



Carboxyl Activation of 2-Mercapto-4,6-dimethylpyrimidine through N-Acyl-4,6-dimethylpyrimidine-2-thione: A Chemical and Spectrophotometric Investigation

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2-Mercapto-4,6-dimethylpyrimidine, as effective carboxyl activating group, has been successfully proved by converting it into respective acyl derivatives and the subsequent conversion to the amides and esters respectively using amines, amino alcohols and alcohols. The aminolysis and esterification were monitored chemically and spectrophotometrically. This paved way to establish that the above mercaptopyrimidine derivative is an efficient carboxyl activating group applicable in solid phase peptide synthesis.

Keywords: Pyrimidine thiols, Activation of carboxyl group, Solid phase peptide synthesis.

INTRODUCTION

Peptide chemistry in association with molecular biology has made great advances in the last two decades and still continue to be a prominent area of active research. Recently, biomedical research including molecular biology^{1,2}, immunology³⁻⁵, pharmacology^{6,7}, enzymology⁸⁻¹⁰ and neurobiology^{11,12} have established their importance. Further, advances in biotechnology has made great contributions in understanding the life process of living organisms and health science. These help in developing new synthetic vaccines that can compete with bacterial and viral infections, enzyme mechanism and also in understanding the action of neuro-peptides. Using synthetic peptides, studies on mechanism of hormone action and of enzyme-substrate, antigen-antibody and protein-DNA interaction have been made possible.

Peptide synthesis got acceleration when oxytoxin was synthesized by du Vigneaud and co-workers. This was followed in rapid succession by the introduction of mixed anhydrides, active esters as carboxyl activating groups and also the discovery of coupling reagents which gave an unprecedented impetus to the development of peptide synthesis. Of course, in these methods high reactivity of carboxyl function towards nucleophilic attack is achieved, but rigorous conditions such as use of base, temperature *etc.* are required. Moreover, the electron withdrawing groups like halogen which enhances the electrophilicity of carboxyl carbon, increases the possibility of racemization.

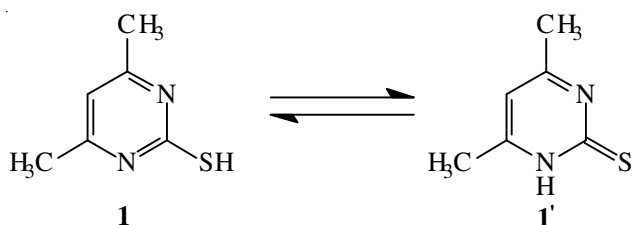
Now-a-days, a number of heterocyclic systems having a thiol function have been proved to be effective in carboxyl group

activation¹³⁻¹⁶. Actually thiol esters are more reactive than esters towards nucleophilic substitution. A number of new methods have been developed for the preparation of thiol esters¹⁷⁻¹⁹. Active role of thiol esters in biochemical processes and their reactivity with various nucleophiles have led investigators to choose them as attractive synthetic intermediates in organic synthesis²⁰⁻²². Their high reactivity may be due to the better leaving group ability of the thiide group than that of the alkoxide.

This led to investigate carboxyl group activation *via* heterocyclic thiols, especially using diazine and triazine thiols²³⁻²⁶. A number of new methods have been developed for the preparation of thiol esters. Active role of thiol esters in biochemical processes and their reactivity with various nucleophiles have led investigators to choose them as attractive synthetic intermediates in organic synthesis. Carboxyl group activated heterocyclic compounds possess enhanced reactivity, which promotes synthesis under mild conditions. This has been found to provide effective synthetic methods for peptides^{25,26}, macrolides^{27,28} and carbohydrates^{29,30}. In recent years, there has been tremendous advance in the chemistry of heterocyclic compounds³¹. Most of them were found to be biologically active and are being used as herbicides³²⁻³⁶, cross linking agents in polymers³⁷, dyes and in pharmaceuticals³⁸⁻⁴⁰. In order to find out an able carboxyl activating group, the studies on 2-mercapto-5,6-dimethylpyrimidine have been carried out and hence the present work here is the investigation of the effectiveness of 2-mercapto-4,6-dimethylpyrimidine as carboxyl activating group.

In order to establish the carboxyl activating nature of 2-mercapto-4,6-dimethylpyrimidine (1), it has been converted

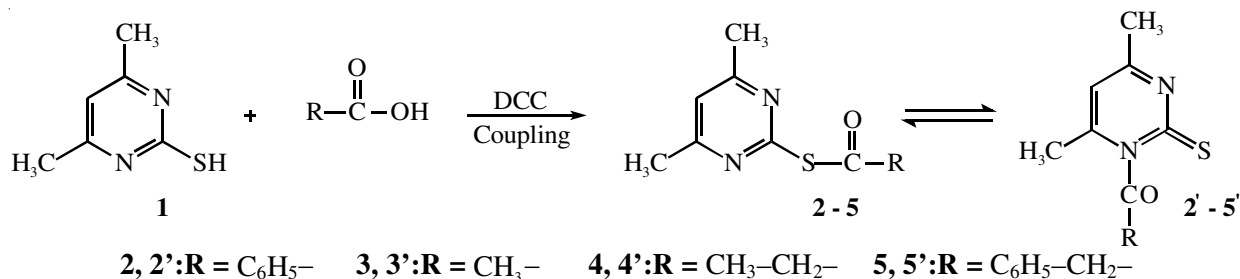
to various acyl derivatives by suitable acylation reactions so that S-acyl derivatives which easily tautomerise to the more stable N-acyl derivatives are formed. These derivatized compounds were found to be very efficient in acylation when subjected to aminolysis and esterification reactions. During the course of these reactions, the amides are isolated in good yield in addition to the formation of equivalent amount of original thiol. The UV-visible spectra of the pyrimidines and other monocyclic azines have been theoretically interpreted by Green and Tong. The spectra of 2- and 4-dimethylmercaptopyrimidines and those of the available S- and N-methyl derivatives, indicate that these compounds exist largely in the thiol form in the neutral aqueous solution. The efficiency of these acyl derivatives in aminolysis and esterification processes were measured spectrophotometrically by scanning the UV-visible spectrum of the compound regenerated during the course of the reaction, in addition to the isolation of amides or esters, in high yield.



EXPERIMENTAL

Synthesis of 2-mercapto-4,6-dimethylpyrimidine hydrochloride: In a typical procedure, conc. hydrochloric acid (75 mL) was added to a suspension of finely powdered thiourea (38 g, 0.5 mol) in acetylacetone (60 g, 0.6 mol) and ethanol (1.25 lit.) and the mixture was then refluxed for 2 h. Yellow needle shaped crystals of 2-mercapto-4,6-dimethylpyrimidine hydrochloride afforded on cooling was separated by filtration. Recrystallization from alcohol gave yellow crystals of 2-mercapto-4,6-dimethylpyrimidine hydrochloride: yield, 80 %, m.p. 240 °C.

2-Mercapto-4,6-dimethylpyrimidine (1): 2-Mercapto-4,6-dimethylpyrimidine hydrochloride was dissolved in water and to this solution, a saturated aqueous solution of sodium carbonate was added in drops with constant stirring. At the neutral point (pH 7-8), yellow crystals were formed. It was then separated by filtration and dried. The product thus obtained was recrystallized to afford yellow crystals of 2-mercapto-4,6-dimethylpyrimidine (1): Yield 70 %, m.p. 206 °C (lit⁴¹, m.p. 209-210 °C).



Scheme-I

N-Acyl-4,6-dimethylpyrimidine-2-thiones (2'), (3'), (4') and (5'): N-Benzoyl-4,6-dimethylpyrimidine (2') was prepared first by DCC coupling method²⁴ and also using the general procedure of acylation with benzoyl chloride in presence of triethylamine as base.

By applying the usual DCC coupling method, 2-mercapto-4,6-dimethylpyrimidine (1, 3.5 g, 25 mmol) and benzoic acid (3.05 g, 25 mmol) were dissolved in 80 mL THF and methylene dichloride (1:4) and this was then added to a solution of DCC (5.2 g, 25 mmol) in 14 mL methylene dichloride in drops with constant stirring in an ice bath. Stirring continued for 1 h and the precipitated DCU was filtered off. The filtrate thus obtained was separated by neutral alumina column using benzene-ethylacetate (3:1) mixture as solvent. The product obtained was recrystallized from benzene to afford yellow crystals of N-benzoyl-4,6-dimethylpyrimidine-2-thione (2') which was identified by different spectra: yield 85 %, m.p. 72 °C.

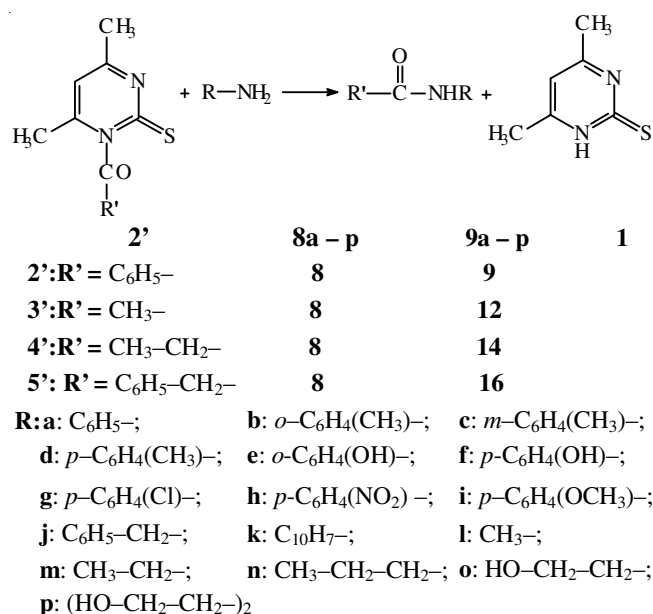
The DCC coupling method was also used to prepare other N-acyl derivatives using acetic acid (1.5 g, 25 mmol), propionic acid (1.8 g, 25 mmol) and phenylacetic acid (2.8 g, 25 mmol) and equimolar proportions of DCC (5.2 g, 25 mmol). The respective acyl derivatives, N-AcDPT (3'), N-PrDPT (4') and N-PaDPT (5') were afforded. They were isolated, purified by column chromatography and characterized (Scheme-I).

Aminolysis of N-acyl-4,6-dimethylpyrimidine-2-thiones: N-Benzoyl-4,6-dimethylpyrimidine-2-thione (2', 1 g, 4 mmol) dissolved in chloroform (15 mL) was mixed with freshly distilled aniline (8a, 0.38 g, 4 mmol). The reaction mixture was agitated well. A pale yellow colouration was developed in the solution within 3-4 min indicating the regeneration of thiol compound 1 which was also confirmed by TLC. From the reaction mixture, the solvent was evaporated off and the residue thus obtained was extracted with water, since DPT (1') is highly soluble in water. The white crystalline product was separated by filtration, purified by chromatography (neutral alumina), then recrystallized from alcohol to get crystals of benzanilide (9a), yield 85 %, m.p. 159 °C (lit⁴⁰, m.p. 163 °C).

The spectrophotometric monitoring of aminolysis was carried out using 0.1 mmol chloroform solution of compound 2' with equimolar amount of aniline compound 8 and the UV-visible spectrum was taken at every 30 s. Absorbance values were gradually increased at room temperature conditions and became steady after 3 min. Simultaneously the colour of the reaction mixture became yellow indicating the regeneration of 2-mercapto-4,6-dimethylpyrimidine (1).

The entire procedure of aminolysis was repeated using other amines 2-methylaniline (8b), 3-methylaniline (8c), 4-methylaniline (8d), 1-naphthylamine (8k), 2-chloraniline (8g)

and 4-nitraniline (**8h**), so that respective amides N-benzoyl-2-methylaniline (**9b**), N-benzoyl-3-methylaniline (**9c**), N-benzoyl-4-methylaniline (**9d**), 1-naphthylbenzamide (**9k**), N-benzoyl-2-chloraniline (**9g**) and N-benzoyl-4-nitraniline (**9h**) were obtained (**Scheme-II**).



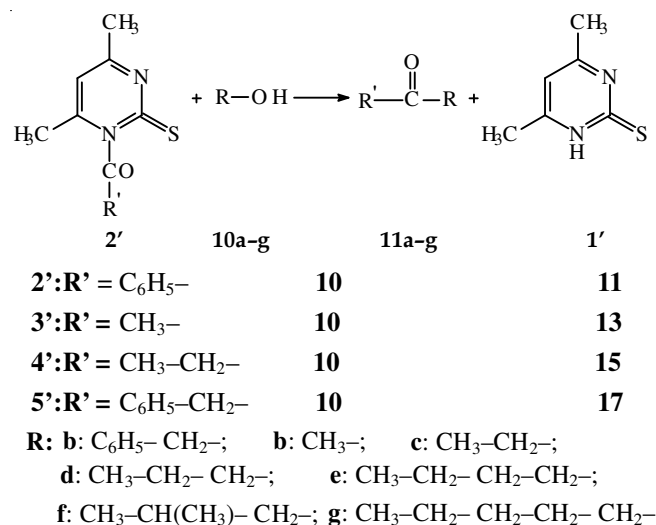
Scheme-II

The aminolysis reaction to isolate amides and spectrophotometric monitoring were repeated using other acyl derivatives N-AcDPT (**3'**), N-PrDPT (**4'**) and N-PaDPT (**5'**).

Reactions of N-acyl-4,6-dimethylpyrimidine-2-thiones with alcohols; formation of esters: N-Benzoyl-4,6-dimethylpyrimidine-2-thione (**2**, 2.5 g, 10 mmol) was dissolved in 40 mL benzyl alcohol (**10a**) and stirred well. There was no indication of the regeneration of compound **1** even after prolonged stirring. Then the reaction mixture was heated on a water bath to 60-70 °C for 5 min. A fruity smell with a simultaneous colour change to pale yellow indicating the regeneration of compound **1** was developed. The product formed was evidenced by TLC. Column chromatographic separation of the mixture using neutral alumina afforded benzyl benzoate (**11a**) bp 304 °C (lit.⁴¹, b.p. 314 °C) and compound **1** in very good yield. The reaction was also followed by UV-visible spectral measurements using 0.1 mmol solutions of compound **2'** and benzyl alcohol (**10a**). Absorbance values were noted at regular interval of 30 s. The increase in the absorbance values were negligibly small.

The esterification reaction was repeated using other alcohols like methyl alcohol (**10b**) and ethyl alcohol (**10c**) and other acyl derivatives under similar conditions. In all

the cases esterification occurred only when heated and the respective esters, methyl benzoate (**11b**) and ethyl benzoate (**11c**) formed were separated by chromatographic method (**Scheme-III**).



Scheme-III

Selective aminolysis of acyl-derivatives with amino-alcohols and phenols: Formation of hydroxy amides: A chloroform solution (15 mL) of N-benzoyl-4,6-dimethylpyrimidine-2-thione (**2**, 1 g, 4 mmol) were treated with ethanolamine (**8o**, 0.24 g, 4 mmol) and stirred well for 10 min at room temperature. The regeneration of 4,6-dimethylpyrimidine-2-thione (**1**), an yellow colour was developed within 2-3 min. This was also evidenced by TLC. The excess chloroform was evaporated off. The residue thus obtained was extracted with water and filtered. The solid product thus obtained was purified by neutral alumina column and recrystallised from benzene to afford N-hydroxyethyl benzamide (**9o**). Yield 80 %, m.p. 156 °C, (lit.⁴¹ m.p. 163 °C).

Similar procedure was repeated using diethanolamine (**8p**) and 4-aminophenol (**8f**) with the same proportion so that N,N-bis(hydroxyethyl)benzamide (**9p**) and 4-(hydroxyphenyl)benzamide (**9f**) were yielded. The similar sets of selective aminolysis using ethanolamine, diethanolamine, 2-aminophenol and 4-aminophenol were also carried out with N-AcDMPT (**3'**), N-PrDMPT (**4'**) and N-PaDMPT (**5'**) derivatives.

RESULTS AND DISCUSSION

Details of different N-acyl derivatives prepared and a representative compound **3'** are presented in Table-1.

Many experimental and theoretical studies have been reported that pyridines and pyrimidines substituted with an -SH or -OH group at 2- or 4-positions are fundamentally tautomeric

TABLE-1
PHYSIOCO-CHEMICAL CHARACTERISTIC DATA OF N-ACETYL-4,6-DIMETHYLPYRIMIDINE-2-THIONE

Acyl derivative	m.p. (°C)	Yield (%)	Spectral data		
			UV (CHCl ₃ , nm)	IR (KBr, ν _{max} , cm ⁻¹)	¹ H NMR (CDCl ₃ , δ)
N-Acetyl-4,6-dimethylpyrimidine-2-thione [N-AcDPT (3')]	210	80	303	1236, C=S	2.35 (9H, m)
			362	1439, C=S 1709, C=O	6.5 (1H, s)

systems. In addition, the formation of the N-acyl derivatives from the tautomeric S-acyl-4,6-dimethylpyrimidine-2-thiones can reasonably be explained as an S→N thermal rearrangement of the kinetic product to the more stable N-acyl-4,6-dimethylpyrimidine-2-thione by close analogy with the rearranged products observed in the case of acyl derivatives of 2-thionothiazolidines⁴².

In order to establish the carboxyl activated nature of N-acyl dimethylpyrimidine-2-thione, the aminolysis reactions were further carried out using other acylpyrimidine derivatives like N-AcDPT (**3'**), N-PrDPT (**4'**), N-PaDPT (**5'**) with similar set of amines. In all cases, the respective amides formed were separated by column chromatography. The amides obtained were in almost quantitative yield except in the case of N-PrDPT (**4'**). The formed amides were evidenced by TLC and characterized by analytical methods. The characterization data of the amides are presented in Table-2.

Further, it has been observed that amide formation with various acyl derivatives of 2-mercapto-4,6-dimethylpyrimidine (**1**) were effective and aminolysis reactions occurred irrespective of the nature of the acyl group present on 4,6-dimethylpyrimidine-2-thione. Another specific observation noticed that all the reactions took place at room temperature conditions and the original thion regenerated was almost in quantitative yield. In all the cases, the time taken for amide formation was around 10-15 min except with N-propionyl 4,6-dimethyl-pyrimidine-2-thione (**4'**).

Spectrophotometric monitoring studies of the acyl transfer reactions were repeated using acyl derivatives **2'**, **3'**, **4'** and **5'** so as to verify the regeneration of original thiol during the amide formation reactions, under room temperature conditions. In all the cases 0.1 mmol solutions of acyl derivatives and respective amines in chloroform solutions were used. The UV-visible scannings, which show the regeneration of 2-mercapto-4,6-dimethylpyrimidine (**1**) were followed in every 30 s. In all the reactions, pale yellow colour was developed within 2-3 min showing the regeneration of thiol with simultaneous formation of respective amides with the exception of N-propionyl-4,6-dimethylpyrimidine-2-thione (**4'**) in which the reaction was very slow.

From the scanning results, slight differences have been observed in the rate of amide formation as, N-BzDPT (**2'**) > N-PaDPT (**5'**) > N-AcDPT (**3'**) > N-PrDPT (**4'**). This order of reactivity is in full agreement with the field effects of benzoyl, phenyl acetyl, acetyl and propionyl groups. Among the phenyl and phenyl acetyl groups, the latter is having a better electron releasing group and therefore acyl group cleavage is most facilitated in benzoyl derivative. The same trend in rate of reactivity in terms of isolated yields of amides has also been observed. In brief, all the N-acyl derivatives could be used as activated carboxyl components, benzoyl derivative being the best among them.

In order to generalize the esterification reactions the other acyl pyrimidine derivatives, N-AcDPT (**3'**), N-PrDPT (**4'**) and N-PaDPT (**5'**) were also subjected to esterification using different alcohols.

The failure in esterification reactions at room temperature also prompted to carry out spectrophotometric monitoring similar to that of aminolysis. It has been clearly found that the esterification reactions using N-acyl-4,6-dimethylpyrimidine-2-thiones were sluggish as in the case of N-acyl-5,6-diphenyl-1,2,4-triazine-3-thiones which points to the weak nucleophilic nature of alcohol/phenols.

The carboxyl activation efficiency of 4,6-dimethylpyrimidine-2-thione (**1**) towards selective aminolysis reactions were again studied using N-AcDPT (**3'**), N-PrDPT (**4'**) and N-PaDPT (**5'**), so that respective hydroxyamides were afforded without much difference in the nature of the reactivity. Anyhow, the selective aminolysis reaction with N-propionyl-4,6-dimethylpyrimidine-2-thione (**4'**) was weak compared to other acyl derivatives. In all the cases, 2-mercapto-4,6-dimethyl-pyrimidine (**1**) was regenerated in very good yield.

Similar to aminolysis reactions using N-acyl-4,6-dimethylpyrimidine-2-thione, selective aminolysis was also followed by spectrophotometric measurements. Here, again, the experiments were conducted using 0.1 mmol solutions of respective acyl derivative and each amino alcohol and the scannings were done in every 30 s at room temperature till the completion of the reaction. The increase in the absorbance clearly indicated the regeneration of 2-mercapto-4,6-dimethylpyrimidine (**1**)

TABLE-2
ACYLATION OF AMINES (**8**)/ALCOHOLS (**10**) USING N-ACDPT (**3'**)

Amines/alcohols/amino alcohols used	Amides/esters formed	m.p./b.p. (lit. m.p./b.p.) (°C)	Reaction time (min)	Yield (%)
Aniline (8a)	Acetanilide (12a)	110 (114) ⁴³	12	82
2-Methyl aniline (8b)	N-(<i>o</i> -Tolyl)acetamide (12b)	108 (110) ⁴³	9	85
3-Methyl aniline (8c)	N-(<i>m</i> -Tolyl)acetamide (12c)	63 (65.5) ⁴³	9	83
4-Methyl aniline (8d)	N-(<i>p</i> -Tolyl)acetamide (12d)	153 (154) ⁴⁴	7	83
Ethyl amine (8m)	N-Ethylacetamide (12m)	190 (205) ⁴⁴	7	77
<i>n</i> -Propyl amine (8n)	<i>n</i> -Propylacetamide (12n)	b.p. 211 (215) ⁴³	8	74
Benzyl amine (8j)	N-Acetyl benzamide (12j)	56 (61) ⁴³	10	78
4-Methoxyaniline (8i)	N-(4-Methoxyphenyl)acetamide (12i)	79 (81) ⁴³	12	75
Ethanol amine (8o)	N-(2-Hydroxyethyl)acetamide (12o)	162 (166) ⁴⁴	14	72
Diethanol amine (8p)	N,N-Bis(2-hydroxyethyl)acetamide (12p)	146 (153) ⁴³	15	59
2-Aminophenol (8e)	N-(2-Hydroxyphenyl)acetamide (12e)	205 (209) ⁴³	14	68
4-Aminophenol (8f)	N-(4-Hydroxyphenyl)acetamide (12f)	174 (170) ⁴³	14	70
Benzyl alcohol (10a)	Benzyl acetate (13a)	b.p. 201 (215.5) ⁴³	23	50*
<i>n</i> -Propyl alcohol (10d)	<i>n</i> -Propyl acetate (13d)	b.p. 92 (101) ⁴³	22	45*
<i>n</i> -Butyl alcohol (10e)	<i>n</i> -Butyl acetate (13e)	b.p. 118 (126.5) ⁴³	22	45*

*Yield calculated based on the amount of DPT regenerated

during the selective aminolysis reactions. In all these experiments, the spectrophotometric measurements were fully in agreement with the rate of observed yield of hydroxy amides.

Conclusion

Carboxyl activation capability of 2-mercapto-4,6-dimethylpyrimidine has been proved chemically by simple aminolysis and esterification of amines and alcohols respectively. Spectrophotometric monitoring of the above aminolysis and esterification confirm the facile carboxyl activation ability of the original pyrimidine thiol.

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