

N-Quaternary Compounds. Part XLI.* Bromination Studies of 2-Pyridylthiovinyl Derivatives

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α -Carbonyl- β -2-pyridylthiovinyl derivatives have been brominated. The preferential reaction path depends on the nature of the pyridine 6-substituent and on the carbonyl group (CONR²R¹, CO₂Et and COMe). Cyclisation to dihydro- and thiazolo[3,2-*a*]pyridinium derivatives constitutes a facile method for the synthesis of the latter; alternative products are the dibromides and the α -bromovinyl thioethers. Stereochemistry and reaction pathways have been rationalised in terms of steric and electronic effects.

In a recent report we have described a facile method for the synthesis of the thiazolo[3,2-*a*]pyridinium system.³ The earlier published methods consist in acid catalysed cyclodehydration of 2-alkylthiopyridines in which the β -carbon of the *S*-side-chain is a carbonyl group.³⁻⁵ In our new synthesis a pyrid-2-thione was added to propiolic or phenylpropiolic acid to form a Michael 1:1-adduct which on treatment with bromine in cold chloroform led to immediate precipitation of the thiazolo[3,2-*a*]pyridinium derivative. The product may be formed by initial bromine addition followed by bromide displacement in the cyclisation, or by direct cyclisation of an intermediate bromonium ion; HBr elimination finally generates the thiazolo system. In this work we report further results on the scope of this reaction by studies of steric and electronic effects. The electronic activation of the double bond was varied through the nature of the attached carbonyl group; the latter was embedded in an ester and a ketone and in amido groups (Scheme 1). Different steric requirements also reside in these

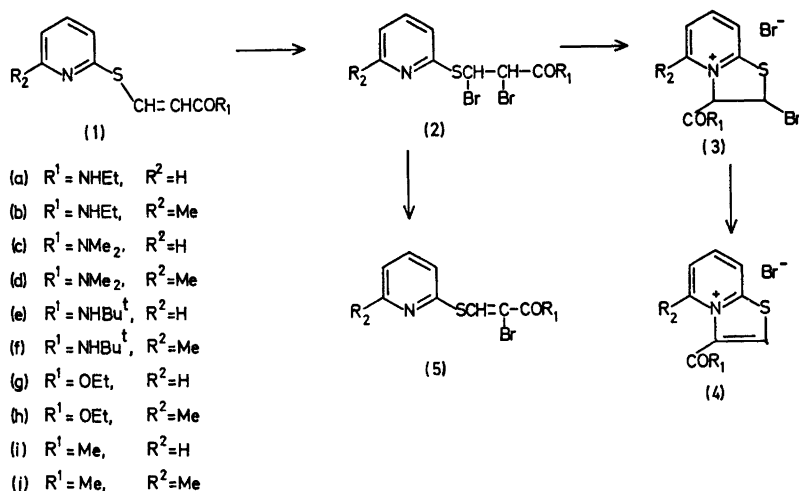
groups; the steric influence of the amido group was further changed by the substitution pattern on the amido nitrogen atom. A methyl group was also introduced into the 6-position of the pyridine ring. The available vinyl thioethers had the *cis* configuration with the exception of the ketone **1i** which was a 1:1 mixture of the *cis* and *trans* isomers and its 6-methyl homologue **1j** which had the *trans* configuration.⁶

The reactions were run in chloroform at 20 °C; bromine was added as a 10 % solution in chloroform. Addition of bromine to the amides **1a**, **1c**, and **1e**, which carry a hydrogen atom in the 6-position, immediately led to precipitation of a product identified by spectroscopy as the dihydrothiazolo derivative (**3**). A minor product left in solution has been identified as the dibromo adduct (**2**) by comparison of its spectroscopic and chromatographic properties with those of **2d** and **2f** discussed below.

The UV spectra of the dihydrothiazolo derivatives (**3**) are significantly different in ethanolic 0.1 N HCl and 0.1 N NaOH; in fact the spectrum in alkaline solution is that of the thiazolo analogue (**4**) which demonstrates HBr elimination from **3**. This is not unexpected as the methine proton on C-3 is activated by both the carbonyl group and the quaternary nitrogen atom; it is readily exchanged in deuterium oxide (NMR) as discussed below. The dihydrothiazolo product has *trans* stereochemistry; this follows from the vicinal coupling constant (TFA) between the C-2 (δ 6.5–6.6) and C-3 (δ 6.9–7.1) protons which is ≤ 1 Hz.^{7,8}

It was pointed out above that in bromination of corresponding acids the product was the

* See Ref. 1.



Scheme 1.

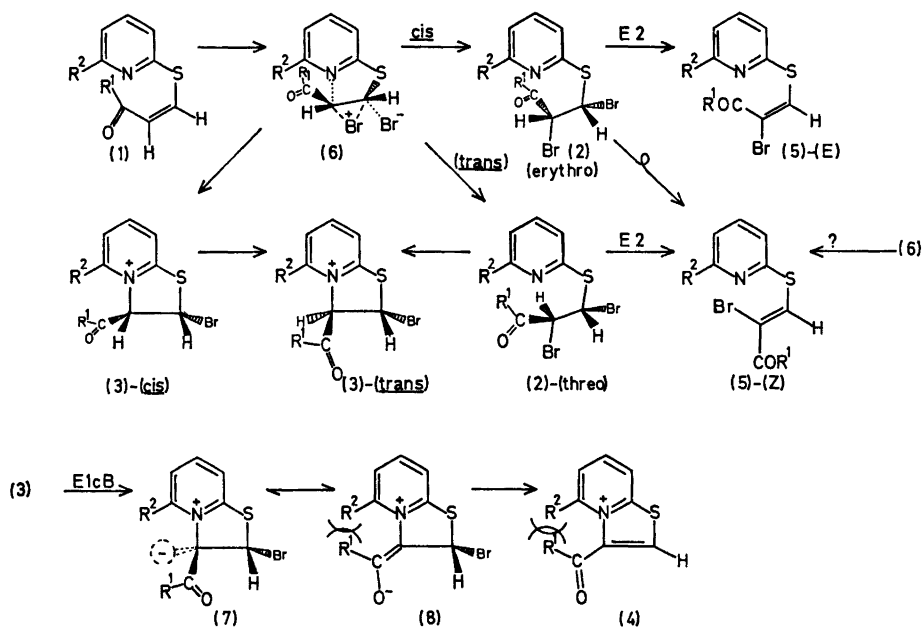
thiazole 4;³ the differential activation by the carbonyl groups may explain the different product formations. Thus further activation by warming led to HBr elimination; the elimination in recrystallisations of 3 was suppressed by HBr additions. Preparatively, however, the thiazole 4 was generated by warming a solution of 3 in the presence of propylene oxide as HBr scavenger. The NMR spectra (TFA) of the thiazolo[3,2-*a*]pyridinium derivatives are characterised by low field absorption for the C-3 proton (δ 8.7–8.9) and the C-5 proton (δ 9.3–9.4).

The 6-methyl substituted amides 1*b*, 1*d*, and 1*f* reacted differently after bromine addition. The initial product was the adduct 2; in the case of the ethylamide 1*b*, HBr elimination had partially occurred. HBr was eliminated from all the adducts on warming in solution; no cyclisation, however, occurred. The products are the vinyl derivatives (5); the *N*-ethyl derivative has the vinyl proton at δ 8.7 (TFA). The analogues 5*d* and 5*f* were considerably contaminated by 6-methylpyrid-2-thione; the latter is thus formed in a competitive elimination reaction where the sulfide and not the bromide ion is the leaving group. These results show that a 6-methyl group effectively blocks cyclisation of the amides. The important non-bonded interaction is presumably between the substituents on the amido nitrogen atom and the 6-methyl

group. In this respect the amido nitrogen in the examples are perhaps best compared with the bulkiness of a secondary and tertiary carbon. In the esters 1*g* and 1*h* the non-bonded interaction in the cyclisation step is reduced; the isolated product was the thiazole 4 as in the case of the acids. In the ketones 1*i* and 1*j*, however, methyl group interference in the cyclisation step was apparent in that the product from the 6-methyl derivative 1*j* was the vinyl thioether 5. The NMR spectrum contained one vinyl proton signal (δ 8.6) suggesting that only one stereoisomer was formed. The desmethyl ketone 1*i*, however, yielded both the vinyl thioether 5 and the thiazolo analogue 4; the vinyl thioether was the major component.

The vinyl thioethers 1 except the ketones 1*i* and 1*j* have the *cis* configuration as pointed out above. *trans*-Addition of bromine to the *cis*-isomers followed by cyclisation with configurational inversion are consistent with the observed *trans* configuration for the dihydrothiazolo derivatives 3*a*, 3*c*, and 3*e*. NMR showed no isomerisation of the vinyl thioether by bromine or by traces of HBr in experiments using excess of the vinyl thioether reactant.

Interconversions of the *cis* and *trans* isomers of (3) cannot be excluded. Reaction paths leading to the *cis* isomer therefore have to be considered. The latter is thought to be thermodynamically the less stable because of steric



Scheme 2.

repulsion between the vicinal substituents (Scheme 2). C-3 is highly activated by the quaternary nitrogen atom and the carbonyl group. Epimerisation on C-3 is therefore quite feasible under the experimental conditions used which would result in isolation of the *trans* product irrespective of the original configuration of the product formed. Support for this view was found in a deuteration experiment with **3a**; dissolution of the latter in a solution of deuterium oxide and acetone-*d*₆ at 20 °C led to very rapid exchange of the proton on C-3 while no significant exchange of the C-2 proton had occurred after 5 h (NMR). At higher temperatures the C-2 proton was also exchanged.

A cyclic bromonium ion is normally assumed in bromine additions to olefins; an ion pair can initially be assumed. In the case of a solvent of low solvating power and where the onium intermediate carries a strongly stabilising substituent the ion pair may collapse with overall *cis*-addition. With better solvation of the bromonium intermediate the bromide ion preferably adds *trans*. For the vinyl thioethers the charge distribution in the bromonium intermediate is presumably unsymmetrical; the posi-

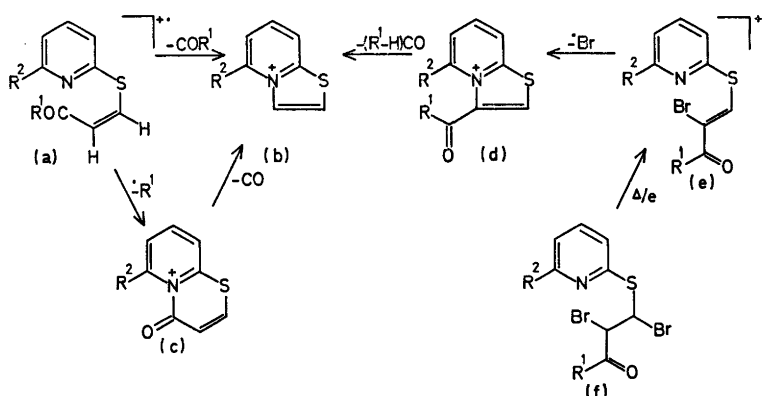
tive charge is better stabilised on the α -carbon to the thioether sulfur atom. The pyridine nitrogen through its lone pair of electrons, however, may be involved in solvation and stabilisation of charge at the other carbon. The solvated onium intermediate **6** may therefore collapse either by *cis/trans* bromide addition or pyridine addition; the latter path leads directly to the *cis* isomer **3** which then is epimerised on C-3 to the *trans* form. The reaction path was further studied by bromination of the ethylamide **1a** with efficient cooling at 0 °C using concentrated bromine and vinylthioether solutions and with rapid addition; the major product was the open-chain dibromide **2a** and the minor product the bicyclic derivative **3a**. The dibromide **2a** was cyclised slowly in dilute chloroform solution in the cold. The slow cyclisation rate compared with the rapid formation of **3a** in the bromination excludes the dibromide **2a** as an intermediate in this reaction and is consistent with direct addition of the pyridine nitrogen to the bromonium intermediate. A 6-methyl group introduces steric repulsion in the approach of the pyridine nitrogen to the bromonium ion **6** for solvation. The activation energy for pyridine addition is thereby increased to the extent

that bromide addition is favoured in the 6-methyl derivatives; the dibromide **2** is thus formed. The esters **1g** and **1h** furnished the bicyclic thiazoles **4** presumably by way of the corresponding dihydrothiazoles **3** as did corresponding acids. The reaction is fast and therefore pyridine attack on the bromonium intermediate is again assumed; this is followed by rapid HBr elimination. The non-bonded interaction between the 6-methyl group and the ester group is thus less than for the amido group. It will be recalled that the 6-methyl ketone yielded the bromovinyl thioether **5j** while the desmethyl derivative **1i** gave a mixture of the bromovinyl product **5i** and the corresponding thiazole **4i**. The observed product formation is explained in terms of steric and electronic effects. The side-chain methyl group is attached directly to the carbonyl carbon which increases the effective non-bonded interaction with the 6-substituent in the pyridine ring. In a bromonium intermediate the proton next to the carbonyl group is highly activated. Intramolecular abstraction of this proton by the basic nitrogen may be a pathway to **5** in the case of the ketones.

The evidence for the formation of only the one stereoisomer of **5** rests on NMR data. Thus the vinyl proton in **5b**, **5i**, and **5j** is in the region δ 8.6–8.7 in TFA solution and at about δ 9.0 in deuteriochloroform solution. These data are used in structural assignment by comparison with data recorded under similar conditions for the parent vinyl thioethers **1**.⁸ In deuteriochloroform solution the β -proton of **1** was at

δ 8.3–8.5 irrespective of the configuration; in TFA a diamagnetic shift (0.4–1.0 ppm) was observed which depended on the configuration. These observations are rationalised through dominating deshielding effects from the aromatic pyridine ring in chloroform solution which is reduced on protonation of the pyridine nitrogen in TFA solution. Similar shift changes were seen in MeOH-*d*₄.DBr. The signal from the β -proton in the *trans* isomer is found at the lower field (0.6 ppm) ascribed to the anisotropy of the carbonyl group. The corresponding signal in the bromovinyl thioethers has undergone a diamagnetic shift of 0.4 ppm from deuteriochloroform to TFA which is interpreted in terms of the (*Z*)-configuration for the bromovinyl ethers **5b**, **5i** and **5j**. The stereochemistry of the bromovinyl derivatives **5b** and **5j** is the same although the parent vinyl thioethers **1b** and **1j** have opposite stereochemistry. As the stereochemical course of bromine addition is uncertain and the adduct presumably can be epimerised because of carbonyl activation, discussion of the elimination mechanism is not warranted.

The bromovinyl thioethers **5** contain groups capable of stabilising negative charge. Nucleophilic vinyl substitution of the bromine by the nitrogen atom to yield the thiazole **4** can be visualised. The bromovinyl ketone **5i**, however, did not undergo this reaction in chloroform solution. This further supports thiazole **4** formation from the dihydrothiazole **3** by HBr elimination. The leaving substituents are *cis* in **3**; hence E2 elimination is less favourable. It will be recalled that H-3 in the amide **3a**



Scheme 3.

was very rapidly exchanged in deuterium oxide-acetone- d_6 . A carbanion on C-3 is well stabilised by resonance with the carbonyl group **7** and inductively by the quaternary ammonium nitrogen. The best resonance stabilisation is obtained with a keto carbonyl group and the poorest stabilisation by the amido carbonyl group. Only the amides were isolated as dihydrothiazoles **3**; the esters and ketones reacted further to the thiazoles **4**. The results are consistent with an E1cB elimination reaction in which the departure of the leaving group with double bond formation is the rate determining step.^{9,10} The E1cB elimination is most often seen in cases with β -proton activation and a poor leaving group. Elimination of the bromide ion is normally encountered in concerted eliminations because of good leaving properties. The unusual behaviour in the present case is attributed to the very good carbanion stabilisation and charge dispersion by the two mentioned groups and to non-bonded interaction as discussed below. On rehybridisation from sp^3 to sp^2 on C-3 the carbonyl group becomes coplanar with the pyridine ring (δ) which results in differential increased non-bonded interaction between the 6-substituent and the carbonyl substituent. The anionic carbon in the ester and especially in the ketones is closer to sp^2 hybridisation than in the amide because of better resonance stabilisation. The activation energy for bromide expulsion with double bond formation is probably increased for the latter because of the more extensive rehybridisation required on C-3.

The base peak in the mass spectra for the vinyl thioethers is found at m/e 136 or at m/e 150 depending on whether the molecule contains the 6-methyl group. These mass numbers correspond to the aromatic thiazolo[3,2-*a*]pyridinium cation **b** and correlate well with previous studies of corresponding acids.¹¹ Secondary fragments are of little importance. The two-step process to **b** with initial R^1 expulsion is also seen, especially in the case of the *t*-butyl derivatives and the esters but hardly any signal at this mass number was present in the spectra of the ketones. In the amides the intensity of the $[M - R^1]$ signal is generally lower in the 6-methyl derivative which suggests non-bonded interaction suppressing a cyclisation reaction such as formation of **c**. Molecular ion intensities for

the amides were of the order 0.2–2.5 %, for the ketones about 2 % and for the esters about 10 %. The molecular ion intensities in the available bromovinyl thioethers were slightly increased (3–6 %). They differ in their fragmentation by initial expulsion of the bromine to give the base peak; the more stable radical is expelled. The other pathway is seen but is of little importance. The $[M - Br]$ species **d** further undergoes rearrangements with transfer of a hydrogen and expulsion of the side-chain to give species with mass number corresponding to the thiazolo[3,2-*a*]pyridinium cation; relative intensity in the range 70–90 %. In the dibromides **2** pyrolytic HBr elimination occurred extensively. The dihydrothiazolo derivatives naturally eliminated HBr; the spectra from the thiazolo cations **4** are superimposed on the spectra from pyrolytic products and therefore variable.

EXPERIMENTAL

NMR spectra were recorded with a Varian A-60A or Varian A-100 instrument, the UV spectra with a Cary 14 instrument and the MS spectra with an AEI MS-902 mass spectrometer.

N-t-Butyl-2,3-dibromo-3-(6-methyl-2-pyridylthio)propionamide HBr (2f). Bromine in chloroform (10 % solution) was added dropwise at 20 °C to a solution of *cis-N-t-butyl-3-(6-methyl-2-pyridylthio)acrylamide* (1.25 g, 0.005 mol) in chloroform (100 ml) until rapid bromine decolouration no longer occurred. The excess bromine was destroyed by acetone additions and a little HBr added. The precipitated hydrobromide was recrystallised from ethanol-ether to which had been added a little aqueous HBr; yield 1.92 g (78 %), m.p. 160 °C (decomp.). (Found: C 31.96; H 4.15; N 5.90. Calc. for $C_{13}H_{18}Br_2N_2OS \cdot HBr$: C 31.79; H 3.90; N 6.05; δ (TFA) 3.0 (Me), 1.5 (*N-t*-Bu), 5.1 (H- β , d), 6.3 (H- α), 7.7–8.6 (3H-pyr).

N,N-Dimethyl-2,3-dibromo-3-(6-methyl-2-pyridylthio)propionamide HBr (2d) was prepared as above from the corresponding *cis*-ethylene (**1f**); m.p. 124 °C (decomp.) after recrystallisation from ethanol/ether with HBr addition (Found: C 28.78; H 3.33; N 5.85. Calc. for $C_{11}H_{14}Br_2N_2OS \cdot HBr$: C 28.53; H 3.26; N 6.05; δ (TFA) 3.0 (Me), 3.4 (NMe₂), 5.5 (H- β), 6.0 (H- α), 7.6–8.7 (3H-pyr.).

*trans-2-Bromo-3-N-ethylcarbamoyldihydrothiazolo[3,2-*a*]pyridinium bromide (3a)*. A bromine solution in chloroform (10 %) was added dropwise at 20 °C to a solution of *cis-N-ethyl-3-(2-pyridylthio)acrylamide* (0.50 g, 0.0025 mol) in chloroform (50 ml) until a permanent colour of bromine remained. An oily product was precipi-

tated as the addition proceeded. The solvent was removed by evaporation below 20 °C. The residual yellow oily material was then dissolved in ethanol (20 ml) and an equal volume of ether added. The title compound was slowly precipitated from this solution and was recrystallized from ethanol/ether to which had been added a few drops of HBr solution; yield 0.6–0.7 g (70–80 %), m.p. 140 °C (decomp.). (Found: C 32.44; H 3.43; N 7.40. Calc. for C₁₀H₁₂Br₂N₂OS: C 32.63; H 3.28; N 7.61); δ (TFA) 1.3 and 3.5 (NEt), 6.5 (H-2, $J < 1$ Hz), 6.9 (H-3), 7.8–9.0 (3 H-pyr); λ_{\max} (0.1 N HCl EtOH) 242 (log ϵ 3.90), 310 (3.74), 323 sh. nm (3.70).

trans-2-Bromo-3-*N,N*-dimethylcarbamoyldihydrothiazolo[3,2-*a*]pyridinium bromide (3c) was prepared as above from the corresponding *cis*-ethylene amide (1c); yield 70–80 %, m.p. 160 °C (decomp.) (EtOH/Et₂O/HBr). (Found: C 32.50; H 3.58; N 7.45. Calc. for C₁₀H₁₂Br₂N₂OS: C 32.63; H 3.28; N 7.61); δ (TFA) 3.2 and 3.5 (NMe₂), 6.6 (H-2, $J < 1$ Hz), 7.1 (H-3), 7.8–9.1 (3 H-pyr.); λ_{\max} (0.1 N HCl EtOH) 240 (log ϵ 3.81), 310 (3.78), 324 sh.nm. (3.7).

trans-2-Bromo-3-*N-t*-butylcarbamoyldihydrothiazolo[3,2-*a*]pyridinium bromide (3e) was prepared as above from the corresponding *cis* ethylene amide (1e); yield 48 %, m.p. 260 °C (decomp.) (EtOH/Et₂O/HBr). (Found: C 36.07; H 3.93; N 6.92. Calc. for C₁₂H₁₆Br₂N₂OS: C 36.38; H 4.07; N 7.07); δ (TFA) 1.5 (*N-t*-Bu), 6.5 (H-2, $J < 1$ Hz), 6.9 (H-3), 7.8–9.1 (3 H-pyr.); λ_{\max} (0.1 N HCl EtOH) 242 (log ϵ 3.90), 323 nm (3.71).

3-*N,N*-Dimethylcarbamoylthiazolo[3,2-*a*]pyridinium bromide (4c). 2-Bromo-3-*N,N*-dimethylcarbamoyldihydrothiazolo[3,2-*a*]pyridinium bromide (0.2 g) was dissolved in ethanol (50 ml) and 1,2-propylene oxide added as HBr acceptor. The resultant solution was heated at 60 °C for 30 min before the solution was evaporated at reduced pressure. The residue was re-dissolved in ethanol before addition of ether and a little pet.ether. The title compound crystallised out in 70 % yield, m.p. 169 °C (decomp.). (Found: C 41.15; H 4.14; N 9.73. Calc. for C₁₀H₁₁BrN₂OS: C 41.82; H 3.86; N 9.75); δ (TFA) 3.4 (NMe₂), 8.7 (H-2), 9.4 (H-5), 8.1–8.8 (3 H-pyr); λ_{\max} (0.1 N HCl EtOH) 225 (log ϵ 4.21), 299 sh. (4.03), 308 nm (4.13).

3-*N-t*-Butylcarbamoylthiazolo[3,2-*a*]pyridinium bromide (4e) was prepared in almost quantitative yield by the above procedure from the corresponding 2-bromodihydrothiazole (3e); m.p. 205 °C (decomp.), (EtOH/Et₂O/light petroleum). (Found: C 45.72; H 4.77; N 8.83. Calc. for C₁₂H₁₆BrN₂OS: C 45.72; H 4.79, N 8.88); δ (TFA) 1.6 (*N-t*-Bu), 8.9 (H-2), 9.3 (H-5), 7.9–8.3 (3 H-pyr); λ_{\max} (0.1 N HCl EtOH) 227 (log ϵ 4.15), 298 sh (3.96), 309 nm (4.05).

3-Ethoxycarbonylthiazolo[3,2-*a*]pyridinium bromide (4g). Bromine in chloroform (10 % solution) was added dropwise at 20 °C to a solution of ethyl *cis*-3-(2-pyridylthio)acrylate (1.05 g, 0.005 mol in chloroform (50 ml) until a

permanent colour of bromine remained. An oily precipitate was slowly formed. The reaction mixture was evaporated at reduced pressure after about $\frac{1}{2}$ h. The residual brown oily material was triturated with acetone (10 ml) which decolourised the material. The resultant white suspension was dissolved by addition of ethanol. A little ether was then added and the solution left to stand in the cold. The precipitated product was collected after 1 week; yield 80 %, m.p. 158 °C (decomp.). (Found: C 41.65; H 3.67; N 4.84. Calc. for C₉H₁₀BrNO₂S: C 41.68; H 3.49; N 4.86); δ (TFA) 1.5 and 4.7 (OEt), 9.1 (H-2), 8.0–8.9 (4 H-pyr); λ_{\max} (0.1 N HCl EtOH) 225 (log ϵ 4.24), 241 (3.83), 247 (3.73), 296 (4.04), 306 nm (4.14).

3-Ethoxycarbonyl-5-methylthiazolo[3,2-*a*]pyridinium bromide (4h) was prepared as described for 4g by bromination of ethyl *cis*-3-(6-methyl-2-pyridylthio)acrylate (1h) yield 80 %, m.p. 140 °C (decomp.) (Acetone/EtOH/Et₂O). (Found: C 43.75; H 3.60; N 4.55. Calc. for C₁₁H₁₂BrNO₂S: C 43.72; H 4.00; N 4.63); δ (TFA) 1.5 and 4.7 (OEt), 3.0 (5-Me), 8.9 (H-2), 7.9–8.7 (3H-pyr.); λ_{\max} (0.1 N HCl EtOH) 228 (log ϵ 4.16), 247 (3.72), 278 (3.49), 308 (4.04), 317 nm (4.12).

3-Acetylthiazolo[3,2-*a*]pyridinium bromide (4i) and 3-bromo-4-(2-pyridylthio)but-3-en-2-one HBr (5i). Bromine in chloroform (10 %) solution was added dropwise at 0–10 °C to a solution of *cis/trans* (1:1) 4-(2-pyridylthio)but-3-en-2-one (0.90 g, 0.005 mol) until the solution assumed the permanent colour of bromine. The product which crystallised out during the bromine addition was triturated with acetone and was recrystallised from ethanol/ether; yield 0.3 g (25 %), m.p. > 260 °C. (Found: C 42.10; H 3.10; N 5.46. Calc. for C₉H₈BrNOS: C 41.88; H 3.12; N 5.43); δ (TFA) 3.0 (Ac), 9.4 (H-2), 10.6 (H-5), 8.9–9.0 (3 H-pyr); λ_{\max} (0.1 N HCl EtOH) 244 (log ϵ 3.93), 298 (3.75), 308 (3.88), 326 nm (3.63).

The filtrate from the reaction solution was decolourised by acetone addition. The precipitated HBr salt was a mixture of the title compounds. The salt was dissolved in water and the solution made alkaline by means of sodium bicarbonate. The bromovinyl derivative 5i was then extracted into chloroform which was dried and evaporated. The residual material was crystallised from ethanol to which had been added a few drops of ethereal HBr; yield 0.68 g (40 %), m.p. 150 °C. Runs on larger reaction scales furnished yields up to 70 %. (Found: C 31.92; H 2.74; N 4.32. Calc. for C₉H₈BrNOS: C 31.88; H 2.67; N 4.13); δ (TFA) 2.7 (Ac), 8.7 (H- β) 8.9 (H-6), 7.7–8.7 (3 H-pyr.); λ_{\max} (0.1 N HCl EtOH) 243 (log ϵ 3.67), 276 (3.83), 320 nm (4.23).

N-Ethyl-2-bromo-3-(6-methyl-2-pyridylthio)acrylamide HBr (5b). Bromine in chloroform (10 % solution) was added dropwise at 20 °C to a solution of *cis-N*-ethyl-3-(6-methyl-2-pyridylthio)acrylamide (0.10 g, 0.005 mol) in chloroform until the colour of bromine was no longer

discharged. The solvent was then distilled off and the product recrystallised from ethanol and ethyl acetate; yield 0.14 g (82 %), m.p. 165 °C (decomp.) (Found: C 34.58; H 3.65; N 7.23. Calc. for $C_{11}H_{13}BrN_2OS.HBr$: C 34.57; H 3.69; N 7.33); δ (TFA) 1.4 and 3.6 (NEt), 3.0 (6-Me), 8.7 (H- β), 7.7–8.7 (3 H-pyr.); λ_{max} (0.1 N HCl EtOH) 272 (log ϵ 4.06), 319 nm (4.18).

3-Bromo-4-(6-methyl-2-pyridylthio)but-3-en-2-one HBr (5j). Bromine in chloroform (10 % solution) was added in the usual way at 0–10 °C to *trans*-4-(6-methyl-2-pyridylthio)but-3-en-2-one (0.96 g, 0.005 mol) in chloroform (100 ml). Acetone was next added to the reaction solution and the precipitated title compound recrystallised from ethanol-ether-HBr; yield 1.57 g (90 %), m.p. 180 °C (decomp.). (Found: C 34.13; H 3.19; N 3.97. Calc. for $C_{10}H_{10}BrNOS.HBr$: C 34.01; H 3.14; N 3.97); δ (TFA) 2.7 (Ac), 3.0 (6-Me), 8.6 (H- β), 7.7–8.5 (3 H-pyr.); λ_{max} (0.1 N HCl EtOH) 250 (log ϵ 3.66), 277 (3.89), 323 nm (4.24).

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