

Addition of Aromatic Nucleophiles to a C=N Double Bond of 1,2,5-Thiadiazole 1,1-Dioxide

M. F. Rozas¹, O.E. Piro², E. E. Castellano³, M. V. Mirífico^{1,4} and E. J. Vasini¹

¹INIFTA Dpto. Qca, Fac. Cs. Exactas.C.C. 16, Suc. 4, 1900 La Plata, Argentine

²Dpto. Física, Fac. Cs. Exactas, UNLP, 47 y 115, 1900 La Plata, Argentine

³Instituto de Física, Univ. De São Paulo, CP 369, 13560 São Carlos (SP) Brazil

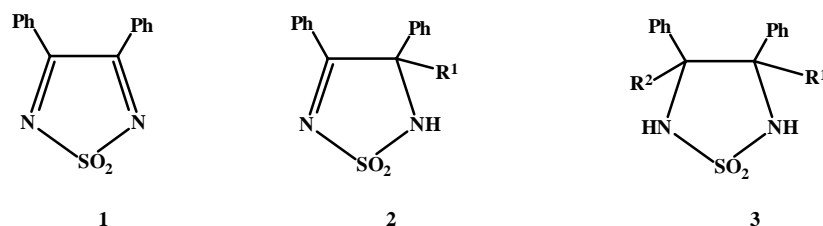
⁴Fac. Ingeniería, Dpto de Ingeniería Química, UNLP, Calle 47 y 1, 1900 La Plata, Argentine

Abstract: A new synthesis of 3,4-diphenyl-4-aryl-1,2,5-thiadiazolines 1,1-dioxide through the addition of aromatic derivatives to 1,2,5-thiadiazole 1,1-dioxide is presented. Anhydrous AlCl₃ is used as catalyst.

Introduction

Compounds of the 1,2,5-thiadiazolidines 1,1-dioxide type (**3**) are interesting owing to a number of therapeutic and synthetic applications [1]. They are almost exclusively obtained through the condensation reaction of vicinal diamines or amino-alcohols with sulfamide. The availability of the precursors limits the synthetic possibilities.

A recently reported new method [2] for the synthesis of **3** uses substituted thiadiazolines intermediates (**2**), obtained from thiadiazoles (**1**) by addition with Grignard reagents.



A new method for the addition of activated aryl nucleophiles to the C=N double bond of **1** is presented in this work. The addition is carried out in solution at room temperature and with adequate yields, using AlCl₃ as a catalyst.

Experimental

The synthesis were carried out in Cl₂CH₂ solution, except in the cases of toluene and anisole addition, were these reagents were also used as solvents.

Anhydrous AlCl_3 was added at room temperature to a magnetically stirred solution of **1**, in a molar ratio $R = [\text{AlCl}_3] / [\mathbf{1}] \cong 10$. The course of the reaction was followed by TLC.

Results and Discussion

The nucleophiles used were anisole, toluene, phenol, N,N-dimethylaniline, resorcinol and benzene. The products and yields obtained were: 3,4-diphenyl-4-(4-methoxyphenyl)- ($\eta = 64\%$), 3,4-diphenyl-4-(4-methylphenyl)- ($\eta = 92\%$), 3,4-diphenyl-4-(4-hydroxyphenyl)- ($\eta = 90\%$) and 3,4-diphenyl-4-(4-N,N-dimethylaminophenyl)-1,2,5-thiadiazoline 1,1-dioxide (η (unoptimized) = 38%).

The products were purified, their EA was obtained and crystals were grown for X-ray diffraction structure measurements. Spectroscopic (IR, ^1H -RMN, ^{13}C -RMN and EM) characterization was also performed.

In the case of benzene, a complex mixture of reaction products, containing mainly polymers derived from benzene, was obtained. Three as yet unidentified reaction products were obtained with resorcinol.

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References and Notes

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