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THE REACTIONS OF SOME BROMO-DERIVATIVES OF COMPOUNDS HAVING REACTIVE METHYLENE GROUPS WITH THIOUREAS, AND OF SOME RESULTANT THIOURONIUM SALTS WITH BASE

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Abstract—Whereas α-bromocarbonyl compounds react with thiourea to give thiazole derivatives, bromomalononitrile and bromobis(phenylsulphonyl)methane underwent protodebromination. With N,N,N',N'-tetramethylthiourea many of the bromo-compounds gave thiouronium salts but protodebromination sometimes supervened. N,N'-Disubstituted thioureas provided examples of salt formation, protodebromination and cyclisation reactions. The only thiouronium salt to provide an ylide on treatment with base was the S-[bis(phenylsulphonyl)methyl]-N,N,N',N'-tetramethylthiouronium bromide. N,N'-Disubstituted salts gave isothioureas rather than ylides. Thiouronium dicyanomethylide underwent cyclisation rather than a Wittig reaction when heated with *p*-nitrobenzaldehyde, and the aldehyde condensed with the resultant 2-aminothiazole.

A number of thiouronium ylides has been isolated, some stabilised by inclusion of the carbanionic moiety in a cyclopentadiene[1-3] or diazacyclopentadiene[2,4] ring, and others by the presence of electron-withdrawing carbonyl[5-8] or cyano[9,10] groups attached to the carbanionic centre. Many of these thiouronium ylides have been made by the action of base on thiouronium salts,[1,3,5-7] the latter in turn being prepared by reaction of suitable halogeno-derivatives with thioureas. In the course of an investigation of thiouronium ylides, the reactions of a number of α-brominated derivatives of compounds having electron-withdrawing groups with thioureas were studied.

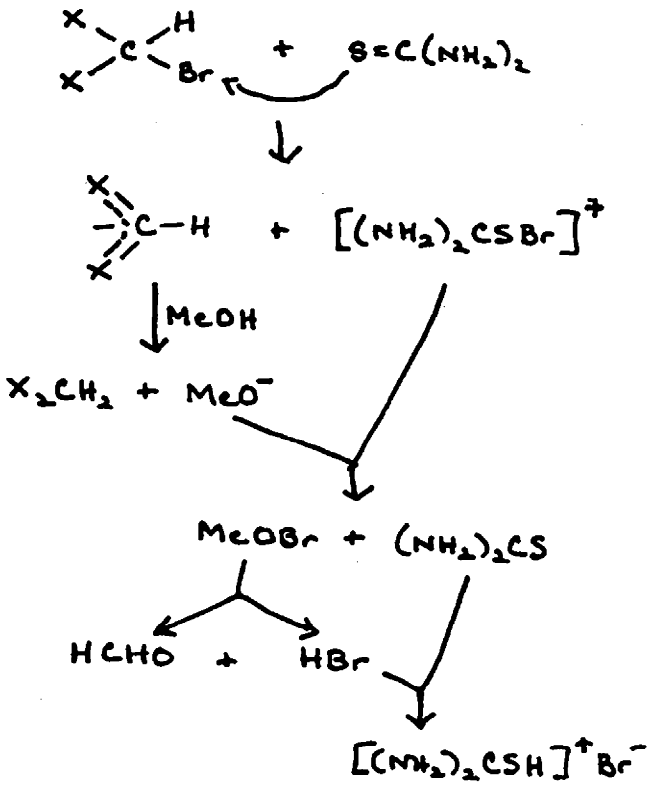
Reactions involving thiourea. If thiourea itself reacts with an α-bromocarbonyl compound then frequently a 2-aminothiazole is formed, this being a standard method for the preparation of such compounds.[11] Thus *p*-nitrophenacyl bromide gives 2-amino-4-*p*-nitrophenylthiazolium bromide in almost quantitative yield, and dimethyl bromomalonate gives the 2-iminothiazolidone (I)[12] in high yield.

Such cyclisation might be avoided by the use of other electron-withdrawing groups than CO, thus permitting thiouronium salts to be isolated. Treatment of bromomalononitrile with thiourea, even at 0°, did not, however, provide a thiouronium salt, but instead led to replacement of the Br by an H atom to generate malononitrile. Thiouronium bromide was also isolated. Bromobis(phenylsulphonyl)methane underwent a similar reaction in methanol either under reflux or at room temperature, providing a good yield of bis(phenylsulphonyl)methane. It seems most likely that in these reactions nucleophilic attack by thiourea at the Br atom is involved, producing initially an S-bromothiouronium salt, $[(NH_2)_2CSBr]^+ [CHX_2]^-$ (X = CN or $PhSO_2$). This reaction is promoted by the accompanying formation of a stabilised carbanion. There is ample precedent for removal of a bromonium ion to leave a stabilised carbanion,[13,14] including cases involving thiourea as debrominating agent.[13] The subsequent reactions leading to formation of malononitrile [or bis(phenylsulphonyl)methane] and thiouronium bromide could involve proton transfer from solvent methanol to the carbanion, and reaction of a resultant methoxide ion (or of methanol itself) with the bromothiouronium cation, culminating in oxidation of the alcohol and formation of thiouronium bromide.

An alternative possibility, which has been suggested for some dehalogenation reactions of aryl iodides, involves initial formation of radical ions.[15]

Reactions involving N,N,N',N'-*tetramethylthiourea.* If all the H atoms on the N atoms are replaced by alkyl groups thiazole formation is prevented, whatever the identity of the bromo-compound. With this tetra-N-substituted thiourea dimethyl bromomalonate, bromobis(phenylsulphonyl)methane and *p*-nitrobenzyl bromide all gave thiouronium salts in straightforward manner, but complications still arose with other substrates. Bromomalononitrile again underwent protodebromination. Bromodibenzoylmethane gave a thiouronium salt in benzene at room temperature but underwent protodebromination in refluxing ethanol. In methanol at room temperature the amide (II) was the product, presumably formed by hydrolytic cleavage of the thiouronium salt; this amide was also formed if the thiouronium salt formed in benzene solution was subjected to aqueous work-up. *p*-Nitrophenacyl bromide likewise provided a thiouronium salt in benzene at room temperature and an amide (III) in refluxing methanol.

Reactions involving N,N'-*disubstituted thioureas.* Not surprisingly the disubstituted thioureas were intermediate in their behaviour. Benzyl bromide and its *p*-nitro derivative gave thiouronium salts. *p*-Nitrophenacyl bromide gave a thiouronium salt with N,N'-dimethylthiourea but the thiazolidinium salt (IV) with N,N'-diphenylthiourea. The formation of a thiazoline rather than a thiazolidine derivative from these reactants had been reported previously,[16] but the earlier workers had used more severe conditions. The

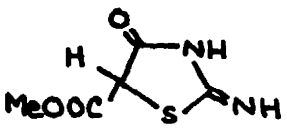


structures of both of the present products follow from their elemental analyses and spectra. This difference in reactivity between the dimethyl- and diphenyl-thioureas is unexpected in that an NMe group is likely to be more nucleophilic than an N-phenyl group and thus would also be expected to undergo cyclisation. Bromobis(phenylsulphonyl)methane provided some N,N′-dimethylthiouronium salt in methanol at room temperature but in refluxing methanol reacted instead predominantly by protodebromination. Dimethyl bromomalonate gave a cyclised product with N,N′-dimethylthiourea for which, by analogy with (I) formed from dimethyl bromomalonate and thiourea, structure (V) might be expected, but structure (VI) cannot be ruled out, for this compound, unlike (I), formed a stable hydrobromide, and its IR spectrum is different in the CO region from that of (I). Bromomalononitrile reacted with N,N′-dimethyl- or with N,N′-ethylene-thiourea to give the 4-amino-5-cyano-2-iminothiazolinium bromides (VII). Cyclisation proceeds as in the case of α-carbonylthiouronium salts.

Action of base upon thiouronium salts. It had been hoped that the action of base upon the N,N,N′,N′-tetrasubstituted thiouronium salts would provide stabilised thiouronium ylides but this was only achieved in the case of the salt derived from bis(phenylsulphonyl)methane, which provided the stable ylide (VIII) in good yield. This ylide is protonated by perchloric acid and is more basic than its triphenylphosphonium analogue.[17] The other tetrasubstituted salts produced intractable mixtures when treated with base; if base was added in the presence of *p*-nitrobenzaldehyde no product from a Wittig reaction of the aldehyde with an ylide was formed. At this stage a publication by Nozaki *et al.*[18] appeared which described the complexity of the reactions which ensue when base is added to such tetrasubstituted thiouronium salts, so studies were discontinued.

Treatment of the N,N′-disubstituted thiouronium salts with base resulted in removal of a proton from a N atom to give isothioureas, e.g. (IX, X) from *p*-nitrophenacyl- and *p*-nitrobenzyl-thiouronium salts, respectively, rather than from the α-C atom to provide an ylide. Thus the N-H atoms must be more acidic than the α-C-H atoms, or alternatively the desired ylides are more basic than these isothioureas. Phenyl lithium or aqueous sodium hydroxide were used as bases; cleavage of the molecules to mercaptans did not appear to take place with the aqueous alkali.

Reaction of a thiouronium ylide with aldehydes. Since thiouronium fluorenylides and cyclopentadienylides reacted with *p*-nitrobenzaldehyde in Wittig reactions,[1] it seemed of interest to investigate such reactions involing other thiouronium ylides. Thiouronium dicyanomethylide (XI) reacted slowly with benzaldehyde and more rapidly with *p*-nitrobenzaldehyde. Instead of a normal Wittig reaction product, however, the thiazole imines (XII) were formed. Their structures were verified by their ready hydrolysis to 2,4-diamino-5-cyanothiazole and benzaldehydes. Obviously this ylide undergoes intramolecular cyclisation faster than it reacts with the aldehydes, and the aldehydes then condense with the resultant aminothiazole. The ylide, like others with electron-withdrawing groups attached to their carbanionic centres, is unreactive in Wittig reactions because of the extensive delocalisation of negative charge.

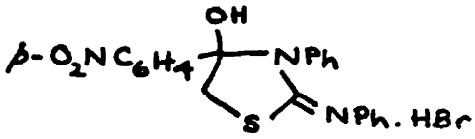


(I)

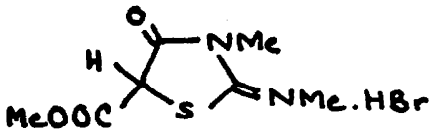
$RSCONMe_2$

(II) R = $(PhCO)_2CH$

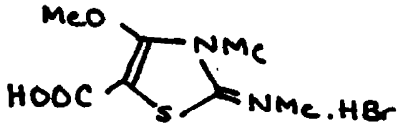
(III) R = $p\text{-}O_2NC_6H_4CH_2$



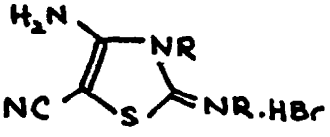
(IV)



(V)



(VI)



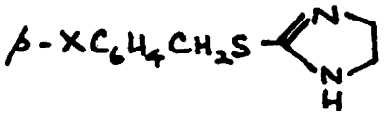
(VII) R = Me or RR = CH_2CH_2

$(PhSO_2)_2\bar{C}-\overset{+}{S}C(NMe_2)_2$

(VIII)

$p\text{-}O_2NC_6H_4COCH_2SC(=NMe)NHMe$

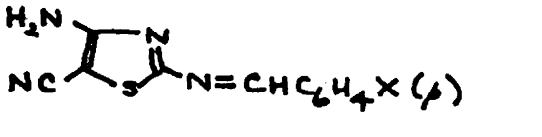
(IX)



(X) X = H or NO_2

$(NC)_2\bar{C}-\overset{+}{S}C(NH_2)_2$

(XI)



X = H or NO_2

(XII)

CONCLUSION

Treatment of α-brominated derivatives of a number of compounds having electron-withdrawing groups with thioureas gave, in the case of thiourea itself thiazole derivatives or protodebrominated products; tetramethylthiourea gave thiouronium salts or protodebrominated products; N,N'-disubstituted thioureas gave in different cases thiouronium salts, thiazole derivatives or protodebrominated products. Treatment of the tetra-N-substituted thiouronium salts with base gave complicated mixtures and only in the case of a bis(phenylsulphonyl)methylthiouronium salt was a thiouronium ylide isolated. On treatment with base N,N'-disubstituted thiouronium salts lost a proton from a nitrogen atom rather than from the α-C atom, providing isothioureas rather than ylides.

EXPERIMENTAL

All m.ps are uncorrected. Electronic spectra were recorded in methanolic soln unless otherwise indicated. IR spectra were recorded using Nujol mulls. NMR spectra were recorded in [$^2H_6$]DMSO unless otherwise indicated. Light petroleum had b.p. 40–60°.

(a) *Reactions of thiourea*

With p-nitrophenacyl bromide. A soln of *p*-nitrophenacyl bromide (980 mg, 4 mmol) and thiourea (304 mg, 4 mmol) in EtOH (25 ml) was heated under reflux. When it was cooled a crystalline ppt formed and was filtered off and washed with ether, providing 2-amino-4-*p*-nitrophenylthiazole hydrobromide (1.20 g, 94%), m.p. 251–256°, which on treatment with 2M NaOH gave the corresponding *aminothiazole*, m.p. 284–288°, λ_{max} 216, 239, 266, 362 nm ($\log\varepsilon$ = 4.14, 4.10, 4.09, 4.02), ν_{max} 1500, 1325 cm^{-1}, τ 1.95 (m, 4 H), 2.69 (s, 1 H), 2.89 (s, 2 H) (Found: C, 48.5; H, 3.1; N, 18.9. $C_9H_7N_3O_2S$ requires: C, 48.9; H, 3.2; N, 19.0%).

With dimethyl bromomalonate. Reaction of dimethyl bromomalonate (3.15 g, 0.015 mol) with thiourea (1.14 g, 0.015 mol) gave I,[12] m.p. 250° (dec) (from EtOH), λ_{max} 214, 249, 309 nm ($\log\varepsilon$ = 4.33, 3.94, 3.20), ν_{max} 1640 cm^{-1}, τ 4.85 br, 6.29 (s).

With α-bromobis(phenylsulphonyl)methane. A soln of the bromo-compound (562 mg, 1.5 mmol) and thiourea (114 mg, 1.5 mmol) in MeOH (12 ml) was heated under reflux for 10 min, and then evaporated *in vacuo* to *ca.* 2 ml. The residue was cooled in ice and scratched. Needles of bis(phenylsulphonyl)methane separated and were filtered off and washed with a small amount of cold MeOH (280 mg, 63%), m.p. and mixed m.p. 118–119°. The same product was obtained if a mixture of the reactants in MeOH was kept at room temp for 16 days.

(b) *Reactions of* N,N,N',N'-*tetramethylthiourea*

With dimethyl bromomalonate. A soln of the bromo-compound (1.05 g, 5 mmol) and tetramethylthiourea (660 mg, 5 mmol) in benzene (5 ml) was heated under reflux for 2 min and then cooled. Ether (15 ml) was added and after 2 hr the pale yellow ppt of the thiouronium bromide was filtered off and washed with ether (1.10 g, 64%). A sample (0.76 g) was dissolved in EtOH (5 ml) and perchloric acid (70%, 0.4 ml) was added, followed by ether (10 ml). Scratching induced crystallisation of S-[*bis(methoxycarbonyl)methyl*]*tetramethylthiouronium perchlorate* (0.65 g, 52% overall yield) m.p. 92–95°, λ_{max} 253, 312 nm, ($\log\varepsilon$ = 4.35, 3.45), ν_{max} 1740 cm^{-1}, τ 4.61 (s, 1 H), 6.20 (s, 6 H), 6.72 (s, 12 H) (Found C, 33.5; H, 5.6; N, 7.7. $C_{10}H_{19}ClN_2O_8S$ requires: C, 33.1; H, 5.2; N, 7.7%).

With bromobis(phenylsulphonyl)methane. The bromo-compound (500 mg, 1.33 mmol) and tetramethylthiourea (175 mg, 1.33 mmol) were stirred in benzene (40 ml) until a clear soln was obtained (*ca* 1 hr). After 10 days at room temp a ppt was filtered off and washed with benzene and then ether, providing the thiouronium salt (300 mg, 58%), m.p. 101–105°, which was characterised by conversion into an ylide. (See below).

With p-nitrobenzyl bromide. p-Nitrobenzyl bromide (6.47 g, 30 mmol) and tetramethylthiourea (3.96 g, 30 mmol) in EtOH (20 ml) were heated under reflux fpr 30 min. Addition of ether precipitated the thiouronium bromide (9.9 g, 95%), which was converted into S-(p-*nitrobenzyl*)*tetramethylthiouronium perchlorate* (81%), m.p. 89–91° (from MeOH), λ_{max} 269 nm ($\log\varepsilon$ = 3.96), ν_{max} 1500, 1340 cm^{-1} (Found C, 39.2; H, 5.1; N, 11.4. $C_{12}H_{18}ClN_3O_6S$ requires: C, 39.2; H, 4.9; N, 11.4%).

With α-bromodibenzoylmethane. When α-bromodibenzoylmethane (456 mg, 1.5 mmol) and tetramethylthiourea (198 mg, 1.5 mmol) were stirred in benzene (5 ml) for 10 min an oil separated. Benzene was decanted off and ether (50 ml) was added. The oil crystallised slowly and after one week was filtered off to provide the yellow highly deliquescent thiouronium bromide (170 mg, 26%), ν_{max} 1660 cm^{-1}, τ 2.5 (m, 10 H), 2.97 (s, 1 H), 7.40 (s, 3 H), 7.45 (s, 6 H), 7.51 (s, 3 H); attempted conversion into the corresponding perchlorate led to formation of II. If a slurry of α-bromodibenzoylmethane (1.82 g, 6 mmol), finely ground tetramethylthiourea (792 mg, 6 mmol) and MeOH (10 ml) was stirred for 5 min and methanolic sodium perchlorate (1.66 M, 3.4 ml, 6 mmol) was added, crystals of II separated (650 mg, 33%), m.p. 184–186°, λ_{max} 251, 335 nm ($\log\varepsilon$ = 4.15, 3.55), ν_{max} 1685, 1665 cm^{-1}, τ 2.48 (m, 10 H), 4.56 (s, 1 H), 6.45 (s, 3 H), 6.49 (s, 3 H).

With p-nitrophenacyl bromide. A soln of tetramethylthiourea (528 mg, 4 mmol) in benzene (4 ml) was added to a stirred soln of the bromide (980 mg, 4 mmol) in benzene (8 ml). After 1 hr the pale yellow *thiouronium bromide* was filtered off and washed with ether (1.40 g, 93%), m.p. 125°, λ_{max} 260, 376 nm ($\log\varepsilon$ = 4.04, 3.61), ν_{max} 1695, 1520, 1350 cm^{-1}, τ 1.61 (m, 4 H), 5.14 (s, 2 H), 6.53 (s, 12 H) (Found: C, 41.3; H, 5.0; N, 10.9. $C_{13}H_{18}BrN_3O_3S$ requires: C, 41.5; H, 4.8; N, 11.2%). If the reactants were heated in MeOH (10 ml) for 5 min, solvent was then removed *in vacuo*, and further MeOH (5 ml) was added, a ppt formed which was washed with MeOH followed by ether to provide III (85 mg, 8%) ν_{max} 1690, 1645, 1525, 1350 cm^{-1}, τ 1.70 (m, 4 H), 5.50 (s, 2 H), 7.05 (s, 6 H) (Found C, 49.1; H, 4.5; N, 10.0. $C_{11}H_{12}N_2O_4S$ requires: C, 49.3; H, 4.5; N, 10.4%).

(c) *Formation of thiazole derivatives from* N,N'-*disubstituted thioureas*

Thiazolidinium salt (IV). A warm soln of *p*-nitrophenacyl bromide (980 mg, 4 mmol) in EtOH (10 ml) was aded to a warm soln of N,N'-diphenylthiourea (912 mg, 4 mmol) in EtOH (25 ml). Crystals formed almost immediately. The soln was cooled in ice for 30 min. Pale yellow crystals were filtered off and washed with ether, providing 4-*hydroxy*-4-p-*nitrophenyl*-3-*phenyl*-2-*phenyliminothiazolidinium bromide* IV (1.55 g, 82%), m.p. 270° (decomp) (from methanol), λ_{max} 263 nm ($\log\varepsilon$ = 4.34), ν_{max} 1510, 1345 cm^{-1}, τ 1.91 (m, 4 H), 2.56 (m, 10 H), 5.4 br, 5.99 (dd, 2 H, *J* = 13 Hz) (Found: C, 53.0; H, 3.9; N, 8.5. $C_{21}H_{18}BrN_3O_3S$ requires: C, 53.3; H, 3.8; N, 8.9%).

Thiazolidone derivative V (or VI). A soln of dimethyl α-bromomalonate (1.05 g, 5 mmol) and N,N'-dimethylthiourea (520 mg, 5 mmol) in EtOH (9 ml) was heated under reflux for 30 min. The soln was cooled in ice, and the resultant ppt was filtered off and washed with a small volume of cold EtOH followed by ether. Addition of ether (50 ml) to the filtrate produced a further crop of crystals, and the combined yield of *thiazole derivative* V or VI (980 mg, 69%) had m.p. 158° (dec) (from EtOH), λ_{max} 217, 253, 260, 311 nm ($\log\varepsilon$ = 3.98, 3.31, 3.30, 3.49), ν_{max} 1765, 1750 cm^{-1}, τ 3.3 vbr, 6.27 (s, 3 H), 6.76 (s, 3 H), 6.89 (s, 3 H) (Found: C, 30.0; H, 3.8; N, 9.6. $C_7H_{11}BrN_2O_3S$ requires: C, 29.8; H, 3.9; N, 9.9%).

Thiazolinium salts (VII). A soln of N,N'-dimethylthiourea (3.12 g, 0.03 mol) in MeOH was added to a methanolic soln containing freshly prepared (*in situ*) bromomalononitrile (0.03 mol). The mixture was warmed to 60° for 5 min and then

cooled on ice for 30 min. Crystals were filtered off and washed with a small amount of MeOH and then ether to provide the product (1.2 g). Addition of ether (*ca* 100 ml) to the filtrate provided a second crop (3.1 g), giving a total yield (58 %) of *4-amino-5-cyano-3-methyl-2-methyliminothiazolinium bromide* VII (R = Me), m.p. 270° (dec) (from MeOH), λ_{max} 252 sh, 292 nm ($\log\varepsilon$ = *ca.* 3.79, 4.24), ν_{max} 2210 cm^{-1}, τ 2.08 br, 6.49 (s, 3 H), 7.03 (s, 3 H) (Found: C, 28.8; H, 3.8, N, 22.7. $C_6H_{10}BrN_4S$ requires: C, 28.8; H, 4.0; N, 22.4 %). A similar procedure provided the thiazolinium salt (VII, RR = CH_2CH_2) (20 %) m.p. 170° (dec), ν_{max} 2205 cm^{-1}, τ 0.23 br (1 H), 1.9 br (2 H), 6.08 (m, 4 H).

S-(p-*Nitrophenacyl*)-N,N'-*dimethylisothiourea* (IX). A soln of *p*-nitrophenacyl bromide (980 mg, 4 mmol) and N,N'-dimethylthiourea (416 mg, 4 mmol) in EtOH (25 ml) was warmed. The ppt was filtered off from the cooled soln and washed with EtOH and ether to give the *p-nitrophenacyldimethylthiouronium bromide* (1.30 g, 92 %), m.p. 250° (dec) (Found: C, 37.7; H, 3.9; N, 12.0. $C_{11}H_{14}BrN_3O_3S$ requires: C, 37.9; H, 4.0, N, 12.1 %). A soln of this salt (522 mg, 1.5 mmol) in warm EtOH (100 ml) was treated with 2M NaOH (0.5 ml) and the mixture was kept for 30 min, being shaken occasionally. Solvent was reduced *in vacuo* to 10 ml. When the resultant soln was cooled, pale yellow crystals formed and were filtered off and washed with EtOH and ether providing the *isothiourea* IX (350 mg, 87 %), m.p. 185° (dec) (from EtOH), λ_{max} 263 nm ($\log\varepsilon$ = 4.06), ν_{max} 1655, 1520, 1350 cm^{-1}, τ 1.94 (m, 4 H), 2.26 br (1 H), 6.31 (s, 2 H), 6.93 (s, 3 H), 7.29 (s, 3 H) (Found: C, 49.1: H, 4.9; N, 15.6. $C_{11}H_{13}N_3O_3S$ requires: C, 49.4; H, 4.9; N, 15.7 %).

S-p-*Nitrobenzyl*-N,N'-*ethyleneisothiourea* (X, X = NO_2). A soln of *p*-nitrobenzyl bromide (6.47 g, 30 mmol) and N,N'-ethylenethiourea (3.06 g, 30 mmol) in EtOH (20 ml) was heated under reflux for 30 min. When the soln cooled crystals of the nitrobenzylthiouronium bromide separated and were filtered off (8.5 g, 89 %), m.p. 146–148°. This salt (2.1 g, 6.6 mmol) in dry THF (50 ml) was treated with a soln of phenyl lithium in ether (0.96 M, 6.85 ml, 6.6 mmol). The mixture was stirred for 20 min and solvent was then removed *in vacuo*. The residue was dissolved in ether (300 ml), and the solution was washed with water (4 × 75 ml) and dried ($MgSO_4$). Solvent was removed *in vacuo* and trituration of the residue with ether provided yellow crystals of S-(p-*nitrobenzyl*)-N,N'-*ethyleneisothiourea* (860 mg, 55 %), m.p. 151–153°, λ_{max} 270 nm ($\log\varepsilon$ = 4.01), ν_{max} 1500, 1340 cm^{-1}, τ ([$^2H_4$]methanol) 2.10 (m, 4 H), 5.66 (s, 2 H), 6.39 (s, 4 H) (Found: C, 51.0; H, 4.8; N, 17.5. $C_{10}H_{11}N_3O_2S$ requires: C, 50.6; H, 4.6; N, 17.7 %).

S-*Benzyl*-N,N'-*ethyleneisothiourea* (X, X=H). Prepared as its *p*-nitrobenzyl analogue, this *isothiourea* (710 mg, 49 %) had m.p. 50–54°, τ (C^2HCl_3) 2.71 (m, 5 H), 5.60 (s, 1 H), 5.70 (s, 2 H), 6.37 (s, 4 H) (Found: C, 62.4; H, 6.3; N, 14.5. $C_{10}H_{12}N_2S$ requires C, 62.5; H, 6.2; N, 14.6 %).

N,N,N',N'-*Tetramethylthiouronium bis(phenylsulphonyl)-methylide* (VIII). Triethylamine (2 drops) was added to a suspension of N,N,N',N'-tetramethyl-S-bis(phenylsulphoyl)-methylthiouronium bromide (100 mg) in MeOH (2 ml). A transient soln resulted from which crystals separated. The *ylide* (50 mg, 60 %) was filtered off and washed with MeOH, and had m.p. 170–173°, λ_{max} 244, 259 sh, 328 sh nm ($\log\varepsilon$ = 4.15,–,–), ν_{max} 1285, 1125 cm^{-1} τ (C^2HCl_3) 2.70 (m, 10 H), 6.80 (s, 12 H) (Found: C, 50.3; H, 5.0; N, 6.7. $C_{18}H_{22}N_2O_4S_3$ requires: C, 51.1; H, 5.2; N, 6.6 %).

Reaction of thiouronium dicyanomethylide (XI) *with benzaldehyde*. A soln of the ylide (350 mg), 2.5 mmol) and freshly purified benzaldehyde (265 mg, 2.5 mmol) in EtOH (20 ml) was heated under reflux for 16 hr. Evaporation of the solvent *in vacuo* left yellow crystals which were filtered off and washed with a small volume of cold EtOH and then ether, providing *4-amino-2-benzylideneamino-5-cyanothiazole* (XII, X = H) (120 mg, 21 %), m.p. 198–200° (from acetonitrile), λ_{max} 218, 227, 273, 356 nm ($\log\varepsilon$ = 3.84, 3.83, 4.29, 3.81) ν_{max} 2205 cm^{-1}, τ 0.92 (s, 1 H), 1.71 (m, 5 H), 6.62 br (2 H) (Found: C, 57.5; H, 3.7; N, 24.0. $C_{11}H_8N_4S$ requires: C, 57.9; H, 3.5; N, 24.5 %). This compound was readily cleaved by methanolic HCl (10 % w/v) to give 2,4-diamino-5-cyanothiazole hydrochloride.

Reaction of thiouronium dicyanomethylide (XI) *with p-nitrobenzaldehyde*. A soln of the ylide (350 mg, 2.5 mmol) and *p*-nitrobenzaldehyde (375 mg, 2.5 mmol) in EtOH (25 ml) was heated under reflux for 1 hr. Evaporation of the solvent *in vacuo* left a residue which crystallised when scratched. The crystals were filtered off to give lustrous orange-red crystals of *4-amino-5-cyano-2-p-nitrobenzylideneaminothiazole* (XII, X = NO_2) (165 mg, 25 %), m.p. 249° (dec) (from EtOH), λ_{max} 228, 288, 394 nm ($\log\varepsilon$ = 4.14, 4.39, 3.93), ν_{max} 2230, 1520, 1350 cm^{-1}, τ 0.89 (s, 1 H), 1.76 (dd, 4 H, J = 8 Hz) (Found: C, 48.2; H, 2.6; N, 25.5. $C_{11}H_7N_5O_2S$ requires: C, 48.4; H, 2.6; N, 25.6 %).

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