639. *Cyanamides. Part III. The Formation of Substituted Triazines from* o-*Halogenophenylureas and Arylsulphonyl Chlorides.*

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The interaction of *o*-halogenophenylureas and arylsulphonyl chlorides yields, in addition to the expected arylsulphonylarylcyanamides, varying quantities of the appropriate substituted melamines, produced by polymerisation. Under suitable conditions the trimers may become the main products of the reaction. A readily realised, novel dehydration of 1 : 1-diarylureas to the corresponding diarylcyanamides by the action of aromatic sulphonyl chlorides is also reported.

The significance of these results is discussed with reference to the mechanism of the reaction.

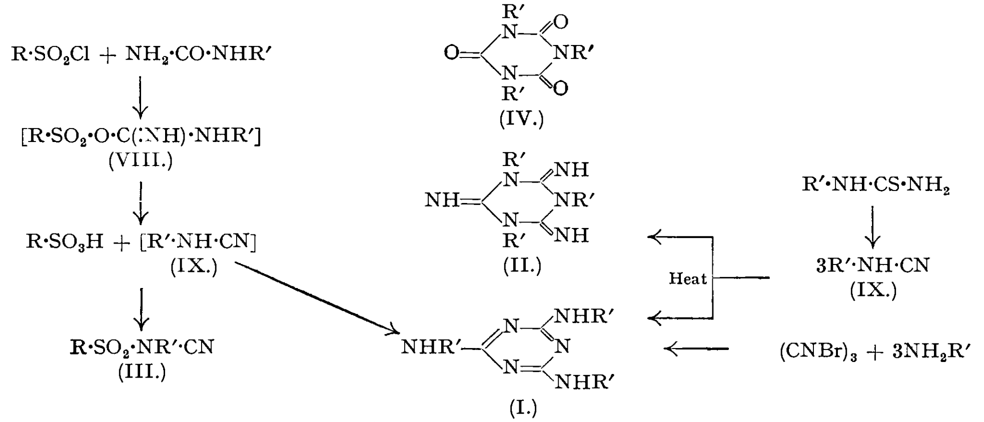
The polymerisation of cyanogen derivatives, particularly to trimers containing the 1 : 3 : 5-triazine ring-system, is a well known reaction. Whilst cyanamide is readily condensed to cyanoguanidine under a variety of conditions, the action of heat on cyanamide or its dimer under pressure produces the trimer, melamine (Drechsel, *J. pr. Chem.*, 1875, **11**, 302; 1876, **13**, 331; B.PP. 525,185 and 598,533; U.S.P. 2,161,940). Owing to the occurrence of tautomerism, cyanuric acid and its amide (melamine) (I or II; R′ = H) exist in only one form; physical evidence suggests the predominance of the amide (I; R′ = H) rather than the imide structure (II; R′ = H) (Lonsdale *et al.*, *Proc. Roy. Soc.*, 1940, *A*, **177**, 140). Melamine derivatives containing alkyl, aryl, or other suitable groups, however, form two distinct series of compounds, depending on the position of the substituents in the molecule. *iso*Melamines (II) contain substituents attached to the nitrogen atoms of the triazine nucleus, whilst the presence of substituents in extranuclear nitrogen atoms gives rise to the normal series (I). Trialkyl- or triaryl-*iso*melamines are almost invariably synthesised by the thermal polymerisation of the appropriate cyanamides (Hofmann, *Ber.*, 1869, **2**, 602; 1885, **18**, 2784, 3223; Heller and Bauer, *J. pr. Chem.*, 1902, **65**, 374). A convenient route to melamines is available by the interaction of primary or secondary amines with cyanuric halides, which are in their turn obtained by the trimerisation of the monomeric cyanogen halides (Friess, *Ber.*, 1886, **19**, 244, 2057; von Meyer and Näbe, *J. pr. Chem.*, 1910, **82**, 531).

It has now been found that the interaction of certain substituted arylureas with aromatic sulphonyl chlorides produces, in addition to the expected arylsulphonylarylcyanamides (see Parts I and II) varying quantities of substituted triazines of type (I). The formation of such melamine derivatives appears to occur particularly readily with *o*-halogenophenylureas: thus, reaction in pyridine under the usual conditions between *o*-bromophenylurea and benzenesulphonyl chloride, toluene-*p*-sulphonyl chloride, or toluene-*o*-sulphonyl chloride, gave abnormally low yields of the appropriate *o*-bromophenylcyanamides (III; R′ = *o*-C_6H_4Br), whilst *tri*-o-*bromophenylmelamine*, m. p. 188—189° (I; R′ = *o*-C_6H_4Br), was isolated in 46, 40, and 25% yield, respectively. The interaction of arylsulphonyl chlorides with *o*-chlorophenylurea occurred more slowly and was therefore carried out with advantage at slightly higher temperatures. In addition to small quantities of unchanged *o*-chlorophenylurea, varying yields of sulphonyl-*o*-chlorophenylcyanamides, and of tri-*o*-chlorophenylmelamine, m. p. 165—166° (I; R′ = *o*-C_6H_4Cl), were obtained. Owing to the solubility differences of the sulphonylcyanamides and triazines formed in these reactions, their separation was effected without difficulty. Under suitable conditions the triazine could be made to become the main product in this reaction. Thus, the interaction of *o*-bromophenylurea and toluene-*p*-sulphonyl chloride at 90° for 15 minutes gave a 65% yield of tri-*o*-bromophenylmelamine, but only a trace of the expected sulphonylcyanamide was isolated.

The triazines obtained in the above reaction were characterised by comparison with melamines synthesised from cyanuric bromide and the appropriate aniline in benzene solution. Apart from determinations of molecular weights, mixed melting points, etc., further proof of the identity of the products obtained from *o*-halogenophenylureas with the authentic melamines from cyanuric bromide was obtained by a comparison of their ultra-violet absorption spectra. The table (p. 3035) illlustrates the identity of the substances concerned.

The formation of triazines during the interaction of arylureas and aromatic sulphonyl chlorides appears to depend on the presence of suitable substituents in the arylurea selected, and on the conditions of the reaction: of sixteen urea derivatives examined under identical conditions, only *o*-halogenophenylureas gave appreciable yields of trimers under the mild conditions employed. Thus, for example, phenylurea and arylsulphonyl chlorides at higher temperatures, which were observed to favour melamine formation in the case of *o*-halogenophenylureas, did not give significant quantities of triazines.

The above results have occasioned an examination of the polymerisation of *o*-halogenophenylcyanamides. The trimerisation of arylcyanamides has previously been investigated in a number of cases, when formation of *iso*melamines, formulated as (II) because of their conversion into triaryl*iso*cyanuric acids (IV), was observed (*e.g.*, Hofmann, *loc. cit.*). o-*Chlorophenylcyanamide*



R′ = *o*-C_6H_4Cl, or *o*-C_6H_4Br

was prepared by the removal of the elements of hydrogen sulphide from the corresponding thiourea (Rathke, *Ber.*, 1879, **12**, 772; Krall *et al.*, *J. Indian Chem. Soc.*, 1942, **19**, 343; 1946,

23, 373). In contrast to *p*-tolyl- and *p*-chlorophenyl-cyanamide, which undergo polymerisation completely at ordinary temperatures within 3—7 days (Krall, *loc. cit.*), *o*-chlorophenylcyanamide did not trimerise in the solid state, or in benzene solution, on storage at temperatures between 20° and 30° for several weeks. Short heating at 100° gave a brittle glass-like material, from which *tri-*o*-chlorophenyl*iso*melamine*, m. p. 260—262° (II; $R' = o\text{-}C_6H_4Cl$), and smaller quantities of tri-*o*-chlorophenylmelamine, m. p. 164—167°, were isolated. Similarly, thermal trimerisation of *o*-bromophenylcyanamide gave *tri-*o*-bromophenyl*iso*melamine*, m. p. 266—268°, (II; $R' = o\text{-}C_6H_4Br$), together with tri-*o*-bromophenylmelamine, m. p. 189—190°. The identity of the melamines thus obtained with the authentic compounds was again confirmed by the examination of their ultra-violet absorption spectra (see Table). For comparison, light-absorption data were also determined for the corresponding *iso*melamines.

		Maximum I		Maximum II	
Tri-*o*-chlorophenylmelamine from :	M. p.	$\lambda_{\text{max.}}$ (mμ.).	$E^{1\%}_{1\text{ cm.}}$.	$\lambda_{\text{max.}}$ (mμ.).	$E^{1\%}_{1\text{ cm.}}$.
cyanuric bromide and *o*-chloroaniline	164—167°	272	1600	278	1600
o-chlorophenylurea and $R\cdot SO_2Cl$	165—166	271	1500	277	1590
o-chlorophenylcyanamide, trimerised	164—167	271	1580	278	1600
Tri-*o*-bromophenylmelamine from :					
cyanuric bromide and *o*-bromoaniline......	189—190	270	1100	276	970
o-bromophenylurea and $R\cdot SO_2Cl$	188—189	270	1050	277	980
o-bromophenylcyanamide, trimerised ...	186—189	270	1080	277	970
Tri-*o*-chlorophenyl*iso*melamine	261—262	247	*	—	—
Tri-*o*-bromophenyl*iso*melamine	266—268	242	*	—	—

* Owing to the very limited solubility of the *iso*melamines in the usual organic solvents, the intensities could not be accurately measured.

The interaction of asymmetrical 1 : 1-diarylureas (V) with aromatic sulphonyl chlorides has been found to afford an excellent route to diarylcyanamides (VII). 1 : 1-Diphenylurea, heated in pyridine with benzene- or toluene-*p*-sulphonyl chloride at 100° for short periods, gave almost theoretical quantities of diphenylcyanamide, also obtained in satisfactory yields by merely storing the reactants at room temperature. Diphenylcyanamide has previously been prepared from 1 : 1-diphenylthiourea (Werner, *Chem. News*, 1892, **65**, 249), and by the interaction of diphenylamine and cyanogen bromide under pressure (von Braun, *Ber.*, 1900, **33**, 1450). The present synthesis, apart from being a very convenient method from the preparative point of view, is of importance with regard to the reaction mechanism of the action of sulphonyl chlorides on arylureas (see below). As was to be expected, *s*-diarylureas did not react under the mild conditions of this synthesis.

$$\underset{\text{(V.)}}{Ar_2N\cdot CO\cdot NH_2} \xrightarrow{R\cdot SO_2Cl} \underset{\text{(VI.)}}{[Ar_2N\cdot C(:NH)\cdot O\cdot SO_2R]} \longrightarrow R\cdot SO_3H + \underset{\text{(VII.)}}{Ar_2N\cdot CN}$$

The new results presented have provided additional information on the mechanism of the synthesis of substituted sulphonylcyanamides (III) from arylureas and aromatic sulphonyl chlorides. The experimental evidence appears to favour a mechanism involving intermediate formation of arylcyanamides. Postulation of the intermediate production of sulphonic esters (of type VIII) from *iso*ureas explains satisfactorily all observations so far made.

In their work on amidines, Short *et al.* (*J.*, 1948, 1514, 1618) adduced reasons for postulating the intermediate formation of sulphonyl esters of structure $R\cdot C(:NR')\cdot O\cdot SO_2R''$ from monosubstituted amides $R\cdot CO\cdot NHR'$ and arylsulphonyl chlorides; the great instability of imidosulphonates of type $R\cdot C(:NH)\cdot O\cdot SO_2R''$, however, was shown by unsuccessful attempts to prepare *N*-phenylbenzamidine from benzamide, benzenesulphonyl chloride, and aniline, the product of the reaction being phenyl cyanide even at low temperatures. It is suggested (cf. Short *et al.*, *Chem. and Ind.*, 1949, 419; Kurzer, *ibid.*, p. 522) that, analogously, the reaction between arylureas and sulphonyl chlorides may involve the intermediate formation of highly unstable *iso*urea derivatives, $R\cdot SO_2\cdot O\cdot C(:NH)\cdot NHR'$, which would decompose spontaneously into the sulphonic acid and the cyanamide (IX), the latter giving the sulphonyl derivative (III) with the excess of the sulphonyl chloride present. This mechanism readily explains the formation of triazines in these reactions: part of the arylcyanamide arising from the unstable *iso*urea compound (VIII) may polymerise before interaction with the excess of sulphonyl chloride, yielding the substituted melamine (I). The synthesis of diarylcyanamides from 1 : 1-diarylureas is also accounted for by postulating the intermediate existence of the unstable imido-sulphonate (VI): the disubstituted cyanamide (VII) cannot, of course, react with the excess of sulphonyl chloride and is readily isolated in theoretical yield. A mechanism involving intermediate formation of arylsulphonylarylureas, on the other hand, justifies the expectation that a diarylsulphonylurea, $Ph_2N\cdot CO\cdot NH\cdot SO_2R$, would result, since loss of water is not possible in this case.

The present mechanism also accounts for the fact that, in contrast to arylureas, ethyl*iso*urea and arylguanidines react with sulphonyl chlorides to yield the expected sulphonyl derivatives (Cox and Raymond, *J. Amer. Chem. Soc.*, 1941, **63**, 300; Marshall *et al.*, *Johns Hopkins Hosp. Bull.*, 1940, **67**, 163; Backer and Moed, *Rec. Trav. chim.*, 1947, **66**, 335), In neither case is the formation of the unstable intermediate of type (VIII) possible, and normal formation of sulphonyl derivatives is observed.

The observations now reported appear to provide strong support for the view that arylcyanamides occur, at some stage, as intermediate products in this reaction. The work of Short *et al.* on amidines, together with the above results, provide indirect evidence for the correctness of a mechanism involving the formation of labile sulphonyl esters (VIII) of *iso*urea. Experiments now in progress should provide further relevant results.

EXPERIMENTAL.

M.p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, Oxford. Experimental conditions recorded are in each case the best of several tried.

*Tri-*o*-bromophenylmelamine.*—(*a*) *Using benzenesulphonyl chloride.* To a solution of *o*-bromophenylurea (10·75 g., 0·05 mol.) in pyridine (45 ml.) at 30°, benzenesulphonyl chloride (26·5 g., 0·15 mol.) was added in one portion. The dark reddish liquid, the temperature of which rose rapidly to 60°, was set aside for 12 minutes. It was then slowly stirred into ice–water (400 ml.) containing hydrochloric acid (10 ml.) and gave a dark-orange oil that solidified partly on storage. The material was extracted with warm chloroform (150, 120, and 100 ml.), and the collected extracts washed successively with sodium hydroxide solution (5%; 2 × 100 ml.; see extracts A), dilute hydrochloric acid, and water until neutral. The semi-solid mass obtained on removal of the solvent was roughly separated into the sulphonylcyanamide and the trimer by brief heating under reflux with acetone (50 ml.) and cooling to room temperature. The sparingly soluble melamine, forming a white granular solid, was filtered off and washed with acetone (giving filtrate B) (weight of dried residue 4·5 g., 46%). Two crystallisations from chloroform–ethanol (approx. 10 and 20 ml., respectively, per g. of crude material) gave white silky needles of *tri-*o*-bromophenylmelamine*, m. p. 188—189° [Found: C, 43·6; H, 2·6; N, 14·1; Br, 41·0%; *M* (Rast), 530 and 550. $C_{21}H_{15}N_6Br_3$ requires C, 42·7; H, 2·5; N, 14·2; Br, 40·6%; *M*, 591], soluble in glacial acetic acid, benzene, hot chloroform, sparingly soluble in acetone and ethanol, and almost insoluble in water and alkalis.

The acetone filtrate B was diluted with ethanol, and further small quantities of the trimer separating out on storage were filtered off. The solvent was removed in a vacuum, and the residual orange oil dissolved in ethanol (25 ml.) and boiled with carbon for 15 minutes. The deep-yellow filtrate deposited lustrous prisms of benzenesulphonyl-*o*-bromophenylcyanamide, m. p. 94—95° (3·1 g., 19%). The alkaline washing liquids A gave, on acidification with hydrochloric acid, a small quantity of unidentified white precipitate (0·5 g.).

When the above reactants were allowed to interact within a higher temperature range (60—90°) and were maintained at 90° for 15 minutes, higher yields (62%) of tri-*o*-bromophenylmelamine were obtained, but only traces of crystalline sulphonylcyanamide could be isolated from the oily acetone-soluble fraction.

(*b*) *Using toluene-*p*-sulphonyl chloride.* A solution of *o*-bromophenylurea (10·75 g.; 0·05 mol.) in pyridine (60 ml.) was treated with toluene-*p*-sulphonyl chloride (28·6 g., 0·15 mol.). The temperature rose to 105°, and the resulting dark red liquid was poured, after 15 minutes, into ice-water (400 ml.). The green semi-solid product was worked up as previously described and gave silky needles of tri-*o*-bromophenylmelamine (3·9 g., 40%), m. p. 188—189°, undepressed on admixture with material prepared by method (*a*) (Found: C, 42·9; H, 2·45%). The acetone-soluble fraction gave compact lustrous prisms of toluene-*p*-sulphonyl-*o*-bromophenylcyanamide, m. p. 111—112° (5·2 g., 30%).

(*c*) Tri-*o*-bromophenylmelamine was also obtained in 25% yield from *o*-bromophenylurea and toluene-*o*-sulphonyl chloride as described in (*a*).

(*d*) *From cyanuric bromide.* To a solution of *o*-bromoaniline (5·2 g., 0·03 mol.) in anhydrous benzene (100 ml.), cyanuric bromide (1·6 g., 0·005 mol.) (Ponomarew, *Ber.*, 1885, **18**, 3261) was added, and the suspension was heated under reflux for 1 hour. The separated *o*-bromoaniline hydrobromide was removed by filtration, and the benzene filtrate evaporated in a vacuum. The residual orange oil was taken up in chloroform (12 ml.), and the solution decanted from a further small quantity of amine hydrobromide and diluted with ethanol (24 ml.). On storage and partial spontaneous evaporation, a white granular mass separated (m. p. 180—184°; 2·55 g., 87%) which gave, on crystallisation from chloroform–ethanol, silky needles of tri-*o*-bromophenylmelamine, m. p. 189—190°, undepressed on admixture with material prepared from *o*-bromophenylurea and arylsulphonyl chlorides [Found: C, 42·6; H, 2·6%; *M* (Rast), 560].

*Tri-*o*-chlorophenylmelamine.*—(*a*) A solution of *o*-chlorophenylurea (17 g., 0·1 mol.) in pyridine (100 ml.) at 50° was treated with benzenesulphonyl chloride (53 g., 0·3 mol.). The resulting hot solution (85°) was poured, after 20 minutes, into ice–water (400 ml.), and the reaction products were extracted with warm chloroform. The combined extracts were washed successively with dilute sodium hydroxide solution, hydrochloric acid, and water until neutral, and the dark orange oil obtained after removal of the solvent was dissolved in acetone (12 ml.)–ethanol (36 ml.). The granular deposit separating during 1—2 hours was filtered off (filtrate A) and gave, on crystallisation from chloroform–ethanol (1 : 4), white silky tri-*o*-chlorophenylmelamine, m. p. 165—166° (Found: C, 55·1; H, 3·25; N, 18·0; Cl, 23·4. Calc.

for $C_{21}H_{15}N_6Cl_3$: C, 55·1 ; H, 3·3 ; N, 18·4 ; Cl, 23·3%) (yield, including material from mother-liquors : 3—4 g., 20—26%).

From filtrate A further small quantities (up to 0·5 g.) of the granular trimer, subsequently separated, were first removed. The filtrate gave, on partial spontaneous evaporation, large glass-like prisms of benzenesulphonyl-*o*-chlorophenylcyanamide, m. p. 106—107° (4—4·5 g., 14—15%). Owing to the greater solubility of tri-*o*-chlorophenylmelamine in acetone, separation from the accompanying sulphonylcyanamide cannot be accomplished by simply heating the mixture with this solvent as for the corresponding bromo-compound.

(*b*) Interaction of *o*-chlorophenylurea (0·1 mol.) and toluene-*p*-sulphonyl chloride (0·3 mol.) in the temperature range 40—105° gave considerable quantities of the unchanged urea (almost insoluble in chloroform), together with tri-*o*-chlorophenylmelamine, m. p. 164—165° (10%), and toluene-*p*-sulphonyl-*o*-chlorophenylcyanamide, m. p. 102—104° (16%). In experiments in which the maximum temperature was kept below 35° by external cooling (initial temp., 5°), the original urea was recovered almost quantitatively. Tri-*o*-chlorophenylmelamine has previously been prepared by the interaction of cyanuric bromide and *o*-chloroaniline (von Meyer and Näbe, *loc. cit.*), m. p. 161° being recorded.

(*c*) Interaction of *o*-chloroaniline and cyanuric bromide (cf. von Meyer and Näbe, *loc. cit.*) gave tri-*o*-chlorophenylmelamine, m. p. 164—165° (Found : C, 55·4; H, 3·4%), undepressed on admixture with material prepared as above.

o-*Chlorophenylthiourea.*—A solution of *o*-chloroaniline (12·75 g., 0·1 mol.) in concentrated hydrochloric acid (12 ml., 0·11 mol.) and water (100 ml.) was heated with ammonium thiocyanate (8·4 g.; 0·11 mol.), in an evaporating dish on the steam-bath for 1 hour. The liquid, from which a mass of needle-shaped crystals had separated, was set aside at room temperature for 2 hours; it was then twice slowly evaporated to dryness (time 4—5 hours), and the crystalline residue heated on the steam-bath for 4 hours. The suspension of the powdered solid in water (150 ml.) was heated to 80° and then allowed to cool to 30°, and the crude product filtered off (yield : 10—11·5 g., 54—62%; m. p. 142—144°). Crystallisation from ethanol–acetone–water (3, 1, and 2 ml., respectively, per g.) gave white crystalline *o*-chlorophenylthiourea, m. p. 144—145° (long needles, m. p. 145—146°, from ethanol–ether). Uninterrupted evaporation of the initial reaction mixture (see above) tended to give an oily product, from which smaller yields were isolated on crystallisation. *o*-Chlorophenylthiourea has previously been obtained from *o*-chlorophenyl*iso*thiocyanate and ammonia (Dyson and George, *J.*, 1924, **125**, 1705), and by the interaction of *o*-chloroaniline hydrochloride with sodium thiocyanate in chlorobenzene (Dalgliesh and Mann, *J.*, 1945, 900).

o-*Chlorophenylcyanamide.*—To a boiling suspension of *o*-chlorophenylthiourea (18·7 g., 0·1 mol.) in water (150 ml.) at 100°, a boiling solution of potassium hydroxide [56 g. (1 mol.) in 150 ml. of water] was added, immediately followed by a hot saturated solution of lead acetate (38 g., 0·1 mol.). The reaction mixture was boiled for 6 minutes and then cooled to 0°, and the lead sulphide removed by filtration under reduced pressure. On acidification of the colourless filtrate with glacial acetic acid (60 ml.) at 0—5° (addition of ice), a white crystalline precipitate of o-*chlorophenylcyanamide* (12·8 g., 84%) separated, forming large lustrous needles, m. p. 104—105°, from benzene–light petroleum (Found : C, 54·9; H, 3·6. $C_7H_5N_2Cl$ requires C, 55·1 ; H, 3·3%). In benzene solution, or in the solid state, the material did not polymerise on storage for several weeks at 20—30°.

Polymerisation of o-*Chlorophenylcyanamide.*—*o*-Chlorophenylcyanamide (10 g.), contained in a dish, was heated at 100° for 1 hour. The viscous melt, which solidified to a transparent brittle mass on cooling, was finely powdered and dissolved in boiling chloroform (50 ml.). After 5 minutes' treatment with charcoal and filtration, the water-clear filtrate was diluted with ethanol (40 ml.); it deposited, on cooling and storage, a white micro-crystalline powder, which on recrystallisation (see below) gave *tri-*o-*chlorophenyl*iso*melamine* in white minute prisms, m. p. 261—262° [Found : C, 55·0; H, 3·7; N, 17·9; Br, 23·8%; *M* (Rast), 475, 510. $C_{21}H_{15}N_6Cl_3$ requires C, 55·1 ; H, 3·3 ; N, 18·4 ; Cl, 23·3% ; *M*, 458].

Evaporation of the filtrate to approx. half its bulk gave further quantities of the *iso*melamine (total yield : 3·5—4 g., 35—40%). Tri-*o*-chlorophenyl*iso*melamine is almost insoluble in acetone, ethanol, and benzene; it is readily soluble in acetic acid and dilute hydrochloric acid in the cold and is reprecipitated therefrom as a white crystalline powder by alkalis. It can be crystallised by dissolving it (0·5 g.) in ethanol (30 ml.) in the presence of concentrated hydrochloric acid (0·3 ml.), followed by adding aqueous ammonia dropwise to alkalinity, resulting in the rapid formation of minute prisms on cooling.

The filtrate, from which the *iso*melamine had crystallised, was evaporated under reduced pressure, and the residual oil dissolved in ethanol (20 ml.). The white granular material obtained on cooling and storage was filtered off (filtrate A), washed with hydrochloric acid (1 : 1; 2 × 10 ml.) to remove small quantities of the *iso*melamine, and crystallised from chloroform–ethanol, giving a silky mass of tri-*o*-chlorophenylmelamine, m. p. 164—167° [Found : C, 54·8; H, 3·4%; *M* (Rast), 480], undepressed on admixture with material prepared from cyanuric bromide. Filtrate A deposited a colourless oil.

Polymerisation of o-*Bromophenylcyanamide.*—Heating *o*-bromophenylcyanamide (5 g.) at 100° for 1 hour and then cooling it gave a brittle mass, which was finely powdered and twice extracted with hydrochloric acid (2 × 25 ml.; 10%) at 60°; the extracts were decanted from the insoluble viscous residue (A). The acid extracts were filtered with charcoal and made alkaline with aqueous ammonia. The white granular precipitate (2·85 g.; m. p. 250—260°) was crystallised from ethanol (25 ml.) with successive addition of hydrochloric acid and ammonia as described above and gave minute white prisms of *tri-*o-*bromophenyl*iso*melamine*, m. p. 266—268° [Found : C, 42·3; H, 2·7; N, 13·8; Br, 40·2%; *M* (Rast), 610. $C_{21}H_{15}N_6Br_3$ requires C, 42·7 ; H, 2·5 ; N, 14·2 ; Br, 40·6% ; *M*, 591].

The acid-insoluble residue A was crystallised from ethanol (15 ml.); the resulting white granular mass was again washed with 10% hydrochloric acid and gave, on crystallisation from chloroform–acetone, a silky mass of tri-*o*-bromophenylmelamine, m. p. 186—189°, undepressed on admixture with material prepared from cyanuric bromide.

Diphenylcyanamide.—(*a*) A solution of *as*-diphenylurea (2·12 g., 0·01 mol.) in pyridine (15 ml.) was treated with excess of toluene-*p*-sulphonyl chloride (5·7 g., 0·03 mol.), and the deep-green liquid heated on the steam-bath for 2 hours. When the dark orange solution was slowly poured into ice–water (150 ml.), an oil separated which solidified on being stirred (1·9 g., 97%). Crystallisation from acetone–ethanol–water gave thin lustrous plates of diphenylcyanamide, m. p. 69—71° (Found: C, 79·7; H, 5·45; N, 14·6. Calc. for $C_{13}H_{10}N_2$: C, 80·4; H, 5·15; N, 14·4%).

(*b*) A solution of *as*-diphenylurea (2·12 g., 0·01 mol.) and benzenesulphonyl chloride (5·25 g., 0·03 mol.) in pyridine (15 ml.), when heated on the steam-bath for 1 hour and worked up as described above, gave diphenylcyanamide (90%), m. p. 70—72° (Found: C, 80·15; H, 4·95%).

(*c*) Diphenylcyanamide was obtained in smaller yield (64%) when the above reaction mixtures were set aside at room temperature for 48 hours.

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