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Synthesis of Thiazolinethione-5-Carbaldehydes by Vilsmeier-Haack formylation and transformation into Imines Chromophores

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Abstract : A new series of Shiff bases chromophores 6 containing thiazole, rhodanine and dicyano moiety have been synthesized in four steps by functionalization of the corresponding Δ-4-thiazolinethione 1a-b via Vilsmeier- Haack reaction. The formylation of 1a has afforded to two aldehydes 3a and 3c. The orientation of this electrophilic substitution has been discussed. The structures of these newly compounds have been established on the basis of their analytical and spectral data

Keywords : Thiazolinethione-5-Carbaldehydes, Synthesis, Vilsmeier-Haack formylation, transformation, Imines Chromophores.

Introduction

In the last three decades, heterocyclic chromophores are of wide interest because of their diverse potential applications in various fields as telecommunications, photovoltaic materials, information processors, optoelectronics and photonics.[1]

Synthetic approach to these chromophores mostly requires an intermediate such as aromatic aldehyde. Chromophores containing thiazole and benzothiazole units are versatile building blocks for the synthesis of donor-acceptor substituted π conjugated systems for several optical applications.[2] Many researchers have demonstrated that heterocyclic chromophores containing thiazole ring exhibit higher hyperpolarizabilities (μβ) than their aryl analogues.[3]

Continuing of our efforts on the use of Δ-4-thiazolinethione **1**[4] as starting material for the synthesis of new heterocycles with interesting chemical and physical properties**,** we have decided to synthesize novel Schiff bases chromophores by the functionalization of the corresponding Δ-4-thiazolinethione **1**.

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In our previous work [5]**,** we have studied the synthesis of several dyes rhodacyanines from a building block molecule, such as Δ-4-thiazolinethione **1**. This compound has been easily prepared in reasonable amounts, ready for further applications. Indeed, we have used this compound as substrate for the functionalization at the 2 and 5-position of derivatives **1a-b**.

The Vilsmeier-Haack reagent (chloromethyleniminium salt) which generated from an interaction of N,N-disubstituted formamides such as DMF with $POCl_3$ has attracted the attention of the synthetic organic chemists since its discovery in 1927.[6] It has been extensively used for formylation of activated compounds and fully conjugated carboxylic system. [7, 8]

In this work we report the synthesis and the reactivity studies of thiazolcarboxaldehyde by Vilsmeier-Haack reaction from Δ-4-thiazolinethione **1a-b** as starting materials. These resulting carboxaldehydes **3a-b** have been used as synthones for the production of new classes of Schiff bases chromophores **6a-d**. The formylation of **1a** has afforded two aldehydes **3a** and **3c** under Vilsmeier –Haack conditions.

As far as we know, the present study is the first one for the synthesis of formyl Δ-4-thiazolinethione **1** using Vilsmeier-Haack reagent. The formylation of thiazole and bisthiazolinnethione derivatives has been previously prepared by the Sommelet réaction and metalation .[9, 10]

Experimental

Melting points were determined on a Kofler melting-point apparatus and are uncorrected .^{1}HNMR spectra were recorded on Bruker ARX 200 (200 MHz) and Bruker AC300P (300 MHz) spectrometers, and ^{13}C NMR spectra were measured on a Bruker AC 300P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. The mass spectra (HRMS) were measured on a Variant MAT 311 at an ionizing potential of 70 eV in the Centre de Mesures Physiques de l'Ouest (CRMPO, Rennes). Elemental analysis was performed at Centre de Mesures Physiques de l' Ouest (CRMPO, Rennes). The UV-Vis spectra were recorded on a UV-vis Spectrometer Pye Unicam at Tiaret University. All solvents and reagents were purchased from Acros Organics and Aldrich Chemic and used without further purification unless otherwise stated.

Starting Materials. The preparation of the compounds **1** was obtained according to the literature [4] from disulfide carbon, amine in aqueous ammonia, and chloroacetone by Hantzsch's cyclization.

General procedure for the synthesis of products 3a and 3b: (Method A, Entry 3). The Δ-4-thiazolinethione **1** (50mmol, 1eq) was dissolved in 60ml of 1, 2 dichloroethane with DMF (51.48mmol, 1.05eq, V= 4ml). The mixture was stirred for 10min at 0°C. The phosphorus oxychloride (51.48mmol, 1.05eq, V= 4.8ml) was added by slow addition. The reaction mixture was left at room temperature for 1h and heated at 80°C for 3h. The cooled reaction mixture was poured into ice cold water (30ml) and basified with NaOH solution (4M) to pH 9. The solid that separated was filtered, washed with water and crystallized from ethanol / water (80/20) to give compounds Δ-4-thiazolinethione -5-carbaldehydes **3.**

2, 3- dihydro -3, 4- dimethyl- 2- thioxothiazole - 5- carbaldehyde (3a). Yield: 75%. Orange crystals; mp: 140°C. **^{1}HNMR (300MHZ, $CDCl_3$/TMS) δppm** = 2.67(s, 3H, *C*H_3-thiazol); 3.69(s, 3H, CH_3-N); 9.8(s,1H, CHO). **^{13}CNMR (75MHZ, $CDCl_3$/TMS) δppm** = 14.20 (q, J = 131.2Hz, *C*H_3-Me,); 34.36 (q, J = 142.6Hz, *C*H_3-N); 122.26(dq, J = 32.01Hz, J = 3.9; C_5); 152.07 (sq, J = 4Hz, C_4); 179.66(d, J = 181Hz, CHO); 190.08(sq, J = 4Hz, C=S). HRMS (EI) $M.^+$ for $C_6H_7N0S_2$ calcd.: 172.9969; found: 172.9964.

2, 3- Dihydro -4- methyl -3- phenyl -2- thioxothiazole -5- carbaldéhyde (3b). Yield: 46%.brown crystals; mp : 234°C. **^{1}HNMR 300MHZ, $CDCl_3$/TMS) δppm** = 2.31(s, 3H, Methiazol); 7.2-7.62 (m,5H); 9.84(s,1H,CHO). **^{13}CNMR (75MHZ, $CDCl_3$/TMS) δppm** = 14.64(q, J= 131.31Hz, *C*H_3thiazol); 123.38; 128.09; 130.34; 130.41 (Car); 136.8(C5); 150.38 C4); 178.49 (d, J = 180.5Hz, CHO); 192.03(C=S). HRMS (EI) $M.^+$ for $C_{11}H_9NOS_2$ calcd.: 235.0125; found: 235.0117.

Synthesis of 2, 3-Dihydro-3-((1E)-2-(2, 3-dihydro-3,4-diméthyl-2- thioxothiazol-5-yl) vinyl)-4- méthyl-2-thioxothiazole-5-carbaldéhyde (3c) Method B. Phosphorus oxychloride (50mmol, V= 4.7ml) was added dropwise at 0°C to DMF (775.2mmol, V = 60ml) and the reaction mixture was stirred for 20min. Thione **1a**

(50mmol, m= 7.25g) dissolved in 20ml of DMF was added and maintained at room temperature for 1h. The mixture reaction was stirred at 80°C for 18h. After cooling, the mixture was poured into ice water and basified with NaOH (4M) and stirring for 4h. The solide was filtered, washed with ethanol /water (80/20).

Yield: 97%. Orange solid; mp > 260°C. **^{1}HNMR 300MHZ, $CDCl_3$/TMS) δppm** = 9.55(s, 1H, CHO); 7.21-7.32(d, 1H, J = 15.2Hz); 6.32-6.37(d, 1H, J = 15.3Hz); 3.77(s, 3H, Me-Nthiazol **1**); 3.75(s, 3H, Me_4 thiazol **1**); 2.9(s, 3H, Me_4thiazol **2**). **^{13}CNMR (75MHZ, $CDCl_3$/TMS) δppm** = 190.8(C=S); 187.86(C=S); 182.87(dq, J=186Hz, J = 4.89Hz, CHO); 155.6 (C_4thiazol **1**); 154.01(C_4thiazol **2**); 132.46(d, J= 161Hz,CH = C) ; 120.6(d,J= 162Hz,CH=C); 116..81 (C_5thiazol); 113.01 (C_5thiaz); 35.27 (q, J = 142.2Hz, Me-Nthiaz **1**); 13.58(q, J = 128.2Hz, Me-thiazol **1**); 13.50(q, J = 18.1Hz, Me-thiazol **2**). HRMS (EI) $M.^+$ for $C_{12}H_{12}N_2OS_4$ calcd.: 327. 9832; found: 327.9838.

General procedure for the preparation of Iminothiazolinethiones 4a-e. An equimolar mixture of **3a-b** (5mmol) and primary aromatic amines (6 mmol) in absolute ethanol (20 mL) was heated under reflux for 1 h. The precipitate formed after cooling was filtered off, washed with cold ethanol, dried, and recrystallized from ethanol to give products **4.**

3, 4-Diméthyl-5-((E)-(phénylimino) méthyl) thiazole-2(3H) -thione (4a). Yield: 82%. Yellow crystals; mp : 188°C. **^{1}HNMR (200MHZ, $CDCl_3$/TMS) δppm** = 2.49(s, 3H, Me_4); 3.68(s, 3H, Me-N); 7.20-7.41(m, 5H); 8.37(s, 1H,CHN). **^{13}CNMR (50MHZ, $CDCl_3$/TMS) δppm** = 13.98(Me_4thiazol) ; 34.25(Me-N) ; 115.13(C_5); 120 .93; 126.50; 129.27; 143.10; (C_{ar}); 147.58 (CH = N, J = 177Hz); 150.88 (C_4); 189.47(C=S). HRMS (EI) $M.^+$ for $C_{12}H_{12}N_2S_2$ calcd.: 248.0443; found: 248.0453.

5-((E)-(1-phényléthylimino) méthyl)-3, 4-diméthylthiazole-2(3H)-thione (4b). Yield : 90% ; yellow solid ; mp : 196°C. **^{1}HNMR (200MHZ, $CDCl_3$/TMS) δppm** =1.58(d, 3H, J= 6.63Hz); 2.4(s,3H, Me_4thiazol); 3.57(s,3H, Me-N); 4.47(q,1H, J= 6.6Hz); 7.2- 7.40(m, 5H); 8.29(s,1H, CH= N).**^{13}C NMR (50MHZ, $CDCl_3$/TMS) δppm** = 13.73 (Me_4thiazol) ; 25.02 (MeCPh) ; 34.17 (Me-N); 69.42 (CHMe); 116.52; 121.87, 126.2, 126.94; 128.2 (Car); 141.10; 144.61(C_4); 147.88 (CH = N, J= 177Hz); 188.93(C = S). **HRMS (EI):** $M.^+$ for $C_{14}H_{16}N_2S_2$ calcd.: 276. 0755; found: 276. 0765.

5-((E)-(p-tolylimino)méthyl)-3,4-diméthylthiazole-2(3H)-thione (4c). Yield: 96%; yellow solid; mp: 146°C. **^{1}HNMR (300MHZ, $CDCl_3$/ TMS) δppm** = 2.29(s, 3H, Me-thiazol); 2.65(s,3H,Me-ptolyl); 3.67(s, 3H, Me-N); 7.05-7.38(2d, 4H); 8.55(s,1H,CH=N). **^{13}C NMR (75MHZ, $CDCl_3$/TMS) δppm**=13.87(q, J= 132.1Hz, Me_4thiaz); 21.17(q, J= 127.2Hz, Me-p tolyl); 35.35(q, J= 143.8Hz); 116.68 (C_5); 120.7; 125.87; 130.20 (Car); 142.95(C_4); 146.68(d, J= 177Hz, CH=N); 190.70(, C=S). HRMS (EI) $M.^+$ for $C_{13}H_{14}N_2S_2$ calcd.: 262,0598; found: 262,0613.

5- ((E)-(Benzylimino) méthyl)-3, 4-diméthylthiazole-2(3H)-thione (4d). Yield: 83%; yellow cristals; mp: 158°C. **^{1}HNMR (300MHZ, DMSO) δppm** = 8.62NMR (s, 1H, CHN); 7.36-7.22 (m, 5H); 4.70 (s, 2H, CH_2Ph); 3.61(s, 3H, Me Nthiazol); 2.50(s, 3H, Me_4-thiazol).**^{13}C(75MHZ, DMSO) δppm** = 187.17(C=S); 152.09 (HC = N, J = 177Hz); 144.07; 139.29; 128.35; 128.27; 127.81; 126.79; 119.96; 63.22; 34.13 (MeN); 13.33 (Methiazol). **HRMS (EI):** $M.^+$ for $C_{13}H_4N_2S_2$ calcd.: 262.0598; found: 262.0591.

4- Méthyl-3-phényl-5-((E)-(phénylimino) methyl) thiazole-2(3H)-thione (4e). Yield: 86%; yellow cristals; mp: 190°C. **^{1}HNMR (300MHZ, $CDCl_3$/TMS) δppm** = 2.15(s, 3H, Me_4 thiazol); 7.1-7.6(m, 10H); 8.4(s,1H, CH=N). **^{13}C NMR (75MHZ, $CDCl_3$/TMS) δppm** = 14.63(Me); 115.4(C_5); 122.70; 126.48; 128.15; 129.1; 129.92; 130.28; 137.26; 143.72 (Car); 147.75(C_4); 150.90(C = N); 191.21 (C = S). **HRMS (EI):** $M.^+$ for $C_{17}H_{14}N_2S_2$ calcd.: 310.0598 ; found: 310.0595.

General procedure for the preparation of Thiazoliums Salts (5 a-c). A mixture of **4** (5 mmol), 15 mmol of CH_3I and 20 ml of CH_3CN is stirred at room temperature during 24 h. The resulting salt is filtered off and dried under vacuum.

3, 4-Diméthyl-2-(méthylthio)-5-[(phénylimino) méthyl]-1,3-thiazol-3-iumiodure(5a). Yield: 85%; yellow cristals; mp: 198°C. **^{1}HNMR (200MHZ, DMSO) δppm** = 2.52(s, 3H, Me_4); 2.6(s, 3H, Me-S); 3.88 (s, 3H, Me-N^+); 7.26-7.6 (m, 5H); 8.7 (s, 1H, CH = N). **HRMS (EI):** $M.^+$ for $C_{13}H_{15}N_2S_2$ calcd. 263, 0676; found: 263, 0673.

3, 4-Diméthyl-2-(méthylthio)-5-{[(1-phényléthyl) imino] méthyl}-1, 3-thiazol-3-ium iodure (5 b). Yield: 80%; dark yellow cristals; mp : 186°C. **^{1}HNMR (300HZ, D_2O) δppm** = 1.72 (s, 3H, Me-tolyl); 2.22 (s, 3H, Me_4); 2.40 (s, 3H, Me-S); 3.29 (s, 3H, Me-N); 6, 66-6.73 (2d, 4H); 9.39 (s,1H, CH = N).

3, 4-Diméthyl-5-{[(4-méthylphényl) imino] méthyl}-2-(méthylthio)-1,3-thiazol-3-ium iodure (5c). Yield: 95%; yellow cristals; mp: 212°C. **^{1}HNMR (300HZ, $CDCl_3$/TMS +TFA) δppm** = 1.8(d, 3H, J = 6.9Hz, Me_4 thiazol); 2.76 (s, Me-S); 2.90 (Me-N); 3.8(s, MeCH); 5.9(m, 1H, CH, J= 6.8Hz); 7.7-7.5(m,).

General procedure for the synthesis of Schiff bases chromophores 6a-d. Activated methylene H_2A (10mmol) was added to a solution of thiazolium salts **5** (10mmol) in acetone (30ml). After stirring 5min at room temperature, triethylamine was added (2ml). The reaction mixture immediately turns red. The magnetic stirring is maintained at room temperature overnight. The solid obtained is filtered and washed with acetone.

(5E)-3-Méthyl-5-(3, 4-diméthyl-5-((phénylimino) méthyl)thiazol -2(3H)-ylidène)-2-thioxo-thiazo lidin-4-one (6a). Yield: 80%; red solid; mp > 260°C. UV-Vis (MeOH) λmax=502nm **^{1}HNMR (200HZ, $CDCl_3$/TMS +TFA) δppm** = 2 .78(s, 3H, Me_4 thiazol); 3.58 (s, 3H, Me-Nrhod); 3.97(s, 3H, Me-N thiazol); 7.4-7.7 (m, 5H); 8.91(s, 1H, CH = N). **HRMS (EI):** M.$^+$ for $C_{16}H_{15}N_3OS_3^+$ calcd.: 361,0377; found: 361, 0352. Anal.calcd for $C_{16}H_{15}N_3OS_3$: C, 53.16; H, 4.18; N, 11.62; S, 26.61. Found: C, 53.20; H, 4.22; N, 11.68; S, 26.70.

(5E)-[3,4-Diméthyl-5-{[(1-phényléthyl)imino]méthyl}-1,3-thiazol-2(3*H*)-ylidène]-3-méthyl-2-thioxo-1,3-thiazolidin-4-one (6b).Yield : 87% ; dark green solid ; mp : > 260°C. UV-Vis(MeOH) λmax=420nm. **^{1}HNMR (300HZ, $CDCl_3$/TMS +TFA) δppm** = = 1.7(d,3H,J= 7.36Hz); 2.4(s, 3H, Me_4); 3.3 (s, 3H, Me-Nrhod); 3.8 (s, 3H, Me_4-thiazol); 4.9 (m,1H, J = 6.8Hz); 7.15-7.3 (m,5H); 8,4 (s, 1H, CH = N).**^{13}CNMR (75MHZ,$CDCl_3$/TMS+ TFA) δppm** = 13.9(s,3H,J= 132.4Hz, Me_4 thiazol);20.30(qd, J = 130Hz, MeCH);31.63 (q, J =1 43Hz, Me-Nrhod) ;35.93 (q, J = 143.7Hz, Me-Nthiazol); 64.2 (dm, J= 143.8, CHMe); 93.05(C5rhod); 109.45(C5thiaz); 112.74; 116.52; 126.66; 129.49; 129.66; 130.08; 136.84; 164.25 (d, J= 197Hz, CH=N); 167.23(C=O), ; 188.22(C=S)150.39(C_4);154.2(C_2thiaz); 167.23(C=O); 188.22(C=S). **HRMS (EI):** M.$^+$ for $C_{18}H_{19}N_3OS_3^+$ calcd: 389, 0690; found: 389, 0694. Anal. Calcd for $C_{18}H_{19}N_3OS_3$: C, 55.50; H, 4.92; N, 10.79; S, 24.69. Found: C, 55.61; H, 5.01; N, 10.86; S, 24.79.

(5E)-[3,4-Diméthyl-5-[(4-méthylphényl)imino]méthyl}-1,3-thiazol-2(3*H*)-ylidène]-3-méthyl-2-thioxo-1,3-thiazolidin-4-one (6c).Yield : 79% ; dark red solid ; mp > 260°C. UV-Vis (MeOH) λmax= 489nm. **^{1}HNMR (300HZ, $CDCl_3$/TMS +TFA) δppm** = 2.4 (s, 3H); 2.72 (s, 3H, Me_4); 3.5(s, 3H, Me-rhod); 3.92 (s, 3H, Me-Nthiazol);7.24-7.40 (m, 4H); 8.83 (s,1H, CH = N). **^{13}C NMR(75MHZ,$CDCl_3$/TMS) δppm** = 13.95 (q, J = 132.Hz, Me_4-thiazol) ;21.15(q, J = 127Hz, Me-tolyl) ;31.7 (q, 143.3Hz, Me-Nrhod) ; 36.3 (q, J = 143.7Hz, Me-Nthiazol);94.58 (C_5rhod) ; 109.53 (C_5thiazol);(119.97 ;134.8 C_{ar}) ;150.58 (C_2thiazol); 163.72(d, J = 190Hz, CH = N) ;168.3 (C = O);189.34 (C = S). **HRMS (EI):** M.$^+$ for $C_{17}H_{17}N_3OS_3^+$ calcd.: 375,0534; found: 375, 0539. Anal. Calcd for $C_{17}H_{17}N_3OS_3$: C, 54.37; H, 4.56; N, 11.19; S, 25.62. Found: C, 54.39; H, 4.62; N, 11.25; S, 25.69

2-(3,4-Diméthyl-5-((phénylimino)méthyl)thiazol-2(3H)-ylidène)malononitrile(6d). Yield: 82% ; dark yellow solid ; mp : > 260°C. UV-Vis (MeOH) λmax= 418nm. **^{1}HNMR (300HZ, $CDCl_3$/TMS +TFA) δppm** = 2.6(s, 3H, Me-$_4$) ; 2.9 (s, 3H, NMe); 7.44-7.6 (m, 5H); 9.01(s, 1H, CH=N). **HRMS (EI):** M.$^+$ for $C_{15}H_{12}N_4OS^+$ calcd.: 280.0782; found: 280.0792. Anal. Calcd for $C_{15}H_{12}N_4S$: C, 64.26; H, 4.31; N, 19.98; S, 11.44. Found: C, 64.32; H, 4.38; N, 11.25; S, 19.26.

Results and Discussion

The formylation reaction of Δ-4-thiazolinethione **1a** using V-H reagent with different amounts of $POCl_3$/DMF and at different reaction temperatures has investigated in order to optimize the reaction conditions. The optimization of the amounts of phosphorus oxychloride and DMF is summarized in Table 1. It has been found that the best yield of the corresponding formyl **3a** has been obtained at 80°C for 3 hours with 1equiv of $POCl_3$/DMF in 1,2 dichloroethane (Table1, Entry 3). Without chlorinated solvents such as 1, 2 dichloroethane, has improved yield of 26% to 55 %.(Entry 1-2). Using 2eq of phosphorus oxychloride/DMF and shorter reaction times at 60°C has led to aldehyde **3a** in 62% yields (Entry 4). At room temperature, **3a** has not been obtained (Entry5).

Therefore, the same V.H formylation of **1a** with DMF/$POCl_3$ at 80°C for 18h has produced a mixture of formyl derivatives. The mixture was purified by column chromatography on silica gel (CH_2Cl_2) to give **3a** (60%) and **3c** (15%) (Table 1, Entry 6).

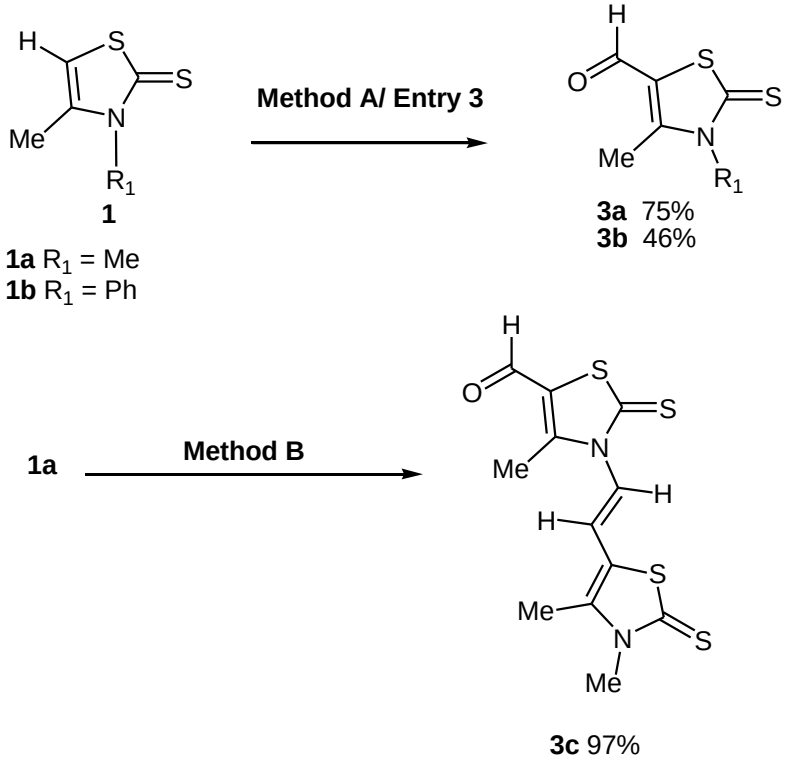
Table1. Selected optimization of Vilsmeier-Haack formylation Δ-4-thiazolinethione **1a (Method A)**

Entry	$POCl_3$(equiv)	DMF(equiv)	DCE[b] (ml)	T°C	Time(h)	Yield(%)[a] 3a/3c
1	1	4	-	60	18	26/00
2	1	1	-	80	18	55/00
3	1	1	60	80	3	75/00
4	2	2	60	60	3	62/00
5	1	4	-	rt	24	00/00
6	1	4	60	80	18	60/15

[a] Isolated yield
[b] 1, 2 dichloroethane

We adopted the experimental protocol according to Entry 3 for the synthesis of **3a** and **3b**.

The formylation reaction of Δ-4-thiazolinethione **1a-b** in dichloroethane (60ml) with DMF/ $POCl_3$(1eq) at 0°C ; followed by stirring reaction mixture at 80°C for 3h and neutralization with NaOH (4M) has afforded to 2,3-dihydro-3,4-dimethyl-2-methylenethiazole-5-carbaldehyde **3a** in 75% yield and 2,3-dihydro-4-methyl-2-methylene-3-phenylthiazole-5-carbaldehyde **3b** in 46% yield (Scheme1).



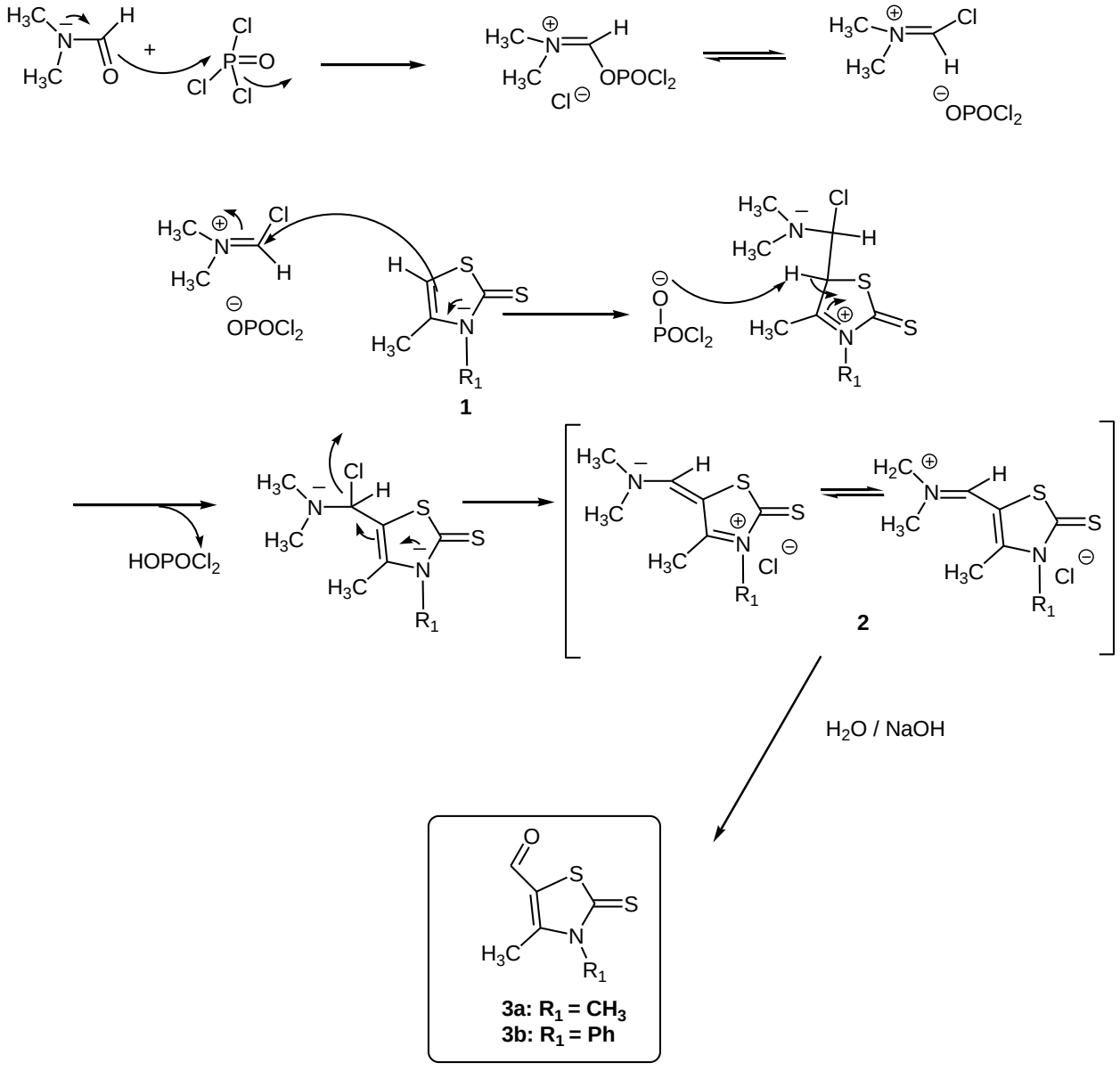
Scheme 1

The structure of the compound **3c** was elucidated from its spectral data.

The ^{1}HNMR spectrum of **3c** showed the presence of two doublet at 6.34 and 7.32ppm corresponding to CH=CH, with coupling constants of J= 15.34Hz, characteristic of E configuration. The proton signal appearing around 9.55ppm confirmed the presence of group formyl CHO at C_5 position of the Δ-4-thiazolinethione Δ-4-thiazolinethione **1a.**

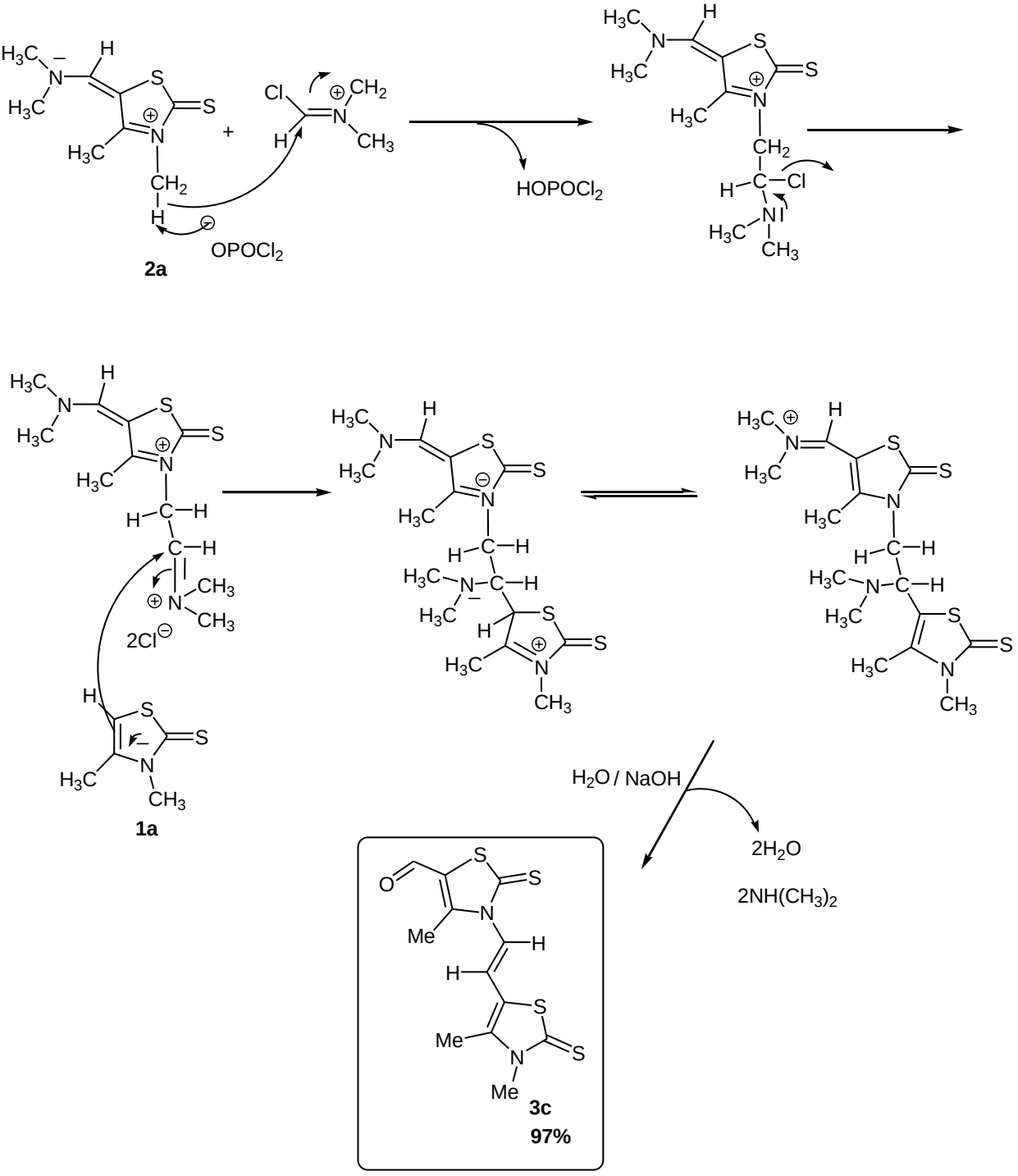
This unexpected result (Table 1, Entry 6) leads us to investigate this formylation using a different procedure from the first, by the direct preparation of the **3c** as exclusive product from **1a** under VH conditions **(Method B)**: The $POCl_3$/DMF (1equiv) /15.5eq) is stirred at 0 ° C, a thione solution **1a** in DMF (20ml) is added to the reactant in small fractions VH. The mixture is brought to réactionnnel 1h at rt, then heated to 80 ° C for 18 h. The aldehyde **3c** is obtained quantitatively (97%) (Scheme1).

These results show that in the case of Vilsmeier formylation of thiazoline thione **1a**, the reaction occurs in the most activated position 3 and 5. The results indicate that the 5-position is still favoured compared to the 3-position. The structures were confirmed by ^{1}H, ^{13}C NMR and HRMS. The formyl group has been introduced at carbon C_5 as proposed in the following mechanisms (Scheme 2).



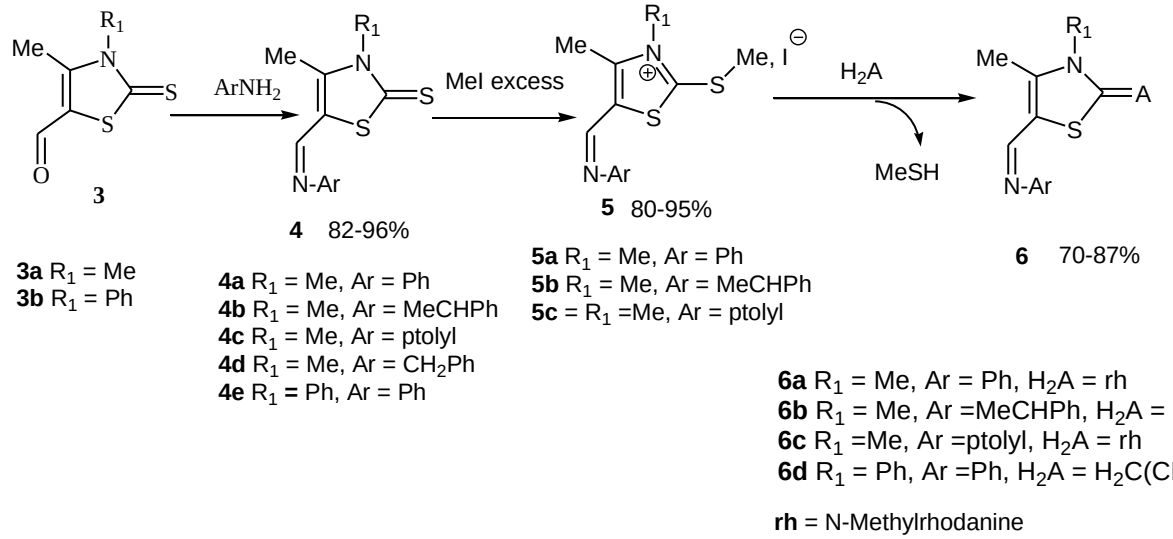
Scheme 2

Initially, chloromethyleniminium salt interacts with the thione **1a** to give in situ the corresponding monomethyliminium salt **2a** which further reacts with another chloromethyleniminium salt to afford after neutralization with NaOH the formyl **3c** (Scheme 3).



Scheme 3

On the other hand, a large number of heterocyclic Schiff bases containing thiazole moiety have been reported to possess several biological activities.[11] Some of the Schiff bases were used as chromophores in NLO applications.[12] The synthetic strategy adopted to obtain the target compounds is depicted in the scheme 4.



Scheme 4

Condensation of thiazolinethione-5-carboxaldehyde **3a-b** with primary aromatic amines in refluxing ethanol gave Schiff bases **4a-e** in good yields (82-96%, Table 2). These Schiff bases are engaged in an alkylation reaction in the presence of an excess of iodomethane at room temperature for 2h. Salts **5a-c** (table 2) obtained were isolated by filtration and purified by simply washing with acetone. The condensation reaction of the salt **5** with activated methylenes in the presence of triethylamine in acetone at room temperature leads to imines chromophores **6** with good yields (70-87%, Table3)). All compounds were unambiguous confirmed by their analytical and spectral data.

Table 2. Physico-chemical data of Schiff bases 4a-e and thiazoliums salts 5a-d

Composés	R_1	R_2	Yield %	F°C
4a	*Me*	*Ph*	*82*	*188*
4b	*Me*	*CHMePh*	*90*	*196*
4c	*Me*	*Ptolyl*	*96*	*146*
4d	*Me*	*CH_2Ph*	*83*	*158*
4e	*Ph*	*Ph*	*86*	*190*
5a	*Me*	*Ph*	*85*	*198*
5b	*Me*	*CHMePh*	*80*	*186*
5c	*Me*	*Ptolyl*	*95*	*212*
5d	*Ph*	*CH_2Ph*	*87*	*202*

Table 3. Physico-chemical data of 6a-h

Compound	R_1	R_2	H_2A	Yield (%)	F°C	Rf Value (CH_2Cl_2)
6a	Me	Ph	N-Me-rhodanine	80	>260	0.55
6b	Me	CHMePh	N-Me-rhodanine	87	>260	0.50
6c	Me	Ptolyl	N-Me-rhodanine	79	>260	0.52
6d	Me	Ph	Malononitrile	82	>260	0.49
6e	Ph	Ph	N-Me-rhodanine	76	>260	0.53
6f	Ph	CHMePh	N-Me-rhodanine	84	>260	0.54
6g	Ph	ptolyl	N-Me-rhodanine	70	>260	0.58
6h	Ph	Ph	Malononitrile	84	>260	0.60

Conclusion

In summary, formyl thiazolinethiones **3** have been synthesized through the V-H reaction starting from easily available precursor as Δ-4-thiazolinethione **1** which is obtained by Hantzsch's reaction. Four synthetic routes have been widely used for the preparation of Schiff bases chromophores **6a-d** ; Formylation of **1a-b**, condensation of an aldehyde **3a-b** with primary aromatic amines, followed by alkylation with an excess iodide methane and finally, condensation with activated methylenes. The formation of formyl **3c** was described and a mechanism was proposed. Formyl derivative **3c** compound containing two thiazoles moiety in a single molecular framework , could be used as important building blocks in the synthesis of various heterocycles which often show high biological activities and promising applications in optoelectronics.

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