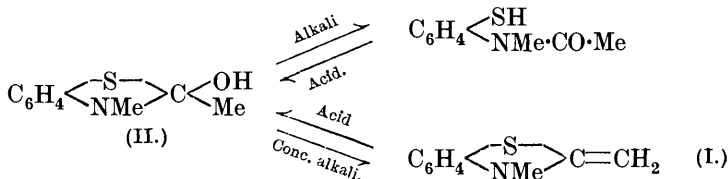


CCCIH.—*The Methylene Bases from 1-Methylbenzthiazole and 1-Methylbenzselenazole Methiodides; with a Note on the Preparation of 1-Substituted Benzthiazoles.*

By LESLIE MARSHALL CLARK.

1-METHYLBENZTHIAZOLE methiodide reacts with ammonium hydroxide in dilute aqueous solution, yielding as the main product the ammonium salt of *o*-acetmethylamidothiophenol, since atmospheric oxidation of the solution gives 2:2'-diacetmethylamido-diphenyl disulphide (J., 1925, 127, 973). König and Meier (*J. pr. Chem.*, 1925, 109, 324) have shown that when 1-methylbenzthiazole methoperchlorate is suspended in acetone and shaken with concentrated sodium hydroxide solution, the acetone extracts a base which they identify as 2-methyl-1-methylenebenzthiazoline (I).

Further examination of the reaction with ammonia and with dilute sodium hydroxide proves that a certain amount of the methylene base is produced in either case, whilst in the latter case the proportion of methylene base to thiophenol is increased by increasing the alkali concentration. It is evident, therefore, that the carbinol (II) decomposes in the presence of alkali in the two directions :



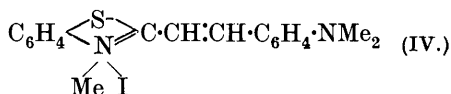
When the compound (I) is heated in alcoholic hydrogen chloride solution or when alkali salts of *o*-acetmethylamidothiophenol are acidified, 1-methylbenzthiazolinium salts result. Each of the directions of reaction in which the carbinol base can decompose under the influence of alkalis is therefore reversible in the presence of acids.

Since quaternary salts in the benzselenazole series react with alkalis to give products similar to those obtained from the analogous benzthiazolinium salts (J., 1927, 2805), the behaviour of 1-methylbenzselenazole methiodide has also been investigated. The base could not be obtained by the action of acetic acid on the zinc salt of *o*-aminoselenophenol, the products of this reaction being selenium and acetanilide, but was readily formed by condensation of the zinc salt with acetyl chloride. The methiodide in aqueous solution reacts

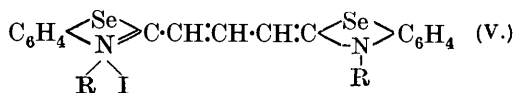
immediately with dilute sodium hydroxide giving 2-methyl-1-methylenebenzselenazoline together with the sodium salt of *o*-acetyl-methylaminoselenophenol.

The course of the reaction may be followed by titration with phenolphthalein as indicator, part of the methiodide yielding a precipitate of the selenazoline (and consequently neutralising one equivalent of alkali), whilst the remainder is converted into the neutral sodium salt of the selenophenol (at the same time neutralising 2 equivs. of alkali). A much higher proportion of the methylene base is formed with 1-methylbenzselenazoline methiodide than with the analogous sulphur compound. 2-Methyl-1-methylenebenzselenazoline, like its sulphur analogue, is reconverted into the ammonium salt by heating with alcoholic hydrogen chloride.

Mills and Raper (J., 1925, 127, 2466) have isolated the highly-coloured condensation product obtained by reaction of *p*-dimethylaminobenzaldehyde with the reactive methylene group in 1-methyl-2-methylene-1 : 2-dihydro- $\beta$ -naphthaquinoline. The aldehyde condenses similarly with 2-methyl-1-methylenebenzthiazoline in alcohol, giving a deep red solution from which no solid material could be isolated. The solution evidently contains the compound (III), since on addition of one mol. of hydriodic acid, *p*-dimethylaminostyrylbenzthiazole methiodide (IV) is formed, addition of the acid evidently taking place in a manner analogous to that described by Mills and Raper (*loc. cit.*).



The presence of the reactive methyl group in 1-methylbenzselenazole methiodide suggested that selenocarbocyanine formation might be possible. By using the general method of preparation of carbocyanines described by Hamer (J., 1927, 2796), *i.e.*, the condensation in pyridine solution of orthoformic ester with the methiodides of bases containing a reactive methyl group, good yields of both 2 : 2'-dimethyl- and 2 : 2'-diethylselenocarbocyanine iodides (V), were obtained. Like the thiocarbocyanines described by Mills (J., 1922, 121, 455), these compounds are powerful sensitizers of the photographic plate.



In *C*-substituted benzoxazoles, fission of the heterocyclic ring is increasingly difficult to bring about as the volume and valency demands of the substituent group increase (Skraup, *Annalen*, 1919, **419**, 1). The influence of the *C*-phenyl group, although well-marked in the benzoxazole series, is insufficient in the benzthiazolinium series to make possible the isolation of a carbinol base of the type (II), even when silver hydroxide is used instead of sodium hydroxide (J., 1925, **127**, 973) as basifying agent.

The well-known Hofmann synthesis of 1-substituted benzthiazoles (*Ber.*, 1880, **13**, 21), whereby *o*-aminothiophenol is heated with the appropriate acid, acid anhydride, or acid chloride, is not entirely satisfactory. An alternative method is therefore described. 2 : 2'-Diaminodiphenyl disulphide is acylated by treatment with the appropriate acid or acid chloride, and this compound is reduced with sodium hydrosulphite yielding the acylamino-thiophenol, which condenses with elimination of water to give the 1-substituted benzthiazole (compare Clark, *loc. cit.*, and Phillips, this vol., p. 172).

#### EXPERIMENTAL.

2-Methyl-1-methylenebenzthiazoline is formed in small yield by the action of ammonia, silver hydroxide, or *N*-sodium hydroxide on 1-methylbenzthiazole methiodide in aqueous solution. The maximum yield was obtained by the following modification of König and Meier's method (*loc. cit.*). The methiodide (4 g.) was suspended in acetone and shaken with 50% sodium hydroxide solution. When no quaternary salt remained undecomposed, the acetone solution was evaporated and the pinkish residue extracted with toluene (5 c.c. and 2 c.c.). A small quantity of dark red oil, which afterwards solidified, remained undissolved; this was separated by acetone into a sparingly soluble, dark red, crystalline substance and a colourless substance which separated in needles, m. p. 164°. These compounds were not further examined. The toluene solution, when cooled, deposited 0.81 g. of stout, colourless tablets of 2-methyl-1-methylenebenzthiazoline, m. p. 170° (König and Meier give 164°) (Found : C, 66.2; H, 5.6; N, 8.7. Calc. : C, 66.3; H, 5.5; N, 8.6%). A mixture of this substance with 2 : 2'-diacetmethylamidodiphenyl disulphide, m. p. 171°, melted at 128°. When these two compounds are heated together they develop a brilliant red colour.

By the action of benzoyl chloride on a solution of the sodium salt of *o*-acetmethylamidothiophenol, the *benzoyl* derivative was obtained; from light petroleum it separated in colourless needles, m. p. 87° (Found : C, 67.0; H, 5.2.  $C_{16}H_{15}O_2NS$  requires C, 67.4; H, 5.3%).

1-Methylbenzthiazole methopicate, prepared from the methiodide

and picric acid, separated from aqueous solution in yellow needles which, when kept in a vacuum over sulphuric acid, became liquid and then resolidified. It then had m. p.  $94^{\circ}$  (Found : N, 14.7.  $C_{15}H_{12}O_7N_4S$  requires N, 14.3%). The *hydrogen sulphate* separated from alcohol-ether in colourless needles, m. p.  $177-178^{\circ}$  (Found :  $SO_4$ , 38.5.  $C_8H_7NS, H_2SO_4$  requires  $SO_4$ , 38.75%); the *methochloroplatinate*, prepared from the methochloride and chloroplatinic acid in alcoholic solution, separated in deep yellow crystals, m. p.  $224^{\circ}$  (decomp.) [Found : Pt, 26.2.  $(C_9H_{10}NS)_2PtCl_6$  requires Pt, 26.5%]; the *perchlorate* separated from alcohol-ether in colourless needles, m. p.  $149^{\circ}$ , and exploded during combustion.

*Action of Silver Hydroxide on 1-Phenylbenzthiazole Methiodide.*—The methiodide (2 g.), dissolved in water (35 c.c.) and acetone (50 c.c.), was shaken for an hour with excess of silver hydroxide; the filtrate from the insoluble material contained none of the expected 1-hydroxy-1-phenyl-2-methylbenzthiazoline, the major portion of the thiazole compound being mixed with the silver oxide and iodide residue, probably as the silver salt of *o*-benzoylmethylaminothiophenol (compare Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353). The sodium salt of *o*-benzoylmethylaminothiophenol was benzoylated by shaking with benzoyl chloride, and the *benzoyl* derivative, when crystallised from light petroleum, had m. p.  $130-131^{\circ}$  (Found : C, 72.6; H, 4.8.  $C_{21}H_{17}O_2NS$  requires C, 72.6; H, 4.85%).

For the characterisation of 1-phenylbenzthiazole quaternary salts, the following compounds were prepared by the usual methods : 1-*Phenylbenzthiazole methochloroplatinate*, m. p.  $243^{\circ}$  (decomp.) [Found : Pt, 22.7.  $(C_{14}H_{12}NS)_2PtCl_6$  requires Pt, 22.7%]; *methopicrate*, orange-yellow plates, m. p.  $125-126^{\circ}$  (Found : N, 12.4.  $C_{20}H_{14}O_7N_4S$  requires N, 12.3%); *methoperchlorate*, colourless needles, m. p.  $220^{\circ}$  (Found : S, 10.0.  $C_{14}H_{12}O_4NSCl$  requires S, 9.8%).

*Preparation of 1-Methylbenzselenazole.*—A preliminary experiment on the action of glacial acetic acid (150 c.c.) on the zinc salt of *o*-aminoselenophenol (17 g.) in an atmosphere of carbon dioxide showed that selenium was deposited; the only product which could be isolated from the filtrate was acetanilide, m. p.  $114^{\circ}$  (Found : C, 71.35; H, 6.1; N, 10.4. Calc. : C, 71.1; H, 6.7; N, 10.4%). When the acetic acid was replaced by acetyl chloride, the condensation took place smoothly : The zinc salt (7 g.) was suspended in benzene (50 c.c.), and acetyl chloride in excess (10 c.c.) was added slowly with constant shaking; the brown oil which separated solidified after 16 hours. The reaction mixture was heated on the water-bath for 1 hour and cooled. Water and excess of ammonia

were then added. The solid slowly dissolved, and the benzene layer was separated. The aqueous solution was extracted with ether, the combined organic extracts were dried over sodium carbonate, and most of the solvent was distilled off. Addition of light petroleum then precipitated a yellowish gum, which was probably 2 : 2'-diacetamidodiphenyl diselenide, but which was not investigated. The solution was removed and concentrated, and the residual oil distilled under reduced pressure. 1-Methylbenz-selenazole (4.6 g.) was thus obtained as an almost colourless liquid, b. p.  $140^{\circ}/51$  mm. It was analysed as the *chloroplatinate*, which separates from alcoholic solutions in yellow needles [Found : C, 24.4; H, 1.95; Pt, 24.6.  $(C_8H_7NSe)_2, H_2PtCl_6$  requires C, 23.9; H, 2.0; Pt, 24.4%]. The *methiodide*, obtained by heating the base (3.8 g.) with methyl iodide (6 g.) at  $100^{\circ}$  for 8 hours, crystallised from alcohol in fine, colourless needles, m. p.  $221^{\circ}$  (decomp.); yield, 5.5 g. (Found : I, 37.4; Se, 23.6.  $C_9H_{10}NISE$  requires I, 37.6; Se, 23.4%); and the *ethiodide*, similarly obtained by 16 hours' heating, crystallised from alcohol in colourless, flattened needles, m. p.  $212^{\circ}$  (decomp.) (Found : I, 35.9.  $C_{10}H_{12}NISE$  requires I, 36.1%). The *methochloroplatinate*, prepared from the methochloride in the usual way, had m. p.  $214^{\circ}$  (decomp.) [Found : Pt, 23.1.  $(C_9H_{10}NSe)_2PtCl_6$  requires Pt, 22.9%].

*Action of Sodium Hydroxide on 1-Methylbenzselenazole Methiodide.*—Addition of *N*/20- or *N*-sodium hydroxide solution to aqueous solutions of the methiodide causes the formation of a voluminous, curdy, pale yellow precipitate of 2-methyl-1-methylenebenzselenazoline, which crystallises from its orange-red alcoholic solution in pale yellow plates, m. p.  $157$ — $158^{\circ}$  (Found : C, 51.4; H, 4.4; N, 7.1.  $C_9H_9NSe$  requires C, 51.4; H, 4.3; N, 6.7%). The compound is sparingly soluble in alcohol and shows a tendency to form a brown mass when warmed with that solvent. From 1 g. of the methiodide, 0.346 g. of methylene base (dried over sulphuric acid) was obtained, and the change of titre was 4.0 c.c. of *N*-alkali; if the reaction proceeded as suggested on p. 2314, the change of titre should have been 4.3 c.c. The alkaline solution, after removal of the methylene base, was oxidised with potassium ferricyanide and gave an oily suspension which rapidly crystallised. The solid product, 2 : 2'-diacetmethylamidodiphenyl diselenide, crystallised from petroleum ether in colourless flat needles, m. p.  $141^{\circ}$  (Found : C, 47.3; H, 4.4; N, 6.3.  $C_{18}H_{20}O_2N_2Se_2$  requires C, 47.6; H, 4.4; N, 6.2%).

*Reversibility of Methylene-base Formation in the Benzthiazole and Benzselenazole Series.*—(1) *Action of hydrochloric acid on 2-methyl-1-methylenebenzthiazoline.* The methylene base (0.2 g.) in alcohol

(5 c.c.) was heated under reflux with hydrochloric acid (2 c.c.) for 2 hours. Addition of chloroplatinic acid then caused the separation of yellow needles which slowly disappeared as a heavy, brown, crystalline deposit was formed. This compound had m. p. 224° (decomp.), not depressed when mixed with authentic 1-methylbenzthiazole methochloroplatinate (Found: Pt, 26.2. Calc.: Pt, 26.5%).

(2) *Action of hydrochloric acid on 2-methyl-1-methylenebenz-selenazoline.* The reaction was carried out as for the sulphur compound, the chloroplatinate separating from the alcoholic solution in stout, yellowish-brown needles, m. p. 214° (decomp.) (Found: Pt, 23.1. Calc.: Pt, 22.9%), not depressed by admixture with 1-methylbenzselenazole methochloroplatinate.

*Condensation of 2-Methyl-1-methylenebenzthiazoline with p-Dimethylaminobenzaldehyde.*—Dimethylaminobenzaldehyde and the methylene base (0.71 g. of each) were heated in alcoholic solution (15 c.c.) for 1 hour. An intense red colour developed, but no solid material separated when the mixture was cooled and kept for 12 hours. To the hot solution, therefore, hydriodic acid (*d* 1.7; 1.1 c.c., 1 mol.) was added. The purple, crystalline precipitate with bronze reflex, which separated on cooling, was easily soluble in alcohol, and was crystallised from that solvent containing a little sulphurous acid; *p*-dimethylaminostyrylbenzthiazole methiodide (Found: S, 7.6. Calc.: S, 7.6%) melted at 244—245°, unchanged by admixture with an authentic specimen, m. p. 245°, prepared by Dr. F. M. Hamer from 1-methylbenzthiazole methiodide and the aldehyde. The absorption spectra in alcohol of the two samples are identical, showing maxima at  $\lambda$  4350 and  $\lambda$  6400.

*Condensation of Orthoformic Ester with 1-Methylbenzselenazole Methiodide.*—The methiodide (1.45 g.) and orthoformic ester (1.5 c.c.) were boiled in dry pyridine solution (15 c.c.) for 1 hour. A deep purple colour rapidly developed, and a crystalline deposit was formed. The mixture was poured into water and kept for 12 hours. 2 : 2' - *Dimethylselenocarbocyanine iodide*, thus obtained, was crystallised from ethyl alcohol (1.3 l.), and separated from the hot deep red solution in flocculent masses of fine, bronze needles, m. p. 267—268° (decomp.); yield 0.8 g. (Found\*: C, 40.5; H, 3.5; N, 4.8.  $C_{19}H_{17}N_2ISe_2$  requires C, 40.8; H, 3.0; N, 5.0%). In alcoholic solution the dye has absorption maxima at  $\lambda$  4500 and  $\lambda$  6400, whilst it confers sensitivity on a bathed plate up to  $\lambda$  7020.

*Condensation of Orthoformic Ester with 1-Methylbenzselenazole Ethiodide.*—The condensation was carried out in the manner described for the methyl compound. The yield of 2 : 2' - *diethyl-*

\* Microanalysis by H. Weil, Munich.

*selenocarbocyanine iodide* from 0.5 g. of 1-methylbenzselenazole ethiodide was 0.27 g. The solubility of the higher homologue is considerably greater than that of the lower, since this amount of dye could be crystallised from 50 c.c. of alcohol. It separates in glistening, dark green needles, m. p. 270—271° (decomp.) (Found \* : N, 4.8.  $C_{21}H_{21}N_2ISe_2$  requires N, 4.8%). The absorption spectrum in alcoholic solution shows maxima at  $\lambda$  4500 and  $\lambda$  6420. The sensitivity band of a bathed plate has a slight maximum at  $\lambda$  6200, falling off steeply to the red at  $\lambda$  6940.

*The Preparation of 1-Substituted Benzthiazoles.*

2 : 2'-*Diacetamidodiphenyl disulphide* was prepared by boiling 2 : 2'-diaminodiphenyl disulphide (8.0 g.) with glacial acetic acid (50 c.c.) and acetic anhydride (10 c.c.) for 5 hours. Dilution of the solution and neutralisation with ammonia precipitated a colourless oil, which rapidly crystallised (9.3 g.); when recrystallised from ethyl acetate, it separated in masses of colourless, flocculent needles, m. p. 165—166° (Found : N, 8.4.  $C_{16}H_{16}O_2N_2S_2$  requires N, 8.4%), readily soluble in alcohol.

1 - *Methylbenzthiazole*.—2 : 2' - Diacetamidodiphenyl disulphide (12.2 g.) was dissolved in hot aqueous alcohol, and excess of solid sodium hydrosulphite (15 g.) was added in three portions. Heating was continued during 15 minutes. After the addition of hydrochloric acid (35 c.c.) the solution was concentrated on the water-bath. Basification with sodium hydroxide solution precipitated an oily paste which was extracted with ether. The ethereal solution was dried over sodium carbonate and evaporated, leaving 3.5 g. of a yellow oil, which, on distillation under reduced pressure, yielded 2.0 g. of pure 1-methylbenzthiazole, identified by means of its picrate, m. p. 155—156°, identical with that obtained from an authentic specimen.

2 : 2' - *Dipropionamidodiphenyl disulphide* was obtained by boiling 2 : 2'-diaminodiphenyl disulphide (6 g.) for 12 hours with propionic acid (50 g.); the disulphide was precipitated as a dark brownish oil on dilution and neutralisation of the acid solution, but solidified on standing over-night. A portion, washed with ether and crystallised from light petroleum (b. p. 60—80°), separated in colourless, flocculent masses, m. p. 138° (Found : N, 7.95.  $C_{18}H_{20}O_2N_2S_2$  requires N, 7.8%).

1 - *Ethylbenzthiazole*.—Reduction of the foregoing unpurified solid with sodium hydrosulphite as described above for the acetyl compound eventually gave a small quantity of dark-coloured oil. This was not distilled, but 1.6 g. of a picrate were obtained from it by addition of a saturated solution of picric acid in alcohol; after

\* Microanalysis by H. Weil, Munich.

recrystallisation from alcohol (charcoal), 1-ethylbenzthiazole picrate had m. p. 138° (Found : C, 45·8; H, 3·0; N, 14·1.  $C_{15}H_{12}O_7N_4S$  requires C, 45·9; H, 3·05; N, 14·3%).

2 : 2'-Dibenzamidodiphenyl Disulphide.—This was obtained in good yield by the Schotten-Baumann method from the base; it crystallised from alcohol, in which it is sparingly soluble, in pale yellow plates, m. p. 143—144·5° (Found : N, 6·3.  $C_{26}H_{20}O_2N_2S_2$  requires N, 6·1%).

*Reduction.* The disulphide (1·2 g.) was dissolved in aqueous acetone, and an excess of sodium hydrosulphite added. The mixture was kept hot for 5 minutes. Hydrochloric acid (10 c.c.) was added and the acetone evaporated. Basification with ammonia precipitated a colourless oil which immediately crystallised. The solid, which when heated had the geranium-like odour characteristic of 1-phenylbenzthiazole, was crystallised from aqueous alcohol, and separated in long needles, m. p. 113°, showing no depression on admixture with an authentic specimen of 1-phenylbenzthiazole; yield 0·9 g.

*Preparation of 2 : 2'-Diaminodiphenyl Disulphide.*—The method described by Hofmann (*Ber.*, 1894, 27, 2808) for the preparation of this compound is not satisfactory. Most of the material used in carrying out the above work was prepared by the method of Möhlau (*Ber.*, 1912, 45, 131). Dr. F. M. Hamer, of Ilford Ltd., kindly prepared 10 g. of the disulphide by Hofmann's method and to her I am indebted for the following note : " After heating aniline (120 g.) and sulphur (35 g.) according to Hofmann's directions, 67% of the aniline was recovered unchanged by steam distillation. From the residue, 400 c.c. of hydrochloric acid (8%) extracted a mixture of bases. The hydrochlorides left on evaporation of this solution were separated by extraction with 400 c.c. of hot water. The sparingly soluble residue was the hydrochloride of a base which had m. p. 81° and was probably 4 : 4'-diaminodiphenyl disulphide. The hot aqueous solution deposited a hydrochloride which on basification gave 5 g. of 2 : 2'-diaminodiphenyl disulphide, m. p. 93°."

I wish to thank Messrs. Ilford Ltd. for the gift of 2 : 2'-diaminodiphenyl disulphide, and for examining the optical and photographic properties of the sensitisers described in this paper. My thanks are due to Dr. F. M. Hamer for the loan of a specimen of *p*-dimethylaminostyrylbenzthiazole methiodide.

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[Received, June 29th, 1928.]