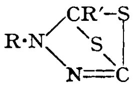
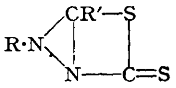
64. *Cyclic Meso-ionic Compounds. Part IV. ψ-4-Aryl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazoles* (" endo*Thiodihydrothiodiazoles* ").

By WILSON BAKER, W. D. OLLIS, A. PHILLIPS, and T. STRAWFORD.

ψ-4 : 5-Diaryl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazoles (III; R and R′ = aryl) containing chlorine have been prepared from *N*-aryl-*N*′-dithiocarboxyhydrazines, NHAr·NH·CS$_2$H, and aromatic acid chlorides in presence of alkali. These compounds were required for dipole moment investigation. The related 4-aryl compounds (III; R = aryl, R′ = H) were prepared in a new manner from aqueous alkaline solutions of *N*-aryl-*N*′-dithiocarboxyhydrazines and sodium dithioformate at room temperature. Benzylhydrazine and carbon disulphide gave 4-benzyl-2-mercapto-5-thio-Δ^2-1-thia-3 : 4-diazoline (V) in presence of alkali.

COMPOUNDS supposed to possess the stereochemically improbable structures (I) or (II) were first prepared by Busch and his co-workers (*Ber.*, 1895, **28**, 2635; *J. pr. Chem.*, 1899, **60**, 218, 228; 1903, **67**, 201, 216, 246, 257), who named them " *endo*thiodihydrothiodiazoles." Schönberg (*J.*, 1938, 824) preferred to represent them as monocyclic compounds containing the five-membered ring shown in (III), but possessing a hybrid structure derived from a number of dipolar forms. This view was supported by the work of Jensen and Friediger (*Kgl. Danske Videnskab. Selskab.*, 1943, **20**, 1) and of Edgerley and Sutton (forthcoming publication), who have shown that they possess high dipole moments. The nature of these and related substances which cannot be represented by simple co-valent formulæ has been discussed in earlier papers of this series (see especially Baker, Ollis, and Poole, Part I, *J.*, 1949, 311; Part III, *J.*, 1950, 1542) dealing mainly with the sydnones, and the term meso-ionic has been used there to describe such molecules. There is some difference between this method of describing the structure of these compounds and the proposals made by Schönberg; the reasons for regarding the resonance method for describing their structures as unsatisfactory were given in Part III. They are represented in, for example, the case of the " *endo*thiodihydrothiodiazoles " as shown in formula (III), and the systematic name given to the sydnones (see Part I) may be extended to these dithio-compounds which are, consequently, ψ-4-aryl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazoles.


(I.)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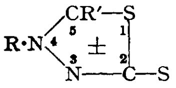
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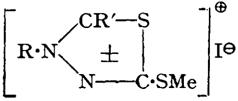
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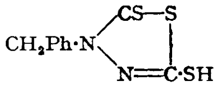
(V).

The ψ-4-aryl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazoles (III; R = aryl, R′ = alkyl or aryl) were prepared by Busch *et al.*, by interaction of an acid chloride with the potassium salt of *N*-aryl-*N*′-dithiocarboxyhydrazine, NHAr·NH·CS$_2$K. We have now prepared by this method, for dipole-moment investigations, the 5-*p*-chlorophenyl-4-phenyl, 4-*p*-chlorophenyl-5-phenyl, and 4 : 5-di-*p*-chlorophenyl compounds (III). In these preparations the formation of colourless intermediates was observed which slowly passed at room temperature into the yellow ψ-thiadiazoles (III). The intermediates were not investigated, but their insolubility in water and their solubility in organic solvents show that they are not salts; they may be mixed anhydrides NHAr·NH·CS·S·CO·R′.

ψ-4-Aryl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazoles unsubstituted in position 5 (III; R = aryl, R′ = H) have previously been prepared from the potassium salts of *N*-aryl-*N*′-dithiocarboxyhydrazines by reaction with ethyl formimidate hydrochloride (Busch and Schneider, *J. pr. Chem.*, 1903, **67**, 246). It has now been found that such compounds are more readily prepared from these potassium salts by treatment with sodium dithioformate in aqueous solution at room temperature, and by this method the 4-phenyl, 4-*p*-chlorophenyl, and 4-*p*-tolyl compounds (III; R′ = H) have been prepared.

All the above ψ-thiadiazoles form methiodides which are probably best represented as containing meso-ionic cations (IV), in agreement with the views of Schönberg, and of Jensen and Friediger (*loc. cit.*).

An attempt was made to prepare ψ-4-benzyl-2 : 4-dihydro-5-methyl-2-thio-1-thia-3 : 4-diazole (III; R = CH$_2$Ph, R′ = Me) from benzylhydrazine by reaction with carbon disulphide and potassium hydroxide, followed by treatment of the product with acetyl chloride. The products isolated—$C_9H_8N_2S_3$, m. p. 57°, and $C_{18}H_{14}N_4S_6$, m. p. 102°—were, however, derived only from benzylhydrazine and carbon disulphide, and were shown by direct synthesis to be 4-benzyl-2-mercapto-5-thio-Δ^2-1-thia-3 : 4-diazoline (V) and its disulphide produced by aerial oxidation. Benzylhydrazine, carbon disulphide, and alcoholic potassium hydroxide gave (V) (cf. Ziegele and Busch, *J. pr. Chem.*, 1899, **60**, 51), which when oxidised by ferric chloride gave the related disulphide previously isolated.

EXPERIMENTAL.

*ψ-5-*p*-Chlorophenyl-2 : 4-dihydro-4-phenyl-2-thio-1-thia-3 : 4-diazole* (III; R = Ph, R′ = *p*-C_6H_4Cl).—*p*-Chlorobenzoyl chloride (23·8 g.) was added dropwise during 2 hours to a stirred solution of the potassium salt of *N*′-dithiocarboxy-*N*-phenylhydrazine (30 g.; cf. Busch, *J. pr. Chem.*, 1899. **60**, 219) in water (200 c.c.) at room temperature. Next day the precipitate was collected and washed with hot ethanol (100 c.c.). The residue was dissolved in hot chloroform (250 c.c.), and hot ethanol (300 c.c.) added, giving *ψ-5-*p*-chlorophenyl-2 : 4-dihydro-4-phenyl-2-thio-1-thia-3 : 4-diazole* (12·5 g., 30%) as long, yellow, fibrous needles, m. p. 233—234° (decomp.) (Found: C, 54·8; H, 3·2; N, 9·6; S, 21·1; Cl, 11·5. $C_{14}H_9N_2S_2Cl$ requires C, 54·6; H, 3·0; N, 9·1; S, 20·8; Cl, 11·5%). The *methiodide* (cf. Busch, Kamphausen, and Schneider, *J. pr. Chem.*, 1903, **67**, 222) formed yellow plates (from ethanol–ether), m. p. 159—160° (Found: C, 40·1; H, 2·7; N, 6·3. $C_{15}H_{12}N_2S_2ClI$ requires C, 40·4; H, 2·7; N, 6·25%).

*ψ-4-*p*-Chlorophenyl-2 : 4-dihydro-5-phenyl-2-thio-1-thia-3 : 4-diazole* (III; R = *p*-C_6H_4Cl, R′ = Ph).—Reaction of benzoyl chloride (20·5 g.) with the potassium salt of *N*-*p*-chlorophenyl-*N*′-dithiocarboxyhydrazine [30 g.; see preparation of (III; R = *p*-C_6H_4Cl, R′ = H) below] in water (200 c.c.) gave a precipitate that was collected, dried, and kept in a desiccator for 5 days. Crystallisation from ethanol then gave *ψ-4-*p*-chlorophenyl-2 : 4-dihydro-5-phenyl-2-thio-1-thia-3 : 4-diazole* (10·5 g., 30%) as large, yellow needles, m. p. 185—187° (Found: C, 54·9; H, 3·0; N, 9·5; S, 21·2; Cl, 11·5. $C_{14}H_9N_2S_2Cl$ requires C, 54·6; H, 3·0; N, 9·1; S, 20·8; Cl, 11·5%). This compound showed a strong yellow fluorescence in ultra-violet light. The *methiodide* formed yellow plates (from chloroform–ether), m. p. 197—198° (decomp.) (Found: C, 41·0; H, 3·1; N, 5·7. $C_{15}H_{12}N_2S_2ClI$ requires C, 40·6; H, 2·7; N, 6·2%).

*ψ-4 : 5-Di-*p*-chlorophenyl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazole* (III; R = R′ = *p*-C_6H_4Cl).—In a similar manner *p*-chlorobenzoyl chloride (20·5 g.) and the potassium salt of *N*-*p*-chlorophenyl-*N*′-dithiocarboxyhydrazine (30 g.; see next paragraph) gave *ψ-4 : 5-di-*p*-chlorophenyl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazole* (10 g., 25%), orange plates (from *n*-butanol), m. p. 241—242° (decomp.) (Found: C, 49·9; H, 2·3; N, 8·55; S, 18·8; Cl, 20·8. $C_{14}H_8N_2S_2Cl_2$ requires C, 49·6; H, 2·4; N, 8·3; S, 18·9; Cl, 20·9%). The *methiodide* forms yellow plates (from chloroform–ether), m. p. 195—196° (decomp.) (Found: C, 37·1; H, 2·4; N, 5·5. $C_{15}H_{11}N_2S_2Cl_2I$ requires C, 37·4; H, 2·3; N, 5·8%).

*ψ-4-*p*-Chlorophenyl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazole* (III; R = *p*-C_6H_4Cl, R′ = H).—Carbon disulphide (9·4 c.c.) was added to a solution of *p*-chlorophenylhydrazine (20 g.) in ethanol (200 c.c.). After a few minutes, when the *p*-chlorophenylhydrazine salt of *N*-*p*-chlorophenyl-*N*′-dithiocarboxyhydrazine, $Cl{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CS_2\}NH_3{\cdot}NH{\cdot}C_6H_4Cl$, had separated, a solution of potassium hydroxide (8·6 g.) in ethanol (60 c.c.) was added. The precipitate dissolved and the crystalline potassium salt of *N*-*p*-chlorophenyl-*N*′-dithiocarboxyhydrazine separated, which was collected, washed with alcohol, then with ether, and dried. To this potassium salt in water (100 c.c.) was added sodium dithioformate (33 g.) in water (100 c.c.), and after 12 hours the crystalline precipitate (10·8 g., 31%) was collected, well washed with water, and dried. Crystallisation from ethanol (*ca.* 2 l.) gave *ψ-4-*p*-chlorophenyl-2 : 4-dihydro-2-thio-1-thia-3 : 4-diazole* as yellow platelets, m. p. 202·5° (decomp.) (Found: C, 42·4; H, 2·6; N, 12·3; Cl, 15·6; S, 28·0. $C_8H_5N_2ClS_2$ requires C, 42·0; H, 2·2; N, 12·3; Cl, 15·5; S, 28·0%).

ψ-2 : 4-Dihydro-4-phenyl-2-thio-1-thia-3 : 4-diazole (III; R = Ph, R′ = H).—This compound was prepared as in the previous case. To the potassium salt of *N*′-dithiocarboxy-*N*-phenylhydrazine in water (200 c.c.) was added sodium dithioformate (24 g.) in water. After 3 hours, the crystalline precipitate was collected, well washed, and crystallised from a large volume of ethanol, giving ψ-2 : 4-dihydro-4-phenyl-2-thio-1-thia-3 : 4-diazole (10 g., 58%) as yellow platelets, m. p. 189° [Busch, *Ber.*, 1895, **28**, 2640, gives m. p. 190° (decomp.)] (Found: C, 49·8; H, 3·1; N, 14·4. Calc. for $C_8H_6N_2S_2$: C, 49·5; H, 3·1; N, 14·4%).

*ψ-2 : 4-Dihydro-2-thio-4-*p*-tolyl-1-thia-3 : 4-diazole* (III; R = *p*-C_6H_4Me, R′ = H).—As in the previous cases, the potassium salt of *N*′-dithiocarboxy-*N*-*p*-tolylhydrazine (20 g.) and sodium dithioformate gave ψ-2 : 4-dihydro-2-thio-4-*p*-tolyl-1-thia-3 : 4-diazole. It separated from a large volume of ethanol as yellow platelets, m. p. 201° (7·7 g., 44%) (Busch, *J. pr. Chem.*, 1899, **60**, 222, gave m. p. 198°) (Found: C, 52·3; H, 3·4; N, 13·8. Calc. for $C_9H_8N_2S_2$: C, 51·9; H, 3·8; N, 13·5%).

4-Benzyl-2-mercapto-5-thio-Δ^2-1-thia-3 : 4-diazoline (V).—Carbon disulphide (3·8 c.c.) was added to a solution of benzylhydrazine (3 g.; Wohl and Oesterlin, *Ber.*, 1900, **33**, 2736) in ethanol (10 c.c.), and to the mixture a solution of potassium hydroxide (2·3 g.) in ethanol (10 c.c.) was added. After being heated under reflux for 8 hours, the mixture was poured into dilute hydrochloric acid and extracted with chloroform (50 c.c.), and the extract washed with water and then with 5% aqueous sodium hydrogen carbonate. Acidification of the alkaline layer and extraction with chloroform yielded a residue (4·0 g.) which solidified. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave the 3 : 4-*diazoline* as thick, yellow needles, m. p. 57° (Found: C, 45·2; H, 3·3; N, 11·8; S, 39·4%; equiv., 250. $C_9H_8N_2S_3$ requires C, 45·1; H, 3·3; N, 11·7; S, 40·1%; equiv., 240).

Di-(4-*benzyl*-5-*thio*-1-*thia*-3 : 4-*diazolin*-2-*yl*) *Disulphide.*—Ferric chloride (1 g.) in water (5 c.c.) was added to the foregoing thiol (150 mg.) in ethanol (3 c.c.), and after a few minutes water was added and the product extracted into chloroform. This extract was washed with aqueous sodium hydrogen carbonate and water and then dried ($MgSO_4$), and the solvent removed, leaving a residue (135 mg., 90%) which was crystallised from chloroform (2 c.c.)–light petroleum (3 c.c.; b. p 60—80°). The *disulphide* separated as light yellow needles, m. p. 102° [Found: C, 45·5; H, 3·1; N, 11·7; S, 39·6%; *M* (Rast) 460, 490. $(C_9H_7N_2S_3)_2$ requires C, 45·2; H, 2·9; N, 11·8; S, 40·2%; *M*, 478].

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[*Received, October* 21*st*, 1950.]