Cyanamides. Part VIII. The Interaction of* 1-*Arylbiurets and Arenesulphonyl Chlorides.*

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The interaction of 1-arylbiurets or *N*-aryl-*N'*-cyanoureas with arenesulphonyl chlorides in pyridine produces aryl *iso*cyanates and triarenesulphonylmelamines as main products. The mechanism of these reactions is discussed.

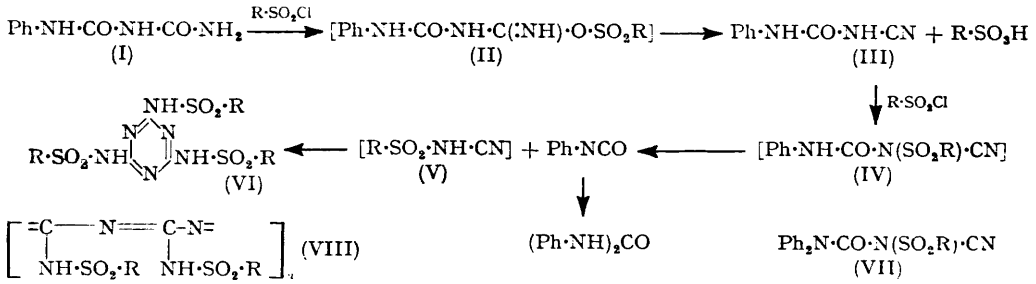
UNLIKE acylureas and their thio-analogues, sulphonylureas and sulphonylthioureas are not obtainable by the direct action of the appropriate acid chlorides upon ureas (Kurzer, *Chem. Reviews*, 1952, **50**, 1, 13). Aromatic ureas and thioureas react with arenesulphonyl chlorides, with elimination of the elements of water or hydrogen sulphide, to yield *N*-arenesulphonyl-*N*-arylcyanamides (Part III, *J.*, 1949, 1034, 3029; Part IV, 1950, 3269). *iso*-Ureas and *iso*thioureas, on the other hand, readily form *N*-sulphonyl derivatives by a modified Hinsberg procedure. The present paper reports analogous reactions of biurets; in their essentials, the results may be correlated satisfactorily with those in the urea series.

The reaction between 1-arylbiurets and arenesulphonyl chlorides in pyridine, under

* Part VII, *J.*, 1954, 4152. Most of the present work has been summarised in *Chem. and Ind.*, 1953, 195.

the usual experimental conditions (Part II, *loc. cit.*), afforded *iso*cyanates and trisulphonylmelamines (VI) as main products. 1-Phenylbiuret and toluene-*p*-sulphonyl chloride, for example, gave *s*-diphenylurea (from the primary product, phenyl *iso*cyanate) and tri(toluene-*p*-sulphonyl)melamine in 60 and 45% yield, respectively. The comparatively low yields of the latter were due to the formation of by-products in a parallel reaction (see below).

The main reaction is accounted for by a mechanism, outlined in the annexed scheme (I—VI), which is closely related to those that have proved satisfactory for the corresponding reactions of aromatic ureas (Part III, *J.*, 1949, 3033) and thioureas (Part IV, *loc. cit.*). In this sequence, the first stage of the interaction is the formation of unstable 1-aryl-4-



O-sulphonyl-4-*iso*biurets (II). In common with other imidosulphonate structures incorporating the ·C(O·SO_2R):NH grouping (Oxley, Partridge, Peak, and Short, *J.*, 1948, 1514, 1618; Kurzer, *Chem. Reviews*, *loc. cit.*), these decompose instantly with elimination of arenesulphonic acids to yield the corresponding cyano-derivative, in this instance *N*-aryl-*N'*-cyanoureas (III). Further interaction of these intermediates with excess of sulphonyl halide affords *N*-aryl-*N'*-cyano-*N'*-sulphonylureas (IV). Observations on the interaction of *N*-cyano-*N'*-sulphonylguanidines and sulphonyl chlorides (Part VI, *J.*, 1953, 2531), and the present results, suggest that structures incorporating a ·N(SO_2R)·CN grouping in proximity to a mobile hydrogen atom are labile, and decompose with elimination of the elements of sulphonylcyanamides. Thus, the postulated intermediate sulphonylcyanoureas (IV) break down into aryl *iso*cyanates and arenesulphonylcyanamides (V), the latter polymerising to trisulphonylmelamines (VI) and other polymeric products (see below). The fact that cyanosulphonylureas (IV) are split spontaneously *during* the reaction, and not by hydrolytic reagents used in the subsequent isolation process (cf. Experimental section), was confirmed by the addition of suitable reaction mixtures to anhydrous light petroleum, aryl *iso*cyanate being then isolated. The formulation of cyanosulphonylureas, as (IV), in preference to alternative *O*-sulphonyl*iso*urea structures [Ph·N:C(O·SO_2·R)·NH·CN and tautomeric forms] is regarded as justified in view of the acidic character of the hydrogen atom of the cyanamide grouping in cyanoureas (III).

The correctness of the suggested mechanism presupposed that *N*-aryl-*N'*-cyanoureas and 1-arylbiurets should form the same products with sulphonyl halides. This requirement was fulfilled, cyanoureas (III) reacting generally more smoothly to give better yields, probably because the two initial stages of the reaction sequence (I—VI) are eliminated. *N*-Cyano-*N'*-phenylurea and toluene-*p*-sulphonyl chloride in pyridine at 80°, for example, produced *s*-diphenylurea and tri(toluene-*p*-sulphonyl)melamine in 65% and 58% yields, respectively.

The last stage of the suggested mechanism [*i.e.*, (V ⟶ VI)] has not been confirmed experimentally because benzene- and toluene-*p*-sulphonylcyanamide were not obtainable except in the form of their metallic salts. In contrast, free aroylcyanamides can be isolated without difficulty (*e.g.*, benzoylcyanamide: Hantzsch and Dollfus, *Ber.*, 1902, **35**, 255; Diels and Wagner, *Ber.*, 1912, **45**, 876; Crowther, Curd, and Rose, *J.*, 1948, 586). Arenesulphonylcyanamide salts have been described by Hebenstreit (*J. prakt. Chem.*, 1890, **41**, 97), who claimed their conversion, by mineral acids, into free sulphonylcyanamides. In the present work, Hebenstreit's experimental observations were confirmed, and the identity

of the salts established by their conversion into sulphonylthioureas with hydrogen sulphide in pyridine–triethylamine by the method of Fairfull, Low, and Peak (*J.*, 1952, 742). All attempts to isolate the free acids from the sulphonylcyanamide salts, however, under Hebenstreit's or other conditions, gave arenesulphonylureas, or resulted, on more drastic treatment, in partial hydrolysis to arenesulphonamides. Excepting the single representative of the alkyl series described, Hebenstreit's alleged sulphonylcyanamides contained, on the basis of their composition " a molecule of water of crystallisation " which was not given off below their decomposition points; their reported stability towards acids, and their thermal decomposition into sulphonamide and cyanuric acid (recently shown to be a reaction of sulphonylureas; cf. Part V, *J.*, 1951, 1258) show plainly that Hebenstreit's aromatic products were arenesulphonylureas. Brief treatment of sodium or calcium sulphonylcyanamides with boiling mineral acid has in fact been used for the preparation of *p*-acetamido- (Winnek, Anderson, Marson, Faith, and Roblin, *J. Amer. Chem. Soc.*, 1942, **64**, 1682) and *p*-nitrobenzenesulphonyl-urea (Backer and Moed, *Rec. Trav. chim.*, 1947, **66**, 335).

The remarks concerning stage (IV ⟶ V) imply that fully substituted sulphonylcyanoureas, which lack mobile hydrogen atoms, should not decompose spontaneously. This expectation was realised by the preparation of a sulphonyl derivative of *N*-cyano-*N'N'*-diphenylurea, formulated as (VII). The required cyanourea was readily obtained from diphenylcarbamoyl chloride (reaction 1); it was remarkably resistant to the action of alkalis, but was rapidly hydrolysed to diphenylamine by boiling hydrochloric acid; brief treatment with concentrated sulphuric acid at 25° gave fair yields of 1 : 1-diphenylbiuret (reaction 2). Reactions (1) and (2) are a useful extension of one of the classical biuret syntheses (Baumann *Ber.*, 1875, **8**, 708; Hecht, *Ber.*, 1892, **25**, 749) to 1 : 1-disubstituted biurets. In this connexion, mention may be made of Biltz and Jeltsch's unsuccessful efforts (*Ber.*, 1923, **56**, 1914) to prepare analogous substituted biurets by condensing dimethylcarbamoyl chloride with urea and its homologues; the present method appears to by-pass these difficulties.

$$Ph_2N{\cdot}COCl + NH_2{\cdot}CN \longrightarrow Ph_2N{\cdot}CO{\cdot}NH{\cdot}CN + HCl \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$Ph_2N{\cdot}CO{\cdot}NH{\cdot}CN + H_2O \longrightarrow Ph_2N{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Both the above reactions (I ⟶ VI, and III ⟶ VI), but more particularly the biuret–arenesulphonyl chloride interaction, gave also varying quantities (20—40%) of non-homogeneous by-products, the composition of which approximated to that of arenesulphonylcyanamides. These products were highly soluble non-crystalline acidic solids of high molecular weight; they were partially fractionated and purified by repeated reprecipitation from their alkaline or alcoholic solution (cf. Experimental section). Hydrolysis, by concentrated sulphuric acid or ethanolic hydrogen chloride (cf. Part VI, *loc. cit.*), afforded the appropriate sulphonic acid or sulphonamide, respectively, thus confirming the presence of arenesulphonamido-residues in their structures.

Analogous products resulted in moderate yields from the interaction of cyanamide and arenesulphonyl chlorides in pyridine. The mode of formation, the ultimate composition, and the non-homogeneous nature of these substances suggest their provisional formulation as polymers (other than melamines) of arenesulphonylcyanamides. While no definite structure can be advanced at this stage, the possible existence of linear polymers (VIII) of varying chain length, analogous in structure with Sidgwick's suggested formula for cyamelide (Taylor and Baker, " Sidgwick's Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 323), may be borne in mind.

In contrast to *iso*urea ethers, which yield *N*-sulphonyl derivatives readily (Cox and Raymond, *J. Amer. Chem. Soc.*, 1941, **63**, 300; 1942, **64**, 2225), the structurally related 4-methyl-1-phenyl-4-*iso*biuret failed to react with sulphonyl chlorides in alkaline media. In pyridine, small quantities (3—8%) of triarenesulphonylmelamine were produced, probably by previous demethylation of the *iso*biuret by the pyridinium chloride formed *in situ* (cf. Kurzer, *J.*, 1953, 3360), followed by the usual reaction (I—VI).

Attention may be drawn to the powerfully sweet taste, previously unrecorded, of *N*-cyano-*N'*-phenylurea. The introduction of the cyano-group into phenylurea, known to

possess a strong bitter taste, thus causes a remarkable reversal of this physiological property. *N*-Cyano-*N'*-α-naphthylurea was tasteless.

Experimental

The pyridine used was the commercially available anhydrous grade. The identity of triarenesulphonylmelamines was confirmed in all cases by mixed m. p. determinations with authentic samples prepared from cyanuric chloride (Part VII, *loc. cit.*), and from *N*-arenesulphonyl-*N'*-cyanoguanidines (Part VI, *loc. cit.*).

1-Phenylbiuret was prepared by McKee's method (*Amer. Chem. J.*, 1901, **26**, 253) in 62—70% yield from 4-methyl-1-phenyl-4-*iso*biuret. After four crystallisations from absolute ethanol it formed compact prisms, m. p. 170—171° (decomp.) (inserted at 145°; temp. raised at 4° per min.). The m. p. of the product depends on the rate of heating, and has variously been given between 156° and 167° (McKee, *loc. cit.*; Blair, *J. Amer. Chem. Soc.*, 1934, **56**, 904).

*4-Methyl-1-α-naphthyl-4-*iso*biuret.*—A solution of methyl*iso*urea hydrochloride (Kurzer and Lawson, *Org. Synth.*, 1954, **34**, 67) (12·2 g., 0·11 mole), in water (15 ml.), rendered alkaline with aqueous potassium hydroxide (27 ml., 25% w/v., 0·12 mole) was slowly treated with α-naphthyl *iso*cyanate (16·9 g., 0·1 mole), with good shaking during 10 min. at <25° (cooling); agitation was then continued for 0·5 hr. The granular solid was collected, air-dried, and extracted with boiling ethanol (4 × 50 ml.). The ethanol-insoluble residue was di-α-naphthylurea, m. p. 286—287° (2·3 g.). The alcoholic extracts deposited, on cooling and partial evaporation, white crystals (m. p. 140—145°; total 13·6 g., 56%) which gave, on crystallisation from ethanol (20 ml. per g.), lustrous platelets of *4-methyl-1-α-naphthyl-4-*iso*biuret*, m. p. 141—142° (decomp.) (Found: C, 64·4; H, 5·4; N, 16·8. $C_{13}H_{13}O_2N_3$ requires C, 64·2; H, 5·35; N, 17·3%).

1-α-Naphthylbiuret.—A suspension of 4-methyl-1-α-naphthyl-4-*iso*biuret (12·15 g., 0·05 mole) in hydrochloric acid (3N, 180 ml.; contained in a large flask; subsequent severe frothing) was slowly heated under reflux until brisk effervescence indicated the beginning of the interaction; the source of heat was then temporarily withdrawn. The reaction was completed by gentle boiling until no more methyl chloride was evolved (15—20 min.). The suspension was cooled to 0°, and the granular solid [m. p. 220—224° (decomp.); 10—10·5 g.] collected, dried, and crystallised from ethanol (150 ml. per g.), white feathery needles of 1-α-naphthylbiuret, m. p. 214—215° (decomp.), being obtained (8·6—9·15 g., 75—80%) (Found: N, 18·6. Calc. for $C_{12}H_{11}O_2N_3$: N, 18·3%).

*Interaction of 1-Phenylbiuret and Toluene-*p*-sulphonyl Chloride.*—A solution of 1-phenylbiuret (3·58 g., 0·02 mole) in pyridine (30 ml.) was treated with toluene-*p*-sulphonyl chloride (11·44 g., 0·06 mole) at 20°. The orange-red liquid (the temperature of which did not rise spontaneously) was kept at 85—90° during 20 min., stirred into ice (250 g.), and acidified to Congo-red with concentrated hydrochloric acid (35 ml.). During several hours' storage, the upper oily orange-brown layer (which smelled powerfully of phenyl *iso*cyanate) solidfied gradually, with simultaneous slow effervescence, to a brittle sponge-like mass. The powdered product was extracted with aqueous sodium hydroxide (12%; 40, 30, and 20 ml.; at 20°, 30°, and 40° respectively). The collected undissolved product (m. p. 215—225°; 1·10—1·30 g., 52—61%) was *s*-diphenylurea, forming needles, m. p. and mixed m. p. 236—238°, from ethanol. Acidification of the alkaline filtrate to Congo-red with concentrated hydrochloric acid gave a white solid; the collected air-dried powder (3·8 g.) was added to boiling ethanol (50 ml.): the red solution rapidly deposited lustrous crystals on cooling. [A second crop was obtainable by evaporating the ethanol filtrates to dryness, redissolving the residual oil in 12% alkali, and adding the product precipitated by acid to a fresh portion of boiling ethanol (ethanolic filtrates therefrom: A).] The collected crystalline solid (m. p. 278—282°; 1·57—1·75 g., 40—45%) gave, on crystallisation from ethanol, platelets of tri(toluene-*p*-sulphonyl)melamine, m. p. 282—284° (Found: C, 49·2; H, 4·6; N, 13·9; S, 15·9. Calc. for $C_{24}H_{24}O_6N_6S_3$: C, 49·0; H, 4·1; N, 14·3; S, 16·3%).

The ethanolic filtrates A, from which no more trisulphonylmelamine separated, contained varying quantities of an oil, highly soluble in organic solvents and alkalis, which was isolated by precipitation from its alkaline solution by mineral acid, as a white to pink powder, of indefinite m. p. The results of analysis and mol. wt. determinations suggest the presence of a higher polymeric form of toluene-*p*-sulphonylcyanamide (yield, 1·2—1·7 g.; 30—43%, calc. as polymeric sulphonylcyanamide) (cf. last paragraph, Experimental).

1-Phenylbiuret was recovered almost quantitatively after treatment with toluene-*p*-sulphonyl chloride in acetone–aqueous alkali (experimental details as in Part VI, *J.*, 1953, 2533).

Cognate Experiments.—The interaction of 1-phenylbiuret and benzenesulphonyl chloride

under the above conditions gave *s*-diphenylurea (68%), ethanol-solvated tribenzenesulphonylmelamine, m. p. 150—152° (decomp.) (38%) (Found: C, 47·0; H, 4·1; N, 14·7. Calc. for $C_{21}H_{18}O_6N_6S_3,C_2H_6O$: C, 46·6; H, 4·05; N, 14·2%), and low-melting (60—70°) acidic material (45%, calc. as polymeric benzenesulphonylcyanamide).

1-Phenylbiuret and toluene-*o*-sulphonyl chloride similarly gave *s*-diphenylurea (62%), tri(toluene-*o*-sulphonyl)melamine, m. p. 292—294° (16%), and low-melting acidic material (45%).

1-α-Naphthylbiuret (2·30 g., 0·01 mole), suspended in pyridine (20 ml.), was treated at 80° with toluene-*p*-sulphonyl chloride (7·6 g., 0·04 mole) during 5 min., and the resulting deep-red liquid kept at 95° during 30 min., and worked up as above. It afforded *s*-di-α-naphthylurea, m. p. 286—287° (decomp.) (82%), tri(toluene-*p*-sulphonyl)melamine, m. p. 282—284° (45%), and low-melting acidic material (35%). Under the less vigorous standard conditions (see above), much unchanged 1-α-naphthylbiuret, m. p. and mixed m. p. 223—225° (up to 40%), was recovered from the alkali-insoluble product and was separated from the *s*-di-α-naphthylurea by its solubility in ethanol.

4-Methyl-1-phenyl-4-*iso*biuret, treated with arenesulphonyl chloride in pyridine, gave 3—8% of triarenesulphonylmelamine (presumably by preliminary demethylation of the *iso*-biuret by pyridinium chloride). It failed to react with arenesulphonyl chloride in aqueous or aqueous acetone media in the presence of alkali.

N-*Cyano*-N′-α-*naphthylurea*.—A solution of cyanamide (6·3 g., 0·15 mole) (*Org. Synth.*, 1954, **34**, 67) in water (25 ml.), made alkaline with sodium hydroxide (12% w/v., 36 ml.; 0·11 mole) was treated, with good shaking, at 20—25° (slight external cooling required) with α-naphthyl *iso*cyanate (18·6 g., 0·11 mole) during 30 min. A trace of separated di-α-naphthylurea was filtered off, and the clear filtrate *just* acidified to Congo-red with concentrated hydrochloric acid (dropwise). The crystalline precipitate was collected at 0°, washed with ice-water (5 × 20 ml.), and dried in a vacuum over phosphoric oxide. The crude product [m. p. 142—145° (decomp., resolidifying at once); 19·7 g., 85%] gave, after two crystallisations from acetone–light petroleum (12 and 6 ml., respectively, per g.; recovery 60% per crystallisation), lustrous prisms of N-*cyano*-N′-α-*naphthylurea*, m. p. 148—149° (decomp.) (Found: N, 19·7. $C_{12}H_9ON_3$ requires N, 19·9%).

Interaction of N-*Cyano*-N′-*phenylurea and Toluene*-p-*sulphonyl Chloride*.—(*a*) *N*-Cyano-*N*′-phenylurea (3·22 g., 0·02 mole), dissolved in pyridine (15 ml.), was treated with toluene-*p*-sulphonyl chloride (7·62 g., 0·04 mole) at room temperature, and the solution kept at 80° during 20 min. The deep-red liquid was added to ice (150 g.), and the whole acidified to Congo-red with concentrated hydrochloric acid (20 ml.). The observations, and the method of isolating the products, were as described for the corresponding reaction of 1-phenylbiuret (see above). In this way, the following were obtained: *s*-diphenylurea (1·38 g., 65%), m. p. and mixed m. p. 236—238°; tri(toluene-*p*-sulphonyl)melamine (2·27 g., 58%), m. p. 282—284°; and low-melting (65—75°) acidic material (1·18 g., 30%, calc. as polymeric toluene-*p*-sulphonylcyanamide).

(*b*) The deep-red reaction mixture obtained as in (*a*) was stirred with anhydrous light petroleum (b. p. 60—80°; 3 × 60 ml.), and the extracts were decanted (combined extracts: A). The residual oil solidified slowly in contact with water (10 ml.); it was separated, as usual, by sodium hydroxide, into *s*-diphenylurea (0·4 g., 19%), and tri(toluene-*p*-sulphonyl)melamine (52%), m. p. 282—284°. Evaporation of the petroleum extracts A gave an oil which smelled powerfully of phenyl *iso*cyanate: addition of aniline (3·7 g., 0·04 mole), followed by heating at 90° during 0·5 hr., gave a product which was extracted with aqueous sodium hydroxide (6%; 3 × 15 ml.). The insoluble residue was *s*-diphenylurea (2·85 g., 67%); acidification of the filtrate precipitated toluene-*p*-sulphonanilide (0·85 g.), m. p. and mixed m. p. 100—102° (from benzene–light petroleum) (Found: C, 63·1; H, 5·3; N, 5·4. Calc. for $C_{13}H_{13}O_2NS$: C, 63·2; H, 5·3; N, 5·7%). The last-mentioned product arose probably from the excess of toluene-*p*-sulphonyl chloride, dissolved by the light petroleum, and the added aniline.

N-Cyano-*N*′-phenylurea was recovered unchanged after treatment with toluene-*p*-sulphonyl chloride in acetone–aqueous alkali (experimental details as in Part VI).

Cognate Experiments.—The reaction of *N*-cyano-*N*′-phenylurea and toluene-*o*-sulphonyl chloride (procedure *a*) gave *s*-diphenylurea (65%), and tri(toluene-*o*-sulphonyl)melamine (36%), m. p. 293—294°. Interaction of *N*-cyano-*N*′-α-naphthylurea (0·01 mole) and toluene-*p*-sulphonyl chloride (0·04 mole) at 95° during 30 min., followed by isolation according to procedure (*a*), afforded *s*-di-α-naphthylurea (54%), m. p. and mixed m. p. 285—287° (decomp.), and tri(toluene-*p*-sulphonyl)melamine (38%), m. p. 282—284°.

N-*Cyano*-N′N′-*diphenylurea*.—To cyanamide (10·1 g., 0·24 mole; *Org. Synth.*, 1954, **34**, 67) in water (40 ml.), previously filtered with carbon, aqueous sodium hydroxide (25 ml., 20% w/v, 0·125 mole) and acetone (50 ml.) were added. This stirred solution was treated, at room temperature, with a solution of diphenylcarbamoyl chloride (13·9 g., 0·06 mole) in acetone (30 ml.) during 2—2½ hr., a further portion of aqueous sodium hydroxide (0·125 mole) being gradually added during the second half of the addition to keep the liquid strongly alkaline to litmus. Stirring was then continued for 1—1½ hr., and more acetone added if necessary, to redissolve any solid which tended to separate. Air was now drawn over the surface of the stirred solution to remove most of the acetone, and the residual liquid (L) diluted with water (100 ml.). A small quantity of separated solid (consisting of unchanged diphenylcarbamoyl chloride, m. p. 86°) was filtered off, and the clear filtrate acidified at 0° with concentrated hydrochloric acid. The precipitated crystalline solid was collected, washed with water, and then with ether (3 × 20 ml.; ethereal washing liquid: A) and air-dried (m. p. 138—144°, after sintering at 130°; 12·1—12·8 g.). Two crystallisations from acetone–light petroleum (10 and 4 ml., respectively, per g.) gave lustrous plates of N-*cyano*-N′N′-*diphenylurea*, m. p. 153—154° (Found: C, 70·35; H, 4·3; N, 17·4. $C_{14}H_{11}ON_3$ requires C, 70·9; H, 4·6; N, 17·7%) (yield, including material from the mother-liquors, 9·25—12·1 g., 65—85%). The ethereal washing liquid A deposited diphenylamine (1·0 g., 10%), m. p. and mixed m. p. 52—54°, on evaporation.

Alternatively, the filtered liquid L, without previous dilution, was set aside at 0° during 48 hr. The separated crystalline solid (m. p. 88—90°; 14—14·8 g., 90—95%) was collected and recrystallised from acetone (5 ml. per g., recovery 80%) and lustrous needles of the *sodium derivative*, m. p. 89—91°, were obtained. Its identity was established by reconversion into *N*-cyano-*N′N′*-diphenylurea (carried out by acidification of its aqueous solution).

N-Cyano-*N′N′*-diphenylurea was recovered almost quantitatively (*a*) after being refluxed with aqueous 1·5N-sodium hydroxide during 1 hr, or (*b*) after treatment with excess of 6% hydrogen peroxide in 1·5N-sodium hydroxide at 50—60° during 3 hr. Brief refluxing with N-hydrochloric acid caused quantitative hydrolysis to diphenylamine.

1 : 1-*Diphenylbiuret*.—Finely powdered *N*-cyano-*N′N′*-diphenylurea (2·37 g., 0·01 mole) was stirred within 4—5 min. into concentrated sulphuric acid (12 ml.) at 25—30° (cooling). Complete dissolution occurred during the next 2—3 min., and stirring at 25° was continued for a total of 15 min. The almost colourless liquid was treated with crushed ice (30 g.) in one portion. The resulting white precipitate was collected immediately, washed with water, and dried in a desiccator over phosphoric oxide. The white solid (2·2 g.) was dissolved in acetone (120 ml.)–ethanol (10 ml.), and the solution filtered with suction, evaporated to small volume (20 ml.) under reduced pressure, and set aside. It deposited a white semicrystalline solid (1·4 g.) which consisted, after two crystallisations from ethanol (30 ml. per g.), of minute prisms of 1 : 1-*diphenylbiuret*, m. p. 175—178° (decomp.) (1·12 g., 44%), soluble in aqueous alkalis, and reprecipitated by acids. Repeated crystallisation from ethanol raised the m. p. to 182—183° (decomp.; somewhat subject to the rate of heating) (Found: C, 66·2; H, 5·1; N, 16·5. $C_{14}H_{13}O_2N_3$ requires C, 65·9; H, 5·1; N, 16·5%).

N-*Cyano*-N-m-*nitrobenzenesulphonyl*-N′N′-*diphenylurea*.—A solution of *N*-cyano-*N′N′*-diphenylurea (2·37 g., 0·01 mole) in pyridine (20 ml.) at room temperature was treated with *m*-nitrobenzenesulphonyl chloride (3·32 g., 0·015 mole) with cooling. After being kept at 15° during 1 hr., the liquid was added to ice (100 g.) and concentrated hydrochloric acid (20 ml.). The collected dried pale-pink solid (4·15 g.) was dissolved in a boiling mixture of ethanol (25 ml.) and acetone (10 ml.); the clear (filtered) liquid deposited, on prolonged storage, a white granular solid (1·7—2·2 g., 40—52%), which gave, on crystallisation from benzene–light petroleum, needles of N-*cyano*-N-m-*nitrobenzenesulphonyl*-N′N′-*diphenylurea*, m. p. 200—202° (decomp.) (Found: C, 56·4; H, 3·7; N, 13·6; S, 7·2. $C_{20}H_{14}O_5N_4S$ requires C, 56·9; H, 3·3; N, 13·3; S, 7·6%).

Hydrolysis. The above product (1·06 g., 0·0025 mole), suspended in absolute ethanol (120 ml.), was refluxed with passage of anhydrous hydrogen chloride during 10 hr. The resulting clear solution was evaporated nearly to dryness in a vacuum; the residue was made alkaline and stirred with sodium hydroxide (12% w/v; 6 ml.); the undissolved solid was filtered off at 0°, and rinsed with a few drops of water (filtrate A); crystallisation from light petroleum (b. p. 60—80°) gave diphenylamine, m. p. and mixed m. p. 52—53° (total, 0·36 g., 86%). Acidification of filtrate A precipitated *m*-nitrobenzenesulphonamide, which was collected at 0° (0·28 g., 56%) and gave needles, m. p. and mixed m. p. 159—161° (from water).

Toluene-p-*sulphonylurea*.—A solution of sodium toluene-*p*-sulphonylcyanamide (4·4 g., 0·02 mole) [Hebenstreit, *J. prakt. Chem.*, 1890, **41**, 97; the salt crystallises from a large volume of

acetone–ether in platelets, m. p. 290—294° (decomp.)] in water (20 ml.) and concentrated hydrochloric acid (8 ml.) was boiled for 2 min. The white granular solid (1·93 g., 45%; m. p. 183—184°), which was deposited on cooling, was collected (filtrate A) and crystallised from water and then from acetone–light petroleum (25 and 5 ml., per g., respectively), giving toluene-*p*-sulphonylurea, m. p. 191—192° (decomp., subject to the rate of heating; the m. p. was erroneously given as 200—202° in Part V, *J.*, 1951, 1258) (Found: C, 45·0; H, 4·5; N, 13·4. Calc. for $C_8H_{10}O_3N_2S$: C, 44·9; H, 4·7; N, 13·1%). The aqueous filtrate A gave varying quantities of toluene-*p*-sulphonamide, m. p. and mixed m. p. 136—137°, on evaporation.

Similar results were obtained by storing acidified solutions of sodium toluene-*p*-sulphonylcyanamide at room temperature for 48—72 hr. The salt (1 g.), when refluxed in concentrated hydrochloric acid (30 ml.) during 30 min., was converted nearly quantitatively into toluene-*p*-sulphonamide.

Benzenesulphonylurea.—Sodium benzenesulphonylcyanamide (2·04 g., 0·01 mole), when dissolved in an equivalent of 0·1N-sulphuric acid and evaporated to small volume during 3 hr., gave white cubes of benzenesulphonylurea, m. p. and mixed m. p. 170—171° [cf. Haak, U.S.P. 2,385,571; Hebenstreit, *loc. cit.*, reported m. p. 158° (decomp.)]. A second crop resulted from further evaporation and recrystallisation from aqueous ethanol (total yield: 0·65 g., 33%). The final fractions consisted of a mixture of benzenesulphonylurea and benzenesulphonamide.

Toluene-p-*sulphonylthiourea.*—A solution of ammonia (0·68 g., 0·04 mole) in anhydrous *n*-butanol (20 ml.) was saturated with hydrogen sulphide at 0°. Sodium toluene-*p*-sulphonylcyanamide (4·35 g., 0·02 mole) (Hebenstreit, *loc. cit.*) was added, and the suspension heated in a closed vessel at 100° for 6 hr. The crystalline product was filtered off at 0°, washed with *n*-butanol, dried, and dissolved in water (30 ml.). The turbid liquid was filtered with carbon and acidified; the resulting yellow oil was dissolved in ethanol (2 ml., 90%), crystalline plates (0·90 g., 20%) of *toluene*-p-*sulphonylthiourea*, m. p. 128—129° (from ethanol), being slowly deposited (Found: C, 41·8; H, 4·6. $C_8H_{10}O_2N_2S_2$ requires C, 41·7; H, 4·35%). Treatment of a solution of the above sodium salt in pyridine (40 ml.)–triethylamine (2·8 ml.) at 60° for 3 hr. failed to yield the required product. The correctness of the structure of this compound was confirmed by the analogous preparation (in 30% yield) of benzenesulphonylthiourea, m. p. and mixed m. p. (B.P. 595,771; U.S.P. 2,498,782) 137—139° (from ethanol).

Interaction of Cyanamide and Toluene-p-*sulphonyl Chloride.*—Cyanamide (4·2 g., 0·1 mole; *Org. Synth.*, 1954, **34**, 67) in pyridine (30 ml.) was treated with toluene-*p*-sulphonyl chloride (21 g., 0·11 mole) during 5 min., and the hot deep-red liquid kept at 80—90° during 15 min. and added to N-hydrochloric acid (300 ml.) at 0°. The air-dried granular buff precipitate (6—9 g.) was dissolved in boiling ethanol (30—50 ml.) and set aside overnight, and the clear liquid (solution A) decanted from a dark viscid deposit. This, on re-dissolution in boiling ethanol, prolonged treatment with carbon, and filtration, gave a solution which deposited small quantities (up to 0·6 g., 3%) of tri(toluene-*p*-sulphonyl)melamine, m. p. 281—283°, in some, but not all, experiments. Addition of solution A to water (300 ml.) containing sodium chloride (2 g.) gave a granular precipitate (5·5—8 g., 28—41% calc. as polymeric toluene-*p*-sulphonylcyanamide), which formed, after two further reprecipitations from alkaline solution, a nearly white amorphous powder, decomposing variously between 70° and 90°. One hour's drying at 80° in a vacuum raised the decomposition range to 135—145° (after sintering at 120—130°). The *substance* was highly soluble in the usual organic solvents except light petroleum (Found: C, 47·9, 48·5; H, 4·3, 4·6; N, 14·7, 14·2; S, 15·0, 15·7. $[C_8H_8O_2N_2S]_n$ requires C, 49·0; H, 4·1; N, 14·3; S, 16·3%). The product did not significantly depress the f. p. of naphthalene or thymol.

Addition of excess of 6N-aqueous potassium hydroxide to an ethanolic solution of the product gave its *potassium salt*, forming lustrous plates when recrystallised from 66% ethanol (Found: C, 40·3; H, 3·25. $[C_8H_7O_2N_2SK]_n$ requires C, 41·0; H, 3·0%). Addition of excess of silver nitrate to an aqueous ammoniacal solution of the product gave the *silver salt* as a white precipitate {Found (volumetrically): Ag, 32·5, 31·9. $[C_8H_7O_2N_2SAg,H_2O]_n$ requires Ag, 33·6%}.

The material was recovered substantially unchanged after being refluxed with acetic acid–acetic anhydride (2 : 3) during 30 min. It did not add the elements of hydrogen sulphide when treated with this gas in ammoniacal butanol under pressure (conditions: cf. Kurzer, *J. Appl. Chem.*, 1951, **1**, 84) or in pyridine–triethylamine (cf. Fairfull, Low, and Peak, *J.*, 1952, 742). It resisted hydrolysis on 1 hour's refluxing in 12% aqueous sodium hydroxide, or on 4 hours' refluxing in 6% ethanolic potassium hydroxide. Hydrolysis of the product by concentrated sulphuric acid (conditions: cf. Part VI, *loc. cit.*) gave toluene-*p*-sulphonic acid (isolated as the

S-benzylthiuronium salt) in 56—64% yields; ethanolic hydrogen chloride (conditions: cf. Part VI) afforded toluene-*p*-sulphonamide (58%) and traces of cyanuric acid.

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