5-Amino-1,2,3,4-thiatriazole: 
Its Acylation with Chloroformates 
and Chlorothioformates as a Route to 1,2,4-Thiadiazoles 
and 1,6,6a,Δ4-Trithia-3,4-diazapentalenes

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Summary. Pyridine catalyzed acylation of 5-amino-1,2,3,4-thiatriazole with chloroformates and chlo-
rothioformates afforded 3,5-bis(ethoxycarbonylamino)-1,2,4-thiadiazoles in the former and 2,5-
bis(phenoxy)-1,6,6a,Δ4-trithia-3,4-diazapentalenes in the latter case. An unstable, but isolable inter-
mediate 2-phenoxy-1-aza-3,4-dithiolium-5-imide has been found if the chlorothioformate acylation 
was performed in acetonitrile in the absence of pyridine. The bis(phenoxy)trithiapentalenes are prone 
to nucleophilic displacement reactions at positions 2 and 5, exchanging in a stepwise manner one or 
both phenoxy groups. The structures of the compounds described could be inferred from their 1H-
NMR 13C-NMR, and mass spectra and were corroborated by the comparison with the data of 
authentic and similar derivatives as well as by chemical means.

Keywords. Chloroformate; Chloro(di)thioformate acylation; 5-Amino-1,2,3,4-thiatriazole; Trithia-
diazapentalenes.

Die Acylierung von 5-Amino-1,2,3,4-thiatriazol mit Chlorformaten und Chlorothioformaten als Route 
zu 1,2,4-Thiadiazolen und 1,6,6a,Δ4-Trithia-3,4-diazapentalenen

Zusammenfassung. Die durch Pyridine katalysierte Acylierung von 5-Amino-1,2,3,4-thiatriazol mit 
Chlorameisensäureethylester führt zu 3,5-bis(ethoxycarbonylamino)-1,2,4-thiadiazolen, während mit 
Chlorothioamisensäureethylester 2,5-bis(phenoxy)-1,6,6a,Δ4-trithia-3,4-diazapentalene erhalten wer-
den. Ohne Pyridin entsteht bei letzterer Reaktion ein wenig stabiles, aber isolierbares Zwischenpro-
dukt: 2-Phenoxy-1-aza-3,4-dithiolium-5-imid. Die Bis(phenoxy)trithiadiazapentalene reagieren leicht 
nukleophilen Reagenzien und tauschen dabei schrittweise eine oder beide Phenoxygruppen aus.

Introduction

5-Amino-1,2,3,4-thiatriazole (1) can easily be further functionalised at the amino 
group. In spite of this obvious possibility and the fact, that 1 is known since 1896 
[2], acylation reactions have hardly been attempted so far.

1 is known to react with isothiocyanates to 5-thioureido-1,2,4-thiadiazolin-3-
thiones and 2,5-bis(aryl-amino)-1,6,6a,Δ4-trithia-3,4-diazapentalenes [1], with iso-
cyanates to 2-substituted 5-ureido-1,2,4-thiadiazolin-3-ones [3]. Acylations with carboxylic acid chlorides resulted in the formation of 2,5-diaryl-3,4-dioxo(dithia or diarylaza)-3a,4-thia-1,6-diazapentalenes, [4, 5] whereas acetic anhydride acylation produced 3,5-bis(acetylamo)-1,2,4-thiadiazole [5]. Cyanic esters gave rise to 5-amino-5-aroxy-1,2,4-thiadiazoles [6].

We now report acylation reactions with chloroformate and chlorothioformate.

Results and Discussion

The reaction of 5-amino-1,2,3,4-thiatriazole (1) with chloroformates in pyridine at 0°C gave after 24h moderate yields of 3,5-bis(alkoxycarbonylamino)-1,2,4-thiadiazoles (4).

\[
\text{N} = \text{S} \quad \text{N} = \text{H}_2 \quad + \quad \text{CICOOR} \quad \xrightarrow{\text{Pyridine}} \quad \text{N} = \text{S} \quad \text{NHCOOR} \\
(1) \quad (2) \quad (3)
\]

Although the mass spectra of thiadiazoles 4 showed the expected molecular ion peaks, the crucial structural information was supplied by \(^1\text{H-}\) and \(^{13}\text{C-NMR}\) spectra, which indicated two different ethyl groups (4a), and two signals of C₃ at 176.8 and 158.2 ppm, respectively. These values are characteristic for bis(acylamino)-1,2,4-thiadiazoles and compare well with the structure assignment of Kurzer [7] for 3,5-bis(benzoylamino)-1,2,4-thiadiazole.

\(^{13}\text{C-NMR}\) signals indicated a nonequivalence of ester groups as well and corroborated the suggested structure of unsymmetrically substituted 1,2,4-thiatriazole.

3,5-Bis(ethoxycarbonylamino)-1,2,4-thiadiazole has previously been prepared in 8% yield by an alternative route, involving an oxidation of N-ethoxycarbonyl thiourea, and according to its analytical data [8], it was identical with the thiadiazole 4a.

The formation of 4 could be rationalised assuming an acylation at the amino group of the thiatriazole 1 to form an unstable carbamic acid derivative 2, which upon loss of nitrogen and of elemental sulphur gives an alkoxycarbonyl cyanamide 3.

Even though the alternative ring-N₃ acylation would eventually lead to the identical cyanamide 3, we base our assumption concerning the structure of the intermediate 2, on analogous derivatives, isolated from the reaction of 5-arylaminio-1,2,3,4-thiatriazoles 5 with chloroformates.

The acylation of 5 occurred at the amino group, since an alternative ring acylation to aryliminothiatriazole 7 would have been indicated by a typical value of \(^{13}\text{C-NMR}\) signal of C₃ at 156 ppm [9, 10], whereas the observed value of 173 ppm is characteristic for C₃ of 6. In addition, structures 6 and 7 could be distinguished.