CCCLXXV.—*Quaternary Salts in the Benzselenazole Series.*

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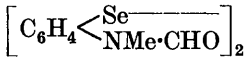
The zinc salt of *o*-aminoselenophenol, which reacts with benzoyl chloride to give phenylbenzselenazole (Bauer, *Ber.*, 1913, **46**, 92), reacts similarly with formic acid to give *benzselenazole* (I).

(I.)

$\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{Se}}{\mathrm{N}}>\mathrm{CH}$



$\left[\mathrm{C_6H_4}<\genfrac{}{}{0pt}{}{\mathrm{Se}\text{———}}{\mathrm{NMe{\cdot}CHO}}\right]_2$

(II.)

Benzselenazole methiodide, when titrated in aqueous solution with sodium hydroxide and phenolphthalein, requires two equivalents of alkali for neutralisation. The neutral solution reduces one equivalent of iodine, a compound, $(C_8H_8ONSe)_2$, being formed. This behaviour of benzselenazole methiodide is clearly analogous to that of benzthiazole methiodide (Mills, Clark, and Aeschlimann, J., 1923, **123**, 2353) and must be ascribed to formation of the carbinol base, subsequent opening of the heterocyclic ring to give the sodium salt of *o*-formylmethylaminoselenophenol, $CHO{\cdot}NMe{\cdot}C_6H_4{\cdot}SeNa$, and oxidation of this by iodine (or other mild oxidising agents) to *di-*o*-formylmethylaminodiphenyl diselenide* (II).

Similar reactions occur when 2-phenylbenzselenazole methiodide is treated with two equivalents of sodium hydroxide, followed by one of iodine, and are, therefore, probably general for all 2-alkyl- and 2-aryl-substituted benzselenazolinium salts.

Atmospheric oxidation of benzselenazole methiodide in ammoniacal solution gives *di-*o*-methylaminodiphenyl diselenide*, the formyl groups of (II) having been removed by contact with ammonium hydroxide. Similar treatment of benzthiazole methiodide gives di-*o*-formylmethylaminodiphenyl disulphide, di-*o*-methylaminodiphenyl disulphide being produced only when sodium hydroxide is substituted for ammonium hydroxide (compare Mills, Clark, and Aeschlimann, *loc. cit.*).

Confirmation of the correctness of the explanations advanced above is obtained by the benzoylation of the di-*o*-methylaminodiphenyl diselenide obtained from benzselenazole methiodide. The product is identical with the compound obtained from 2-phenylbenzselenazole methiodide by treatment with alkali and oxidation.

During the preparation of benzselenazole, *di-*o*-formylaminodiphenyl diselenide* was isolated as a by-product. This compound, when treated in alcoholic solution with stannous chloride, gave some benzselenazole by preliminary reduction to *o*-formylaminoselenophenol, which then underwent condensation by loss of water.

The formyl groups in di-*o*-formylaminodiphenyl diselenide are readily removed by heating with phenylhydrazine, since α-formylphenylhydrazine is obtained from the reaction mixture.

EXPERIMENTAL.

The zinc salt of *o*-aminoselenophenol was prepared by Bauer's method (*loc. cit.*), but a better yield (56%) of di-*o*-aminodiphenyl diselenide was obtained by oxidising the solution of *o*-aminoselenophenol, well stirred and cooled below 6°, with potassium ferricyanide instead of hydrogen peroxide.

Benzselenazole (I).—The zinc salt of *o*-aminoselenophenol (17 g.) was boiled during 14 hours with anhydrous formic acid (140 c.c.), and the solution poured into water; a light-coloured oil, which rapidly solidified, was then precipitated. Excess of ammonium hydroxide was added and the oily suspension and the solid deposit (A) were extracted by means of ether. The extract was dried over sodium carbonate, the solvent removed, and the residue distilled, giving *benzselenazole* (4·5 g.), a slightly yellow liquid, b. p. 154°/45 mm., having an odour very similar to that of benzthiazole (Found : N, 8·0. C_7H_5NSe requires N, 7·7%).

Benzselenazole Methiodide.—A mixture of the base (4·2 g.) and methyl iodide (5 g.) was kept for 24 hours and then heated on the water-bath for 3 hours. The resulting solid, after being washed with ether, crystallised from alcohol in very pale yellow needles (yield, 80%), m. p. 188—189° (Found : C, 29·4; H, 2·45; N, 4·2; I, 39·1; Se, 24·1. C_8H_8NISe requires C, 29·6; H, 2·5; N, 4·3; I, 39·2; Se, 24·4%). *Benzselenazole methopicrate*, obtained from the methiodide and picric acid in alcoholic solution, had m. p. 173° (Found : N, 12·8. $C_{14}H_{10}O_7N_4Se$ requires N, 13·2%).

Action of Sodium Hydroxide on Benzselenazole Methiodide.—Benzselenazole methiodide (1·500 g.) in aqueous solution required 9·3 c.c. of 1·02*N*-sodium hydroxide for neutralisation (Calc. for two equivs. of NaOH, 9·1 c.c.). On oxidation of the cold solution with potassium ferricyanide a yellowish, oily substance was precipitated. This was extracted with benzene, and the extract was dried over sodium carbonate and concentrated, and light petroleum added until a permanent turbidity appeared; *di*-o-*formylmethylaminodiphenyl diselenide* (II) slowly separated in small, colourless prisms, m. p. 104° (Found : C, 45·0; H, 3·8; N, 6·7; *M*, cryoscopic in camphor, 424. $C_{16}H_{16}O_2N_2Se_2$ requires C, 45·1; H, 3·75; N, 6·6%; *M*, 426).

Oxidation of o-*Formylmethylaminoselenophenol by Iodine.*—Benzselenazole methiodide (0·3240 g.), dissolved in water, was treated with two equivalents of sodium hydroxide. The slightly yellow solution required 9·3 c.c. of *N*/10-iodine for oxidation (Calc. for 1 equiv., 10·0 c.c.). The error in the titration is undoubtedly due to atmospheric oxidation, which appears to be more rapid in the case of the selenophenols than in that of the thiophenols. Di-*o*-formylmethylaminodiphenyl diselenide, m. p. 104°, was isolated as before.

Atmospheric Oxidation of o-*Formylmethylaminoselenophenol.*—Benzselenazole methiodide (0·3 g.) was dissolved in water (30 c.c.), and ammonium hydroxide (2 c.c.; *d*, 0·880) added. The solution became yellow and slightly turbid; after it had been kept for several hours in the dark, a crystalline, yellow substance separated on the surface. If the concentration of ammonium hydroxide was greater than that stated, the crystals were accompanied by a yellow oil. When the solution had lost its yellow colour, the crystals were removed and purified by evaporation of a solution in light petroleum. After several repetitions of this procedure, *di-*o*-methylaminodiphenyl diselenide* was obtained, m. p. 89° (Found: C, 45·3; H, 4·2; N, 7·5. $C_{14}H_{16}N_2Se_2$ requires C, 45·4; H, 4·3; N, 7·6%). This diselenide is very readily soluble in organic solvents. It separates from ether in yellow, hexagonal tablets, very similar in appearance to those of di-*o*-methylaminodiphenyl disulphide (Mills, Clark, and Aeschlimann, *loc. cit.*).

Di-*o*-methylaminodiphenyl diselenide (0·2 g.), shaken with benzoyl chloride and sodium hydroxide, gave a pasty mass; after crystallisation from aqueous alcohol, this had m. p. 170°, alone or when mixed with di-*o*-benzoylmethylaminodiphenyl diselenide obtained from 1-phenylbenzselenazole methiodide (see below).

1-*Phenylbenzselenazole Methiodide.*—1-Phenylbenzselenazole (2 g.), prepared by Bogert and Chen's method (*J. Amer. Chem. Soc.*, 1922, **44**, 2355), was heated at 100° during 26 hours with methyl iodide (2·5 c.c.). After removal of the excess of methyl halide, the residue was extracted with ether to remove unchanged base. The crude *methiodide* crystallised from alcohol in golden-yellow needles, m. p. 211—212° (decomp.) (Found: I, 31·5. $C_{14}H_{12}NISe$ requires I, 31·75%). 1-*Phenylbenzselenazole chloroplatinate* was prepared from alcoholic-hydrochloric acid solutions of the base and platinic chloride and separated in flattened, yellowish-brown needles [Found: Pt, 20·8. $(C_{13}H_9NSe)_2H_2PtCl_6$ requires Pt, 21·0%].

Action of Sodium Hydroxide on 1-*Phenylbenzselenazole Methiodide: Di-*o*-benzoylmethylaminodiphenyl Diselenide.*—The methiodide (0·210 g.), dissolved in water, was titrated at 50° with sodium hydroxide and phenolphthalein. The addition of each portion of alkali caused the transient red coloration of the indicator which is characteristic of pseudo-base formation (Required: 19·3 c.c. of *N*/20-sodium hydroxide. Calc. for two equivs., 19·5 c.c.). This solution, cooled and titrated with 0·0625*N*-iodine, required 7·0 c.c. for complete oxidation, whereas the amount calculated for one equivalent of iodine is 8·4 c.c. This discrepancy must again be ascribed to atmospheric oxidation. The colourless solid, *di*-o-*benzoylmethylaminodiphenyl diselenide*, which separated after the iodine oxidation crystallised from aqueous alcohol in stout needles, m. p. 170° (Found : C, 58·4 ; H, 4·1 ; N, 5·1 ; Se, 27·0. $C_{28}H_{24}O_2N_2Se_2$ requires C, 58·1 ; H, 4·15 ; N, 4·8 ; Se, 27·3%).

Di-o-*formylaminodiphenyl Diselenide*.—The deposit A, obtained from the formylation of *o*-aminoselenophenol, crystallised from alcohol (charcoal) in soft, pale yellow needles, m. p. 174°. Analysis showed it to be *di*-o-*formylaminodiphenyl diselenide*, which must have been produced by atmospheric oxidation of aminoselenophenol to the corresponding diselenide, followed by formylation of the amino-groups (Found : C, 42·4 ; H, 3·1 ; N, 7·0. $C_{14}H_{12}O_2N_2Se_2$ requires C, 42·2 ; H, 3·0 ; N, 7·0%).

Preparation of Benzselenazole from Di-o-*formylaminodiphenyl Diselenide*.—The diselenide (1·8 g.), dissolved in alcohol–acetone, was reduced with excess of stannous chloride in dilute hydrochloric acid solution. The mixture was heated at 100° for ½ hour and then evaporated to dryness. The residue was treated with sodium hydroxide solution and the oil liberated was taken up in ether, dried over sodium carbonate, and distilled in a vacuum. The distillate was heated with excess of methyl iodide at 70—80° for 4 hours, the uncombined methyl iodide boiled off, and the partly crystalline residue dissolved in acetone; on addition of ether to this solution a crystalline deposit was formed which, after purification, melted at 187°, alone or when mixed with authentic benzselenazole methiodide.

Reaction between o-*Diformylaminodiphenyl Diselenide and Phenylhydrazine*.—The diselenide (0·5 g.) was heated with phenylhydrazine (1·2 g.) at 100° for 3 hours and the orange-red oil produced was cooled and diluted with ether; colourless plates of α-formylphenylhydrazine were deposited; these, after crystallisation from water, had m. p. 144°, alone or when mixed with an authentic specimen.

A satisfactory method for the estimation of selenium in organic compounds of the type described in this paper is as follows : The compound is decomposed by treatment with 50 c.c. of 8% potassium permanganate solution and 10 c.c. of concentrated nitric acid. The mixture is evaporated to dryness on the steam-bath, 10 c.c. of the permanganate solution and 5 c.c. of nitric acid are added to the residue, and the evaporation is repeated. The addition of permanganate and acid and the evaporation are repeated, 80 c.c. of concentrated hydrochloric acid are added to the residue, and the mixture is boiled until chlorine and nitric acid are removed. The solution is then diluted and selenium determined by reduction with sulphurous acid.

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