Nucleophilic attack on 2,1-benzisothiazolium salts

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Received August 10, 1981

DAVID M. MCKINNON, K. ANN DUNCAN, and LESLEY M. MILLAR. Can. J. Chem. **60**, 440 (1982).

2,1-Benzisothiazolium salts react with several stabilized carbanions to give products that are derived by attack at the carbon atom of the heterocyclic ring.

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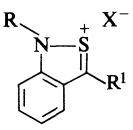
Les sels de benzisothiazolium-2,1 réagissent avec plusieurs carbanions stabilisés en donnant des produits qui proviennent de l'attaque au niveau de l'atome de carbone de l'hétérocycle.

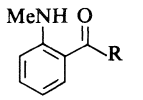
[Traduit par le journal]

Although the site of nucleophilic attack of carbanions on monocyclic isothiazolium salts and the 1,2-benzisothiazolium cation appears to be at ring sulfur rather than at a carbon atom (1–4), little work is reported of the attack of carbanions on 2,1-benzisothiazolium salts. It is known that nucleophilic attack occurs at a ring carbon, i.e. the 3-position by certain oxygen (5), sulfur (6), and nitrogen (7) nucleophiles, and by *N*,*N*-dimethylaniline (on its *para* position) (6). For this investigation we used the salts **1** *a*–*e* which were available from reported syntheses (5–7) or simple modifications. For the reactions of cations of type **1**, a number of reaction possibilities may be envisaged by analogies with other isothiazoles or related heterocyclic species: reaction at ring sulfur with subsequent ring opening (1, 2) as for the isothiazolium (1, 2) and 1,2-benzisothiazolium system (2–4); addition at carbon 3 followed by ring fission or replacement of a reactive substituent with retention of the isothiazole ring (5, 7); dealkylation by nucleophilic displacement at an *N*-alkyl substituent (8), or removal of a C-3 proton giving a carbene (or zwitterion) or further acyclic derivative as for the monocyclic system (9). Other possible reactions of the salts, involving deprotonation of a C-3 alkyl substituent (10), are not possible with the examples we used.

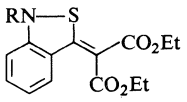


1

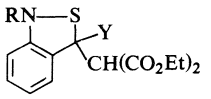
	R	R[1]	Y
a	Me	H	I
b	Me	SMe	I
c	Ph	SMe	I
d	Ph	Cl	Cl
e	Me	Ph	ClO_4
f	Me	$CH(CO_2H)_2$	ClO_4
g	Me	CH_2CO_2H	ClO_4
h	Me	Me	ClO_4



2
a R = H
b R = Ph



3
R = Me
R = Ph



4
R = Me; Y = H
R = Me; Y = SMe

The reaction of the anion of diethyl malonate with **1***a* afforded a mixture of products, from which 2-methylaminobenzaldehyde (**2***a*) and diethyl 1-methyl-2,1-benzisothiazol-3-ylidenemalonate (**3***a*) were isolated. The formation of the latter may be rationalized in terms of nucleophilic attack at carbon to form a saturated derivative **4***a* which is then oxidized by possibly unreacted **1***a* to form **3***a*. The reduction of **1***a* would provide 2-methylaminothiobenzaldehyde which might be expected to convert to **2***a* under the reaction conditions. It is known (11, 12) that the structurally related 1,2-dithiolium salts react with ketones to produce 3-acylmethylene-1,2-dithioles. On the other hand, if malonate were displaced from **4** by water during the work-up process, ring opening reactions would lead to **2***a*, as described (5). The ester **3***a* was obtained in much better yield by reaction of **1***b* with diethyl malonate. This is again obviously formed by nucleophilic attack at carbon to form **4***b*, which then eliminates methanethiol.

When **1***a* was treated with triethylamine or pyridine and the product worked up, the only products obtained were the thione **5** and **2***a*. No products derived from proton abstraction were isolated. The formation of **5** and **2***a* represents a dismutation reaction of a product formed by nucleophilic attack of water on **1***a*, with sulfur being transferred between two molecules. This could have arisen by the mechanism shown (Fig. 1). The addition of extra sulfur to the reaction mixture did not affect the relative yield of the products and therefore this reaction would then appear to pro-

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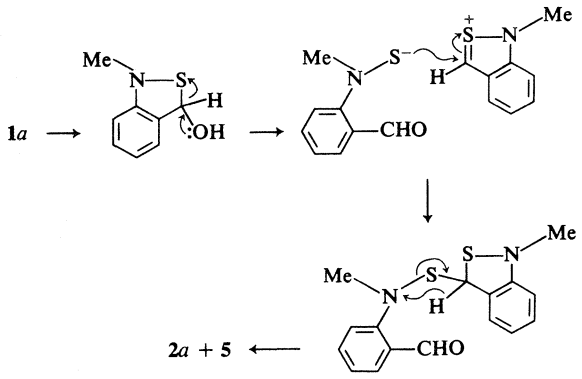
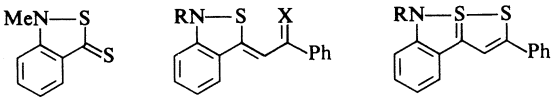


FIG. 1.

ceed via a different mechanism to the base catalysed sulfurizations of 1,2-dithiolium salts to 1,2-dithiole-3-thiones (13) and of isothiazolium salts to isothiazoline 3- and 5-thiones (9). Davis *et al.* (5) obtained **2***a* by treatment of **1***a* with sodium bicarbonate, without reporting the isolation of **5**. In our hands a repeat of this reaction did also yield some thione. The treatment of **1***b* with sodium benzoylacetate in ethanol yielded the ketone **6***a* as a yellow oil. This reaction is analogous to the reactions of sodium benzoylacetate with 3-alkylthio-1,2-dithiolium salts to form 3-phenacylidene-1,2-dithioles (14). The product **6***a* upon thionation with phosphorus pentasulfide yielded the thione **6***b* which is probably best represented by the hypervalent sulfur structure **7**. The product **6***a* was accompanied by small amounts of a red oil, whose properties are consistent with methyl 2-methylaminodithiobenzoate **8***a*, likely formed by reduction of **1***b* with methanethiolate eliminated in the reaction, as for monocyclic isothiazolium salts (1).

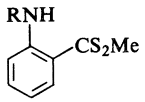
Also, treatment of **1***b* with the anion of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's Acid) afforded the cyclic ester **9***a*. When this was treated with perchloric acid in acetic acid it rapidly converted to the acid derivative **1***f* by ketal hydrolysis and decarboxylation of the malonic acid derivative **1***g*. We were unsuccessful, however, in converting this further to the 1,3-dimethyl-2,1-benzisothiazolium salt **1***h* by further decarboxylation as is described for 1,2-dithioles (15). Similarly **1***d* reacted with Meldrum's acid to form **9***d*.

Reactions of **1***c* or *d* with various anions proceeded similarly with little difference, other than in side products. Thus **1***c* reacted with diethyl malonate or sodium benzoylacetate to yield **3***b* and **6***c* respectively. A side product in these reactions was methyl 2-(*N*-phenylamino)dithiobenzoate (**8***b*) produced by reduction of **1***c* with eliminating methanethiolate. To check this, a sample of **1***c* was treated with methanethiol, giving **8***b* in excellent yield. This product was contaminated, however, with a small amount of 9-methylthioacridine (**10**). This does not appear to arise from **8***b* by base catalysed cyclization since its prolonged treatment with methanethiolate gave no acridine **10**. It therefore may be that it is some initial reduction product of **1***c*, possibly a radical species, that is the direct percursor of **10**. Alternatively it may be formed by initial nucleophilic attack at carbon, with subsequent production of the species **11**, which eventually cyclizes to **10**.[2]



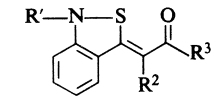
5 **6** **7**

a R = Me; X = O
b R = Me; X = S
c R = Ph; X = O



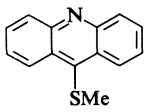
8

a R = Me
b R = Ph

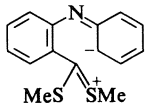


9

a R^1 = Me; R_2, R_3 = $-C(=O)-O-CMe_2-O-$
b R^1 = Ph; R_2 = 2-Py; R_3 = OMe
c R^1 = Ph; R_2 = OMe; R_3 = 2-Py
d R^1 = Ph; R_2, R_3 = $-C(=O)-O-CMe_2-O-$



10

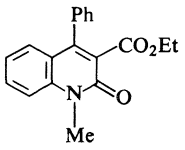


11

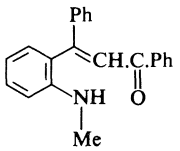
The treatment of **1***d* with sodium benzoylacetate also afforded **6***c*, and reaction with methyl pyridyl-2-acetate gave a dark yellow oil which could not be separated, but appears to be a mixture of the ester **9***b* and its geometrical isomer **9***c*. With the anion of 2,2-dimethyl-1,3-dioxane-2,6-dione, **9***d* was obtained. Attempted hydrolysis and decarboxylation of this gave only brown polymeric material. Both **9***a* and **9***d* exhibited low field absorptions at ~9.3 δ, no doubt due to the shielding effect of a dioxane-ring carbonyl group on the neighboring aromatic proton. These are in close proximity, due to the steric constraints of the conjugated ring systems.

[2]We are indebted to one of the referees for this suggestion.

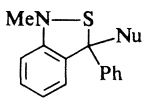
Treatment of 1-methyl-3-phenyl-2,1-benzisothiazolium perchlorate (**1***e*) with diethyl malonate under a number of conditions gave only 3-phenyl-2,1-benzisothiazole and 2-methylaminobenzophenone (**2***b*). Only a trace of material was isolated whose mass spectrum corresponded to the quinolone **12**, formed by nucleophilic attack on carbon, ring opening, and recyclization. Likewise treatment of **1***e* with sodium benzoylacetate gave 3-phenyl-2,1-benzisothiazole and **2***b*, along with what appear to be traces of the aminoketone **13**, or a tautomer, formed by nucleophilic attack of a phenacyl ion, actual or potential at ring carbon, followed by ring opening, and extrusion of a sulfur atom.



12



13



14

The low yields of the reaction products with the nucleophiles may be rationalized in terms of initial production of 1:1 addition products which are relatively resistant to ring opening. Nakagawa and co-workers (7) report the isolation of initial products of amines on 2,1-benzisothiazolium salts. Redissociation of adducts of type **14**, with dealkylation, or attack of water on the regenerated cation as alternate reaction pathways could produce the main products isolated. Indeed when **1***e* was treated with sodium bicarbonate, 2-methylaminobenzophenone was isolated. This is comparable to earlier reactions of simpler 2,1-benzisothiazoles (5). Two other unstable products were formed in lesser amounts which may represent side reactions.

Thus all of the products obtained in these reactions, other than dimethylation products, are consistent with nucleophilic attack at ring carbon, in contrast to isothiazolium and 1,2-benzisothiazolium salts which give products by attack of carbanions at sulfur. In terms of "Hard and Soft" acid and base theory, it implies that in the 2,1-system the carbon is "softer," and the sulfur is the "harder" in the latter systems. The low frequencies of the carbonyl stretching frequencies in **6***a* and **6***c*, as well as the two greatly different carbonyl frequencies in **3***a* and **3***c*, are indicative of partial bonding between carbonyl oxygen and sulfur atom. Similar data are available for closely related 1,6,6aS^{iv} trithiapentalenes (16).

Experimental

The ^1H nmr spectra were obtained in deuteriochloroform solution, unless otherwise stated, on a Varian model EM 360 spectrometer using tetramethyl silane as an internal standard. Mass spectra were obtained on a Finnegan 1015 spectrometer. Chromatography was performed on Camag silica gel type D.S.F. 5, supplied by Terochem Laboratories, and elution, unless otherwise stated, was by benzene with varying proportions of chloroform. Unless otherwise stated, solutions were dried over anhydrous magnesium sulfate.

*2,1-Benzisothiazolium salts (1*a–e*)*

These were prepared by literature methods (5–7) or simple modifications of them.

*Reaction of 1-methyl-2,1-benzisothiazolium iodide (1*a*) with sodium bicarbonate*

This was performed as described (5). Examination of the product obtained by tlc afforded 2-methylaminobenzaldehyde (**2***a*) (34%) and 1-methyl-2,1-benzisothiazoline-3-thione (**5***a*) (22%) identical with an authentic sample (6)

Reaction of 1-methyl-3-phenyl-2,1-benzisothiazolium perchlorate (1e) with sodium bicarbonate

The perchlorate (326 mg, 1 mmol) was stirred in a warm mixture of ether and saturated sodium bicarbonate. After 30 min the red ether layer was separated, washed with water, dried, and evaporated to give a red oil which on chromatography yielded a broad yellow band. On elution this yielded 2-methylaminobenzophenone (**2***b*) as bright yellow needles from hexane (73%), mp 69°C (lit. (17) mp 69°C).

Two other bands gave small amounts of oily material which appeared to be unstable.

*Reaction of 1-methyl-2,1-benzisothiazolium iodide (1*a*) with triethylamine*

The salt (277 mg, 1 mmol) was added to dry triethylamine and stirred for 30 min. The solution was filtered and partitioned between dilute hydrochloric acid (10%) and ether. The ether layer on evaporation yielded a red oil which on examination by chromatography yielded 2-methylaminobenzaldehyde (36%) and 1-methyl-2,1-benziothiazoline-3-thione (21%), both identical (mixture mp) with authentic specimens (refs. 5 and 6 respectively). Use of pyridine gave similar results.

*Reaction of 1-methyl-2,1-benzisothiazolium iodide (1*a*) with diethyl malonate to form 3*a

The salt (277 mg, 1 mmol) was added to the equivalent quantity of sodium diethyl malonate in ethanol. On stirring, an orange solution resulted which was evaporated and examined by chromatography. Two main bands were evident. A yellow band was found to be 2-methylaminobenzaldehyde (20%), and a slower moving band was isolated as an orange oil which crystallized on standing under ethanol and was recrystallized from hexane as pale orange needles, mp 78–80°C. This is assigned the structure **3***a* (28%). The ir spectrum: 1611, 1702 cm^{-1} (C=O str, the two different carbonyl groups) (in liquid paraffin). The nmr spectrum, δ: 1.20–1.53 (6H, two superimposed methyl triplets), 3.49 (3H, s, the N methyl), 4.12–4.65 (4H, two superimposed methylene quartlets), 6.95–8.02 (4H bands, the aromatic protons). The mass spectrum M^+ 307, M calcd. 307.

Anal. calcd. for $C_{15}H_{17}NO_4S$: C 58.63, H 5.54, N 4.56, S 10.42; found: C 58.51, H 5.61, N 4.59, S 10.53%.

*Reactions of 3-methylthio- or 3-chloro-2,1-benzisothiazolium salts 1*b, c, d *with diethyl malonate, 2,2-dimethyl-1,3-dioxane-4,6-dione, or benzoylacetic acid*

These were performed under similar conditions. The salts

were added to slight excesses (1.1 equiv.) of the anions in anhydrous ethanol (prepared by adding the ester or acid to a solution of sodium ethoxide in ethanol). The mixtures were warmed gently until homogeneous, then diluted with water, extracted with chloroform, dried, and examined by chromatography. Products from 2,2-dimethyldioxane-4,6-dione crystallized on dilution of the ethanol with water and were collected. Results of individual experiments are summarized below.

*1-Methyl-3-methylthio-2,1-benzisothiazolium iodide (**1**b) and sodium benzoyl acetate to form **6**a*

Chromatography gave a dark yellow strongly adsorbed material and small amounts of 1-methyl-2,1-benzisothiazoline-3-thione. Separation of the dark yellow material gave an oil which could not be crystallized but had properties consistent with **6***a* (76%). It was not analysed.

The ir spectrum: 1000 cm^{-1} (C=O str) (as a liquid film). The nmr spectrum: δ: 3.46 (3 H, s, the *N* methyl protons), 6.85–8.25 (10H bonds, the aromatic and methine protons). The mass spectrum M^+ 267, M calcd. 267.

*1-Phenyl-3-methylthio-2,1-benzisothiazolium iodide (**1**c) and sodium benzoylacetate to form **6**c*

Chromatography of the reaction mixture afforded two main products. A dark yellow band on elution and evaporation gave a viscous oil which crystallized on standing under ethanol. Compound **6***c* was recrystallized from ethanol as orange prisms, mp 148–50°C (49%). The ir spectrum: 1604 cm^{-1} (C=O str) (in liquid paraffin). The nmr spectrum only exhibited complex bands between δ 7.0 and 8.35. The mass spectrum, M^+ 329, M calcd. 329.

Anal. calcd. for $C_{21}H_{15}NOS$: C 76.60, H 4.50, N 4.26, S 9.73; found: C 76.73, H 4.31, N 4.28, S 9.80.

A dark orange band on elution and evaporation gave a viscous red oil whose properties were consistent with **8***b* (15%). This was identical (R_f, nmr) to the product of a preparation described below.

*1-Phenyl-3-chloro-2,1-benzisothiazolium chloride (**1**d) and sodium benzoylacetate*

This reaction was performed as above. A yellow band obtained on chromatography yielded **6***c* as an oil which crystallized under ethanol and was identical to that obtained above (62%).

*Reaction of 1-methyl-3-methylthio-2,1-benzisothiazolium iodide (**1**b) with 2,2-dimethyl-1,3-dioxane-4,6-dione to form **9**a*

The reaction mixture diluted with water gave red needles which recrystallized from ethanol as pale orange needles, mp 165–166°C (43%). The aqueous filtrate on extraction with chloroform yielded more product (19%). The ir spectrum: 1610, 1699 cm^{-1} (C=O str, the two different carbonyl groups) (in liquid paraffin). The nmr spectrum, δ: 1.90 (6H, s, the two C methyl groups), 3.84 (3H, s, the *N*-methyl). The aromatic protons were evident as groups at 7.05–7.83 and 9.15–9.45. The mass spectrum M^+ 291, M calcd. 291.

Anal. calcd. for $C_{14}H_{13}NO_4S$: C 57.73, H 6.47, N 4.81, S 11.00; found: C 57.62, H 4.48, N 4.90, S 11.13.

*Reaction of 3-chloro-1-phenyl-2,1-benzisothiazolium chloride (**1**d) with 2,2-dimethyl-1,3-dioxane-4,6-dione to form **9**d*

This was performed as above. Dilution with water afforded a dark yellow precipitate which was recrystallized from ethanol as dark yellow prisms, mp 189–190°C (65%). The ir spectrum: 1609, 1699 cm^{-1} (C=O str, the two carbonyl groups) (in liquid paraffin). The nmr spectrum, δ: 1.91 (6H, s, the two methyl groups). The aromatic protons were evident as groups at 7.01–7.86 and 9.13–9.41. The mass spectrum M^+ 352, M calcd. 353.

Anal. calcd. for $C_{19}H_{15}NO_4S$: C 64.59, H 4.25, N 3.97, S 9.07; found: C 64.81, H 4.26, N 3.83, S 8.94.

*Reaction of 1-methyl-3-methylthio-2,1-benzisothiazolium iodide (**1**b) with diethyl malonate*

On chromatography a broad yellow band was obtained which on evaporation and standing under ethanol gave **3***a* as orange needles from hexane (56%) identical to above.

A faster running orange band gave ~10 mg of a red oil, assigned tentatively to the dithioester **8***a*; M^+ 197, M calcd. 197.

*Reaction of 3-methylthio-1-phenyl-2,1-benzisothiazolium iodide (**1**c) with diethyl malonate to form* **3**b

Chromatography of the reaction mixture gave a broad strongly absorbed yellow band which on elution gave **3***b* as a yellow oil which crystallized from hexane as yellow needles, mp 80°C (42%). The ir spectrum: 1621, 1701 cm^{-1} (C=O str) (in liquid paraffin). The nmr spectrum, δ: 1.31–1.62 (6H, two superimposed methyl triplets), 4.20–4.73 (4H, two superimposed methylene quartets), 6.95–8.11 (9H bands, the aromatic protons). The mass spectrum M^+ 369, M calcd. 369.

Anal. calcd. for $C_{20}H_{19}NO_4S$: C 65.04, H 5.15, N 3.79, S 8.67; found: C 64.97, H 5.23, N 3.88, S 8.53.

The reaction also yielded **8***b* (10%) and small amounts of 1-phenyl-2,1-benzisothiazoline-3-thione as side products.

*Reaction of 3-chloro-1-phenyl-2.1-benzisothiazolium chloride (**1**d) with methyl 2-pyridylacetate*

The isothiazolium salt (282 mg, 1 mmol) and methyl 2-pyridylacetate (151 mg, 1 mmol) in anhydrous pyridine (10 mL) were refluxed 3 h. The mixture was diluted with water and partitioned between 10% dilute hydrochloric acid and chloroform. The chloroform layer was dried and evaporated to give a dark oil. Chromatography gave a broad yellow band which on elution gave an orange oil. This failed to crystallize and could not be further separated. It was not analysed but its spectral properties are consistent with a mixture of **9***b* and **9***c*.

The nmr spectrum, δ: 3.78, 4.01 (two singlets of the two isomers). Other protons were evident as bands between 6.95 and 8.85. The mass spectrum M^+ 360, M calcd. 360.

*Reaction of 1-methyl-3-phenyl-2,1-benzisothiazolium perchlorate (**1**e) with diethyl malonate*

The isothiazolium salt (**1***e*) (32.6 mg, 1 mmol) and diethyl malonate (~0.2 g) were refluxed together in pyridine for 1.5 h. The pyridine was evaporated under reduced pressure and the product partitioned between dilute hydrochloric acid and chloroform. Examination of the chloroform solution by tlc afforded 3-phenyl-2,1-benzisothiazole (38%) and 2-methylaminobenzophenone (26%), both identical with authentic specimens (refs. 7 and 18, respectively) and only traces of a pale yellow material, mp 135°C, tentatively assigned to **12**.

The mass spectrum M^+ 307, M calcd. 307. The use of other reaction conditions gave poorer results.

*Reaction of 1-methyl-3-phenyl-2,1-benzisothiazolium perchlorate (**1**e) with sodium benzoylacetate*

The perchlorate (326 mg, 1 mmol) was added to a solution of sodium benzoylacetate, prepared from benzoylacetic acid (164 mg, 1 mmol) added to a solution of sodium (23 mg, 1 mmol) in ethanol (10 mL). The mixture was warmed until homogeneous, evaporated under reduced pressure, and examined by chromatography.

The reaction yielded only 3-phenyl-2,1-benzisothiazole, 2-methylaminobenzophenone, and traces of pale orange crystals, mp 68°C, tentatively assigned to **13**.

The mass spectrum M^+ 313, M calcd. 313.

1-Methyl-2,1-benzisothiazole[2,3-b]-5-phenyl-1,2-dithiole (7)

1-Methyl-3-phenacylidene-2,1-benzisothiazole (**6***a*) (133 mg, 0.5 mmol) in toluene (10 mL) was refluxed with phosphorus pentasulfide (0.5 g) for 30 min. The mixture was cooled and treated with saturated sodium bicarbonate solution and extracted with chloroform. Evaporation yielded a red oil which was separated by chromatography. Elution of the crimson band gave a red oil which crystallized on trituration with ethanol. Dark red prisms, mp 152–153°C, were obtained (61%). The nmr spectrum, δ: 3.60 (3H, s, the *N*-methyl), 6.95–8.29 (9H bands, the aromatic protons), 8.51 (1H, s, the methine proton). The mass spectrum M^+ 283, M calcd. 283.

Anal. calcd. for $C_{16}H_{13}NS_2$: C 67.84, H 4.59, N 4.95, S 22.61%; found: C 67.91, H 4.66, N 4.61, S 22.89%.

1-Methyl-3-carboxymethyl-2,1-benzisothiazolium perchlorate (1f)

The dioxane **9***a* (145 mg, 0.5 mmol) in acetic acid (3 mL) was treated with 70% perchloric acid (0.05 mL) and warmed briefly. The red solution turned pale yellow with gas evolution and separation of a crystalline precipitate. This was recrystallized from acetic acid containing a trace of perchloric acid as buff needles, mp 155°C (dec.).

The ir spectrum: 1710 cm^{-1} (C=O str). It also exhibited a broad absorption between 2800 and 3200 cm^{-1}. *Anal.* calcd. for $C_{10}H_{10}ClNO_6S$: C 39.02, H 3.25, Cl 11.54, N 4.55, S 10.41; found: C 39.31, H 3.51, Cl 11.60, N 4.62, S 10.59%.

Further heating of this gave dark yellow polymeric material.

Methyl 2-phenylaminodithiobenzoate (8b)

Excess methanethiol was passed into a solution of sodium ethoxide in ethanol (10 mL) (from 13.8 mg sodium). To the solution was added 3-methylthio-1-phenyl-2,1-benzisothiazolium iodide (230 mg, 0.6 mmol), and the mixture warmed until homogeneous. The resulting red solution was treated with charcoal, filtered, and evaporated. The red oil was chromatographed and gave a red and a pale yellow band. The red band on elution gave a red oil which had properties consistent with **8***b* (73%). It was not analysed. The nmr spectrum, δ: 2.80 (3H, s), 6.83–8.40 (9H bands), 9.50–10.03 (1H, broad, the hydrogen bonded NH). The mass spectrum M^+ 259, M calcd. 259.

The pale yellow band on elution gave a pale yellow crystalline solid, mp 113°C, identical to a sample of **10** prepared below (5%).

Prolonged treatment of **8***b* with sodium methanethiolate did not produce any of the acridine **10**. Instead a polymeric material was obtained.

9-Methylthioacridine (10)

9-Chloracridine (2.13 g, 10 mmol) was treated with excess sodium methanethiolate in methanol (prepared from sodium methoxide and methanethiol) and stirred 4 h. Dilution with water and work-up afforded pale yellow crystals, mp 113–114°C (lit. (17) mp 113–114°C) (81%).

Acknowledgements

We wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work, and Mr. W. Buchannon for the preparation of mass spectra.

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