825. 1,2,3-*Benzothiadiazole. Part V.*[1] *Further Investigations in the Quaternisation of* 1,2,3-*Benzothiadiazole. Propyl, Hydroxyethyl, and Polymethylene Bis*-1,2,3-*benzothiadiazolium Salts*

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Even reactive alkyl iodides are shown to be of limited usefulness for obtaining the corresponding 1,2,3-benzothiadiazole quaternary salts. Reactions between n-propyl, butyl, and substituted alkyl 2,4-dinitrobenzenesulphonates and 1,2,3-benzothiadiazole are described. The use of tetramethylene and hexamethylene bis-2,4-dinitrobenzenesulphonates provided a satisfactory method for obtaining the corresponding bisquaternary salts. A convenient one-stage process is mentioned.

1,2,3-BENZOTHIADIAZOLE has been quaternised with isopropyl iodide in a low yield (4·4%) by heating the reactants in nitrobenzene 100° for 10 hours. Quaternisations with methyl iodide and ethyl iodide are reported to give similar low yields.[1] By heating 1,2,3-benzothiadiazole with either allyl iodide or benzyl iodide at 100° for up to 7 days, none of the required quaternary salts could be obtained.

Direct fusion of 1,2,3-benzothiadiazole with n-propyl 2,4-dinitrobenzenesulphonate at 100° for 4 hours yielded 81% of almost pure n-propyl-1,2,3-benzothiadiazolium 2,4-dinitrobenzenesulphonate. However, neither these reaction conditions, nor use of longer times, lower temperatures, and polar solvents enabled n-butyl-, or isobutyl-1,2,3-benzothiadiazolium 2,4-dinitrobenenesulphonate to be isolated. This was surprising since benzothiazole gave nearly as high yields of quaternary salts with these reagents as it did with the n-propyl ester under the same conditions.[2]

2′-Hydroxyethyl 2,4-dinitrobenzenesulphonate when fused with 1,2,3-benzothiadiazole at 155° gave a 10% yield of the quaternary salt. At a reaction temperature of 135° the yield was halved. Polar solvents could not be used in this case as the ester is insoluble in such media.

2-Cyanoethyl, 2-halogenoethyl, and 3-halogenopropyl 2,4-dinitrobenzenesulphonates failed to quaternise 1,2,3-benzothiadiazole under a wide range of conditions. This may be due to the electron-attracting effect of the cyano- and the halogeno-groups. The effect should be more pronounced with the 2-substituted, than with the 3-substituted alkyl esters.[3] This was apparent in quaternisation experiments with benzothiazole [2] (pK_a 1·2),[4] a slightly stronger base than 1,2,3-benzothiadiazole (pK_a − 3).[1]

The preparation of hexamethylenebis-1,2,3-benzothiadiazolium bis-2,4-dinitrobenzenesulphonate has been studied in several different conditions. Direct fusion of 1,2,3-benzothiadiazole with the bis-ester at 100° for 1 day gave a 22% yield of quaternary salt. This yield was increased to 31% by heating a solution of the reactants in nitrobenzene at 50° for 14 days. The reaction of 1,2,3-benzothiadiazole with tetramethylene bis-2,4-dinitrobenzenesulphonate in nitrobenzene solution at 50° took place more rapidly than with the hexamethylenebis-ester. After 7 days a yield of 61% was obtained. However pentamethylene and decamethylene bis-2,4-dinitrobenzenesulphonates did not appear to quaternise 1,2,3-benzothiadiazole under these conditions even after 10 weeks. Both the reaction of silver 2,4-dinitrobenzenesulphonate with an alkyl iodide to give the ester, and the reaction of this ester with 1,2,3-benzothiadiazole to form the quaternary salt can be carried out in one operation. Heating the silver salt with a solution of 1,4-di-iodobutane and 1,2,3-benzothiadiazole in ether for 6 hours gave 34% of the quaternary salt. Using this method with 1,6-di-iodohexane, we obtained a yield of 31%. As isopropyl and t-butyl

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[1] Part IV, A. J. Nunn, D. J. Chadbourne, and J. T. Ralph, *J.*, 1964, 6061.

[2] D. J. Chadbourne and A. J. Nunn, preceding Paper

[3] J. Hine, " Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, 1962, 2nd ed., p. 175.

[4] A. Albert, R. Goodacre, and J. Phillips, *J.*, 1948, 2240.

2,4-dinitrobenzenesulphonate could not be prepared,[2] this method was used in an attempt to obtain isopropyl- and t-butyl-1,2,3-benzothiadiazolium 2,4-dinitrobenzenesulphonates. However, in both cases, only 2,4-dinitrobenzenesulphonic acid could be isolated, as was the case without the 1,2,3-benzothiadiazole.[2] Similar results were obtained by shaking the suspension at room temperature for 3 days.

EXPERIMENTAL

*2-Isopropyl-*1,2,3-*benzothiadiazolium Iodide.*—1,2,3-Benzothiadiazole (13·6 g., 0·1 mole) and isopropyl iodide (17·0 g., 0·1 mole) were dissolved in nitrobenzene (20 ml.) and heated at 100° for 10 hr. The mixture was filtered, and the solid crystallised from ethanol to give orange needles (0·912 g., 3·0%), m. p. 186—187° (decomp.). The nitrobenzene filtrate was treated with excess of ether, and the precipitate crystallised from ethanol to give orange-yellow needles (0·429 g., 1·4%), m. p. 185—186° (decomp.). Recrystallisation of the total product from ethanol gave orange-yellow needles (1·152 g., 3·8%), m. p. 189—190° (decomp.), of 3-*isopropyl-*1,2,3-*benzothiadiazolium iodide* (Found: C, 35·3; H, 3·5; I, 41·3; N, 9·3; S, 10·0. $C_9H_{11}IN_2S$ requires C, 35·3; H, 3·6; I, 41·45; N, 9·15; S, 10·5%).

The alkyl and substituted alkyl 2,4-dinitrobenzenesulphonates, and polymethylene bis-2,4-dinitrobenzenesulphonates were prepared as described in a preceding Paper.[2]

3-*n-Propyl-*1,2,3-*benzothiadiazolium* 2,4-*Dinitrobenzene Sulphonate.*—1,2,3-Benzothiadiazole (0·68 g., 0·005 mole) and n-propyl 2,4-dinitrobenzenesulphonate (1·45 g., 0·005 mole) were fused on a water-bath for 4 hr. The dark brown oil obtained was crystallised from ethanol, giving a pale brown solid (1·731 g., 81·4%), m. p. 117—118°. Further recrystallisation from ethanol gave white needles, m. p. 118—119°, of 3-*n-propyl-*1,2,3-*benzothiadiazolium* 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%).

3-2-*Hydroxyethyl-*1,2,3-*benzothiadiazolium* 2,4-*Dinitrobenzenesulphonate.*—1,2,3-Benzothiadiazole (0·272 g., 0·002 mole) and 2-hydroxyethyl 2,4-dinitrobenzenesulphonate (0·584 g., 0·002 mole) were fused and heated at 155° for 1 hr. The dark brown solid obtained was crystallised from ethanol to give a fawn solid (0·085 g., 9·9%), m. p. 145—148°. Recrystallisation from ethanol gave white needles, m. p. 159—160°, of 3-2-*hydroxyethyl-*1,2,3-*benzothiadiazolium* 2,4-*dinitrobenzenesulphonate* (Found: C, 38·8; H, 2·9; N, 12·6. $C_{14}H_{12}N_4O_8S_2$ requires C, 39·25; H, 2·8; N, 13·1%).

*Hexamethylenebis-*1,2,3-*benzothiadiazolium Bis-*2,4-*dinitrobenzenesulphonate.*—1,2,3-Benzothiadiazole (0·544 g., 0·004 mole) and hexamethylene bis-(2,4-dinitrobenzenesulphonate (1·156 g., 0·004 mole) were fused or dissolved in dry nitrobenzene, and heated at the temperature and for the time stated. Excess of ether was added to the nitrobenzene solution, and the precipitate, or the reaction mixture in those cases where nitrobenzene was not used, was crystallised from water to give the product as a pale brown solid. Further recrystallisation from water or methanol gave white needles, m. p. 194—195° (decomp.), of *hexamethylenebis-*1,2,3-*benzothiadiazolium bis-*2,4-*dinitrobenzenesulphonate* (Found: C, 42·5; H, 3·0; N, 13·0. $C_{30}H_{26}N_8O_{14}S_4$ requires C, 42·4; H, 3·1; N, 13·2%).

The results are tabulated.

Expt. No.	Volume of nitrobenzene	Temp.	Time	Yield (g.)	Yield (%)	Product (m. p.)
1	0	100°	24 hr.	0·368	21·6	186—188°
2	0	100	7 days	0·298	17·5	186—188
3	5 ml.	100	24 hr.	0·112	6·6	185—187
4	5 ml.	50	14 days	0·535	31·4	184—186
5	5 ml.	50	28 days	0·585	34·3	178—180

*Tetramethylenebis-*1,2,3-*benzothiadiazolium Bis-*2,4-*dinitrobenzenesulphonate.*—1,2,3-Benzothiadazole (0·272 g., 0·002 mole) and tetramethylene bis-2,4-dinitrobenzenesulphonate (0·55 g., 0·001 mole) were dissolved in dry nitrobenzene (5 ml.) and the solution heated at 50° for 7 days. The mixture was filtered and the white solid (0·582 g.) crystallised from water, giving white needles (0·501 g., 61%), m. p. 238—239° (decomp.). Recrystallisation from water gave white needles, m. p. 241—242° (decomp.), of tetramethylenebis-1,2,3-benzothiadiazolium bis-2,4-dinitrobenzenesulphonate (Found: C, 41·1; H, 2·7; N, 13·9; S, 15·4. $C_{28}H_{22}N_8O_{14}S_4$ requires C, 40·9; H, 2·7; N, 13·6; S, 15·6%).

Tetramethylenebis-1,2,3-*benzothiadiazolium Bis*-2,4-*dinitrobenzenesulphonate from Silver* 2,4-*Dinitrobenzenesulphonate*.—Silver 2,4-dinitrobenzenesulphonate (3·55 g., 0·01 mole) was added to a solution of 1,2,3-benzothiadiazole (1·36 g., 0·01 mole) and 1,4-di-iodobutane (1·55 g., 0·005 mole) in dry ether (15 ml.), and the suspension heated under reflux for 6 hr. The ether was evaporated, and the residue extracted with boiling water (4 × 50 ml.). The aqueous solution was cooled to give fawn needles (1·76 g.), m. p. 218—220° (decomp.). Recrystallisation from water gave white needles (1·42 g., 34%), m. p. 238—240° (decomp.).

Hexamethylenebis-1,2,3-*benzothiadiazolium Bis*-2,4-*dinitrobenzenesulphonate from Silver* 2,4-*Dinitrobenzenesulphonate*.—The method described above for the tetramethylene compound was used with 1,6-di-iodohexane (1·69 g., 0·005 mole). The product was obtained as a yellow solid (1·72 g.), m. p. 184—186° (decomp.). Crystallisation from water gave white needles (1·31 g., 30·8%), m. p. 192—194° (decomp.).

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