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Chlorination of 3-Arylsydones with Iodine Monochloride

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Abstract
An improved method for the chlorination at the 4-position of 3-arylsydones I was developed, utilizing iodine monochloride (ICl) dissolved in DCM. 1,3,4-Oxadiazol-2(3H)-ones 3 were then synthesized from the result of 4-chloro-3-arylsydones 2. The scope and limitations will be presented.

Scheme 1: Overall scheme for chlorination of sydones and subsequent transformation into 5-aryl-1,3,4-oxadiazol-2(3H)-ones

Introduction to Sydones
Sydones are unique, dipolar heterocycles, which are archetypal members of the class of compounds known as mesoionic.1,2

Synthesis of Sydones
N-arylhydrazines can be converted to the corresponding 3-arylsydones by transformation into the N-aminonitriles followed by cyclization with acetic anhydride.1,3

Reactions of Sydones
The process of electrophilic aromatic substitution is an integral part of sydone research. When the aromatic carbon is unsubstituted at the 4-position it becomes very susceptible to electrophilic attack and this allows for a variety of different substitutions of the sydnone.1,3

Spectroscopic Properties of Sydones

IR Spectrum
Sydones C=O stretch: ~1744 cm⁻¹
Sydones C-H stretch: ~3150 cm⁻¹

1H NMR Spectrum
Sydones CH: ~6.8
13C NMR Spectrum
Sydones C-4: ~95 ppm
Sydones C-5: ~165 ppm

Introduction of 1,3,4-oxadiazol-2(3H)-ones
Biological and Structure-Activity Relationship (SAR) studies have been performed on 1,3,4-oxadiazol-2(3H)-ones. It was observed that these chemical species could be utilized as herbicidal, anti-tumoral, anti-bacterial and anti-fungal agents.2,3

Remost (Oxadizone) an herbicide, is an example of a commercially available 5-aryl-1,3,4-oxadiazol-2(3H)-one.

Figure 1. 1,3,4-Oxadiazol-2(3H)-ones

Synthesis of 5-alkyl-3-aryl-1,3,4-oxadiazol-2(3H)-ones
Many 5-alkyl-3-aryl-1,3,4-oxadiazol-2(3H)-ones have been prepared previously from 3-arylsydones,12,14 hydrazides15, carbamates16 and phosgene.17

Reactivity 1,3,4-oxadiazol-2(3H)-ones
Previous work from our lab has shown that 5-alkyl-3-aryl-1,3,4-oxadiazol-2(3H)-ones are susceptible to electrophilic aromatic substitutions (EAS). Common examples include halogenation and nitration.

In further work from our lab, 5-alkyl-3-aryl-1,3,4-oxadiazol-2(3H)-ones have also been shown to react at the carbon of the C=O with “hard” nucleophiles such as methoxide and ethoxide ions, resulting in a ring-opening reaction.

Spectroscopic Properties of 5-Alkyl-3aryl-1,3,4-oxadiazol-2(3H)-ones
IR Spectrum
C=O stretch: ~1780 cm⁻¹
C=H stretch: ~2930 cm⁻¹
CN stretch: ~1490 cm⁻¹

1H NMR Spectrum
Aliphatic CH: ~2.4 ppm
13C NMR Spectrum
C-2: ~153.79 ppm
C-5: ~151.09 ppm

Background to Aims (sydones)
In 1997, Dimitrakos observed iodination of 3-phenylsydnone with ICl in acetic acid19

Scheme 3: Reaction of 3-arylsydones with “nour” ICl to A-GH

Table 3: Optimum parameters for ICl chlorination of sydones

| IC | Solution | Substrate | Reaction Time (hr) | Product Composition | Yield (%)
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**Results (Chlorination with ICl)**

• Complete chlorination of 3-phenylsydnone occurred in 30 minutes using 3 equivalents of ICl (1 mmol in DCM).

• The procedure was extended to a variety of 3-arylsydones on the basis of three results (scheme 6).

Conclusion
4-Chloro-3-arylsydones were synthesized in high yields and purity by the optimized procedure. 5-Methyl-1,3,4-oxadiazol-2(3H)-ones 3 were synthesized from (2) in high yields and purity, all in a novel one-pot synthetic procedure.

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