

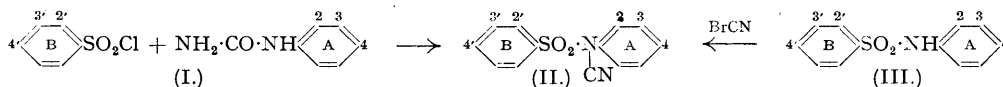
### 638. Cyanamides. Part II. The Influence of Substituents in the Synthesis of Arylsulphonylarylcyanamides.

By FREDERICK KURZER.

A series of arylsulphonylarylcyanamides has been prepared from arylureas by the general method described in Part I (this vol., p. 1034). The velocity of cyanamide formation, compared approximately by the yield of product obtained under standard conditions, was not appreciably influenced by the presence of methyl, phenyl, ethoxy-, or halogen substituents in the arylurea, but was affected noticeably by the choice of the arylsulphonyl chloride. A further hydrolytic fission of sulphonylcyanamides has been examined.

It was shown in Part I of this series (this vol., p. 1034) that condensation of arylureas and aromatic sulphonyl chlorides in pyridine under restrained conditions does not yield arylsulphonylarylcyanamides, but occurs with simultaneous dehydration and results in the formation of arylsulphonylarylcyanamides (II) in good yield. In marked contrast, arylureas react with aromatic carboxyl chlorides under analogous conditions to produce the expected arylacylarylureas,  $\text{ArNH}\cdot\text{CO}\cdot\text{NH}\cdot\text{COAr}'$ , without difficulty (Beckmann and Köster, *Annalen*, 1893, 274, 28; Walther and Wlodkowski, *J. pr. Chem.*, 1899, 59, 271). The action of sulphonyl chlorides on urea itself, first shown by Remsen and Garner (*Amer. Chem. J.*, 1901, 25, 175) to give amidinourea sulphonates  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)_2\cdot\text{NH}_2\}\text{ArSO}_3$ , has recently been claimed to yield sulphonylureas,  $\text{ArSO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , provided that the reaction temperatures are carefully controlled (Swiss P. 224,070).

Arylsulphonylarylcyanamides (II) were first prepared by the action of cyanogen bromide on arylsulphonanilides (III) in the presence of alkali (von Braun, *Ber.*, 1904, 37, 2809). The reaction, which was reported to occur only slowly with sulphonamides derived from aliphatic amines, failed entirely with arylsulphonanilides containing substituents in the *ortho*-position of ring A. In the present investigation a series of 46 sulphonylcyanamides of type (II) was prepared by the general method described in Part I (*loc. cit.*) in order to obtain further information on the general applicability of this reaction and the influence of substituents on its course. By performing the synthesis under carefully controlled standard conditions, the yield of product obtained could be taken as an approximate measure of the influence of structural changes on the relative ease of the formation of the desired compounds. By preparing arylsulphonylarylcyanamides from substituted phenylureas (I) containing either a methyl, phenyl, ethoxy-, or bromo-group in the *ortho*-, *meta*-, or *para*-position to the ureido-grouping, a series of cyanamides (II) with these substituents in positions 2, 3, or 4 was obtained.



An examination of the yields obtained under standard conditions in these experiments reveals that the formation of cyanamides was not appreciably affected by the presence of the selected substituents, irrespective of their position, in the arylurea, but was influenced noticeably by the choice of the sulphonyl chloride employed. It is seen from the Table that, regardless of the presence of substituents in ring A, benzenesulphonylarylcyanamides were almost invariably obtained in 70—80% yields. Similarly, 60—70% and 40—50% conversion appeared to be the rule with toluene-*p*-, and toluene-*o*-sulphonyl chlorides, respectively, whilst the yields of *m*-nitrobenzenesulphonylarylcyanamides were somewhat more variable. The marked reduction in the yields resulting when a methyl group in ring B is moved from position 4' to position 2' suggests the operation of steric factors, since polar effects would not be expected to cause quantitative differences of the order of magnitude now recorded. This observation contrasts strongly with the behaviour of substituents in ring A, where the presence of larger substituents (*e.g.*, a phenyl group, cf. diphenylcyanamides) appears not to retard cyanamide formation by steric hindrance.

Arylsulphonylarylcyanamides substituted in position 2, previously reported to be unobtainable by the action of cyanogen bromide on the corresponding sulphonanilides (III) (von Braun, *loc. cit.*) are readily available by the present synthesis. The exceptionally low yields of cyanamides obtained from *o*-halogenophenylureas are caused by the formation of polymeric products; the reaction is described in detail in the subsequent paper.

## Arylsulphonylarylcyanamides,

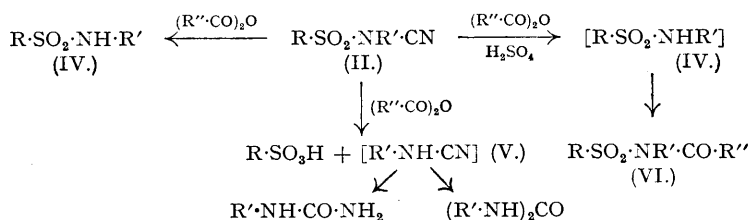
Compound.	Crystal form. <sup>1</sup>	M. p.	Yield, <sup>2</sup> %.	Formula.	Found.			Required.		
					C, %.	H, %.	N, %.	C, %.	H, %.	N, %.
Benzenesulphonyl- <i>p</i> -tolylcyanamide	Compact prisms	91—93°	76	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> S	61.6	4.75	10.4	61.8	4.4	10.3
Toluene- <i>p</i> -sulphonyl- <i>p</i> -tolylcyanamide	Thick plates	124—126	72	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	62.6	5.1	10.0	62.9	4.9	9.8
Toluene- <i>o</i> -sulphonyl- <i>p</i> -tolylcyanamide <sup>4</sup>	Small prisms	116—117	45	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	62.75	4.6	9.9	62.9	4.9	9.8
m-Nitrobenzenesulphonyl- <i>p</i> -tolylcyanamide	Thick needles	103—105	62	C <sub>14</sub> H <sub>11</sub> O <sub>4</sub> N <sub>3</sub> S	53.15	3.65	13.2	53.0	3.5	13.25
Benzenesulphonyl- <i>m</i> -tolylcyanamide	Compact prisms	81—82	72	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> S	61.4	4.4	—	61.8	4.4	—
Toluene- <i>p</i> -sulphonyl- <i>m</i> -tolylcyanamide	Thick plates	98—100	58	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	62.3	4.65	—	62.9	4.9	—
Toluene- <i>o</i> -sulphonyl- <i>m</i> -tolylcyanamide <sup>3</sup>	Small prisms	79—81	52	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	63.0	5.0	—	62.9	4.9	—
m-Nitrobenzenesulphonyl- <i>m</i> -tolylcyanamide	Very pale yellow needles	119—121	50	C <sub>14</sub> H <sub>11</sub> O <sub>4</sub> N <sub>3</sub> S	52.7	3.5	—	53.0	3.5	—
Benzenesulphonyl- <i>o</i> -tolylcyanamide <sup>3, 10</sup>	Compact prisms	70—72	70	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub> N <sub>2</sub> S	61.6	4.7	—	61.8	4.4	—
Toluene- <i>p</i> -sulphonyl- <i>o</i> -tolylcyanamide <sup>3</sup>	Compact prisms	104—106	62	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	62.8	4.95	—	62.9	4.9	—
Toluene- <i>o</i> -sulphonyl- <i>o</i> -tolylcyanamide <sup>4</sup>	Elongated prisms	73—75	40	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	63.3	4.9	—	62.9	4.9	—
m-Nitrobenzenesulphonyl- <i>o</i> -tolylcyanamide	Thin needles	110—111	45	C <sub>14</sub> H <sub>11</sub> O <sub>4</sub> N <sub>3</sub> S	53.3	3.6	—	53.0	3.5	—
Benzenesulphonyl-4-diphenylcyanamide	Massive plates	102—104	80	C <sub>19</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	67.9	4.1	8.6	68.3	4.2	8.4
Toluene- <i>p</i> -sulphonyl-4-diphenylcyanamide	Elongated plates	121—122	60	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> S	68.7	4.6	8.1	69.0	4.6	8.0
Toluene- <i>o</i> -sulphonyl-4-diphenylcyanamide <sup>4</sup>	Plates	82—84	32	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> S	68.9	4.45	8.2	69.0	4.6	8.0
m-Nitrobenzenesulphonyl-4-diphenylcyanamide	Pale yellow needles	165—167	32	C <sub>19</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub> S	60.1	3.35	10.9	60.2	3.4	11.1
Benzenesulphonyl-2-diphenylcyanamide	Small prisms	131—132	80	C <sub>19</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	68.3	4.4	—	68.3	4.2	—
Toluene- <i>p</i> -sulphonyl-2-diphenylcyanamide	Large needles	160—161	60	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> S	68.8	4.55	—	69.0	4.6	—
Toluene- <i>o</i> -sulphonyl-2-diphenylcyanamide <sup>3</sup>	Small prisms	101—104	10	C <sub>20</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> S	69.1	4.6	—	69.0	4.6	—
m-Nitrobenzenesulphonyl-2-diphenylcyanamide	Minute prisms	156—157	15	C <sub>19</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub> S	60.0	3.3	—	60.2	3.4	—
Benzenesulphonyl- <i>p</i> -ethoxyphenylcyanamide	Massive needles	102—104	80	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	59.35	4.6	9.3	59.6	4.6	9.3
Toluene- <i>p</i> -sulphonyl- <i>p</i> -ethoxyphenylcyanamide	Massive needles	105—106	72	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S	60.1	5.15	9.1	60.8	5.1	8.9
Toluene- <i>o</i> -sulphonyl- <i>p</i> -ethoxyphenylcyanamide <sup>3</sup>	Massive needles	92—94	56	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S	60.4	5.1	9.0	60.8	5.1	8.9
m-Nitrobenzenesulphonyl- <i>p</i> -ethoxyphenylcyanamide	Pale yellow plates	111—113	45	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub> S	52.3	3.75	12.2	51.9	3.75	12.1
Benzenesulphonyl- <i>m</i> -ethoxyphenylcyanamide <sup>4</sup>	Oil <sup>5</sup>	—	70	C <sub>15</sub> H <sub>14</sub> O <sub>3</sub> N <sub>2</sub> S	59.2	4.1	—	59.6	4.6	—
Toluene- <i>p</i> -sulphonyl- <i>m</i> -ethoxyphenylcyanamide	Massive plates	68—70	60	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S	60.8	5.2	—	60.8	5.1	—
Toluene- <i>o</i> -sulphonyl- <i>m</i> -ethoxyphenylcyanamide <sup>4</sup>	Oil <sup>5</sup>	—	45	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S	59.3	4.7	—	60.8	5.1	—
m-Nitrobenzenesulphonyl- <i>m</i> -ethoxyphenylcyanamide	Pale yellow plates	82—83	40	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub> S	51.8	4.0	—	51.9	3.75	—
Benzenesulphonyl- <i>o</i> -ethoxyphenylcyanamide <sup>3, 10</sup>	Large plates	84—85	52	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> S	59.85	4.9	—	59.6	4.6	—
Toluene- <i>p</i> -sulphonyl- <i>o</i> -ethoxyphenylcyanamide	Massive plates	96—97	62	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S	60.9	5.1	—	60.8	5.1	—
Toluene- <i>o</i> -sulphonyl- <i>o</i> -ethoxyphenylcyanamide <sup>3</sup>	Massive plates	99—101	40	C <sub>16</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub> S	61.2	4.9	—	60.8	5.1	—
m-Nitrobenzenesulphonyl- <i>o</i> -ethoxyphenylcyanamide	Pale yellow plates	130—132	30	C <sub>16</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub> S	51.7	3.55	—	51.9	3.75	—

<i>Benzenesulphonyl-p-bromophenylcyanamide</i> .....	Compact prisms	95—96	74	$C_{13}H_9O_2N_3SBr$	46.3	2.8	8.4	46.3	2.7	8.3
<i>Toluene-p-sulphonyl-p-bromophenylcyanamide</i> .....	Compact prisms	143—145	68	$C_{14}H_{11}O_2N_3SBr$	47.7	3.3	8.0	47.9	3.1	8.0
<i>Toluene-o-sulphonyl-p-bromophenylcyanamide</i> <sup>4</sup> .....	Flat prisms	62—63	54	$C_{13}H_9O_2N_3SBr$	48.0	3.0	8.4	47.9	3.1	8.0
<i>m-Nitrobenzenesulphonyl-p-bromophenylcyanamide</i> .....	Pale yellow plates	140—142	60	$C_{13}H_8O_4N_3SBr$	40.25	1.9	10.9	40.85	2.1	11.0
<i>Benzenesulphonyl-m-bromophenylcyanamide</i> .....	Small prisms	91—92	72	$C_{13}H_9O_2N_3SBr$	45.9	2.6	—	46.3	2.7	—
<i>Toluene-p-sulphonyl-m-bromophenylcyanamide</i> .....	Small prisms	112—114	45	$C_{14}H_{11}O_2N_3SBr$	47.4	3.0	—	47.9	3.1	—
<i>Toluene-o-sulphonyl-m-bromophenylcyanamide</i> <sup>6</sup> .....	Thick needles	79—81	54	$C_{13}H_9O_2N_3SBr$	47.45	3.1	—	47.9	3.1	—
<i>m-Nitrobenzenesulphonyl-m-bromophenylcyanamide</i> .....	Pale yellow needles	133—134	50	$C_{13}H_8O_4N_3SBr$	40.65	2.0	—	40.85	2.1	—
<i>Benzenesulphonyl-o-bromophenylcyanamide</i> <sup>7, 8a</sup> .....	Elongated plates	94—95	35.8	$C_{13}H_9O_2N_3SBr$	46.1	2.7	—	46.3	2.7	—
<i>Toluene-p-sulphonyl-o-bromophenylcyanamide</i> <sup>7, 8b</sup> .....	Elongated plates	111—112	30.8	$C_{14}H_{11}O_2N_3SBr$	48.2	3.2	—	47.9	3.1	—
<i>Toluene-o-sulphonyl-o-bromophenylcyanamide</i> <sup>7, 8c</sup> .....	Oil <sup>5</sup>	—	25.8	$C_{13}H_9O_2N_3SBr$	47.1	3.1	—	47.9	3.1	—
<i>m-Nitrobenzenesulphonyl-o-bromophenylcyanamide</i> <sup>6</sup> .....	—	—	0	$C_{13}H_8O_4N_3SBr$	—	—	—	—	—	—
<i>Benzenesulphonyl-o-chlorophenylcyanamide</i> <sup>7, 10</sup> .....	Small prisms	106—107	20.8	$C_{13}H_9O_2N_3SCl$	53.0	3.1	9.7	53.3	3.1	9.6
<i>Toluene-p-sulphonyl-o-chlorophenylcyanamide</i> <sup>7</sup> .....	Small prisms	102—104	15.8	$C_{14}H_{11}O_2N_3SCl$	54.4	3.5	9.0	54.8	3.6	9.1

<sup>1</sup> Unless otherwise stated, the cyanamides formed colourless lustrous crystals. <sup>2</sup> The values reported are the average yields obtained in two, and in some cases in three, experiments carried out under the standard conditions specified. <sup>3</sup> When the reaction mixture was poured into water, the crude material solidified only partly on prolonged storage. <sup>4</sup> The crude product failed to solidify on prolonged storage, and the sulphonylcyanamide was therefore isolated by extraction with chloroform. The combined extracts were washed successively with hydrochloric acid, sodium hydroxide solution, and water until neutral, and the solvent was removed in a vacuum; the orange oily residue was purified by treatment of its acetone solution with charcoal, and the product crystallised from the usual solvents. On acidification, the alkaline washing liquids gave traces of white substances, which have not yet been closely examined. <sup>5</sup> The substance failed to crystallise on prolonged storage. Since arylsulphonylarylcyanamides decomposed with some violence above their m. p.s., isolation by vacuum-distillation proved impracticable; the three compounds concerned were accordingly obtained by long storage in a vacuum, whereupon highly viscous substances, eventually showing signs of crystallisation, resulted. <sup>6</sup> In contrast to other toluene-*o*-sulphonyl derivatives which proved difficult to crystallise, the crude toluene-*o*-sulphonyl-*m*-bromophenylcyanamide solidified rapidly and was readily crystallised. <sup>7</sup> *o*-Halogenophenylarenes reacted slowly, and more favourable results were obtained when the reaction was carried out at higher temperatures. This was particularly apparent with *o*-chlorophenylurea, considerable quantities of which were recovered unchanged amongst the reaction products. A few selected details are given in Part III (following paper) (see also note 8). <sup>8</sup> The exceptionally low yields of arylsulphonylarylcyanamides obtained from *o*-halogenophenylureas are due to the formation of polymeric by-products (see Part III, following paper). The following bromine contents were found: (a) 23.1 (Required, 23.7%); (b) 22.4 (Required, 22.8%); (c) 22.2 (Required, 22.8%). <sup>9</sup> Preparation of this compound by the present method was not successful. <sup>10</sup> Von Braun (*loc. cit.*) failed to prepare this compound by the action of cyanogen bromide on the appropriate substituted benzenesulphonamide.

In the synthesis of *m*-nitrobenzenesulphonylarylcyanamides, the reaction mixture generally set to a yellow crystalline mass; on addition of ice-water to the material the pyridinium sulphonate dissolved readily, while the precipitate of the crude cyanamide appeared in suspension.

A further hydrolytic reaction of sulphonylcyanamides prepared by the above method has been examined. Toluene-*p*-sulphonylphenylcyanamide is not attacked by acetic anhydride at 100°, but a slow fission of the molecule in two distinct ways occurs on prolonged boiling of the solution, giving a mixture of varying quantities of toluene-*p*-sulphonanilide, phenylurea, and carbanilide (cf. Part I, *loc. cit.*); the last two products are no doubt formed from the intermediate phenylcyanamide. It has now been found that arylsulphonylarylcyanamides, when heated under reflux for short periods with an aliphatic acid anhydride in the presence of a few drops of concentrated sulphuric acid, yield *N*-acylsulphonanilides (VI) almost quantitatively. Thus, for example, acetic or propionic anhydride with toluene-*p*-sulphonylphenylcyanamide gave *N*-acetyl- and *N*-propionyl-toluene-*p*-sulphonanilide, respectively. *N*-Acylbenzenesulphonanilides have previously been prepared by the interaction of the sodium salt of benzenesulphonanilide with acid anhydrides (Wheeler, Smith, and Warren, *Amer. Chem. J.*, 1897, **19**, 760) and were identical with specimens prepared as above from the appropriate sulphonylcyanamide. The reaction probably involves the intermediate formation of the sulphonanilide (IV), as this is isolated in the absence of sulphuric acid, immediately followed by acylation. The ready acetylation of sulphonanilides under the present conditions has been previously observed (Reverdin, *Helv. Chim. Acta*, 1930, **13**, 696).



The arylureas required in this work were prepared in excellent yield by the action of excess of sodium cyanate (2 moles) on the corresponding aromatic amine (1 mole) in acetic acid of suitable concentration. This convenient method appears to be an improvement over previous syntheses of 2- and 4-diphenylureas from the diphenyl isocyanate and ammonia (Van Gelderen, *Rec. Trav. chim.*, 1933, **52**, 976; Morgan and Walls, *J.*, 1932, 2225).

#### EXPERIMENTAL.

M. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss.

*Arylsulphonylarylcyanamides*.—Forty-six compounds (see Table) were prepared by the following general procedure. A solution or suspension of the substituted arylurea (0.05 mol.) in pyridine (40 ml.) was treated with the appropriate sulphonyl chloride (0.15 mol.) in 2 portions. The temperature of the reaction mixture rose rapidly but was maintained below 60° by external cooling if necessary. After 12–15 minutes, during which the orange liquid was allowed to cool spontaneously, the whole was slowly poured, with stirring, into ice-water (400 ml.) whereupon the crude cyanamide separated as an oil which generally solidified rapidly on being stirred (see, however, the Table, footnotes 3 and 4). The product was filtered, finely ground, and washed successively with hydrochloric acid, dilute sodium hydroxide solution, and water. Purification with carbon and 3 crystallisations from acetone-ethanol-water (approx. 1.5 ml., 6 ml., and 1 ml., respectively, per g. of crude material) gave the pure sulphonylcyanamide.

*N*-Acetylbenzenesulphonanilide.—A solution of benzenesulphonylphenylcyanamide (6 g.) in acetic anhydride (50 ml.) was treated with concentrated sulphuric acid (6 drops) and heated under reflux for 2 hours. On slowly pouring the dark-brown liquid into ice-water (300 ml.) a black pitch-like material separated, which solidified to a brittle amorphous material when kept overnight. On prolonged heating of the alcoholic solution (60 ml.) with charcoal, filtering, and cooling, a pale yellow crystalline material (5.2 g., 80%) was obtained, which gave, after 2 crystallisations from ethanol, colourless lustrous needles of *N*-acetylbenzenesulphonanilide, m. p. 117–118° (Found: C, 61.3; H, 4.8. Calc. for C<sub>14</sub>H<sub>13</sub>O<sub>3</sub>NS: C, 61.1; H, 4.7%).

*N*-Propionylbenzenesulphonanilide.—This, similarly prepared from benzenesulphonylphenylcyanamide (1 g.) and propionic anhydride (12 ml.) in the presence of sulphuric acid, formed blades, m. p. 117–118° (Found: C, 62.4; H, 4.9. Calc. for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub>NS: C, 62.3; H, 5.2%).

*N*-Acetyltoluene-*p*-sulphonanilide.—A solution of toluene-*p*-sulphonylphenylcyanamide (6 g.) in acetic anhydride (40 ml.) containing concentrated sulphuric acid (6 drops) was boiled for 2 hours. The dark brown brittle solid (4.9 g., 76%) obtained on pouring the liquid into ice-water (200 ml.) was crystallised twice from ethanol (60 and 50 ml., respectively) and gave colourless needles of *N*-acetyltoluene-*p*-sulphonanilide, m. p. 154–155° (Found: C, 61.8; H, 4.8; N, 4.75; S, 10.8. Calc. for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub>NS: C, 62.3; H, 5.2; N, 4.8; S, 11.1%) (Chaplin and Hunter, *J.*, 1937, 1114, report m. p. 149–150°).

*N*-Propionyltoluene-*p*-sulphonanilide.—A solution of toluene-*p*-sulphonylphenylcyanamide (5 g.) in propionic anhydride (40 ml.) was treated with sulphuric acid (6 drops) and heated under reflux for

1½ hours. The dark liquid was poured into ice-water and gave a deep-brown oil which solidified when kept for 24 hours. Purification of its alcoholic solution with carbon, and 2 crystallisations from ethanol gave elongated prisms of *N-propionyltoluene-p-sulphonanilide*, m. p. 143—144° (Found: C, 63.0; H, 5.3; N, 4.5; S, 10.5.  $C_{16}H_{17}O_3NS$  requires C, 63.4; H, 5.6; N, 4.6; S, 10.6%).

*N-Acetylbenzenesulphon-p-anisidide*.—This was prepared by heating benzenesulphonyl-*p*-methoxyphenylcyanamide (5 g.), acetic anhydride (50 ml.), and concentrated sulphuric acid (8 drops) under reflux, and isolating the product as before. Crystallisation from ethanol gave colourless flat needles of *N*-acetylbenzenesulphonanisidide, m. p. 145—146° (85%) (Found: C, 58.8; H, 4.8; N, 4.7; S, 10.2. Calc. for  $C_{15}H_{15}O_4NS$ : C, 59.0; H, 4.9; N, 4.95; S, 10.5%). No depression in m. p. was observed on admixture with a specimen prepared according to Reverdin (*loc. cit.*).

*N-Acetyl-p-toluenesulphon-p-phenetidide*.—This was obtained by the same procedure from toluene-*p*-sulphonyl-*p*-ethoxyphenylcyanamide (31.6 g.), acetic anhydride (320 ml.) and concentrated sulphuric acid (2 ml.). The dark brown crude product gave, on decolorisation and 2 crystallisations from ethanol (350 ml. and 250 ml., respectively), white lustrous plates of *N*-acetyl-*p*-toluenesulphon-*p*-phenetidide (28 g., 84%), m. p. 151—152° (Found: C, 61.1; H, 5.7; N, 4.7. Calc. for  $C_{17}H_{19}O_4NS$ : C, 61.3; H, 5.7; N, 4.2%).

*2-Diphenyllylurea*.—To a cooled solution of 2-aminodiphenyl (42 g., 0.25 mol.) in acetic acid (1 l.; 50% v/v) sodium cyanate (33 g., 0.5 mol.) was added with mechanical stirring during ½ hour. The gradual separation of 2-diphenyllylurea, accompanied by a slow rise in temperature to 35°, was completed by setting the reaction mixture aside overnight. The product, m. p. 158—160° (48 g., 90%), forming white micro-crystalline prisms, was satisfactory for conversion into the sulphonylcyanamides. Recrystallisation from ethanol gave plates, m. p. 160—161°.

*4-Diphenyllylurea*.—A solution of 4-aminodiphenyl (56 g., 0.33 mol.) in acetic acid (800 ml.; 60% v/v) at 60° was treated, with vigorous stirring, in one portion, with a suspension of sodium cyanate (43 g., 0.66 mol.) in water (120 ml.). The product separated immediately as a finely divided precipitate; after a short time, it was filtered off under reduced pressure using a large funnel (12" diameter), washed by successive suspension, at 60°, in dilute hydrochloric acid (1% w/v; 1 l.) and water (1 l.), filtered, and dried (yield: 54 g., 76%). Crystallisation by dissolution in a large volume of acetone (20 ml. per c.c.), treatment with charcoal, and evaporation of the pale yellow filtrate to approx. half its volume gave short, prismatic, minute needles of 4-diphenyllylurea, m. p. 198—200° (determined by insertion into the bath at 200°) (Found: C, 73.4; H, 5.5; N, 13.1. Calc. for  $C_{13}H_{12}ON_2$ : C, 73.6; H, 5.7; N, 13.2%). The reported m. p. [250° (decomp.)] (Van Gelderen, *loc. cit.*) is due to the formation of the symmetrical di-4-diphenyllylurea, which occurs rapidly on heating 4-diphenyllylurea above its m. p. (cf. Kurzer, this vol., p. 2292).

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