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CYCLOCONDENSATION OF 2-LITHIOMETHYLTHIAZOLES AND 2-LITHIOMETHYLTHIAZOLINE WITH α-OXOKETENE DITHIOACETALS: SYNTHESIS OF SUBSTITUTED AND ANNELATED THIAZOLO- AND DIHYDROTHIAZOLO[3,2-*a*]PYRIDINIUM COMPOUNDS

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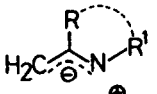
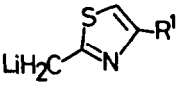
Abstract: *The oxoketene dithioacetals* **1** *undergo regioselective 1,2-addition with 2-lithiomethyl-4-methylthiazole (***2a***) and 2-lithiomethylthiazoline (3) to afford the carbinol acetals* **4** *which on borontrifluoride etherate assisted cyclization yield the corresponding substituted and annelated 3-methyl-5-methylthiothiazolo[3,2-a]pyridinium tetrafluoroborates (***5a-q***, **8a,b**, **10**, **12**) and the dihydro derivatives (***23-25***) respectively in good yields. The corresponding 2-methyl-5-phenylthiazole (***16***) however underwent both nuclear and side chain deprotonation and yielded a mixture of products under similar reaction conditions.*

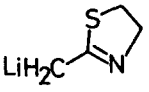
The α-oxoketene dithioacetals have been the subject of intensive investigation in this and other laboratories for the chemo-, stereo- and regioselective construction of new C-C bond forming reactions using organometallic reagents[1]. As a part of this strategy, we have developed a general method for aromatic and heteroaromatic annelation by reacting these intermediates with 1,3-binucleophilic species like allyl, benzyl, propargyl Grignard reagents, 5-lithiomethylisoxazole and lithioacetonitrile[2-7]. The resulting carbinolacetals obtained by regioselective 1,2-addition of these reagents underwent facile acid assisted cyclization to afford fully aromatized ring systems. This methodology was particularly useful to construct the bridgehead heteroaromatic systems through the reaction of α-oxoketene dithioacetals with azaallyl anions of the general formula **A**. Thus, the 2-picolyllithium underwent smooth 1,2-addition with **1** to give the corresponding carbinolacetals which on borontrifluoride etherate catalyzed cyclization yielded the corresponding substituted and fused quinolizinium tetrafluoroborate salts in high yields[8]. In continuation of these studies, we have investigated the reaction of 2-lithiomethylthiazoles (**2a,b**) and 2-



A



2a R^1=Me
2b R^1=C_6H_5

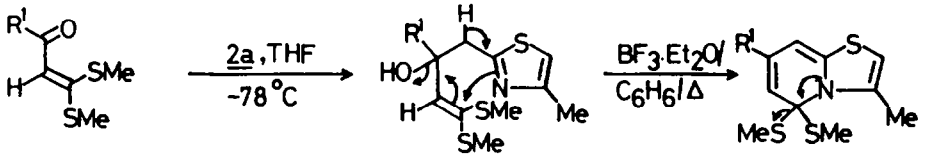


3

lithiomethylthiazoline (**3**) with α-oxoketene dithioacetals with a view to formulating an efficient methodology for the synthesis of thiazolo- and

dihydrothiazolo[3,2-*a*]pyridinium salts and our results are presented in this paper.

In principle, the construction of thiazolo[3,2-*a*]pyridine ring systems can be achieved either from a preconstructed 2-thiopyridine (azine approach) or from the thiazole derivatives (azole approach). Generally, most literature methods are confined to azine approach and the azole approach starting from the preconstructed thiazole ring to build the pyridine ring is scantly described in the literature[9,10]. However, both the approaches do not offer much scope for substituent variation in the pyridine ring. The α-oxoketene dithioacetal approach for heteroaromatic annelation to construct thiazolo- and dihydrothiazolopyridine ring systems *via* their reaction with respective lithiomethylthiazole and thiazoline appeared to be an attractive method which would greatly enhance the synthetic scope for this class of compounds. Thus, in an optimized reaction condition, 2-lithiomethyl-4-methylthiazole (2a) generated by deprotonation of the corresponding 2,4-dimethylthiazole with n-butyllithium, was reacted with 1a, when the corresponding carbinolacetal 4a was obtained in nearly quantitative yield. The carbinol 4a was directly treated with borontrifluoride etherate in refluxing benzene to afford the expected 3-methyl-5-methylthio-7-phenylthiazolo[3,2-a]-pyridinium tetrafluoroborate (5a) in 55% yield. The other substituted thiazolopyridines 5b-f were similarly obtained from the respective 1b-f in 51-68% overall yields. Similarly, the carbinolacetal 4g was obtained in high yield when the α-cinnamoylketene dithioacetal 1g was reacted with 2a to afford the corresponding cyclized product 5g only in 42% yield (Scheme 1).



1 4 6

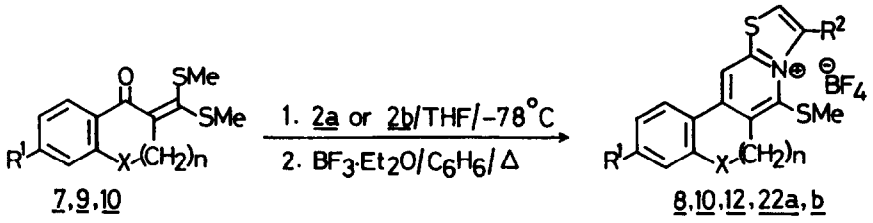
1, 4, 5a $R^1 = C_6H_5$
b $R^1 = 4\text{-}MeOC_6H_4$
c R^1 = 2-naphthyl
d R^1 = 2-furyl
e R^1 = 2-thienyl
f R^1 = Me
g $R^1 = 3\text{-}MeOC_6H_4CH{=}CH$
1h $R^1 = C_6H_5CH{=}CH$
1i $R^1 = C_6H_5CH{=}CH{-}CH{=}CH$

5

Scheme 1

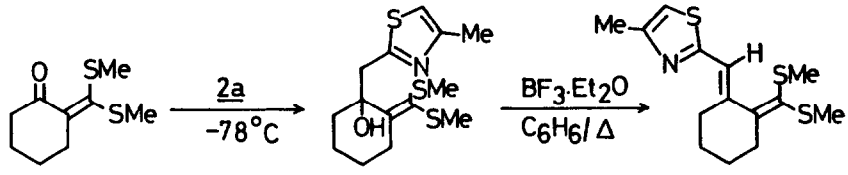
The reaction of 2a with cylic α-oxoketene dithioacetals was next examined to extend the methodology to annelated thiazolopyridines (Scheme 2). Thus, the hitherto ureported thiazolopyridinium salts 8a,b, 10 and 12 were obtained in good yields from the respective 7a,b, 9 and 11 under the described conditions. However, the corresponding carbinolacetal 14 derived from

dithioacetal of cyclohexanone failed to give the thiazolopyridinium salt under similar reaction conditions and the product isolated was characterized as the open-chain diene 15 on the basis of its IR and ^{1}H NMR spectral data.



7,9,10 8,10,12,22a,b

7,8a R^1=H ; X = CH_2 ; n=1 ; R^2=Me
b R^1=MeO ; X = CH_2 ; n=1 ; R^2=Me
9,10 R^1=H ; X=CH_2 ; n=2 ; R^2=Me
11,12 R^1=Me ; X=S ; n=2 ; R^2=Me
7,22a R^1=H ; X=CH_2 ; n=1 ; R^2=C_6H_5
7,22b R^1=MeO ; X=CH_2 ; n=1 ; R^2=C_6H_5

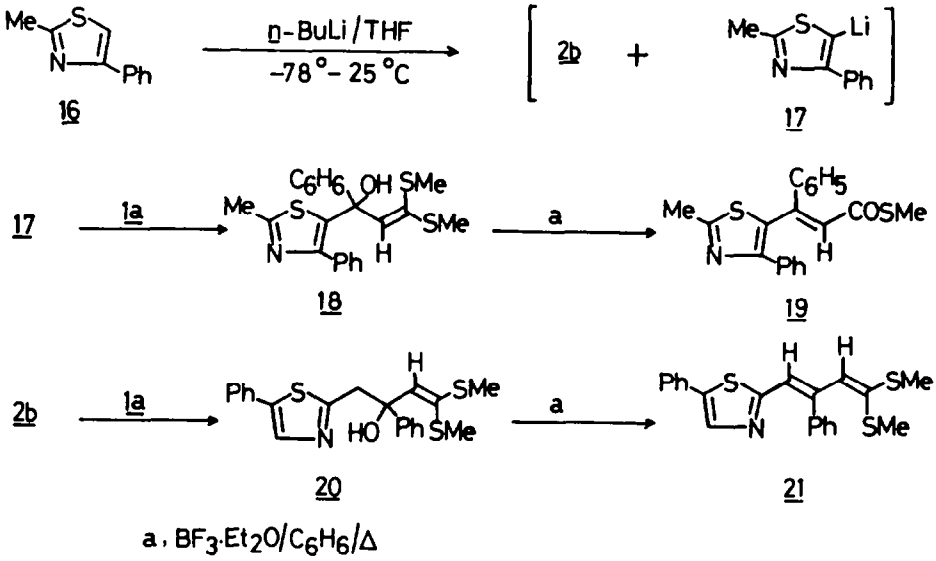


13 14 15

Scheme 2

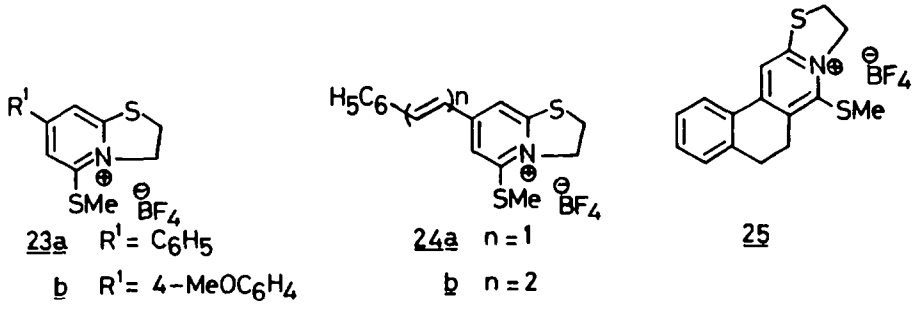
The reaction of 2-lithiomethyl-4-phenylthiazole (2b) with 1a was next investigated. The acidities of C-5 and 2-methyl protons in 2-methyl-4-phenylthiazole (16) are reported to be very close and it has been shown that the 5-lithio salt 17 is formed kinetically with n-butyllithium at low temperature (-78°C), while at higher temperature (25°C), the thermodynamic acidity prevails, producing the lithiomethyl anion 2b[11]. The metallation, at these two positions, is also dependent on the strength and bulk of the base employed. In one of the experiments, when 1a was reacted with lithiated 16 at -78°C, the reaction mixture after work-up and treatment with borontrifluoride etherate afford two products which were characterized as the enethioester 19 (22%) and the diene 21 (38%) (Scheme 3). The products 19 and 21 are evidently derived from the corresponding carbinolacetals 18 and 20 formed by 1,2-addition of 1a to lithio salts 17 and 2b respectively. When the reaction was carried out at higher temperature (25°C), yield of the diene 21 was increased to 45% while that of thioester 19 was reduced to a poor 10%. However, attempted deprotonation of 16 with other bases (LDA, t-BuLi) and its subsequent reaction with 1a under varying conditions yielded either the same products (19 and 21) in varying yields or resulted in an intractable mixture of products[12]. On the otherhand, when the dithioacetals 7a,b from α-tetralones, were reacted with lithiated 16 either at low or

higher temperature under the described reaction conditions, only the corresponding 6,7-annelated thiazolopyridinium salts 22a and 22b were obtained in moderate yields.



Scheme 3

Cycloaromatization was next investigated on the reaction of 2-lithiomethylthiazoline (3) with 1 leading to the synthesis of dihydrothiazolopyridinium compounds. Thus, 3 underwent facile 1,2-addition and borontrifluoride etherate cyclization with acyclic (1a, 1b, 1h, 1i) and cyclic (7a) oxoketene dithioacetals to afford the corresponding dihydro derivatives 23-25 in overall high yields (Scheme 4).



Scheme 4

The present cycloaromatization involving the reaction of 2-lithiomethylthiazoles and the corresponding thiazoline with α-oxoketene dithioacetals provides a novel entry to the thiazolopyridinium compounds with a greater degree of substitutent variations.

EXPERIMENTAL SECTION

Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer. ^{1}H NMR spectra were determined on a Varian EM-390 (90 MHz) spectrometer in TFA/$CDCl_3$ unless otherwise indicated and chemical shift values are expressed in ppm downfield from the internal standard tetramethylsilane. ^{13}C NMR spectrum was recorded on a Brucker WM-400 spectrometer. Mass spectra were obtained on a Jeol JMS D-300 spectrometer. Elemental analysis were performed on a Heraeus CHN-O-RAPID instrument. THF was freshly distilled from sodium-benzophenone ketyl prior to use.

2,4-Dimethylthiazole and 2-methyl-4-phenylthiazole were prepared as reported[13]. 2-Methylthiazoline was purchased from Aldrich Co. and used as received without further purification and the required α-oxoketene dithioacetals were prepared according to the reported procedure[14,15].

Reaction of 2-lithiomethyl-4-methylthiazole (2a) with α-oxoketene dithioacetals (1a-g,7a,b,9,11): General procedure.- To a stirred and cooled (-78°C) solution of freshly distilled 2,4-dimethylthiazole (1.13g, 10 mmol), in THF (20 ml) n-butyllithium (12 mmol) in diethylether was added *via* a syringe under nitrogen atmosphere and the suspension was further stirred for 30 min. maintaining the temperature at -78°C. Lithiation was indicated by the appearance of a reddish brown colour. A solution of oxoketene dithioacetal (10 mmol) in THF (20 ml) was added *via* a syringe and the reaction mixture was further stirred for 1 hr. After warming to room temperature, it was quenched with saturated NH_4Cl solution (200 ml) and the organic layer was separated. The aqueous layer was extracted with ether (100 ml) and the combined organic layer was washed with water (200 ml), dried (Na_2SO_4) and evaporated to afford the crude carbinolacetals (4) in nearly quantitative yield.

Cyclization of Carbinolacetals with Borontrifluoride Etherate: Synthesis of Thiazolo[3,2-*a*]pyridinium tetrafluoroborates (5a-g,8a,b,10,12): General Procedure.- To a solution of carbinolacetals (ca. 10 mmol, obtained from the previous reaction) in dry benzene (50 ml), $BF_3.Et_2O$ (6 ml) was added and the reaction mixture was refluxed with stirring for 2.5 hr. The benzene layer was separated by decantation after cooling and the solid residue dissolved in minimum amount of EtOAc and neutralized with saturated $NaHCO_3$ solution. The thiazolopyridinium salts thus separated were filtered, washed with water (2x50 ml) and Et_2O (2x20 ml). Analytically pure products were obtained by recrystallization from suitable solvent.

3-Methyl-5-methylthio-7-phenylthiazolo[3,2-*a*]pyridinium tetrafluoroborate (5a) yellow solid (acetone), yield 55%, m.p. 247-248°C; IR(KBr) 1601,1500,1420,1020-1119 (br) cm^{-1}; δ_H2.91 (3H,s,CH_3), 3.30 (3H,s,SCH_3), 7.56-7.93 (7H,m,arom), 8.31 (1H,s,H-8). (Found: C, 49.99; H, 3.81; N,4.02. $C_{15}H_{14}NS_2BF_4$ requires: C, 50.15; H,3.93; N,3.90%); m/z 272 (34%, M^+-BF_4), 271(100), 256(62).

3-Methyl-5-methylthio-7-(4-methoxyphenyl)thiazolo[3,2-*a*]pyridinium tetrafluoroborate (5b) yellow solid (acetone), yield 68%; m.p. 284-285°C; IR(KBr) 1604, 1505, 1433, 1021-1122(br) cm^{-1}; δ_H2.90(3H,s,CH_3), 3.29 (3H,s,SCH_3), 4.00 (3H,s,OCH_3), 7.27 (2H,d,J=8.5Hz,arom), 7.61 (1H, s,arom), 7.74 (1H,s,arom), 7.89 (2H,d,J=8.5Hz,arom), 8.30 (1H,s,H-8). (Found: C,49.21; H, 4.03;N,3.71. $C_{16}H_{16}NOS_2BF_4$ requires: C,49.37; H,4.14; N,3.60%); m/z302 (33%, M^+-BF_4), 301 (55), 287(100).

3-Methyl-5-methylthio-7-(2-naphthyl)thiazolo[3,2-*a*]pyridinium tetrafluoroborate (5c) yellow solid (acetone), yield 66%; m.p. 312-313°C; IR(KBr) 1601,1491,1434, 1030-1119 (br) cm^{-1}; δ_H2.88(3H,s,CH_3), 3.20 (3H,s, SCH_3), 7.44-7.68 (5H,m,arom), 7.77-8.04 (4H,m,arom), 8.22 (1H,s,H-8). (Found: C,55.58; H,4.02; N,3.60. $C_{19}H_{16}NS_2BF_4$ requires: C, 55.76; H, 3.94; N,3.42%); m/z 322(24%, M^+-BF_4), 321(48), 306(84).

3-Methyl-5-methylthio-7-(2-furyl)thiazolo[3,2-*a*]pyridinium tetrafluoroborate (5d) yellow solid (acetone), yield 53%; m.p. 249-250°C; IR(KBr) 1609, 1501, 1477, 1421, 1009-1122(br) cm^{-1}; δ_H2.91(3H,s,CH_3), 3.26 (3H,s,SCH_3), 6.75 (1H,brs,H-3'furyl), 7.41 (1H,distorted t,H-4' furyl), 7.54 (1H,s,arom), 7.70 (1H.s,arom), 7.77 (1H,d,H-5' furyl), 8.26 (1H,s,H-8). (Found: C, 44.80; H, 3.53; N,4.22. $C_{13}H_{12}NOS_2BF_4$ requires: C, 44.71; H, 3.47; N, 4.01%); m/z 262 (42%, M^+-BF_4), 261(96), 246(100).

3-Methyl-5-methylthio-7-(2-thienyl)thiazolo[3,2-*a*]pyridinium tetrafluoroborate (5e) yellow solid (acetone), yield 62% m.p. 273-274°C; IR(KBr) 1600,1493,1433,1416,1026-1120(br) cm^{-1}; δ_H2.90(3H, s, CH_3), 3.23 (3H,s, SCH_3), 7.29 (1H,t,J=4.5Hz,H-4'thienyl), 7.53(1H,brs,arom), 7.67 (1H, brs,arom), 7.76 (1H,d,J=4.5Hz,H-3' thienyl), 7.88 (1H,d,J=4.0Hz,H-5' thienyl), 8.22 (1H,s,H-8). Found: C, 42.66; H,3.32; N,4.01. $C_{13}H_{12}NS_3BF_4$ requires: C,42.75; H,3.31;N,3.84%); m/z 278(37%,M^+-BF_4), 277(100), 262(97).

3-Methyl-5-methylthio-7-methylthiazolo[3,2-*a*]pyridinium tetrafluoroborate (5f) colourless solid (ethylacetate), yield 51%; m.p. 154-155°C; IR(KBr) 1609, 1515, 1457, 1440, 1422, 1025-1120 (br) cm^{-1}; δ_H2.65 (3H,s,CH_3), 2.83 (3H,s,CH_3), 3.23 (3H,s,SCH_3), 7.44 (1H,s,H-2), 7.59 (1H,s,H-6), 7.97 (1H,s,H-8). (Found: C,40.58; H,4.01; N,4.88. $C_{10}H_{12}NS_2BF_4$ requires: C,40.42; H,4.07; N, 4.71%); m/z 210 (44%, M^+-BF_4), 194(28).

3-Methyl-5-methylthio-7-(3-methoxystyryl)thiazolo[3,2-*a*]pyridinium tetrafluoroborate (5g) yellow solid (acetone), yield 42%; m.p. 293-294°C; IR(KBr) 1604,1530,1461,1430,1030-1125(br) cm^{-1}; δ_H2.88(3H,s,CH_3), 3.20 (3H,s,SCH_3), 3.98 (3H,s,OCH_3), 6.97-7.71 (8H,m,arom and olefinic), 8.13 (1H,brs,H-8). (Found: C,51.96; H,4.30; N,3.48. $C_{18}H_{18}NOS_2BF_4$ requires: C, 52.06; H,4.37; N,3.37%); m/z 328 (2%, M^+-BF_4), 313(79), 312(44).

3-Methyl-5-methylthio-6,7-dihydrothiazolo[3,2-*a*]phenanthroquinolinium tetrafluoroborate (8a) yellow solid (acetone), yield 69%; m.p. 193-194°C; IR(KBr) 1600,1581,1505,1431,1412,1028-1125(br) cm^{-1}; δ_H2.57(3H,s,CH_3), 3.11 (2H,t,J=7.0Hz,CH_2), 3.30 (3H,s,SCH_3), 3.64 (2H,t,J=7.0Hz,CH_2), 7.41-7.64(3H,m,arom), 7.77 (1H,s,H-2), 7.98 (1H,m,arom), 8.69 (1H,s,H-12). (Found: C, 53.21; H,4.13; N,3.70. $C_{17}H_{16}NS_2BF_4$ requires: C, 53.00; H,4.19; N,3.64%); m/z 283 [98%,M^+-BF_4 and CH_3], 250(44).

3-Methyl-5-methylthio-9-methoxy-6,7-dihydrothiazolo[3,2-*a*]phenanthroquinolinium tetrafluoroborate (8b) yellow solid (acetone), yield 68%; m.p. 278-279°C; IR(KBr) 1590, 1577, 1511, 1430, 1412, 1020-1121(br) cm^{-1}; δ_H2.56 (3H,s,CH_3), 3.10(2H,t,J=7.0Hz,CH_2) 3.29(3H,s,SCH_3), 3.60 (2H,t,J=7.0Hz,CH_2), 4.03 (3H,s,OCH_3), 6.99-7.23 (2H,m,arom), 7.70 (1H,s,H-2), 7.97 (1H,d,J=8.5Hz, H-11), 8.57 (1H, s,H-12). (Found:C,51.91; H,4.13; N,3.44. $C_{18}H_{18}NOS_2BF_4$ requires: C, 52.06; H, 4.37; N,3.37%); m/z 328 (6%, M^+-BF_4), 313(100).

3-Methyl-5-methylthio-7,8-dihydro-6H-benzocyclohepta[2,1-*d*]thiazolo[3,2-*a*]pyridinium tetrafluoroborate (10) colourless crystals (ethylacetate:hexane), yield 60%; m.p. 156-157°C; IR(KBr) 1602,1588,1500,1440,1412,1028-1116(br) cm^{-1}; δ_H($CDCl_3$) 2.26-2.78 (4H,m,CH_2), 2.57 (3H,s,CH_3), 2.77-3.36 (2H,m,CH_2), 3.29 (3H,s,SCH_3), 7.25-7.62 (4H,m,arom), 7.63 (1H,s,H-2), 8.13 (1H,s,H-13), δ_C($CDCl_3$) 21.01 (CH_3), 22.29 (SCH_3), 29.40, 30.51, 31.59(CH_2), 121.75, 122.40, 127.61, 128.78, 128.92, 131.05(CH,arom), 135.81, 139.47, 142.01, 142.79, 143.33, 150.06, 156.62 (quaternary C). (Found: C, 54.30; H,4.52; N,3.56. $C_{18}H_{18}NS_2BF_4$ requires: C, 54.15; H, 4.54; N, 3.51%); m/z 312(2%, M^+-BF_4), 311(3), 297(12).

3-Methyl-11-methyl-5-methylthio-6,7-dihydro[1]benzothiepino[4,5-*d*]thiazolo[3,2-*a*]pyridinium tetrafluoroborate (12) yellow solid (acetone), yield 69%; m.p. 239-240°C; IR(KBr) 1598,1576,1433,1411,1389,1030-1109(br) cm^{-1}; δ_H2.47(3H,s,CH_3), 2.57 (3H,s,CH_3), 3.34 (3H,s,SCH_3), 2.74-3.40 (2H,m,CH_2 merged with SCH_3), 3.59-4.23 (2H,m,CH_2), 7.50 (2H,brs,arom), 7.59 (1H,s,arom),7.88 (1H,brs,H-2), 8.29 (1H,s,H-13). (Found: C, 50.11; H, 4.30; N,3.38. $C_{18}H_{18}NS_3BF_4$ requires: C, 50.12; H,4.21; N, 3.25%); m/z 329 (2%, M^+-BF_4 and CH_3), 314(22), 313 (100), 298(85).

1,1-Bis(methylthio)methylene-2-(4-methylthiazolo)methylenecyclohexane (15) was obtained on treatment of carbinolacetal (14) with $BF_3.Et_2O$ under similar conditions. Work-up and silica gel column chromatography (EtOAc/hexane 1:20 as eluent) gave 15 as viscous brown liquid; yield 48%; IR(neat) 1598,1581,1505 cm^{-1}; $\delta_H(CDCl_3)$ 1.56-1.98 (4H,m,CH_2), 2.14 (3H,s,SCH_3), 2.40 (3H,s,SCH_3), 2.56-3.90 (4H,m,CH_2), 3.21 (3H,s,CH_3), 6.59 (1H,s,vinylic), 6.81 (1H,s,H-2). The diene (14) was found to be thermally unstable and its analytically pure sample could not be isolated.

Reaction of Lithiated 2-Methyl-4-Phenylthiazole (16) with α-Oxoketene Dithioacetals: Lithiation of 16 (1.75g, 10 mmol) with n-BuLi (12 mmol) at -78°C, and its reaction with 1a, 7a,b was carried out in the same manner as described for the reaction of 2a except for the longer stirring time (2 hr) after addition of oxoketene dithioacetals (procedure A). Work-up as described afforded viscous residues which were directly refluxed with $BF_3.Et_2O$ (6 ml) in C_6H_6 (50 ml) for 3 hr. The reaction mixture (from 1a) after cooling was neutralized with satd. $NaHCO_3$, the organic layer was separated and the aqueous layer was extracted with EtOAc (50 ml). The combined organic extracts were washed with water (50 ml) dried (Na_2SO_4) and evaporated to give a viscous residue which was subjected to column chromatography over silica gel. Elution with EtOAc/hexane (1:20) gave first the diene 21 followed by thioester (19).

In the case of thiazolopyridinium salts 22a,b the work-up after $BF_3.Et_2O$ treatment was similar to that described earlier. In an alternate reaction (Procedure B) the dithioacetal 1a was added after warming the lithiated salt of 16 to 25°C.

3-(2-Methyl-4-phenylthiazol-5-yl)-S-methylthiocinnamate (19) was isolated as yellow crystals (CH_2Cl_2: hexane), yield 22%(A); 10%(B); m.p. 115-116°C; IR(KBr) 1655,1589 cm^{-1}; $\delta_H(CDCl_3)$ 2.20 (3H,s,CH_3), 2.76 (3H,s,SCH_3), 6.69 (1H,s,=CH), 7.11-7.46 (8H,m,arom), 7.60-7.74 (2H,m,arom). (Found: C,68.19; H,4.76; N,4.09. $C_{20}H_{17}NOS_2$ requires: C, 68.34; H,4.88; N,3.99%); m/z 351 (9%, M^+), 304(100).

1,1-Bis(methylthio)-3-phenyl-4-(4-phenylthiazol-2-yl)butadiene (21) viscous brown liquid, yield 38%;IR(neat) 1598,1545,1472 cm^{-1}; $\delta_H(CDCl_3)$ 2.04 (3H,s,SCH_3), 2.39 (3H,s,SCH_3), 6.71 (7H, brs,vinylic), 7.19-7.61 (10H,m,arom and vinylic), 7.72-8.06 (2H,m,arom). The diene was found to be unstable and could not be purified for elemental data.

5-Methylthio-3-phenyl-6,7-dihydrothiazolo[3,2-*a*]phenanthroquinolinium tetrafluoroborate (22a) yellow solid (acetone), yield 43%; m.p. 254-255°C; IR(KBr) 1589,1510,1410,1027-1110(br)cm^{-1}; δ_H2.15 (3H,s,SCH_3), 3.06 (2H, distorted t, CH_2), 3.46 (2H,distorted t, CH_2), 7.34-7.71 (7H,m,arom), 7.82 (1H,s,H-2), 7.90-8.09 (2H,m,arom), 8.70 (1H,s,H-12). (Found: C,59.21; H,4.15; N,3.26. $C_{22}H_{18}NS_2BF_4$ requires: C, 59.07; H, 4.06; N, 3.13%).

9-Methoxy-5-methylthio-3-phenyl-6,7-dihydrothiazolo[3,2-*a*]phenanthroquinolinium tetrafluoroborate (22b) was isolated as yellow solid (acetone), yield 41%; m.p. 226-228°C;IR(KBr) 1587,1509,1411,1020-1101(br) cm^{-1}; δ_H2.13 (3H,s,SCH_3), 3.03 (2H,distorted t, CH_2), 3.43 (2H, distorted t, CH_2), 3.98 (3H,s,OCH_3), 6.88-7.13 (2H,m,arom), 7.33-7.64 (5H,m,arom), 7.74 (1H,s,H-2), 7.94 (1H,d,J=8.5Hz,arom), 8.54 (1H,s,H-12). (Found: C,58.02; H,4.38; N,3.20. $C_{23}H_{20}NOS_2BF_4$ requires: C,57.87; H,4.22; N,2.93%).

Reaction of α-Oxoketene Dithioacetals with 2-Lithiomethylthiazoline (3)[16]: Synthesis of 2,3-Dihydrothiazolo[3,2-*a*]pyridinium Tetrafluoroborates 23a,b,24a,b and 25: General Procedure.- The lithio salt 3 was generated by the general procedure described for 2a from 2-methyl-2-thiazoline (10 mmol) and n-BuLi (12 mmol) in THF at -78°C. The resulting pale yellow suspension was further stirred at -78°C (1.5 hr) followed by addition of appropriate oxoketene dithioacetal (10 mmol) in THF (20 ml). The reaction mixture was slowly warmed to room temperature (2 hr) with stirring and worked-up as described to give the corresponding carbinolacetals which were cyclized with $BF_3.Et_2O$ according to the general procedure (refluxing time 1.5 hr) followed by work-up to afford 23a,b,24a,b and 25.

5-Methylthio-7-phenyl-2,3-dihydrothiazolo[3,2-*a*]pyridinium tetrafluoroborate (23a) yellow solid (acetone), yield 84%; m.p. 260-262°C; IR(KBr) 1598, 1521, 1018-1121 (br) cm^{-1}; δ_H2.91 (3H,s,SCH_3), 3.90 (2H,t,J=7.5Hz,CH_2), 4.98 (2H,t,J=7.5Hz,CH_2), 7.50 (1H,brs,H-6), 7.58-7.89 (6H,m,H-8,arom). (Found: C, 48.61; H, 4.08; N,4.20. $C_{14}H_{14}NS_2BF_4$ requires: C, 48.43; H,4.06; N,4.03%).

5-Methylthio-7-(4-methoxyphenyl)-2,3-dihydrothiazolo[3,2-*a*]pyridinium tetrafluoroborate (23b) yellow solid (acetone), yield 86%; m.p. 203-204°C; IR(KBr) 1602,1518,1003-1120(br) cm^{-1}; δ_H2.87 (3H,s,SCH_3), 3.88 (2H,t,J=7.5Hz,CH_2), 4.01 (3H,s,OCH_3), 4.90 (2H,t,J=7.5Hz,CH_2), 7.19 (2H, d, J=9Hz,arom), 7.45 (1H,brs,H-6), 7.64 (1H,brs,H-8), 7.83 (2H,d,J=9Hz,arom). (Found: C, 47.88; H,4.32; N,3.90. $C_{15}H_{16}NOS_2BF_4$ requires: C,47.76; H,4.28; N,3.71%).

5-Methylthio-7-styryl-2,3-dihydrothiazolo[3,2-*a*]pyridinium tetrafluoroborate (24a) yellow solid (acetone), yield 82%; m.p. 265-67°C; IR(KBr) 1631, 1590, 1522, 1020-1118 (br)cm^{-1}; δ_H2.86 (3H,s,SCH_3), 3.81 (2H,t,J=7.5Hz,CH_2), 4.82 (2H,t,J=7.5Hz,CH_2), 7.13 (1H,d,J=16Hz,=CH), 7.31 (1H,brs,H-6), 7.37-7.78 (7H,m,arom and =CH). (Found: C,51.32; H,4.30; N,3.81. $C_{16}H_{16}NS_2BF_4$ requires: C, 51.49; H,4.32; N,3.75%).

5-Methylthio-7-(4-phenyl-1,3-butadienyl)-2,3-dihydrothiazolopyridinium tetrafluoroborate (24b) orange solid (acetone), yield 92%; m.p. 239-240°C; IR(KBr) 1618,1586,1515,1427,1022-1105(br)cm^{-1}; δ_H2.78 (3H,s,SCH_3), 3.66 (2H,t,J=7.5Hz,CH_2), 4.62 (2H,t,J=7.5Hz,CH_2), 6.56 (1H,d,J=16Hz,=CH), 6.88-7.15 (3H,m,=CH), 7.24-7.56 (7H,m,arom). (Found: C,54.40; H,4.50; N,3.62. $C_{18}H_{18}NS_2BF_4$ requires: C, 54.15; H,4.54; N,3.51%).

5-Methylthio-2,3,6,7-tetrahydrothiazolo[3,2-*a*]phenanthroquinolinium tetrafluoroborate (25) yellow crystals (acetone), yield 89%; m.p. 210-211°C; IR(KBr) 1581,1519,1409,1005-1118(br) cm^{-1}; δ_H2.27(3H,s,SCH_3), 2.74-3.71 (4H,m,CH_2), 3.49 (2H,t,J=7.5Hz,CH_2), 5.08(2H,t,J=7.5Hz, CH_2), 7.01-7.32 (3H,m,arom), 7.48-7.68 (1H,m,arom), 7.69 (1H,s,H-12). (Found: C,51.21; H, 4.36; N,3.88. $C_{16}H_{16}NS_2BF_4$ requires: C,51.49; H,4.32;N,3.75%).

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