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Synthesis and crystal structure of N^1-tosylacetylamidrazone

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ABSTRACT

The condensation of two molar equivalents of N^1-tosylhydrazonate **1** with one molar equivalent of 1,2-diaminoethane give birth to amidrazone in good yields. The structure of the synthesized compound was identified by X-ray diffraction, IR spectroscopy and nuclear magnetic resonance.

Keywords

N^1-tosyltylhydrazonate; amidrazone; 1,2-diaminoethane; X-ray diffraction; nuclear magnetic resonnance.

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INTRODUCTION

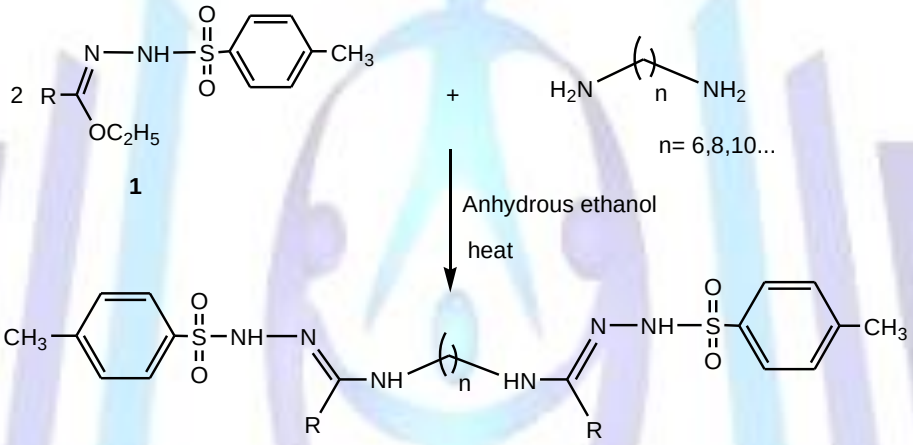
Amidrazones have emerged as an important class of intermediates particularly for the synthesis of heterocyclic compounds [1-3]. They are organic compounds of great interest mainly thanks to their application in different areas such as photography [4], fungicides [5] and herbicides [6].

According to the literature and depending on the type of substituents, the derivatives of N^1-tosylamidrazones have been proved to have a high potential for antibacterial [7] and anti-cancer activities [8]. Moreover, heterocyclic compounds, containing an amidrazone fragment have been applied in the pharmaceutical field owing to their diverse biological properties [9]. Recently, some bis-amidrazone derivatives endowed with antibacterial activities have been reported from our laboratory [10].

The present paper proposes a new method for obtaining N^1-tosylamidrazone **3** as a result of the reaction of 1,2-diaminoethane **2** with N^1-tosylhydrazonate **1**.

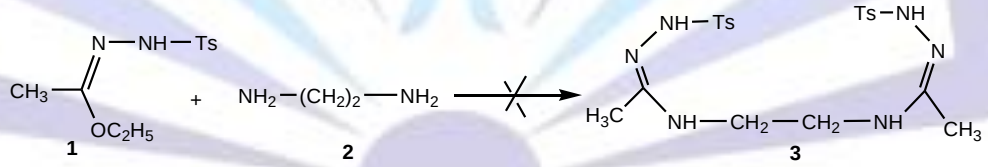
RESULTS AND DISCUSSION

The required N^1-tosylthydrazonates **1** were prepared as described in the literature [12]. The N^1-tosylhydrazonates **1** have electrophilic centers and are very reactive with reactants having NH_2-moiety such as amines, hydrazide, etc [11-12]. In recent years, refluxing in ethanol of two moles of N^1-tosylhydrazonates with one mole of diamine derivatives leads to the corresponding bis-(1-tosyl amidrazones)alkanes [13] (Scheme 1).



Scheme 1: Synthetic of bis-(1-tosyl amidrazones)alkanes

However, there was a different behavior in the case of 1,2-diaminoethane with N^1-tosylthydrazonate **1**. Indeed, the condensation of two molar equivalents of substrate **1** with a molar equivalent of reagent **2** under refluxing ethanol did not produce the bis-amidrazone **3** (Scheme 2).



Scheme 2

The product formed from this reaction, is represented in the form of a white solid and purified by the recrystallization in ethanol. The NMR spectra of this compound did not elucidate the structure of the product **3**. For example, the ^{1}H-NMR spectral analysis showed two singlets relating to 3H and 6H that appeared at δ : 1.88 and 2.39 ppm, respectively. Furthermore, the signals relating to the ^{1}H-aromatic appeared at 7.41-7.59 ppm. In particular, the absence of the -CH_2-N- signal emanating from 1,2-diaminoethane can be noted.

Since the spectroscopic data can not determine the exact molecular structure of product **3**, we used the crystallographic study by X-ray diffraction of a single crystal of the compound obtained to determine the final structure. As Shown in Figure 1, the examination of the molecular structure of $C_9H_{12}N_3O_2S$ shows the existence of a linear chain of amidrazone fragment formed by three nitrogen atoms (*N1*, *N2* and *N3*).

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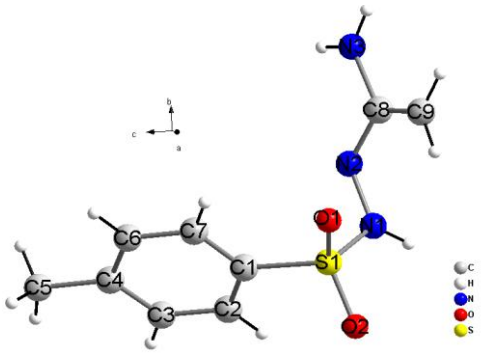
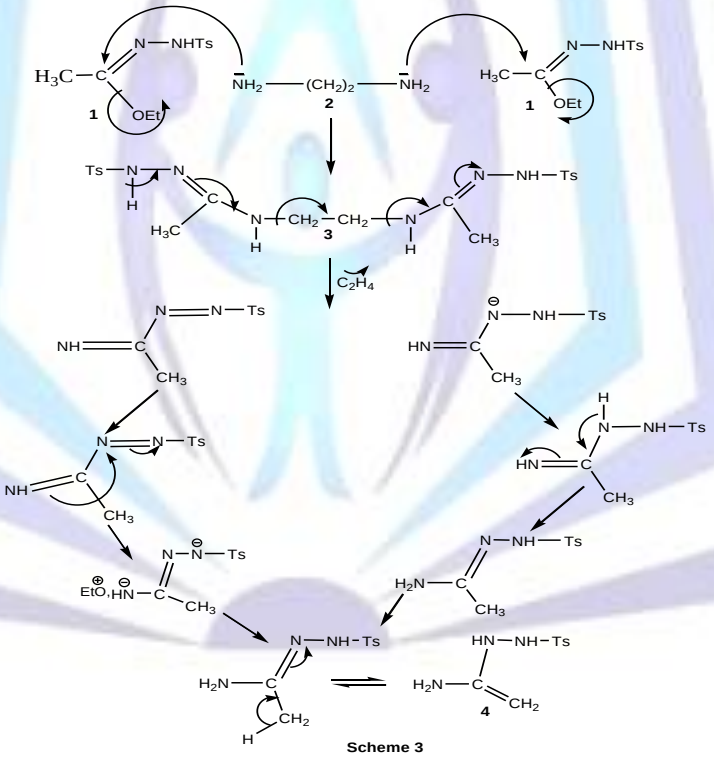


Figure 1: Spatial representation of amidrazone

X-ray data diffraction of compound **4**: $C_9H_{12}N_3O_2S$, M= 226.28 g/ mol^{-1}, orthorhombic, space group $P2_12_12_1$, a = 5.203 (5), b = 8.769 (5), c = 23.010 (5) Å, V = 1049.8 (1) $Å^3$, Z = 4. 2757 reflections with I>2σ (I) used for the refinement of the crystal structure. The final discrepancy factors R_1 and WR_2 were found to be 0.0655 and 0.2176.

Normally, the proposed mechanism started with a double nucleophilic attack of the two nitrogen atoms of 1,2-diaminoethane on the electrophilic center of the two moles of substrate **1**, followed by the elimination of two moles of ethanol to give rise to bis-amidrazone **3** (Scheme 3). However, this structure did not fit with the crystallographic data. So, the obtension of a structure that accords well with the crystallographic data may be due to the instability of compound **3** followed by the formation of two molecular amidrazones after the elimination of one mole of ethene (C_2H_4). From this crystallographic study, the reaction was found to be in the unexpected direction.



Scheme 3

CONCLUSION

In conclusion, the present research work reports the success of a new method in the synthesis of a novel class of amidrazone, used as a good precursor for the synthesis of new heterocyclic compounds due to the existence of nucleophyl centers.

EXPERIMENTAL

All melting points were measured on an Electrothermal apparatus. The IR spectra were recorded on a Perkin–Elmer 100 infrared spectrophotometer whose precision is $2cm^{-1}$ covering 400–4000 cm^{-1}. The NMR spectra were recorded on a Bruker Avance spectrometer. The ^1H spectra were run at 300 MHz and ^{13}C spectra were run at 75 MHz in dimethylsulfoxide (DMSO-d_6) as solvent.The chemical shifts are expressed in parts per million (ppm) by using tetramethylsilane (TMS) as internal reference. The multiplicities of the signals are indicated by the following abbreviations: s, singlet; d, doublet and coupling constants are expressed in Hertz. The single crystal X-ray diffraction studies were

realized on a KPPACCD diffractometer.The elemental analyses were performed at the Service of Microanalyse, Sidi Thabet, Tunisia.

A suitable crystal was carefully selected under a polarizing microscope and mounted at the end of a thin glass fiber. The crystal structure determination was performed using a BRUKER SMART APEX CCD diffractometer which uses graphite monochromatized MoKα radiation (0.71073). The unit cell parameters, optimized by least-squares refinement were calculated and refined using indexation of collected intensities. The structures were solved by direct methods using SHELXS-97 [14] and refined by full-matrix least-squares procedures using the SHELXL-97 program [15].

GENERAL EXPERIMENTAL PROCEDURE

A mixture of N^1-tosylhydrazonate **1** (0,002 mol), 1,2-diaminoethane (0,001mol) and 30 mL of anhydrous ethanol was refluxed. After the reaction completion (6 h), as indicated by TLC, the solvent was removed by evaporation and the precipitated product obtained by the addition of diethyl ether was re-crystallised from methanol.

Spectral Data of New Compound

***N^1*-tosylacéthyamidrazone 4:** Yield: 70%, white crystal, mp 150-152°C; IR (v/cm^{-1}): 1651 (C=N), 3215 (NH), ^{1}H-NMR: (DMSO-d_6): δ (ppm): 1.88 (s, 6 H), 2.40 (s, 3H), 7.43 (d, 2H, J= 8.10 Hz). 7.57 (d, 2H, J= 8.10 Hz). ^{13}C-NMR (DMSO-d_6): δ (ppm): 9.8 (C_9), 21.6 (C_5) 136.3 (C_2 and C_5), 128.1 (C_4), 130.7 (C_3 and C_6), 145.1 (C_1), 151.6 (C_8).

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