Chemistry of the Benzothiazole System: Ring-opening Reaction in a Non-basic Medium promoted by Co-ordination to Silver(I)

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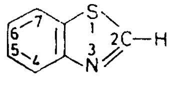
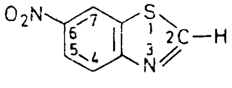
Reaction of the ligand (L) benzothiazole (bt) and 6-nitrobenzothiazole (nbt) with $Ag[NO_3]$ or $Ag[ClO_4]$ affords ionic complexes of formula $[AgL][NO_3]$ and $[AgL_2]X$ ($X = NO_3$ or ClO_4). The $[Ag(nbt)][NO_3]$ and $[Ag(nbt)_2]X$ complexes react with alcohols (MeOH, EtOH, or $PhCH_2OH$) at room temperature to give ring-opening reactions and 2-amino-5-nitrobenzenethiolatosilver(I) *via* the corresponding 2-(methoxymethylene)amino-derivative. This is the first example of a thiazole ring-opening reaction in non-basic media.

THE chemistry of the thiazole system has been extensively studied as the C^2 of the thiazole ring is the active site of Vitamin B_1 (thiamine pyrophosphate).[1,2] Metal complexes with substituted benzothiazoles[3] and benzothiazolines[4] have been recently described. The substituents in the thiazole ring, essentially in the 2, 4, and 5 positions, modify both the stoicheiometry and the stereochemistry of the complexes.[5,6] More recently, the oxidative addition of 2-chloro-derivatives of 5-methyl-1,3-thiazole and benzothiazole to d^8 and d^{10} metal complexes has been reported, and the N-protonation reaction to give cationic cyclic carbene complexes.[7] We report here the preparation of complexes of Ag^I with the ligands (L) benzothiazole(bt) and 6-nitrobenzothiazole (nbt) of formula $[AgL][NO_3]$ and $[AgL_2]X$ ($X = NO_3$ or ClO_4), and the reaction of the co-ordinated ligand nbt with alcohols (MeOH, EtOH, and $PhCH_2OH$) at room temperature to give 2-amino-5-nitrobenzenethiolatosilver(I).



(bt)



(nbt)

RESULTS AND DISCUSSION

The reaction of $Ag[NO_3]$ with bt or nbt affords complexes of formula $[AgL][NO_3]$ and $[AgL_2][NO_3]$ depending on the temperature and on the solvent used. Silver(I) perchlorate gave complexes of formula $[AgL_2][ClO_4]$ only.† Conductivity measurements on the solutions of the complexes in *NN*-dimethylformamide (dmf) show that the $[AgL_2]X$ complexes behave as 1 : 1 electrolytes (see Table 1). The complexes of formula $[AgL][NO_3]$ gave lower values of Λ_m, strongly dependent on concentration, suggesting ion-pair formation.

The i.r. spectra (Nujol mull) of the $[AgL_2]X$ complexes did not show any band attributable to co-ordinated anions, suggesting the existence of two-co-ordinate Ag^I also in the solid state (see Table 2). The complexes $[Ag(bt)][NO_3]$ and $[Ag(nbt)][NO_3]$ exhibited strong bands at 1.375 and 1 380 cm^{-1} respectively in their i.r. spectra (Nujol mulls), in the range for ionic nitrate,[8] but no bands in the range 1 500—1 280 cm^{-1} attributable to co-ordinated nitrate.[9] These figures would suggest that silver is only co-ordinated to the ligand L in the solid state in the complexes of formula $[AgL][NO_3]$, but these complexes are probably not monomeric. The analysis of the 600—1 600 cm^{-1} region of the vibrational spectrum of the complexes $[AgL_2]X$ and $[AgL]X$ shows that several absorptions attributable to vibrations of the benzothiazole ring are modified on co-ordination to the metal.

The benzothiazoles could co-ordinate to silver through the N or the S atom of the ring. Although various substituted thiazoles have been found to be N-bonded[6] to metal ions such as Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, in the present case the ligand could be bonded to the metal through the S atom, due to the soft character of Ag^I, which could give a d_π–d_π interaction with S.[10] For example, N-substituted thioureas are S-bonded to Ag^I.[11] Comparing the i.r. spectra of $[Ag(bt)][NO_3]$ and $[Ag(bt)_2]X$ with that of benzothiazole, we find that the most significant changes, in the range 600—1 600 cm^{-1}, are the shift of the bands at 1 475 and 667 cm^{-1} in the spectrum of the free ligand. The former band is found at lower wavenumbers in the complexes, while the latter is shifted towards higher values of ν (Table 2). These bands can

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† The different behaviour can be related to packing in the solid state.

[1] S. F. Dyke, 'The Chemistry of the Vitamins,' Interscience, New York, 1965, p. 4.

[2] R. Breslow, 'The Mechanism of Action of Water Soluble Vitamins,' CIBA Study Group No. II, Little Brown and Co., Boston, p. 65.

[3] N. N. Y. Chan, M. Goodgame, and M. J. Weeks, *J. Chem. Soc.* (*A*), 1968, 2499; P. S. Chia and S. E. Livingstone, *Inorg. Chim. Acta*, 1968, **2**, 427; E. J. Duff, M. N. Hughes, and K. J. Rutt, *J. Chem. Soc.* (*A*), 1968, 2354; 1969, 2126; J. E. House and Pik-Shing Lau, *J. Inorg. Nuclear Chem.*, 1974, **36**, 223; A. Ouchi, T. Takeuchi, and I. Taminaga, *Bull. Chem. Soc. Japan*, 1970, **43**, 2840; W. Beck, J. Chr. Weis, and J. Wieczorek, *J. Organometallic Chem.*, 1971, **30**, 89; P. Powell, *ibid.*, 1974, **65**, 89; O. A. Osipov, L. V. Surpina, A. D. Garnovskii, and Yu. V. Kolodyazhuii, *Zhur. obshchei Khim.*, 1971, **41**, 2279; M. N. Hughes and K. J. Rutt, *Spectrochim. Acta*, 1971, **A27**, 924.

[4] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 1968, **2**, 119.

[5] M. J. M. Campbell, D. W. Card, R. Grzeskowiak, and M. Goldstein, *J. Chem. Soc.* (*A*), 1970, 672.

[6] E. J. Duff, M. N. Hughes, and K. J. Rutt, *J. Chem. Soc.* (*A*), 1969, 2101.

[7] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 102.

[8] R. H. Nuttall and D. W. Taylor, *Chem. Comm.*, 1968, 1417; G. Topping, *Spectrochim. Acta*, 1965, **21**, 1743.

[9] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' John Wiley, 1967, p. 92.

[10] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[11] N. Dash and Rao D. V. Ramana, *Indian J. Chem.*, 1973, **11**, 603.

be ascribed[12] to vibrations of the thiazole ring,* mainly ν(N=C), and to C–S stretching respectively.

The shift to higher values of ν of the C–S stretching band must be related to a stronger C–S bond due to an increased d_π–d_π contribution between sulphur and the ring π system.[14] The band at 1 425 cm^{-1} [ν(N=C–S)] in the free ligand is similarly lowered on co-ordination. On the basis of these figures we assume that the ligand is N-bonded to silver, which would adopt a linear *sp* hybridization in the complexes [AgL$_2$]X, while for [AgL][NO$_3$] a polymeric structure can be proposed with some intermolecular silver–sulphur bonding. In the 200—600 cm^{-1} region the ligand itself has strong absorptions due to ring deformations. This makes it difficult to assign the metal–nitrogen stretching vibration. A poorly resolved band at 220 cm^{-1} cannot be unambiguously assigned. The nbt complexes showed similar features (Table 2).

U.v. and visible spectroscopic data provided no additional useful information. Kuznik and Sulikowska[15] reported identical features for complexes of Ag^{I} with thioureas.

^{1}H N.m.r. spectra (Table 2) show that the resonance due to the C^2 hydrogen is shifted to lower values of τ with respect to the free ligands as a consequence of the deshielding of H^2 on co-ordination. The downfield shift was more pronounced in the 1 : 1 complexes than in the 1 : 2 complexes. Moreover, the effect of co-ordination to silver is more pronounced in the bt than in the nbt complexes.

TABLE 1

Analytical[a] and physical data for the complexes

Complex[b]	M.p.[c] (θ_c/°C)	Analysis (%) C	H	Ag	N	Cl	Λ_m[d] S cm^2 mol^{-1}
[Ag(bt)][NO$_3$]	113	27.5 (27.5)	1.80 (1.55)	35.2 (35.35)	9.00 (9.20)		35.6
[Ag(bt)$_2$][NO$_3$]	128	37.85 (38.2)	2.15 (2.30)	24.5 (24.5)	9.55 (9.55)		71.2
[Ag(nbt)][NO$_3$]	238	23.85 (24.0)	1.20 (1.15)	30.65 (30.8)	11.9 (12.1)		32.7
[Ag(nbt)$_2$][NO$_3$]	232	31.5 (31.7)	1.50 (1.50)	20.3 (20.35)	13.2 (13.2)		69.4
[Ag(bt)$_2$][ClO$_4$]	147	35.0 (35.2)	2.15 (2.10)	22.3 (22.6)	5.80 (5.85)	7.40 (7.40)	78.3
[Ag(nbt)$_2$][ClO$_4$]	303 explodes	29.5 (29.65)	1.40 (1.40)	18.75 (19.0)	9.80 (9.85)	6.20 (6.25)	74.0
Ag[SC$_6$H$_3$(NH$_2$)(NO$_2$)]	Decomp. from 180	26.0 (26.0)	1.85 (1.90)	39.0 (38.95)	10.0 (10.1)		12.0

[a] Calculated values are given in parentheses. [b] All the complexes are white, except the last which is dark yellow. [c] Uncorrected. [d] For 10^{-3} mol dm^{-3} solutions in dmf; Λ_m 73.0 S cm^2 mol^{-1} for tetrapentylammonium bromide (10^{-3} mol dm^{-3}) in dmf (C. Fragale, Ph.D. Thesis, Istituto di Chimica Analitica, Università, Bari, 1969).

TABLE 2

Spectral data for the free ligands and the complexes

	I.r. (cm^{-1})					^{1}H N.m.r. (τ)[a]		
Compound	ν(C=N)	ν(N=C–S)	ν(C–S)	ν(NO$_2$)	ν(NO$_3^-$)			
bt	1 473m	1 425m	667mw			2.46 (m, 2 H, H^{4,7})	1.82 (m, 2 H, H^{5,6})	0.55 (s, 1 H, H^2)
[Ag(bt)][NO$_3$]	1 463m	1 415m	690mw		1 370s, br	2.42 (m, 2 H, H^{4,7})	1.80 (m, 2 H, H^{5,6})	0.45 (s, 1 H, H^2)
[Ag(bt)$_2$][NO$_3$]	1 466m	1 417—1 423m	695mw		1 370s, br	2.45 (m, 2 H, H^{4,7})	1.80 (m, 2 H, H^{5,6})	0.52 (s, 1 H, H^2)
[Ag(bt)$_2$][ClO$_4$][b]	1 466m	1 415—1 421m	697mw			2.44 (m, 2 H, H^{4,7})	1.80 (m, 2 H, H^{5,6})	0.51 (s, 1 H, H^2)
nbt	1 462m	1 435m	675mw	1 603s, 1 571s		1.68 (m, 2 H, H^{4,5})	0.77 (m, 1 H, H^7)	0.25 (s, 1 H, H^2)
[Ag(nbt)][NO$_3$]	1 455m	1 430m	691w	1 597s, 1 569s	1 380s, br	1.64 (m, 2 H, H^{4,5})	0.75 (m, 1 H, H^7)	0.21 (s, 1 H, H^2)
[Ag(nbt)$_2$][NO$_3$]	1 450m	1 423m	705w	1 602s, 1 572s	1 380s, br	1.65 (m, 2 H, H^{4,5})	0.76 (m, 1 H, H^7)	0.22 (s, 1 H, H^2)
[Ag(nbt)$_2$][ClO$_4$][c]	1 455m	1 432m	703w	1 602s, 1 572s		1.65 (m, 2 H, H^{4,5})	0.76 (m, 1 H, H^7)	0.22 (s, 1 H, H^2)
Ag[SC$_6$H$_3$(NH$_2$-2)(NO$_2$-5)][d]				1 603s, 1 580s		3.53 (s, br, 2 H, NH$_2$) 1.57 (d, 1 H, H^6)	3.42 (d, 1 H, H^3)	2.39 (dd, 1 H, H^4)

s = strong, m = medium, w = weak, and br = broad.

[a] Measured in [^{2}H$_6$]dmso at 60 MHz; SiMe$_4$ was the internal standard. [b] ν(ClO$_4^-$) at 622—1 100 cm^{-1}. [c] ν(ClO$_4^-$) at 623—1 100 cm^{-1}. [d] ν(NH$_2$) at 3 357ms and 3 455m cm^{-1}; n.m.r. spectrum measured at 100 MHz [*J*(H^{4}H^6) 2.5, *J*(H^{3}H^4) 9.0 Hz].

Reaction with Alcohols.—The thiamine pyrophosphate system is the biologically active centre of the carboxylase enzyme, which consists of a specific protein, the coenzyme, and metal ions (like Mg^{2+}). Breslow[2,16] has shown that the base-catalyzed exchange of the C^2 proton of the thiazolium ion is essential for the thiamine activity. The role of the thiazolium ylide stabilized by a *d*–σ inter-

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* Rao[13] emphasizes that it is not easy to assign the pure ν(C=N) band in this kind of system.

[12] J. M. Bonnier, M. Gelus, and B. Papoz, *Bull. Soc. chim. France*, 1965, 2485.

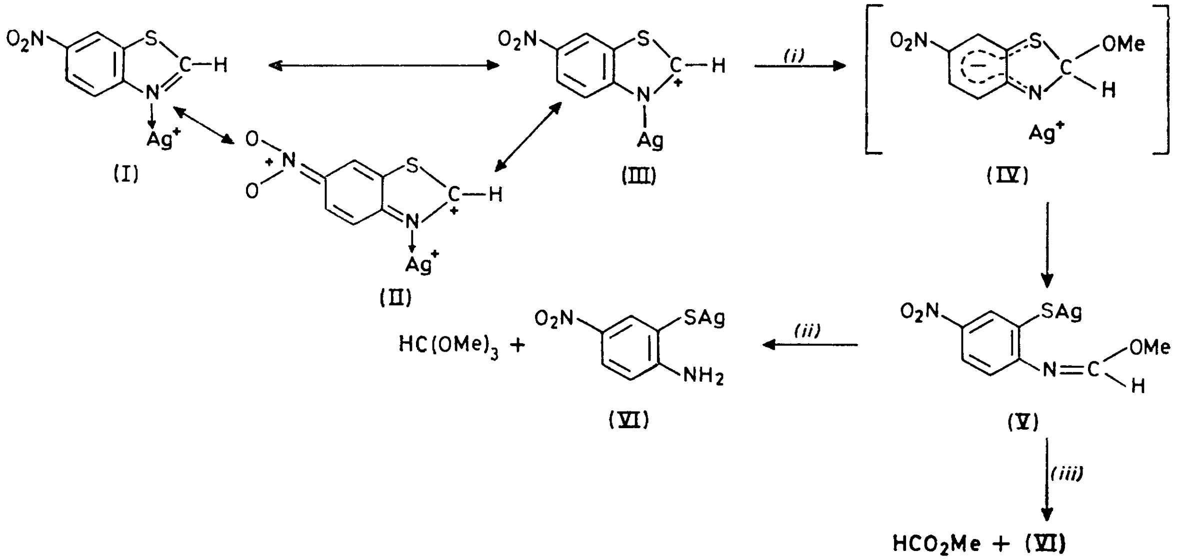
[13] C. N. R. Rao and R. Venkataraghavan, *Canad. J. Chem.*, 1964, **42**, 43.

[14] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 1954, 332.

[15] B. Kuznik and D. M. Czakis Sulikowska, *Zeszyty Nauk. Politech. lodz.* (*Chem.*), 1971, **21**, 43.

[16] (*a*) R. Breslow, *J. Amer. Chem. Soc.*, 1957, **79**, 1762; (*b*) *ibid.*, 1958, **80**, 3719; (*c*) *Ann. New York Acad. Sci.*, 1962, **98**, 445; (*d*) R. Breslow and E. McNelis, *J. Amer. Chem. Soc.*, 1959, **81**, 3080.

action through a *d* orbital of the sulphur and the σ orbital of C^2 is known.[16,17] On the other hand, it has been shown that OH^- can cause opening of the thiazole ring.[18-21] More recently, ring opening has been reported by the action of secondary aliphatic amines on 2-halogeno-5-nitrothiazoles,[22] and the reaction of 6-nitrobenzothiazoles with methoxide ion in dimethyl sulphoxide (dmso) gives reversible opening of the ring.[23] Despite the considerable amount of work done on thiazole–metal complexes, no data are available about how co-ordination to a metal can influence the reactivity of the heterocyclic system.



SCHEME (*i*), MeOH, $-H^+$; (*ii*), H^+ and MeOH; (*iii*), H^+ and H_2O

We find that alcohols (MeOH, EtOH, and $PhCH_2OH$) react with the complexes $[Ag(nbt)][NO_3]$ and $[Ag(nbt)_2]X$ at room temperature under nitrogen to give ring-opening reactions. When $[Ag(nbt)][NO_3]$ was suspended in freshly distilled, anhydrous methanol and shaken under nitrogen, a yellow-orange product separated which analysed for 2-amino-5-nitrobenzenethiolatosilver(I) [see (VI) in the Scheme]. The ^1H n.m.r. spectrum in $[^2H_6]$-dmso showed four resonances at τ 1.57, 2.39, 3.42, and 3.53 assigned as in Table 2. The i.r. spectrum (Nujol mull) showed bands at 3 455m and 3 357ms cm^{-1} [$\nu(NH_2)$ stretching], at 1 570ms cm^{-1} [N–H deformation], and at 1 603s and 1 580s cm^{-1} [$\nu(NO_2)$ (in the ring)]. In the range 600—1 600 cm^{-1} the spectrum was strongly modified with respect to that of the parent complex, as a consequence of the collapse of the thiazole ring. No bands due to an N=C–S moiety were evident. The complex does not conduct in dmf (Λ_m 12 S cm^2 mol^{-1}). The low solubility in common solvents (benzene, chlorohydrocarbons, and alcohols) can be explained on the basis of a polymeric structure. Starting from $[Ag(nbt)_2]$-$[NO_3]$ in MeOH, besides the complex (VI), unchanged nbt was also found (*ca.* 1 mol per mol of starting material) showing that the alcohol does not react with free ligand released during the reaction.

A comparison can be made between the nitrogen atom in the N-bonded thiazole–metal complexes and the nitrogen atom in thiamine or in thiazolium salts. Breslow [16b–d] observed that the catalytic ability of thiazolium salts depends on the withdrawing effect of the R group bonded to the N atom. The electron-withdrawal and inductive effects of such groups strongly influence the exchange rate of the C^2 hydrogen. Similarly the nature of the metal bonded to the nitrogen atom in the thiazole complexes can influence the reactivity of C^2.

Considering that nbt does not react with alcohols even at the boiling point of the solutions, the reactivity of the bonded thiazole system cannot be ruled out only on the basis of the withdrawing effect of the conjugated nitro-group. It is evident that silver plays an important role in the ring-opening reaction.* The poor tendency to increase its co-ordination number, especially with ' hard ' donor atoms, the electronic configuration, and the charge density can contribute to a polarization of the N=C bond, thus enhancing the positive charge at C^2 and making possible an interaction with the poor nucleophile MeOH (see Scheme).

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* We have evidence of a ring-opening reaction on the $[Ag(bt)]$-$[NO_3]$ and $[Ag(bt)_2]X$ complexes. This is of some relevance since benzothiazole does not react with methoxide ion to give a ring-opening reaction and supports the role of silver in activating the C^2 position. These systems will be discussed in a subsequent paper, together with 2-substituted benzothiazole.

[17] P. Haake, L. P. Bausher, and W. B. Miller, *J. Amer. Chem. Soc.*, 1969, **91**, 111.

[18] (*a*) R. R. Williams and A. E. Ruchle, *J. Amer. Chem. Soc.*, 1935, **57**, 1856; (*b*) R. R. Williams and O. Zima, *Ber.*, 1940, **73**, 941.

[19] P. Sykes and A. R. Todd, *J. Chem. Soc.*, 1951, 534.

[20] G. D. Mayer and D. E. Metzler, *J. Amer. Chem. Soc.*, 1957, **79**, 4386.

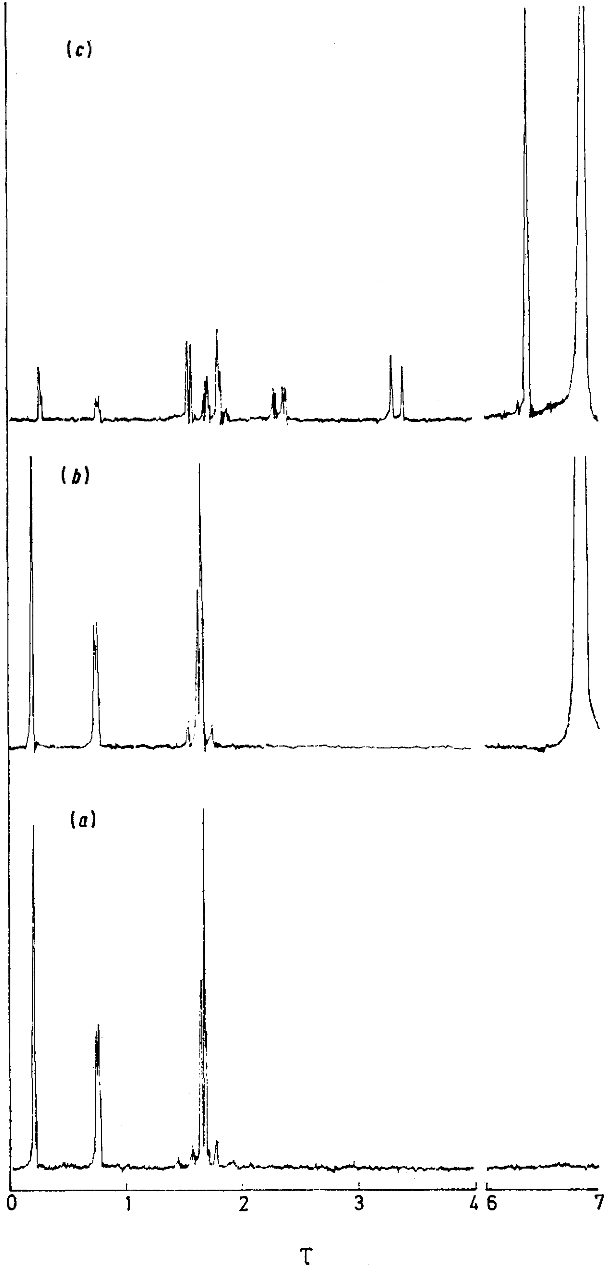
[21] P. Haake and J. M. Duclos, *Tetrahedron Letters*, 1970, 461.

[22] A. O. Ilvespaa, *Helv. Chim. Acta*, 1968, **51**, 1723.

[23] G. Bartoli, F. Ciminale, M. Fiorentino, and P. E. Todesco, *J.C.S. Chem. Comm.*, 1974, 732.

As no strong base is present, the proton-extraction process, with formation of an ylide system, does not take place. The intermediate (IV) (see Scheme), a Meisenheimer-like adduct, undergoes cleavage of the S–C^2 bond to give (V).* The presence of a large excess of alcohol gives cleavage of the N=C bond. It is known that imidates, $R^1C(=NR^2)OR^3$, react with alcohols, R^3OH, at room temperature, the rate of reaction (from a few days to weeks) being dependent on the alcohol (increasing in the order R^3 = Me < Et < Pr),[24] the products being the primary amines R^2NH_2 and orthoesters $R^1C(OR^3)_3$. In our case, trimethyl orthoformate should be formed on alcoholysis. In an acidic medium and in the presence of water, the hydrolysis gives alkylammonium salts and esters RCO_2R. Under our experimental conditions, water was carefully excluded and this second path seems not to be relevant.

In a study of the influence of alcohol, we found that the rate of the alcoholysis process increases in the order MeOH < EtOH < $PhCH_2OH$, in accordance with the literature data. The cleavage of the N=C bond in this case could be accelerated by the acidity of the medium, resulting from the reaction of ROH with C^2 (see Scheme).† Gas-chromatographic analysis has shown the presence of trimethyl orthoformate in the MeOH solution after isolation of (VI). In order to confirm the formation of (V) during the reaction, we carried out the reaction of $[Ag(nbt)][NO_3]$ with MeOD in $[^2H_6]$dmso in a sealed n.m.r. tube, and ^1H n.m.r. spectra were recorded at various times (see Figure). Spectrum (*c*) clearly shows two classes of signal. The resonances at τ 0.28(s), 0.78(m), and 1.71(m) (1 : 1 : 2 relative intensities) are due to unchanged starting material (*ca.* 20%) and are assigned to H^2, H^7, and H^4 + H^5 respectively. The peaks at τ 1.56(d), 1.81(s), 2.34(dd), 3.35(d), and 6.37(s) (1 : 1 : 1 : 1 : 3 relative intensities) are assigned to the open form of the thiazole and can be interpreted on the basis of an imidate form. The doublet at τ 1.56 is assigned to H^7 of (V) coupled with H^5 [$J(H^5H^7)$ 2.5 Hz]; the apparent singlet at τ 1.81 is consistent with the N=C–H hydrogen. Careful investigation shows that this signal is a quartet resulting from coupling with the methoxy-protons [$J(H\text{–}CH_3)$ 0.8 Hz]. The resonance at τ 2.34 (a doublet of doublets)‡ is assigned to H^5 coupled with H^7 [$J(H^5H^7)$ 2.5 Hz] and with H^4 [$J(H^4H^5)$ 9.0 Hz]; the doublet at τ 3.35 is due to H^4 coupled with H^5 [$J(H^4H^5)$ 9.0 Hz]. The signal at τ 6.37, apparently a singlet, can be resolved into a doublet and is assigned to the methoxy-protons coupled with the hydrogen atom in the N=CH(OMe) moiety [$J(H\text{–}CH_3)$ 0.8 Hz]. No other signals were evident in the spectrum other than that due to the unchanged MeOD. Working with CD_3OD, the signal at τ 6.37 (methoxy-group of the imidate form) did not appear, the other resonances being unchanged, thus confirming the assignment made. For longer reaction times, the spectrum changed to that of (VI), which can be isolated from the solution. Addition of an excess of alcohol accelerated the conversion of (V) into (VI). The reaction of the perchlorate complex followed an identical path. The same final silver complex was isolated also with EtOH and $PhCH_2OH$.



^1H N.m.r. spectrum in $[^2H_6]$dmso of: (*a*), $[Ag(nbt)][NO_3]$; (*b*), $[Ag(nbt)][NO_3]$ and MeOD (1 : 3), *t* = 0; and (*c*), (*b*) after 12 h

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* The reaction of MeO$^-$ with nbt follows an identical path,[23] the conversion of the Meisenheimer adduct to the imine having been assumed as an equilibrium process. In our work the presence of Ag^I can make the S–C^2 bond cleavage an irreversible reaction. Thus, a double role can be inferred for silver in the ring-opening reaction: (*i*) promotion of nucleophilic attack by MeOH; (*ii*) stabilization of the open form.

[24] R. Roger and D. G. Neilson, *Chem. Rev.*, 1962, **61**, 179.

† Preliminary studies have demonstrated that strong acids (HNO_3) can positively affect the rate of cleavage of the N=C bond.

‡ For the sake of simplicity, the hydrogen atoms of the aromatic ring are numbered as in the starting benzothiazole system.

This provides the first example of a ring-opening reaction of the thiazole system in non-basic media. Studies are in progress in order to ascertain the role of the metal and of the substituents in this reaction.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 557 spectrophotometer. Gas-chromatographic analyses were made with a 5750 HP instrument. ^{1}H N.m.r. spectra were recorded on Varian 60 and HA100 spectrometers. Solvents were dried and distilled under nitrogen before use. All reactions were carried out in an atmosphere of pure dry nitrogen.

The compounds [$^2H_6$]dmso, CD_3OH, and CD_3OD were from J. T. Baker Chemicals. Benzothiazole was distilled before use (b.p. 231 °C) and 6-nitrobenzothiazole was crystallized from methanol and carbon tetrachloride (m.p. 170 °C).

Preparations.—*(Benzothiazole)silver*(I) *nitrate*, [Ag(bt)][NO_3]. To a solution of Ag[NO_3] (1.7 g, 1 mol) in absolute ethanol was added dropwise a solution of bt (1.35 g, 1 mol) in OEt_2 at 0 °C with stirring. An excess of diethyl ether (50 cm^3), cooled to 0 °C, was added and a white crystalline *complex* precipitated, which was filtered off, washed with water, diethyl ether, and pentane, and dried *in vacuo*. The complex is soluble in dmf and in dmso.

Bis(benzothiazole)silver(I) *nitrate*, [Ag(bt)$_2$][NO_3]. To a solution of Ag[NO_3] (0.85 g, 1 mol) in distilled air-free water, was added bt (1.35 g, 2 mol) in EtOH. A white solid precipitated which was filtered off, washed with water, ethanol, and pentane, and dried *in vacuo*. Crystallization from *NN*-dimethylformamide–toluene afforded the pure *product* (1.9 g). The complex is soluble in dmf and dmso, sparingly soluble in ethanol and acetone.

(6-*Nitrobenzothiazole)silver*(I) *nitrate*, [Ag(nbt)][NO_3]. Addition of a solution of nbt (0.90 g, 1 mol) in EtOH to a solution of Ag[NO_3] (0.85 g, 1 mol) in hot EtOH caused precipitation of an off-white *solid* which was washed with ethanol and pentane and dried *in vacuo*. The complex is soluble in dmf and dmso.

Bis(6-*nitrobenzothiazole)silver*(I) *nitrate*, [Ag(nbt)$_2$][NO_3]. This *complex* was similarly prepared with a ligand to silver molar ratio of 2 : 1. It was crystallized from *NN*-dimethylformamide–toluene.

The complexes [Ag(bt)$_2$][ClO_4] *and* [Ag(nbt)$_2$][ClO_4]. These complexes were obtained by adding a solution of the ligand (2 mol) in toluene to a solution of Ag[ClO_4] (1 mol) in toluene. Crystallization from *NN*-dimethylformamide–toluene afforded the pure *products* which are soluble in dmf and dmso, and sparingly soluble in hot acetone and ethanol. Attempts to isolate the [AgL][ClO_4] complexes failed, and [AgL_2][ClO_4] were also obtained with a ligand to silver molar ratio of $<1:1$.

Reaction with Alcohols.—The [Ag(nbt)$_n$]X ($n = 1$ or 2; X = NO_3 or ClO_4) complex (0.5 g) was suspended in dry alcohol (10 cm^3; MeOH, EtOH, or $PhCH_2OH$) under nitrogen and the suspension shaken vigorously. A yellow complex was formed in a few hours, and was filtered off, washed with water, CH_2Cl_2, alcohol, and pentane, and dried *in vacuo*. In all the cases the same compound 2-amino-5-nitrobenzenethiolatosilver(I), (VI), was obtained (*ca.* 70% yield), and is soluble in dmf and dmso. Addition of MeI to a solution of (VI) produced precipitation of AgI and gave a compound characterized as methyl 2-amino-5-nitrobenzenethiolate by comparison with an authentic sample.

Gas-chromatographic Determination of the Orthoesters.—The alcoholic solutions, after filtering off compound (VI), were analysed by means of gas chromatography using 4-m columns (3-mm internal diameter) of silicone (250 °C) or polyethylene glycol 4 000 (150 °C); the carrier gas (nitrogen) flow rate was 45 cm^3 min^{-1}. The presence of the orthoesters was revealed by comparison with a standard, and the estimated yield was *ca.* 75% with respect to the starting material [1 : 1 ratio with compound (VI)].

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