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A FACILE PROCEDURE FOR PREPARATION OF CARBOXYLIC SULFONIC ANHYDRIDES UNDER SOLVENT-FREE CONDITIONS

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A manipulatively one-pot and rapid method for the synthesis of carboxylic sulfonic anhydride from acid chloride or sulfonyl chloride and potassium salt of carboxylic or sulfonic acid under solvent-free conditions is reported. The reaction has been carried out in excellent yield and short reaction time in the presence of DABCO under solvent-free conditions.

Keywords: Carboxylic sulfonic anhydride; DABCO; solid-state; sulfonyl chloride

INTRODUCTION

Acid anhydrides are among the most important class of reagents used in organic synthesis. They are the preferred reactive acid derivatives for the preparation of amides, esters, and peptides.^{1,2} Further, the use of acid anhydrides does not require any acid scavengers unlike in the case of acid chloride. This article presents a general method that may be applied to the preparation of anhydride unlikely or difficult to obtain by the other known methods, exclusively.

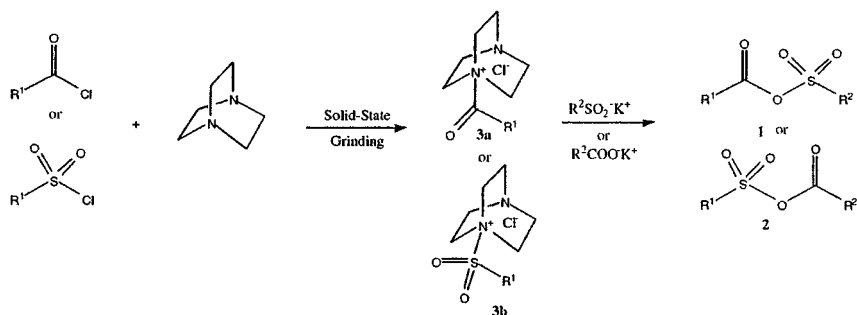
Heterogeneous reaction under solvent-free conditions have received attention in recent years.^{3–7} The advantage of these methods over conventional homogenous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products, and manipulative simplicity.⁷

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RESULTS AND DISCUSSION

In connection with our ongoing program to develop environmentally benign methods using solid supports,⁷ herein we wish to report an extremely convenient method for preparation of different anhydride with different potassium salt of acid and acid chloride in the presence of DABCO under solvent-free conditions (Scheme 1). The process in its entirety involves a simple mixing of carboxylic acid chloride or sulfonyl chloride and potassium salt of carboxylic or sulfonic acid in the presence of DABCO in a mortar and grinding the mixture for the time specified in Table I at room temperature. This method is very fast and purification of product is very easy (Scheme 1).



SCHEME 1

We believe that the effect of DABCO is to react with acid chloride or sulfonyl chloride to produce 1-aza-acyl-4-azoniabicyclo[2.2.2]octane chloride **3a** or 1-aza-sulfonyl-4-azoniabicyclo[2.2.2]octane chloride **3b**. These salts then react with potassium salt of carboxylic or sulfonic acids to produce corresponding carboxylic sulfonic anhydride, the probably mechanism is shown in Scheme 1.

The carboxylic sulfonic anhydrides have been identified by 1H NMR, IR, and CHN analysis. The IR of carboxylic sulfonic anhydride obtained in this work showed two very strong and sharp absorption bands in the region $1800-1720\text{ cm}^{-1}$, arising due to symmetric and asymmetric carbonyl stretching vibrations and two very strong and sharp absorption bands in the region $145-1100\text{ cm}^{-1}$, arising due to symmetric and asymmetric sulfonyl stretching vibrations, characteristic of carboxylic sulfonic anhydride. The results of these efforts are presented in Table I. The desired product was usually isolated in excellent yield (Table I). As shown in Table I, a series of acid chlorides were reacted with potassium salt of acid in the presence of DABCO under solvent-free conditions. Potassium salt of acid could be easily reacted with different sulfonyl

TABLE I Preparation of Carboxylic Sulfonic Anhydrides

Product	R ¹	R ²	Reaction time (min)	Yield (%) ^a	m.p. °C	Mol. formula	Found (%) (calcd.) C, H
1a	C ₆ H ₅	C ₆ H ₅	10	94	Semi Solid	C ₁₃ H ₁₉ O ₄ S	59.40, 3.80 (59.53, 3.84)
2a	C ₆ H ₅	C ₆ H ₅	12	96	—	—	—
1b	C ₆ H ₅	<i>p</i> -ClC ₆ H ₅	11	99	198–200	C ₁₃ H ₉ O ₄ SCl	52.62, 3.00 (52.62, 3.05)
1b	<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	14	97	—	—	—
1c	C ₆ H ₅	<i>p</i> -MeC ₆ H ₄	10	94	108–111	C ₁₄ H ₁₃ O ₄ S	60.80, 4.30 (59.53, 3.84)
1c	<i>p</i> -MeC ₆ H ₄	C ₆ H ₅	10	98	—	—	—
1d	C ₆ H ₅	<i>p</i> -NO ₂ C ₆ H ₄	9	93	188–190	C ₁₃ H ₉ NO ₆ S	50.80, 2.90 (50.81, 2.95)
1d	<i>p</i> -NO ₂ C ₆ H ₄	C ₆ H ₅	8	96	—	—	—
1e	C ₆ H ₅	<i>m</i> -MeOC ₆ H ₄	10	97	60–61	C ₁₄ H ₁₂ O ₃ S	57.40, 4.10 (57.52, 4.14)
1e	<i>m</i> -MeOC ₆ H ₄	<i>m</i> -MeOC ₆ H ₄	7	95	—	—	—

^aIsolated yield after simple extraction.

chloride or carboxylic acid chlorides at room temperature. It is noteworthy that DABCO could recovered easily by filtration and washing with NaOH 10% and extraction with CH₂Cl₂ and could be reused again without significant decrease in its activity.

In conclusion a simple and efficient method for synthesis of carboxylic sulfonic anhydrides under solvent-free conditions at room temperature has been developed. This work also is a rapid and very convenient method for the synthesis of carboxylic sulfonic anhydrides in excellent yields with high purity. By this method a variety of acid carboxylic sulfonic anhydrides can be readily prepared in short reaction time. This methodology is superior to the reported method⁸ from point of view of yield, short reaction time, and the straightforward work-up of the product.

EXPERIMENTAL

General

Products were characterized by comparison with authentic samples (IR, ¹H-NMR spectrum, CHN analysis, melting point, mixed melting point, and co-TLC analysis) with those obtained by literature method⁸ and using alternative method of synthesis. The structure of all the carboxylic sulfonic anhydrides that obtained in this work showed two very strong

and sharp absorption bands in the region 1800–1720 cm^{-1} , arising due to symmetric and asymmetric carbonyl stretching, characteristic of acid carboxylic sulfonic anhydrides. All m.p.s were taken on a Gallenkamp melting apparatus and are uncorrected. ^1H NMR spectra were recorded on a Varian EM-390 NMR Spectrometer operating at 90 MHz. The spectra were measured in CCl_4 and CDCl_3 relative to TMS (0.00 ppm). IR spectra were recorded on a Shimadzu 435 IR spectrophotometer. Spectra of solids were performed using KBr pellets. The Research Institute of Petroleum Industry, Tehran, I.R. Iran performed elemental analysis.

General Procedure

A mortar was charged with acid chloride (1 mmol), DABCO (0.11 g, 1 mmol); the mixture was ground with a pestle for 1 min until the reaction mixture solidified. Then potassium salts of carboxylic acid (1 mmol) were added to the mixture. The reaction mixture was ground for the time specified in Table I. Then the reaction mixture was poured into a mixture of ether (20 ml) and H_2O (5 ml). The ethereal layer was dried (CaCl_2), and evaporated to dryness using a rotary evaporator to give the pure product (>95% base on TLC analysis). The products could be further purified by column chromatography on silica gel using a mixture of n-hexane:EtOAc (80:20).

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