217. *Urea and Related Compounds. Part VI.** sym-*Diaryldithioformamidines.*

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sym-Diaryldithioformamidines are obtained by oxidising aromatic thioureas with bromine and are isolated in the form of suitable salts. Hydrolysis of *sym*-diaryldithioformamidines in alkaline media yields, according to the conditions, sulphur, arylthioureas, *sym*-diarylguanidines, arylcyanamides, and 2 : 4-diaryl-3 : 5-di-imino-1 : 2 : 4-thiadiazolidines.

An improved technique of preparing 2 : 4-diaryl-3 : 5-di-imino-1 : 2 : 4-thiadiazolidines by oxidising aromatic thioureas with hydrogen peroxide is described.

Whereas thiourea and its alkyl derivatives are readily oxidised to the corresponding disulphides (I; R = H or Alk), the existence of *sym*-diaryldithioformamidines (I; R = Ar) has long been doubted. Oxidation of arylthioureas, expected to furnish the desired disulphides (I; R = Ar), invariably gave heterocyclic products. The relevant literature has been summarised briefly before.[1]

We have recently [1] reported the conversion of aromatic thioureas into dithioformamidines, but our work was restricted to *ortho*-substituted arylthioureas: this choice of starting material was intended to exclude the possibility of the ring closure to benzothiazoles,[2,3] which, according to the literature, is the prevalent reaction under these conditions. It was desirable to examine the applicability of this synthesis to arylthioureas which lacked *ortho*-substituents; *sym*-diaryldithioformamidines were expected to prove useful in the study of the hydrolysis of dithioformamidine and of the course of the oxidation of arylthioureas to 2 : 4-diaryl-3 : 5-di-imino-1 : 2 : 4-thiadiazolidines.†

Experiments have shown that blocking the *ortho*-positions of the aromatic nuclei of arylthioureas is not essential to prevent cyclisation and that, under proper conditions, *sym*-diaryldithioformamidines (I; R = Ar) appear to be generally obtainable. Arylthioureas, suspended in inert organic solvents, reacted rapidly with the calculated quantity of bromine at room temperature and gave excellent yields of the dithioformamidines (I; R = Ar), which were isolated as hydrobromides. The oxidation was promoted by the

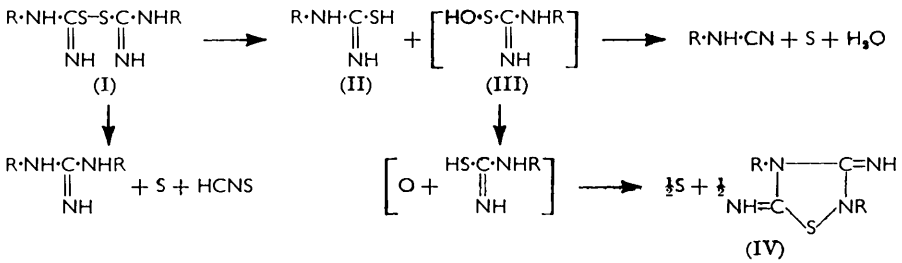
* Part V, *J.*, 1958, 1571.

† Following accepted practice, we continue to represent, with the usual reservations (cf. Part IV [1]), so-called Hector's bases as 2 : 4-diaryl-3 : 5-di-imino-1 : 2 : 4-thiadiazolidines.

[1] Kurzer and Sanderson, *J.*, 1957, 4461.
[2] Hugershoff, *Ber.*, 1901, **34**, 3130; 1903, **36**, 3121, 3134; 1906, **39**, 1014.
[3] Sahasrabudhey and Krall, *J. Indian Chem. Soc.*, 1944, **21**, 17.

presence of small quantities of water; under anhydrous conditions, the rate of bromine uptake was much reduced, and reaction stopped completely after 60—70% of the halogen had been added. Since dithioformamidines (I) are unobtainable as free bases, they were further characterised as picrates and picrolonates. All salts, though reasonably stable as the dry solid, decomposed rapidly in contact with solvents, including non-polar ones, and could not, therefore be purified by crystallisation. A technique was devised, however, which afforded excellent yields of analytically pure salts in one stage; with careful attention to correct conditions (cf. Experimental) results were consistently reproducible. It is known [4] that salts of the parent compound (I; R = H) also tend to decompose on attempted crystallisation and are best prepared under conditions that afford pure specimens in one operation. Fichter *et al.*, during a study of the electrolytic oxidation of organic sulphur compounds,[5] converted thioureas into dithioformamidines; [6] although they obviously succeeded in preparing *sym*-diphenyldithioformamidine hydrochloride, the only aromatic example studied, their attempts to isolate the salt resulted in its partial decomposition.

As expected, bis-(*N*-alkyl-*N*-aryl)dithioformamidines are also obtained by this reaction. *N*-Ethyl-*N*-phenylthiourea, for example, was oxidised more smoothly than any of the arylthioureas, the reaction being completed rapidly even in the absence of water; in contrast, dialkylthioureas are preferably oxidised in aqueous media.[1,7] Bis-(*N*-ethyl-*N*-phenyl)dithioformamidine hydrobromide thus obtained was more stable than the *sym*-diaryl derivatives (I; R = Ar), being crystallisable from suitable solvents in the cold. On the other hand, attempts to prepare dithioformamidines from *sym*- and *asym*-diphenylthioureas were unsuccessful. Although both thioureas absorbed the correct amount of halogen the solutions thus obtained gave an uncrystallisable yellow oil from the *sym*- and solids of variable composition and m. p. from the *asym*-material. Both substances dissolved in mineral acids and deposited sulphur on basification, and no doubt consisted substantially of the desired products.



The course of the reaction between arylthioureas and halogens in non-polar solvents thus depends clearly on the conditions: the use of equimolar quantities or excess of bromine at higher temperatures provides an excellent route to 2-aminobenzothiazoles (" Hugershoff's synthesis "),[2,3,8] but half-molar proportions of the oxidising agent under mild conditions afford dithioformamidines.

Dithioformamidines exist only as the salts, solutions of which deposit sulphur immediately when attempts are made to liberate the free bases. Precise information is, however, not available on the decomposition of these disulphides in alkaline media. Claus,[9] hydrolysing dithioformamidine hydrobromide in boiling water, obtained sulphur, and impure thiourea containing a sulphur-free by-product, the latter components being

[4] McGowan, *J.*, 1886, **49**, 190; *J. prakt. Chem.*, 1886, **33**, 188.
[5] Fichter and Sjöstedt, *Ber.*, 1910, **43**, 3422; Fichter and Wenk, *ibid.*, 1912, **45**, 1373.
[6] Fichter and Braun, *Ber.*, 1914, **47**, 1528.
[7] Sahasrabudhey and Singh, *J. Indian Chem. Soc.*, 1952, **29**, 636.
[8] Sprague and Land, in Elderfield (Ed.), " Heterocyclic Compounds," Wiley, New York, 1957, Vol. 5, p. 581.
[9] Claus, *Annalen*, 1875, **179**, 135, 140.

only incompletely separable from one another; he represented the decomposition by (1). Later workers,[4,10,11] observing the deposition of sulphur, interpreted the alkaline hydrolysis in the same way without further experimental evidence. Analogous assumptions were made for the decomposition of *sym*-diphenyldithioformamidine hydrochloride in contact with water.[6]

$$C_2H_6N_4S_2,2HBr \longrightarrow 2HBr + S + CS(NH_2)_2 + NH_2{\cdot}CN \quad . \quad . \quad . \quad . \quad . \quad (I)$$

Diaryldithioformamidines appeared to be particularly suitable for hydrolysis studies because of the ease with which products can be isolated and characterised. Results show that the alkaline hydrolysis of *sym*-diaryldithioformamidines (I) cannot be represented by a simple equation such as (1), but appears to involve simultaneous and consecutive changes. Alkali rapidly decomposed *sym*-diphenyldithioformamidine into sulphur, phenylthiourea, phenylcyanamide, and *sym*-diphenylguanidine, while the action of ammonia afforded sulphur, phenylthiourea, and, unexpectedly, 3 : 5-di-imino-2 : 4-diphenyl-1 : 2 : 4-thiadiazolidine. Although the results do not establish the route by which the products are formed, it is suggested that in both cases, the first stage may be the hydrolytic cleavage of the disulphide link of (I) to form the arylthiourea (II) and an intermediate highly labile sulphenic acid (III). The existence of an analogous sulphinic acid, $NH_2{\cdot}C(:NH){\cdot}SO_2H$, obtainable from thiourea or dithioformamidine salts on oxidation, is well established.[12,13] Decomposition of the hypothetical intermediate (III) might proceed, in the former hydrolysis, to yield cyanamide and sulphur, but may take place, in ammoniacal medium, with preliminary elimination of oxygen, which thus becomes available for converting half the total arylthiourea formed into the thiadiazolidine (IV). The yields of products obtained in the reaction with ammonia are in agreement with this interpretation. The formation of " Hector's bases " (IV), the existence of which appears to be confined to the aromatic series,[14] presumably has no parallel in the hydrolysis of dithioformamidine itself and its alkyl derivatives, but suggests that oxidative changes may occur during their hydrolysis. *sym*-Diarylguanidine, isolated in relatively low yield, may arise more directly from (I), with elimination of sulphur and thiocyanic acid, which is always present in the hydrolysate. Further work in this connexion is in progress.

Finally, we report an improved procedure for preparing 2 : 4-diaryl-3 : 5-di-imino-1 : 2 : 4-thiadiazolidines (IV) from arylthioureas by oxidation. On decreasing the proportion of water present in the reaction mixture, by using 30% (instead of the usual 6%) hydrogen peroxide, and absolute ethanol as solvent, the heterocyclic compounds were obtained in significantly increased yields. Thus, thiadiazolidines (IV) derived from phenyl- and *p*-tolyl-thiourea, which we obtained by Hector's method [15] in 50 and 30% yield, were formed in 75—80% and 50% yield, respectively, by the improved technique. It is probable that the modified conditions prevent loss of reactant by hydrolytic side-reactions: the oxidation of phenylthiourea by 6% hydrogen peroxide in aqueous ethanol, for example, gave up to 15% of *sym*-diphenylguanidine as by-product (see also Part IV [1]).

Experimental

The solvent used for preparing M-bromine was chloroform, unless otherwise stated.

Bromide in *sym*-diphenyl- and bis-(*N*-ethyl-*N*-phenyl)-dithioformamidine dihydrobromides was estimated by Volhard's method, including the use of nitrobenzene (cf. Part IV [1]). The other dithioformamidine hydrobromides precipitated silver sulphide rapidly from 0·1N-silver nitrate, and bromide was estimated gravimetrically in these cases.

[10] Storch, *Monatsh.*, 1890, **11**, 458.
[11] Sahasrabudhey, *J. Indian Chem. Soc.*, 1950, **27**, 433.
[12] Barnett, *J.*, 1910, **97**, 63.
[13] Boeseken, *Proc. Akad. Sci. Amsterdam*, 1936, **39**, 717; *Rec. Trav. chim.*, 1936, **55**, 1044; 1948, **67**, 603.
[14] Hector, *J. prakt. Chem.*, 1891, **44**, 492, and own unpublished observations.
[15] Hector, *Ber.*, 1889, **22**, 1177; 1890, **23**, 357.

Contact of wet dithioformamidine salts with metal spatulas must be avoided to prevent local decomposition.

sym-*Diphenyldithioformamidine.*—(*a*) A suspension of finely ground phenylthiourea (6·08 g., 0·04 mole) in chloroform (100 ml.), to which water (6 ml.) was added, was treated with M-bromine (20 ml., 0·02 mole) with shaking and external cooling (ice–water) during 8—10 min. The product was filtered off, washed successively with much chloroform and light petroleum, ground in a mortar with more chloroform, collected, and dried at room temperature. The resulting white granular powder (8·0—9·2 g., 80—92%) was sym-*diphenyldithioformamidine dihydrobromide dihydrate*, m. p. 96—100° (decomp., frothing at 110—115°) [Found: C, 33·45; H, 4·0; N, 11·6; S, 13·0; Br (gravimetrically), 32·2; Br (volumetrically), 32·1. $C_{14}H_{14}N_4S_2,2HBr,2H_2O$ requires C, 33·6; H, 4·0; N, 11·2; S, 12·8; Br, 32·0%]. The product dissolved in 3N-hydrochloric or sulphuric acid when slightly warmed, but the solutions deposited colloidal sulphur when boiled, or in the cold on being basified. The salt was almost insoluble in hot benzene, light petroleum, or ether. It dissolved in warm ethanol or cold methanol; the former solution gave colloidal sulphur rapidly, the latter more slowly.

(*b*) Specimens of phenylthiourea consisting of large prisms, in spite of being finely ground, tended to absorb bromine erratically and form bright orange specks that were only slowly decolorised In such cases, satisfactory results were obtained by continuously grinding the reactant (0·04 mole) with chloroform (15—20 ml.)–water (2 ml.) in a mortar and introducing 0·2M-bromine (0·02 mole) during 10—15 min. The yield of product, isolated as before, averaged 75% of the theoretical.

Addition of water to the reaction mixture in this and the subsequent preparations increases the rate and completeness of oxidation (see p. 1058), and appears to prevent local production of perbromide.

The absence of Hector's base [1] in the *sym*-diphenyldithioformamidine salt was demonstrated by extracting a sample (4 g.) with 3N-hydrochloric acid (10 ml.): the filtered extract when basified gave a precipitate that was not soluble in acid.

sym-*Di*-p-*tolyldithioformamidine.*—In a mortar, a suspension of finely powdered *p*-tolylthiourea (3·32 g., 0·02 mole) in chloroform (25 ml.)–water (2 ml.) was treated, with continuous grinding during 20—30 min., with M-bromine (10 ml.; 0·01 mole), more chloroform being added to make up for losses due to evaporation. The resulting white creamy precipitate was collected and washed with much chloroform, and the compact filter-cake ground with more chloroform and again collected. The white sym-*di*-p-*tolyldithioformamidine dihydrobromide* (3·9—4·4 g., 80—90%) had m. p. 95—98° (decomp., after sintering at 85°) (Found: C, 38 6; H, 4·1; N, 11·3; S, 13·0. $C_{16}H_{18}N_4S_2,2HBr$ requires C, 39·0; H, 4·1; N, 11·4; S, 13·0%). The product dissolved rapidly in cold methanol (absence of the sparingly soluble *p*-tolylthiourea); the solution slowly depositing colloidal sulphur.

o-Tolylthiourea (0·20 mole) absorbed the correct quantity of bromine on treatment by the above method, but gave clear chloroform solutions from which the soluble dithioformamidine salt could not be isolated without extensive decomposition.

Di-p-*chlorophenyldithioformamidine.*—*p*-Chlorophenylthiourea (1·87 g., 0·01 mole) was oxidised with bromine (0·005 mole) as described for the *p*-tolyl analogue. The precipitated salt was washed, re-ground with much chloroform, and dried, giving *di*-p-*chlorophenyldithioformamidine dihydrobromide* (2·25 g., 85%), m. p. 145—146° (decomp.; discolouring at 140°) (Found: C, 31·9; H, 2·9; N, 10·2; S, 11·7. $C_{14}H_{12}N_4S_2Cl_2,2HBr$ requires C, 31·5; H, 2·6; N, 10·5; S, 12·0%).

Bis-(N-*ethyl*-N-*phenyl*)*dithioformamidine.*—(i) *N*-Ethyl-*N*-phenylthiourea was prepared by a modification of Gerhardt's method [16] as follows: In a porcelain dish, *N*-ethylanilinium chloride (63 g., 0·4 mole), dissolved in warm water (300 ml.) containing concentrated hydrochloric acid (6 ml.), and ammonium thiocyanate (38 g., 0·5 mole) were kept at 100° during 1 hr. The liquid was set aside at room temperature during 2 hr., then slowly evaporated, and the residue heated on the steam-bath (total, 8—10 hr.). The residue was ground with water (3 × 100 ml.), and the product collected and crystallised from ethanol (2 ml. per g.). It formed massive needles, m. p. 111—112° (lit.[16] 113°) (yield, including material from the mother liquors, 48—56%).

(ii) A solution of *N*-ethyl-*N*-phenylthiourea (1·80 g., 0·01 mole) in cold chloroform (10 ml.) rapidly decolorised 1M-bromine (5 ml., 0·005 mole). The resulting liquid was diluted with ether to incipient precipitation; it deposited crystals, which were collected at 0°, washed with

[16] Gerhardt, *Ber.*, 1884, **17**, 2094.

cold chloroform, and air-dried [m. p. 158—160° (decomp.); 2·2—2·35 g., 85—90%]. Two crystallisations, by dissolution in the minimum of cold methanol, dilution with an equal volume of acetone, and dilution with ether to incipient turbidity (recovery 50—60%), gave lustrous prismatic *bis*-(N-*ethyl*-N-*phenyl*)*dithioformamidine dihydrobromide*, m. p. 162—163° (decomp.) (Found: C, 41·7; H, 4·6; N, 10·6; S, 12·1; Br, 30·9. $C_{18}H_{22}N_4S_2,2HBr$ requires C, 41·6; H, 4·6; N, 10·8; S, 12·3; Br, 30·7%). The salt was highly soluble in cold methanol, soluble in hot chloroform (slight decomp.), and sparingly soluble in water and cold chloroform.

Picrates.—These were prepared in 50—60% yield as follows: The finely powdered hydrobromide (0·001 mole) was dissolved in successive small quantities of the cold solvent [for (i): 40 ml. of 0·3N-hydrochloric acid; for (ii)—(iv): minimum (10—15 ml.) of methanol] and filtered into stirred cold 0·05N-aqueous picric acid (40—50 ml.; 0·002—0·0025 mole). The coagulated yellow powdery precipitate was collected, washed with 0·1N-hydrochloric acid, and air-dried.

Picrolonates.—These were similarly obtained in 60—90% yield as follows: A solution of the finely powdered hydrobromide (0·0004 mole) in cold hydrochloric acid [for (i): 30 ml. of 0·3N; (ii) 10 ml. of 1·5N; (iii) 25 ml. of 1·5N; (iv) 30 ml. of 1·5N + 30 ml. of methanol] was filtered into a stirred solution of picrolonic acid (0·26 g., 0·001 mole) in 0·3N-hydrochloric acid (60—80 ml.). The powdery yellow precipitate was collected, washed with very dilute hydrochloric acid, and dried at room temperature.

Specimens of *picrates* and *picrolonates* so obtained were analytically pure (cf. Table) but

				Found (%)		Required (%)	
R	R′	Formula	M. p.*	C	H	C	H
		Picrates $[RR'N\cdot C(:NH)\cdot S]_2,\ 2C_6H_3O_6N_3$					
(i) Ph	H	$C_{26}H_{20}O_{14}N_{10}S_2$	105—106°	41·3	2·6	41·05	2·6
(ii) Ph	Et	$C_{30}H_{28}O_{14}N_{10}S_2$	99—100°	44·2	3·4	44·1	3·4
(iii) *p*-$CH_3\cdot C_6H_4$	H	$C_{28}H_{24}O_{14}N_{10}S_2$	68—71°	43·0	3·0	42·6	3·0
(iv) *p*-ClC_6H_4	H	$C_{26}H_{18}O_{14}N_{10}S_2Cl_2$	125—126°	38·1	2·6	37·6	2·2
		Picrolonates $[RR'N\cdot C(:NH)\cdot S]_2,2C_{10}H_8O_5N_4$					
(i) Ph	H	$C_{34}H_{30}O_{10}N_{12}S_2,2H_2O$	130—132°	47·2	3·7	47·1	3·9
(ii) Ph	Et	$C_{38}H_{38}O_{10}N_{12}S_2$	103—105°	51·2	3·9	51·5	4·3
(iii) *p*-$CH_3\cdot C_6H_4$	H	$C_{36}H_{34}O_{10}N_{12}S_2,2H_2O$	149—150°	48·6	3·9	48·3	4·25
(iv) *p*-ClC_6H_4	H	$C_{34}H_{28}O_{10}N_{12}S_2Cl_2$	132—133°	45·4	2·8	45·4	3·1

* All products melted with decomposition.

decomposed on attempted crystallisation from the usual solvents. Because of the rapidity with which some of the *NN′*-diaryldithioformamidine hydrobromides decompose in solution, the procedure is not suitable for preparing picrates or picrolonates on a considerably larger scale.

sym-*Diphenyldithioformamidine.*—(a) *Reaction with ammonia.* Freshly prepared, finely powdered *sym*-diphenyldithioformamidine dihydrobromide dihydrate (10 g., 0·02 mole) was dissolved in boiling methanol (20 ml.), treated with aqueous ammonia (*d* 0·88; 6 ml., 0·12 mole), and the liquid swirled and boiled during 5 min. Colloidal sulphur, followed by a white crystalline solid, appeared in suspension; the whole was allowed to cool to room temperature and diluted with water (30 ml.), and the solids were collected at 0° and washed with a little water (ammoniacal filtrate: F) (5·26—5·65 g.). (i) The substance was exhaustively extracted with cold 3N-hydrochloric acid (2 × 10, 2 × 8 ml. successively), the undissolved solid collected (filtrate: E), and the dried product (2·9—3·2 g.) crystallised from methanol–water (1 : 3): the insoluble residue, removed by vacuum filtration, was sulphur (0·24—0·3 g.; 75—94%); the filtrates deposited phenylthiourea, m. p. and mixed m. p. 152—153° (2·6—2·8 g., 85—92%, including material from the mother-liquors). Filtrates E were basified with 3N-sodium hydroxide, and the precipitate was collected at 0°, washed with water, dried (1·95—2·4 g.) and crystallised from acetone–methanol (1 : 1), affording 3 : 5-di-imino-2 : 4-diphenyl-1 : 2 : 4-thiadiazolidine, m. p. and mixed m. p. 186—187° (deep red melt, decomp.) (total, including material from the mother-liquors, 1·5 g., 56%).

(ii) Alternatively, the crude base from E was treated, in pyridine, with toluene-*p*-sulphonyl chloride; the product, crystallised from acetone–ethanol, was the toluene-*p*-sulphonyl derivative of 3 : 5-di-imino-2 : 4-diphenyl-1 : 2 : 4-thiadiazolidine, m. p. and mixed m. p. 230—232° (2·70 g., 64%).

The ammoniacal filtrate F, having evaporated spontaneously at room temperature to quarter volume, gave a little solid (0·25 g.) consisting substantially of phenylthiourea.

Reaction using N- or 2N-aqueous ammonia (30 ml.) was more difficult, the reactant being converted, without completely dissolving, into a lumpy mass. This was fractionated into the same products as above, though in lower yields.

(b) *Alkaline hydrolysis.* Finely powdered dihydrobromide (5·0 g., 0·01 mole) was quickly dissolved in warm methanol (10 ml.) and treated with 3N-aqueous sodium hydroxide (10 ml., 0·03 mole). The mixture was boiled gently, with frequent swirling, during 5 min., set aside at room temperature, and the white precipitate (2·05—2·15 g.) collected at 0° (alkaline filtrate: G). It was extracted with cold 3N-hydrochloric acid (3 × 5 ml.), and the undissolved residue R collected and rinsed with water (filtrate: H). Product R (m. p. 147—149°) was crystallised from boiling methanol–water (1 : 3; 10 ml. per g.), a little undissolved sulphur (0·2—0·25 g.) being removed, and gave phenylthiourea, m. p. and mixed m. p. 152—153° (total, 1·05—1·22 g., corresponding to a 35—40% conversion of the reactant into thiourea). Filtrate H was basified with 3N-sodium hydroxide and the washed, dried precipitate (0·55 g.) was crystallised by dissolution in ethanol (1 ml. per g.) and slow dilution of the filtered solution with drops of water, affording *NN'*-diphenylguanidine, m. p. and mixed m. p. 147—149° (total, 0·38—0·51 g., 18—24% conversion).

Spontaneous evaporation of filtrate G to small volume at room temperature gave crystalline solid (0·06—0·1 g.) consisting of phenylthiourea and sulphur. The filtrate therefrom, after being strongly acidified with concentrated hydrochloric acid, slowly deposited oily droplets of phenylcyanamide, identified by conversion into the benzoyl derivative, m. p. 124—125° (from ethanol; 0·55 g., 25%) (Found: C, 75·6; H, 4·3. Calc. for $C_{14}H_{10}ON_2$: C, 75·7; H, 4·5%), by the Schotten–Baumann method [40% sodium hydroxide (20 ml.) and benzoyl chloride (5 ml.)].

Hydrolysis in boiling aqueous N-sodium hydroxide (30 ml.) during 10 min. gave a cruder product (2·2 g.) which was fractionated as above, affording the same products, though in somewhat lower yield.

3 : 5-*Di-imino*-2 : 4-*diphenyl*-1 : 2 : 4-*thiadiazolidine.*—(*a*) Phenylthiourea (30·4 g., 0·2 mole) in boiling ethanol (350 ml.) was treated with concentrated hydrochloric acid (20 ml., 0·2 mole), withdrawn from the heat source, and oxidised with 30% hydrogen peroxide (23 ml., 0·2 mole) (dropwise addition during 10—15 min.; the mixture boiled vigorously throughout); boiling was then continued for another 10 min. The cooled solution was decanted from the coagulated sulphur (3·0 g., 94%), diluted with water (1200 ml.), filtered (charcoal), and basified at 0° with ammonia. The dried precipitate (m. p. 183—184°, decomp., after sintering at 178°; 22—24 g., 82—90%) was crystallised from boiling methanol–acetone (1 : 1; 25—28 ml. per g.) and gave lustrous prisms, m. p. 184—185° (decomp.) (yield, 20·9—22 g., 78—82% in three successive crops).

(*b*) Phenylthiourea (0·2 mole) in boiling 50% ethanol (500 ml.) containing concentrated hydrochloric acid (5 ml.) was treated with 6% hydrogen peroxide (0·3 mole) during 20 min., the liquid refluxed for another 20 min., decanted from the sulphur, filtered (carbon), and basified with 20% sodium hydroxide (30 ml.), and the precipitate collected at once (Filtrate F). Crystallisation as above gave the thiadiazolidine in 43—52% yield. The warm filtrate F deposited lustrous crystals (m. p. 144—146°, 7—9%) on storage at 0°, which consisted of *sym*-diphenylguanidine, m. p. and mixed m. p. 146—148° (from 60% aqueous ethanol); more (6%) was isolated as the most soluble fraction in the crystallisation of the main product.

The yields of 1 : 2 : 4-thiadiazolidine from *p*-tolylthiourea obtained by procedure (*a*) and (*b*) were 50 and 30% respectively.

2 : 4-*Di*-p-*chlorophenyl*-3 : 5-*di*-*imino*-1 : 2 : 4-*thiadiazolidine.*—To a boiling solution of *p*-chlorophenylthiourea (7·46 g., 0·04 mole) in ethanol (40 ml.), concentrated hydrochloric acid (4 ml., 0·04 mole) was added, followed by 30% hydrogen peroxide (5 ml., 0·045 mole) with good mixing within 2—3 min. The swirled mixture was boiled during 3 min., and nearly filled with white solid. It was diluted with water (100 ml.) and concentrated hydrochloric acid (10 ml.), heated to boiling, and cooled to 0°. The collected product (7·35 g.) was extracted with successive portions of 50% aqueous acetone, and the undissolved coagulated sulphur (0·60 g., 94%) removed. The filtrate deposited crystals which were collected at 0° (6·4 g., 86%) and consisted, after a further crystallisation from 75% aqueous acetone, of prisms of 2 : 4-*di*-p-*chlorophenyl*-3 : 5-*di*-*imino*-1 : 2 : 4-*thiadiazolidine hydrochloride*, m. p. 265—266° (decomp., dependent on rate of heating) (Found: C, 44·7; H, 3·1. $C_{14}H_{10}N_4Cl_2S$,HCl requires C, 45·0; H, 2·9%).

Alternatively, the crude hydrochloride (6·3 g.) was dissolved in nearly boiling water (350 ml.), and the solution basified with 3N-ammonium hydroxide. The precipitate (m. p. 165—167°; 5·4 g., 80%) was crystallised from ethanol (10 ml. per g.; with addition of a few drops of acetone) or from methanol–acetone (1 : 1, 2—3 ml. per g.). 2 : 4-*Di*-p-*chlorophenyl*-3 : 5-*di-imino*-1 : 2 : 4-*thiadiazolidine* had m. p. 167—168° (decomp.) (Found: C, 49·8; H, 2·9; N, 16·8; Cl, 20·8. $C_{14}H_{10}N_4Cl_2S$ requires C, 49·9; H, 3·0; N, 16·6; Cl, 21·05%).

The use of 6% hydrogen peroxide (0·04 mole) afforded, by the same procedure, the crude thiadiazolidine in 65% yield.

A solution of the 1 : 2 : 4-thiadiazolidine (0·5 g., 0·0015 mole) in acetic anhydride (10 ml.) was heated on the steam-bath during 0·5 hr., and the liquid then stirred into water. The precipitate (m. p. 204—205°, decomp.; 0·55 g., 96%) gave, after crystallisation from acetone–ethanol, glass-like prisms of the *monoacetyl derivative*, m. p. 207—209° (decomp.) (Found: C, 50·6; H, 3·3. $C_{16}H_{12}ON_4Cl_2S$ requires C, 50·7; H, 3·2%).

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