1254. *Quaternisation of* 2,1,3-*Benzothiadiazole and* 2,1,3-*Benzoselenadiazole. Part I. Preparation of Methyl- and Ethyl-*2,1,3-*benzothiadiazolium and -benzoselenadiazolium Salts*

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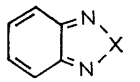
The preparation of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole is discussed. Only mono-quaternary salts of the parent bases have been obtained; there is little doubt about the structure of such compounds as it is unlikely that a sulphonium or selenonium salt is involved. The merits of various quaternising agents (alkyl iodides, dialkyl sulphates, alkyl toluene-*p*-sulphonates, and alkyl 2,4-dinitrobenzenesulphonates) for the preparation of methyl- and ethyl-2,1,3-benzothia- and -selenadiazolium salts are discussed, with a view to finding a suitable method of obtaining higher members of the series. 2,1,3-Benzoselenadiazole appears considerably more reactive towards quaternisation than 2,1,3-benzothiadiazole and the salts formed are much more stable, especially to water.

2,1,3-Benzothiadiazole (I) can be prepared by the action of thionyl chloride or thionylaniline on *o*-phenylenediamine or its hydrochloride. This method of ring-closure was first suggested by Michaelis.[1] Khaletsky and Pesin [2] obtained an 84% yield by this method

[1] A. Michaelis, *Annalen*, 1893, **274**, 262.
[2] A. M. Khaletsky and V. G. Pesin, *J. Gen. Chem.* (*U.S.S.R.*), 1950, **20**, 1981.

on heating *o*-phenylenediamine and thionyl chloride with toluene; in a similar manner, Efros and Levit [3] obtained an 86·5% yield of 2,1,3-benzothiadiazole. We have found that boiling the reactants under reflux for 3 hr. and distillation of the product at normal pressure gives an 85% yield of the heterocycle. Little advantage is gained by the use of other solvent media, except that in the presence of tertiary bases the reaction proceeds with great vigour.[4,5] It is only necessary to employ thionylaniline in place of thionyl chloride when using an *o*-phenylenediamine derivative containing reactive substituents.



(I: X = S)
(II: X = Se)

The ready formation of 2,1,3-benzoselenadiazoles from *o*-phenylenediamines and selenious acid has been known since the time of Hinsberg.[6] The parent compound (II) is best prepared by mixing warm aqueous solutions of equivalent quantities of *o*-phenylenediamine and selenium dioxide, when 2,1,3-benzoselenadiazole separates in almost quantitative yield; variations of this method have been used previously by various authors.[7-10]

The review of quaternisation in heterocyclic compounds by Duffin [11] shows that the commonest reagents for such reactions are the alkyl iodides; *N*-phenyl quaternary salts are most frequently prepared by ring-closure reactions. However, as we found with 1,2,3,-benzothiadiazole,[12] methyl and ethyl iodides are unsuitable for the quaternisation of very weak bases, although limited success with methyl iodide is claimed by Poesche.[13] No quaternary salt could be isolated when 2,1,3-benzothiadiazole was boiled under reflux with methyl or ethyl iodide for a period of 9 hr., even when a polar solvent like nitrobenzene was added to the reaction mixture. Similar experiments with 2,1,3,-benzoselenadiazole gave small yields of unsatisfactory product. Sealed-tube reactions were not attempted; Hinsberg [7] said that 5-methyl-2,1,3-benzothiadiazole would not react with methyl iodide at 160°, but he succeeded in isolating a methiodide of 5-methyl-2,1,3-benzoselenadiazole [6] on heating the reaction mixture at 100° for several hours, though later workers [14] had some doubt as to the authenticity of this compound.

The only known, well-defined quaternary salts of the systems under investigation are a series of phenyl-2,1,3-benzoselenadiazolium chlorides prepared by Battegay and Véchot [14] as a result of condensing selenious acid in dilute hydrochloric acid with salts of *o*-aminodiphenylamine. We therefore set out to prepare a series of methyl and ethyl quaternary salts of 2,1,3-beznothiadiazole and 2,1,3-benzoselenadiazole.

2,1,3,-Benzoselenadiazole reacted violently with dimethyl sulphate to give methyl-2,1,3,-benzoselenadiazolium methosulphate in 95% yield. The anion could be readily exchanged and was converted by double decomposition in cold aqueous medium into chloride, bromide, iodide, thiocyanate, or perchlorate; methyl-2,1,3-benzoselenadiazolium cyanide proved to be unstable and the acetate and phosphate could not be obtained. 2,1,3-Benzothiadiazole and dimethyl sulphate heated for 4 hr. at 100° gave a 95% yield of methyl-2,1,3-benzothiadiazolium hydrogen sulphate. Double decomposition reactions gave only the iodide, thioycanate, and perchlorate, methyl-2,1,3-benzothiadiazolium cyanide being very unstable. Methyl-2,1,3-benzothiadiazolium chloride and bromide were obtained by ion-exchange of the methohydrogen sulphate in ethanol.

[3] L. S. Efros and R. M. Levit, *J. Gen. Chem.* (*U.S.S.R.*), 1953, **23**, 1629.
[4] A. M. Khaletsky, V. G. Pesin, and Chzhao Chzhi-Chzhun, *Proc. Akad. Sci.* (*U.S.S.R.*), 1956, **106**, 31.
[5] A. M. Khaletsky, V. G. Pesin and Chzhao Chzhi-Chzhun, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1643.
[6] O. Hinsberg, *Ber.*, 1889, **22**, 862.
[7] O. Hinsberg, *Ber.*, 1889, **22**, 2895.
[8] E. Sawickl and A. Carr, *J. Org. Chem.*, 1957, **22**, 503.
[9] L. S. Efros and Z. V. Todres-Selektor, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1064.
[10] C. W. Bird, G. W. H. Cheeseman, and A. A. Sarsfield, *J.*, 1963, 4767.
[11] G. F. Duffin, " The Quaternisation of Heterocyclic Compounds " in Recent Advances in Heterocyclic Chemistry, vol. III, ed. Katrizky, Academic Press, London and New York, 1964.
[12] A. J. Nunn, D. J. Chadbourne, and J. T. Ralph, *J.*, 1964, 6061.
[13] W. H. Poesche, *J.*, 1964, 5426.
[14] M. Battegay and J. Véchot, *Bull. Soc. Chim. France*, 1925, **37**, 1271.

Both 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole reacted with diethyl sulphate but the quaternary salts formed could not be isolated. Aqueous solutions of the compounds could be readily converted into the iodide, thiocyanate, and perchlorate, but only the quaternary salt from 2,1,3-benzoselenadiazole gave an ethochloride or an ethobromide.

The applicability of some commercially available alkyl toluene-*p*-sulphonates was next examined; their reactivity was as expected.[15,16] Direct fusion of methyl toluene-*p*-sulphonate and 2,1,3-benzoselenadiazole at 100° for 3 hr. gave an 80% yield of methyl-2,1,3-benzoselenadiazolium toluene-*p*-sulphonate. With ethyl toluene-*p*-sulphonate, the best yield of quaternary salt (40%) was obtained by direct fusion of the reactants at 110° for 6 hr. These methyl and ethyl compounds underwent ready conversion into the iodide, perchlorate, and thiocyanate only.

2,1,3-Benzothiadiazole gave some methyl-2,1,3-benzothiadiazolium toluene-*p*-sulphonate (25%) on heating with methyl toluene-*p*-sulphonate, but no quaternary salt could be isolated when ethyl toluene-*p*-sulphonate was used. Only conversion into iodide, perchlorate, and thiocyanate was possible.

The alkyl esters of nitro-substituted benzenesulphonic acids are known to be more reactive than those of other aromatic sulphonic acids [17-22] and Kiprianov and Tolmatschev [20,21] found that the alkyl 2,4-dinitrobenzenesulphonates were the most reactive of these compounds while Lunt [22] showed that such esters were effective for the quaternisation of weak bases. Both 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole reacted rapidly with methyl and ethyl 2,4-dinitrobenzenesulphonates; the yields of product obtained demonstrated, first, the greater reactivity of 2,1,3-benzoselenadiazole in quaternisation reactions, and second, that the methyl is more effective than the ethyl ester.*

Methyl- and ethyl-2,1,3-benzothiadiazolium and -benzoselenadiazolium 2,4-dinitrobenzenesulphonates were not particularly suitable for conversion into other methyl and, particularly, ethyl quaternary salts, owing to poor solubility in water. Hot aqueous solutions of alkyl-2,1,3-benzoselenadiazolium 2,4-dinitrobenzenesulphonates with potassium iodide gave the corresponding iodides (the least soluble quaternary salts in the series), but this method was not particularly suitable for the sulphur analogues, owing to decomposition. However, it was possible to obtain the outstanding ethyl-2,1,3-benzothiadiazolium chloride and bromide by ion-exchange in ethanolic medium.

At first it was thought that exchange of anions by the double-decomposition method was dependent solely on the solubility of the quaternary salt formed, but it soon became apparent that the nature of the anions involved was important. Indeed, it appeared that chlorides and bromides could only be obtained from the alkosulphate anions; the results therefore suggest that 2,1,3-benzoselenadiazole and diethyl sulphate give ethyl-2,1,3-benzoselenadiazolium ethosulphate.

Trouble was experienced in obtaining pure samples of some of the quaternary iodides and this was presumably due to their ability to form complexes with free iodine. Satisfactory analytical data were obtained when the iodides were converted into the picrates.

Only the properties of alkyl-2,1,3-benzothia- and -selenadiazolium salts which establish the structure of the compounds are dealt with in this Paper. In the 1,2,3-benzothiadiazole system, the evidence [12,13] is against formation of sulphonium salts, so it is unlikely that the

* Further experiments on the quaternisation of 1,2,3-benzothiadiazole with methyl and ethyl 2,4-dinitrobenzenesulphonate gave yields of 98 and 90%, respectively, and established the expected order of reactivity (cf. ref. 12).

[15] C. K. Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 341.
[16] W. Pritzkow and K. H. Schöppler, *Ber.*, 1962, **95**, 834.
[17] L. Demény, *Rec. Trav. chim.*, 1931, **50**, 60.
[18] M. S. Morgan and L. H. Cretcher, *J. Amer. Chem. Soc.*, 1948, **70**, 375.
[19] R. E. Robertson, *Canad. J. Chem.*, 1953, **31**, 589.
[20] A. I. Kiprianov and A. I. Tolmatschev, *Comm. XIV Int. Congr. Pure and Applied Chem.* (*Zurich*), 1955, 320.
[21] A. I. Kiprianov and A. I. Tolmatschev, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 157.
[22] E. Lunt, May and Baker Laboratory Bulletin, 1958, **3**, 13.

sulphur or selenium atom is involved here, more especially since decomposition of the salts in water yields sulphurous or selenious acid. Reaction of 2,1,3-benzoselenadiazole with excess of methyl 2,4-dinitrobenzenesulphonate gave only the monoquaternary salt; as with 1,2,3-benzothiadiazole, di-quaternary salts are never obtained.

The selenium-containing quaternary salts were considerably more stable to water than the sulphur compounds and none was hygroscopic. All the methyl- and ethyl-2,1,3-benzothiadiazolium salts showed decomposition in the presence of water, giving sulphurous acid and, presumably, the *N*-alkyl-*o*-phenylenediamine. The selenium compounds were little affected by cold water but slow decomposition took place with hot water.

Our studies show that 2,1,3-benzoselenadiazole undergoes quaternisation more readily than 2,1,3-benzothiadiazole and the quaternary salts formed are more stable.

While methyl toluene-*p*-sulphonate gave product with both the 2,1,3-benzodiazoles, only ethyl-2,1,3-benzoselenadiazolium toluene-*p*-sulphonate could be prepared directly, but in smaller yield than the methyl compound. Both dimethyl and diethyl sulphates produced quaternary salts with each of the parent bases, but we were unable to solve the difficulties of isolation of the ethyl compounds; furthermore, the higher dialkyl sulphates are not readily available. It is the alkyl 2,4-dinitrobenzenesulphonates which appear to offer the best scope for obtaining higher alkyl quaternaries.

Experimental

2,1,3-*Benzothiadiazole*.—A mixture of o-phenylenediamine (100 g.), thionyl chloride (300 ml., freshly-distilled), and dry toluene (1 litre), was boiled in a large flask under reflux for 3 hr. Distillation removed first the toluene and excess of thionyl chloride, then gave 2,1,3-benzothiadiazole. All fractions boiling above 200° were collected and on cooling, the distillate solidified to a pale yellow material (107 g., 85%, m. p. 42—44°), which was dissolved in ethanol and and reprecipitated with water, giving an off-white solid (100 g., 80%), m. p. 44—45°, considered suitable for quaternisations. Pure material was obtained as long, white, needle-shaped crystals (m. p. 44·5—45·5°), with characteristic smell, on recrystallisation from ethanol, or by vacuum sublimation.

2,1,3-*Benzoselenadiazole*.—Warm aqueous solutions of selenium dioxide (50 g. in 100 ml.) and *o*-phenylenediamine (50 g. in 400 ml.) were mixed and stirred, resulting in rapid deposition of a pale brown solid, which, after cooling of the reaction mixture, was collected and dried (80·5 g., 95%, m. p. 72—74°). Reprecipitation from ethanol with water afforded an off-white material, m. p. 74—75° (75 g., 88·5%), suitable for quaternisations. Pure material was obtained as off-white needles (m. p. 75—76°), with a characteristic smell, on recrystallisation from ethanol.

Action of Dialkyl Sulphates on 2,1,3-*Benzothiadiazole*.—(a) *Dimethyl sulphate* (0·1 *mole scale*). 2,1,3-Benzothiadiazole (13·6 g.) and dimethyl sulphate (9·5 ml.) were heated at 100° for a total period of 4 hr. The mixture solidified after 3 hr. but heating was continued for a further hour. The crude yellow solid was dissolved in ethanol (*ca.* 50 ml.), boiled, and cooled. A sticky, brownish-yellow solid (23·5 g., 95%), suitable for exchange experiments, was collected and washed with ether. Recrystallisation from ethanol afforded light yellow hygroscopic crystals of *methyl-2,1,3-benzothiadiazolium hydrogen sulphate*, m. p. 157—158° (Found: C, 33·7; H, 3·4; N, 11·1; S, 25·9. $C_7H_8N_2O_4S_2$ requires C, 33·9; H, 3·3; N, 11·3; S, 25·8%).

(b) *Diethyl sulphate* (0·025 *mole scale*). 2,1,3-Benzothiadiazole (3·4 g.) and diethyl sulphate (3·2 ml.) were heated at 100° for 12 hr.; no solidification occurred. The material was lixiviated several times with ether (4 × 25 ml.) and the ether solutions discarded. Water (20 ml.) was added to the oily residue and the mixture treated with aqueous potassium iodide (2·5 g. in 5 ml.), resulting in immediate deposition of a bright red solid (2·3 g.), which was quickly collected, washed with ether, and dried. Addition of more potassium iodide solution to the filtrate gave no further ethyl-2,1,3-benzothiadiazolium iodide.

Action of Dialkyl Sulphates on 2,1,3-*Benzoselenadiazole*.—(a) *Dimethyl sulphate* (0·1 *mole scale*). A mixture of 2,1,3-benzoselenadiazole (18·3 g.) and dimethyl sulphate (9·5 ml.) was carefully warmed until reaction commenced (85—90°), whereupon the reactants were plunged rapidly into an ice-bath. Despite this cooling, the temperature rose quickly to 140°; the mixture soon solidified and did not melt again when heated at 100° for 1 hr. to ensure completion of the reaction. The bright yellow solid was washed with ether and weighed (29·5 g. 95%).

Precipitation by ether from an ethanolic solution gave material of m. p. 130—132°, suitable for exchange experiments. Recrystallisation from ethanol afforded pale yellow crystals of *methyl-2,1,3-benzoselenadiazolium methosulphate*, m. p. 133—134° (Found: C, 31·5; H, 3·5; N, 9·0; S, 10·2. $C_7H_8N_2O_4SSe$ requires C, 31·1; H, 3·3; N, 9·1; S, 10·4%). The compound was little affected by water and in aqueous solution showed no effervescence on treatment with a solution of sodium carbonate.

(b) *Diethyl sulphate* (0·025 *mole scale*). After treatment of 2,1,3-benzoselenadiazole (4·6 g.) with diethyl sulphate (3·2 ml.) at 100° for 12 hr., the quaternary salt could not be isolated, so it was converted into the iodide (4·6 g.) by the method used for 2,1,3-benzothiadiazole.

*Action of Alkyl Toluene-*p*-sulphonates on 2,1,3-Benzothiadiazole and 2,1,3-Benzoselenadiazole.*—The methyl and ethyl toluene-*p*-sulphonates were purified before use by treatment with water, drying, and distillation under reduced pressure.

2,1,3-Benzothiadiazole. (a) *Methyl toluene-*p*-sulphonate* (0·025 *mole scale*). 2,1,3-Benzothiadiazole (3·4 g.) and methyl toluene-*p*-sulphonate (4·7 g.) were heated at 100° (see below) for 6 hr. The colourless mixture gradually became orange-red but did not solidify. Ether (100 ml.) was added and the insoluble pink material collected, washed with ether, and dried. Recrystallisation from ethanol afforded pale yellow leaflets of *methyl-2,1,3-benzothiadiazolium toluene-*p*-sulphonate*, m. p. 171—172° (Found: C, 52·7; H, 4·5; N, 8·8; S, 20·4. $C_{14}H_{14}N_2O_3S_2$ requires C, 52·2; H, 4·4; N, 8·7; S, 19·9%). The compound did not store well, slowly becoming pink and sticky. [Heating at 100°; crude material 0·45 g., m. p. ~165°, recryst. 0·30 g., m. p. 170—171°; Heating at 110°; crude material 2·05 g. (25%), m. p. ~165°, recryst. 1·75 g., m. p. 170—171°; Heating at 140°; unsatisfactory product (would not convert into the iodide) owing to thermal decomposition of the ester.]

(b) *Ethyl toluene-*p*-sulphonate*. Treatment as for the methyl ester (above) gave no product, even when polar solvents were used.

2,1,3-Benzoselenadiazole. (a) *Methyl toluene-*p*-sulphonate* (0·025 *mole scale*). 2,1,3-Benzoselenadiazole (4·6 g.) and methyl toluene-*p*-sulphonate (4·7 g.) were heated at 100° for 3 hr. The bright yellow solid was treated with ether (50 ml.), collected, and dried (7·5 g., 80%). Recrystallisation from ethanol afforded bright yellow crystalline *methyl-2,1,3-benzoselenadiazolium toluene-*p*-sulphonate*, m. p. 191—192° (Found: C, 45·5; H, 3·9; N, 7·5; S, 8·9. $C_{14}H_{14}N_2O_3SSe$ requires C, 45·5; H, 3·8; N, 7·6; S, 8·7%).

(b) *Ethyl toluene-*p*-sulphonate* (0·025 *mole scale*). Direct fusion of 2,1,3-benzoselenadiazole (4·6 g.) and ethyl toluene-*p*-sulphonate (5·0 g.) for 6 hr. gave ethyl-2,1,3-benzoselenadiazolium toluene-*p*-sulphonate. The crude material of indefinite m. p. obtained by addition of ether (50 ml.) was purified by dissolution in ethanol and reprecipitation with ether. Recrystallisation from ethanol gave bright yellow *crystals*, m. p. 174—175° (Found: C, 47·0; H, 4·2; N, 7·1; S, 8·6. $C_{15}H_{16}N_2O_3SSe$ requires C, 47·0; H, 4·2; N, 7·3; S, 8·4%). [Heating at 100°; crude material, 1·7 g.; after reprecipitation 1·5 g., m. p. ~170°; Heating at 110°; crude material, 3·8 g. (40%); after reprecipitation 2·6 g., m. p. ~170°; Heating at 140°; unsatisfactory product (would not convert into the iodide) owing to thermal decomposition of the ester.]

Action of Alkyl 2,4-Dinitrobenzenesulphonates on 2,1,3-Benzothiadiazole and 2,1,3-Benzoselenadiazole.—Methyl and ethyl 2,4-dinitrobenzenesulphonates were prepared from 2,4-dinitrobenzenesulphonyl chloride and the sodium alkoxide, according to the method of Chadbourne and Nunn.[23] However, the products contained a small amount of a water-soluble impurity (sodium salt or free acid) which could be removed by extraction of the ester with chloroform.

General method (0·01 *mole scale*). The 2,1,3-benzodiazole and the alkyl 2,4-dinitrobenzenesulphonate were heated at 100° for ½ hr. The product was isolated by treatment with ether (50—100 ml.), then collected and dried. Recrystallisation from ethanol afforded pure material, though some compounds were only sparingly soluble in this solvent. 1,2,3-Benzothiadiazole was treated in the same way. Details are given in Table 1.

Interconversion of Anions (*Tables* 2—5).—The instability in water of methyl hydrogen sulphates or methosulphates, methotoluene-*p*-sulphonates, metho-2,4-dinitrobenzenesulphonates, and the corresponding ethyl compounds of 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole, prevented their undergoing ion-exchange in a like manner to those of 1,2,3-benzothiadiazole,[12] although small amounts of methyl-2,1,3-benzothiadiazolium iodide (from methohydrogen sulphate) and methyl-2,1,3-benzoselenadiazolium iodide (from dimethosulphate) were obtained

[23] D. J. Chadbourne and A. J. Nunn, *J.*, 1965, 4458.

by ion-exchange in aqueous medium, owing to their low solubility. By means of double decomposition in a cold aqueous medium, and working quickly to prevent losses due to reaction with water, a considerable number of quaternary salts were obtained. Others were produced

TABLE 1

Action of alkyl 2,4-dinitrobenzenesulphonates on the various heterocyclic systems

No.	System	Alkyl ester used	Max. temp. attained *	Yield of crude product (g.)	Yield of crude product (%)	Cryst. form	M. p. of pure compound
1	2,1,3-Benzothiadiazole (1·36 g.)	Methyl (2·62 g.)	*ca.* 140°	3·80	95	Off-white needles	200—201°
2		Ethyl (2·76 g.)	*ca.* 110	2·65	64	Pale yellow needles	136—137
			ca. 110 †	3·25	79		
3	2,1,3-Benzoselenadiazole (1·83 g.)	Methyl (2·62 g.)	*ca.* 155	4·45	100	Bright yellow needles	240—241
		Methyl (5·25 g.)		4·50 ‡			239—240
4		Ethyl (2·76 g.)	*ca.* 125	4·50	98	Bright yellow needles	186—187
		Ethyl (5·52 g.)		4·50 ‡			185—186
5	1,2,3-Benzothiadiazole (1·36 g.)	Methyl (2·62 g.)	*ca.* 125	3·90	98	Cream needles	196—197
6		Ethyl (2·76 g.)	*ca.* 120	3·70	90	White needles	150—151

		Found (%)				Required (%)			
No.	Formula	C	H	N	S	C	H	N	S
1	$C_{13}H_{10}N_4O_7S_2$	39·7	2·6	14·25	15·85	39·2	2·5	14·1	16·1
2	$C_{14}H_{12}N_4O_7S_2$	40·2	2·9	14·2	15·6	40·8	2·9	13·6	15·6
3	$C_{13}H_{10}N_4O_7SSe$	35·0	2·3	12·45	7·55	35·1	2·3	12·6	7·2
4	$C_{14}H_{12}N_4O_7SSe$	36·5	2·7	12·4	6·2	36·6	2·6	12·2	7·0
5	$C_{13}H_{10}N_4O_7S_2$	Reported previously [12]							
6	$C_{14}H_{12}N_4O_7S_2$	,, ,, [12]							

* The maximum temperatures give some indication of the reactivities of the various heterocyclic systems. † Heating time 1 hr. ‡ Reaction product treated with both ether and chloroform.

TABLE 2

Methyl-2,1,3-benzothiadiazolium salts

No.	Anion	Metho-quaternary used (anion)	Method	Reagent used	Wt. of crude product (g.)	Cryst. form	M. p. of pure compound
1	Cl	Hydrogen sulphate	*D*	Ion-exchange column in chloride form	1·45	Pale yellow crystals (*b*)	109—110° (decomp.) *
2	Br	Hydrogen sulphate	*D*	Ion-exchange column in bromide form	1·65	Yellow microcrystalline solid (*a*)	153—155 (decomp.) *
3	I	Hydrogen sulphate	*A*	KI	0·55	Shiny red needles (*a*)	149—150 (decomp.) *
		Toluene-*p*-sulphonate	*A*		0·60		
4	ClO_4	Hydrogen sulphate	*A*	$NaClO_4,2H_2O$	0·65	Light yellow needles (*a*)	148—149
		Toluene-*p*-sulphonate	*A*		0·50		
5	CNS	Hydrogen sulphate	*A*	NaCNS	0·45	Bright yellow needles (*a*)	135—136
		Toluene-*p*-sulphonate	*A*		0·40		
6	Picrate	Iodide	*F*	Picric acid	1·10	Yellowish-brown crystals (*a*)	156—157
7	CN	Hydrogen sulphate	*A*	KCN	The yellow-brown material deposited decomposed rapidly to a black oil		
		Toluene-*p*-sulphonate	*A*				

		Found (%)							Required (%)				
No.	Formula	C	H	Br	Cl	I	N	S	C	H	Halogen	N	S
1	$C_7H_7ClN_2S,H_2O$	40·9	4·6		17·4		13·8	15·8	41·1	4·4	17·3	13·7	15·7
2	$C_7H_7BrN_2S$	36·3	3·1	34·0			12·2	14·1	36·4	3·1	34·6	12·1	13·9
3	$C_7H_7IN_2S$	30·8	2·9			45·4	9·9	11·5	30·2	2·5	45·6	10·1	11·5
4	$C_7H_7ClN_2O_4S$	32·6	2·8		14·2		11·4	12·9	33·6	2·8	14·2	11·2	12·8
5	$C_8H_7N_3S_2$	45·7	3·4				19·7	31·5	45·9	3·4		20·1	30·6
6	$C_{13}H_9N_5O_7S$	41·4	2·5				18·1	8·5	41·2	2·4		18·5	8·4

(*a*), (*b*) and *: see footnotes to Table 5.

TABLE 3

Ethyl-2,1,3-benzothiadiazolium salts

No.	Anion	Etho-quaternary used (anion)	Method	Reagent used	Wt. of crude product (g.)	Cryst. form	M. p. of pure compound
1	Cl	2,4-Dinitrobenzene-sulphonate	*E*	Ion-exchange column in chloride form	0·40	Pale yellow needles (*b*)	Indefinite (slow decomp.)
2	Br	2,4-Dinitrobenzene-sulphonate	*E*	Ion-exchange column in bromide form	0·55	Bright yellow needles (*a*)	132—133° (decomp.)
3	I	Hydrogen sulphate	*C*	KI	2·30	Dark red needles (*a*)	133—134
4	ClO_4	Hydrogen sulphate	*C*	$NaClO_4,2H_2O$	2·10	Pale yellow plates (*a*)	117—118
5	CNS	Hydrogen sulphate	*C*	NaCNS	1·50	Bright yellow needles (*b*)	64—66
6	Picrate	Iodide	*F*	Picric acid	1·00	Bright yellow crystals (*a*)	142—143

		Found (%)							Required (%)				
No.	Formula	C	H	Br	Cl	I	N	S	C	H	Halogen	N	S
1	$C_8H_9ClN_2S$	47·9	4·7		18·0		13·9	15·3	47·9	4·5	17·7	14·0	16·0
2	$C_8H_9BrN_2S$	39·7	3·5	32·6			12·2	12·6	39·2	3·7	32·6	11·4	13·1
3	$C_8H_9IN_2S$	32·8	3·2			42·8	9·3	11·5	32·9	3·1	43·5	9·6	11·0
4	$C_8H_9ClN_2O_4S$	36·0	3·5		13·5		10·5	12·2	36·3	3·4	13·4	10·6	12·1
5	$C_9H_9N_3S_2$ †	46·5	4·2				18·5	27·2	48·4	4·1		18·8	28·7
6	$C_{14}H_{11}N_5O_7S$	42·7	2·9				17·9	8·1	42·8	2·8		17·8	8·2

(*a*) and (*b*), see footnotes to Table 5. † Slight decomp. on standing.

TABLE 4

Methyl-2,1,3-benzoselenadiazolium salts

No.	Anion	Metho-quaternary used (anion)	Method	Reagent used	Wt. of crude product (g.)	Cryst. form	M. p. of pure compound
1	Cl	Methosulphate	*A*	KCl	0·40	Yellow needles (*a*)	177—178° (decomp.) *
2	Br	Methosulphate	*A*	KBr	0·65	Yellowish-brown needles (*c*)	189—190 (decomp.) *
						Bright yellow needles (*a*)	
3	I	Methosulphate	*A*	KI	1·00	Dark red cubes (*c*)	171—172
		Toluene-*p*-sulphonate	*A*		0·90	Dark red needles	
		2,4-Dinitrobenzene-sulphonate	*B*		0·70	(*a*)	
4	ClO_4	Methosulphate	*A*	$NaClO_4,2H_2O$	0·80	Lemon-yellow	205—206
		Toluene-*p*-sulphonate	*A*		0·70	crystals (*a*)	
5	CNS	Methosulphate	*A*	NaCNS	0·80	Orange-yellow	151—152
		Toluene-*p*-sulphonate	*A*		0·65	crystals (*a*)	
6	Picrate	Iodide	*F*	Picric acid	1·25	Yellow-brown crystals (*a*)	187—188
7	CN	Methosulphate	*A*	KCN	The yellow-brown material deposited slowly decomposed to a black oil		
		Toluene-*p*-sulphonate	*A*				

		Found (%)							Required (%)				
No.	Formula	C	H	Br	Cl	I	N	S	C	H	Halogen	N	S
1	$C_7H_7ClN_2Se$	35·2	2·9		14·9		12·2		36·0	3·0	15·2	12·0	
2	$C_7H_7BrN_2Se$	29·9	2·5	28·1			9·8		30·3	2·5	28·7	10·1	
3	$C_7H_7IN_2Se$	26·0	2·2			39·4	8·7		25·9	2·2	39·1	8·6	
4	$C_7H_7ClN_2O_4Se$	27·7	2·3		11·4		9·5		28·2	2·4	11·9	9·4	
5	$C_8H_7N_3SSe$	38·0	2·7				16·5	12·5	37·5	2·8		16·4	12·5
6	$C_{13}H_9N_5O_7Se$	36·7	2·2				16·4		36·6	2·1		16·4	

(*a*), (*c*) and *, see footnotes to Table 5.

TABLE 5

Ethyl-2,1,3-benzoselenadiazolium salts

No.	Anion	Etho-quaternary used (anion)	Method	Reagent used	Wt. of crude product (g.)	Cryst. form	M. p. of pure compound
1	Cl	Ethosulphate	*C*	KCl	2·55	Yellow needles (*a*)	151—152° (decomp.) *
2	Br	Ethosulphate	*C*	KBr	4·25	Orange-yellow needles (*a*)	159—160 (decomp.) *
3	I	Ethosulphate	*C*	KI	4·60	Dark red needles (*c*)	143—144
		Toluene-*p*-sulphonate	*A*		0·80		
		2,4-Dinitrobenzene-sulphonate	*B*		0·70	Red needles (*a*)	
4	ClO_4	Ethosulphate	*C*	$NaClO_4,2H_2O$	3·25	Brownish-yellow plates (*a*)	161—162
		Toluene-*p*-sulphonate	*A*		0·75		
5	CNS	Ethosulphate	*C*	NaCNS	3·15	Brownish-yellow needles (*a*)	112—113 (prelim. softening)
		Toluene-*p*-sulphonate	*A*		0·65		
6	Picrate	Iodide	*F*	Picric acid	1·15	Bright yellow crystals (*a*)	162—163

		Found (%)							Required (%)				
No.	Formula	C	H	Br	Cl	I	N	S	C	H	Halogen	N	S
1	$C_8H_9ClN_2Se$	38·8	3·7		14·4		11·2		38·9	3·7	14·4	11·3	
2	$C_8H_9BrN_2Se$	32·9	3·2	27·8			9·7		32·9	3·1	27·4	9·6	
3	$C_8H_9IN_2Se$	28·4	2·7			37·2	8·1		28·3	2·7	37·4	8·3	
4	$C_8H_9ClN_2O_4Se$	30·6	2·9		11·8		9·2		30·8	2·9	11·4	9·0	
5	$C_9H_9N_3SSe$	39·3	3·2				15·9	12·4	40·0	3·4		15·6	11·9
6	$C_{14}H_{11}N_5O_7Se$	38·3	2·5				16·3		38·2	2·5		15·9	

(*a*) Recrystallised from ethanol. (*b*) Recrystallised from ethanol–ether. (*c*) Recrystallised from water.

* The material darkens on heating and decomposes on melting (with bubbling), leaving a red tar.

by ion-exchange in ethanol; these procedures were evaluated by the preparation of small quantities of the methiodide and ethiodide of 2,1,3-benzothiadiazole.

Method A. An aqueous solution of quaternary salt (1·0 g. in 10 ml.) was treated with a solution of a suitable inorganic salt (1·0 g. in 5 ml. water). After stirring and cooling the reactants, the deposited solid was filtered off, washed with ether, and dried. Purification was usually effected by recrystallisation from ethanol.

Method B. To a hot aqueous solution of methyl- or ethyl-2,1,3-benzoselenadiazolium 2,4-dinitrobenzenesulphonate (1·0 g. in 20 ml.) was added potassium iodide solution (1·0 g. in 5 ml. water). The mixture was heated to boiling, stirred vigorously, and then cooled in an ice-bath. The quaternary iodide was filtered off, washed with ether, and dried.

Method C. An aqueous solution of the required quaternary salt was obtained by reaction (0·025 *mole scale*) of the parent (2,1,3-benzothiadiazole or 2,1,3-benzoselenadiazole base with diethyl sulphate at 100° for 12 hr., lixiviation of the mixture with ether, and treatment with water (10 ml.). To this was added a solution of a suitable inorganic salt (2·5 g. in 10 ml. water); the deposited solid was filtered off, washed with ether, and dried.

Method D. An ethanolic solution of methyl-2,1,3-benzothiadiazolium hydrogen sulphate (2·5 g. in 25 ml.) was ion-exchanged on De-Acidite FF resin (SRA 65; 20 g.) in the appropriate form. The chloride or bromide formed was eluted with ethanol (25—50 ml.) and to this solution was added ether (*ca.* 200 ml.). The solid deposited was collected, washed with ether, and dried. Addition of further ether usually resulted in some unchanged starting material being obtained, showing incomplete exchange.

Method E. Procedure was at in *D* above, but ethyl-2,1,3-benzothiadiazolium 2,4-dinitrobenzenesulphonate (1·0 g. in 100 ml. of warm ethanol) was used in the ion-exchange (20 g. of resin). After elution with ethanol (*ca.* 50 ml.), the volume was made up to 250 ml. with ether and any unchanged starting material which separated was filtered off. Addition of further ether (1 l.) gave the required product.

Method F. The quaternary iodide (1·0 g.) was dissolved in the minimum quantity of ethanol

and treated with an ethanolic solution of picric acid. The mixture was boiled for a few minutes, cooled, and the precipitate washed with ether, and dried. The crude products were recrystallised from ethanol. The solubility of the selenium-containing iodides in ethanol was so low that 50% aqueous ethanol had to be used as the reaction medium.

Stability and Decomposition of the Quaternary Salts.—A cold aqueous solution of methyl-2,1,3-benzoselenadiazolium methosulphate which had been left to stand for a week showed little discoloration and gave almost the expected yield of methiodide on treatment with potassium iodide solution. A similar solution which had been refluxed for 1 hr. gave much less product.

On standing, a cold aqueous solution of methyl-2,1,3-benzothiadiazolium hydrogen sulphate, which was initially pale yellow, became yellow, orange, and then dark red. Sulphur dioxide was evolved. Evaporation of an aqueous solution to dryness gave only a sticky, dark red tar, which could be diazotised and coupled to β-naphthol.

Such instability was characteristic of all the 2,1,3-benzothiadiazole and 2,1,3-benzoselenadiazole quaternary salts prepared.

We thank Professor L. Hunter for his interest.

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