692. *The Preparation and Reactivity of Some 2-Methanesulphonylbenzazoles.*

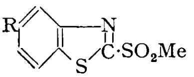
By Eric Hoggarth.

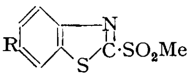
2-Methanesulphonyl-benzoxazole, -benziminazole, and -benzthiazole and derivatives thereof have been prepared and their reactions with amines examined. Convenient preparations of 2-alkylamino-, 2-hydroxy-, and 2-alkoxy-benzthiazoles from the corresponding methanesulphonyl compounds are described.

Whilst the methanesulphonyl group of 5-methanesulphonyl-3-phenyl-1 : 2 : 4-triazole is apparently inert towards amines (Hoggarth, this vol., p. 1163), the same group in 2-methanesulphonyl-5-phenyl-1 : 3 : 4-oxadiazoles is very easily replaced by primary amines (this vol., p. 1918). An examination has now been made of the displacement of the methanesulphonyl group by amines in a number of benzazolyl sulphones. 2-*Methanesulphonylbenziminazole*, readily obtained by oxidation of the corresponding *methylthio*-compound, was more reactive than the methanesulphonyl triazole and reacted (with difficulty) with 2-diethylaminoethylamine, though not with *iso*propylamine, at the highest temperature tried. 2-*Methanesulphonylbenzoxazole*, obtained similarly, was very reactive and on crystallisation from water gave 2-hydroxybenzoxazole; like the methanesulphonyl-oxadiazole, it reacted with 2-diethylaminoethylamine and *iso*propylamine very easily, giving the corresponding substituted 2-*aminobenzoxazoles*. The reactivity of a number of 2-methanesulphonylbenzthiazoles was intermediate between that of the two preceding benzazolyl sulphones, and these compounds have been used for the preparation of 2-aminobenzthiazoles with substituents on the amino-group. Tuda, Sakamoto, Matsuda, and Kanno (*J. Pharm. Soc. Japan*, 1940, **60**, 184) showed that heating 2-aminobenzthiazoles with 3-diethylaminopropyl bromide gave 2-imino-3-3′-diethylaminopropylbenzthiazolines and that

2-acetamidobenzthiazoles under similar conditions gave 2-acetimidobenzthiazolines. 2-Dialkylaminoalkylaminobenzthiazoles were obtained by treating the alkali-metal salts of 2-acetamidobenzthiazoles with dialkylaminoalkyl halides or 2-chlorobenzthiazoles with dialkylaminoalkylamines. The present route, starting from the readily accessible benzthiazole-2-thiols, is more convenient.

Methylation of 5-chloro- and 5-methoxy-benzthiazole-2-thiol gave 5-*chloro*-2-*methylthio*- and 2-*methylthio*-5-*methoxy-benzthiazole*, and these were oxidised to the corresponding *sulphones* (I; R = Cl or OMe). Similarly were prepared (II; R = H or NO_2). In these compounds the methanesulphonyl group was readily displaced by warming them with various primary amines, and nine benzthiazole *derivatives* were thus obtained in good yield. The compound (IV; R = NO_2, R′ = $NH\cdot[CH_2]_2\cdot NEt_2$) was also obtained by nitrating (III; R = H, R′ = $NH\cdot[CH_2]_2\cdot NEt_2$), and this nitro-compound and (IV; R = NO_2, R′ = $NHPr^i$) were reduced to the corresponding *diamines*. Reaction with ammonia or secondary amines was much less easy, gave poor yields, and needed temperatures much higher than were necessary for primary amines.


(I.)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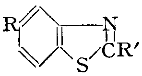
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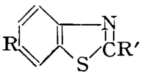
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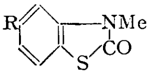
(V.)

The methanesulphonyl group of 2-methanesulphonyl-benzthiazoles is also easily removed by mineral acids, giving 2-hydroxybenzthiazoles (benzthiazolones) in excellent yield. Further, by the action of a solution of sodium alkoxide in an excess of the corresponding alcohol, five 2-*alkoxy*-derivatives were obtained in good yield. The properties of 2-methoxybenzthiazole prepared in this way agreed with those recorded by Davies and Sexton (*J.*, 1942, 304), and it was converted by heat into 3-methylbenzthiazolone (V; R = H). Isomerisation under similar conditions took place with (III; R = Cl or OMe, R′ = OMe) to give the corresponding 3-*methylbenzthiazolones* (V; R = Cl or OMe). When the *iso*propyl compounds (III; R = H or Cl, R′ = OPr^i) were heated, an unsaturated inflammable gas, presumed to be propylene, was rapidly evolved and the pure hydroxy-compounds (III; R = H or Cl, R′ = OH) were obtained.

Johnson and Sprague (*J. Amer. Chem. Soc.*, 1935, **57**, 2252) have suggested that, when 2-ethanesulphonyl groups were displaced from certain pyrimidine derivatives by acids, ethanesulphinic acid was formed and that this decomposed to give (mainly) sulphur dioxide. We have proved that, when the methanesulphonyl groups of 2-methanesulphonylbenzthiazoles are displaced by a solution of sodium in an excess of *iso*propyl alcohol, a colourless crystalline substance which separates is sodium methanesulphinate, for its reaction with benzyl chloride gave benzyl methyl sulphone.

EXPERIMENTAL.

2-*Methylthiobenziminazole*.—Benziminazole-2-thiol (15·0 g.) in N-sodium hydroxide (100 c.c.) was shaken with methyl iodide (10 c.c.) and alcohol (50 c.c.) for 0·5 hour; the solid *product* crystallised from ethyl acetate in colourless needles (13·0 g.), m. p. 201° (Found: C, 58·8; H, 5·0; S, 19·7. $C_8H_8N_2S$ requires C, 58·55; H, 4·9; S, 19·5%).

2-*Methanesulphonylbenziminazole*.—The methylthio-compound (24·0 g.) in acetic acid (300 c.c.) was stirred whilst a solution of potassium permanganate (66·0 g.) in water (1 l.) was added during 2 hours, the temperature being kept below 30° by cooling as necessary. After 1 hour, ice (1 kg.) was added, sulphur dioxide was passed in until the solution was bleached, and the white *sulphone* collected and crystallised from ethyl acetate, giving colourless needles (14·8 g.), m. p. 202° (depressed to 174° by the methylthio-compound) (Found: C, 49·4; H, 4·2; S, 16·5. $C_8H_8O_2N_2S$ requires C, 49·0; H, 4·1; S, 16·3%).

2-2′-*Diethylaminoethylaminobenziminazole*.—2-Methanesulphonylbenziminazole (4·0 g.), and 2-diethylaminoethylamine (5·0 c.c.) were heated at 160—170° for 3 hours and then cooled, and the product was dissolved in 10% acetic acid. After filtration from a small residue, the clear orange solution was made alkaline (sodium hydroxide), and the oily *amine* extracted with ether, dried, and distilled, giving a yellow oil, b. p. 320—322°/0·1 mm., which solidified to a crystalline mass (3·9 g.), m. p. 120—122°. From benzene–light petroleum (b. p. 60—80°) stout colourless needles, m. p. 126—128°, were obtained (Found: C, 67·5; H, 8·7. $C_{13}H_{20}N_4$ requires C, 67·2; H, 8·6%). When this experiment was repeated, but at 130° for 6 hours, the solid insoluble in 10% acetic acid was crystallised from ethyl acetate, giving unchanged sulphone (3·5 g.), m. p. 198—199° (Found: C, 49·0; H, 4·4; S, 16·2%). The sulphone was also recovered unchanged after being heated with *iso*propylamine for 6 hours at 140—150° (sealed tube).

2-*Methanesulphonylbenzoxazole*.—2-Methylthiobenzoxazole, b. p. 146—147°/28 mm. (Found: C, 58·3; H, 4·3; S, 19·2. Calc. for C_8H_7ONS: C, 58·2; H, 4·2; S, 19·4%), prepared as for the benziminazole compound (cf. Kendall, B.P. 475,647), was oxidised in the same way. After removal of the manganese dioxide, the crystalline solid was collected, quickly dried in a vacuum over phosphoric oxide, and dissolved in cold dry benzene. The filtered solution (charcoal) was treated with an equal volume of warm light petroleum (b. p. 60—80°), whereupon colourless prisms of the *sulphone* rapidly formed. The crystals were collected, washed with benzene–light petroleum, and dried in a vacuum over wax (Found : C, 49·1, 48·8; H, 3·5, 3·5; S, 15·9. $C_8H_7O_3NS$ requires C, 48·8; H, 3·6; S, 16·2%). The crystals had no definite m. p., appearing to sinter at 45°, and gradually decomposed giving a clear melt at 110—115°. On storage in the air they rapidly decomposed, becoming moist-looking; they lost their crystalline form in a few days in a desiccator. When the crude sulphone was crystallised from water, colourless prisms of 2-hydroxybenziminazole, m. p. 137° not depressed by an authentic specimen (Sandmeyer, *Ber.*, 1886, **19**, 2656), were obtained (Found : C, 62·2; H, 3·9; N, 10·4. Calc. for $C_7H_5O_2N$: C, 62·2; H, 3·7; N, 10·4%).

2-2′-*Diethylaminoethylaminobenzoxazole*.—2-Diethylaminoethylamine (2 c.c.) at 50° was stirred and treated with the powdered methanesulphonyl compound (2·0 g.) during 0·5 hour. The reaction was very violent and the temperature rose to 110—120°. The residue was dissolved in 10% acetic acid, filtered, and made alkaline (sodium hydroxide), and the precipitate extracted with ether, dried, and distilled, giving the yellow oily *amine* (1·0 g.), b. p. 148—150°/0·5 mm. (Found : C, 66·5; H, 8·2. $C_{13}H_{19}ON_3$ requires C, 67·0; H, 8·2%). A *hydrate* was formed exothermally on rubbing the compound with water and crystallised in colourless needles, m. p. 60°, from light petroleum (b. p. 40—60°) on cooling in ice (Found : C, 61·8; H, 8·3. $C_{13}H_{19}ON_3,H_2O$ requires C, 62·2; H, 8·4%). The *dipicrate* crystallised from alcohol in yellow needles, m. p. 176—178° (Found : C, 43·4; H, 3·7. $C_{13}H_{19}ON_3,2C_6H_3O_7N_3$ requires C, 43·5; H, 3·6%).

2-iso*Propylaminobenzoxazole*.—The sulphone was added to an excess of cold *iso*propylamine (under reflux), a vigorous reaction then taking place. The residue was dissolved in N-hydrochloric acid, filtered, and precipitated with sodium hydroxide. From aqueous alcohol, a *hemihydrate* forming colourless plates, m. p. 88°, was obtained (Found : C, 64·5; H, 7·3. $C_{10}H_{12}ON_2,\frac{1}{2}H_2O$ requires C, 64·8; H, 7·0%); when dried at 60° these plates effloresced, giving the anhydrous *base* as a white powder, m. p. 78—79° (Found : C, 67·9; H, 6·5. $C_{10}H_{12}ON_2$ requires C, 68·2; H, 6·8%).

5-*Chloro*-2-*methylthiobenzthiazole*.—5-Chlorobenzthiazole-2-thiol was prepared from 1 : 4-dichloro-2-nitrobenzene by the method used by Dunbrook and Zimmermann (*J. Amer. Chem. Soc.*, 1934, **56**, 2734) for preparation of benzthiazole-2-thiol from *o*-chloronitrobenzene; it formed large, colourless, refractive prisms, m. p. 202°, from ethyl acetate (Tschunkur and Herdieckeroff, G.P. 518,206, give m. p. 195°). The thiol (10·0 g.) was triturated with N-sodium hydroxide (100 c.c.), filtered, and shaken with methyl iodide (4·0 c.c.) in alcohol (10 c.c.) for ¼ hour. After 1 hour the solid *product* was collected, washed with water, dried at 50°, and crystallised from alcohol or light petroleum (b. p. 60—80°), giving colourless flattened needles (7·1 g.), m. p. 76° (Found : C, 44·7; H, 3·0; S, 30·3. $C_8H_6NClS_2$ requires C, 44·55; H, 2·8; S, 29·8%).

2-*Methylthio*-5-*methoxybenzthiazole*.—This *compound*, prepared from the corresponding thiol [prepared as for the 5-chloro-compound from 4-chloro-3-nitroanisole; needles, m. p. 199°; Ney (U.S.P. 1,788,585) gives m. p. 201°], was distilled, giving a colourless oil, b. p. 146—148°/0·2 mm., which crystallised, on cooling, to a mass of large prisms, m. p, 43° (Found : S, 30·6. $C_9H_9ONS_2$ requires S, 30·3%).

5-*Chloro*-2-*methanesulphonylbenzthiazole* (I; R = Cl).—The methylthio-compound (10·6 g.) in acetic acid (75 c.c.) was stirred whilst a solution of potassium permanganate (16·5 g.) in water (250 c.c.) was added during 0·5 hour, the temperature not being allowed to rise above 35°. After 1 hour, water (500 c.c.) was added and, with good cooling, sulphur dioxide was passed until the colour was discharged. The *sulphone* was collected, dried at 70° (11·0 g.; m. p. 145—146°), and crystallised from benzene, giving colourless plates (8·6 g.), m. p. 149° (Found : C, 39·1; H, 2·6; S, 25·9. $C_8H_6O_2NClS_2$ requires C, 38·8; H, 2·4; S, 25·8%).

The following benzthiazoles were obtained in similar experiments : 2-*methanesulphonyl*-5-*methoxy*- (I; R = OMe), stout colourless needles, m. p. 108—109°, from benzene–light petroleum (b. p. 60—80°) (Found : C, 44·6; H, 3·8; S, 26·7. $C_9H_9O_3NS_2$ requires C, 44·4; H, 3·7; S, 26·4%), 2-*methanesulphonyl*- (I; R = H),* colourless prisms, m. p. 92—93°, from alcohol (Found : S, 30·2. $C_8H_7O_2NS_2$ requires S, 30·0%), and 6-nitro-2-methanesulphonyl- (II; R = NO_2), faintly yellow needles, m. p. 186—188° from alcohol (Cutter and Golden, *J. Amer. Chem. Soc.*, 1947, **69**, 832, give m. p. 186°).

5-*Chloro*-2-iso*propylaminobenzthiazole* (III; R = Cl, R′ = $NHPr^i$).—The methanesulphonyl compound (20·0 g.) and dry *iso*propylamine (40·0 c.c) were heated for 1 hour in a sealed tube, cooled, and ground with N-hydrochloric acid. The insoluble *hydrochloride* was collected and crystallised from alcohol, giving colourless prisms, m. p. 248—250° (Found : N, 11·1; Cl, 26·5; S, 12·5. $C_{10}H_{11}N_2ClS,HCl$ requires N, 10·6; Cl, 27·0; S, 12·2%). The salt was decomposed with warm N-sodium hydroxide, and the *base* collected and crystallised from light petroleum (b. p. 60—80°), giving colourless fibrous needles (9·5 g.), m. p. 125—126° (Found : C, 52·9; H, 4·9; S, 14·1. $C_{10}H_{11}N_2ClS$ requires C, 53·0; H, 4·9; S, 14·1%).

5-*Chloro*-2-2′-*diethylaminoethylaminobenzthiazole* (III; R = Cl, R′ = $NH{\cdot}[CH_2]_2{\cdot}NEt_2$).—2-Diethylaminoethylamine (6·0 c.c.) was heated to 100° and the methanesulphonyl compound (5·0 g.) was added at such a rate that the temperature did not rise above 110°. After 5 minutes the mixture was cooled, diluted with water (100 c.c.), made just acid (acetic acid), and filtered (charcoal), and the filtrate stirred with cooling in ice whilst 10N-sodium hydroxide was added to strong alkalinity. The crystalline precipitate was collected, washed with water, dried at 80° (6·0 g.; m. p. 90°), and crystallised from light petroleum (b. p. 60—80°), giving large colourless needles (4·5 g.), m. p. 92° (Found : C, 55·3; H, 6·3; S, 11·6. $C_{13}H_{18}N_3ClS$ requires C, 55·0; H, 6·3; S, 11·3%).

The following *benzthiazoles* were obtained in similar experiments from the corresponding sulphones and amines : 2-iso*propylamino*-5-*methoxy*- (III; R = OMe, R′ = $NHPr^i$), fine colourless needles, m. p. 158°, from benzene–light petroleum (b. p. 60—80°) (Found : C, 59·3; H, 5·8; S, 14·9. $C_{11}H_{14}ON_2S$ requires C, 59·5; H, 6·3; S, 14·4%), 2-2′-*diethylaminoethylamino*-5-*methoxy*- (III; R = OMe, R′ = $NH{\cdot}[CH_2]_2{\cdot}NEt_2$), large colourless prisms, m. p. 56—57°, from light petroleum (b. p. 60—80°) (Found : C, 59·9; H, 7·7; S, 11·5. $C_{14}H_{21}ON_3S$ requires C, 60·2; H, 7·5; S, 11·5%), 2-iso*propylamino*-

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* This compound had been obtained previously in these laboratories by Dr. G. Swain who obtained it from the corresponding sulphide by oxidation with chlorine.

(III; R = H, R′ = $NHPr^i$), colourless square plates, m. p. 95°, from light petroleum (b. p. 60—80°) (Found: C, 62·2; H, 6·5. $C_{10}H_{12}N_2S$ requires C, 62·5; H, 6·25%), 2-*benzylamino*- (III; R = H, R′ = $NH{\cdot}CH_2Ph$), colourless plates, m. p. 160—161°, from benzene (Found: C, 70·1; H, 5·0; S, 13·8. $C_{14}H_{12}N_2S$ requires C, 70·0; H, 5·0; S, 13·3%), 2-2′-diethylaminoethylamino- (III; R = H, R′ = $NH{\cdot}[CH_2]_2{\cdot}NEt_2$), a colourless oil, b. p. 160—161°/1·0 mm. (Found: C, 62·7; H, 7·5. Calc. for $C_{13}H_{19}N_3S$: C, 62·65; H, 7·6%) [the dipicrate crystallised from 2-ethoxyethanol in yellow flattened needles, m. p. 195° (Found: C, 42·6; H, 3·6. Calc. for $C_{13}H_{19}N_3S,2C_6H_3O_7N_3$: C, 42·4; H, 3·5%) (Tuda *et al., loc. cit.*, give m. p. 195°)], and 6-*nitro*-2-iso*propylamino*- (IV; R = NO_2, R′ = Pr^i), small sulphur-yellow needles, m. p. 150°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 50·7; H, 4·5; S, 13·6. $C_{10}H_{11}O_2N_3S$ requires C, 50·6; H, 4·6; S, 13·5%). On reduction in methyl alcohol by hydrogen (Raney nickel) this nitro-compound gave the corresponding *diamine* which crystallised from benzene–light petroleum (b. p. 60—80°) in faintly coloured prisms, m. p. 155° (Found: C, 58·3; H, 6·4; S, 15·2. $C_{10}H_{13}N_3S$ requires C, 58·0; H, 6·3; S, 15·45%).

6-*Nitro*-2-2′-*diethylaminoethylaminobenzthiazole* (IV; R = NO_2, R′ = $NH{\cdot}[CH_2]_2{\cdot}NEt_2$).—(*a*) This *compound*, obtained as above from the nitro-sulphone, crystallised from benzene–light petroleum (b. p. 60—80°) in large flattened golden-yellow needles, m. p. 107° (Found: C, 53·2; H, 6·1; S, 11·3. $C_{13}H_{18}O_2N_4S$ requires C, 53·1; H, 6·1; S, 10·9%).

(*b*) 2-2′-Diethylaminoethylaminobenzthiazole (6·2 g.) was added to a mixture of 100% nitric acid (25 c.c.) and 100% sulphuric acid (25 c.c.) during 0·5 hour at 0—5°. After the mixture had been poured on ice, the base was liberated with 10N-sodium hydroxide and extracted with ether, and the filtered extract shaken with several small amounts of 10% acetic acid. The united extracts were filtered (charcoal) and basified, and the precipitate allowed to harden. From light petroleum (b. p. 60—80°) deep-yellow needles (3·5 g.), m. p. 108° not depressed by the compound prepared as previously, were obtained (Found: C, 53·4; H, 6·0; S, 10·9%).

6-*Amino*-2-2′-*diethylaminoethylaminobenzthiazole* (IV; R = NH_2, R′ = $NH{\cdot}[CH_2]_2{\cdot}NEt_2$)—Reduction of the above nitro-compound with hydrogen (Raney nickel) gave the corresponding *diamine* which crystallised from benzene–light petroleum (b. p. 60—80°) in clumps of colourless needles, m. p. 106° (Found: C, 59·5; H, 7·8. $C_{13}H_{20}N_4S$ requires C, 59·1; H, 7·6%).

2-*Aminobenzthiazole*.—2-Methanesulphonylbenzthiazole (1·8 g.) and ammonia solution (*d* 0·88; 20 c.c.) were heated for 18 hours at 180° (sealed tube), the mixture cooled, the solid collected and dissolved in N-hydrochloric acid, and the filtered solution (charcoal) made alkaline with 10N-sodium hydroxide. The precipitated solid (0·6 g.; m. p. 120°) was crystallised from water, giving colourless leaflets (0·4 g.), m. p. 128—129° not depressed by an authentic specimen (Found: S, 21·5. Calc. for $C_7H_6N_2S$: S, 21·3%).

2-*Diethylamino*-5-*methoxybenzthiazole* (III; R = OMe, R′ = NEt_2).—Dry diethylamine (10·0 c.c.) and 2-methanesulphonyl-5-methoxybenzthiazole (4·8 g.) were heated for 3 hours at 130° (sealed tube). To the cold mixture 2N-hydrochloric acid (100 c.c.) was added, and the solid was collected and washed with 2N-hydrochloric acid. This solid (2·6 g.; m. p. 102—104°) crystallised from benzene–light petroleum (b. p. 60—80°) in colourless needles, m. p. 106° not depressed by the original sulphone (Found: S, 14·0%). The acid filtrates were made strongly alkaline (10N-sodium hydroxide), and the oil extracted with ether, dried and distilled, giving a colourless oily *base* which darkened on storage (1·5 g.), b. p. 158—160°/0·4 mm. (Found: C, 60·9; H, 6·6. $C_{12}H_{16}ON_2S$ requires C, 61·0; H, 6·8%).

5-*Chloro*-2-*hydroxybenzthiazole* (III; R = Cl, R′ = OH).—5-Chloro-2-methanesulphonylbenzthiazole (2·5 g.), concentrated hydrochloric acid (20·0 c.c.), and alcohol (2·0 c.c.) were refluxed for 4 hours, diluted with water (100 c.c.), and made alkaline with 10N-sodium hydroxide. After filtration from a small insoluble residue the filtrate was precipitated with acetic acid, and the solid collected, dried, and crystallised from methyl alcohol, giving long silky needles (1·2 g.), m. p. 230—231° (Found: S, 17·6. Calc. for C_7H_4ONClS: S, 17·3%). Herdieckeroff and Tschunkur (G.P. 615,131) give m. p. 218°.

6-Nitro-2-hydroxy- (IV; R = NO_2, R′ = OH), silky, faintly buff needles, m. p. 248°, from methyl alcohol (Found: S, 16·7. Calc. for $C_7H_4O_3N_2S$: S, 16·3%) (Jacobsen and Kwaysser, *Annalen*, 1893, **277**, 240, give m. p. 252°), and 2-hydroxy-benzthiazole (IV; R = H, R′ = OH), large colourless prisms, m. p. 140—141°, from benzene–light petroleum (b. p. 60—80°) (Found: S, 21·0. Calc. for C_7H_5ONS: S, 21·2%) (Hunter, *J.*, 1930, 135, gives m. p. 138°), were similarly prepared.

5-*Chloro*-2-*methoxybenzthiazole* (III; R = Cl, R′ = OMe).—5-Chloro-2-methanesulphonylbenzthiazole (12·5 g.) was added to a solution of sodium (1·2 g.) in dry methyl alcohol (150 c.c.) and refluxed for 3 hours. The solvent was removed under reduced pressure, water (100 c.c.) added, and the solid collected and crystallised from a small volume of light petroleum (b. p. 40—60°), giving colourless leaflets (6·9 g.), m. p. 71—72° (Found: C, 48·3; H, 3·0; S, 16·4. C_8H_6ONClS requires C, 48·0; H, 3·0; S, 16·0%).

The following were obtained from the corresponding sulphones and sodium alkoxides. 5-*Chloro*-2-iso-*propoxybenzthiazole* (III; R = Cl, R′ = OPr^i) crystallised from a small volume of light petroleum (b. p. 40—60°) in colourless leaflets, m. p. 62° (Found: S, 14·0. $C_{10}H_{10}ONClS$ requires S, 14·1%); when this compound (1·0 g.) was heated at 180° a rapid evolution of an unsaturated inflammable gas took place and the residue solidified; crystallisation from alcohol gave large colourless needles (0·6 g.), m. p. 230° not depressed by admixture with 5-chloro-2-hydroxybenzthiazole prepared as above. 2-Methoxybenzthiazole (III; R = H, R′ = OMe), large colourless prisms, m. p. 36—37°, from light petroleum (b. p. 40—60°) cooled to 0° (Found: C, 58·1; H, 4·3; S, 19·5. Calc. for C_8H_7ONS: C, 58·2; H, 4·2; S, 19·4%) (Davies and Sexton, *loc. cit.*, give m. p. 31—33°). 2-iso*Propoxybenzthiazole* (III; R = H, R′ = OPr^i), a colourless oil, b. p. 80—81°/0·05 mm. (Found: C, 62·3; H, 5·8; S, 16·3. $C_{10}H_{11}ONS$ requires C, 62·2; H, 5·7; S, 16·6%); this compound (1·0 g.) on heating at 250° (oil-bath) gave 2-hydroxybenzthiazole which crystallised from benzene–light petroleum (b. p. 60—80°) in large colourless prisms (0·6 g.), m. p. 140—141°. 2 : 5-*Dimethoxybenzthiazole* (III; R = R′ = OMe), a colourless oil, b. p. 114—116°/0·15 mm. (Found: C, 55·5; H, 4·6; S, 16·6. $C_9H_9O_2NS$ requires C, 55·4; H, 4·5; S, 16·5%).

The following *benzthiazolones* were prepared by heating the corresponding 2-methoxybenzthiazoles at 180° and crystallising the residue from benzene–light petroleum (b. p. 60—80°): 3-methyl- (V; R = H), large colourless plates, m. p. 72—73° (Found: S, 19·1. Calc. for C_8H_7ONS: S, 19·4%), 5-*chloro*-3-

methyl- (V; R = Cl), colourless needles, m. p. 105—106° (Found: C, 47·8; H, 3·1; S, 16·4. C_8H_6ONClS requires C, 48·0; H, 3·0; S, 16·1%), and 5-*methoxy*-3-*methyl-* (V; R = OMe), colourless needles, m. p. 106—107° (Found: C, 55·2; H, 4·6. $C_9H_9O_2NS$ requires C, 55·4; H, 4·6%).

Identification of Sodium Methanesulphinate.—2-Methanesulphonylbenzthiazole (10·7 g.) was refluxed with a solution of sodium (1·2 g.) in dry *iso*propyl alcohol (150 c.c.) for 3 hours and then cooled, and the deliquescent colourless needles (3·8 g.) were collected, washed with ether, and dried in a vacuum over phosphoric oxide. On refluxing of this salt with benzyl chloride (10·0 g.) in alcohol (40 c.c.) and water (40 c.c.) for 3 hours and evaporation of the alcohol, benzyl methyl sulphone was obtained which crystallised from water in large, colourless needles (4·0 g.), m. p. 125—126° not depressed by an authentic sample (Fromm and Palma, *Ber.*, 1906, **39**, 3315) (Found: S, 18·8. Calc. for $C_8H_{10}O_2S$: S, 18·8%).

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