824. *Some Alkyl and Substituted Alkyl 2,4-Dinitrobenzenesulphonates and Polymethylene Bis-2,4-dinitrobenzenesulphonates*

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Known methods for the preparation of methyl, ethyl, n-propyl, and n-butyl 2,4-dinitrobenzenesulphonates have been investigated and improved. 2-Cyano-, 2-halogeno-, and 2-hydroxy-ethyl esters and the corresponding 3-substituted propyl esters have been obtained. Tetra-, penta-, hexa-, and deca-methylene bis-2,4-dinitrobenzenesulphonates have been synthesised and their comparative reactivity assessed by quaternisation experiments with benzothiazole.

In a search for suitable quaternising agents for weakly basic heterocyclic compounds our attention was directed to the work of Kiprianov and Tolmachev [1-3] and Lunt [4] on alkyl 2,4-dinitrobenzenesulphonates. Methyl 2,4-dinitrobenzenesulphonate was described as being 60 times as active as dimethyl sulphate in the quaternisation of benzothiazole under

[1] A. I. Kiprianov and A. I. Tolmachev, *Zhur. obshchei Khim.*, 1957, **27**, 142.
[2] A. I. Kiprianov and A. I. Tolmachev, *Zhur. obshchei Khim.*, 1957, **27**, 486.
[3] A. I. Kiprianov and A. I. Tolmachev, *Comm. XIV Int. Congr. Pure and Applied Chem.* (*Zurich*), 1955, p. 320.
[4] E. Lunt, *May & Baker Laboratory Bulletin*, 1958, **3**, 13.

comparable conditions. Moreover, it was reported that these esters could be used at room temperature even with normally unreactive heterocyclic systems.

Three main methods for the production of alkyl 2,4-dinitrobenzenesulphonates have been utilised. First the reaction between 2,4-dinitrobenzenesulphonyl chloride and sodium alkoxides, secondly the removal of hydrogen chloride between the sulphonyl chloride and the alcohol by means of 2,6-lutidine, and thirdly the reaction between the silver salt of the acid and an alkyl halide.

Kiprianov and Tolmachev [2] obtained methyl 2,4-dinitrobenzenesulphonate in a moderate yield (50%) by adding a methanolic solution of sodium methoxide to the acid chloride in toluene at −5°. By a similar method Lunt obtained the same compound in a slightly higher yield (57%). In the present work the addition of a small amount of magnesium methoxide, to dry the methanol *in situ*,[5] gave a much improved yield (82%). Ethyl 2,4-dinitrobenzenesulphonate had also been prepared by the sodium alkoxide method.[2,4] A slightly modified method employing a trace of magnesium ethoxide in the ethanolic sodium ethoxide and a different method of extraction gave a high yield. A slightly better yield was obtained from a mixture of silver 2,4-dinitrobenzenesulphonate and ethyl iodide in refluxing benzene. The replacement of benzene by acetonitrile in which both reactants were soluble gave an unexpectedly low yield of ester (cf. Emmons and Ferris [6]).

n-Propyl and n-butyl 2,4-dinitrobenzenesulphonates were prepared by the modified sodium alkoxide method in good yield. Some difficulty was encountered with Lunt's lutidine method [4] with n-butanol, because the ester was difficult to purify from contamination by unchanged sulphonyl chloride. This problem was overcome by using a hundredfold excess of n-butanol and a slightly modified method. In the same way n-propyl and isobutyl esters were prepared. High yields of n-propyl and n-butyl esters were obtained by shaking the alkyl iodide with silver 2,4-dinitrobenzenesulphonate. None of these methods could be used to synthesise secondary or tertiary alkyl esters, nor the benzyl or allyl esters; the only product that could be isolated was 2,4-dinitrobenzenesulphonic acid. This could have arisen by dehydrohalogenation when the silver salt method was used.[6]

2-Halogenoethyl, 3-halogenopropyl, and 2-cyanoethyl 2,4-dinitrobenzenesulphonates were prepared by both a chloroform–lutidine method and a toluene–lutidine method. The method of Szabó and Ostwald [7] is unsuitable for the preparation of these esters, since even traces of sodium hydroxide hydrolyse 2,4-dinitrobenzenesulphonyl chloride.

Attempts to prepare polymethylene bis-2,4-dinitrobenzenesulphonates by reaction of the disodium derivative of the appropriate diol with 2,4-dinitrobenzenesulphonyl chloride were unsuccessful. Authentic disodium derivatives were difficult to obtain. Even with known methods,[8,9] the disodium salt of ethylene glycol so obtained was shown to contain a proportion of monosodium salt. Hexamethylene bis-2,4-dinitrobenzenesulphonate was obtained in low yield (9%) by Lunt's lutidine method.[4] This method was unsuccessful with the other diols, but in the case of ethylene glycol it gave a 37% yield of 2-hydroxyethyl 2,4-dinitrobenzenesulphonate. (This ester would not react with further sulphonyl chloride, owing to its insolubility in all the solvents suitable for this type of reaction.) Likewise trimethylene glycol formed the 3-hydroxypropyl ester, but in much lower yield. Tetra-, penta-, hexa-, and deca-methylene bis-2,4-dinitrobenzenesulphonates were obtained by shaking the appropriate di-iodide with the silver salt of the acid suspended in ether, at room temperature. 1,3-Di-iodopropane, however, gave 3-iodopropyl 2,4-dinitrobenzenesulphonate and not the diester. 1,2-Di-iodoethane gave a crystalline product which has not been identified.

Benzothiazole was used to evaluate these new quaternising agents, in particular

[5] E. Lunt, personal communication.
[6] W. D. Emmons and A. F. Ferris, *J. Amer. Chem. Soc.*, 1953, **75**, 2257.
[7] K. Szabó and E. Ostwald, *Magyar Kém. Folyóirat*, 1954, **60**, 99.
[8] Sh. Mamedov, *Trudy Akad. Nauk, S.S.S.R. Azerbaidzhan*, 1938, **55**, 187.
[9] D. Vorländer, *Annalen*, 1894, **280**, 182.

cyanoethyl, the halogenoalkyl, and the polymethylene bis-esters. When benzothiazole was heated with 2-cyanoethyl 2,4-dinitrobenzenesulphonate at 100° for 3 days, 55% of quaternary salt was obtained, but with 2-chloroethyl and 2-bromoethyl 2,4-dinitrobenzenesulphonates under the same conditions and also after longer heating no quaternary salt could be isolated. This was in marked contrast to the unsubstituted ethyl ester which gave 85% of quaternary salt after 15 min. at 100°. When benzothiazole (pK_a 1·2)[10] was heated at 100° for 1 hr. with penta-, hexa-, and deca-methylene bis-2,4-dinitrobenzenesulphonate yields of 48, 92, and 26% of the respective bisquaternary salts were obtained. 1,2,3-Benzothiadiazole (pK_a — 3)[11] was quaternised with the hexa-, but not with the penta- nor the deca-methylene bis-esters.[12] It is hard to explain why the hexa- should be almost twice as reactive as the penta-methylene bisester, especially as the tetramethylene bisester is even more reactive than the hexamethylene bis-ester with 1,2,3-benzothiadiazole.[12] With 3-chloropropyl, 3-bromopropyl, and 3-iodopropyl 2,4-dinitrobenzenesulphonates instead of the expected 3-(3-halogenopropyl)benzothiazolium 2,4-dinitrobenzenesulphonates being formed, trimethylene bis-3-benzothiazolium bis-2,4-dinitrobenzenesulphonate was formed in all three cases. This unexpected result might be due to the halogen of any initially formed 3-halogenopropyl quaternary salt quaternising a further molecule of benzothiazole, followed by exchange of the halide by 2,4-dinitrobenzenesulphonate.

Experimental

General Methods for the Preparation of the Alkyl 2,4-Dinitrobenzenesulphonates listed in Table 1.—(*a*) "The dried alcohol"[13] (20 ml.) was treated with magnesium alkoxide[14] (*ca.* 10 mg.) and the mixture set aside for a few hours. Sodium (0·92 g., 0·04 mole) was then added gradually. The solution of sodium alkoxide was cooled and added dropwise during 20 min. to a stirred solution of 2,4-dinitrobenzenesulphonyl chloride (10·66 g., 0·04 mole) in dry toluene (60 ml.) at −10 to −15°. The stirred mixture was allowed to warm slowly to room temperature

Table 1

		Method				
		(*a*)	(*b*)	(*c*)		
No.	Ester	Yield (%)	Yield (%)	Yield (%)	Crystalline form	M. p.
1	Me	82	—	—	White needles	84—85° *
2	Et	84	—	90	,,	101—102 †
3	Pr^n	86	83	78·5	,,	106—107
4	Bu^n	69	67·5	83	,,	68—69 ‡
5	Bu^i	—	73	—	Pale yellow prisms	85—86

		Found (%)				Required (%)			
No.	Formula	C	H	N	S	C	H	N	S
1	$C_7H_6N_2O_7S$	32·4	2·4	10·5	12·3	32·1	2·3	10·7	12·2
2	$C_8H_8N_2O_7S$	34·8	3·0	10·7	11·5	34·8	2·9	10·2	11·6
3	$C_9H_{10}N_2O_7S$	37·3	3·5	9·7	11·1	37·2	3·5	9·65	11·05
4	$C_{10}H_{12}N_2O_7S$	39·2	4·0			39·5	4·0		
5	$C_{10}H_{12}N_2O_7S$	39·2	4·15	9·45	10·85	39·5	4·0	9·2	10·6

* Kiprianov and Tolmachev[2] give m. p. 86·5°; Lunt[4] gives 82—83°. † Kipranov and Tolmachev[2] give 97°; Lunt[4] gives 97°. ‡ Lunt[4] gives 68°.

during 1 hr. and then filtered. The residual salts were washed with dry toluene. The combined filtrate and washings were diluted with dry light petroleum (b. p. 60—80°) (*ca.* 900 ml.) and the whole set aside at 0° overnight. The product was crystallised from toluene–light petroleum.

(*b*) 2,4-Dinitrobenzenesulphonyl chloride (5·33 g., 0·02 mole) was added portionwise to a

[10] A. Albert, R. Goldacre, and J. Phillips, *J.*, 1948, 2240.
[11] A. J. Nunn, D. J. Chadbourne, and J. T. Ralph, *J.*, 1964, 6061.
[12] D. J. Chadbourne and A. J. Nunn, following Paper.
[13] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green & Co. Ltd., London, 1957, 3rd edn., pp. 167—170.
[14] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green & Co. Ltd., London, 1959, 3rd edn., pp. 108.

stirred solution of the alcohol (0·04 mole) in 2,6-lutidine (20 ml.) at 0° during 45 min. After further stirring for 15 min., toluene (35 ml.) was added. After being stirred at 0° for 15 min., the whole was poured into a mixture of concentrated hydrochloric acid (20 ml.) and ice–water (150 g.) and shaken well. The toluene layer was separated, shaken with dilute hydrochloric acid (50 ml.) and water (2 × 50 ml.), dried (Na_2SO_4 then $MgSO_4$), and filtered. The filtrate was diluted with light petroleum (b. p. 60—80°) (450 ml.) and kept at 0° overnight. The white needles were crystallised from toluene–light petroleum (b. p. 60—80°).

(*c*) The alkyl iodide (0·01 mole) was added to a suspension of silver 2,4-dinitrobenzenesulphonate (3·55 g., 0·01 mole) in dry ether (15 ml.) and shaken in the dark at room temperature for 3 days. The ether was evaporated and the residue extracted with dry chloroform in a Soxhlet apparatus. Concentration and cooling of the extract gave a solid. Crystallisation from chloroform gave the pure product.

In the case of the ethyl ester the reactants were refluxed in dry benzene for 1 hr., then Soxhlet extracted and crystallised from the same solvent.

General Methods for the Preparation of the Halogenoalkyl 2,4-Dinitrobenzenesulphonates listed in Table 2.—(*a*) 2,4-Dinitrobenzenesulphonyl chloride (0·02 mole) was added portionwise to a solution of dry halogenohydrin (0·02 mole) in dry 2,6-lutidine (20 ml.) during 60 min. at −10°. Chloroform (50 ml., precooled to 0°) was added and, after being stirred for 5 min., the whole was poured into a mixture of concentrated hydrochloric acid (20 ml.) and ice (150 g.) and well shaken. Any precipitate was filtered off. The chloroform layer was washed with dilute hydrochloric acid (50 ml.) and water (2 × 50 ml.) and dried (Na_2SO_4). The solvent was evaporated and the residue, together with any precipitate obtained earlier, recrystallised from benzene.

(*b*) Method (*b*) described for the n-propyl ester was used, with halogenohydrin (0·04 mole) and 2,4-dinitrobenzenesulphonyl chloride (0·02 mole). The toluene and acidic ice–water mixture was filtered to remove precipitated ester. Addition of light petroleum to the dried toluene solution gave further product. The total crude ester was crystallised from toluene–light petroleum (b. p. 60—80°).

TABLE 2

		Method				
		(*a*)	(*b*)			
No.	Ester	Yield (%)	Yield (%)	Crystalline form	M. p.	Formula
1	2-Chloroethyl	46·0	63·2	Very pale yellow needles	104—105° *	$C_8H_7ClN_2O_7S$
2	2-Bromoethyl	39·4	65·0	White needles	110—111	$C_8H_7BrN_2O_7S$
3	2-Iodoethyl	—	13·5	,, †	93—94(d)	$C_8H_7IN_2O_7S$
4	3-Chloropropyl	57·0	63·0	Pale yellow needles †	90—91	$C_9H_9ClN_2O_7S$
5	3-Bromopropyl	52·0	43·5	White prisms	98—99	$C_9H_9BrN_2O_7S$
6	3-Iodopropyl	38·0	43·0	Pale yellow needles †	106—107	$C_9H_9IN_2O_7S$
7	2-Cyanoethyl ‡	43·0	31·5	White needles †	105—106	$C_9H_7N_3O_7S$

	Found (%)							Required (%)						
	C	H	Br	Cl	I	N	S	C	H	Br	Cl	I	N	S
1	30·9	2·2		14·2		8·2	9·9	30·9	2·3		14·4		9·0	10·3
2	27·2	1·9	22·1			7·7		27·1	2·0	22·5			7·9	
3	23·7	2·2			29·0	7·0	8·1	23·9	1·8			31·55	7·0	8·0
4	33·1	2·8		11·4		8·3	9·6	33·3	2·8		10·9		8·6	9·9
5	29·25	2·35	21·5			7·5		29·3	2·45	21·65			7·95	
6	25·9	2·3			29·8	6·5		26·0	2·2			30·5	6·7	
7	35·8	2·3				13·3	10·8	35·9	2·3				13·95	10·6

* Ross and Davis [15] give m. p. 104—106°. † Crystallised from chloroform. ‡ Ethylene cyanhydrin was used instead of halohydrin.

2-Hydroxyethyl 2,4-Dinitrobenzenesulphonate.—Lunt's lutidine method [4] was used with ethylene glycol (1·24 g., 0·02 mole) and 2,4-dinitrobenzenesulphonyl chloride (10·66 g., 0·04 mole). The 2-hydroxyethyl ester was obtained by filtering the chloroform and acidic ice–water mixture, as this ester is insoluble in both layers. Crystallisation from dioxan–ethanol gave pale yellow needles (2·13 g., 36·5%), m. p. 177—178°, of 2-hydroxyethyl 2,4-dinitrobenzenesulphonate (Found: C, 32·6; H, 2·4; N, 9·8; S, 10·95. $C_8H_8N_2O_8S$ requires C, 32·9; H, 2·75; N, 9·6; S, 10·95%).

[15] W. C. J. Ross and W. Davis, *J.*, 1957, 2420.

3-*Hydroxypropyl* 2,4-*Dinitrobenzenesulphonate*.—When the above method was used with trimethylene glycol, the main product was unchanged sulphonyl chloride. However, several recrystallisations from toluene–light petroleum (b. p. 60—80°) of the residue obtained by evaporation of the chloroform layer, gave pale brown needles, m. p. 89—90°, of 3-*hydroxypropyl* 2,4-*dinitrobenzenesulphonate* (Found: C, 34·8; H, 3·4; N, 9·2. $C_9H_{10}N_2O_8S$ requires C, 35·3; H, 3·3; N, 9·15%).

Hexamethylene Bis-2,4-*dinitrobenzenesulphonate*.—Lunt's method [4] was used with hexamethylene glycol (0·01 mole) and 2,4-dinitrobenzenesulphonyl chloride (0·02 mole), and reaction time of 40 min. without chloroform and 60 min. with chloroform. Crystallisation from chloroform gave white needles, m. p. 110—111°, of *hexamethylene bis*-2,4-*dinitrobenzenesulphonate* (Found: C, 37·6; H, 3·1; N, 9·35; S, 11·3. $C_{18}H_{18}N_4O_{14}S_2$ requires C, 37·4; H, 3·1; N, 9·7; S, 11·1%).

General Method for the Preparation of the Polymethylene Bisdinitrobenzenesulphonates listed in Table 3.—To a suspension of silver 2,4-dinitrobenzenesulphonate (3·55 g., 0·01 mole) in sodium-dried ether (15 ml.) was added αω-di-iodoalkane (0·005 mole) and the whole shaken at room temperature (*ca.* 20°) in the dark for 1 week. The reaction mixture was evaporated to dryness, and the residue extracted with dry chloroform in a Soxhlet apparatus. The extract was allowed to evaporate spontaneously at room temperature. Crystallisation gave white needles, of *polymethylene bis*-2,4-*dinitrobenzenesulphonate*.

TABLE 3

No.	Bis-ester	Yield (%)	Crystallisation solvent	M. p.
1	Tetramethylene	30·5	Chloroform–acetone	158—159°
2	Pentamethylene	47·6	,,	132—134
3	Hexamethylene	75·0	Chloroform	110—111
4	Decamethylene	67·8	,,	95—96

		Found (%)				Required (%)			
No.	Formula	C	H	N	S	C	H	N	S
1	$C_{16}H_{14}N_4O_{14}S_2$	35·0	2·7	10·0	1·5	34·9	2·6	10·2	11·6
2	$C_{17}H_{16}N_4O_{14}S_2$	35·9	2·9	9·7	11·5	36·2	2·9	9·9	11·4
3	$C_{18}H_{18}N_4O_{14}S_2$	37·6	3·1	9·35	11·3	37·4	3·1	9·7	11·1
4	$C_{22}H_{26}N_4O_{14}S_2$	41·9	4·1	8·9	10·4	41·6	4·1	8·8	10·1

Reaction of Silver 2,4-*Dinitrobenzenesulphonate with* 1,3-*Dihalogenopropanes*.—(*a*) Silver 2,4-dinitrobenzenesulphonate (1·42 g., 0·004 mole), sodium-dried benzene (5 ml.), and 1,3-dibromopropane (0·404 g., 0·002 mole) were heated under reflux for 6 hr. The reaction mixture was extracted with benzene in a Soxhlet apparatus. The crude solid (0·712 g.) obtained by evaporation of the solvent was extracted with chloroform and toluene, and light petroleum (b. p. 40—60°) added to the combined extracts to precipitate a pale brown solid. Crystallisation from chloroform gave white needles (0·303 g.), m. p. 96—97°, of 3-bromopropyl 2,4-dinitrobenzenesulphonate (identified by mixed m. p. with an authentic sample prepared by the lutidine method).

(*b*) The method described for polymethylene bis-2,4-dinitrobenzenesulphonates was used with 1,3-di-iodopropane (1·48 g., 0·005 mole). Crystallisation from dry chloroform (charcoal) gave white needles (1·25 g.), m. p. 104—105°, of 3-iodopropyl 2,4-dinitrobenzenesulphonate (identified by mixed m. p. using an authentic sample prepared by the lutidine method).

(*c*) The method (*b*) above was repeated, but the reaction mixture was heatedunder reflux for 6 hr. Pale yellow needles (0·906 g.), m. p. 104—105°, of 3-iodopropyl 2,4-dinitrobenzenesulphonate were obtained.

3-*Ethylbenzothiazolium* 2,4-*Dinitrobenzenesulphonate*.—Benzothiazole (1·35 g., 0·01 mole) and ethyl 2,4-dinitrobenzenesulphonate (2·76 g., 0·01 mole) were heated on a water-bath. After 15 min., the crude solid was crystallised from ethanol to give fawn needles (3·5 g., 85·0%), m. p. 175—177°. Recrystallisation from ethanol gave white needles, m. p. 178—179°, of 3-*ethylbenzothiazolium* 2,4-*dinitrobenzenesulphonate* (Found: C, 43·5; H, 3·4; N, 10·2; S, 15·2. $C_{15}H_{13}N_3O_7S_2$ requires C, 43·8; H, 3·2; N, 10·2; S, 15·6%).

3-*n-Propylbenzothiazolium* 2,4-*Dinitrobenzenesulphonate*.—Benzothiazole (0·675 g., 0·005 mole) and n-propyl 2,4-dinitrobenzenesulphonate (1·45 g., 0·005 mole) were heated on a water-bath. After 1 hr., the solid mass was crystallised from ethanol to give white needles (2·02 g., 94·7%), m. p. 141—142°. Recrystallisation from ethanol gave white needles, m. p. 143—144°

(decomp.), of 3-*n-propylbenzothiazolium* 2,4-*dinitrobenzenesulphonate* (Found: C, 42·3; H, 3·3; N, 13·1; S, 15·1. $C_{15}H_{14}N_4O_7S_2$ requires C, 42·25; H, 3·3; N, 13·1; S, 15·0%).

3-*n-Butylbenzothiazolium* 2,4-*Dinitrobenzenesulphonate*.—The method described for the n-propyl compound above was used with n-butyl 2,4-dinitrobenzenesulphonate (1·52 g.). Crystallisation from ethanol gave white needles (1·87 g., 85·3%), m. p. 118—120°. Recrystallisation from ethanol gave white needles, m. p. 119—120°, of 3-*n-butylbenzothiazolium* 2,4-*dinitrobenzenesulphonate* (Found: C, 46·0; H, 3·9; N, 9·5; S, 14·85. $C_{17}H_{17}N_3O_7S_2$ requires C, 46·45; H, 3·9; N, 9·6; S, 14·6%).

3-(2-*Hydroxyethyl*)*benzothiazolium* 2,4-*Dinitrobenzenesulphonate*.—2-Hydroxyethyl 2,4-dinitrobenzenesulphonate (0·584 g., 0·002 mole) was suspended in a solution of benzothiazole (0·270 g., 0·002 mole) in dry nitrobenzene (2 ml.) and heated on a water-bath for 1 hr. Excess of ether was added to the cooled suspension, and the filtered solid crystallised from water to give a yellow product (0·384 g., 45·0%), m. p. 222—224° (decomp.). Recrystallisation from water gave yellow needles, m. p. 226—227° (decomp.), of 3-(2-*hydroxyethyl*)*benzothiazolium* 2,4-*dinitrobenzenesulphonate* (Found: C, 42·2; H, 3·0; N, 10·2; S, 15·4. $C_{15}H_{13}N_3O_8S_2$ requires C, 42·15; H, 3·1; N, 9·8; S, 15·0%).

3-(2-*Cyanoethyl*)*benzothiazolium* 2,4-*Dinitrobenzenesulphonate*.—Benzothiazole (0·270 g., 0·002 mole) and 2-cyanoethyl 2,4-dinitrobenzenesulphonate (0·602 g., 0·002 mole) were heated at 100° for 3 days. The mixture was extracted with water (25 ml.) and the extract cooled and set aside for a few days to deposit a brown oil and yellow needles. The yellow needles (0·482 g., 55·3%), m. p. 137—138°, were crystallised from ethanol to give pale yellow needles, m. p. 137—138°, of 3-(2-*cyanoethyl*)*benzothiazolium* 2,4-*dinitrobenzenesulphonate* (Found: C, 43·9; H, 2·9; N, 13·1; S, 13·9. $C_{16}H_{12}N_4O_7S_2$ requires C, 44·0; H, 2·8; N, 12·8; S, 14·7%).

Reaction of Benzothiazole with 3-*Halogenoethyl* 2,4-*Dinitrobenzenesulphonates*.—Benzothiazole (0·270 g.) and one of 3-chloropropyl 2,4-dinitrobenzenesulphonate (0·649 g.) or 3-bromopropyl 2,4-dinitrobenzenesulphonate (0·738 g.) or 3-iodopropyl 2,4-dinitrobenzenesulphonate (0·838 g.) were heated at 100° for 50, 8, and 6 hr., respectively. The crude solids produced were crystallised from water to give yellow-green products (0·625, 0·345, and 0·152 g., respectively), m. p. 228—230° (decomp.). Recrystallisation from water or ethanol gave yellow needles, m. p. 230—231° (decomp.) of *trimethylenebis*-3-*benzothiazolium bis*-2,4-*dinitrobenzenesulphonate* (Found: C, 44·0; H, 2·95; N, 10·2; S, 16·3. $C_{29}H_{22}N_6O_{14}S_4$ requires C, 43·2; H, 2·75; N, 10·4; S, 15·9%).

Pentamethylenebis-3-*benzothiazolium Bis*-2,4-*dinitrobenzenesulphonate*.—Benzothiazole (0·540 g., 0·004 mole) and pentamethylene bis-2,4-dinitrobenzenesulphonate (1·128 g., 0·002 mole) dissolved in dry nitrobenzene (2 ml.) were heated on a water-bath. After 1 hr., the solid was filtered off and washed with ether. The fawn solid (0·812 g., 48·7%), m. p. 184—186°, was crystallised from water to give white needles, m. p. 187—188°, of *pentamethylenebis*-3-*benzothiazolium bis*-2,4-*dinitrobenzenesulphonate* (Found: C, 44·8; H, 3·3; N, 10·0; S, 15·7. $C_{31}H_{26}N_6O_{14}S_4$ requires C, 44·6; H, 3·1; N, 10·1; S, 15·4%).

Hexamethylenebis-3-*benzothiazolium Bis*-2,4-*dinitrobenzenesulphonate*.—The above method was repeated with hexamethylene bis-2,4-dinitrobenzenesulphonate (1·156 g., 0·002 mole). A fawn solid (1·561 g., 92·2%), m. p. 193—195° (decomp.), was obtained. Crystallisation from water gave white needles, m. p. 197—198° (decomp.), of *hexamethylenebis*-3-*benzothiazolium bis*-2,4-*dinitrobenzenesulphonate* (Found: C, 45·8; H, 3·3; N, 10·0; S, 14·7. $C_{32}H_{28}N_6O_{14}S_4$ requires C, 45·3; H, 3·3; N, 9·9; S, 15·1%).

Decamethylenebis-3-*benzothiazolium Bis*-2,4-*dinitrobenzenesulphonate*.—The above method was repeated with decamethylene bis-2,4-dinitrobenzenesulphonate (1·270 g., 0·002 mole). The solid, crystallised from ethanol, gave white needles (0·467 g., 25·8%), m. p. 139—141°. Recrystallisation from ethanol gave white needles, m. p. 143—144°, of *decamethylenebis*-3-*benzothiazolium bis*-2,4-*dinitrobenzenesulphonate* (Found: C, 47·9; H, 4·1; N, 9·3; S, 13·8. $C_{36}H_{36}N_6O_{14}S_4$ requires C, 47·8; H, 4·0; N, 9·3; S, 14·2%).

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