Journal of the Korean Chemical Society
2008, *Vol. 52, No. 4*
Printed in the Republic of Korea

단 신

Microwave Irradiation 및 촉매로서 실리카 지지 술팜산을 사용한 아닐리드의 합성(Beckmann 자리옮김 반응)

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(2008. 1. 22 접수)

Silica Supported Sulphamic Acid as Mild Catalyst for Synthesis of Anilides (Beckmann Rearrangement), Using Microwave Irradiation

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(Received January 22, 2008)

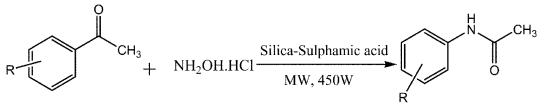
주제어: 실리카, 술팜산, 아닐리드, 아세토페논(케톤), Microwave irradiation, Beckmann 자리옮김 반응
Keywords: Silica, Sulphamic Acid, Anilides, Acetophenones (ketone), Microwave Irradiation, Beckmann Rearrangement

INTRODUCTION

A unique product of 1;2 Shift, Beckmann reaction has it's good many synthesis application. Beckmann reaction is a general tool in organic chemistry. The reaction requires high reaction temperature; strong acidic conditions and dehydrating media.[1,2] Amides are important biological and commercial compounds. Because amide constitutes the backbone of protein molecules, their chemistry is of extreme importance. The penicillin and cephalosporin antibiotics are among the best-known products of the pharmaceutical industry.[3] Keep all such things in mind we go for preparation of anilides, which also contribute excellent role to synthesis, various organic compounds.

The Beckmann rearrangement requires strong acidic conditions such as conc. Sulphuric acid or Phosphoric acid these have a large amount of side products and serious corrosion problems. So, In recent days the milder conditions were tried and investigated on clean, simple, ecofriendly benign and excellent process became the chemists interesting undertaking.[4,5] Several improved or developed process are reported using modified reagents[6] and solid acid catalyst like clay,[7] zeolites[8] and silica sulfuric acid.[8(c)] However, the reactions are sluggish when they are performed in the liquid phase.[5-8,10] Relatively few solid phase methods have been developed.[11] Also the Beckman reaction using a Stoichiometic amount of cynuric chloride and Dimethyl formamide salt, Reactions was observed with solvents other than Dimethyl formamide and the reaction rate decreased noticeably with a reduced amount of cyanuric chloride in Dimethyl formamide.[9]

Also some methods are available for one-pot Beckmann reaction of Acetophenone (ketone).[12-15] Hence, overcome all such disadvantages we report clean, effective, and simple method for one-pot synthesis of anilides in presence of catalytic amount of silica supported Sulphamic acid using microwave irradiation under solvent free condition.



Scheme 1.

RESULTS AND DISCUSION

Silica supported Sulphamic acid is an excellent mild catalyst over Sulphuric acid and Chlorosulphonic acid[16] in organic reactions without any limitations such as use of rather toxic, harmful solvents and expensive reagents. Hence, we tries mild acid catalyst Sulphamic acid[17] which shows rather slow rate of reaction and lower yield, therefore on using solid support (silica), which gives enhancement in the rate of reaction and better yields. Reaction goes through simple, clean and environmental friendly.

To prepare anilides various acetophenones (ketones) were mixed with hydroxyl amine hydrochloride and Silica-Sulphamic acid using mortar and pestle. The reaction mixture was irradiated in microwave oven for 7-15 min. The Corresponding anilides was obtained in excellent yield. The experimental results are summarized in *Table* 1.

As Shown in *Table* 1 several structurally varied acetophenones undergo clean, remarkably fast and direct nitrogen insertion by a one pot Beckmann type reaction to the corresponding anilides. This simple, clean, mild acid catalyst use for prepare different anilides. In *Table* 2 shows correlation between Sulphamic acid and silica supported Sulphamic acid for the model reaction, we examine three different derivatives and observed there is better result for reaction time and yield using silica supported Sulphamic acid catalyst.

Table 1. Silica-Sulphamic acid as mild catalyst for synthesis of anilides (Beckman Rearrangement)

Entry	Ar.	Time (Min)	M.P. (°C)	Yield[a] (%)
1	H	7	115	88
2	4-CH_3	8	150	86
3	4-NO_2	10	216	80
4	4-OC_2H_5	9	135	85
5	2-CH_3	10	112	83
6	3-CH_3	11	66	80
7	2-C_2H_5	8	96	88
8	3-OCH_3	9	78	90
9	3-F	13	83	76
10	4-OCH_3	8	131	90
11	3-Cl,4-F	15	76	81
12	2-Br	12	99	88

[a]Products yield are isolated yield.

Table 2. Correlation between Sulphamic acid and Silica-Sulphamic acid catalyzed reaction

Entry	Ar.	Catalysts			
		Sulphamic acid		Silica-Sulphamic acid	
		Time (min.)	Yield (%)	Time (min.)	Yield (%)
1	H	14	79	7	88
2	4-OC_2H_5	13	75	9	85
3	2-NO_2	17	71	10	80

In conclusion, a green benign method for synthesis of anilides has been developed with easy workup, high selectivity, without formation of bi-products such as tetrazole, amino tetrazoles, nitriles, ureas, etc.

EXPERIMENTAL SECTION

Melting points were uncorrected and recorded in open capillary. IR spectra were recorded on FT/IR-410 type(A) spectrophotometer in KBr. ^{1}HNMR spectra were measured in DMSO-d6 solution on a Bruker spectrophotometer at 400 MHz. Silica gel 60(230-400 mesh) was purchased from fluka and was dried in an oven at 120°C for 2 h.

Preparation of silica supported Sulphamic acid: For this preparation Silica gel (230-400 mesh) about 0.5 gm with 1mmole of Sulphamic acid (0.96 gm) was taken and mill that mixture for few minutes by using mortar and piston at room temperature. The mixture of Silica -Sulphamic acid used for further reaction.

General procedure: A mixture of acetophenone (2 mmol), Hydroxyl amine hydrochloride (4 mmol) and Silica-Sulphamic acid (1.96 gm) was grounded in mortar and reaction mixture was irradiated in domestic microwave oven at 450 W for optimized time indicated in *Table* 1. The progress of reaction monitored by TLC. After the completion of reaction, reaction mass dissolved in dichloromethane and catalyst was separated by filtration and product washed by water and dried over sodium Sulphate and solvent evaporated in vacuum to obtained crude product. The purification of crude product done by recrystallization in ethanol. Products are known compounds and were characterized by com-

parison of their spectral data (IR, ^{1}HNMR) and physical properties.

Compound **(4)** ^{1}HNMR (DMSO; d6) 2.0 ppm (s, 3H), 4.0 ppm (q, 2H), 1.3 ppm (t, 3H), 6.8 ppm (d, 2H), 7.8 ppm(d, 2H), 9.8 ppm (s, 1H). IR (KBR): 3300cm^{-1}, 1670 cm^{-1}.

Compound **(12)** ^{1}HNMR (DMSO; d6) 2.0 ppm (s, 3H), 7-7.6 ppm (m, 4H), 9.4 ppm (s, 1H). IR (KBR): 3250 cm^{-1}, 1665 cm^{-1}.

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