Indian Journal of Heterocyclic Chemistry
Vol. 24, Oct.-Dec., 2014, pp.119-126

CARBOXYL ACTIVATION OF 3-MERCAPTO-5,6-DIPHENYL-1,2,4-TRIAZINE THROUGH N-PHENYLACETYL-5,6-DIPHENYL-1,2,4-TRIAZINE-3-THIONE

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Received 29 April 2014; Accepted 6 Sept. 2014

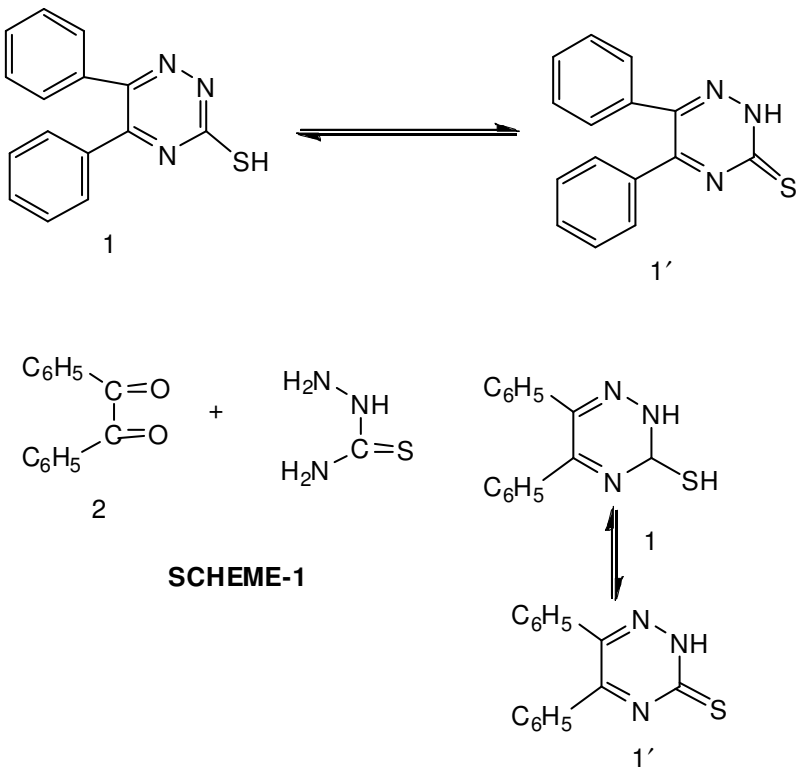
The carboxyl activation ability of 3-mercapto-5,6-diphenyl-1,2,4-triazine has been established by coverting it into N-phenylacetyl-5,6-diphenyl-1,2,4-triazine-3-thione and this was then subjected to aminolysis and esterification with amines and alcohols respectively and selective aminolysis with aminoalcohols-monitoring chemically and confirmed spectrophotometrically by UV-Visible scannings. It could be proved that 3-mercapto-5,6-diphenyl-1,2,4-triazine is an efficient carboxyl activating group which can be successfully applied in solid phase peptide synthesis.

Research activities in peptides are growing at an unassuming pace, since synthetic peptides have emerged as a powerful tool for studying peptide or protein structures and their complexities. Synthesis of peptides, chemically confirms the structures of naturally occurring peptides and enable them to obtain in bulkier quantities for further investigation and in the preparation of artificial vaccines and new potent drugs. The goal of peptides synthesis principally lies with the formation of amide bonds in which the union of amino and carboxyl groups is the key step. Activation and coupling of amino acids often results in overall loss of free energy which is achieved either by catalysts or by the use of activated functional groups. Till now, no practical approach is reported for the activation of amino group.

Carboxyl group activation which eventually leads to the peptide synthesis has been history of more than a century old and benzoyl glycine was the first activated synthetic derivative achieved. Afterwards the peptide bond formation by converting to azides and chlorides got established. In recent years there has been tremendous advances in the chemistry of heterocyclic compounds. A number of heterocyclic systems having a thiol function have been proved to be effective in carboxyl group activation[1-4]. Biomedical research including molecular biology[5,6], immunology[7-9], pharmacology[10,11], enzymology[12-14] and neurobiology[15,16] have established their importance.

Among the heterocyclic compounds triazines have drawn much attention as plant growth regulators[17-22], disinfectants and bleaching agents. The facile formation of triazine thiols from easily available precursors prompted to exploit the utility of triazine as carboxyl activating group in organic synthesis. Thus the present work deals with the study of 2-mercapto-5,6-diphenyl-1,2,4-triazine (**1**) which can easily be tautomerised to thione function **1′** to serve as a novel carboxyl activating group under mild conditions.

The investigation concentrated mainly to, the synthesis of 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**) and its characterization using different analytical and spectral methods. Derivatisation of compound **1** with phenylacetic acid to yield N-phenylacetyl derivative and characterization of the derivatised compound. Aminolysis and esterification of N-phenylacetyl-5,6-diphenyl-1,2,4-triazine-3-thione (**3′**) with various aliphatic and aromatic amines, alcohols and selective aminolysis using amino alcohols and characterization of the product formed to demonstrate the suitability of N-PaDDT (**3′**) as mild carboxyl activating moiety and spectrophotometric monitoring studies of aminolysis and esterification reactions using N-



SCHEME-1

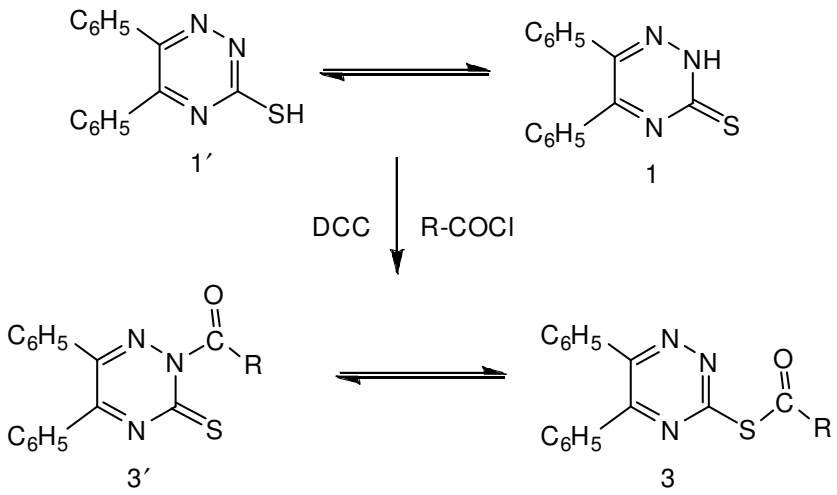
phenylacetyl-5,6-diphenyl-1,2,4-triazine-3-thione in order to give further support to carboxyl activation.

Phenylacetelation of (**1**) was also done by DCC coupling method. Here to an equimolar solution of phenylacetic acid and 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**) in THF & CH_2Cl_2 mixture (1:4), an equivalent amount of DCC in CH_2Cl_2 was added with constant stirring for 1 hr in an ice bath. DCU precipitated was filtered off.The concentrated filtrate was separated using silica gel column. The product separated was recrystallised from ethanol to afford pale yellow crystals with m.p. 125^0 in 90% yield. Mixed melting point with the compound obtained by Schotten-Baumann reaction of **1** did not show any depression and it was homogeneous to tlc.

N-PaDTT (**3**') has also been found to be an activated carboxyl derivative by conducting various aminolysis reactions. Here, when a chloroform solution of N-PaDTT (**3**′) was treated with a solution of freshly distilled aniline (**8**a), immediate colour change was noticed and within 5 min the orange red colour developed became intense. The mixture was stirred for another 10 min and separated by column chromatographic method using neutral alumina column. The first fraction of the product was identified as phenyl acetyl amino benzene (**18**a): yield 95%, m.. 116^0 (lit[58] m.p. 118^0). 3-Mercapto-5,6-diphenyl-1,2,4-triazine (**1**) was isolated as another compound.

The behaviour of N-PaDTT (**3**′) was also studied using other amines. The products formed in the different reactions were separated by column chromatographic method and characterized. Characterization data are given in Table-2. In all the above cases, DTT (**1**′) was isolated in almost quantitative yield.

When a solution of N-PaDTT (**3**′) in chloroform (40 ml) was treated with ethyl alcohol (**10**b), there was no indication for the regeneration of DTT (**1**′) even after stirring for about 2 hr at room temp. Anyhow, when the mixture was heated to about 70^0, for 5 minutes fruity smell of the ester was noticed with a simultaneous orange red colour indicating the regeneration of DTT (**1**′). Column chromatographic separation afforded ethyl phenyl acetate (**19**b) with



SCHEME-2 $R=C_6H_5\text{-}CH_2\text{-}$

bp 220^0 (lit[24], bp 227^0) and the regeneration of DTT (**1′**). The other esterification reactions carried out using N-PaDTT (**3′**) and alcohols are presented in Table-2 in all the above cases, DTT (**1′**) has been isolated.

Due to the better nucleophilicity of amines than alcohols, it could be seen that the esterification of N-PaDTT (**3′**) with alcohols are very sluggish in nature. This led to carry out selective aminolysis reaction using amino alcohols. Thus, when an equimolar solution of N-PaDTT (**3′**) in chloroform was stirred with ethanolamine (8m) in chloroform for 15 min, the pale orange red colour was gradually developed. The mixture was separated using neutral alumina column and the products obtained were recrystallised from alcohol and identified as N-(2-hydroxyethyl) phenyl acetamide (**20**m) m.p. 150^0 (lit,[22], m.p. 152^0) in 80% yield. Simultaneously 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1′**) was also isolated almost quantitatively.

To generalize the above selective aminolysis reaction, the reaction was repeated with a few amino alcohols and phenols. Hence, diethanolamine (**8**m), 4-aminophenol (**8**p) gave N,N-bis (2-hydroxy ethyl) benzamide (**20**m), N-(2-hydroxyphenyl) phenyl benzamide (**20**p) respectively. Characterization data has been provided in Table-2. In all the above cases DTT (**1′**) was regenerated. Regeneration of DTT (**1′**) was again evidenced by spectrophotometric monitoring studies.

When a dilute solution of aniline (0.01 mmol) was mixed with an equimolar solution of N-PaDTT (**3′**) in chloroform and then more DTT (**1′**) is regenerated so that absorbance value gradually increased. After 5 min, absorbance value remained unchanged. Initial sudden jump in the absorbance shows that the major portion of the aminolysis would have completed with in 2-4 min. The gradual increase in the absorbance after the above period is a clear indication of the slow process. The clear demonstration of the aminolysis reaction as a spectrophotometric tool paved the way to extend the reaction using different aliphatic and aromatic primary amines and also selective aminolysis with amino alcohols. Thus, the spectrophotometric scannings were repeated using *o*-toluidine, *n*-propylamine, *n*-butylamine and benzyl alcohol. In all spectral scannings the regeneration of DTT (**1′**) is in conformity with the nucleophilicity of NH_2 group or OH group present.

From the experimental observations, it is very much obvious that the esterification reactions of N-PaDTT (**3′**) is sluggish at room temp conditions. As already evidenced, the weak nucleophilic nature of the alcohols and phenols were also established by the spectrophotometric studies by carrying out

Table-1
Characterisation data of N-acyl-5,6-diphenyl-1,2,4-triazine-3-thione (**3′**)

Acyl derivatives	M.P. (^{0}C)	Yield (%)	Spectral data UV ($CHCl_3$, nm)	IR (KBr, cm^{-1})	^{1}H NMR (DMSO-d_6 δ)
N-Phenylacetyl-5,6 diphenyl-1,2,4-triazine [N-PaDTT (**3′**)]	191	85	315	1127(C=S) 1471(C=S) 1686 (C=O)	3.3 (2H, s) 7.2-7.7 (15H, *m*)

esterification reactions using N-PaDTT (**3′**) with different alcohols like ethanol, benzyl alcohol, *m*-nitrophenol and *m*-cresol. Thus, when a chloroform solution of benzyl alcohol (0.1 mmol) was added to an equimolar solution of N-PaDTT (**3′**) followed by scanning the UV-Visible spectrum at definite time intervals of 30 secs, only a very slow increase in the absorption of the characteristic peak at 321 nm was observed. This shows that the regeneration of DTT (**1′**) i.e. rate of esterification is very slow.

Fundamentally, electronic effects like inductive/ mesomeric effects and the nucleophilicity of the amines or alcoholic group play an important role in the rate of different reactions. Therefore, in addition to the investigation on the extent of aminolysis/ esterification of individual reactions, a comparative study on different amines, amino-alcohols and alcohols/phenols in order to make a correlation with the electronic arrangement of nucleophiles was also carried out. Effort is made here only to get a qualitative idea on the electronic effects operating and not for a quantitative treatment on the various kinetic parameters involved in it.

Aliphatic and aromatic amines like ethylamine, *n*-propylamine, *n*-butylamine, aniline, *o*-toluidine, *p*-chloroaniline, *o*-ethylaniline, polyfunctional compounds like ethylenediamine, ethanolamine, diethanolamine, 4-aminophenol and hydroxyl compounds like benzyl alcohol, *n*-butylacohol, *m*-nitrophenol and *m*-cresol were used to study the rate of benzoylation/esterification using N-PaDTT (**3**.).

The relative absorbance in aminolysis using various amines and amino alcohols has been plotted against time in seconds so that the extent of the reaction could easily be studied and compared. It is observed that aliphatic amines showed better reactivity than aromatic amines towards benzoylation. This may be due to the electron releasing effect of the alkyl groups in aliphatic amines and consequent increase in nucleophilicity on nitrogen centre of the amino group so that the extent of aminolysis is comparatively higher than that of aromatic amines. Amongst aliphatic amines, *n*-butyl amine showed the highest rate than that of *n*-propyl amine and ethyl amine, which is undoubtedly in agreement with the influence of electron releasing inductive effect of alkyl groups. Aniline showed the least reactivity towards benzoylation. Here electron withdrawing effect of the phenyl group would have influenced the reactivity at the nitrogen centre of the amino group. In the case of *m*-toluidine, a better reactivity than aniline has been observed. This may be due to the positive inductive effect of methyl group at the *meta* position which in tum makes the reaction faster than aniline.

Further, *o*-ethylaniline showed more reactivity than *m*-toluidine. This could be due to the presence of electron donating ethyl group at the *o*-position of the benzene ring. In aliphatic polyfunctional compounds like ethylenediamine, ethanolamine and diethanolamine an increase in the reaction trend was observed. This again may be due to the increase in availability of electrons at the nitrogen atom of the amino group. An exceptional behaviour was observed

Table-2
Acylation of amines/alcohols using N-PaDTT (**3′**)

Amines/alcohols/ amino alcohols used	Amides/esters formed	mp/bp (lit. mp/bp) ^{0}C	Time of reaction (min)	Yield (%)
Aniline (**8**a)	Phenyl acetyl amino benzene (**18**a)	116 (118)[23]	8	85
2-Methylaniline (**8**b)	Phenyl acetyl amino (2-methyl) benzene (**18**b)	156 (159)[24]	7	70
4-Methylaniline (**8**d)	Phenyl acetyl amino (4-methyl) benene (**18**d)	135 (136)[24]	7	73
Benzyl amine (**8**g)	N-Benzoyl-2-phenyl ethanamide (**18**g)	118 (122)[23]	8	70
Ethyl amine (**8**j)	Phenyl acetyl aminoethane (**18**j)	169(174)[23]	8	82
Methanol (**10**a)	Methyl phenyl acetate (**19**a)	bp 209 (215)[24]	15	55*
Ethanol (**10**b)	Ethyl phenyl acetate (**19**b)	bp 220 (227)[24]	15	52*
1-Pentanol (**10**e)	*n*-Pentyl phenyl acetate (**19**e)	bp 260(265)[24]	20	45*
Benzyl alcohol (**10**f)	Benzyl phenyl acetate (**19**f)	bp 305 (317)[24]	18	43*
Ethanolamine (**8**m)	N-(2-Hydroxyethyl) phenyl acetamide (**20**)	150 (157)[24]	10	78
Diethanolamine (**8**n)	N,N-bis (2-hydroxyethyl) benzamide (**20**n)	130 (136)[23]	12	72
4-Aminophenol (**8**p)	N-(2-hydroxyphenyl) benzamide (**20**p)	180 (190)[23]	15	70

*Yield calculated based on the regenerated amount of DTT.

in the case of *o*-chloroaniline where a very high reactivity was noticed. This anomalous behaviour could not be explained on the basis of electronic effect.

It has already been discussed that esterification of N-PaDTT (**3′**) using alcohols and phenols are sluggish in nature, probably due to the less nucleophilicity of the hydroxyl group than amino group. Therefore, a thorough and systematic comparative spectrophotometric investigation using different alcohols/phenols could not be conducted. However, the behaviour of benzyl alcohol towards the reactivity with N-PaDTT (**3′**) was compared with that of *m*-nitrophenol.

The relative ease of aminolsyis of benzoyl derivative with alphatic, aromatic and hydroxyamines and its very poor response in esterification with alcohols and phenols at room temp have been discussed earlier. Spectrophotometric monitoring has been found to be very successful in the case of phenylacetyl derivative, N-PaDTT (**3′**), of 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**).

Experimental

Melting points were determined in open capillaries on a Toshniwal capillary melting point apparatus and are uncorrected. Thin layer chromatography was carried out by using precoated silica gel plates. In column chromatography (100 cm x 2 cm) natural alumina and silica gel were used as adsorbants and the solvent systems used were petroleum ether-ethyl acetate (4:1), chloroform, methanol and water.

UV-Visible spectra were recorded on a Shimadzu UV-1601 spectrophotometer. Monitoring studies were carried out spectrophotometrically by conducting the reactions in the cuvette of spectrophotometer. IR spectra were recorded on Shimadzu IR-470 spectrophotometer using KBr pellets. ^{1}H NMR and ^{13}C NMR and mass spectroscopic measurements were recorded elsewhere.

3-Mercapto-5,6-diphenyl-1,2,4-triazine (1)

A solution of benzil (4.2g, 0.01 mol) in ethanol (60 ml) was refluxed and to the refluxing solution an equimolar solution of thiosemicarbazide (1.82g, 0.02 mol) in water (12 ml) was added. To the reaction mixture, ammonium acetate crystals were added till the solution became turbid. The orange red colour appeared initially became deep red orange after 1 hr. The mixture was refluxed for another 10 hr. After 10 hr the reaction mixture was cooled in ice and the crystals separated were filtered. Recrystalised from alcohol to afford yellow crystals of 3-mercapto-5,6-diphenyl-1,2,4-triazine (**2**). Yield 2.52g (95%), m.p. 205^{0}.

UV-visible spectrum in chloroform gave absorption band λ_{max} 321 nm at an absorbance value of 3.48. IR (KBr) spectrum of the compound **1** showed characteristic SH stretching frequency at 2360 (w) cm^{-1} and C=S stretching frequency at 1128(s). It is clear from the above signals that two tautomeric structures are possible for the triazine thiol as **1** & **1′**. ^{1}H NMR (DMSO-d_6) spectrum gave two characteristic signals. The multiplet, at δ 7.5-7.2 ppm (10H, *m*) and a singlet for NH proton at 5.2 (1H, s). The mass spectrum gave the molecular ion peak at m/z 265. The base peak occurs at m/z 178 for fragment Ph-C≡C-Ph^{+}. The other prominent peaks at m/z 89, 76 and 51 could also be explained.

Synthesis of N-PaDTT (3′)

An equimolar solution of phenyl acetic acid (2.68g; 20 mmol) and 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**, 5.3g, 20 mmol) in 40 ml THF and CH_2Cl_2 mixture (1:4) were treated with an equivalent quantity of DCC (4.12g; 20 mol) in 7 ml CH_2Cl_2 with constant stirring in an ice bath. The reaction mixture was stirred for 1 hr in the ice bath. Precipitated DCU was filtered off and the concentrated reaction mixture was separated using silica gel column. Product recrystallised from alcohol to afford dark green amorphous mass of N-PaDTT (**3′**).

Aminolysis of N-PaDTT (3′) with amines (8) : formation of amides (18)

N-PaDTT (**3′**, 0.268g, 2 mmol) in chloroform (10 ml) was mixed up with freshly distilled aniline (**8**a, 0.2 ml, 2 mmol). The reaction mixture was stirred for 5 min under the room temp conditions. During the course of reaction, the dark green colour changed to red orange indicating the regeneration of 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**). The products were separated using alumina column. The first fraction was identified as phenyl acetyl aminobenzene (**18**a) yield 0.31g (85%), m.p. 117^{0} (lit[23] 118^{0}). 3-Mercapto-5,6-diphenyl-1,2,4-triazine (**1**) was also separated as by product in almost quantitative yield.

To verify the generality of the above reaction, aminolysis was extended to other amines like 2-methylaniline (**8**b), 4-methylaniline (**8**d), benzyl amine (**8**g), ethyl amine (**8**j). The respective amides, phenyl acetyl amino (2-methyl) benzene (**18**b), phenyl acetyl amino (4-methyl) benzene (**18**d), N-Benzoyl-2-phenylethanamide (**18**g), phenyl acetylamino ethane (**18**j), were obtained in 70-80% yield. The reactions were also followed by tlc and spectrophotometrically. Using neutral alumina column all the products were separated and characterized. The characterization data are given in Table-1. In all aminolysis reactions 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**) was isolated almost in quantitative yield.

Reaction of N-PaDTT (3′) with alcohols & phenols (10): formation of esters (20)

Ethyl alcohol (**10**b, 20 ml) was treated with a solution of N-PaDTT (**3′**, 1.34g, 10 mmol) in chloroform

(40 ml). Even after stirring thoroughly for about 2 hr at room temp, there was no indication for the regeneration of 3-mercapto-5,6-diphenyl-1,2,4-triazine (**1**). But, when the reaction mixture heated to about 70^0, dark green colour was gradually changed to red orange. Simultaneously the pleasant fruity odour of the ester formed was also noticed. The colour change to red orange was the indication of the regeneration of 3-mercapto-5,6-diphenyl-1,2,4-trazine (**1**). Column chromatographic separation (neutral alumina) afforded ethyl phenyl acetate (**19**b) which was also evidenced by tlc.

The esterification reaction was then repeated with other alcohols like methanol (**10**a), 1-pentanol (**10**e), benzyl alcohol (**10**f). The corresponding esters obtained were methyl phenyl acetate (**19**a), *n*-pentyl phenyl acetate (**19**e), benzyl phenyl acetate (**19**f). 3-Mercapto-5,6-diphenyl-1,2,4-triazine (**1**) was isolated in all the above cases as a byproduct. The course of reactions were evidenced by tlc and spectrophotometric measurements. Characterization data have been produced in Table-1.

Selective aminolysis reaction of N-PaDTT (3′) with amino alcohols and phenols (20)

A chloroform solution (20 ml) of N-PaDTT (**3**′, 1.34g, 10 mmol) was stirred with ethanolamine (**8**m, 0.6ml, 10 mmol). The dark green coloured solution, thus obtained, was gradually changed to a pale red orange solution indicating the regeneration of DTT (**1**′). The mixture, after 15 minutes stirring was then separated using neutral alumina column. The first fraction obtained was recrystallized from alcohol and identified as N-(2-hydroxyethyl) phenyl acetamide (**20**m) yield 1.4g (80%), m.p. 150^0 (lit[23] m.p. 152^0). Simultaneously 2-mercapto-5,6-diphenyl-1,2,4-triazine (**1**) was also regenerated almost in quantitative yield.

Selective aminolysis was then generalized by extending to diethanolamine (**8**m) and 4-aminophenol (**8**p) so that N,N-bis (2-hydroxyethyl) benzamide (**20**n) and N-(2-hydroxyphenyl) benzamide (**20**p) were obtained in addition with the regeneration of 2-mercapto-4,5-diphenyl-1,2,4-triazine (**1**) Table-2.

UV-Visible absorption spectra of N-PaDTT (3′) during aminolysis and esterification

To carry out the spectrophotometric investigation on aminolysis of N-PaDTT (**3**′), a very dilute solution (0.1 mmol) was prepared in chloroform and taken in the cuvette of Schimadzu UV-160A spectrophotometer. The initial absorbance value was noted. Then a 0.01 mmol solution of ethylamine in chloroform was transferred to the cuvette. Stirred well with the aid of a capillary tube and the absorbance value measured immediately. Then the solution was stirred again and absorbance values were measured. The procedure was repeated at an interval of 30 secs.

The same procedure was repeated for the spectrophotometric monitoring of aminolysis/ esterification of N-PaDTT (**3**′) with different amines and alcohols at regular time intervals of 30 sec (Fig.-1-4).

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