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Selective Oxidation of Aryl Ketones to α-Diketones with 4-Aminoperoxybenzoic Acid Supported on Silica Gel in Presence of Air

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Summary. 4-Aminoperoxybenzoic acid supported on silica gel in presence of air was found to be a selective and convenient oxidant for the oxidation of methylene groups in aryl ketones to convert them to α-diketones.

Keywords. Aryl ketones; 4-Aminoperoxybenzoic acid; Oxidation; Silica gel; α-Diketones.

Introduction

Oxidation of a methylene group α to a carbonyl can be carried out with SeO_2, N_2O_3, and other oxidizing agents [1–3]. There have been few reports concerning the conversion of unactivated α-methylene ketones to corresponding α-diketones. The representative examples include the selenium dioxide oxidation of ketones [4, 5], the reaction of α-bromo ketones with dimethyl sulfoxide (*DMSO*) in presence of sodium carbonate [6], reaction of pyridine *N*-oxide with α-nosyloxy ketone intermediates [7], and oxidation of enamino ketone intermediates with singlet oxygen [3]. Although some of these reactions are carried out under mild and neutral conditions [3, 7], some of them have the drawback of using either strong acidic or basic reaction conditions [4–6] and they suffer from inherent vigorous reaction conditions and tedious purification steps [4, 5]. Therefore, development of a more convenient method for oxidation of α-methylene ketones to α-diketones to permit better yields under mild, neutral reaction conditions and easier work up is required.

The use of mineral support attracted much attention because of improved selectivity and reactivity associated ease of manipulation [8–13]. Peroxyacids are used

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for oxidation of organic compounds [14–19]. We have previously presented a convenient and selective method for the oxidation of benzylic methylene compounds to corresponding ketones by 4-aminoperoxybenzoic acid supported on silica gel in presence of oxygen or air [20]. Herein, we wish to report that α-methylene aryl ketones can also be oxidized to α-diketones with this supported reagent in presence of air in high yields.

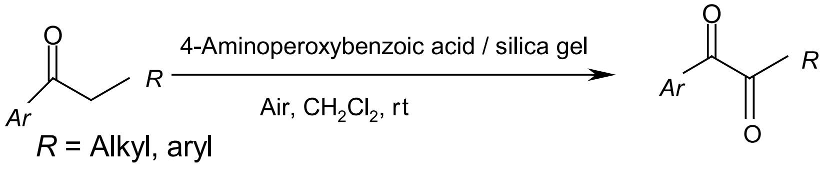
Results and Discussions

Our approach to a clean and efficient preparation of α-diketones is to make use of 4-aminoperoxybenzoic acid supported on silica gel in presence of air. 4-Aminoperoxybenzoic acid easily prepared by the reaction of 4-aminobenzoic acid with activated silica gel which then was oxidized to 4-aminoperoxybenzoic acid using hydrogen peroxide as an oxidant. When the supported reagent was mixed with a solution of p-$CH_3OC_6H_4COCH_2CH_3$ in CH_2Cl_2 and the mixture was stirred at room temperature in presence of air, the reaction was completed in 11 h in 96% yield. The work up procedure involves mere filtration, evaporation of the solvent, and passing the residue through a small pad of silica gel using a suitable solvent. It is noteworthy to mention that the reaction remained incomplete in absence of air (in presence of nitrogen), even with a higher ratio of reagent (1:3) or longer reaction time (16 h).

To assess the generality of the method, a variety of α-methylene ketones were treated likewise to afford the corresponding α-diketones in high yield (Scheme 1, Table 1). As shown in Table 1, various types of α-methylene aryl ketones were oxidized efficiently to their corresponding α-diketones in 88–97% yields without any side products (entries 1–6). It is noteworthy to mention that benzylacetone was converted to benzoylacetone (entry 7), clearly showing that oxidation of a benzylic methylene is easier than that of a methylene α to a carbonyl group. Other α-methylene ketones remained intact under these reaction conditions (entries 11–12), furthermore partial oxidation of cyclic ketones (entries 8–10) to corresponding lactones was observed.

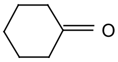
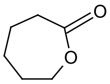
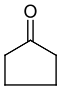
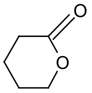
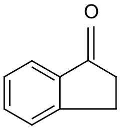
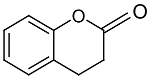
In order to show chemoselectivity of this method for the oxidation of different α-methylene ketones, we have performed a number of competitive reactions and their results are summarized in Table 2. These results clearly show that the presented procedure is potentially applicable for the chemoselective oxidation of aryl ketones versus other ketones.

The supported reagent is recovered in each experiment and can be reused. Table 3 demonstrates the reusability of this supported reagent after three times of oxidation of p-$CH_3OC_6H_4COCH_2CH_3$ to the corresponding α-diketone. In each experiment the supported 4-aminobenzoic acid was recovered quantitatively.



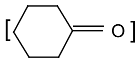
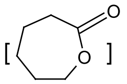
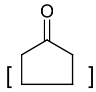
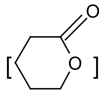
Scheme 1

Table 1. Oxidation of α-methylene ketones with 4-aminoperoxybenzoic acid supported on silica gel in presence of air

Entry	Substrate	Time/h	Product	Yield/%[a]
1	$C_6H_5COCH_2C_6H_5$	10	$C_6H_5COCOC_6H_5$	97
2	$C_6H_5CO(CH_2)_2CH_3$	11	$C_6H_5COCOCH_2CH_3$	91
3	$C_6H_5CO(CH_2)_3CH_3$	11	$C_6H_5COCO(CH_2)_2CH_3$	94
4	*p-Me*$OC_6H_4COCH_2CH_3$	11	*p-Me*$OC_6H_4COCOCH_3$	96
5	*p-Me*$C_6H_4COCH_2CH_3$	11	*p-Me*$C_6H_4COCOCH_3$	88
6	*p*-$ClC_6H_4COCH_2CH_3$	12	*p*-$ClC_6H_4COCOCH_3$	92
7	$C_6H_5(CH_2)_2COCH_3$	12	$C_6H_5COCH_2COCH_3$	90
8		15		22
9		15		31
10		14		50
11	$CH_3(CH_2)_2CO(CH_2)_2CH_3$	15	$CH_3(CH_2)_2(CO)_2CH_2CH_3$	–
12	$CH_3CH_2COCH_2CH_3$	15	$CH_3(CO)_2CH_2CH_3$	–

[a] Isolated yields

Table 2. Selective oxidation of α-methylene ketones with 4-aminoperoxybenzoic acid supported on silica gel in presence of air

Entry	Substrate	Product	Yield/%[a]
1	$C_6H_5COCH_2C_6H_5$	$C_6H_5COCOC_6H_5$	100
	$[CH_3(CH_2)_2CO(CH_2)_2CH_3]$	$[CH_3(CH_2)_2(CO)_2CH_2CH_3]$	[0]
2	*p-Me*$OC_6H_4COCH_2CH_3$	*p-Me*$OC_6H_4COCOCH_3$	100
	$[CH_3(CH_2)_2CO(CH_2)_2CH_3]$	$[CH_3(CH_2)_2(CO)_2CH_2CH_3]$	[0]
3	$C_6H_5COCH_2C_6H_5$	$C_6H_5COCOC_6H_5$	85
			[15]
4	*p-Me*$OC_6H_4COCH_2CH_3$	*p-Me*$OC_6H_4COCOCH_3$	70
			[20]

[a] GC yield

In summary, the present method for oxidation of α-methylene ketones has all these advantages of using supported 4-aminoperoxybenzoic acid as a nontoxic material, mild reaction conditions, high selectivity of the method, an easy work up procedure, high yields, and reusability of the supported reagent.

Table 3. Reusability of 4-aminoperoxybenzoic acid supported on silica gel for oxidation of *p*-$CH_3OC_6H_4COCH_2CH_3$ to the corresponding α-diketone

Experiment	Yield/%
1st	96
2nd	88
3rd	87

Experimental

Chemical 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 identified 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 water ($5\times20\,cm^3$), 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.

General Procedure for the Oxidation of α-Methylene Ketones to the Corresponding α-Diketones

α-Methylen ketones (20 mmol) were 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 the indicated time during which air was bubbled into the solution at a rate of 50 $cm^3\,min^{-1}$. Progress of the reaction was monitored by TLC (petroleum ether:ethylacetate = 3:1). 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 products were obtained in yields indicated in Table 1.

Reusability of Silica Gel Supported 4-Aminoperoxybenzoic Acid

After using silica gel supported 4-aminoperoxybenzoic acid as oxidant for the oxidation of α-methylene ketones, it can be reconverted to the corresponding peroxyacid by treatment with hydrogen peroxide. Then it was reused for the oxidation of p-$CH_3OC_6H_4COCH_2CH_3$ to the corresponding α-diketone. The second use of this reagent for the oxidation of p-$CH_3OC_6H_4COCH_2CH_3$ to the corresponding α-diketone showed about 8% decrease in reactivity. However, the third use showed no further decrease in the reaction yields (*cf.* Table 3).

Acknowledgement

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