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Transformation of *β*-Nitrostyrenes to Carboxylic Acids Using Amberlyst A-26 Supported Hydroperoxide

Moslem M. Lakouraj[1,*], **Barahman Movassagh**[2,*], and **Kyumars Bahrami**[2]

[1] Institute of Chemistry, Mazandaran University, 47415 Babolsar, Iran
[2] Department of Chemistry, Razi University, 67149 Kermanshah, Iran

Summary. Nitrostyrenes are conveniently converted to the corresponding carboxylic acids in high yields at room temperature with Amberlyst A-26 supported hydroperoxide which is prepared *in situ* from 35% hydrogen peroxide and amberlyst A-26 (OH^-).

Keywords. Nitrostyrenes; Amberlyst A-26; Carboxylic acids; Hydroperoxide.

Introduction

Oxidative cleavage of carbon–carbon double bonds resulting in the formation of carboxylic acids is of importance in organic chemistry [1]. It is usually accomplished with potassium permanganate or tetraalkylammonium permanganate [2], potassium dichromate in sulfuric acid [3], chromium trioxide in sulfuric acid or acetic acid [4], sodium hypochlorite [5], ruthenium tetroxide/sodium periodate [6], and ozonolysis [7]. Over the past two decades, nitroalkenes have been found to be important intermediates both in industry and in organic chemistry [8]. However, to the best of our knowledge, neither homogeneous nor heterogeneous oxidations of nitroalkenes have been reported.

More recently, we have described an efficient method for the selective conversion of nitriles to amides and convenient epoxidation of α,β-unsaturated ketones using Amberlyst A-26 supported hydroperoxide [9]. In connection with our research in this area we have investigated the synthetic potential of this polymeric oxidizing agent for the epoxidation of nitrostyrenes.

Results and Discussion

Surprisingly enough, upon reaction of nitrostyrenes with Amberlyst A-26, carbon–carbon double bond scission was exclusively observed instead of epoxidation (Scheme 1).

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[*] Corresponding authors. E-mail: mlakouraj@yahoo.com

$$\text{Ar}-\text{CH}=\text{CH}-\text{NO}_2 \xrightarrow[\text{dioxane/room temperature}]{Q^{+}\text{OOH}^{-}} \text{Ar-CO}_2\text{H}$$

$Q^{+}OOH^{-}$ = Amberlyst A-26 supported hydroperoxide

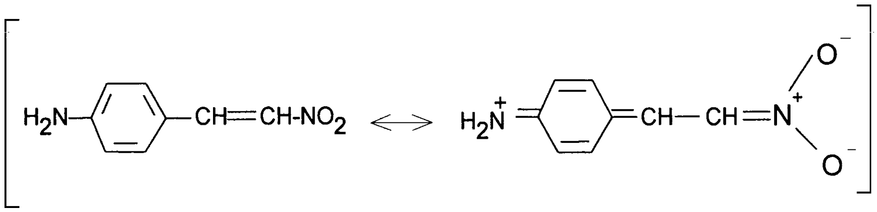
Scheme 1

Table 1. Conversion of β-nitrostyrenes to carboxylic acids with $Q^{+}OOH^{-}$[a]

Entry	Ar	t/h	Yield/%[b,c]
1	C_6H_5	10	92
2	4-MeC_6H_4	12	91
3	4-ClC_6H_4	9.5	94
4	4-BrC_6H_4	10	93
5	3-BrC_6H_4	9	95
6	4-PhC_6H_4	8	86
7	4-$NO_2C_6H_4$	7	89
8	3-$NO_2C_6H_4$	7.5	84
9	2-$NO_2C_6H_4$	8	82
10	$H_2NC_6H_4$	18	0
11	$(Me)_2N-C_6H_4$	18	0
12	2-Naphthyl	10	89
13	4-$MeOC_6H_4$	14	82
14	3,4-$(MeO)_2C_6H_3$	15	78
15	3-$MeOC_6H_4$	12	83

[a] Reactions were conducted in dioxane using a ratio of substrate:H_2O_2:A-26 (OH^{-}) = 1:4:0.1; [b] yields refer to isolated products; [c] all products were characterized by IR, ^{1}H NMR, and comparison with authentic samples

A number of examples illustrating this new and convenient procedure for the oxidation of nitrostyrenes to the corresponding carboxylic acids are summarized in Table 1. Reactions were performed in 1,4-dioxane by stirring the nitrostyrenes and commercial 35% hydrogen peroxide in the presence of catalytic amounts of Amberlyst A-26 (OH^{-}-form) at room temperature. The work-up is exceedingly simple and involves merely filtration; the yields are high to excellent. However, nitrostyrenes containing strong electron donating groups at the aromatic ring system (Table 1, entries 10 and 11) failed to give any acid, even when the reaction mixtures were stirred for 18 h. As an explanation of this result we propose that the charged resonance form in Eq. (1) strongly decreases the reactivity of the carbon–carbon double bond toward hydroperoxide ion attack.



(1)

In the case of 1-nitro-2-(β-naphthyl) ethylene (Table 1, entry 12), 2-naphthaldehyde is obtained exclusively. It is worth mentioning that the carbon–carbon double bond in styrene, α-methylstyrene, stilbene, methyl methacrylate, and acrylamide remains intact under the conditions applied. Therefore, the presence of a nitro substituent at the carbon–carbon double bond seems essential for the transformation described.

In summary, this method can be used for effective carbon–carbon double bond cleavage of nitrostyrenes to carboxylic acids under mild conditions. In addition, the insolubility of the reagent in the reaction media and simple work-up are advantages of this procedure.

Experimental

IR spectra were obtained using a Shimadzu 470 instrument. ^{1}H NMR spectra were recorded on a JEOL JNM-PMX 60 MHz NMR spectrometer employing *TMS* as internal standard. Nitrostyrenes were prepared by a standard method [10]. Amberlyst A-26 (OH^--form) was purchased from Merck or prepared by exchange reaction of the chloride form of the resin with 1.0 N aqueous NaOH. All products were characterized by comparison of their spectroscopic and physical data with those of known samples.

General procedure

To a suspension of 4.85 mmol nitrostyrene in 5 cm^3 1,4-dioxane and 0.48 mmol amberlyst A-26 (wet, OH^--form), 19.4 mmol H_2O_2 (35% w/v solution) were added. After a few minutes, the reaction mixture was stirred magnetically at room temperature for 7–15 h. The progress of the reaction was monitored by TLC (eluent:n-hexane:acetone = 2:1). After completion of the reaction the mixture was filtered. The solid material was washed with 1,4-dioxane (2×5 cm^3). Removal of the solvent under reduced pressure produced the corresponding acid in good yield and almost pure form.

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