The Synthesis of 3-Aryl-5-dialkylamino-1,4,2-dithiazol-1-ium Salts

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(Received December 24, 1985)

Synopsis. *N*-(Dialkylthiocarbamoylthio)arenecarboxamides, prepared by acylation of the corresponding *S*-dialkylthiocarbamoyl-substituted sulfenamides, cyclized with dehydration in a strong acidic media to form a number of 3-aryl-5-dialkylamino-1,4,2-dithiazol-1-ium salts in good yields.

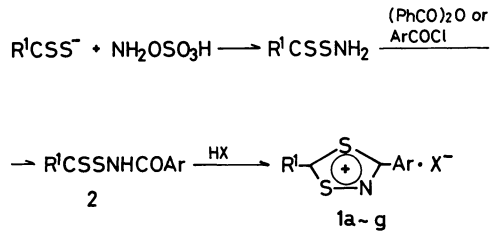
The syntheses and reactions of 1,2- and 1,3-dithiolium cations have been investigated extensively, and their results have been summarized in some excellent reviews.[1-3] The synthesis of 3,5-diaryl-1,2,4-dithiazolium cations, the aza analogs of 1,2-dithiolium, were generalized by Liebscher and the author, and their reactivity has also been studied.[4-7] These five-membered heterocyclic cations are very reactive toward nucleophiles and produce many kinds of derivatives. Therefore, it can be anticipated that 1,4,2-dithiazolium cations, the aza analogs of 1,3-dithiolium, are also reactive and lead to many derivatives. It is interesting to investigate their syntheses and reactivies.

Recently, Paton et al prepared 3-aryl-5-methylthio derivatives by methylation of the corresponding 1,4,2-dithiazol-5-thiones;[8] however, by this method the dithiazol-5-thiones are given only in poor yields.

In addition, Sammes et al prepared 3-aryl-5-dialkylamino compounds quite recently by the reaction between sodium dithiocarbamate and α-chloro oxime *O*-sulfonate,[9] however the chloro oxime sulfonates are special reagents and not available easily.[10]

We now report that a number of 1,4,2-dithiazolium cations were obtained in high yields by another simple method. The approach to preparing 3-aryl-5-dialkylamino-1,4,2-dithiazol-1-ium salts, (**1**), was attained via the pathway shown as Scheme 1, which could be postulated based on the synthetic route of the corresponding 1,3-dithiolium salts.[11]

N-(Dialkylthiocarbamoylthio)arenecarboxamides, (**2**), the precursors for **1**, could not be obtained directly by a reaction of dithiocarbamic acids with *N*-bromoarenecarboxamides; however, the dithiocarbamic acids led to sulfenamides upon treating with hydroxylamine-*O*-sulfonic acid in aqueous sodium hydroxide. The sulfenamides were acylated smoothly with benzoic anhydride to give *N*-benzoyl sulfenamides, while other aroyl compounds were also accessible by treating with aroyl chlorides. Cyclization of **2** was carried out with dehydration in a strong acidic media to afford white crystalline compounds of **1a—g**. Their mps, yields, and analytical data are summarized in Table 1, and satisfactory analytical results were obtained for all products. The IR spectrum of **1a** was almost superimposable to that of 2-diethylamino-4-phenyl-1,3-dithiolium perchlorate. Two absorptions, at δ=166.79 and 192.47, are assignable to the C-3 and C-5 carbons of 1,4,2-dithiazolium ring, respectively. These were observed in the ^{13}C NMR spectrum of **1a**, and the spectral data agreed with the results of Sammes.[9] These facts showed that **1a** is identical with 3-phenyl-5-diethylamino-1,4,2-dithiazol-1-ium perchlorate, and it was found that a number of 3-aryl-5-dialkylamino compounds, **1a—g**, could be obtained in good yields using a simple method, Scheme 1. This process is more convenient and applicable than the two when 1,4,2-dithiazolium salts are supposed to be versatile intermediates to lead to various heterocycles. A study concerning the reaction of the 1,4,2-dithiazolium salts with nucleophiles is in progress.



Scheme 1.

Experimental

***S*-Diethylthiocarbamoyl-Substituted Sulfenamide.** Into an aqueous solution (10 ml) of sodium diethyldithiocarbamate trihydrate (2.30 g, 0.01 mol) was added with stirring at a temperature below 10 °C an aqueous solution (10 ml) of hydroxylamine-*O*-sulfonic acid (1.70 g, 0.015 mol), neutralized with sodium hydroxide. The resulting precipitate was separated by filtration and air-dried. The crude product was dissolved in dichloromethane and filtered to remove any insoluble substance. The solvent was evaporated under a reduced pressure to give 1.56 g of the sulfenamide; yield 95%, mp 30—31 °C. ^1H NMR ($CDCl_3$) δ=1.26 (6H, t), 3.08 (2H, br s), 3.80 (4H, br q); IR (KBr): 3336, 3248, 2979, 2932, 1571, 1493, 1420, 1354, 1274, and 1205 cm^{-1}. Found: C, 36.77; H, 7.42; N, 16.80%. Calcd for $C_5H_{12}N_2S_2$: C, 36.59; H, 7.36; N, 17.05%.

Other *S*-dialkylthiocarbamoyl-substituted sulfenamides were also accessible in the same manner as described above almost quantitatively.

***N*-(Diethylthiocarbamoylthio)benzamide (2a). Reaction with Benzoic Anhydride:** Into a solution of *S*-diethylthiocarbamoyl-substituted sulfenamide (1.64 g, 0.01 mol) in chloroform (10 ml), benzoic anhydride (2.71 g, 0.012 mol) was added. The reaction mixture was then kept at 50 °C for 2 h. After removing the solvent under a reduced pressure, the resulting residue was washed with an excess of ether and recrystallized from ethanol to give 2.09 g of **2a**; yield 78%, mp 129 °C. ^1H NMR ($CDCl_3$) δ=1.34 (6H, br t), 3.87 (4H, br), 7.56 (3H, m), and 8.03 (2H, m). IR (KBr): 3315, 2980, 2935, 1672, 1503, 1455, 1423, 1278, and 710 cm^{-1}. Found: C, 53.85; H, 6.02; N, 10.40%. Calcd for $C_{12}H_{16}N_2S_2O$: C, 53.70; H, 6.01; N, 10.44%.

Reaction with Benzoyl Chloride: A solution of *S*-diethylcarbamoyl-substituted sulfenamide (0.82 g, 5 mmol) and

Table 1. 3-Aryl-5-dialkylamino-1,4,2-dithiazol-1-ium Salts, (**1a—g**)

Compd	R^1-	Ar-	X^-	Mp	Yield	Found (Calcd)/%		
				θ_m/°C	%	C	H	N
1a	Et_2N-	Ph-	ClO_4^-	141	80	41.08 (41.02)	4.31 (4.30)	7.98 (8.07)
1b	Et_2N-	*p*-$CH_3OC_6H_4$-	ClO_4^-	121	54	40.85 (41.00)	4.46 (4.50)	7.43 (7.27)
1c	Et_2N-	*p*-$CH_3C_6H_4$-	ClO_4^-	137	52	42.75 (42.79)	4.62 (4.70)	7.67 (7.68)
1d	Et_2N-	*p*-ClC_6H_4-	ClO_4^-	140	79	37.44 (37.41)	3.63 (3.66)	7.33 (7.68)
1e	Me_2N-	Ph-	ClO_4^-	175	63	37.18 (37.21)	3.39 (3.43)	8.70 (8.68)
1f	$(CH_2)_5N$-	Ph-	ClO_4^-	212	82	42.83 (43.03)	4.09 (4.17)	7.61 (7.72)
1g	Et_2N-	Ph-	BF_4^-	120	56	42.62 (42.58)	4.47 (4.43)	8.28 (8.29)

benzoyl chloride (1.05 g, 7.5 mmol) in ether (20 ml) was vigorously stirred with 2 mol dm^{-3} aqueous sodium hydroxide (20 ml) for 3 h at a temperature below 10 °C. The resulting precipitate was filtered, and recrystallized from ethanol to give 0.85 g of **2a**; yield 32%. Other *N*-benzoyl sulfenamide were given in 30—41% using the same procedure mentioned above.

Preparation of 3-Aryl-5-alkylamino-1,4,2-dithiazol-1-ium Salts (1a—g). To a solution of an *N*-benzoyl sulfenamide (0.01 mol) in acetic anhydride (20 ml), 70% perchloric acid (1 ml) or 40% tetrafluoroboric acid (2 ml) was added dropwise with stirring. The reaction mixture was kept at 60 °C for 2 h. After cooling to room temperature, the mixture was poured into an excess of ether to afford a white powder and recrystallized from acetonitrile to give **1a—g**. Their mps, yields, and analytical results are given in Table 1.

1a: ^{1}H NMR (DMSO-d_6) δ=1.38 (3H, t), 1.42 (3H, t), 3.87 (2H, q), 3.98 (2H, q), 7.02 (3H, m), and 7,99 (2H, m). ^{13}C NMR (DMSO-d_6, ppm from TMS) 10.36 (-CH_3), 54.47 (-CH_2-), 57.06 (-CH_2-), 128.82—133.44 (arom), 166,79 (C-3), 192.47 (C-5). IR (KBr): 1576, 1528, 1473, 1447, 1087, 769, 686, and 617 cm^{-1}.

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