Heterocyclic Compounds from Urea Derivatives. Part XXIII.[1] Thiobenzoylated Thiocarbonohydrazides and their Cyclisation

By **Roshan Esmail** and **Frederick Kurzer,*** Royal Free Hospital School of Medicine (University of London), 8 Hunter Street, London WC1

Thiobenzoylation of thiocarbonohydrazide produces successively 1-thiobenzoyl- and 1,5-bis(thiobenzoyl)-thiocarbonohydrazide in moderate yield, together with their cyclisation products, principally 4-amino-3-mercapto-5-phenyl-1,2,4-triazole. *S*-Methylisothiocarbonohydrazide yields 2,3-dihydro-1-methylthio-4-phenyl-2,3,5,6-tetrazine as the main product in this reaction. The labile 5-thiobenzoyl derivative of 1-phenylthiocarbonohydrazide is cyclised to 2-phenyl-5-phenylhydrazino-1,3,4-thiadiazole in acid, and to 4-anilino-3-mercapto-5-phenyl-1,2,4-triazole in alkaline media. 2-Aryl-5-phenylazo-1,3,4-thiadiazoles arising as by-products in the alkaline cyclisation are the principal products of the oxidation of the 5-phenylhydrazino-analogues.

In conjunction with our study of thioacylcarbonohydrazides,[1] we have examined the thiobenzoylation of thiocarbonohydrazides and the cyclisation of the resulting derivatives.

The synthesis of thiobenzoylthiocarbonohydrazide [(V) ⟶ (VII)] has been described by Sandstrom.[2] The product (VII) gave mixtures of substituted 1,3,4-thiadiazoles, (II) and (XVI), together with small quantities of the 1,2,4-triazole (XIV), on pyrolysis or when treated with acid, but was reported to be unaffected by alkali.[2] In our experience, the thiobenzoylation of thiocarbonohydrazide (V) gave decidedly less satisfactory results. The product (VII) was obtainable in only moderate yield (30—40%); it was invariably contaminated with cyclised material, formed by loss of hydrogen sulphide, and it continued to decompose. Contrary to the report,[2] it was rapidly cyclised by alkali, principally to 4-amino-3-mercapto-5-phenyl-1,2,4-triazole (XIV). Attempts to isolate the thiobenzoyl compound (VII) in the form of stable derivatives were unsuccessful. Its attempted *S*-alkylation was attended by simultaneous ring closure to 3-alkylthio-1,2,4-triazoles (XII). The action of acetylacetone gave 2-mercapto-5-phenyl-1,3,4-thiadiazole (II), no doubt by the scission and cyclisation of the desired pyrazolyl derivative (I) first formed. The reaction thus resembles the production of 2-hydroxy-5-phenyl-1,3,4-thiadiazole from the oxygen analogue of (VII),[1] and of 2-benzamido-5-mercapto-1,3,4-thiadiazole from 4-benzoyl-1-thiocarbazoyl-3-thiosemicarbazide (PhCO·NH·CS·NH·NH·CS·NH·NH_2) under the influence of the same reagent.[3] The scission, in each case, of an *N*-(thioacyl)pyrazole is in accord with the known instability of ring *N*-acyl derivatives of five-membered heterocyclic systems.[4]

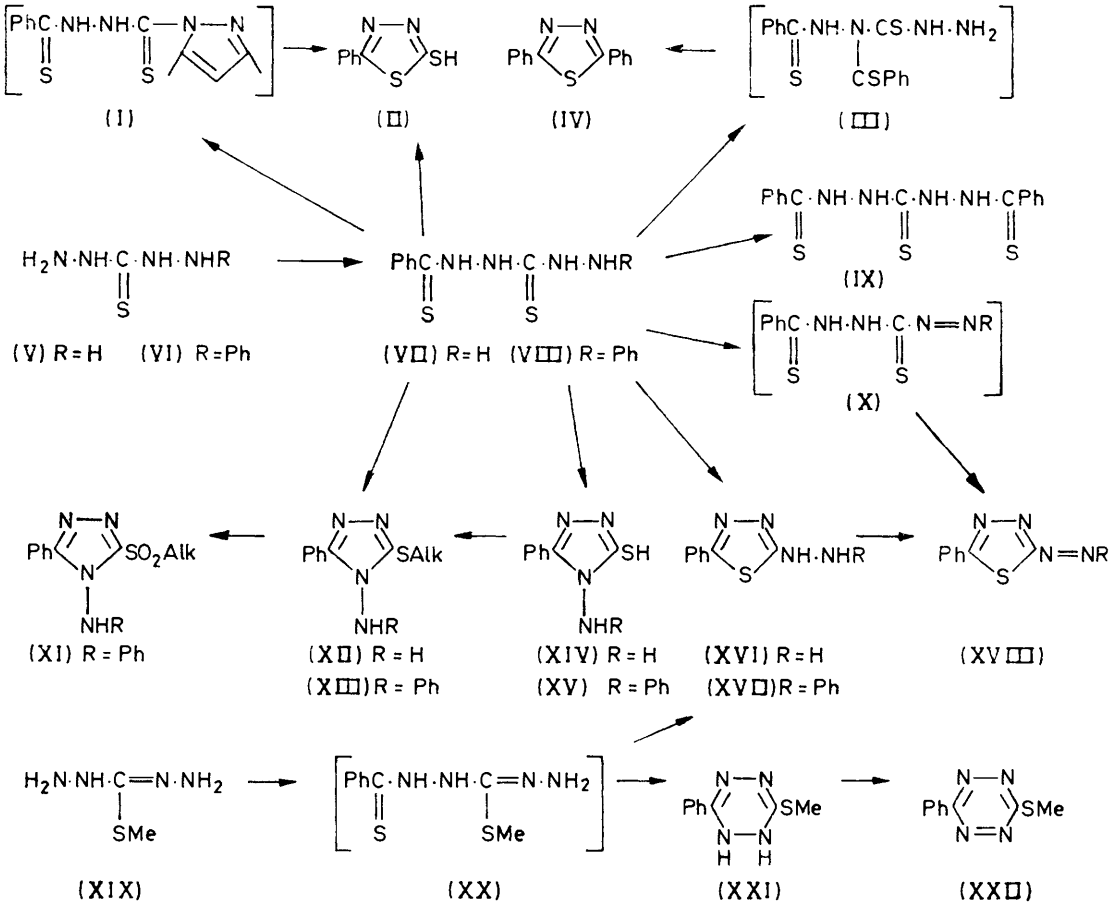
The action of 2 mol. equiv. of thiobenzoylthioacetic acid on thiocarbonohydrazide in aqueous alkali gave small yields (15—25%) of the linear diadduct (IX), together with 4-amino-3-mercapto-5-phenyl-1,2,4-triazole (XIV) (10—15%) and varying amounts of 2,5-diphenyl-1,3,4-thiadiazole (IV), the latter arising [1] *via* (III).

The thiobenzoylation of *S*-methylisothiocarbonohydrazide (XIX) also proceeded with simultaneous cyclisation, chiefly with loss of hydrogen sulphide. Instead of the expected 4-amino-3-methylthio-5-phenyl-1,2,4-triazole (XII; Alk = Me), which arose only in traces, the major product was 2,3-dihydro-1-methylthio-4-phenyl-2,3,5,6-tetrazine (XXI) (35—52%). In a parallel cyclisation, loss of methanethiol from the presumed intermediate (XX) resulted in 2-hydrazino-5-phenyl-1,3,4-thiadiazole (XVI), which was isolable as the isopropylidene derivative (up to 25%).

Tetrazine formation [(XIX) ⟶ (XXI)] is thought

[1] Part XXII, R. Esmail and F. Kurzer, preceding paper.
[2] J. Sandström, *Acta Chem. Scand.*, 1963, **17**, 1595.
[3] F. Kurzer, *J. Chem. Soc.* (*C*), 1971, 2932.
[4] H. A. Staab, *Annalen*, 1957, **609**, 75; *Angew. Chem. Internat. Edn.*, 1962, **1**, 355; H. A. Staab and G. Seel, *Chem. Ber.*, 1959, **92**, 1302.

to involve an intramolecular nucleophilic attack, in the intermediate (XX), of the ultimate amino-group on the thioxo-carbon; it is noteworthy in producing a partially reduced six-membered in preference to the usual fully resonance-stabilised five-membered heteroaromatic system. The formulation of the reduced tetrazine (XXI) is based on its rapid dehydrogenation by acidified hydrogen peroxide to the corresponding 2,3,5,6-tetrazine (XXII), which displays the intense deep-purple colour and spectral properties characteristic of this structure.[5]



In common with 3,6-disubstituted tetrazines,[5,6] it gives rise to intense i.r. peaks near 900, 1 200, and 1 400 cm^{-1}, but shows no significant absorption beyond that range.

The thiobenzoylation of 1-phenylthiocarbonohydrazide (VI) in aqueous alkali, proceeding with slight evolution of hydrogen sulphide, gave a labile derivative (VIII) contaminated with cyclised material. Since its attempted purification caused progressive ring closure, it was immediately cyclised. The main products of the action of hydrochloric acid were 2-phenyl-5-phenylhydrazino-1,3,4-thiadiazole (XVII) (25—40%) and 4-anilino-3-mercapto-5-phenyl-1,2,4-triazole (XV) (*ca.* 35%).

The formulation of the latter (XV) agrees with its ready conversion into *S*-alkyl (XIII) and thence alkylsulphonyl derivatives (XI; Alk = Me or CH_2Ph), the i.r. spectrum of which featured maxima at 1 350 and 1 150 cm^{-1} characteristic of sulphones of this type.[7,8]

The action of alkali gave the triazole (XV) as main product (56—64%) as expected, but the thiadiazole arose also, as the 5-phenylazo-compound (XVIII) (10—15%).

The cyclisation of compounds of type YC(SH):N·N:C(NHX)Z,[9,10] including the specially relevant bithioureas,[11] normally yields exclusively 2-amino-1,3,4-thiadiazoles in acid, and 3-mercapto-1,2,4-triazoles in alkaline media. The present apparently anomalous production of the 1,3,4-thiadiazole (XVIII) in alkali is

[5] V. P. Wystrach in 'Heterocyclic Compounds,' ed. R. C. Elderfield, vol. 8, Wiley, New York and London, pp. 105, 113.

[6] L. A. Franks, A. J. Merer, and K. K. Innes, *J. Mol. Spectroscopy*, 1968, **26**, 458; J. H. Kiefer, *Diss. Abs.*, 1965, **22**, 2604; V. I. Berezin, *Optics and Spectroscopy*, 1964, **16**, 131; G. H. Spencer, P. C. Cross, and K. B. Wiberg, *J. Chem. Phys.*, 1961, **35**, 1939; F. Dallaker, *Monatsh.*, 1960, **91**, 294.

[7] L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, pp. 219 *et seq.*; E. A. Robinson, *Canad. J. Chem.*, 1961, **39**, 247.

[8] F. Kurzer and M. Wilkinson, *J. Chem. Soc.* (*C*), 1968, 2099.

[9] J. F. Willems, *Fortschr. Chem. Forsch.*, 1965, **5**, 147.

[10] F. Arndt and E. Milde, *Ber.*, 1921, **54**, 2089; F. Arndt, E. Milde, and F. Tschenscher, *ibid.*, 1922, **55**, 341, 349; F. Arndt and F. Bielich, *ibid.*, 1923, **56**, 2276.

[11] W. R. Sherman in 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1961, vol. 7, pp. 607—610.

explicable in terms of the intermediate formation of the linear phenylazo-compound (X), which cannot cyclise to a triazole, but can form the thiadiazole (XVIII), with loss of hydrogen sulphide. The analogous formation of 2-anilino-[12] and 2-benzamido-5-phenylazo-1,3,4-thiadiazole[3] has been described previously. The appearance of the triazole (XV) amongst the *acidic* cyclisation products is ascribed to its presence in the impure reactant (VIII), which is itself produced in alkaline media.

2-Phenyl-5-phenylhydrazino-1,3,4-thiadiazole (XVII) was smoothly dehydrogenated to the deep-orange 5-phenylazo-analogue (XVIII) by acidified hydrogen peroxide, less completely by molecular oxygen in alkaline media, and to a small extent even on recrystallisation, and on storage of the solid. 2-Phenyl-5-phenylazo-1,3,4-thiadiazole has been obtained[13,14] (30%) by the action of dimethyl azodicarboxylate on 4,5-diphenyl-1,3,4-thiadiazolium-2-thiolate; its original erroneous formulation[13] as a mesoionic tetrazine was corrected[14] by its synthesis from 2-amino-5-phenyl-1,3,4-thiadiazole and nitrosobenzene. The product of the action of iron(III) chloride on benzaldehyde phenylthiocarbonohydrazone (PhNH·NH·CS·NH·N=CHPh), formulated by Guha and Roy-Choudhury[15] as 2-phenyl-5-phenylhydrazino-1,3,4-thiadiazole [(XVII), 'orange needles, m.p. 172°'] is without doubt the 5-phenylazo-compound (XVIII) and the incorrect structures of analogues[15] obtained by this oxidative route should be revised in the same sense.

The action of thiobenzoylthioacetic acid on 1-benzylidenethiocarbonohydrazide is known[2] to yield 2-benzylidenehydrazino-5-phenyl-1,3,4-thiadiazole in boiling pyridine but intractable material in aqueous media. Our attempts to find conditions for producing linear adducts of type PhCS·NH·NH·CS·NH·N:CRR' have not met with success; in dimethylformamide at room temperature, thiobenzoylation was slow, but cyclisation occurred simultaneously even under these restrained conditions, giving the usual[2] thiadiazole (in 22 or 55% yield after 2 or 24 h, respectively), and starting material.

The pronounced inclination to ring closure of all the thiobenzoylthiocarbonohydrazides [(VII), (VIII), (XX)] now described, contrasting with the stability of thiobenzoylcarbonohydrazides,[1] recalls the behaviour of the comparable semicarbazides: thioacylthiosemicarbazides (ArCS·NH·NH·CS·NH_2) undergo spontaneous ring closure as soon as they are formed, but their oxygen analogues (ArCS·NH·NH·CO·NH_2) are isolable.[16] However, not all relevant structures display the cyclising tendency to the same degree: the reactivity of the XCS·NH·NH·CS·NHY system is evidently influenced by its structural environment; bithioureas, for example, are sufficiently stable to be isolated and purified.[2,3]

The cyclisations of thioacylated carbono- (A)[1] and thiocarbono-hydrazides (B) under like conditions show differences of some significance. The conversion in acidic media of thiobenzoylcarbonohydrazides (A) into 2-hydroxy-1,3,4-thiadiazoles by loss of hydrazines is without parallel in the sulphur series (B), in which 2-hydrazino- in preference to 2-mercapto-1,3,4-thiadiazoles are formed. The comparable structural patterns thus eliminate hydrogen sulphide, hydrazine, and water in descending order of preference.

ArCS·NH·NH·CO·NH·NHR (A) ArCS·NH·NH·CS·NH·NHR (B)

Conversely, the ready cyclisation in alkaline media of thiobenzoylthiocarbonohydrazides (B) to 3-mercapto-1,2,4-triazoles has no counterpart in the oxygen series, members of which are largely unaffected by alkali. Reaction conditions and structural patterns [(A), (B)] being identical, the reactivity of the sulphur series (B) is ascribed to the only structural difference [from (A)], *i.e.* the effect of their thioureido-sulphur atom. However, the nature of the hetero-products arising from the thiocarbonohydrazides [(VII) ⟶ (XIV), (VIII) ⟶ (XV), (XX) ⟶ (XXI)] shows that, barring rearrangements, the eliminated hydrogen sulphide originates from the thiobenzoyl group. The thioureido-sulphur atom may thus be regarded as rendering the adjacent penultimate N(4) atom [of (B)] sufficiently nucleophilic (possibly by a delocalisation of its negative charge, in the alkaline medium) to attack successfully the thiocarbonyl carbon atom, with ejection of the attached mercapto-group, the stabilisation of which in alkali is insufficient to prevent its displacement.

Unlike thiobenzoylcarbonohydrazides (A), which generally afford single isolable products in good yield upon cyclisation,[1] their sulphur analogues (B) tend to form more than one heterocyclic product in parallel reactions, not always in the same ratio or in reproducible yields. As a synthetic method, the thioacylation of thiocarbonohydrazides is therefore less useful than that of the oxygen analogues.

EXPERIMENTAL

The usual general remarks[17] regarding apparatus and reagents are applicable. Ethyl acetate was the preferred solvent, and iodine the developing reagent, for separating the heterocycles by t.l.c.

Cyclisations of thiobenzoylthiocarbonohydrazide and of its 1-benzylidene derivative, and the preparation of simple derivatives, are described in Supplementary Publication No. SUP 21424 (4 pp.).*

1,5-*Bis(thiobenzoyl)thiocarbonohydrazide*.— Thiocarbonohydrazide (2.12 g, 0.02 mol), dissolved in N-sodium hydroxide (20 ml, 0.02 mol), was added dropwise at room temperature during 10 min to a stirred solution of thiobenzoylthioacetic acid (8.48 g, 0.04 mol) in N-sodium

* For details of Supplementary Publications, see Notice to Authors No. 7, in *J.C.S. Perkin I*, 1974, Index issue.

[12] F. Kurzer and M. Wilkinson, *J. Chem. Soc.* (*C*), 1970, 26.
[13] R. M. Moriarty, J. M. Kliegeman, and R. B. Desai, *Chem. Comm.*, 1967, 1045.
[14] W. L. Mosby and M. L. Vega, *Chem. Comm.*, 1971, 837.
[15] P. C. Guha and S. K. Roy-Choudhury, *J. Indian Chem. Soc.*, 1928, **5**, 149.
[16] A. Lawson and C. E. Searle, *J. Chem. Soc.*, 1957, 1556; F. Kurzer, *ibid.*, 1961, 1617.
[17] F. Kurzer and M. Wilkinson, *J. Chem. Soc.* (*C*), 1970, 19.

hydroxide (40 ml, 0.04 mol). The precipitate which appeared gradually was filtered off after 30 min (solid A) and the filtrate was stirred for 2 h, filtered again if necessary, then acidified at 0 °C with 3N-acetic acid. The soft precipitate was collected (it usually turned resinous), air-dried, and crystallised from butanol (23—30 ml) giving minute prisms (1.04—1.72 g, 15—25%) of *1,5-bis(thiobenzoyl)thiocarbonohydrazide*, m.p. 178—182° (Found: C, 52.5; H, 3.4; N, 16.4; S, 27.4. $C_{15}H_{14}N_4S_3$ requires C, 52.0; H, 4.05; N, 16.2; S, 27.7%), $\nu_{max.}$ 3 100m, 2 930m, 2 880m (NH), 1 495m, 760s, 685s (Ph), and 1 065s cm^{-1} (CS?). The final crops (*ca.* 0.4 g) from the butanol filtrates were 2,5-diphenyl-1,3,4-thiadiazole, m.p. 136—138° (from ethanol), identified by its i.r. spectrum.[1] Solid A (0.38—0.57 g, 10—15%) gave prisms of 4-amino-3-mercapto-5-phenyl-1,2,4-triazole, m.p. and mixed m.p. 201—202° (from acetone–ethanol), identified by its i.r. spectrum.[18]

Reverse addition of the reactants gave even less favourable results, producing increased yields of 4-amino-3-mercapto-5-phenyl-1,2,4-triazole (25—30%) and reduced yields of the diadduct (10—15%). Dimethylformamide was not a suitable solvent, much thiobenzoylthioacetic acid being recovered when it was used.

2,3-Dihydro-1-methylthio-4-phenyl-2,3,5,6-tetrazine.— A stirred solution of *S*-methylisothiocarbonohydrazide hydriodide [19] (1.24 g, 0.005 mol) in water (10 ml) was treated dropwise with thiobenzoylthioacetic acid (1.06 g, 0.005 mol) in 3N-sodium hydroxide (3.3 ml, 0.01 mol); a pale-orange precipitate appeared and methanethiol was evolved. The mixture was acidified with 3N-acetic acid, and the solid was collected and air-dried. Crystallisation from ethanol (*ca.* 10 ml per g) gave *2,3-dihydro-1-methylthio-4-phenyl-2,3,5,6-tetrazine* as faintly orange felted needles, m.p. 152—154° (0.36—0.54 g, 35—52%) (Found: C, 52.0; H, 4.85; N, 28.0; S, 15.8%; M^+, 206. $C_9H_{10}N_4S$ requires C, 52.4; H, 4.85; N, 27.2; S, 15.5%; *M*, 206), $\nu_{max.}$ 3 300s, 3 060m, 2 930m (NH), 1 575m,br (NH/CN), 770s, and 690s cm^{-1} (Ph). The crystallisation filtrates gave only deep-red resinous material.

In some experiments, in which the evolution of methanethiol was especially marked, crystallisation of the crude product, first from ethanol, then from acetone–ethanol, gave faintly yellow needles (0.29 g, 25%) of 2-isopropylidenehydrazino-5-phenyl-1,3,4-thiadiazole, m.p. and mixed [2] m.p. 238—240° (Found: C, 57.3; H, 5.1; N, 24.2; S, 13.4. Calc. for $C_{11}H_{12}N_4S$: C, 56.9; H, 5.2; N, 24.1; S, 13.8%), also identified by its i.r. spectrum; $\nu_{max.}$ 3 140s, 3 060s, 2 940s (NH), 1 570—1 560s,br (NH/CN), 765s, and 690s cm^{-1} (Ph).

Reaction did not occur in dimethylformamide, the thiobenzoylthioacetic acid being recovered (85%) after 2 h interaction at room temperature.

1-Methylthio-4-phenyl-2,3,5,6-tetrazine.—The foregoing 2,3-dihydrotetrazine (1.03 g, 0.005 mol) dissolved almost completely in ethanol (20 ml)–3N-hydrochloric acid (20 ml) on warming. Addition of 6% hydrogen peroxide (11.3 ml, 0.02 mol), and heating to *ca.* 60 °C for 5 min gave a clear orange liquid which rapidly turned scarlet and deposited a dark-purple solid. Crystallisation from chloroform–light petroleum (with addition of a little methanol) gave deep scarlet prisms (0.51 g, 50%) of the *substituted tetrazine*, m.p. 96—98° (Found: C, 53.3; H, 3.8; N, 26.8; S, 14.9. $C_9H_8N_4S$ requires C, 52.9; H, 3.9; N, 27.45; S, 15.7%), $\nu_{max.}$ 1 195s, 905s (tetrazine), [12,13] 760s, and 695s cm^{-1} (Ph).

1-Phenylthiocarbonohydrazide.—Thiobenzoylation and treatment with acid. A stirred solution of 1-phenylthiocarbonohydrazide (1.82 g, 0.01 mol) in N-sodium hydroxide (0.0125 mol) was treated dropwise during 5—10 min at room temperature with a solution of thiobenzoylthioacetic acid (2.12 g, 0.01 mol) in N-sodium hydroxide (0.011 mol). Stirring was continued for 30 min (odour of hydrogen sulphide), and the finally clear deep orange-brown solution was acidified with 3N-acetic acid (with addition of ice). The creamy pink precipitate was collected, washed with water, and well drained.

It was refluxed without delay in ethanol (60 ml)–5N-hydrochloric acid (15 ml) for 30 min, and the liquid was distilled under reduced pressure to *ca.* half-volume, until the appearance of solid. This was collected at 0 °C (m.p. 206—208°; 0.8—1.08 g, 30—40%) (filtrate F), and crystallised from ethanol (20 ml per g; recovery 60%), giving silky felted needles of *4-anilino-3-mercapto-5-phenyl-1,2,4-triazole*, m.p. 214—215° (Found: C, 62.9; H, 4.6; N, 20.8; S, 12.1%; M^+, 268. $C_{14}H_{12}N_4S$ requires C, 62.7; H, 4.5; N, 20.9; S, 11.9%; *M*, 268), $\nu_{max.}$ 3 170s, 3 020s, 2 860s, 2 700m (NH), 1 605s (C=N), 1 550s (NH/CN), 1 500s (doublet), 775s, 760s, and 695s cm^{-1} (Ph). The compound was soluble in 3N-sodium hydroxide in the cold, and reprecipitated by 3N-acetic acid. It did not give a picrate in ethanol under the usual conditions.

Filtrate F was distilled to smaller volume if necessary and stirred into ice–water (80 ml), and the resulting precipitate (soft at first) was collected after several hours storage (1—1.5 g). It was extracted with warm 1.5N-sodium hydroxide (20—25 ml), and the pale orange residue was collected (filtrate G) (m.p. 185—190°; 0.60—0.95 g, 22—35%; almost pure by t.l.c. and i.r. spectrum). Crystallisation from acetone–ethanol (10 ml each per g; recovery 60%) gave opaque microcrystalline *2-phenyl-5-phenylhydrazino-1,3,4-thiadiazole*, m.p. 197—198° (Found: C, 62.75; H, 4.65; N, 20.85; S, 12.0. $C_{14}H_{12}N_4S$ requires C, 62.7; H, 4.5; N, 20.9; S, 11.9%), $\nu_{max.}$ 3 280, 3 220s,br, 3 120, 3 080ms,br (doublet), 2 950s (NH), 1 605 (C=N), 1 505s, 765s, and 690s cm^{-1} (Ph). On storage, its colour deepens to yellow-orange (see below). Similarly, the mother liquors from the crystallisation of even pure samples of the 5-phenylhydrazino-compound always gave some orange needles of the 5-phenylazo-compound, m.p. 170—172°.

Filtrate G was acidified with 3N-acetic acid, and the precipitate (0.6—0.7 g; m.p. 190—195°) crystallised from a small volume of ethanol; this gave successive crops (0.2—0.32 g, 8—12%) of 4-anilino-3-mercapto-5-phenyl-1,2,4-triazole (see above).

Thiobenzoylation and treatment with alkali. The crude adduct obtained as above (from 0.02 mol of the reactants) was suspended in 2N-sodium hydroxide (90 ml) and refluxed for 15—20 min. The deep reddish-brown liquid became lighter in colour, but darkened again on exposure to air. It was diluted with ice (100 g), and acidified with 3N-acetic acid, to give a creamy partly resinous precipitate, which solidified on stirring. It was collected, air-dried, and dissolved in boiling ethanol (*ca.* 80 ml). The separated white crystalline solid (3.0—3.45 g, 56—64%) was 4-anilino-3-mercapto-5-phenyl-1,2,4-triazole (see above). The filtrates therefrom deposited non-homogeneous orange and white material, which gave, on crystallisation from acetone–

[18] F. Kurzer and M. Wilkinson, *J. Chem. Soc.* (*C*), 1969, 1218.
[19] E. S. Scott and L. F. Audrieth, *J. Org. Chem.*, 1954, **19**, 1231.

ethanol, orange needles (0.53—0.8 g, 10—15%) of 2-phenyl-5-phenylazo-1,3,4-thiadiazole, m.p. 171—172° (see below).

4-Anilino-3-mercapto-5-phenyl-1,2,4-triazole was converted into the following derivatives by standard procedures: *4-anilino-3-methylthio-5-phenyl-1,2,4-triazole*, lustrous prisms (75—85%), m.p. 218—220° (from methanol–acetone) (Found: C, 63.5; H, 5.0; N, 19.7; S, 11.4. $C_{15}H_{14}N_4S$ requires C, 63.8; H, 5.0; N, 19.9; S, 11.35%), $\nu_{max.}$ 3 170s, 3 110s, 3 000s, 2 950s (doublet) (NH), 1 605s (C=N), 1 505s, 750s, and 695s cm^{-1} (Ph); *4-anilino-3-ethylthio-5-phenyl-1,2,4-triazole*, opaque white prisms, m.p. 199—200° (from ethanol) (56%) (Found: C, 64.7; H, 5.3; N, 19.5; S, 10.7. $C_{16}H_{16}N_4S$ requires C, 64.9; H, 5.4; N, 18.9; S, 10.8%), $\nu_{max.}$ 3 200s, 3 100ms, 3 000, 2 900s (doublet, NH), 1 605s (C=N), 1 500s, 755s,br, and 695s cm^{-1} (Ph); *4-anilino-3-benzylthio-5-phenyl-1,2,4-triazole*, microcrystalline opaque powder, m.p. 193—194° (from chloroform–light petroleum) 92% (Found: C, 69.9; H, 4.9; N, 15.5; S, 8.35. $C_{21}H_{18}N_4S$ requires C, 70.4; H, 5.0; N, 15.6; S, 8.9%), $\nu_{max.}$ 3 170s, 2 930s (NH), 1 605s (C=N), 1 505s, 775, 770s (doublet), 700, 695s (doublet) (Ph), and 1 465s cm^{-1} (CH_2 in CH_2Ph).

4-Anilino-3-phenyl-1,2,4-triazol-5-yl Benzyl Sulphone.—A stirred solution of 4-anilino-3-benzylthio-5-phenyl-1,2,4-triazole (1.07 g, 0.003 mol) in glacial acetic acid (15 ml) was treated with 30% hydrogen peroxide (3.4 ml, 0.03 mol) at 80 °C during 10 min, and the liquid was stirred at this temperature for 1 h. Addition of the brown solution to ice–water precipitated an orange solid which gave faintly yellow microprisms of the *sulphone*, m.p. 215—216° (0.61 g, 52%) (from ethanol–acetone) (Found: C, 64.8; H, 4.7; N, 14.1; S, 8.15. $C_{21}H_{18}N_4O_2S$ requires C, 64.6; H, 4.6; N, 14.4; S, 8.2%), $\nu_{max.}$ 3 300s, 3 020m, 2 980m, 2 930m (NH), 1 610s (C=N), 1 510s, 780, 770s (doublet), 755s, 700s,br (doublet) (Ph), 1 470s (CH_2 in CH_2Ph), 1 345s, and 1 150s cm^{-1} (SO_2).

4-Anilino-3-phenyl-1,2,4-triazol-5-yl methyl sulphone, similarly obtained in low yield, formed off-white opaque prismatic needles, m.p. 145—148° (from 95% ethanol) (Found: C, 57.3; H, 4.8; N, 17.2; S, 9.8. $C_{15}H_{14}N_4O_2S$ requires C, 57.3; H, 4.5; N, 17.8; S, 10.2%), $\nu_{max.}$ 3 250, 3 200s (doublet), 3 050s (doublet), 2 950s (NH), 1 605s (C=N), 1 510s, 780—760s,br, 695s (Ph), 1 350s,br, and 1 155s cm^{-1} (SO_2).

2-Phenyl-5-phenylazo-1,3,4-thiadiazole.—To a suspension of 2-phenyl-5-phenylhydrazino-1,3,4-thiadiazole (0.54 g, 0.002 mol) in hot ethanol (20 ml), 6% hydrogen peroxide (1.70 ml, 0.003 mol) containing concentrated hydrochloric acid (0.25 ml) was added during 1 min. The dark-brown solution was kept on a steam-bath for 10 min, then stirred into ice–water. The finely divided orange precipitate coagulated on being stirred; crystallisation gave 2-phenyl-5-phenylazo-1,3,4-thiadiazole (0.38 g, 72%), m.p. 171—172° (pale-orange felted needles from methanol, or deep orange prismatic needles from ethanol) (Found: C, 63.1; H, 3.9; N, 20.9; S, 12.0. Calc. for $C_{14}H_{10}N_4S$: C, 63.2; H, 3.8; N, 21.05; S, 12.0%), $\nu_{max.}$ 1 580w (C=N), 780s, 770s, and 690s cm^{-1} (Ph) (lit.,[14] m.p. 173—174°).

2-p-Chlorophenyl-5-phenylazo-1,3,4-thiadiazole.— 1-Phenylthiocarbonohydrazide (0.01 mol) was converted into the (crude) 5-*p*-chlorothiobenzoyl derivative in the usual manner. This was suspended in a mixture of ethanol (60 ml), concentrated hydrochloric acid (15 ml), and 6% hydrogen peroxide (17 ml, 0.03 mol) and refluxed for 20 min, and the deep-orange solution was distilled to *ca.* half-volume. The separated dark solid (m.p. 166—169°; 1.9—2.15 g, 64—72%) gave, on crystallisation from ethanol, orange needles of *2-p-chlorophenyl-5-phenylazo-1,3,4-thiadiazole*, m.p. 170—171° (Found: C, 55.9; H, 3.4; Cl, 11.9; N, 18.6. $C_{14}H_9ClN_4S$ requires C, 55.9; H, 3.0; Cl, 11.8; N, 18.6%), $\nu_{max.}$ 1 600s (C=N), 835s (1,4-disubst. aryl), 770s, and 685s cm^{-1} (Ph).

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