CXXVIII.—*Derivatives of 2-Keto-1 : 2-dihydrobenziso-thiazole.**

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IT has been suggested (McClelland and Longwell, J., 1923, **123**, 3310) that the first stage in the production of the disulphide (I) from 2-dithiobenzoyl and a primary amine is the formation of

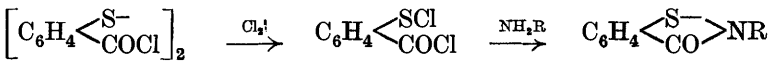
* Named " 2-thiobenzimide " in previous papers.

hydrogen sulphide and a ketodihydrobenz*iso*thiazole (II). It was pointed out that these benz*iso*thiazoles, if formed, would be

very easily reduced to the corresponding disulphides and that the failure to isolate them was probably due to their reduction by the hydrogen sulphide.

Such compounds appear to be unknown and the present investigation was undertaken with the object of synthesising them and examining their stability towards hydrogen sulphide.

Attempts to prepare 2-keto-1-phenyl-1 : 2-dihydrobenz*iso*thiazole by the intramolecular condensation of (I; R = Ph), which in the presence of sulphuric acid might be expected to react as the sulphenic acid, $NHPh{\cdot}CO{\cdot}C_6H_4{\cdot}S{\cdot}OH$ (compare Prescott and Smiles, J., 1911, **99**, 640), were unsuccessful. According to patent literature (D.R.P.-anm. F. 35230), 2 : 2′-dithiobenzoic acid on treatment with chlorine yields a sulphur chloride, $CO_2H{\cdot}C_6H_4{\cdot}SCl$. It was therefore to be expected that 2 : 2′-dithiobenzoyl chloride would also yield a sulphur chloride (III) and that this dichloride would condense with primary amines to give the required *N*-substituted ketodihydrobenz*iso*thiazoles (II) thus :



2 : 2′-Dithiobenzoyl chloride, suspended in carbon tetrachloride, dissolved on treatment with dry chlorine, presumably owing to the formation of the dichloride (III). This chlorinated solution reacted with aqueous ammonia to give 2-keto-1 : 2-dihydrobenz*iso*thiazole. In a similar way the chlorinated solution reacted with aniline, *o*-toluidine, and aqueous methylamine to give compounds of the type (II) in which R is Ph, o-C_6H_4Me, and Me, respectively. On oxidation with hydrogen peroxide these compounds were converted into the corresponding "saccharins." The interaction of the chlorinated solution of 2 : 2′-dithiobenzoyl chloride with *n*-propylamine yielded an oily substance which was undoubtedly 2-*keto*-1-n-*propyl*-1 : 2-*dihydrobenz*iso*thiazole*, as on oxidation it was converted into N-n-*propyl*-o-*benzoicsulphinide*.

The 1-*phenyl*, 1-o-*tolyl*, and 1-*methyl* derivatives of 2-keto-1 : 2-dihydrobenz*iso*thiazole in alcoholic solution are rapidly reduced by hydrogen sulphide with deposition of sulphur and formation of disulphides identical with the products obtained by the action of the corresponding amines on 2-dithiobenzoyl. The afore-mentioned suggestion of McClelland and Longwell hereby receives strong

confirmation. 2-Keto-1 : 2-dihydrobenz*iso*thiazole also is reduced by hydrogen sulphide. The fact that it can be isolated by the action of ammonia on 2-dithiobenzoyl may be due to its being slightly more stable than its derivatives towards hydrogen sulphide, as previously suggested.

Selenium analogues of 2-keto-1 : 2-dihydrobenz*iso*thiazole and certain of its derivatives have been prepared by an analogous method (Lesser and Weiss, *Ber.*, 1924, **57**, 1077).

EXPERIMENTAL.

2 : 2′-Dithiobenzoyl chloride was prepared by the action of phosphorus pentachloride on 2 : 2′-dithiobenzoic acid (*Ber.*, 1898, **31**, 1670) and was crystallised from benzene before use in the following experiments.

The derivatives of 2-keto-1 : 2-dihydrobenz*iso*thiazole described below were prepared by the following general method. Dry chlorine was bubbled through a suspension of 2 : 2′-dithiobenzoyl chloride (5 g.) in carbon tetrachloride (40 c.c.; dried over calcium chloride) until solution was complete. The excess of chlorine having been removed by a current of dry air, the solution was added slowly, with vigorous stirring, to aqueous ammonia (40 c.c.; *d* 0·880), 30% aqueous methylamine (excess), or the amine (aniline, 8 g.; *o*-toluidine, 10 g.) diluted with carbon tetrachloride. During the addition the aqueous ammonia and the solutions of the amines were cooled in ice. The product of the reaction was either precipitated or obtained by evaporation of the dried carbon tetrachloride solution.

2-*Keto*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = H) was precipitated on addition of the chlorinated solution of 2 : 2′-dithiobenzoyl chloride to the aqueous ammonia and was crystallised from methyl alcohol and finally from water (yield 80%). It melted at 155—156°, alone or mixed with a specimen prepared by the action of ammonia on 2-dithiobenzoyl.

2-*Keto*-1-*phenyl*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = Ph). — In this preparation aniline hydrochloride was precipitated; it was filtered off and the carbon tetrachloride allowed to evaporate at room temperature. The residual solid crystallised from methyl alcohol in fine, colourless needles, m. p. 140° (Found: C, 68·4; H, 4·1; S, 13·9. $C_{13}H_9ONS$ requires C, 68·7; H, 4·0; S, 14·1%).

2-*Keto*-1-o-*tolyl*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = *o*-C_6H_4Me) was obtained as a brown oil which slowly solidified; after crystallisation from methyl alcohol it melted at 122—123° (Found: C, 69·7; H, 4·5; S, 13·4. $C_{14}H_{11}ONS$ requires C, 69·7; H, 4·5; S, 13·3%).

2-*Keto*-1-*methyl*-1 : 2-*dihydrobenz*iso*thiazole* (II; R = CH_3) was

obtained from the carbon tetrachloride after separation from the aqueous solution, as a brown oil which slowly solidified; it crystallised from benzene–light petroleum in fine, colourless needles, m. p. 51—52° (Found: C, 58·0; H, 4·3; S, 19·5. C_8H_7ONS requires C, 58·1; H, 4·3; S, 19·4%).

This *iso*thiazole is sparingly soluble in ether and light petroleum and very soluble in alcohol or benzene. On treatment with hydrochloric acid the crude oil obtained above yielded a *hydrochloride*, which was readily hydrolysed by water but crystallised from hydrochloric acid in colourless needles, m. p. 124—127°. The hydrochloride appears to be unstable, as varying results were obtained in the estimation of the chlorine and its melting point gradually fell on keeping in a vacuum desiccator.

N-n-*Propyl*-o-*benzoicsulphinide*, $C_6H_4<^{SO_2}_{CO}>N\cdot C_3H_7$.—A chlorinated solution of 2 : 2′-dithiobenzoyl chloride, prepared by the general method, was added to an excess of propylamine diluted with carbon tetrachloride. The solid material was filtered off, and the carbon tetrachloride evaporated. The oil thus obtained was oxidised in glacial acetic acid with hydrogen peroxide (30%). The product crystallised from water in fine, colourless needles, m. p. 73—75° (Found: S, 14·1; N, 6·1. $C_{10}H_{11}O_3NS$ requires S, 14·2; N, 6·2%).

*Oxidation of the Benziso*thiazoles.—A solution of 2-keto-1-phenyl-1 : 2-dihydrobenz*iso*thiazole (0·2 g.) in glacial acetic acid was heated with 30% hydrogen peroxide (1 c.c.) for 1 hour at 100°. On cooling, a white, crystalline product was obtained. This, after recrystallisation from glacial acetic acid, melted at 189—190°, and at 189° when mixed with authentic *N*-phenyl-*o*-benzoicsulphinide, m. p. 190·5° (*Amer. Chem. J.*, 1895, **17**, 320).

In a similar way 2-keto-1-*o*-tolyl-1 : 2-dihydrobenz*iso*thiazole yielded a substance, m. p. 171—173° (*N*-*o*-tolyl-*o*-benzoicsulphinide has m. p. 172—175°; *loc. cit.*, p. 327).

2-Keto-1-methyl-1 : 2-dihydrobenz*iso*thiazole (the crude oil) was instantly converted by cold hydrogen peroxide (30%) into a white, crystalline substance. This, after recrystallisation from glacial acetic acid and finally from methyl alcohol, melted at 129—130°, alone or mixed with *N*-methyl-*o*-benzoicsulphinide.

*Reduction of the Benziso*thiazoles.—Hydrogen sulphide was bubbled slowly through a solution of 2-keto-1-phenyl-1 : 2-dihydrobenz*iso*-thiazole in ethyl alcohol at 50°. In a few minutes a precipitate of sulphur appeared; the current of gas was then stopped, and the solution filtered as quickly as possible. The filtrate slowly deposited colourless needles contaminated with sulphur. After several crystallisations from glacial acetic acid, the product was obtained free from

sulphur; it melted at 236—238°, and at 237° when mixed with 2 : 2′-dithiobenzophenylamide (m. p. 239°), prepared by the action of aniline on 2-dithiobenzoyl.

2-Keto-1-*o*-tolyl-1 : 2-dihydrobenz*iso*thiazole, reduced in a similar way, gave a product which after recrystallisation from methyl alcohol melted at 219—220°, alone or mixed with the product obtained by the action of *o*-toluidine on 2-dithiobenzoyl.

The reduction of 2-keto-1-methyl-1 : 2-dihydrobenz*iso*thiazole by hydrogen sulphide, under the same conditions, yielded a substance which after crystallisation from glacial acetic acid and methyl alcohol melted at 220—221°, alone or mixed with 2 : 2′dithiobenzomethylamide, prepared by the action of methylamine on 2-dithiobenzoyl.

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