Preparation of Dithiadiazafulvalene Precursors: 2-Piperidino-2,3-dihydro-1,3-thiazoles or 2-Unsubstituted 2,3-Dihydro-1,3-thiazoles from the Reduction of the Corresponding 2-Piperidino Mesoionic Thiazoles

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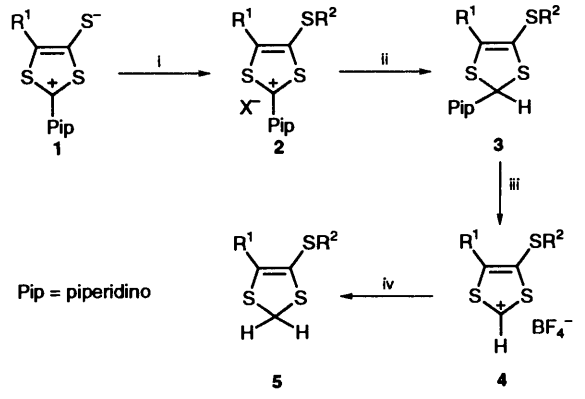
Depending on the experimental conditions, either the 2-piperidino-3-aryl-4-alkylthio-5-aryl- or -alkyl-2,3-dihydro-1,3-thiazoles **8** or the 2-unsubstituted 3-aryl-4-alkylthio-5-aryl- or -alkyl-2,3-dihydro-1,3-thiazoles **10** have been prepared starting from mesoionic 5-alkyl- or 5-aryl-2-piperidino-1,3-thiazole-4-thiolates **6**. After alkylation of the mesoionic compound, the best conditions to isolate these two dihydrothiazoles were established from a mechanistic study of the reduction. Compound **8** is known to give dithiadiazafulvalenes[1] through its thiazolium tetrafluoroborate salts. We show here that such salts can also be obtained from **10**.

Although dithiadiazafulvalenes† (DTDAF) are very good donors, their sensitivity to air is probably the reason why they have been so little investigated.[1-5] We recently described a synthesis of DTDAF using mild reaction conditions and in which DTDAF was trapped as a charge transfer salt.[1] The key step of the reaction was the formation of DTDAF from thiazolium salt **12** obtained through the 2-amino-2,3-dihydro-1,3-thiazole **8**. During the preparation of these 2-amino-2,3-dihydrothiazoles **8**, through the reduction of mesoionic thiazoles **6** it appeared that contrary to what was observed with the corresponding 1,3-dithioles,[6] the major products obtained were the 2-unsubstituted dihydrothiazoles **10**. We decided to study the mechanism of this reduction in order to design the best synthetic route to compounds **8** or **10**. To us, such a study seemed to be of interest since, to the best of our knowledge, the only reported 2,3-dihydrothiazoles unsubstituted on the 2 position are dihydrothiamine (the reduced form of vitamin B_1) and the derived phosphates.[7] Furthermore, it can be discounted that, like the corresponding 1,3-dithioles, the dihydrothiazoles **10** will be amphoteric derivatives giving, according to the experimental conditions, either 1,3-thiazolium anions or 1,3-thiazolium cations,[8,9] which could be of particular interest for DTDAF synthesis.[1-4] We report here the mechanism of $NaBH_4$ reduction of mesoionic thiazoles **6**, and described the best way to prepare either compounds **8** or **10**.

We have already shown that alkylation of a mesoionic dithiole **1** gives the dithiolium salt **2**, which is quantitatively reduced by $NaBH_4$ to give a 2-aminodithiole **3**. Tetrafluoroboric acid converts **3** into the dithiolium salt 4 which is reduced by lithium aluminium hydride to give the 2-unsubstituted dithiole **5** (see Scheme 1).[9]

When mesoionic thiazoles **6** were the starting materials, alkylation followed by $NaBH_4$ reduction gave the 2-unsubstituted dihydrothiazoles **10** directly. Only with $R^3 = p\text{-}NO_2C_6H_4$ was the major product the corresponding 2-aminodihydrothiazole **8**, which was then easily reduced *in situ* under acidic conditions to give quantitatively the corresponding dihydrothiazole **10**. It seemed likely that the 2-aminodihydrothiazole **8** and the thiazolium salt **9** were intermediates leading to the dihydrothiazole **10** (see Scheme 2). However, in contrast to the observations with the dithiole series, the 2-aminodihydrothiazoles **8** with $R^3 \neq p\text{-}NO_2C_6H_4$ were unstable even under non-acidic conditions.

† Dithiadiazafulvalene = 2,2'-bi(1,3[3*H*]-thiazol-2-ylidene).



Scheme 1 *Reagents:* i, R^2X; ii, $NaBH_4$, EtOH; iii, HBF_4; iv, $LiAlH_4$

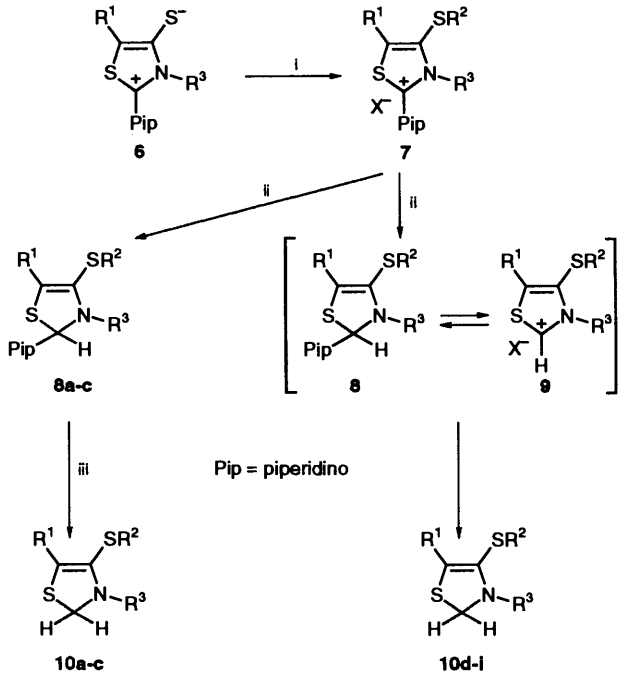
The following experiments were designed in order to confirm the postulated mechanism of Scheme 2:

(*a*) In order to establish that compounds **8** and **9** were in equilibrium we treated compound **7** with $NaBH_4$ in CH_2Cl_2, in the presence of a large excess of piperidine to give the 2-piperidinodihydrothiazoles **8** quantitatively. Similarly, in the presence of an excess of morpholine, the sole product isolated, in good yield, was the corresponding 2-morpholinodihydrothiazole **11** (see Scheme 3). It was also shown that the reaction of the 2-piperidinodihydro-1,3-thiazole **8d** with morpholine gave the corresponding 2-morpholinodihydro-1,3-thiazole **11** quantitatively.

(*b*) In order to establish that compound **8** is an intermediate leading to compound **10**, we prepared the former according to the experimental conditions shown in Scheme 3 (excess of piperidine) and subjected it to the experimental conditions described in Scheme 2 to give compound **10** quantitatively.

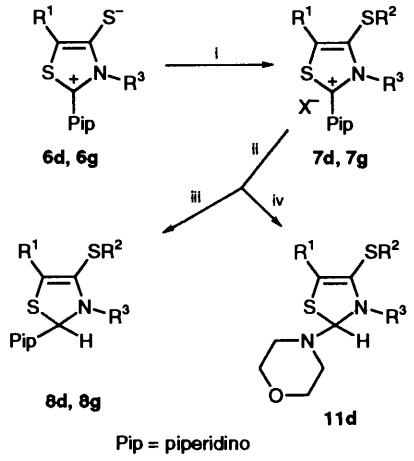
(*c*) It was also possible to prove in one case that compound **9** is a likely intermediate which is then reduced to give compound **10**. The reduction of the thiazolium iodide **7a** according to the procedure described in Scheme 2 gave **10a** together with a small quantity of the thiazolium iodide **9a** which was isolated and characterized. The $NaBH_4$ reduction of **9a** gave **10a** quantitatively.

Since the 2-unsubstituted dihydrothiazoles **10** were easily prepared, it was also of interest to prove their usefulness for the preparation of thiazolium tetrafluoroborate salts **12** which are key starting materials for the synthesis of DTDAF. When the dihydrothiazoles **10** were treated with a stoichiometric quantity

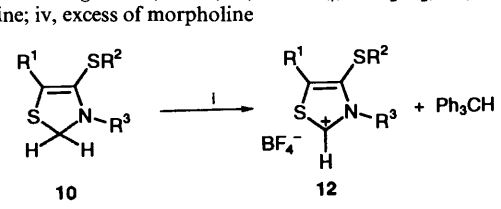


a $R^1 = p\text{-}ClC_6H_4$, $R^2 = Me$, $R^3 = p\text{-}NO_2C_6H_4$
b $R^1 = p\text{-}MeC_6H_4$, $R^2 = Me$, $R^3 = p\text{-}NO_2C_6H_4$
c $R^1 = Me$, $R^2 = C_6F_5CH_2$, $R^3 = p\text{-}NO_2C_6H_4$
d $R^1 = p\text{-}ClC_6H_4$, $R^2 = Me$, $R^3 = Ph$
e $R^1 = p\text{-}ClC_6H_4$, $R^2 = Et$, $R^3 = Ph$
f $R^1 = p\text{-}ClC_6H_4$, $R^2 = C_6F_5CH_2$, $R^3 = Ph$
g $R^1 = p\text{-}MeC_6H_4$, $R^2 = Me$, $R^3 = Ph$
h $R^1 = p\text{-}MeC_6H_4$, $R^2 = Et$, $R^3 = Ph$
i $R^1 = Me$, $R^2 = Me$, $R^3 = Ph$

Scheme 2 *Reagents:* i, R^2X (X = Br or I); ii, $NaBH_4$, EtOH; iii, HCl, EtOH



Scheme 3 *Reagents:* i, R^2X; ii, $NaBH_4$, CH_2Cl_2; iii, excess of piperidine; iv, excess of morpholine



Scheme 4 *Reagents:* i, Ph_3CBF_4, CH_2Cl_2

of triphenylcarbenium tetrafluoroborate, the corresponding thiazolium salts **12** were isolated and characterized (51–88%) (see Scheme 4).

Conclusions

While mesoionic 2-piperidino-1,3-dithioles **1** are alkylated and then reduced by $NaBH_4$ in EtOH to give exclusively the 2-piperidinodithioles **3**, the corresponding mesoionic 2-piperidino-1,3-thiazoles **6** lead to good yields of the 2-unsubstituted dihydrothiazoles **10** under the same conditions. A study of the mechanism of this reaction has allowed us to identify the best experimental conditions (CH_2Cl_2 solvent and excess of piperidine) to obtain good yields of the 2-piperidinodihydrothiazoles **8**. We have also shown that the dihydrothiazoles **10** are good starting materials for the perparation of the thiazolium salts **12**.

Experimental

^1H NMR spectra were recorded at 80 MHz on a Bruker WP 80 spectrometer and ^{13}C NMR spectra at 75 MHz on a Bruker AM 300 spectrometer with tetramethylsilane as internal reference. Mass spectra were determined with a Varian Mat 311 Spectrometer. M.p.s were taken with a Kofler hot stage apparatus. Ether refers to diethyl ether.

Mesoionic Thiazoles **6**.—For R^1 = aryl, we prepared the derivatives according to ref. 10. For R^1 = Me, the following method was employed. Phenyl isothiocyanate (40 mmol) or *p*-nitrophenyl isothiocyanate (3 mmol) was added to a suspension of the dithiole **1** (R^1 = Me) (2 mmol) in dry C_6H_6 (100 cm^3) and the mixture was refluxed for 15 h (R^3 = Ph) or 8 h ($R^3 = p\text{-}NO_2C_6H_4$). Evaporation of the solvent and addition of dry ether (100 cm^3) to the residue gave a precipitate which was filtered off and recrystallized from MeCN; **6** (R^1 = Me, R^3 = Ph): 63%, m.p. 146 °C; $\delta_H(CDCl_3)$ 1.10 [6 H, m, $N(CH_2)_5$], 3.10 [4 H, m, $N(CH_2)_5$], 2.39 (3 H, s, SMe) and 7.49 (5 H, m, ArH); **6** (R^1 = Me, $R^3 = p\text{-}NO_2C_6H_4$): 72%, m.p. 195 °C (MeCN) (Found: C, 13.8; H, 5.0; N, 12.4. $C_{15}H_{17}N_2O_2S$ requires C, 13.71; H, 5.11; N, 12.13%); $\delta_H(CDCl_3)$ 1.12 [6 H, m, $N(CH_2)_5$], 3.10 [4 H, m, $N(CH_2)_5$], 2.39 (3 H, s, SMe), 7.62 and 8.42 (4 H, AA'XX', $p\text{-}NO_2C_6H_4$).

Thiazolium Cations **7a**, **7b**, **7d**, **7e** *and* **7g–i**.—R^2X (X = Br or I) (25 mmol) was added to a suspension of compound **6** (5 mmol) in CH_2Cl_2 (20 cm^3). The mixture, which became homogeneous, was left at room temperature for 12 h after which it was evaporated. For $R^3 = p\text{-}NO_2C_6H_4$, addition of EtOH to the mixture precipitated the thiazolium salt **7** which was filtered off and washed with EtOH. The other salts **7** were obtained as oils which were carefully washed with dry ether and directly used for further reactions. **7a** (X = I), m.p. 200 °C (EtOH) (Found: C, 43.95; H, 3.7; N, 7.3; Cl, 6.2; I, 22.1. $C_{21}H_{21}ClIN_3O_2S_2$ requires C, 43.80; H, 3.55; N, 7.27; Cl, 6.23; I, 22.19%); $\delta_C(CDCl_3)$ 20 (q, SCH_3), 22, 24, 54 [tm, $N(CH_2)_5$], 130 (m, C-5), 133 (q, C-4), 168 (m, C-2), 125, 127, 129, 130.9, 131, 136, 142 and 149 (aromatic C). Yields and ^1H NMR data for salts **7** are summarized in Table 1.

Thiazolium Cations **7c** *and* **7f**.—$BrCH_2C_6F_5$ (5 mmol) was added to a suspension of compound **6** (5 mmol) in CH_2Cl_2 (20 cm^3) and the reaction mixture boiled for 12 h. Evaporation of the mixture gave the salt **7** (X = Br) as an oil, which was washed with dry ether and used without further purification. Yields and ^1H NMR data for salts **7** are summarized in Table 1.

2-Piperidino-2,3-dihydro-1,3-thiazoles **8a–8c** ($R^3 = p\text{-}NO_2C_6H_4$).—Sodium borohydride (250 mg) was added to a suspension of compound **7** (5 mmol) in EtOH (20 cm^3) at O °C. After 3 min, the product **8** was filtered off and recrystallized from MeCN; **8a** (Found: C, 56.35; H, 4.95; N, 9.4; Cl, 8.00. $C_{21}H_{22}ClN_3O_2S_2$ requires C, 56.30; H, 4.95; Cl, 7.91; N, 9.38%); **8b** (Found: C, 61.7; H, 5.85; N, 9.9. $C_{22}H_{25}N_3O_2S_2$ requires

Table 1 Physical data for 2-piperidino-1,3-thiazolium salts **7**

			$\delta_H(CDCl_3)$		
	X	Yield (%)	$N(CH_2)_5$	R^2	R^1 and R^3
a	I	95	1.65 (m, 6 H), 3.50 (m, 4 H)	2.00 (s, 3 H)	8.50 (s, 4 H), 7.55 (AB, 4 H)
b	I	94	1.65 (m, 6 H), 3.50 (m, 4 H)	2.00 (s, 3 H)	2.45 (s, 3 H), 7.50–8.50 (m, 9 H)
c	Br	97	1.67 (m, 6 H), 3.53 (m, 4 H)	3.58 (s, 2 H)	2.45 (s, 3 H), 8.48 (s, 4 H)
d	I	98	1.62 (m, 6 H), 3.47 (m, 4 H)	1.97 (s, 3 H)	7.67 (m, 9 H)
e	Br	96	1.62 (m, 6 H), 3.53 (m, 4 H)	0.85 (t, 3 H), 2.35 (q, 2 H)	7.65 (m, 9 H)
f	Br	95	1.67 (m, 6 H), 3.58 (m, 4 H)	3.70 (s, 2 H)	7.65 (m, 9 H)
g	I	97	1.60 (m, 6 H), 3.50 (m, 4 H)	1.97 (s, 3 H)	2.40 (s, 3 H), 7.00–8.00 (m, 9 H)
h	Br	96	1.60 (m, 6 H), 3.50 (m, 4 H)	0.85 (t, 3 H), 2.30 (q, 2 H)	2.35 (s, 3 H), 7.12–7.92 (m, 9 H)
i	I	93	1.65 (m, 6 H), 3.45 (m, 4 H)	2.05 (s, 3 H)	2.57 (s, 3 H), 7.67 (m, 5 H)

Table 2 Physical data for 2-piperidino-2,3-dihydro-1,3-thiazoles **8**

			$\delta_H(CDCl_3)$			
	M.p./(*T*/°C)	Yield (%)	$N(CH_2)_5$	R^2	H	R^1 and R^3
a	182	80	1.55 (m, 6 H), 2.60 (m, 4 H)	1.90 (s, 3 H)	6.00 (s, 1 H)	7.45 (AB, 4 H), 7.55, 8.23 (AA'XX', 4 H)
b	172	82	1.55 (m, 6 H), 2.62 (m, 4 H)	1.87 (s, 3 H)	5.98 (s, 1 H)	2.35 (s, 3 H), 7.33 (AB, 4 H) 7.55, 8.20 (AA'XX', 4 H)
c	132	60	1.55 (m, 6 H), 2.55 (m, 4 H)	3.75 (s, 2 H)	5.95 (s, 1 H)	2.15 (s, 3 H), 7.30, 8.10 (AA'XX', 4 H)
d	128	62	1.50 (m, 6 H), 2.55 (m, 4 H)	1.85 (s, 3 H)	5.85 (s, 1 H)	7.20–7.62 (m, 9 H)
g	155	50	1.52 (m, 6 H), 2.60 (m, 4 H)	1.90 (s, 3 H)	5.87 (s, 1 H)	2.30 (s, 3 H), 7.10–7.30 (m, 9 H)

Table 3 Physical data for thiazoles **10**

			$\delta_H(CDCl_3)$		
	M.p./(*T*/°C)	Yield (%)	R^2	CH_2	R^1 and R^3
a	166	92	2.00 (s, 3 H)	5.25 (s, 2 H)	7.48 (AB, 4 H), 7.25, 8.20 (AA'XX', 4 H)
b	172	90	1.97 (s, 3 H)	5.23 (s, 2 H)	2.37 (s, 3 H), 7.36 (AB, 4 H), 7.23, 8.20 (AA'XX', 4 H)
c	120	70	3.67 (s, 2 H)	5.12 (s, 2 H)	1.97 (s, 3 H), 6.98, 8.13 (AA'XX', 5 H)
d	124	88	2.00 (s, 3 H)	5.12 (s, 2 H)	7.00–7.62 (m, 9 H)
e	70	82	1.07 (t, 3 H), 2.47 (q, 2 H)	5.15 (s, 2 H)	7.00–7.65 (m, 9 H)
f	139	95	3.70 (s, 2 H)	5.20 (s, 2 H)	7.28–8.00 (m, 9 H)
g	103	94	2.00 (s, 3 H)	5.12 (s, 2 H)	2.35 (s, 3 H), 7.05–7.60 (m, 9 H)
i	Oil	85	2.05 (s, 3 H)	5.02 (s, 2 H)	2.15 (s, 3 H), 7.00–7.35 (m, 5 H)

C, 61.80; H, 5.89; N, 9.83%); **8c** (Found: C, 51,1; H, 3.9; N, 8.1; F, 18.35. $C_{22}H_{20}F_5N_3O_2S_2$ requires C, 50.97; H, 3.95; N, 8.00; F, 18.40%). Yields, m.p.s and ^1H NMR data for 2-piperidino-2,3-dihydro-1,3-thiazoles **8** are summarized in Table 2.

2-Piperidino-2,3-dihydro-1,3-thiazoles **8d** *and* **8g** ($R^3 \neq p$-$NO_2C_6H_4$).—To a solution of **7** (5 mmol) in CH_2Cl_2 (25 cm^3), piperidine (25 mmol) and sodium borohydride (10 mmol) were added, successively. The reaction mixture was stirred for 20 min at room temperature and washed with NaOH (1 mol dm^{-3}; 5 × 25 cm^3). The organic phase was dried (Na_2SO_4) and concentrated. Compound **8**, precipitated by addition of ether (25 cm^3) was recrystallized from EtOH; **8d** (Found: C, 62.25; H, 5.6; N, 7.1; Cl, 9.1%; M^+, 402.0990. $C_{21}H_{23}ClN_2S_2$ requires C, 62.59; H, 5.75; Cl, 8.80; N, 6.95%; *M*, 402.09911); $\delta_C(CDCl_3)$ 16 (q, SCH_3), 24, 25, 46 [tm, $N(CH_2)_5$], 93 (d, C-2), 117 (q, C-4), 132.2 (t, C-5), 122, 124, 126, 128, 128.5, 131, 132.7 and 145 (aromatic C); *m/z* 402 (M^+) and 318 {$[M - N(CH_2)_5]^+$}. **8g** (Found: C, 69.1; H, 6.85; N, 7.3. $C_{22}H_{26}N_2S_2$ requires C, 68.99; H, 6.93; N, 7.41%). Yields, m.p.s and ^1H NMR data for 2-piperidino-2,3-dihydro-1,3-thiazoles **8** are summarized in Table 2.

2,3-Dihydrothiazoles **10a–c** ($R^3 = p$-$NO_2C_6H_4$).—$NaBH_4$ (500 mg) was slowly added to a suspension of compound **7** (5 mmol) in EtOH (20 cm^3) after which the reaction mixture was stirred for 5 min and then treated with HCl (6 mol dm^{-3}; 4 cm^3). After 10 min, the precipitate was filtered off and recrystallized from EtOH. **10a** (Found: C, 52.55; H, 4.0; Cl, 9.8; N, 7.7. $C_{16}H_{13}ClN_2O_2S_2$ requires C, 52.67; H, 3.59; N, 7.68; Cl, 9.72%); **10b** (Found: C, 59.38; H, 4.7; N, 8.1. $C_{17}H_{16}N_2O_2S_2$ requires C, 59.15; H, 4.73; N, 8.22%); **10c** (Found: C, 47.0; H, 2.55; N, 6.45; F, 21.9. $C_{17}H_{11}F_5N_2O_2S_2$ requires C, 46.91; H, 2.65; N, 6.51; F, 21.77%). Yields, m.p.s and ^1H NMR data for dihydrothiazoles **10** are summarized in Table 3.

2,3-Dihydrothiazoles **10d–i** ($R^3 \neq p$-$NO_2C_6H_4$).—$NaBH_4$ (250 mg) was added to a solution of compound **7** (5 mmol) in EtOH (25 cm^3). Compound **10** either formed a precipitate in which case it was filtered off and recrystallized from EtOH, or the mixture was diluted with water (75 cm^3) and extracted with ether (2 × 25 cm^3). The extract was then washed with water, dried (Na_2SO_4) and evaporated to give an oily residue which was sufficiently pure (NMR analysis) to use without further purification. **10d** (Found: C, 59.9; H, 4.55; Cl, 10.95; N, 4.5%; M^+, 319.0253. $C_{16}H_{14}ClNS_2$ requires C, 60.10; H, 4.38; Cl, 11.09; N, 4.38%; *M*, 319.02562); *m/z* 319 (M^+) and 155 (p-$ClC_6H_4CS^+$); $\delta_C(CDCl_3)$ 17 (q, SMe), 60 (t, C-2), 129.6 (m,

Table 4 Physical data for thiazolium tetrafluoroborate salts **12**

			$\delta_H(CDCl_3)$		
	M.p./(*T*/°C)	Yield (%)	R^2	R^1 and R^3	H
12a	132 (EtOH)	72	2.05 (s, 3 H)	7.60 (AB, 4 H), 7.85, 8.48 (AA'XX', 4 H)	9.97 (s, 1 H)
12c	90	70	3.83 (s, 2 H)[a]	2.60 (s, 3 H), 7.83, 8.48 (AA'XX', 4 H)[a]	9.97 (s, 1 H)[a]
12d	145 (EtOH)	88	1.97 (s, 3 H)	7.37–7.70 (m, 9 H)	9.80 (s, 1 H)
12f	>260	56	3.67 (s, 2 H)[a]	7.60–7.75 (m, 9 H)[a]	10.00 (s, 1 H)[a]
12g	98 (EtOH)	85	1.95 (s, 3 H)	2.40 (s, 3 H), 7.20–7.62 (m, 9 H)	9.85 (s, 1 H)
12i	Oil	51	2.05 (s, 3 H)	2.70 (s, 3 H), 7.15–7.55 (m, 5 H)	9.65 (s, 1 H)

[a] ^1H NMR in CD_3CN.

C-4), 131 (t, C-5), 122.6, 123.5, 124, 128.1, 128.9, 131.2, 133 and 145 (aromatic C); **10e** (Found: C, 60.8; H, 4.6; Cl, 10.6; N, 4.1. $C_{17}H_{16}ClNS_2$ requires C, 61,17; H, 4.79; Cl, 10.6; N, 4.20%); **10f** (Found: C, 54.4; H, 2.7; Cl, 7.2; N, 2.8. $C_{22}H_{13}ClF_5S_2$ requires C, 54.38; H, 2.70; Cl, 7.30; N, 2.70%); **10g** (Found: C, 68.2; H, 5.7; N, 4.7. $C_{17}H_{17}NS_2$ requires C, 68.05; H, 5.81; N, 4.73%). The obtained oil **10i** was used directly for further reactions without purification. Yields, m.p.s and ^1H NMR data for the dihydrothiazoles **10** are summarized in Table 3.

Thiazolium Salts **12**.—Triphenylcarbenium tetrafluoroborate (4 mmol) was added to a solution of the dihydrothiazole **10** (4 mmol) in CH_2Cl_2 (30 cm^3) at 0 °C. After the reaction mixture had been stirred for 2 h it was diluted with anhydrous ether (50 cm^3) to precipitate the thiazolium salts **12**. These were filtered off and recrystallized from EtOH. **12a** (Found: C, 42.8; H, 2.7; N, 6.5; Cl, 7.4. $C_{16}H_{12}BClF_4O_2S_2$ requires C, 42.64; H, 2.68; Cl, 7.87; N, 6.22%); **12d** (Found: C, 47.1; H, 3.1; Cl, 8.6; N, 3.4. $C_{16}H_{13}BClF_4NS_2$ requires C, 47.37; H, 3.23; Cl, 8.74; N, 3.45%); $\delta_C(CDCl_3)$ 18 (q, SMe), 137.2 (m, C-5), 144 (q, C-4), 152 (d, C-2), 126.3, 126.5, 129.6, 129.9, 131.3, 131.7, 137.3 and 140 (ArC); **12g** (Found: C, 53.0; H, 4.2; N, 3.6. $C_{17}H_{16}BF_4NS_2$ requires C, 52.89; H, 4.25; N, 3.70%). Thiazolium salts **12c** and **12f** were insufficiently stable to be purified, being easily thermolysed during recrystallization from EtOH to give the corresponding DTDAFs. The oil **12i** obtained was directly used for further reactions without purification. Yields, m.p.s and ^1H NMR data for thiazolium salts **12** are summarized in Table 4.

Mechanistic Study.—Equilibrium between **8d** *and* **9d**: *Formation of 2-Morpholino-2,3-dihydro-1,3-thiazole* **11** (R^1 = *p*-ClC_6H_4, R^2 = Me, R^3 = C_6H_5). Morpholine (20 mmol) was added to a solution of 2-piperidino-2,3-dihydro-1,3-thiazole **8d** (2 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred for 30 h at room temperature and then washed with water (3 × 20 cm^3) dried (Na_2SO_4) and evaporated. Addition of ether (10 cm^3) to the residue precipitated compound **11** (R^1 = *p*-ClC_6H_4, R^2 = Me, R^3 = C_6H_5) which was recrystallized from MeCN (93%), m.p. 145 °C (Found: C, 59.8; H, 5.2; Cl, 8.8; N, 7.1. $C_{20}H_{21}ClN_2OS_2$ requires C, 59.31; H, 5.23; Cl, 8.75; N, 6.92%); $\delta_H(CDCl_3)$ 1.94 (3 H, s, SCH_3), 2.69 [4 H, m, $N(CH_2)_4O$], 3.80 [4 H, t, $N(CH_2)_4O$], 5.88 (1 H, s, H) and 7.16–7.56 (9 H, m, aromatic H); $\delta_C(CDCl_3)$ 16 (q, SCH_3), 45.66 [tm, $N(CH_2)_4O$], 92 (d, C-2), 117 (q, C-4), 132 (t, C-5), 123, 125, 126, 128.1, 128.7, 131, 133 and 145 (aromatic C).

Isolation of the Intermediate **9a**. After isolation of the dihydrothiazole **10a** according to the process described above, refrigeration of the filtrate obtained for 48 h, precipitated compound **9a**. This was filtered off and recrystallized from EtOH (5%), m.p. 188 °C (Found: C, 39.1; H, 2.6; Cl, 6.8; I, 25.3; N, 5.7. $C_{16}H_{12}ClIN_2O_2S_2$ requires C, 39.16; H, 2.46; Cl, 7.22; I, 25.86; N, 5.70%). $\delta_H(CDCl_3$ and $CF_3CO_2H)$; 2.08 (3 H, s, SCH_3), 7.66 (4 H, AB, *p*-ClC_6H_4), 7.87, 8.53 (4 H, AA'XX', *p*-$NO_2C_6H_4$) and 10.13 (1 H, s, CH); $\delta_C(CDCl_3$ and $CF_3CO_2H)$ 18 (q, SCH_3), 140 (tq, C-5), 145 (q, C-4), 159 (d, C-2), 125, 125.5, 128, 130.3, 130.4, 139, 140.5 and 150 (ArC).

Preparation of Compound **10d** *from Compound* **8d**. Sodium borohydride (50 mg) was added to a solution of **8d** (1 mmol) in EtOH (25 cm^3). The reaction mixture was stirred for 2 min, diluted with water (75 cm^3) and extracted with ether (2 × 25 cm^3). The combined extracts were washed, dried (Na_2SO_4) and concentrated. Addition of EtOH (5 cm^3) to the residue precipitated compound **10d** which was recrystallized from EtOH (90%), m.p. 124 °C; $\delta_H(CDCl_3)$ 2.00 (s, 3 H, SMe), 5.12 (2 H, s, CH_2) and 7.00–7.62 (9 H, m ArH).

Preparation of Compound **10a** *from Compound* **9a**. Sodium borohydride (25 mg) was added to a suspension of compound **9a** (0.5 mmol) in EtOH (5 cm^3). The reaction mixture was stirred for 5 min after which the precipitate was filtered off, washed with EtOH and recrystallized from EtOH to yield **10a** (90%), m.p. 166 °C; $\delta_H(CDCl_3)$ 2.00 (3 H, s, SMe), 5.27 (2 H, s, CH_2), 7.25, 8.20 (4 H, AA'XX', *p*-$NO_2C_6H_4$) and 7.47 (4 H, AB, *p*-ClC_6H_4).

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