Gel

Chromatographic grade silica gel (30 g, 70–230 mesh) was heated in an electric furnace at 700°C for 3 h. Then it was cooled to room temperature to obtain 27.9 g of activated silica gel.

Supporting of 4-Aminobenzoic Acid on Activated Silica Gel

To a stirred solution of 6.9 g of 4-aminobenzoic acid (50 mmol) in 200 cm^3 of ethylacetate 27.9 g of activated silica gel were added and the mixture was refluxed under magnetic stirring for 16 h. Then it was cooled to room temperature, filtered, and the solid matter was continuously extracted with ethylacetate in a *Soxhlet* apparatus for 18 h. Then it was dried at 80°C for 3 h to yield 33.7 g of silica gel supported 4-aminobenzoic acid. 4-Aminobenzoic acid (5.8 g, 42 mmol) was supported on 27.9 g of activated silica gel.

Oxidation of Silica Gel Supported 4-Aminobenzoic Acid to the Corresponding Peroxyacid

Silica gel supported 4-aminobenzoic acid (33.7 g) containing 5.8 g of 4-aminobenzoic acid was added to a stirred solution of a commercial 30% solution of H_2O_2 at room temperature and the reaction mixture was stirred for 8 h. Then it was filtered, washed with distilled H_2O ($5\times20\,cm^3$), and dried over anhydrous $CaCl_2$ at room temperature in vacuum (40 torr) to obtain 34.3 g of silica gel supported 4-aminoperoxybenzoic acid.

Typical Procedure for the Oxidation of Diphenylmethane to Benzophenone

Diphenylmethane (3.4 g, 20 mmol) was dissolved in 100 cm^3 of CH_2Cl_2, then 33 g of silica gel supported 4-aminoperoxybenzoic acid (containing 40 mmol of 4-aminoperoxybenzoic acid) were added and the mixture was stirred at room temperature for 9 h during which time oxygen was bubbled at a rate of $10\,cm^3\,min^{-1}$ into the solution. Progress of the reaction was monitored by TLC (petroleum ether:ethylacetate = 4:1). Then the reaction mixture was filtered to recover the solid material. The solid material was washed with $2\times10\,cm^3$ of CH_2Cl_2. The solvent was evaporated and the product purified by column chromatography using silica gel. The pure benzophenone was obtained in 98% yield (3.6 g).

Similar conditions were examined for the use of air instead of molecular oxygen. The reaction was run for 16 h to give benzophenone in 95% yield (3.5 g).

Reusability of Silica Gel Supported 4-Aminoperoxybenzoic Acid

After using silica gel supported 4-aminoperoxybenzoic acid as oxidant for the oxidation of benzylic methylene compounds it can be reconverted to the corresponding peroxyacid by treatment with hydrogen peroxide. Then it was used for the oxidation of diphenylmethane to benzophenone. The second use of this reagent for the oxidation of diphenylmethane to benzophenone showed about 10% decrease in reactivity. However, the third use showed no further decrease in the reaction yields (*cf.* Table 2).

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