619. *Thiadiazoles. Part XIV.* A Link Between* sym-*Diaryldithioformamidines and "Hector's Bases."*

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sym-Diaryldithioformamidine hydrobromides are converted in methanol, with loss of sulphur, into *N*-aryl-*N*-arylamidinothiourea salts, also obtainable by oxidation of arylthioureas under specified conditions. *N*-Aryl-*N*-arylamidinothioureas and "Hector's bases" are interconvertible into each other by oxidation–reduction.

The results lend support to the formulation of "Hector's bases" as 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidines, and to the view that their formation by oxidation of arylthioureas involves *sym*-diaryldithioformamidines as intermediates.

THE part played by aromatic dithioformamidines (I) in the formation of so-called "Hector's bases" [1-3] by oxidation of arylthioureas has so far remained undecided: the possibility of their intermediate formation was favoured [4,5] or rejected [6] by different workers. *sym*-Diaryldithioformamidines (I), first described recently,[7,8] are labile compounds: the free bases decompose instantly with elimination of sulphur, and their salts, though stable in the solid state, also tend to deposit sulphur more or less rapidly, according to the conditions, when dissolved in polar solvents.[7,8] The nature of this reaction, and the interrelation of the resulting products with Hector's bases, are now described.[9]

In boiling methanol, *sym*-diphenyldithioformamidine dihydrobromide (I; R = Ph, X = Br) rapidly eliminated one gram-atom of sulphur, affording good yields of *N*-phenyl-*N*-phenylamidinothiourea hydrobromide (VII; R = Ph, X = Br). The same change occurred more slowly at lower temperatures; in other solvents, *e.g.*, acetone, the yields were somewhat reduced. The formulation of the product (as VII; R = Ph) is based on its chemical behaviour and on an alternative synthesis (see below).

N-Aryl-*N*-arylamidinothioureas (VII) were cleaved remarkably readily into the *sym*-diarylguanidines (VIII) and thiocyanic acid. Thus, alkalis precipitated diphenylguanidine

* Part XIII, preceding paper.

[1] Hector, *Ber.*, 1889, **22**, 1176; 1890, **23**, 357; *Oefvers. Kongl. Vet. Akad.*, 1892, 79 (*Ber.*, 1892, **25**, 799 ref.).

[2] Bambas, "The Chemistry of Heterocyclic Compounds," Interscience Publ., Inc., New York, 1952, Vol. IV, pp. 35, 54.

[3] Sherman, in Elderfield's "Heterocyclic Compounds," Wiley, New York, 1961, Vol. VII, pp. 558, 573.

[4] Fromm and Heyder, *Ber.*, 1909, **42**, 3804.

[5] Patel and Chakravarty, *J. Indian Inst. Sci.*, 1930, **13**, *A*, 85; De and Chakravarty, *J. Indian Chem. Soc.*, 1928, **5**, 661.

[6] Lal and Krall, *J. Indian Chem. Soc.*, 1939, **16**, 31; Krall and Sagar, *ibid.*, 1940, **17**, 475; Sahasrabudhey and Krall, *ibid.*, 1945, **22**, 37.

[7] Kurzer and Sanderson, *J.*, 1957, 4461.

[8] Kurzer and Sanderson, *J.*, 1959, 1058.

[9] A preliminary summary of the present results appeared in *Chem. and Ind.*, 1962, 1681.

from boiling solutions of *N*-phenyl-*N*-phenylamidinothiourea hydrobromide (VII; R = Ph, X = Br), thiocyanate being titratable in the filtrate. At lower temperatures, diphenylguanidine thiocyanate was precipitated almost quantitatively. The use of ammonia at 0° afforded the free base (cf. VII) as a low-melting labile solid, the identity of which was demonstrated by its immediate conversion into *N*-phenyl-*N*-phenylamidinothiourea picrate. However, on brief storage, contact with water, or attempted crystallisation from organic solvents, it was again rapidly converted into diphenylguanidine thiocyanate. Salts (VII) of the amidinothioureas were reasonably stable, but underwent the same reaction under certain conditions: aqueous solutions of the hydrobromide (VII; R = Ph, X = Br) gave, after short boiling, a positive thiocyanate reaction. The picrate (VII; R = Ph, X = $C_6H_2N_3O_7$), though crystallising from suitable solvents in the cold, was converted into diphenylguanidine picrate at higher temperatures.

By condensing phenylthiourea (III; R = Ph) and phenylcyanamide (II; R = Ph) in the presence of hydrochloric acid, Joshua, Verma, and Suresh [10] have recently synthesised *N*-phenyl-*N*-phenylamidinothiourea hydrochloride (VII; R = Ph, X = Cl). Its identity with our product from *sym*-diphenyldithioformamidine (I; R = Ph) has now been proved by comparison of the hydrobromides and picrates obtained by both methods. The structure assigned by Joshua *et al.*[10] to the thiourea–cyanamide condensation product is confirmed. Of the three possible structures (IV, VII, and IX), structure (IV) is excluded by the non-identity of the product with authentic *N*-phenyl-*N'*-phenylamidinothiourea, the structure of which is established in the preceding paper.[11] The alternative monosulphide formulation (IX) is not reconciled as readily with the observed rapid fission of the product into diarylguanidine and thiocyanate as is structure (VII). Moreover, bisamidino-sulphides of type (IX) would be expected to be diacid bases.[12,13] The present synthesis of compounds (VII) is thus an extension of Matsui and Ishikawa's general method [12,14] of preparing *N*-thioaroylamidines from thioamides and nitriles in the presence of hydrogen chloride:

$$RCN + R{\cdot}CS{\cdot}NH_2 \longrightarrow R{\cdot}C(:NH){\cdot}NH{\cdot}CS{\cdot}R$$

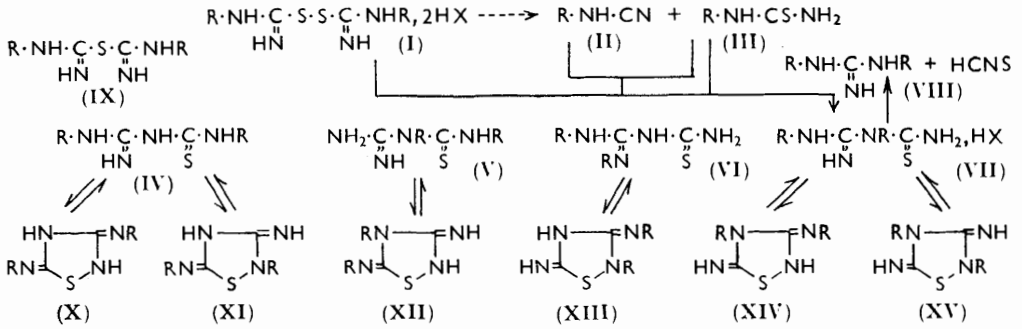
The results of this synthesis (II + III ⟶ VII) also suggest that the conversion of *sym*-dithioformamidine salts (I) into *N*-aryl-*N*-arylamidinothioureas (VII) now reported involves their preliminary fission into sulphur, cyanamide (II), thiourea (III), and hydrohalide: the resulting fragments thus arise under precisely the conditions of the synthesis of compound (VII). Support for this view is provided by the isolation of small quantities of arylthioureas (III) as by-products in this reaction, particularly in the case of the *p*-tolyl homologue, where recombination to (VII) appears to be less complete. Also, oxidation of phenylthiourea by 0·5 mol. of hydrogen peroxide in boiling methanol containing hydrohalide afforded good yields of *N*-phenyl-*N*-phenylamidinothiourea (VII), which was presumably formed from the primary diphenyldithioformamidine (I) by the same mechanism. The isolation of a diaryldithioformamidine (I; R = 2,6-$C_6H_3Me_2$) by this procedure, except for the use of low temperatures, is on record.[7]

The reduction of Hector's bases (XIV) under a variety of conditions yields *sym*-diarylguanidines.[1–3,10,15] The use of hydrogen sulphide at room temperature, in conjunction with aqueous or preferably methanolic hydrohalogen acids as solvents, has now provided a fourth route to *N*-aryl-*N*-arylamidinothioureas, affording the appropriate salts (VII; R = Ph, *p*-C_6H_4Me, or *p*-C_6H_4Cl) in excellent yields. On the basis of the proposed structure (XIV) for Hector's bases (see below), this reduction involves simply the usual

[10] Joshua, Verma, and Suresh, *Tetrahedron Letters*, 1961, 663.
[11] Kurzer and Sanderson, preceding paper.
[12] Goerdeler and Porrmann, *Chem. Ber.*, 1961, **94**, 2856; 1962, **95**, 627.
[13] Chabrier, Renard, and Renier, *Compt. rend.*, 1952, **235**, 64.
[14] Matsui, *Mem. Coll. Sci. (Eng.), Kyoto Imperial Univ.*, 1909—1910, **2**, 401; Ishikawa, *J. Chem. Soc. Japan*, 1921, **42**, 579; *Sci. Papers Inst. Phys. Chem. Res., Tokyo*, 1925, **3**, 147; 1928, **7**, 277.
[15] Dost, *Ber.*, 1906, **39**, 863.

cleaving of the S–N bond of the heterocyclic system, already familiar from a variety of related 1,2,4-thiadiazoles.[16] It proceeded so smoothly without side-reactions that it may well be the first stage in all reductions of Hector's bases to diarylguanidines. *N*-Aryl-*N*-arylamidinothioureas were readily re-oxidised to Hector's bases by bromine or hydrogen peroxide (see also ref. 10).

N-Aryl-*N*-arylamidinothioureas (VII) thus form a link between aromatic dithioformamidines (I) and Hector's bases; this relationship provides additional information concerning the structure and mechanism of formation of the latter. Hector's bases, readily obtained by oxidation of arylthioureas in polar solvents in the presence of mineral acids, were originally represented as 2,4-diaryl-3,5-di-imino-1,2,4-thiadiazolidines (XV) by their discoverer.[1] Certain shortcomings of this formulation revealed by later work,



For the purpose of uniformity, thiadiazolidine structures are written throughout, tautomeric forms being implied whenever applicable.

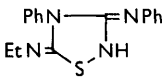
and alternative isomeric thiadiazolidine structures that were considered at various times, have been summarised by Bambas [2] and by Sherman.[3] Because of the inadequacy of the available evidence, however, the original formulation (XV) was in general retained.

The correctness of a 1,2,4-thiadiazolidine structure for Hector's bases is supported by the analogous oxidation of aromatic thioamides [17] to 3,5-diaryl-1,2,4-thiadiazoles of established structure.[12,14] On this basis, the oxidation product of phenylthiourea may have one of six possible structures (X—XV; R = Ph), reducible theoretically by the usual ring-opening at the S–N bond [16] to one of four substituted amidinothioureas (IV—VII), and re-formed therefrom on oxidation. Of these six alternatives, (X) and (XI) are excluded by the non-identity of Hector's base (R = Ph) with the oxidation product of authentic *N*-phenyl-*N'*-phenylamidinothiourea (IV).[11] Structures (X), (XI), and (XII) are ruled out by the demonstrated near-quantitative reduction of Hector's bases to *sym*-diarylguanidines.[1-3,10,15] Barring rearrangements, neither amidinothiourea (V) nor (VI) can arise from phenylcyanamide and phenylthiourea, so that structures (XII) and (XIII) are also excluded. The ready interconvertibility of Hector's bases and compound (VII) by reduction–oxidation thus leaves a choice between (XIV) and (XV) for the structure of the former compounds. A decision in favour of (XIV) is based on the assumption that a free amino- rather than the anilino-group is involved in the oxidative cyclisation to the 1,2,4-thiadiazolidine system (VII ⟶ XIV). Although anilino-groups have been observed to participate in cyclisations of this type, no free amino-groups were available in such examples.[18] With this reservation, Hector's bases are now represented, in agreement with the proposal of Joshua, Verma, and Suresh,[10] as 4-aryl-3-arylimino-5-imino-1,2,4-thiadiazolidines (XIV).

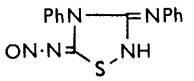
Although both formulations (XIV) and (XV) for Hector's bases agree with their formation from arylthioureas [1-3] and their reduction to *sym*-diarylguanidines,[1-3,10,15] the

[16] Kurzer, *J.*, 1955, 1, and subsequent papers.
[17] Hofmann, *Ber.*, 1869, **2**, 645; Hofmann and Gabriel, *Ber.*, 1892, **25**, 1578.
[18] Kurzer and Sanderson, *J.*, 1960, 3240.

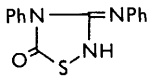
properties of these monoacid [1,4] bases are reflected more truly by structure (XIV) than by (XV). The presence of only one imino-group in the preferred formulation (XIV) accounts particularly for the observed exclusive formation of monoalkyl,[1] monoacyl,[1] and mononitroso-derivatives [1] of Hector's bases, and for their conversion into monoketo-compounds.[15] The *N*-ethyl derivative of (XIV; R = Ph), reducible to *sym*-diphenylguanidine and ethylamine, is therefore regarded as (XVI), and the nitroso-derivative as (XVII). Dost's non-basic keto-compound,[15] which is also reducible to *sym*-diphenylguanidine but no longer yields acyl-derivatives,[15] is represented by (XVIII). Finally, the isomerisation of Hector's bases to 3,5-diarylamino-1,2,4-thiadiazoles [11,15] is accounted for more simply in terms of structure (XIV) than (XV). Whatever the mechanism, the former requires the migration of only one aryl group, while the latter presupposes two such changes.



(XVI)



(XVII)



(XVIII)

The connexion between diaryldithioformamidines (I) and Hector's bases (XIV) now demonstrated provides strong evidence for the view that the oxidation of aromatic thioureas proceeds by the following sequence of changes: I ⟶ II + III ⟶ VII ⟶ XIV. In particular, this interpretation accounts for the contrasting oxidation of arylthioureas to Hector's bases in acidic polar solvents where intermediate disulphide formation is favoured, and to benzothiazoles [19] in non-polar neutral solvents where a free-radical mechanism may operate.

Experimental

The solvent of M-bromine was chloroform, unless otherwise stated. Light petroleum had b. p. 60—80°.

N-*Phenyl*-N-*phenylamidinothiourea* (cf. VII; R = Ph).—(*a*) *From the dithioformamidine.* Freshly prepared *sym*-diphenyldithioformamidine dihydrobromide dihydrate (36·0 g., 0·072 mole) [obtained,[8] in three batches, from phenylthiourea (3 × 7·6 g., 0·15 mole)] was dissolved in methanol (75 ml.) with heating, and the liquid boiled during 5 min. to coagulate the precipitated sulphur. The mixture was allowed to cool to room temperature, the sulphur (1·25—1·4 g., 55—60%) filtered off and rinsed with cold acetone (30—40 ml.), and the clear filtrate was gradually diluted with ether (250—300 ml., each time to incipient turbidity). When stored at 0° during 2—3 days, the solution slowly deposited prisms of the product which were collected at 0° and rinsed with ether [m. p. 165—167° (decomp.); 12·6—15·7 g., 50—62%] (filtrate F). Crystallisation from methanol–acetone–ether (4, 4, and 30 ml. per g., recovery 90%) gave prisms of N-*phenyl*-N-*phenylamidinothiourea hydrobromide*, m. p. 165—167° (decomp. to a yellow froth, after sintering at 162—164°). The salt may also be crystallised from boiling acetone–water(18 and 3 ml. per g.)–ether (recovery, 75%), yielding microprisms (Found: C, 47·4, 48·5; H, 4·4, 4·1; N, 15·7, 15·9; S, 8·7; Br, 21·45. $C_{14}H_{14}N_4S$,HBr requires C, 47·9; H, 4·3; N, 16·0; S, 9·1; Br, 22·8%). The bromine was determined gravimetrically: Volhard's method (use of nitrobenzene), applicable to *sym*-diphenyldithioformamidine dihydrobromide,[8] failed with the present hydrobromide, the end-point being obscured, probably owing to liberation of thiocyanate from the amidinothiourea salt (see below).

On spontaneous evaporation at room temperature, filtrate F gave an orange, syrupy, strongly acid liquid containing a crystalline deposit. The liquid (L) was decanted, and the solid (3—4 g.) was collected, washed with a little water and fractionated by methanol as above, into sulphur (0·3 g., 13%) and *N*-phenyl-*N*-phenylamidinothiourea hydrobromide, m. p. and mixed m. p. 166—168° (decomp.) (up to 2·5 g., 10%). The final filtrates therefrom gave, in some but not all experiments, small quantities (0·2—0·5 g.) of phenylthiourea, m. p. and mixed m. p. 152—153°. The viscous liquid L contained only intractable oils.

N-Phenyl-*N*-phenylamidinothiourea hydrobromide is sparingly soluble in cold, fairly

[19] Sprague and Land, in Elderfield's "Heterocyclic Compounds," Wiley, New York, 1957, Vol. V, pp. 511, 581.

soluble in hot water. Its aqueous solution gives no deep-red colour with ferric chloride, but does so after having been briefly boiled. Hot alkaline sodium plumbite gives black lead sulphide.

Boiling aqueous acetone (6 ml. of acetone and 1 ml. of water per g. of dithioformamidine salt) was less suitable for performing the above reaction; the resulting yellow liquid retained some of the sulphur in solution, and yields were lower (30—40%). The dithioformamidine salt also decomposed slowly in the same way when its cold methanolic solution was kept at room temperature for several hours or at 0° for longer periods, or when its cold methanolic solution (3 g. in 20 ml.) was diluted to incipient turbidity with ether; in the last case, the resulting yellow liquid slowly deposited the amidinothiourea salt (45%) directly.

A solution of the hydrobromide (0·88 g., 0·0025 mole) in cold water (120 ml.), treated with aqueous 0·05M-picric acid (50 ml., 0·0025 mole), gave a precipitate (m. p. 143—145°; 1·12 g., 90%) which consisted, after crystallisation from cold acetone–methanol (1 : 1, partial evaporation), of felted yellow needles of N-*phenyl*-N-*phenylamidinothiourea picrate*, m. p. 144—145° (decomp.) (Found: C, 48·3; H, 3·3; N, 19·4; S, 6·15. $C_{14}H_{14}N_4S,C_6H_3N_3O_7$ requires C, 48·1; H, 3·4; N, 19·6; S, 6·4%). An attempted crystallisation from warm acetone, followed by addition of water, converted the material into *sym*-diphenylguanidine picrate, m. p. and mixed m. p. 171—172°.

(*b*) *By reduction of* 5-*imino*-4-*phenyl*-3-*phenylimino*-1,2,4-*thiadiazolidine*. A slow stream of dry hydrogen sulphide was passed through a solution of the reactant (1·34 g., 0·005 mole) in methanol (15 ml.) and 60% hydrobromic acid (0·75 ml.) at room temperature during 1 hr.; sulphur was precipitated rapidly. The dissolved hydrogen sulphide was boiled off, and the cooled liquid was filtered from the coagulated sulphur and diluted with ether to incipient crystallisation. The deposited crystals, collected at 0° [m. p. 164—166° (decomp.); 1·5 g., 85%] were *N*-phenyl-*N*-phenylamidinothiourea hydrobromide, m. p. 164—165° (decomp.) (from methanol–ether), the identity of which was confirmed by conversion into the picrate, m. p. and mixed m. p. 144—145° (decomp.), and into *sym*-diphenylguanidine thiocyanate (see below), m. p. and mixed m. p. 119—120°.

The use of concentrated hydrochloric acid (instead of 60% hydrobromic acid) gave the corresponding hydrochloride, m. p. and mixed m. p. (with product *d*, below) 157—158° (decomp.), in 90% yield. The use of 3% aqueous hydrobromic acid (12 ml.) as solvent gave, on storage, a mixture of sulphur and the above hydrobromide; the latter, when extracted by boiling methanol (5 and 3 ml.) and crystallised as before, was obtained in 70—75% yield.

The thiadiazolidine was recovered when sulphur dioxide was used in place of hydrogen sulphide as reducing agent, under the above conditions.

5-Imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine, when treated in boiling 3N-hydrochloric acid with a stream of hydrogen sulphide, gave a precipitate of sulphur. Basification of the filtered solution with 3N-sodium hydroxide gave *sym*-diphenylguanidine in good yield.

(*c*) *By oxidation of phenylthiourea*. A boiling solution of phenylthiourea (3·04 g., 0·02 mole) in methanol (10 ml.) and 60% aqueous hydrobromic acid (1 ml.) was treated dropwise with 30% hydrogen peroxide (1·1 ml., 0·01 mole), heated on the steam-bath until the precipitated sulphur (0·24 g., 75%) had coagulated (5—10 min.), and allowed to cool to room temperature. The filtrate therefrom, when diluted with acetone and ether (as above), gave *N*-phenyl-*N*-phenylamidinothiourea hydrobromide, m. p. 164—165° (decomp.) (2·15 g., 62%).

The alternative use of 10N-hydrochloric acid (1 ml.) and ethanol (10 ml.) gave the corresponding hydrochloride, m. p. 157—158° (decomp.) (45%). This was convertible almost quantitatively into the picrate, m. p. and mixed m. p. (with picrate from *a*) 144—145° (decomp.).

(*d*) A solution of phenylthiourea (1·52 g., 0·01 mole) in acetone (25 ml.), methanol (5 ml.), and 60% hydrobromic acid (1·5 ml.) was treated at room temperature with phenylcyanamide (1·18 g., 0·01 mole) and heated to the b. p. The cooled clear liquid was diluted with ether to incipient turbidity. Storage at room temperature and later at 0° gave prisms (3·15 g., 90%) of *N*-phenyl-*N*-phenylamidinothiourea hydrobromide, m. p. and mixed m. p. (with specimen *a*) 164—165° (decomp.). The picrate therefrom had m. p. and mixed m. p. (with picrate *a*) 144—145° (decomp.).

The corresponding hydrochloride, m. p. 157—158° (decomp.) was similarly obtained in 80% yield by using hydrochloric acid, *i.e.*, by the method of Joshua, Verma, and Suresh.[10] The picrate therefrom had m. p. and mixed m. p. (with the above picrate, and that from *a*) 144—145° (decomp.).

(*e*) *Free base.* The hydrobromide (1·75 g., 0·005 mole) was dissolved in water (50 ml.) by heat, then the solution was cooled to 0° and carefully basified (ice) with 3N-ammonia. The white precipitate was collected at once and washed with small portions of water (the aqueous filtrate was free from thiocyanate ions). Small portions of the base, dried rapidly on a porous plate, had m. p. 75—77° (resolidifying at ~80°, and remelting at about 120°), but on short storage, or on dissolution in organic solvents (including ether, ethanol, chloroform), or on contact with water, the base changed rapidly and quantitatively into *sym*-diphenylguanidine thiocyanate, m. p. and mixed m. p. 119—120°.

The *freshly* precipitated base was reconvertible into the picrate, m. p. and mixed m. p. 145—146° (decomp.) (overall recovery 65%) (Found: C, 48·5; H, 3·8%), on being added to stirred hot 5% ethanolic picric acid (23 ml., 0·005 mole), or into the hydrobromide, m. p. and mixed m. p. 165—166° (decomp.) (overall recovery, 70%), by means of methanol–hydrobromic acid–ether.

Reactions of N-*Phenyl*-N-*phenylamidinothiourea.*—(*a*) *Action of alkali.* (i) The hydrobromide (3·51 g., 0·01 mole) was dissolved in the minimum of boiling water (25 ml.), and the liquid was filtered to remove a turbidity of sulphur if necessary, cooled to 0°, and just made alkaline with 3N-sodium hydroxide. The resulting precipitate was collected at 0°, rinsed with a little ice–water, dried (m. p. 115—116°; 2·25—2·5 g., 84—92%), and crystallised from a little acetone–ether, affording needles of sym-*diphenylguanidine thiocyanate*, m. p. and mixed m. p. (see below) 119—120° (Found: C, 61·9; H, 5·2; N, 20·6; S, 11·7. $C_{13}H_{13}N_3$,HCNS requires C, 62·2; H, 5·2; N, 20·7; S, 11·85%). This salt was converted by picric acid in aqueous solution almost quantitatively into *sym*-diphenylguanidine picrate, m. p. 171—172° (decomp.) (Found: C, 51·9; H, 3·6. Calc. for $C_{13}H_{13}N_3$,$C_6H_3N_3O_7$: C, 51·8; H, 3·6%).

(ii) The finely powdered hydrobromide (0·88 g., 0·0025 mole) was refluxed with 1·5N-sodium hydroxide (10 ml.) during 15 min. The resulting white suspended solid, collected at room temperature, was *sym*-diphenylguanidine (0·45 g., 85%; m. p. and mixed m. p. 147—148°, from aqueous ethanol). The aqueous filtrate, acidified with 10N-nitric acid, was treated with 0·2N-silver nitrate (30 ml., 0·006 mole) and rapidly filtered quantitatively: the filtrate required 12·5 ml. of 0·1N-potassium thiocyanate (indicator, ferric alum), corresponding to a 90% yield of thiocyanate in the above hydrolytic decomposition.

(*b*) *Action of alkaline sodium plumbite.* The hydrobromide (1·75 g., 0·005 mole) was added to a boiling solution of lead acetate trihydrate (3·80 g., 0·01 mole) in 3N-sodium hydroxide (50 ml.), and boiling was continued during 5 min. The resulting black precipitate was collected at room temperature, dried, and exhaustively extracted with boiling ethanol (4 × 10 ml.). The combined filtered extracts gave, on partial evaporation and dilution with water, *sym*-diphenylguanidine, m. p. and mixed m. p. 146—148° (90%).

(*c*) *Oxidation.* (i) A solution of the hydrobromide (0·88 g., 0·0025 mole) in methanol (6 ml.) rapidly absorbed M-bromine (2·5 ml., 0·0025 mole). The soft semicrystalline residue obtained on spontaneous evaporation of the resulting liquid at room temperature was dissolved in 3N-hydrochloric acid. Basification of the filtered solution with ammonia gave a white precipitate (0·6 g.), which crystallised from methanol–acetone (1 : 1) to afford lustrous cubes of 5-imino-4-phenyl-3-phenylimino-1,2,4-thiadiazolidine, m. p. and mixed m. p. 185—186° (after shrinking at 180°) (0·49 g., 73%).

(ii) A boiling solution of the reactant (0·0025 mole) in methanol (10 ml.) containing concentrated hydrochloric acid (2 drops) was treated with 30% hydrogen peroxide (0·6 ml., 0·005 mole) dropwise during 1 min. The resulting slightly turbid liquid was boiled during 5 min., cooled, filtered, diluted with water (50 ml.), and basified with 3N-sodium hydroxide. The precipitate was the same 1,2,4-thiadiazolidine, m. p. and mixed m. p. 185—186° (from methanol–acetone) (0·45 g., 67%).

sym-*Diphenylguanidine Thiocyanate.*—*sym*-Diphenylguanidine (2·10 g., 0·01 mole) was dissolved in water (30 ml.) and concentrated hydrochloric acid (1 ml., 0·01 mole) with heat, and the filtered cooled solution was treated with ammonium thiocyanate (0·76 g., 0·01 mole) in water (5 ml.). The precipitated oil solidified on occasional stirring and cooling; it was collected at 0° (m. p. 117—119°; 2·10 g., 78%) and crystallised from acetone–ether, giving needles of the thiocyanate, m. p. 119—120°.

N-p-*Tolyl*-N-p-*tolylamidinothiourea.*—(*a*) *From the dithioformamidine. sym*-Di-*p*-tolyldithioformamidine dihydrobromide [8] (4·92 g., 0·01 mole) was boiled in methanol (10 ml.) during 2—3 min., and the coagulated sulphur filtered off. On cooling to room temperature, the filtrate

gave (in some but not all experiments) *p*-tolylthiourea, m. p. and mixed m. p. 181—182° (up to 0·6 g., 36%). The filtrate therefrom, after being diluted with acetone (10 ml.) and with ether (to incipient turbidity) gave crystals (1·35—1·85 g., 33—45%), which consisted, after crystallisation from cold methanol–acetone–ether, of prisms of the *hydrobromide*, m. p. 162—164° (decomp.) (Found: C, 49·5; H, 4·9; N, 13·5; S, 8·0; Br, 20·5. $C_{16}H_{18}N_4S$,HBr,MeOH requires C, 49·65; H, 5·6; N, 13·6; S, 7·8; Br, 19·4%). The salt remained solvated after being kept at 110—115° during 1 hr. [m. p. 162—164° (decomp.)] (Found: C, 49·7; H, 4·7%). The high solubility of the salt in cold methanol partly accounts for the low yields.

The hydrobromide was water-soluble; the solution gave no reaction with ferric chloride (absence of thiocyanate). Dilute nitric acid and silver nitrate gave a yellow precipitate presently becoming black.

A freshly prepared solution of the finely powdered hydrobromide (0·205 g., 0·0005 mole) in cold water (50 ml.), when treated with 0·05M-aqueous picric acid (10 ml., 0·0005 mole), gave a crystalline precipitate of the *picrate*, m. p. 144—145° (decomp., after sintering from 140°) almost quantitatively (Found: C, 49·7; H, 3·9; N, 18·0; S, 5·8. $C_{16}H_{18}N_4S,C_6H_3N_3O_7$ requires C, 50·1; H, 4·0; N, 18·6; S, 6·1%).

(*b*) *By reduction of* 5-*imino*-4-p-*tolyl*-3-p-*tolylimino*-1,2,4-*thiadiazolidine*. A solution of the reactant (3·0 g., 0·01 mole) in methanol (10 ml.) and 60% hydrobromic acid (1 ml.) was treated at room temperature with hydrogen sulphide during 30 min. The dissolved hydrogen sulphide was expelled by short boiling, the coagulated sulphur filtered off, and the filtrate diluted with ether gradually during several hours. The deposited crystals, collected after prolonged storage [m. p. 160—162° (decomp.); 3·10 g., 75%] and then crystallised as above, consisted of (solvated) *N*-*p*-tolyl-*N*-*p*-tolylamidinothiourea hydrobromide, m. p. and mixed m. p. (with product from *a*) 161—163° (decomp.) (Found: C, 49·2, 50·3; H, 5·3, 4·8; N, 13·9, 14·1; S, 7·9, 7·9; Br, 19·9%).

(*c*) Interaction of *p*-tolylthiourea and *p*-tolylcyanamide (0·01 mole each) in methanol (5 ml.), acetone (10 ml.), and hydrobromic acid (as described for the phenyl homologue) gave the solvated hydrobromide, m. p. 162—163° (decomp.) (2·85 g., 70%). The picrate therefrom had m. p. and mixed m. p. (with picrate *a*) 145—146° (decomp.).

Reactions of N-p-*Tolyl*-N-p-*tolylamidinothiourea*.—(*a*) *Action of alkali*. Treatment of the hydrobromide (0·001 mole) with boiling 1·5N-sodium hydroxide (as described for the phenyl homologue, procedure *b*) gave *sym*-di-*p*-tolylguanidine, m. p. 169—170° (lit.,[20] m. p. 169—170°), and thiocyanate (by titration) in nearly quantitative yields.

(*b*) *Oxidation*. Treatment of the hydrobromide (2·06 g., 0·005 mole) in methanol with M-bromine (as described for the phenyl homologue; procedure *a*) gave 5-imino-4-*p*-tolyl-3-*p*-tolylimino-1,2,4-thiadiazolidine, m. p. and mixed m. p. 128—129° (from methanol–acetone–water) in 70% yield.

N-p-*Chlorophenyl*-N-p-*chlorophenylamidinothiourea*.—A suspension of 4-*p*-chlorophenyl-3-*p*-chlorophenylimino-5-imino-1,2,4-thiadiazolidine [8] (1·35 g., 0·004 mole) in methanol (10 ml.) and 60% hydrobromic acid (1 ml.) was treated at room temperature with a slow stream of hydrogen sulphide during 1 hr. The material gradually dissolved completely and sulphur was deposited. The mixture was boiled, filtered, and set aside at 0°. The deposited *hydrobromide* formed prisms, m. p. 161—162° (decomp.) (from methanol–ether) (0·87 g., 52%) (Found: C, 39·5; H, 3·5; N, 13·7; S, 8·2. $C_{14}H_{12}Cl_2N_4S$,HBr requires C, 40·0; H, 3·1; N, 13·3; S, 7·6%).

The *picrate*, obtained (60%) by adding water (6 drops) to a solution of the components (0·001 mole each) in methanol (5 ml.), formed deep-yellow needles, m. p. 147—149° (decomp.) (Found: C, 42·3; H, 2·6. $C_{14}H_{12}Cl_2N_4S,C_6H_3N_3O_7$ requires C, 42·3; H, 2·6%).

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[20] Perkin, *J.*, 1880, **37**, 696; Naunton, *J. Soc. Chem. Ind.*, 1926, **45**, 378T.