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N, N, N´, N´-Tetraacetylethylenediamin And Sodium Percarbonate Reagents As An *In Situ* Produsing Of Peracetic Acid For Baeyer-Villiger Oxidation Of Ketones

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ABSTRACT

In-situ production of per acetic acid using N, N, N´, N´-tetraacetylethylene diamin and sodium percarbonate for Baeyer-Villiger oxidation of cyclic and acyclic ketones to lactones and esters in ethylacetate at reflux condition is experienced in low reaction time and high yields.

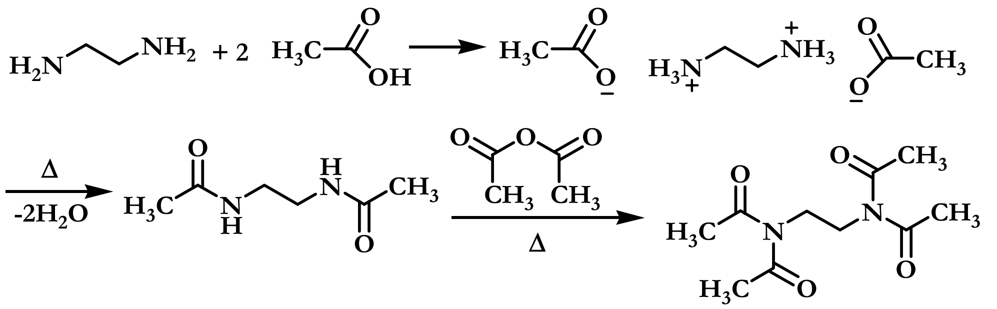
KEYWORDS

Baeyer-Villiger;
Peracetic acid;
N,N,N´,N´-tetraacetyl ethylenediamin(TAED);
sodium percarbonate(SPC).

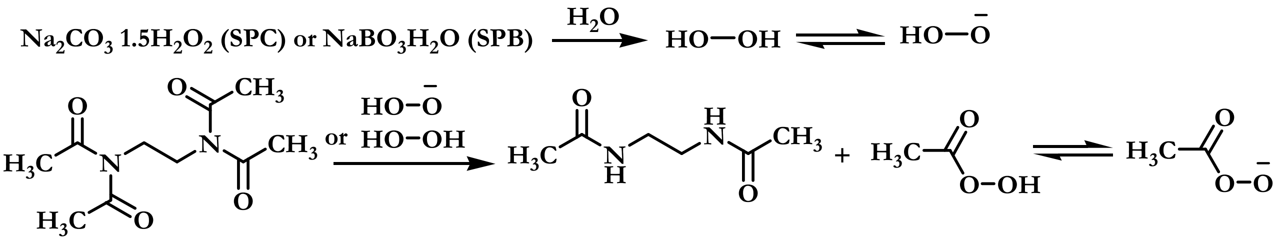
INTRODUCTION

The Baeyer-Villiger oxidation of ketones to lactones or esters is one of the most important reactions in organic chemistry[1,2]. This oxidation is carried using m-chloro perbenzoic acid catalyzed by different Lewis acids such as sulfonic acids[3], Nafion-H[4], CF_3COOH[5], hydrotalicite[6], $SnCl_4$[7], scandium triflate[8], boron trifluoride[9], and bismuth triflate [10]. Recently, we reported the Baeyer-Villiger oxidation of ketones using molecular oxygen with acidic resin[11]. Also the reaction is accelerated by bases[12], or metal complexes[13]. However, many of these methods suffer from drawbacks such as unsatisfactory yields and the use of large amounts and very expensive catalysts and impermanency of peracids. Thus, the development of general and facile new reagent for Baeyer-Villiger oxidation is an active field of research[13].

N, N, N´, N´-tetraacetylethylenediamin (TAED) was synthesised for the first time in 1911 by Franchimont et al [14] and since then there are so many



SCHEME 1: Production prosecutor of TAED



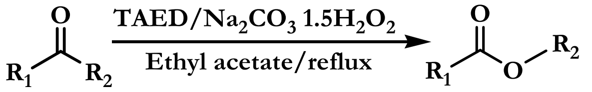
SCHEME 2: In situ production of peracetic acid using TAED and SPC

reports about synthesis[15] and modification of producing methods for it[16]. But one of the best methods for synthesis of TAED is carried in two steps[17]. In which the first step, the 1,2-diammoniumethan diacetate salt is converted to N, N′-diacetylethylenediamin (DAED) on heating and removing of water during the reaction. In the second step, DAED is converted to TAED in the presence of excess amount of acetic anhydride at reflux condition by removing acetic acid (SCHEME 1).

After synthesis of TAED many research have been done about application of TAED in the presence of peroxy scaffold compounds such as sodium perborate (SPB) and sodium percarbonate (SPC) in designing new detergent formulation for low temperature bleaching purposes[18], the mechanism of this bleaching as shown in (SCHEME 2) involve nucleophilic attack of peroxide anion to electrophil carbonyls group of (TAED) and in situ production of per acetic acid that equilibrated with its anion[19].

RESULTS AND DISCUSSION

Insitu production of peracetic acid and its anion allowed us using this reagent (TAED and SPC) for Bayer-Villiger oxidation of cyclic and acyclic ketones to related lactones and esters (SCHEME 3).



SCHEME 3: Bayer-villiger oxidation of ketones using TAED and SPC

In order to optimize the oxidant activity of TAED and SPC, we have studied the Baeyer-Villiger oxidation of acetophenone (TABLE 1, entry 3) as a model substrate with 1 equivalent of TAED using

TABLE 1: The oxidation of ketones by TAED and sodium percarbonate in acetonitril at reflux condition[a]

Entry	R¹	R²	Time(h)	Yield (%) [b]
1	$(-CH_2-)_4$		3.30	81
2	$(-CH_2-)_5$		3.30	78
3	CH_3	C_6H_5	2.30	80
4	CH_3	$4\text{-Cl-}C_6H_4$	2.45	79
5	CH_3	$4\text{-Br-}C_6H_4$	2.45	84
6	C_6H_5	C_6H_5	4	80
7	CH_3	$C_6H_5\text{-}CH_2$	2	91
8	C_6H_5	$C_6H_5\text{-}CH_2$	2.15	83

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples. [b]Isolated yields are based on ketones.

various amount of SPC. The most satisfactory result was obtained when 1.33 equivalent of SPC was used to give the desired ester quantitatively in a much shorter reaction time. Good yields were obtained when dichloromethane was used as solvent; however, it was found that ethylacetate was the best solvent for this reaction.

The reaction procedure was simple and the generality of this process was illustrated by the wide range of cyclic and acyclic aromatic and aliphatic ketones. The results are shown in TABLE 1.

In summary, we have introduced a simple, fast and chemoselective TAED and SPC as new reagent procedure for Baeyer-Villiger oxidation of ketones.

Taking advantages of availability, mild reaction condition via not direct using of peracids and low cost of reagent and accelerating the oxidation. The method provides a simple and efficient alternative to existing procedures for conducting Baeyer-Villiger reaction.

EXPERIMENTAL

Melting points were measured on the Electrothermal 9100 apparatus and are uncorrected. IR spectra were measured on a Bomen FT-IR-MB 100 spectrometer. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500.1 and 125.8 MHz using TMS as internal standard. All chemicals were obtained from Merck or Fluka, and used without further purification.

General procedure: Ketone (2 mmol), TAED (1mmol, 0.23g), sodium percarbonate (1.33 mmol, 0.21g) and ethylacetate (10 ml) were placed in a round bottomed flask with a magnetic stirrer. The reaction was refluxed in a period of time (TABLE 1). After the completion of the reaction (the progress of the reaction was monitored by TLC), the mixture was cooled to room temperature, the reaction mixture was washed with water for extraction by-products of the reactions (DAED, Na_2CO_3, sodium acetate) and unreacted SPC. The organic extract dried over anhydrous $NaSO_4$. All the organic phase was evaporated; the crude product was isolated and purified (silica gel column chromatography). All products are known compounds which were characterized by IR, ^{1}HNMR, ^{13}CNMR and mass spectral data and their melting points compared with literature reports.

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