517. *Cyanamides. Part VI.* Sulphonyl Derivatives related to Dicyandiamide and Melamine.*

By Frederick Kurzer and J. Roy Powell.

N-Aryl(or -alkyl)sulphonyl-*N'*-cyanoguanidines are converted into *N*-(sulphonylamidino)ureas, *N*-(sulphonylamidino)thioureas, and *N*-sulphonyldiguanides, by hydrolysis, addition of hydrogen sulphide, and ammonolysis, respectively. They react with sulphonyl halides in pyridine to yield trisulphonylmelamines, the structures of which are established by degradation.

In continuation of work on the interaction of sulphonyl halides with compounds incorporating the urea structure (Kurzer, *Chem. Reviews*, 1952, **50**, 1), the behaviour of 1-arylbiurets in this reaction has been examined (Kurzer and Powell, *Chem. and Ind.*, 1953, 195). The observed production of polymeric forms of sulphonylcyanamides necessitated a closer examination of sulphonyl derivatives of dicyandiamide and related compounds.

The introduction of two sulphonyl groups into dicyandiamide appeared to be a possible route to dimeric sulphonylcyanamides. Monosulphonyl derivatives of dicyandiamide, and their hydrolytic conversion into sulphonylamidinoureas, have been described by Kaiser and Thurston (U.S.P. 2,368,841; 2,426,882; B.P. 566,864). The results of their parallel work on carbonyldicyandiamides (*J. Org. Chem.*, 1952, **17**, 185, 1162) and the observations now presented suggest that sulphonyldicyandiamides may be regarded as *N*-cyano-*N'*-sulphonylguanidines (I).

By Kaiser and Thurston's method, a number of *N*-cyano-*N'*-sulphonylguanidines (I) were prepared in fair yields from dicyandiamide and sulphonyl chlorides in alkaline media containing a suitable organic solvent, *e.g.*, acetone; the presence of the latter proved essential since interaction in purely aqueous alkalis afforded only negligible yields of (I), the bulk of the dicyandiamide being recovered as amidinourea arylsulphonate. The products (I), though rapidly and quantitatively hydrolysed to the sulphonylamidinoureas (III) by dilute hydrochloric acid, or more slowly by mixtures of water and organic solvents (Kaiser and Thurston, *loc. cit.*), were sufficiently unaffected by boiling water to be readily recrystallised therefrom; they were quite stable towards alkalis.

The results of the addition of hydrogen sulphide and ammonia, respectively, to the products (I) thus obtained confirmed the presence of a cyanamide grouping. Hydrogen sulphide and *N*-cyano-*N'*-sulphonylguanidines, in pyridine–triethylamine (cf. Fairfull, Low, and Peak, *J.*, 1952, 742) gave good yields of *N*-(sulphonylamidino)thioureas (IV), reconvertible into the starting materials (I) by lead acetate in alkali. *N*-Arylsulphonyl-*N'*-cyanoguanidines (I) reacted with aqueous ammonia on prolonged treatment under pressure at 110°, in the presence of copper sulphate, to give small yields (7—12%) of the characteristic pink copper complexes of diguanides from which the free arylsulphonyldiguanides (V) were readily isolated; much of the starting material (30—40%) remained unchanged, however, and part of it was consumed in a side reaction, being hydrolysed to the corresponding arylsulphonylguanidine (12—32%). Depending on the particular reactants selected, the rates of conversion of dicyandiamides into diguanides are known to lie between wide limits (cf. Curd and Rose, *J.*, 1946, 729). In the present case, the low rate of condensation of the substituted dicyandiamide with ammonia and the loss of starting material in the simultaneous hydrolysis undoubtedly combined to lower the yields, which could, therefore, not be greatly improved by prolonging the time of reaction. *N*-Arylsulphonyldiguanides (V) thus obtained were identical with specimens prepared from arylsulphonyl halides and diguanide by the procedure described for the synthesis of sulphanilyldiguanide (Rose, B.P. 550,538). Since, in the latter reaction, the sulphonyl halide may be assumed to attack a terminal nitrogen of the diguanide molecule, the arylsulphonyldiguanides obtained by both routes may be regarded as (V). This evidence rules out the alternative structures (II) for the original sulphonyldicyandiamides. Their solubility in aqueous alkalis and non-solubility in acids are in agreement with this view.

* Part V, *J.*, 1951, 1258.

Although acyldicyandiamides are readily convertible into the corresponding acylbiurets by hydrolysis in a variety of acid media (Adams, U.S.P. 2,401,599), attempts to obtain arylsulphonylbiurets (VI) from *N*-cyano-*N'*-sulphonylguanidines were unsuccessful. With moderately concentrated aqueous-ethanolic sulphuric acid, the reaction proceeded only to the amidinourea stage; under more vigorous conditions the molecule was ruptured, arylsulphonamide being formed as one of the main products.

$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CN$ (I)

$NH_2{\cdot}C(:NH){\cdot}N(SO_2R){\cdot}CN$ (II)

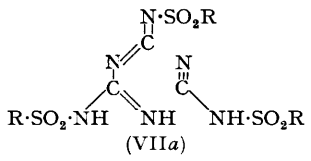
$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CO{\cdot}NH_2$ (III)

$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CS{\cdot}NH_2$ (IV)

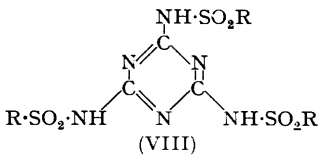
$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C(:NH){\cdot}NH_2$ (V)

$R{\cdot}SO_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$ (VI)

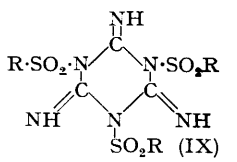
$R{\cdot}SO_2{\cdot}NH{\cdot}C(:NH){\cdot}N(SO_2R){\cdot}CN$ (VII)



(VII*a*)



(VIII)



(IX)

The attempted introduction of a second sulphonyl residue into *N*-cyano-*N'*-sulphonylguanidines (I) did not result in formation of disulphonyldicyandiamides. Since sulphonyldicyandiamides (I) are prepared by the use of an excess of sulphonyl halide, it was not unexpected that they failed to react with a second equivalent of sulphonyl chloride in alkalis. Interaction in pyridine at moderate temperatures, however, rapidly afforded good yields of products which were identified as tri-aryl (or -alkyl)sulphonylmelamines. Their suggested structure (VIII) was proved by molecular-weight determinations and hydrolytic degradation. Concentrated sulphuric acid, known as a suitable reagent for splitting the nitrogen–sulphur link of the sulphonamide group (Ciba, Swiss P. 88,561; Kuhn and Reinemund, *Ber.*, 1934, **67**, 1932; Hodgson and Birtwell, *J.*, 1943, 433; Thorp and Walton, *J.*, 1948, 559), afforded melamine and the appropriate sulphonic acid. Prolonged treatment with ethanolic hydrochloric acid gave satisfactory yields of cyanuric acid and the requisite sulphonamide. In the absence of rearrangements, the latter observations exclude the alternative *iso*melamine structure (IX) : sulphonamides cannot presumably be formed from sulphonyl*iso*melamines without the disruption of the triazine nucleus. Formula (VIII) derives further support from the observed acidic nature of the compounds; *iso*melamines (IX) may be expected to be predominantly basic (cf. Part III, *J.*, 1949, 3033).

In order to establish that the triazine system had not been formed from a dimeric sulphonylcyanamide during the above hydrolyses, a sulphonyldicyandiamide (I) was subjected to these reactions under identical conditions. In sulphuric acid, *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine decomposed with evolution of carbon dioxide and gave guanidine, isolated as the toluene-*p*-sulphonate. Dicyandiamide itself is known to yield guanidine under similar conditions (Lidholm, *Ber.*, 1913, **46**, 158; Davis, *J. Amer. Chem. Soc.*, 1921, **43**, 670). Ethanolic hydrochloric acid gave a mixture of sulphonylamidinourea (III), sulphonylguanidine, and sulphonamide. The non-formation of triazines during the original degradation experiments appeared therefore to be confirmed.

The production of trisulphonylmelamines (VIII) in the present reaction may be regarded as an extension of the well-known synthesis involving the corresponding parent compounds : melamine is prepared on the industrial scale by heating dicyandiamide, usually in the presence of ammonia as a diluent (for a review, see McClellan, *Ind. Eng. Chem.*, 1940, **32**, 1181), or by heating solutions of this dimer with or without the addition of cyanamide (B.P. 598,533) in anhydrous tertiary bases (B.P. 599,702). As suggested by Davis and Underwood (*J. Amer. Chem. Soc.*, 1922, **44**, 2595), melamine may be regarded as arising by combination of dicyandiamide and cyanamide, which in turn originates from the breakdown of part of the dimer.

The results of experiments on the interaction of *N*-aryl-*N'*-cyanoureas (Kurzer and

Powell, *loc. cit.*), and those of the present investigation suggest that structures incorporating a ·N(SO_2R)·CN grouping in proximity to a mobile hydrogen atom are labile and decompose immediately in pyridine solution with elimination of the elements of sulphonylcyanamide (R·SO_2·NH·CN). A possible mechanism for the present synthesis of trisulphonylmelamines (VIII) may therefore involve the intermediate formation of *N*-cyano-*NN'*-disulphonylguanidines (VII); their fission into two molecules of sulphonylcyanamides would provide the fragments (*i.e.*, the unchanged dimer, and monomer being formed) from which the triazine is built up. In addition to chemical evidence, *X*-ray analyses (Hughes, *J. Amer. Chem. Soc.*, 1940, **62**, 1258) and measurements of dipole moments (Schneider, *ibid.*, 1950, **72**, 761) have recently led to the suggestion that the dicyandiamide molecule is best represented as a resonance hybrid, to which di-imide structures contribute significantly. Interaction of the carbodi-imide configuration of the dimeric sulphonylcyanamide (VII*a*) and the monomer would lead directly to sulphonylmelamines (VIII).

Experimental

(The pyridine used was the commercially available anhydrous grade.)

N-*Cyano*-N'-*toluene*-p-*sulphonylguanidine*.—A suspension of dicyandiamide (25·2 g., 0·3 mole) in aqueous potassium hydroxide (14·0 g., 0·25 mole; dissolved in 28 ml. of water) was mechanically stirred at 30° for 10 min., after which acetone (100 ml.) was added. The well-stirred, two-phase system was treated, during 1—1½ hr., with a solution of toluene-*p*-sulphonyl chloride (47·6 g., 0·25 mole) in acetone (80 ml.) at 30—32° (cooling), alkalinity being maintained, towards the end, by simultaneous dropwise addition of more potassium hydroxide solution (20 g., 0·36 mole, in 20 ml. of water). The suspension of the resulting crystalline potassium salt was then stirred at 30—32° for a further ½ hr. and cooled to 0°, and the white solid (52—55 g.) filtered off and washed with a little acetone (recovery of further quantities of this salt from the filtrates by evaporation proved impracticable). The salt was dissolved in water (450—550 ml.) at 80—85°, the liquid quickly filtered while hot, and the filtrate allowed to cool until crystallisation had just set in. Concentrated hydrochloric acid (40 ml.) was then quickly added, and the crystallisation of the free acid completed by slowly cooling the suspension to 0°. The product (m. p. 195—210°, decomp.; 30—32·7 g., 50—55%), crystallised several times from boiling water (150 ml. per g.), affords needles of N-*cyano*-N'-*toluene*-p-*sulphonylguanidine*, m.p. 215—218° (decomp.) (slight sintering at 193°) (recovery per crystallisation: over 85%) (Found: C, 45·4, 45·3; H, 4·25, 4·3; N, 23·8; S, 12·9. $C_9H_{10}O_2N_4S$ requires C, 45·4; H, 4·2; N, 23·5; S, 13·4%). The substance was recovered unchanged after 2 hr.' refluxing in aqueous sodium hydroxide (2% w/v).

The interaction of dicyandiamide (0·05 mole) and toluene-*p*-sulphonyl chloride (0·1 mole) in 10% aqueous sodium hydroxide (0·2 mole) at 20—40° gave a solution which deposited, on acidification at room temperature, *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine, m. p. (193°) 215—217° (decomp.) (2—5%). Partial evaporation of the aqueous acid (Congo-red) filtrate gave amidinourea toluene-*p*-sulphonate (60—80%), m. p. and mixed m. p. 244—246° (decomp.) (Found: N, 20·4; S, 11·8. Calc. for $C_9H_{14}O_4N_4S$: N, 20·4; S, 11·7%).

Addition of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (2·38 g., 0·01 mole) to liquid ammonia (30 ml.) and spontaneous evaporation of the clear solution gave its *ammonium* salt (92—96%), which formed flat prisms, m. p. 219—220° (decomp.), when crystallised from water (20 ml. per g.) (Found: C, 42·85; H, 4·8; N, 27·8. $C_9H_{13}O_2N_5S$ requires C, 42·35; H, 5·1; N, 27·45%). The *ammonium* salts of *N*-benzenesulphonyl-*N'*-cyanoguanidine, m. p. 220—223° (decomp.) (from water, 10 ml. per g.) (Found: N, 28·0. $C_8H_{11}O_2N_5S$ requires N, 29·05%), and of *N*-*p*-aminobenzenesulphonyl-*N'*-cyanoguanidine, m. p. 228—229° (decomp.) (from water, 3 ml. per g.) (Found: N, 32·4. $C_8H_{12}O_2N_6S$ requires N, 32·8%), were similarly prepared.

N-*Cyano*-N'-*toluene*-o-*sulphonylguanidine* was similarly prepared, first as potassium salt, which, on dissolution in water (600—650 ml. at 75°, in experiments starting with 0·3 mole of dicyandiamide), precipitation with hydrochloric acid, and cooling, gave the almost pure *compound* (m. p. 170—174°, decomp.) in 20—25% yield. It formed prisms, m. p. 173—174° (decomp.), from boiling ethanol (2—3 ml. per g.) (Found: C, 45·5; H, 4·4. $C_9H_{10}O_2N_4S$ requires C, 45·4; H, 4·2%).

N-*Cyano*-N'-*methanesulphonylguanidine* was prepared by simultaneous addition, during 1½ hr., of a solution of methanesulphonyl chloride (28·6 g., 0·25 mole) in acetone (40 ml.), and

aqueous potassium hydroxide (28 ml., 60% w/v, 0·3 mole), to a stirred suspension of dicyandiamide (16·8 g., 0·2 mole) in aqueous potassium hydroxide (19 ml., 60% w/v, 0·2 mole)–acetone (60 ml.). The temperature was kept below 8° by external ice-cooling. The separated potassium salt was dissolved in water (40 ml.) at 60°; the product was precipitated with hydrochloric acid, filtered off at 0° (12—14 g.; 37—43%), and crystallised from boiling ethanol (50 ml. per g.), giving prisms of the *guanidine*, m. p. 179—180° (decomp.) (Found: C, 22·5; H, 4·0; N, 35·0; S, 19·9. $C_3H_6O_2N_4S$ requires C, 22·2; H, 3·7; N, 34·6; S, 19·75%). The use of excess of dicyandiamide, of less concentrated potassium hydroxide solutions, or temperatures exceeding 8° resulted in much diminished yields.

N-(*Benzenesulphonylamidino*)*thiourea*.—A solution of *N*-benzenesulphonyl-*N'*-cyanoguanidine (2·24 g., 0·01 mole) in a mixture of anhydrous pyridine (10 ml.) and anhydrous triethylamine (1·0 g., 0·01 mole), kept at 40—50°, was slowly treated (12 hr.) with a stream of dry hydrogen sulphide. The deep orange-red liquid was poured into water (20 ml.), freed from colloidal sulphur by filtration with carbon, and acidified (to Congo-red) with dilute hydrochloric acid. The collected precipitate was crystallised four times from ethanol (20 ml. per g.), the solution being each time decanted from traces of undissolved sulphur, and gave lustrous platelets of N-(*benzenesulphonylamidino*)*thiourea*, m. p. 202—203° (decomp.) (Found: C, 36·8; H, 3·8; S, 25·2. $C_8H_{10}O_2N_4S_2$ requires C, 37·2; H, 3·9; S, 24·8%) (yield, including material recovered from the ethanolic filtrates: 1·74 g., 67%). Hydrogen sulphide treatment over shorter periods resulted in incomplete conversion of the reactant.

N-(*Toluene*-p-*sulphonylamidino*)*thiourea*, similarly prepared from *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine, crystallised from ethanol (10 ml. per g.) in needles, m. p. 201—202° (decomp.) (83%) [Found: C, 40·1; H, 4·6; S, 22·8%; *M* (Rast), 300. $C_9H_{12}O_2N_4S_2$ requires C, 39·7; H, 4·4; S, 23·5%; *M*, 272]. N-(p-*Aminobenzenesulphonylamidino*)*thiourea*, similarly prepared (in 76% total yield), formed needles, m. p. 195—197° (decomp.), after two crystallisations from water (30 ml. per g.) and one from ethanol (20 ml. per g.), (Found: C, 35·9; H, 3·8; S, 22·8. Calc. for $C_8H_{11}O_2N_5S_2$: C, 35·2; H, 4·0; S, 23·4%). [This compound was prepared from amidinothiourea and *p*-nitrobenzenesulphonyl chloride, followed by reduction (Winnek, U.S.P. 2,303,972), but the m. p. was not given.]

Desulphurisation of N-(*Toluene*-p-*sulphonylamidino*)*thiourea*.—A boiling solution of this thiourea (2·72 g., 0·01 mole) in aqueous potassium hydroxide (56 ml., 5% w/v, 0·05 mole) was treated with a saturated aqueous solution of lead acetate trihydrate (7·6 g., 0·02 mole). The suspension was stirred at 80—60° for 5 min., the lead sulphide filtered off at the pump, and the cooled filtrate acidified to Congo-red. The collected precipitate (1·35 g., 57%) was crystallised from water and gave needles of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (m. p. undepressed by authentic material) (Found: C, 44·5; H, 4·1%).

Toluene-p-*sulphonyldiguanide*.*—(a) *From diguanide*. A stirred suspension of diguanide sulphate (preparation: Ostrogovich, *Chem. Zentr.*, 1910, II, 1890; isolation as sulphate: Rackmann, *Annalen*, 1910, **376**, 170) (2·20 g., 0·01 mole) in acetone (10 ml.) and aqueous sodium hydroxide (20% w/v; 4 ml., 0·02 mole) was treated, during 15 min. at 3—8°, with a solution of toluene-*p*-sulphonyl chloride (1·90 g., 0·01 mole) in acetone (4 ml.), followed by more aqueous sodium hydroxide (2 ml., 0·01 mole). The separated product (m. p. 238—242°, decomp.; 2·15 g., 85%), collected after a further 15 min.' stirring, was crystallised successively from water (180 ml. per g.) and ethanol (100 ml. per g.) and gave plates of *toluene*-p-*sulphonyldiguanide*, m. p. 246—247° (decomp.) (Found: C, 42·7; H, 5·1; N, 27·1. $C_9H_{13}O_2N_5S$ requires C, 42·35; H, 5·1; N, 27·45%).

(b) *From* N-*cyano*-N'-*toluene*-p-*sulphonylguanidine*. A suspension of this guanidine (2·38 g., 0·01 mole) and powdered copper sulphate pentahydrate (2·50 g., 0·01 mole) in ammonia (8·5% w/v, 40 ml.), contained in a closed vessel, was heated for 18 hr. in a brine-bath (108—110°). The resulting suspension was heated to boiling, the supernatant deep blue liquid decanted (through a funnel), and the remaining solid, after having been once again extracted with boiling water (50 ml.), collected on the same funnel (combined filtrates B). The pink solid (0·65 g.) was extracted with boiling ethanol (2 × 20 ml.), and filtered off (filtrates A). The residual pink copper salt (0·35 g.) was dissolved in warm hydrochloric acid (10%; 8 ml.), the copper removed by precipitation with hydrogen sulphide and filtration, and the crude product precipitated from the filtrate with concentrated aqueous ammonia. Crystallisation from water (30 ml.), followed by extraction of the crystalline solid with boiling ethanol (3 ml.) to remove traces of

* The m. p. given for this compound in the preliminary note (*Chem. and Ind.*, 1953, 195) is incorrectly stated and is in fact the m. p. of the ammonium salt of the corresponding *N*-arylsulphonyl-*N'*-cyanoguanidine.

toluene-*p*-sulphonylguanidine, gave toluene-*p*-sulphonyldiguanide (0·18 g., 7%), m. p. 243—245° (decomp.), mixed m. p. with material prepared by method (a) 241—243° (Found: C, 42·5; H, 5·15; N, 26·9%). Filtrates (A) deposited toluene-*p*-sulphonylguanidine (0·23 g.), m. p. and mixed m. p. 203—204°. The alkaline filtrates (B) were acidified with concentrated hydrochloric acid (Congo-red), and the white crystalline precipitate collected at 0° (1·50 g.). Extraction with aqueous sodium hydroxide (4% w/v, 25 and 10 ml.) left a residue of toluene-*p*-sulphonylguanidine, m. p. 203—204° (from ethanol) (0·20 g., *i.e.*, total yield 20%). Acidification of the alkaline extracts gave unchanged starting material (1·10 g., 45%).

Benzenesulphonyldiguanide * was prepared by method (a) in 90% yield; successive crystallisation from water (50 ml. per g.) and ethanol (60 ml. per g.) gave the *diguanide* as platelets, m. p. 232—234° (decomp.) (Found: C, 40·0; H, 4·7; N, 29·7; S, 13·5. $C_8H_{11}O_2N_5S$ requires C, 39·8; H, 4·6; N, 29·05; S, 13·3%). The interaction of *N*-benzenesulphonyl-*N'*-cyanoguanidine and ammonia in the presence of copper sulphate (quantities, conditions, and isolation as above) gave the following products: unchanged starting material (30%); benzenesulphonylguanidine, m. p. and mixed m. p. 210—211° (0·63 g., 32%) [picrate: m. p. and mixed m. p. (Clarke and Gillespie, *J. Amer. Chem. Soc.*, 1932, **54**, 1964) 188—189° (decomp.)]; benzenesulphonyldiguanide, m. p. and mixed m. p. with material prepared by method (a) 231—233° (decomp.) (0·29 g., 12%).

Toluene-p-*sulphonylamidinourea*.—To a boiling suspension of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (7·14 g., 0·03 mole) in aqueous sulphuric acid (12%, 30 ml.), ethanolic sulphuric acid (12%, 90 ml.) was added, and the resulting solution refluxed for 1 hr. Deposition of solid began after 20—30 min.; the separated material was collected at 0° (m. p. 224—230°; 6·3 g., 82%). Two crystallisations from ethanol (100 ml. per g., 60% recovery per crystn.) gave platelets of the *urea*, m. p. 238—242° (decomp.) (Found: C, 42·1; H, 4·8; N, 21·6. $C_9H_{12}O_3N_4S$ requires C, 42·2; H, 4·7; N, 21·9%). The same material, m. p. and mixed m. p. 239—242° (decomp.), was obtained (60%) by Kaiser and Thurston's procedure (*loc. cit.*), *i.e.*, hydrolysis with boiling 10% hydrochloric acid during 10 min. Prolonged boiling (6 hr.) with 12% or 25% aqueous-ethanolic sulphuric acid gave the above amidinourea (in 35—5% yield) and toluene-*p*-sulphonamide (in 30—60% yield).

Toluene-o-*sulphonylamidinourea* was similarly prepared in 78% yield. Two crystallisations from ethanol (80 ml. per g.) gave plates of the *product*, m. p. 228—230° (decomp.) (Found: C, 42·3; H, 4·55; N, 21·2. $C_9H_{12}O_3N_4S$ requires C, 42·2; H, 4·7; N, 21·9%). *Methanesulphonylamidinourea* was similarly prepared (by use of 12% aqueous sulphuric acid only) in 40% yield. Crystallisation from ethanol (150 ml. per g.) gave needles, m. p. 217—219° (decomp.) (Found: C, 19·8; H, 4·15; N, 30·9. $C_3H_8O_3N_4S$ requires C, 20·0; H, 4·4; N, 31·1%).

Tri(*toluene*-p-*sulphonyl*)*melamine*.—A solution of *N*-cyano-*N'*-toluene-*p*-sulphonylguanidine (7·14 g., 0·03 mole) in anhydrous pyridine (40 ml.) at 25° was treated with toluene-*p*-sulphonyl chloride (8·55 g., 0·045 mole). The clear, orange liquid was kept at 90—95° for ½ hr. and then slowly stirred into a mixture of ice (120 g.), water (120 ml.), and concentrated hydrochloric acid (50 ml.). The white granular solid was filtered off and stirred with aqueous sodium hydroxide (6% w/v; 150 ml.), a small insoluble fraction filtered off (0·5—0·8 g.; m. p. >360°), and the product slowly reprecipitated with hydrochloric acid (1 : 1; 60 ml.). The collected air-dried powder [12—14 g., m. p. 130—150° (sintering at 110—125°, and finally giving a deep orange melt)] was added to boiling ethanol (100 ml.) in which it dissolved almost instantly. The orange solution rapidly deposited crystalline scales which were filtered off at 0° (m. p. 280—282°; 8·8—10·0 g., 75—85%) (ethanolic filtrate A). Crystallisation from boiling ethanol (60 ml. per g., recovery approx. 75% per crystallisation) gave platelets of *tri*(*toluene*-p-*sulphonyl*)*melamine*, m. p. 284—285° [Found: C, 48·7; H, 4·6; N, 14·2; S, 15·9%; *M* (Rast), 560, 590. $C_{24}H_{24}O_6N_6S_3$ requires C, 49·0; H, 4·1; N, 14·3; S, 16·3%; *M*, 588]. Filtrates A very slowly deposited more product (m. p. 280—282°). The melamine derivative was readily soluble in pyridine and liquid ammonia, moderately soluble in warm dilute caustic alkalis and boiling acetone, sparingly soluble in boiling benzene, and practically insoluble in ether. When reprecipitated by acids from its solution in dilute aqueous alkali, it formed a white amorphous powder (m. p. 150—175°, resolidifying at 180—190° and finally melting at 270—275°) of greatly increased solubility when added to boiling ethanol (probably owing to hydration). Dissolution in ethanol gave once again platelets, m. p. 285°.

Tri(*toluene*-o-*sulphonyl*)*melamine*.—*N*-Cyano-*N'*-toluene-*o*-sulphonylguanidine (7·14 g., 0·03 mole) in pyridine (90 ml.) was treated with toluene-*o*-sulphonyl chloride (11·4 g., 0·06 mole) at 30° and kept at 90—95° for 20 min. The crude air-dried reprecipitated product, isolated as

above, was added to boiling ethanol (60 ml.) (or to boiling chloroform, 100 ml.); the clear solution rapidly deposited crystalline prisms on cooling (m. p. 280°; 5·3 g., 45%). The filtrate therefrom was evaporated in a vacuum, the oily residue dissolved in aqueous alkali (12% w/w, 30 ml.) and filtered (carbon), and the product reprecipitated with acid. Dissolution of the air-dried precipitate in ethanol gave a second crop of crystalline material; a third crop was similarly obtained (total, 1·2—1·75 g., 10—15%). Two crystallisations from acetone (150 ml. per g., recovery approx. 20% per crystn.) gave *tri(toluene-o-sulphonyl)melamine*, m. p. 294—295° (Found: C, 49·5; H, 4·1; N, 14·4; S, 16·6. $C_{24}H_{24}O_6N_6S_3$ requires C, 49·0; H, 4·1; N, 14·3; S, 16·3%); it was not sufficiently soluble in camphor for a Rast determination.

Tribenzenesulphonylmelamine.—Interaction of *N'*-benzenesulphonyl-*N*-cyanoguanidine (4·5 g., 0·02 mole) and benzenesulphonyl chloride (5·3 g., 0·03 mole) in pyridine (20 ml.) (addition at 15°; spontaneous temperature rise to 60—75°; storage at room temperature for 15 min.), and treatment as previously described gave a white granular solid (7—7·5 g.) which was added to boiling chloroform (50 ml.). The deposited crystalline solid (3—4 g.) was collected; two similar fractions were successively isolated by removal of the solvent under reduced pressure, reprecipitation of the residue from alkaline solution by hydrochloric acid, and dissolution of the dried product in chloroform (total recovery: 5—5·3 g., 69—73%) (final chloroform filtrates A). (*a*) Two crystallisations from ethanol (approx. 15 ml. per g.; recovery per crystn. 70—75%) gave prisms of solvated *tribenzenesulphonylmelamine*, m. p. 149—151° (decomp.) (Found: C, 46·8; H, 4·25. $C_{21}H_{18}O_6N_6S_3,C_2H_6O$ requires C, 46·6; H, 4·05%). (*b*) Alternatively, two crystallisations from ethanol–benzene (15 and 6 ml. per g. respectively; recovery 90%) gave the *melamine* solvated with benzene, m. p. 190—192° (decomp., slight sintering at 187—189°) (Found: C, 52·2; H, 3·7; N, 13·4; S, 15·2. $C_{21}H_{18}O_6N_6S_3,C_6H_6$ requires C, 51·9; H, 3·8; N, 13·5; S, 15·4%).

Heating of solvates (*a*) or (*b*) slowly to 190° during 1 hr., and keeping them at this temperature for a further hour (loss in wt.: 6·9, 10·5%. Calc.: 7·7, 12·5%, respectively), gave *tribenzenesulphonylmelamine*, m. p. 229—231° (decomp.) as a white powder [Found: C, 46·0; H, 3·1; N, 15·4; S, 17·1%; *M* (Rast), 580. $C_{21}H_{18}O_6N_6S_3$ requires C 46·15; H, 3·3; N, 15·4; S, 17·6%; *M*, 546]. Dissolution of this product in ethanol or benzene regenerated the corresponding solvate.

The final chloroform filtrates (A) contained varying quantities of a residue, highly soluble in organic solvents, which could be isolated by precipitation from its alkaline solution by acids. The results of analyses and molecular-weight determinations suggest the presence of a higher polymeric form of benzenesulphonylcyanamide.

Trimethanesulphonylmelamine.—Methanesulphonyl chloride (11·45 g., 0·1 mole) was added in four portions at 5-min. intervals to a suspension of *N*-cyano-*N'*-methanesulphonylguanidine (3·24 g., 0·02 mole) in pyridine (25 ml.). The resulting solution was kept at 55—60° for another 30 min., cooled to room temperature, and added to hydrochloric acid (15% w/v, 60 ml.). The brown liquid deposited, after one day's (or occasionally more prolonged) storage at room temperature, deep brown crystals (m. p. 295—298°, decomp.) (1·45—1·75 g., 30—36%). Two crystallisations (carbon) from ethanol (80 ml. per g., recovery: 65%) gave platelets of solvated *trimethanesulphonylmelamine*, m. p. 309—311° (decomp.) (Found: C, 23·4; H, 4·3; N, 19·6; S, 23·4. $C_6H_{12}O_6N_6S_3,C_2H_6O$ requires C, 23·6; H, 4·4; N, 20·7; S, 23·6%), sparingly soluble in water, but not sufficiently soluble in camphor for a Rast determination.

Hydrolysis of Sulphonylmelamines by Concentrated Sulphuric Acid.—(*a*) A suspension of finely powdered tri(toluene-*p*-sulphonyl)melamine (2·35 g., 0·004 mole) in concentrated sulphuric acid (6 ml.) was heated to 70°. The resulting pale yellow solution was kept at this temperature for 15 min., and then added to ice (30 g.). The white solid which separated during several hours' storage at 0° was melamine sulphate (0·65 g., 84%) (Found, for specimens recrystallised from water: SO_4, 24·8. Calc. for $2C_3H_6N_6,H_2SO_4,2H_2O$: SO_4, 24·9%). It was filtered off at 0° (filtrate A), suspended in boiling water (10 ml.), and dissolved by addition of aqueous sodium hydroxide (12% w/w; 1 ml.). The clear (filtered) liquid deposited a white solid (0·28 g., 55%), which gave melamine, m. p. and mixed m. p. 352—354° (decomp.) (from water) (Found: C, 28·5; H, 4·8; N, 66·6. Calc. for $C_3H_6N_6$: C, 28·6; H, 4·8; N, 66·7%). Filtrate A was partly neutralised with aqueous sodium hydroxide (20% w/w; 10 ml.) and treated with a saturated warm solution of *S*-benzyl*iso*thiuronium chloride (3 g.); the precipitated salt was filtered off at 0°, and gave benzylthiuronium toluene-*p*-sulphonate, m. p. and mixed m. p. 178—179° (from aqueous ethanol) (2·43 g., 60%). A control experiment showed that a solution of melamine (0·5 g., 0·004 mole) in concentrated sulphuric acid (6 ml.), kept at 70° for 15 min. and poured into ice-water (30 ml.), gave 85% of melamine sulphate monohydrate.

(*b*) By the same procedure, tri(toluene-*o*-sulphonyl)melamine was hydrolysed to melamine (60%) and benzylthiuronium toluene-*o*-sulphonate (74%), m. p. and mixed m. p. 172—173°.

(*c*) Similarly, tribenzenesulphonylmelamine (containing benzene of crystallisation, m. p. 188—191°) gave melamine (58%) and benzylthiuronium benzenesulphonate (78%), m. p. and mixed m. p. 146—147°.

Hydrolysis of Sulphonylmelamines by Ethanolic Hydrochloric Acid.—(*a*) A solution of tri-(toluene-*p*-sulphonyl)melamine (1·18 g., 0·002 mole) in absolute ethanol (150 ml.), saturated with dry hydrogen chloride, was refluxed during 12 hr., a slow stream of hydrogen chloride being continuously passed through the solution. Cyanuric acid gradually appeared in suspension; the liquid was evaporated under reduced pressure to one-third of its volume and cooled to 0°, and the solid collected (0·19 g., 75%) (filtrate A). One crystallisation from water gave cyanuric acid (identified as complex copper salt; Venable and Moore, *J. Amer. Chem. Soc.*, 1917, **39**, 1750) (Found: N, 33·2. Calc. for $C_3H_3O_3N_3$: N, 32·6%). Filtrates A were further evaporated (5—10 ml.) and a trace of cyanuric acid filtered off. On being cooled to 0°, the liquid deposited toluene-*p*-sulphonamide, m. p. and mixed m. p. 136—137° (yield, including material from mother-liquors, 0·84 g., 82%).

(*b*) A suspension of tri(toluene-*o*-sulphonyl)melamine (0·002 mole) gave, on analogous treatment, cyanuric acid (92%) and toluene-*o*-sulphonamide, m. p. and mixed m. p. 152—153° (87%).

(*c*) Trimethanesulphonylmelamine (0·02 mole) gave, after 18 hr.' refluxing, cyanuric acid (72%) and methanesulphonamide, m. p. 87° (59%).

Other Hydrolysis Attempts.—Tri(toluene-*p*-sulphonyl)melamine was recovered unchanged (i) after 6 hr.' boiling in 3% aqueous sodium hydroxide or 6% ethanolic potassium hydroxide; (ii) after 5 min.' boiling of its solution in acetic anhydride (15 ml.) containing concentrated sulphuric acid (5 drops).

Hydrolysis of N-*Cyano*-N′-*toluene*-p-*sulphonylguanidine.*—(a) *By sulphuric acid.* The compound (4·76 g., 0·02 mole) was dissolved in concentrated sulphuric acid (8 ml.), and the resulting hot solution kept at 70° for 30 min., evolution of carbon dioxide occurring. On dilution with ice (15 g.) and storage at 0°, a crystalline solid was deposited (2·60 g., 56%), which gave guanidine toluene-*p*-sulphonate, m. p. and mixed m. p. 225—226°, after successive crystallisation from small volumes of water and ethanol (Found: C, 41·8; H, 5·9; N, 17·85; S, 13·8. Calc. for $C_8H_{13}O_3N_3S$: C, 41·6; H, 5·6; N, 18·2; S, 13·85%).

(b) *By ethanolic hydrochloric acid.* A solution of the substance (2·38 g., 0·01 mole) in saturated ethanolic hydrochloric acid (150 ml.) was refluxed during 8 hr., and the liquid evaporated to one-third of the original volume under reduced pressure. The crystalline solid which separated on cooling (1·23 g., 48%) was crystallised from ethanol and consisted of toluene-*p*-sulphonylamidinourea, m. p. and mixed m. p. 238—242° (decomp.). The ethanolic filtrates were evaporated nearly to dryness, the residue dissolved in warm water (10 ml.), and the filtered solution made alkaline with ammonia. The collected solid (0·68 g., 32%), crystallised from ethanol, was toluene-*p*-sulphonylguanidine, m. p. and mixed m. p. 203—204°. The aqueous alkaline filtrates contained toluene-*p*-sulphonamide (0·26 g., 15%), m. p. and mixed m. p. 136°, which was isolated by precipitation with acid and crystallised from boiling water.

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