Reaction between 2,2'-Dithiodianiline and Activated Alkynes. Synthesis of 4*H*-1,4-Benzothiazines

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By the title reaction acetylenic esters (2a—c), ketones (2d—g), and the nitrile (2h) gave in all cases the corresponding 4*H*-1,4-benzothiazines (3) together with other products whose nature depends on the alkyne used. Thus benzothiazoline and/or benzothiazole, benzothiazepine, and vinylsulphides were obtained in the representative cases (2c, f, h) studied in detail. Some of these latter compounds have been independently synthesised by reaction of 2-aminobenzenethiol with corresponding alkyne (2). In particular conditions by the reactions between 2,2'-dithiodianiline (1) and alkynes (2f, d) we isolated bis-enamine compounds (19) and (20) respectively and their intermediacy in formation of the corresponding benzothiazines (3f) and (3d) was achieved. The mechanisms of the observed reactions are also suggested.

Both 2*H*- and 4*H*-1,4-benzothiazines are of interest to us as starting substrates for the synthesis of molecules with potential pharmacological activity; such systems also occur in natural pigments [1] and dyes.[2] They have been prepared by (i) reaction of α-halogenoketones [3] or α-cyano-α-methylthioacetophenone [4] with 2-aminobenzenethiol, (ii) reaction of enolizable ketones with 2,2 -dithiodianiline [5] or 2-aminobenzenethiol,[6] and (iii) ring expansion of benzothiazolines; [7] a recent review summarises the current status of the chemistry of the compounds.[8]

We have reported the preliminary results of a new synthetic approach to 1,4-benzothiazines involving a reaction between 2,2 -dithiodianiline (1) and activated acetylenes.[9] In particular, we established that reaction of the disulphide (1) with the alkynes (2a, b, g) in a 1 : 2 molar ratio gave the corresponding 4*H*-1,4-benzothiazines (3a, b, g) in high yield; (3g) is difficult to obtain by other methods. Furthermore, it was found that compounds (3a, b) and their benzothiazoline co-products (4a, b) were obtained in roughly equimolar amounts according to equation (1).

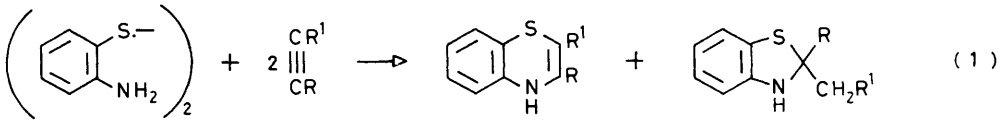
In order to check the general applicability of this reaction we extended our study to alkynes (2c—f, h) and this paper reports the results obtained.

T.l.c. monitoring of the reaction between the disulphide (1) and the alkyne (2a) in a 1 : 1 molar ratio showed complete disappearance of the alkyne but only partial utilization of the disulphide; with a 2 : 1 molar ratio of alkyne to disulphide, both reagents were conveniently consumed. All subsequent reactions, therefore, employed this latter molar ratio. Reactions between the disulphide (1) and the activated alkynes (2c—f, h) carried out under nitrogen and refluxing polar solvent [methanol (2d—f), *N*,*N*-dimethylformamide (DMF) (2c, h)], led in all cases to the corresponding 4*H*-1,4-benzothiazines (3c—f, h) in 76—87% yield. In particular, compounds (3d—f) precipitating from the reaction mixture, like 1,4-benzothiazine (3g), were very easily isolated while the other benzothiazines (3c, h) were isolated by column chromatography. The structures of the new compounds (3d—f) are fully supported by their ^{1}H n.m.r. spectra; all of them show a characteristic signal (doublet) in the range δ 6.90—7.22 due to the vinylic proton at C-3 coupled to aminic hydrogen (*J* 7 Hz). Compounds (3c, h) were identical (i.r., ^{1}H n.m.r. and t.l.c.) with authentic samples.[10,11]

By the above reported reactions other products were obtained together with the 1,4-benzothiazines (3c—f, h). We isolated and characterised all the compounds obtained from the reactions of the representative alkynes (2c, f, h).

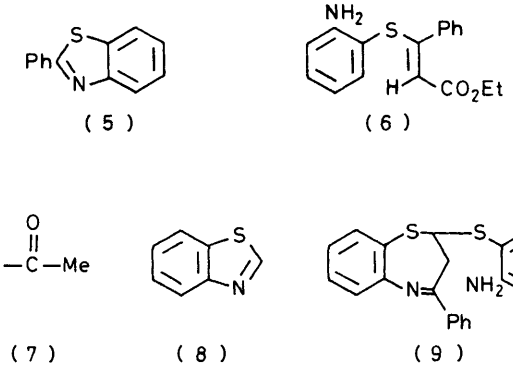
In the case of the alkyne (2c) along with the benzothiazoline (4c), which was formed in lower yield than expected, the following two products were obtained: 2-phenylbenzothiazole (5) and (*E*)-ethyl 1-(2-aminophenylthio)-1-phenylethylene-2-carboxylate (6).

To gain insight into the formation of these latter products, we verified that under the above conditions the following reactions also occurred: (i) thermal decomposition [12] of benzothiazoline (4c) yielded only the expected benzothiazole (5) in 42% yield, (ii) cyclisation (6) ⟶ (4c) did not go to completion; the benzothiazoline (4c) and the benzothiazole (5) were obtained in 13% and 9% yield respectively together with 74% of recovered starting material. (iii) The known [11] β-

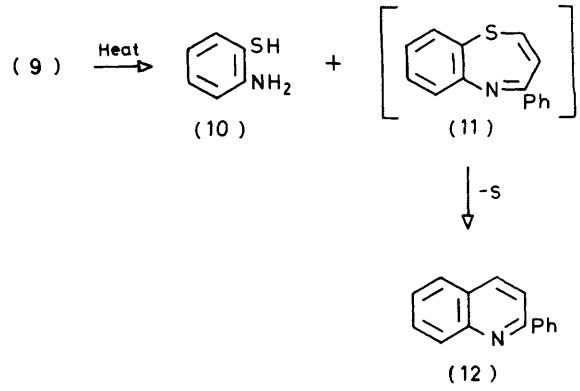


(1)

a; R = R^1 = CO_2Me
b; R = H, R^1 = CO_2Et
c; R = Ph, R^1 = CO_2Et
d; R = H, R^1 = COMe
e; R = H, R^1 = $COPr^n$
f; R = H, R^1 = COPh
g; R = Ph, R^1 = COMe
h; R = Ph, R^1 = CN



(5) (6) (7) (8) (9)



(10) (11) (12)

Scheme 1

arylthiocinnamates, *i.e.* (6) and its (*Z*)-isomer [very probably arising from an ionic rather than radical addition of 2-aminobenzenethiol to alkyne (2c) *], cyclised at a different rate to compound (4c). It follows that, contrary to what was previously observed for the cyclisation of (6), its (*Z*)-isomer under *identical* conditions yielded the benzothiazoline (4c) quantitatively in *ca.* 2.5 h.†

On the basis of these findings we can rationalise some results obtained from the reaction between the disulphide (1) and the alkyne (2c), namely: (*a*) benzothiazole (5) formation, (*b*) a possible way for benzothiazoline (4c) formation, and (*c*) the absence of the (*Z*)-isomer of compound (6).

From the reaction between the disulphide (1) and the alkyne (2f) together with the benzothiazine (3f) the following three products were obtained: acetophenone (7), benzothiazole (8), and 2-(2′-aminophenylthio)-4-phenyl-2,3-dihydro-1,5-benzothiazepine (9).

The benzothiazepine (9) structure was established by a combination of spectral and chemical evidence. Its i.r. spectrum showed absorptions attributable to a primary amino-group (3 460 and 3 360 cm^{-1}) and to a C=N group (1 600 cm^{-1}) and the ^1H n.m.r. spectrum revealed the presence of three hydrogens coupled by an AMX system (δ_A 2.77, δ_M 3.30, δ_X 5.18, J_{AM} and J_{AX} 13.0 Hz, J_{MX} 5.0 Hz). On refluxing a toluene solution of compound (9) the formation of 2-amino-benzenethiol (10) and 2-phenylquinoline (12) was obtained. The latter compound is supposed to have arisen from intermediate 4-phenyl-1,5-benzothiazepine (11) ‡ (Scheme 1). Furthermore, compound (9) was independently synthesised by reaction of the alkyne (2f) with the thiol (10). §

It is noteworthy that the nature of the products obtained by this last reaction at room temperature appears to depend strongly on the molar ratio used. Thus, employing equimolar quantities of reactants compound (9), its derivative (13), and the benzothiazoline (4f) were obtained (reaction a in Scheme 2). When 2 mol equiv. of thiol and 1 mol equiv. of alkyne were used compound (9) was obtained as the main product, while compound (14) was obtained in high yield by using the reactants in reverse molar ratio (reactions b and c respectively in Scheme 2). The structure of compounds (4f), (13), and (14), fully supported by ^1H n.m.r. spectra (see Experimental section) were further confirmed by the following chemical evidence: compound (4f) in refluxing methanol yielded an equimolar mixture of compounds (7) and (8); ¶ compound (13) was obtained by an addition reaction between the benzothiazepine (9) and the alkyne (2f); compound (14) was cyclised when heated under reflux in ethanol containing $N(Et)_3$ to give the known [16] benzothiazoline (15).

Possible modes of (4f), (9), and (14) formation by reaction of the thiol (10) and the alkyne (2f) involving the key intermediate (16) are summarised in Scheme 3.

The verified thermal instability of benzothiazoline (4f) accounts for both its absence and the formation of compounds (8) and (7) in the reaction of the disulphide (1) with the alkyne (2f). Thus, in this last reaction too, the formation of the benzothiazoline (4f) should occur as observed in the previously examined cases.

In the third case examined, namely the reaction between the disulphide (1) and the alkyne (2h), instead of the expected benzothiazoline compound (4h), we obtained a 4 : 1 (*E*)/(*Z*) mixture of 3-(2-aminophenylthio)-3-phenylprop-3-enenitrile (18).[11]

Finally, from the reaction of the disulphide (1) with the alkyne (2f) performed for shorter time we obtained a solid which by t.l.c. was found to be a mixture of two compounds. By mixture fractional crystallisation the two compounds were separated and identified as 1,4-benzothiazine (3f) and bis-enamine-disulphide (19). Similarly the analogous intermediate (20) was isolated by the reaction of the disulphide (1) with the alkyne (2d). In the i.r. spectra of these compounds S–H bands were absent while a strong band at 1 630 or 1 640 cm^{-1} respectively indicated the presence of the enaminoketo-group. This was also confirmed by ^1H n.m.r. spectroscopic examination which showed the enamine system protons characteristically coupled [*trans*-NH–CH=, *J* 13 Hz, *cis*-CH=CH, *J* 8 Hz] and high δ values for aminic protons due to an intramolecular hydrogen bond as expected for vinylogous amide.[17]

Evidence that the bisenamino-disulphide (19) is an intermediate in the reaction between the disulphide (1) and the alkyne (2f) follows from the observation that on refluxing its methanol solution under N_2, a mixture of compounds (3f), (4f), (7), and (8) was obtained. This was established by ^1H n.m.r. spectroscopic examination of the crude reaction mixture after the benzothiazine (3f) had been filtered off. Hence, taking into account that compounds (7) and (8) arise from thermal decomposition of the benzothiazoline (4f), we can conclude that the benzothiazine (3f) and benzothiazoline (4f)

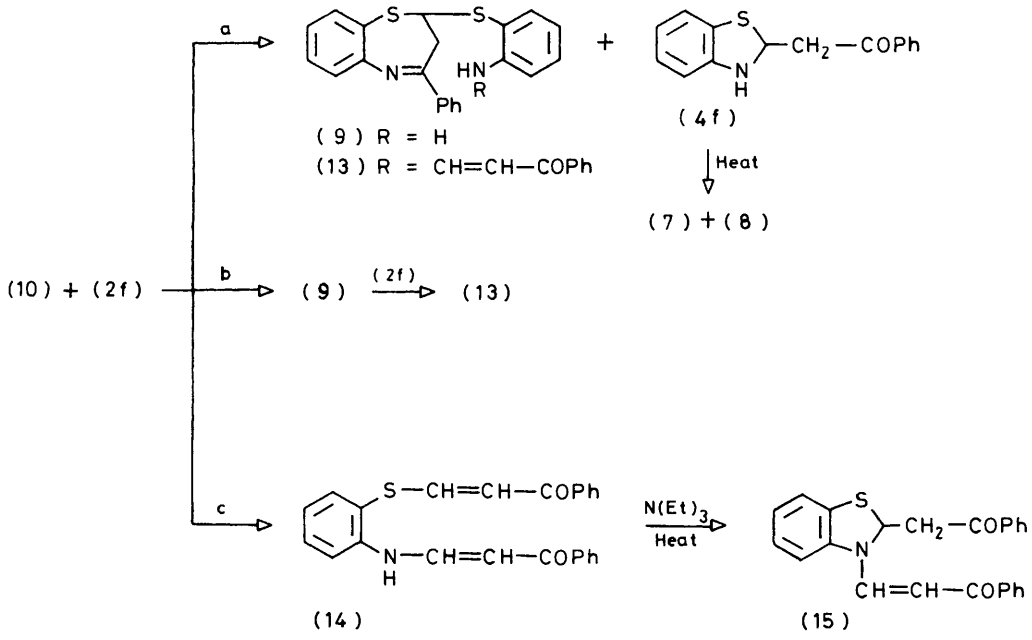
* This assumption follows from Wadsworth and Detty's work [13] namely, that α- or β-vinyl sulphides respectively are obtained by a radical or ionic addition of arenethiols to aryl propiolates.

† Very probably steric effects cause (6) to cyclise slower than its (*Z*)-isomer.

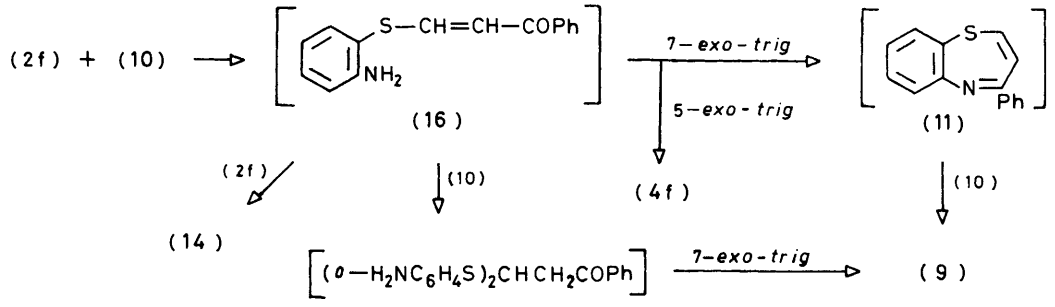
‡ Analogous examples of thermal sulphur extrusion in benzothiazepine compounds have been previously reported.[14]

§ 1,5-Benzothiazepines have been previously synthesised by this way.[15]

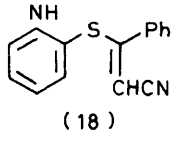
¶ Hitherto, only examples of thermal decomposition of 2,2-disubstituted benzothiazoline to benzothiazole compounds were known.



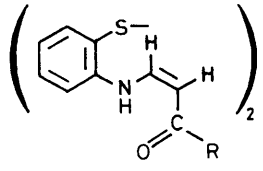
Scheme 2



Scheme 3



(18)



(19) R = Ph
(20) R = Me

(19)

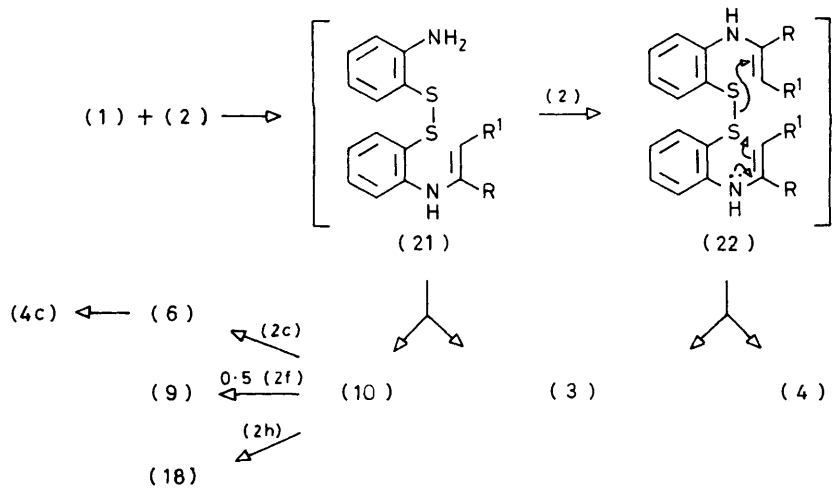
(3f) + (4f) + (7) + (8)

are simultaneously produced by cyclisation of the bisenamino-disulphide (19).

Also, compound (20) underwent cyclization to yield 1,4-benzothiazine (3d) together with unidentified products.

A very plausible mechanism explaining the results obtained by the reactions between the disulphide (1) and the alkynes (2) is shown in Scheme 4. Such a mechanism involves initial formation of the mono-enamine intermediate (21) which could either cyclise by cleavage of a sulphur–sulphur bond [like the bisenamino-disulphides (19) and (20)] to yield benzothiazine (3) together with thiol (10), or react with the alkyne (2) to give the bis-enamine intermediate (22). The latter, in turn, should yield benzothiazine (3) and benzothiazoline (4) as previously found for compound (19). Furthermore, it being possible to rule out the intermediacy of benzothiazolines in the formation of compounds (9), (6), and (18),* and taking into account that these compounds were independently synthesised by reaction of the thiol (10) with the corresponding alkyne (2c, f, h), it appears reasonable to hypothesise an ionic addition to alkyne of an arenethiol moiety arising from mono-enamine cyclisation. Thus, cyclisation to (3) of the two enamine intermediates (21) and (22) should occur by scission of a sulphur–sulphur bond upon nucleophilic attack by the β-enamine carbon. Moreover, we believe that only in the case of the bis-enamine adduct (22) formed from the cyanoalkyne (2h) would not so react, since the β-vinyl sulphide (18) and not the benzothiazoline (4h) or its thermal decomposition products were obtained as co-products of the benzothiazine (3h).

* By benzothiazoline ring-opening the enamino-thiols rather than the vinyl sulphide isomers would be the expected products since the C–S bond is weaker than the C–N bond (normal bond energies are C–S 66 kcal/mol [18] and C–N 69—75 kcal/mol [19]).



Scheme 4

The results obtained indicate that it is possible to employ successfully readily available acetylenic esters, ketones or nitriles as starting material for the synthesis of the corresponding 2-functionalised-4*H*-1,4-benzothiazines. It is also noteworthy that up to now alkyne compounds have been utilised for the synthesis of several heterocyclic systems [20] but not including the 1,4-benzothiazine one.

Experimental

M.p.s are uncorrected. I.r. spectra were taken on a Perkin-Elmer 257 instrument and mass spectra recorded on a Perkin-Elmer 270 low-resolution spectrometer. ^{1}H N.m.r. spectra were recorded on a Varian EM-360 A or Varian XL-200 operating at 60 and 200 MHz, respectively. Chemical shifts are given in δ from tetramethylsilane as internal standard. Preparative t.l.c. on Carlo Erba SI F_{254} silica-gel plates (2 mm thickness) and column chromatography on silica gel (Merck 70—325 mesh) were carried out using light petroleum (b.p. 40—70 °C)–ethyl acetate (9 : 1, v/v) as eluant unless otherwise stated.

2,2′-Dithiodianiline (1) was obtained as yellow needles (92% yield) by bubbling air into an ethanolic solution of commercial 2-aminobenzenethiol; the crude product, collected by filtration and crystallised from ethanol, had m.p. 93 °C (lit.,[21] 93 °C). The alkynes (2c) and (2d) were obtained from commercial sources and used without further purification. Hex-1-yn-3-one (2e) and 1-phenylprop-2-yn-1-one (2f) were prepared by chromic oxidation of the corresponding commercial carbinols according to literature procedure.[22] 3-Phenylprop-2-ynenitrile (2h) was obtained (81% yield) dehydrating, by the procedure of Casini *et al.*,[23] the phenylpropiolamide; the latter was quantitatively prepared by refluxing for 7 h an ethanol–ammonium hydroxide (28 °Be′) (1,5 : 1, v/v) solution of the alkyne (2g).

All the following reactions were carried out under a nitrogen atmosphere.

Reaction between 2,2′-*Dithiodianiline* (1) *and the Acetylenic Ester* (2c).—A solution of 2,2′-dithiodianiline (1) (0.01 mol) and ethyl phenylpropiolate (2c) (0.02 mol) in *N*,*N*-dimethylformamide (50 ml) was refluxed for 15 h. Removal of the solvent under reduced pressure and column chromatography of the residue afforded the following products, in the order given: (i) 2-*phenylbenzothiazole* (5) (14%), m.p. 114 °C (lit.,[21] 114 °C); (ii) 2-*phenyl*-2-*ethoxycarbonylmethyl*-2,3-*dihydrobenzothiazole* (4c) (12%) as a pale yellow oil (Found: C, 68.05; H, 5.7; N, 4.7. $C_{17}H_{17}NO_2S$ requires C, 68.21; H, 5.73; N, 4.68%); $\nu_{max.}$ 3 340 and 1 720 cm^{-1}; δ ($CDCl_3$) 1.06 (3 H, t, *J* 7 Hz, CH_3), AB system, δ_A 3.32, δ_B 3.64 (J_{AB} 16 Hz, CH_2CO), 4.02 (2 H, q, *J* 7 Hz, OCH_2), 5.74 (1 H, bs, NH), and 6.10—7.82 (9 H, m, aromatic); (iii) 2-*ethoxycarbonyl*-3-*phenyl*-4H-1,4-*benzothiazine* (3c) (86%) as yellow-orange prisms, m.p. 142—144 °C (from ethanol) (lit.,[10] 145—146 °C); (iv) (E)-*ethyl*-1-(2-*aminophenylthio*)-1-*phenylethylene*-2-*carboxylate* (6) (70%) as white needles, m.p. 113 °C (from propan-2-ol) (lit.,[11] 113 °C).

Reactions between 2,2′-*Dithiodianiline* (1) *and the Ynones* (2d—f): *General Procedure.*—A solution of 2,2′-dithiodianiline (1) (0.01 mol) and the ynone (0.02 mol) in methanol (30 ml) was refluxed for 20 h. The reaction mixture was cooled at room temperature and filtered. The red precipitate corresponding to the 2-acyl-4*H*-1,4-benzothiazine was washed with a small amount of methanol: the following compounds were prepared.

2-*Acetyl*-4H-1,4-*benzothiazine* (3d) (87%), m.p. 240—242 °C (decomp.) (Found: C, 63.0; H, 4.55; N, 7.35. $C_{10}H_9NOS$ requires C, 62.82; H, 4.75; N, 7.33%); $\nu_{max.}$ 3 270 and 1 640 cm^{-1}; δ [$(CD_3)_2$ SO] 2.10 (3 H, s, CH_3), 6.33—6.98 (4 H, m, aromatic), 7.18 (1 H, d, *J* 7 Hz, collapsed to a singlet on exchange with D_2O, =C*H*NH), 8.88 (1 H, d, *J* 7 Hz, NH); *m*/*z* 191 (M^+, 66%), 148 ($M^+ - COCH_3$, base).

2-*Butyryl*-4H-1,4-*benzothiazine* (4e) (76%), m.p. 208—210 °C (Found: C, 65.9; H, 5.9; N, 6.4. $C_{12}H_{13}NOS$ requires C, 65.74; H, 5.98; N, 6.39%); $\nu_{max.}$ 3 250 and 1 640 cm^{-1}; δ [$(CD_3)_2SO$] 0.82 (3 H, t, CH_3), 1.48 (2 H, m, CH_2CH_3), 2.38 (2 H, t, $COCH_2$), 6.33—6.98 (4 H, m, aromatic), 7.22 (1 H, d, *J* 7 Hz, collapsed a singlet on exchange with D_2O, =C*H*NH), 8.82 (1 H, d, *J* 7 Hz, NH); *m*/*z* 219 (M^+, base) and 148 ($M^+ - COC_3H_7$, 69%).

2-*Benzoyl*-4H-1,4-*benzothiazine* (4f) (86%), m.p. 245—246 °C (decomp.) (Found: C, 71.25; H, 4.35; N, 5.5. $C_{15}H_{11}NOS$ requires C, 71.14; H, 4.37; N, 5.53%); $\nu_{max.}$ 3 300 and 1 630 cm^{-1}; δ [$(CD_3)_2SO$] 6.40—7.10 (5 H, m, aromatic + =C*H*NH), and 9.10 (1 H, d, *J* 7 Hz, NH); *m*/*z* 253 (M^+ 27%), 148 ($M^+ - COPh$, 10%), and 105 (COPh, base). The residue obtained by concentrating the mother-liquor of (4f) was chromatographed on column and the following products were obtained, in the order given: *acetophenone* (7) (22%), *benzothiazole* (8) (32%), 2-(2-*aminophenylthio*)-4-*phenyl*-2,3-*dihydrobenzothiazepine* (9) (200 mg), m.p. 161—162 °C (from methanol–chloroform) (Found: C, 69.45; H, 4.9; N, 7.6.

$C_{21}H_{18}N_2S_2$ requires C, 69.60; H, 5.00; N, 7.73%); $\nu_{max.}$ 3 460, 3 360, and 1 600 cm^{-1}; δ ($CDCl_3$), AMX system, δ_A 2.77, δ_M 3.30, δ_X 5.18 (J_{AM} and J_{AX} 13.0 Hz, J_{MX} 5.0 Hz, $CHCH_2$), 4.38 (2 H, s, NH_2).

Reaction between 2,2'-Dithiodianiline (1) *and Acetylenic Nitrile* (2h).—A solution of 2,2'-dithiodianiline (1) (0.01 mol) and 3-phenylprop-2-ynenitrile (2h) (0.01 mol) in *N,N*-dimethylformamide (50 ml) was refluxed for 6 h. Evaporation of the solvent under reduced pressure and column chromatography of the residue yielded the following products, in the order stated. (i) (E)- and (Z)-3-(2-*Aminophenylthio*)-3-*phenylprop-2-enenitrile* (18) (72%) as colourless oil, $\nu_{max.}$ 2 200 cm^{-1} (C≡N) [11] [(*E*)/(*Z*) ratio 4 : 1, determined by integration of olefinic protons in the ^1H n.m.r. spectrum]; (ii) 2-*cyano*-3-*phenyl*-4H-1,4-*benzothiazine* (3f) (76%) as red-orange crystals, m.p. 211 °C (from propan-2-ol) (lit.,[11] 211 °C).

Reactions between 2,2'-Dithiodianiline (1) *and Alkynes* (2f, d) *for a Shorter Time.*—The solution of the reactants, prepared as before stated, was refluxed for 3 h. The resulting red precipitate, consisting of 1,4-benzothiazine (3f) or (3d) was filtered off from the hot reaction mixture. On cooling the filtrate, a new red-brownish precipitate consisting of the bis-enamine disulphide (19) or (20) respectively was obtained:

N,N'-*Bis*-(β-*benzoylvinyl*)-2,2-*dithiodianiline* (19) (40%), m.p. 169—171 °C (decomp.) (Found: C, 70.9; H, 4.6; N, 5.4. $C_{30}H_{24}N_2O_2S_2$ requires C, 70.85; H, 4.76; N, 5.51); $\nu_{max.}$ 3 180w and 1 630 cm^{-1}; δ ($CDCl_3$) 5.98 (1 H, d, *J* 8 Hz, =CHCO), 6.68—8.20 (10 H, m, aromatic + HN*CH*=) 12.30 1 H, d, *J* 13 Hz, NH); *m/z* peak corresponding to $(M)^+$ ion is absent. The peaks with the highest *m/z* value at 255 and 253 are ascribed to benzothiazoline (4f) and benzothiazine (3f) respectively, both cyclisation products of (19).

N,N-*Bis*-(β-*acetylvinyl*)-2,2-*dithiodianiline* (20) (21%), m.p. 115—117 °C (decomp.) (Found: C, 63.7; H, 5.4; N, 7.35. $C_{20}H_{20}N_2O_2S_2$ requires C, 62.49; H, 5.24; N, 7.29%), $\nu_{max.}$ 3 190w and 1 640 cm^{-1}; δ ($CDCl_3$) 2.12 (3 H, s, CH_3), 5.30 (1 H, d, *J* 8 Hz, =CHCO), 6.67—7.50 (5 H, m, aromatic + HN*CH*=), and 12.15 (1 H, d, *J* 13 Hz, NH); *m/z* [(20) behaved similarly to (19) on electron impact]; the peaks with the highest *m/z* value at 193 and 191 are assigned to the benzothiazoline (4d) and the benzothiazine (3d) respectively, both cyclisation products of compound (19).

Reaction between 2-Aminobenzenethiol (10) *and Alkyne* (2f).—(i) *Molar ratio* 1 : 1. To a solution of 2-aminobenzenethiol (10) (1.25 g) in methanol (35 ml) a solution of 1-phenylprop-2-yn-1-one (2f) (1.30 g) in methanol (15 ml) was added at room temperature and stirred for 24 h. The resulting yellow precipitate (1.20 g) was filtered off and by column chromatography yielded the following products in the order given: (a) 2-(*benzoylmethyl*)-2,3-*dihydrobenzothiazole* (4f) (550 mg), as yellow crystals, m.p. 119—120 °C (from light petroleum–ethyl acetate) (Found: C, 70.3; H, 5.05; N, 5.2. $C_{15}H_{13}NOS$ requires C, 70.58; H, 5.13; N, 5.49%), $\nu_{max.}$ 3 350 and 1 680 cm^{-1}; δ ($CDCl_3$) ABX system, δ_A 3.44, δ_B 3.67, δ_X 5.76 [J_{AB} 9 Hz, J_{BX} 5 Hz, J_{AX} 2 Hz $CHCH_2CO$], 4.86 (1 H, s, NH), and 6.53—8.11 (9 H, m, aromatic); (b) 2-(2-*aminophenylthio*)-4-*phenyl*-2,3-*dihydro*-1,5-*benzothiazepine* (9) (500 mg); removal of the solvent from the filtrate and column chromatography of the residue yielded as main product a yellow solid which was identified as 2-[2-(β-*benzoylvinyl*)*aminophenylthio*]-4-*phenyl*-2,3-*dihydro*-1,5-*benzothiazepine* (13) (1.10 g), m.p. 156 °C (from methanol–chloroform) (Found: C, 72.95; H, 4.9; N, 5.5. $C_{30}H_{24}N_2OS_2$ requires C, 73.16; H, 4.91; N, 5.69%), $\nu_{max.}$ 1 630 cm^{-1}; δ ($CDCl_3$), AMX system, δ_A 2.76, δ_M 3.97, δ_X 5.17 (J_{AM} and J_{AX} 13.0 Hz, J_{MX} 5.0 Hz, $CHCH_2$), 6.19 (1 H, d, *J* 8.0 Hz, =CHCO), 7.11—8.12 (19 H, m, aromatic + HN-*CH*=), and 12.95 (1 H, d, *J* 13 Hz, NH).

(ii) *Molar ratio* 2 : 1. To a solution of 2-aminobenzenethiol (10) (2.50 g) in methanol (35 ml) a solution of 1-phenylprop-2-yn-1-one (2f) (1.30 g) in methanol (15 ml) was added at room temperature and the mixture stirred for 8 h. The precipitate formed was filtered off and crystallised from methanol–chloroform to give compound (9) (2.40 g).

(iii) *Molar ratio* 1 : 2. To a solution of 2-aminobenzenethiol (10) (630 mg) in methanol (35 ml) a solution of 1-phenylprop-2-yn-1-one (2f) (1.30 g) in methanol (15 ml) was added at room temperature and the mixture stirred for 24 h. The precipitate formed was filtered off and crystallised from absolute ethanol to give N,S-*bis*-(β-*benzoylvinyl*)-2-*aminobenzenethiol* (14) (850 mg) as yellow needles, m.p. 172—174 °C (from absolute ethanol) (Found: C, 75.0; H, 5.15; N, 3.65. $C_{24}H_{19}NO_2S$ requires C, 74.79; H, 4.97; N, 6.63%), $\nu_{max.}$ 1 630 cm^{-1}; δ [$(CD_3)_2SO$] 6.23 (1 H, d, *J* 8.0 Hz, =CHCO), 7.12—8.09 (17 H, m, aromatic + HN*CH*= + S*CH*=*CH*), and 12.43 (1 H, d, *J* 13 Hz, NH); *m/z* 385 (M^+, 11%), 280 (M^+ − PhCO, 53%), 266 (M^+ − $PhCOCH_2$, 76%), and 105 (COPh, base).

Thermolysis of the Dihydro-1,5-*benzothiazepine* (9).—A solution of compound (9) (150 mg) in toluene (40 ml) was refluxed for 4 h. Removal of the solvent followed by column chromatography of the residue gave 2-*phenylquinoline* (12) (80 mg, 95%) [24] and a mixture consisting of 2-aminobenzenethiol (10) and disulphide (1) (42 mg).

Thermolysis of the Benzothiazoline (4c).—A solution of the benzothiazoline (4c) (500 mg) in *N,N*-dimethylformamide (20 ml) was refluxed for 15 h. Removal of the solvent under reduced pressure and preparative t.l.c. of the residue yielded benzothiazole (5) in 42% yield.

Thermolysis of the Benzothiazoline (4f).—A solution of the benzothiazoline (4f) (120 mg) in methanol (60 ml) was refluxed for 20 h. Removal of the solvent by evaporation under reduced pressure and preparative t.l.c. of the residue [light petroleum–ethyl acetate (8 : 2, v/v) as eluant] yielded compounds (7) and (8) in roughly quantitative yield.

Cyclisation of Disulphide (19).—A solution of compound (19) (1.50 g) in methanol (100 ml) was refluxed for 20 h. The red precipitate obtained was collected by filtration and identified as 1,4-benzothiazine (4f) (700 mg, 95%). After removal of the methanol from the filtrate, the ^1H n.m.r. spectrum ($CDCl_3$) of the residue revealed that acetophenone (7) and the benzothiazole (8) in roughly equimolar amounts were present as the main products along with a little of the benzothiazoline (4f).

Cyclisation of Disulphide (20).—A solution of compound (20) (250 mg) in methanol (20 ml) was refluxed for 15 h. The red precipitate obtained was collected by filtration and identified as the 1,4-benzothiazine (3d) (110 mg, 89%).

Cyclisation of the Vinyl Sulphide (6) *and Its* (Z)-*Isomer.*—A solution of the vinyl sulphide (6) (700 mg) in *N,N*-dimethylformamide (20 ml) was refluxed for 15 h. Removal of the solvent under reduced pressure and preparative t.l.c. of the residue yielded the following products, stated in decreasing order of R_F values: the benzothiazole (5) (9% yield), the benzothiazoline (4c) (13% yield) and starting material (6) (74%). Under identical conditions the (*Z*)-*ethyl*-1-(2-*aminophenylthio*)-1-*phenylethylene*-2-*carboxylate* yielded benzothiazoline (4c) in 97% yield after only 2.5 h.

Cyclisation of Compound (14).—A mixture of compound (14) (250 mg) in ethanol–water (6 : 4, v/v) (15 ml) and triethylamine (1 ml) was refluxed for 8 h. After cooling the yellow precipitate formed (210 mg, 84%) was filtered off and crystallised from propan-2-ol–chloroform to give N-(β-*benzoylvinyl*)-2-*benzoylmethyl*-2,3-*dihydrobenzothiazole* (15), m.p. 182—183 °C (lit.,[16] 179—181 °C).

Reaction between Dihydro-1,5-*benzothiazepine* (9) *and the Alkyne* (2f).—A mixture of compound (9) (500 mg) and the alkyne (2f) (200 mg) in methanol (80 ml) was stirred at room temperature for 2 days. The resulting yellow precipitate was filtered off and crystallised from methanol–chloroform to give compound (13) in 82% yield.

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