# Some Nucleophilic Reactions of Cyanuric Chloride and of Certain 2,4-Dichloro-1,3,5-Triazines with Compounds containing Reactive Hydrogen

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Cyanuric chloride and 2,4-dichloro-1,3,5-triazines react with carbohydrazides, diarylguanidines, phthalimides, arylsulphonamides, and isopropylidene arylsulphonohydrazides in well-defined, stepwise manner as with amines, but with several other types of reactive compound, demarcation of the successive stages of replacement is less clear, and substantially homogeneous products are obtained only in specific instances and under narrow ranges of conditions. Such reactive compounds include alcohols, phenols, aliphatic, aromatic, and heterocyclic thiols, alkyl dithiocarbamates, alkyl xanthates, and alkyl trithiocarbonates. Details are given for preparing new monochloro- and dichloro-triazines bearing a variety of substituent groups linked through nitrogen, oxygen, or sulphur.

THE invention of fibre-reactive dyes based upon cyanuric chloride stimulated interest in the chemistry of chlorinated 1,3,5-triazines, and especially in their capacity to undergo stepwise reactions. It was already known that replacement of one nuclear chlorine atom in cyanuric chloride by an amino- or substituted amino-group so strongly deactivates the remaining two that well-defined, stepwise reactions are easily realised,[1] and also that the deactivating effects of alkoxy- or aryloxy-groups are considerably weaker,[2,3] but little other detailed information was available as to the scope of the stepwise replacement where deactivation is weak.

It has been found that in addition to amino- and substituted amino-groups, aroylhydrazino-, diarylguanidino-, phthalimido-, arylsulphonamido-, and isopropylidene arylsulphonohydrazino-groups also cause powerful deactivation of chlorine atoms in 1,3,5-triazine; in the absence of other substituents, however, deactivation resulting from substituent alkoxy-, aryloxy-,

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[1] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaeffer, and D. Holm-Hansen, *J. Amer. Chem. Soc.*, 1951, **73**, 2981.

[2] J. R. Dudley, J. T. Thurston, F. C. Schaeffer, D. Holm-Hansen, C. J. Hull, and P. Adams, *J. Amer. Chem. Soc.*, 1951, **73**, 2986.

[3] F. C. Schaeffer, J. T. Thurston, and J. R. Dudley, *J. Amer. Chem. Soc.*, 1951, **73**, 2990.

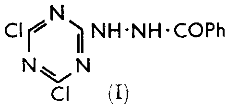
mercapto-, alkylthio-, arylthio-, benzothiazol-2-ylthio-, benzoxazol-2-ylthio-, benzimidazol-2-ylthio-, dialkyldithiocarbamate, *O*-alkylxanthate, and alkyltrithiocarbonate groups is very much weaker, and substantially homogeneous mono-condensation with cyanuric chloride is often much more difficult to achieve. Stepwise replacements involving such groups are more easily realised with selected dichlorotriazines than with cyanuric chloride, but variation of substituents in the reactants, and such factors as solvent solubility, usually affect the proportions of mono-, di-, and tri-condensates formed to a much greater extent than is the case where deactivation is strong. It is not surprising, therefore, that most of the previously known 1,3,5-triazines bearing this type of substituent have been tris-derivatives.

The well-known stepwise reaction between cyanuric chloride and amines is very well-defined, and high yields of aminodichlorotriazines were obtained irrespective of substituents present in the amine. Amino-groups in hydroxy-amines, such as 2-aminoethanol or 4-amino-3-methyl-*N*-ethyl-*N*-(2-hydroxyethyl)aniline, condensed normally, the hydroxyl groups remaining substantially unaffected. Most primary diamines, such as ethylenediamine and *m*- and *p*-phenylenediamine, gave only bis-dichlorotriazinyl derivatives, although in certain instances, such as 4-chloro-1,3-phenylenediamine and 1,3-diaminobenzenesulphondiethylamide, the mono-dichlorotriazinyl derivatives were easily obtained. Aromatic *NN*-dialkyldiamines condensed normally, whilst arylaminodichlorotriazines bearing quaternary salt groups were most readily prepared from cyanuric chloride and amines already bearing such groups. Condensation of cyanuric chloride with 2-cyanoamino-4,6-dimethylpyrimidine proceeded readily to give 2-[*N*-cyano-*N*-(4,6-dichloro-1,3,5-triazin-2-yl)]amino-4,6-dimethylpyrimidine.

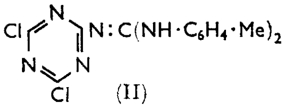
With benzohydrazide, di-*o*-tolylguanidine, and phthalimide, cyanuric chloride gave, respectively, *N*'-(4,6-dichloro-1,3,5-triazin-2-yl)benzohydrazide, (I), *N*''-(4,6-dichloro-1,3,5-triazin-2-yl)-*N*'*N*'''-di-*o*-tolylguanidine, (II), and 2,4-dichloro-6-phthalimido-1,3,5-triazine, (III). Attempts to prepare the monochlorotriazines derived from 2 mol. of benzohydrazide or toluene-*p*-sulphonamide and 1 mol. of cyanuric chloride were unsuccessful, only dichlorotriazines or their hydrolysis products being obtained, and cyanuric chloride failed to react at all with toluene-*p*-sulphonmethylamide. As both the benzohydrazide derivative, (I), and 2,4-dichloro-6-(toluene-*p*-sulphonamido)-1,3,5-triazine,[4] reacted readily with dialkylamines and with phenols, their failure to condense with benzohydrazide and toluene-*p*-sulphonamide, respectively, suggests low reactivity on the part of the latter compounds towards the two dichlorotriazines.

No pure compound was isolated when cyanuric chloride was treated with toluene-*p*-sulphonohydrazide in the absence of acetone, but in its presence, *N*-(4,6-dichloro-1,3,5-triazin-2-yl)-*N*'-isopropylidene toluene-*p*-sulphonohydrazide, (IV), was formed. No doubt this condensation involves the *N*'-isopropylidene derivatives of toluene-*p*-sulphonohydrazide, which is known[5] to be formed very readily from the hydrazide and acetone.

2,4-Dichloro-6-methoxy-1,3,5-triazine was obtained in good yield from cyanuric chloride in benzene with *NN*-dimethylaniline as base and without using a large excess of methanol as previously described,[2] so providing a convenient method for preparing analogues derived from less easily accessible alcohols. Considerable lowering of yield occurred, however, when methanol was replaced by less reactive alcohols such as butanol or 2-chloroethanol; t-butyl alcohol and 2-cyanoethanol gave none of the required products.



(I)



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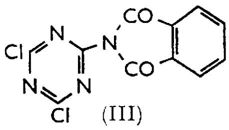

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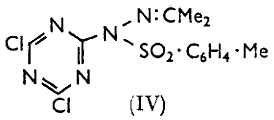
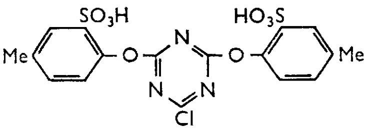


(IV)

Products obtained by condensing cyanuric chloride with phenols or naphthols varied considerably in composition according to the conditions used. Dichlorotriazinyl derivatives of simple, unsulphonated phenols or naphthols were frequently best obtained by working in two-phase chloroform–water mixtures, although substantially pure dichlorotriazines were obtained from β-naphthol and from 1-chloro-2-naphthol under dilute aqueous conditions without an immiscible solvent.

No suitable conditions were discovered for obtaining pure dichlorotriazinyl derivatives of sulphonated phenols and naphthols; there would appear to be little difference in reactivity between cyanuric chloride and the primary products, *viz.*, dichlorotriazines, and, because the latter are water-soluble, any uncondensed phenolsulphonic or naphtholsulphonic acid present would tend to react with them rather than with the insoluble cyanuric chloride. 4-Methylphenol-2-sulphonic acid gave with cyanuric chloride predominantly the monochlorotriazine (V), although a minor proportion of the dichlorotriazine, isolated and identified as the bisdiethylamino-compound (VI), was also formed; from 2-nitrophenol-4-sulphonic acid, only the monochlorotriazine and its derivatives were isolated.



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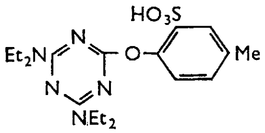

(VI)

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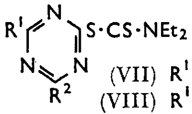
[4] S. Horrobin, *J. Chem. Soc.*, 1963, 4130.

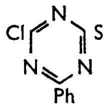
[5] W. Borsche and R. Frank, *Annalen*, 1926, **450**, 81.

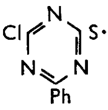
All condensations of cyanuric chloride with compounds containing mercapto-groups were greatly influenced by the nature of substituents present in the thiol; whilst ethanethiol gave only a comparatively poor yield of 2,4-dichloro-6-ethylthio-1,3,5-triazine, ethyl mercaptoacetate yielded, under similar conditions, predominantly the dichlorotriazine,[6] as did also 4-methylthiophenol and thiophenol-3-sulphonic acid. Thiophenol itself, however, and its 4-chloro-, 2,5-dichloro-, 4-chloro-2-methyl-, and 4-hydroxy-derivatives, all gave mixtures containing a preponderance of dichlorotriazine with varying amounts of monochlorotriazine; 4-nitrothiophenol gave almost exclusively monochlorotriazine.

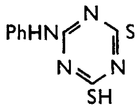
Cyanuric chloride condensed very readily with 3 mol. of 2-mercaptobenzothiazole to form 2,4,6-tris(benzothiazol-2-ylthio)-1,3,5-triazine; even under carefully chosen conditions, the product initially obtained by condensing 1 mol. of mercapto-compound with cyanuric chloride [6] contained some of the monochlorotriazine. Much greater homogeneity of product resulted when cyanuric chloride was replaced by certain 2,4-dichlorotriazines,[6] *e.g.*, the 6-diethylamino and 6-phenyl derivatives, and similar results [6] were also obtained with 2-mercaptobenzoxazole and 2-mercaptobenzimidazole.

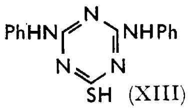
Sodium diethyldithiocarbamate gave with cyanuric chloride, 2,4-dichloro-6-methoxy-1,3,5-triazine, and 2,4-dichloro-6-phenyl-1,3,5-triazine, respectively, predominantly the triazinyl *NN*-diethyldithiocarbamates (VII), (VIII), and (IX),[6] although even under carefully chosen conditions, the crude products were far from homogeneous. No pure products were isolated from condensations of cyanuric chloride with potassium ethylxanthate or potassium ethyl trithiocarbonate, but the latter compounds gave principally the monochlorotriazines (X) and (XI) with 2,4-dichloro-6-phenyl-1,3,5-triazine.[6]


(VII) $R^1 = R^2 = Cl$
(VIII) $R^1 = Cl, R^2 = OMe$
(IX) $R^1 = Cl, R^2 = Ph$


(X)


(XI)


(XII)


(XIII)

Stepwise replacement of chlorine by mercapto-groups was not realised even with dichlorotriazines containing strongly deactivating groups, 2-anilino-4,6-dichloro-1,3,5-triazine, for example, giving with sodium hydrogen sulphide only the dithiol (XII). When the latter was refluxed with aniline, only one of the mercapto-groups was replaced, and the monothiol (XIII) was formed.

## EXPERIMENTAL

Cyanuric chloride was technical material purified by crystallisation from light petroleum (b. p. 100—120°).

Unless otherwise stated, suspensions of cyanuric chloride were prepared by adding solutions in the specified volumes of acetone to stirred mixtures of the specified amounts of water and ice; products isolated from aqueous solutions were washed on the filter with ice-cold water and dried *in vacuo* at room temperature over anhydrous calcium chloride.

*Preparation of* N-(4,6-*Dichloro*-1,3,5-*triazin*-2-*yl*) *Derivatives of Amines*.—A suspension of cyanuric chloride was stirred with an aqueous or acetone solution of the amine or a soluble salt, and aqueous sodium hydroxide or carbonate was added to establish and maintain during 1—2 hr. a pH of 6·5—7·0, at 0—5°. The products were isolated by filtration, washed with ice-cold water, and, where possible, crystallised from organic solvents.

The mono-dichlorotriazinyl derivatives listed in the Table were prepared by using approximately equimolecular amounts of reactants, whilst the bis-derivatives were obtained from 2 mol. of cyanuric chloride and *ca.* 1 mol. of diamine.

Replacement of one or both of the chlorine atoms of aminodichlorotriazines by amino- or aryloxy-groups usually required elevated temperatures, and the following examples were typical:

2-*Anilino*-4-*chloro*-6-*phenoxy*-1,3,5-*triazine*.—Phenol (3·1 g.) in water (80 c.c.) and sodium hydroxide (1·3 g.) was added during 15 min. to 2-anilino-4,6-dichloro-1,3,5-triazine (8·0 g.) in acetone (80 c.c.) with stirring. After 2 hr. at 20° and 15 min. at 50°, the acetone was distilled and the residual solution diluted with water. The *phenoxytriazine*, after being collected and recrystallised from methylcyclohexane, had m. p. 129—130° (Found: C, 60·3; H, 3·6; Cl, 11·4; N, 18·25. $C_{15}H_{11}ClN_4O$ requires C, 60·3; H, 3·7; Cl, 11·9; N, 18·75%). The corresponding (3-*sulphoanilino*)*phenoxytriazine* was obtained in similar manner from 2,4-dichloro-6-(3-sulphoanilino)-1,3,5-triazine and phenol in water at 35—40°, and was recrystallised from water (Found: Cl, 7·7; S, 7·1. $C_{15}H_{10}ClN_4NaO_4S,3H_2O$ requires Cl, 7·8; S, 7·05%).

2-*Anilino*-4,6-*diphenoxy*-1,3,5-*triazine*.—2-Anilino-4,6-dichloro-1,3,5-triazine (4·8 g.) in acetone (30 c.c.) was heated under reflux for 1·5 hr. with phenol (4·0 g.) in 10% aqueous sodium hydroxide (18 c.c.). The solution was diluted with water and the product collected. After recrystallisation from methanol, the *diphenoxytriazine* had m. p. 153—154° (Found: N, 15·6. $C_{21}H_{16}N_4O_2$ requires N, 15·75%).

*Preparation of Alkoxy- and Aryloxy*-1,3,5-*triazines*: 2,4-*Dichloro*-6-*methoxy*-1,3,5-*triazine*.—A mixture of methanol (8·1 c.c.), *NN*-dimethylaniline (24·2 g.), and benzene (50 c.c.) was added dropwise to cyanuric chloride (36·9 g.) in benzene (200 c.c.) at 0·5° during 25 min. After being stirred for 2 hr. at 10—15° and for 30 min. at 30—35°, the mixture was cooled to 5° and shaken with ice-cold water (100 c.c.). The benzene layer was freed from dimethylaniline by extraction with ice-cold 0·1N-hydrochloric acid, washed with water, dried ($MgSO_4$), and evaporated. Recrystallisation of the residue (34 g.), m. p. 72—80°, from light petroleum (b. p. 80—100°) gave the pure compound (26 g.; 72%), m. p. 88—90° (lit.,[2] 88—90°) (Found: Cl, 39·8. Calc. for $C_4H_3Cl_2N_3O$: Cl, 39·4%).

The same procedure was used to prepare 6-β-*chloroethoxy*-2,4-*dichloro*-1,3,5-*triazine* (32%), b. p. 150°/11 mm.

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[6] B.P. 908,352/1962, to Imperial Chemical Industries, Limited.

(Found: C, 26·7; H, 2·0; Cl, 46·0; N, 18·3. $C_5H_4Cl_3N_3O$ requires C, 26·25; H, 1·75; Cl, 46·6; N, 18·4%), and 2-*butoxy*-4,6-*dichloro*-1,3,5-*triazine* (41%), b. p. 146—148°/22 mm. (Found: C, 38·2; H, 4·1; Cl, 32·2. $C_7H_9Cl_2N_3O$ requires C, 37·85; H, 4·05; Cl, 32·0%).

2,4-*Dichloro*-6-(4-*methylphenoxy*)-1,3,5-*triazine*.—A solution of *p*-cresol (21·6 g.) in water (80 c.c.) and sodium hydroxide (8·0 g.) was added during 20 min. to stirred cyanuric chloride (37·2 g.) in chloroform (200 c.c.); the temperature rose to 40°. After 1 hr. at 50°, the chloroform layer was separated, extracted with cold 2N-sodium hydroxide, dried ($MgSO_4$), and evaporated. Distillation of the residue gave an oil (b. p. 234—240°/20 mm.) which solidified when cooled. Recrystallisation from methylcyclohexane gave the pure *compound* (20·4 g.), m. p. 89—90° (Found: Cl, 27·2; N, 15·9. $C_{10}H_7Cl_2N_3O$ requires Cl, 27·7; N, 16·4%).

*N*-(4,6-Dichloro-1,3,5-triazin-2-yl) derivatives of amines

| Amine | Yield (%) | M. p. | Re-cryst. from | Found (%) C | H | Cl | N | Others | Formula | Required (%) C | H | Cl | N | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Mono-derivatives* | | | | | | | | | | | | | | |
| *p*-Amino-*NN*-diethylaniline | 95 | 133—134° | B | 50·5 | 5·1 | 22·6 | 23·0 | | $C_{13}H_{15}Cl_2N_5$ | 50·0 | 4·8 | 22·75 | 22·45 | |
| *p*-Aminophenacyltrimethylammonium chloride | 86 | 245 (dec.) | W | 42·5 | 5·0 | 26·0 | | $Cl^-$ 8·6 | $C_{14}H_{16}Cl_3N_5O + H_2O$ | 42·55 | 4·55 | 27·0 | | $Cl^-$ 9·0 |
| 2-Aminoethanol † | 90 | 116 | A | | | 33·5 | | | $C_5H_6Cl_2N_4O$ | | | 34·0 | | |
| *m*-Aminophenyltrimethylammonium bromide | 75 | (dec.) | W | 39·3 | 4·0 | 21·7 | 18·9 | $Br^-$ 15·8 | $\frac{1}{4}(C_{12}H_{14}Cl_3N_5) + \frac{3}{4}(C_{12}H_{14}BrCl_2N_5)$ | 39·15 | 3·8 | 21·7 | 19·05 | $Br^-$ 16·3 |
| 3-Amino-4′-dimethylaminobenzophenone | 90 | 230 (dec.) | C | | | 17·8 | | | $C_{18}H_{15}Cl_2N_5O$ | | | 18·3 | | |
| 4-Amino-3-methyl-*N*-ethyl-*N*-(2-hydroxyethyl)aniline | 88 | 158—159 | B | | | 20·8 | 20·1 | | $C_{14}H_{17}Cl_2N_5O$ | | | 20·8 | 20·5 | |
| 2-Cyanoamino-4,6-dimethylpyrimidine | 83 | 150 | M | | | 23·5 | 32·6 | | $C_{10}H_7Cl_2N_7$ | | | 24·0 | 33·1 | |
| 4-Chloro-1,3-phenylenediamine | 93 | 120 (dec.) | B | 37·7 | 2·6 | 36·7 | 23·8 | | $C_9H_6Cl_3N_5$ | 37·2 | 2·1 | 36·65 | 24·1 | |
| 2,4-Diaminobenzenesulphondiethylamide * | 98 | >300 | — | | | | 21·3 | S 7·7 | $C_{13}H_{16}Cl_2N_6O_2S$ | | | | 21·5 | S 8·2 |
| *Bis-derivatives* | | | | | | | | | | | | | | |
| Ethylenediamine | >95 | >300 | — | | | 39·8 | | | $C_8H_6Cl_4N_8$ | | | 39·9 | | |
| *m*-Phenylenediamine | >95 | 230—231 (dec.) | B | | | 34·8 | | | $C_{12}H_6Cl_4N_8$ | | | 35·15 | | |
| *p*-Phenylenediamine | >95 | >300 | A | | | 35·0 | | | $C_{12}H_5Cl_4N_6$ | | | 35·15 | | |

A = Acetone, B = benzene, C = chlorobenzene, M = methylcyclohexane, W = water (rapid crystallisation).

* The 1 : 2 condensation product was not obtained even by use of a large excess of cyanuric chloride.

† Acetylation of the dichlorotriazinyl derivative gave the *acetate*, m. p. 111—112° (Found: C, 33·8; H, 3·7; N, 21·8; Cl, 27·8. $C_7H_8Cl_2N_4O_2$ requires C, 33·45; H, 3·2; N, 22·25; Cl, 28·3%), and caused the appearance in the infrared spectrum of a strong band at 5·75μ unaccompanied by any new band at 6·0—6·1μ, consistent with attachment of acetyl through oxygen.

2,4-*Dichloro*-6-β-*naphthyloxy*-1,3,5-*triazine*.— β-Naphthol (28·8 g.) in water (2 l.) and sodium hydroxide (8·0 g.) was added to a stirred suspension of cyanuric chloride (37·2 g.) in water (2 l.) at 0—5° during 2 hr. After a further 2 hr., the product (51·6 g.), m. p. 148—154°, was collected and dried. Recrystallisation from light petroleum (b. p. 80—100°) or methylcyclohexane gave the pure *compound*, m. p. 156—157° (Found: C, 53·4; H, 2·6; Cl, 24·2; N, 14·7. $C_{13}H_7Cl_2N_3O$ requires C, 53·4; H, 2·4; Cl, 24·3; N, 14·4%).

By increasing the concentration of the foregoing condensation twentyfold, a mixture of m. p. 120—140° was obtained. Recrystallisation from benzene gave 2-*chloro*-4,6-*di*-β-*naphthyloxy*-1,3,5-*triazine* (27%), m. p. 180—181° (Found: C, 69·4; H, 3·6; Cl, 8·6; N, 11·0. $C_{23}H_{14}ClN_3O_2$ requires C, 69·1; H, 3·5; Cl, 8·9; N, 10·5%).

2-(1-*Chloro*-2-*naphthyloxy*)-4,6-*dichloro*-1,3,5-*triazine*.—Cyanuric chloride (9·3 g.) was condensed with 1-chloro-2-naphthol (8·93 g.) in water (1 l.) and sodium hydroxide (2·0 g.) at 0—5°. After recrystallisation from benzene, the *compound* had m. p. 172° (Found: Cl, 32·0; hydrolysable Cl, 22·0. $C_{13}H_6Cl_3N_3O$ requires Cl, 32·6; hydrolysable Cl, 21·75%).

*Condensations of Cyanuric Chloride with Phenolsulphonic Acids*.—(*a*) 4-*Methylphenol*-2-*sulphonic acid*. To a stirred solution of 4-methylphenol-2-sulphonic acid (0·2 g. mol.; monopotassium salt) in water (800 c.c.), there was added ice (200 g.) and cyanuric chloride (18·6 g.) in acetone (100 c.c.). The mixture was treated at 0—5° during 2 hr. with potassium hydroxide (11·2 g.) in water (1 l.) and stirred for 1 hr. at 10—15° and 1 hr. at 25°, after which the resulting clear solution was divided into two equal parts.

One part of the solution was stirred with a large excess of diethylamine for 2 hr. at 25° and for 4 hr. at 95°, after which it was evaporated to dryness. The residue was boiled with acetone and the extract removed from the solid, which was recrystallised from ethyl acetate, giving a small amount of 2,4-*bisdiethylamino*-6-(4-*methyl*-2-*sulphophenoxy*)-1,3,5-*triazine* (Found: C, 53·3; H, 7·0; N, 16·8. $C_{18}H_{27}N_5O_4S$ requires C, 52·8; H, 6·6; N, 17·1%).

The remainder of the aqueous solution was stirred with potassium chloride (200 g.) and the product (18·6 g.) was collected and dried, giving the *dipotassium salt* of 2-*chloro*-4,6-*bis*-(4-*methyl*-2-*sulphophenoxy*)-1,3,5-*triazine* containing ~8% of potassium chloride (Found: Hydrolysable Cl, 5·8. $C_{17}H_{12}ClK_2N_3O_8S_2$ requires Cl, 6·3%).

When heated under reflux with an excess of aqueous diethylamine, the foregoing product gave the *dipotassium salt* of 2-*diethylamino*-4,6-*bis*-(4-*methyl*-2-*sulphophenoxy*)-1,3,5-*triazine* (Found: C, 38·5; H, 4·8; K, 11·7; N, 9·1; S, 9·6. $C_{21}H_{22}K_2N_4O_8S_2,3H_2O$ requires C, 38·55; H, 4·3; K, 11·9; N, 8·55; S, 9·8%); the corresponding 2-*anilino-derivative*, formed with aniline under similar conditions, was isolated as the *barium salt* (Found: C, 39·5; H, 3·1; Ba, 19·85; N, 7·9. $C_{23}H_{18}BaN_4O_8S_2,H_2O$ requires C, 39·6; H, 2·85; Ba, 19·7; N, 8·05%).

(*b*) 2-*Nitrophenol*-4-*sulphonic acid*. Attempts to isolate the dichlorotriazine were unsuccessful. The *disodium salt* of 2-*chloro*-4,6-*bis*-(2-*nitro*-4-*sulphophenoxy*)-1,3,5-*triazine* was obtained by dropwise addition of cyanuric chloride (9·3 g.) in acetone (50 c.c.) to stirred 2-nitrophenol-4-sulphonic acid (0·1 g. mol.; sodium salt) in water (40 c.c.) and ice (100 g.), and subsequent treatment during 2 hr. at 0—5° with sodium hydroxide (4·0 g.) in water (500 c.c.). The product was isolated by addition of sodium chloride, and purified by crystallisation from water (Found: C, 28·9; H, 1·8; Cl, 5·7; Na, 6·8; S, 9·7. $C_{15}H_6ClN_5Na_2O_{12}S_2,2H_2O$ requires C, 28·6; H, 1·6; Cl, 5·65; Na, 7·3; S, 10·15%). Treatment of this compound with boiling aqueous diethylamine gave the corresponding 2-*diethylamino-derivative* (Found: C, 34·9; H, 2·4; N, 12·3; S, 9·5. $C_{19}H_{16}N_6Na_2O_{12}S_2,H_2O$ requires C, 35·2; H, 2·8; N, 12·9; S, 9·9%).

When the foregoing diethylamino-derivative (3·2 g.) was heated under reflux with *p*-chlorophenol (2·0 g.) and N-sodium hydroxide (15·3 c.c.) in water for 1 hr., ready formation of 2,4-*di*-p-*chlorophenoxy*-6-*diethylamino*-1,3,5-*triazine* (1·2 g.) occurred, m. p. 144—145° after recrystallisation from cyclohexane (Found: C, 56·6; H, 4·7; Cl, 17·3; N, 13·3. $C_{19}H_{18}Cl_2N_4O_2$ requires C, 56·3; H, 4·45; Cl, 17·55; N, 13·8%).

*Condensation of Cyanuric Chloride with Benzohydrazide*.—Cyanuric chloride (9·3 g.) in acetone (50 c.c.) was added dropwise to a stirred mixture of benzohydrazide (6·8 g.), water (400 c.c.), and ice (100 g.). Sodium hydroxide (2·0 g.) in water (500 c.c.) was added portionwise to the mixture at 0—5° during 2 hr. After a further 2 hr. the product (12·6 g.) was collected and dried. Recrystallised from chlorobenzene or dioxan, N′-(4,6-*dichloro*-1,3,5-*triazin*-2-*yl*)-*benzohydrazide* had m. p. 198° (decomp.) (Found: C, 42·6; H, 2·7; Cl, 25·4; N, 25·0. $C_{10}H_7Cl_2N_5O$ requires C, 42·25; H, 2·45; Cl, 25·0; N, 24·65%).

Although the foregoing compound reacted with diethylamine in boiling acetone to form N′-(4-*chloro*-6-*diethylamino*-1,3,5-*triazin*-2-*yl*)*benzohydrazide*, m. p. 216° (from acetone) (Found: Cl, 10·8; N, 26·7. $C_{14}H_{17}ClN_6O$ requires Cl, 11·1; N, 26·2%), and with sodium *p*-chlorophenoxide in aqueous acetone at 50° to give N′-(4-*chloro*-6-*p*-*chlorophenoxy*-1,3,5-*triazin*-2-*yl*)*benzohydrazide*, m. p. 172° (decomp.) after crystallisation from benzene (Found: C, 51·5; H, 3·3; Cl, 19·4; N, 18·8. $C_{16}H_{11}Cl_2N_5O_2$ requires C, 51·05; H, 2·95; Cl, 18·9; N, 18·6%), attempts to condense it with a further molecule of benzohydrazide proved abortive.

In similar manner, although 2,4-dichloro-6-(toluene-*p*-sulphonamido)-1,3,5-triazine [4] reacted with diethylamine in boiling acetone to give 2-*chloro*-4-*diethylamino*-6-(*toluene*-p-*sulphonamido*)-1,3,5-*triazine*, m. p. 174—175° after recrystallisation from methylcyclohexane (Found: C, 47·4; H, 5·2; Cl, 10·5; N, 19·2; S, 9·1. $C_{14}H_{18}ClN_5O_2S$ requires C, 47·25; H, 5·05; Cl, 10·0; N, 19·7; S, 9·0%), and with sodium *p*-chlorophenoxide in acetone at 50° to give 2-*chloro*-4-p-*chlorophenoxy*-6-(*toluene*-p-*sulphonamido*)-1,3,5-*triazine*, m. p. 146—147° (Found: Cl, 17·6; N, 13·9. $C_{16}H_{12}Cl_2N_4O_3S$ requires Cl, 17·3; N, 13·6%), attempts to condense it with a further molecule of toluene-*p*-sulphonamide under slightly alkaline aqueous conditions did not give the 1 : 2 condensation product but only 2,4-*dihydroxy*-6-(*toluene*-p-*sulphonamido*)-1,3,5-*triazine*, m. p. 256° after crystallisation from acetone–chloroform (Found: C, 42·5; H, 3·8; N, 19·4; S. 10·8. $C_{10}H_{10}N_4O_4S$ requires C, 42·55; H, 3·55; N, 19·85; S, 11·3%).

All attempts to condense cyanuric chloride with *N*-methyltoluene-*p*-sulphonamide under slightly alkaline aqueous conditions were unsuccessful.

*Condensation of Cyanuric Chloride with Phthalimide*.—Cyanuric chloride (37·4 g.) in acetone (400 c.c.) was stirred with potassium phthalimide (37·4 g.) for 10 hr. at 0—5° and for a further 10 hr. at 20—25°. The product was collected, washed with cold acetone (50—100 c.c.), stirred with ice-cold water (500 c.c.), re-collected, dried, and continuously extracted with boiling acetone. Evaporation of the extract and crystallisation of the residue from benzene gave 2,4-*dichloro*-6-*phthalimido*-1,3,5-*triazine* (14·1 g.), m. p. 180—181° (Found: C, 45·2; H, 1·7; Cl, 23·5; N, 19·1. $C_{11}H_4Cl_2N_4O_2$ requires C, 44·75; H, 1·35; Cl, 24·0; N, 19·0%).

The foregoing compound reacted vigorously with an excess of diethylamine to form 2,4-*bisdiethylamino*-6-*phthalimido*-1,3,5-*triazine*, m. p. 169—170° after crystallisation from ethanol (Found: C, 62·2; H, 6·6; N, 22·4. $C_{19}H_{24}N_6O_2$ requires C, 61·95; H, 6·5; N, 22·85%).

*Condensation of Cyanuric Chloride with Di*-o-*tolylguanidine*.—Cyanuric chloride (9·3 g.) suspended in ice-cold water (50 c.c.) and acetone (50 c.c.) was stirred with di-*o*-tolylguanidine (11·96 g.) in 2N-hydrochloric acid (25 c.c.), and the mixture was treated at 0—5° during 30 min. with sodium hydroxide (4·0 g.) in water (100 c.c.). After a further 1 hr., N″-(4,6-*dichloro*-1,3,5-*triazin*-2-*yl*)-N′N‴-*di*-o-*tolylguanidine* (16·5 g.) was collected and dried (Found: Cl, 18·9. $C_{18}H_{16}Cl_2N_6$ requires Cl, 18·4%).

*Condensation of Cyanuric Chloride with Toluene*-p-*sulphonohydrazide*.—By using conditions similar to those previously described [4] for condensing cyanuric chloride with toluene-*p*-sulphonamide, the hydrazide (9·3 g.) gave N-(4,6-*dichloro*-1,3,5-*triazin*-2-*yl*)-N′-*isopropylidene*-p-*methylbenzenesulphonohydrazide* (9·9 g.), m. p. 184—185° (decomp.) after recrystallisation from benzene (Found: Cl, 19·0; N, 18·9; S, 8·2. $C_{13}H_{13}Cl_2N_5O_2S$ requires Cl, 19·0; N, 18·7; S, 8·55%). When the acetone used in making the suspension of cyanuric chloride was replaced by dioxan, no well-defined product other than cyanuric acid was isolated.

The foregoing compound reacted with diethylamine in boiling acetone to form N-(4-*chloro*-6-*diethylamino*-1,3,5-*triazin*-2-*yl*)-N′-*isopropylidene*-p-*methylbenzenesulphonohydrazide*, m. p. 118—119° after recrystallisation from methylcyclohexane (Found: C, 50·2; H, 5·7; Cl, 8·4. $C_{17}H_{23}ClN_6O_2S$ requires C, 49·7; H, 5·6; Cl, 8·65%).

*Preparation of* 1,3,5-*Triazines containing Thio Links*: [6] 2,4-*Dichloro*-6-*ethylthio*-1,3,5-*triazine*.—A stirred suspension of cyanuric chloride (36·9 g.) in water (120 c.c.) was treated at 0—5° with ethanethiol (14·8 c.c.) and sodium hydrogen carbonate (16·8 g.) in water (100 c.c.) was added during 30 min. to maintain neutral conditions. After 1 hr. at 10—15°, 1 hr. at 20—25°, and 30 min. at 40°, the mixture was cooled and the oily product was extracted with ether. The ether solution was dried ($MgSO_4$) and distilled; the fraction (9·2 g.) of b. p. 140—160°/17 mm. was redistilled to give the *ethylthio-compound*, b. p. 145°/17 mm. (Found: C, 29·1; H, 2·7; Cl, 32·8; N, 20·1; S, 15·8. $C_5H_5Cl_2N_3S$ requires C, 28·6; H, 2·4; Cl, 33·8; N, 20·0; S, 15·25%).

2-*Anilino*-1,3,5-*triazine*-4,6-*dithiol*.—N-Hydrochloric acid (100 c.c.) was added dropwise to stirred sodium sulphide (24 g.; nonahydrate) in water (100 c.c.) at a temperature of below 12°. To this solution, there was added 2-anilino-4,6-dichloro-1,3,5-triazine (6 g.) in acetone (25 c.c.) and the mixture was stirred at 25° for 2 hr. and then filtered. The filtrate was acidified with hydrochloric acid, and the *compound* (5·2 g.), m. p. 255° (decomp.), was collected and dried (Found: S, 26·6. $C_9H_8N_4S_2$ requires S, 27·1%).

Rapid evolution of hydrogen sulphide occurred when the foregoing compound (1·5 g.) was heated under reflux with aniline (30 c.c.) for 1 hr. The product was isolated by filtration, boiled with benzene, re-collected, and dried, giving 2,4-dianilino-1,3,5-triazine-6-thiol.[7] (Found: C, 61·2; H, 4·4; N, 23·8; S, 10·6. Calc. for $C_{15}H_{13}N_5S$: C, 61·0; H, 4·4; N, 23·75; S, 10·85%).

2,4-*Dichloro*-6-(*ethoxycarbonylmethylthio*)-1,3,5-*triazine*.—Ethyl mercaptoacetate (12 g.) and a solution of sodium hydrogen carbonate (8·5 g.) in water (100 c.c.) were added simultaneously to a stirred suspension of cyanuric chloride (18·5 g.) in water (130 c.c.) at 0—5°. The temperature of the mixture was gradually raised to 25° during 2·5 hr., and the product was extracted with ether. The ether solution was dried ($MgSO_4$) and distilled, giving the *compound*, b. p. 140—145°/0·2 mm., which formed crystals, m. p. 52—53°, on being cooled (Found: C, 31·3; H, 2·4; Cl, 26·3; N, 15·7; S, 11·7. $C_7H_7Cl_2N_3O_2S$ requires C, 31·35; H, 2·6; Cl, 26·5; N, 15·65; S, 11·95%).

2,4-*Dichloro*-6-(4-*methylphenylthio*)-1,3,5-*triazine*.— Dropwise addition of thio-*p*-cresol (6·2 g.) in water (500 c.c.) and sodium hydroxide (2·0 g.) to a stirred suspension of cyanuric chloride (9·3 g.) in water (500 c.c.) and acetone (40 c.c.) at 0—5° during 2 hr. gave 2,4-*dichloro*-6-(4-*methylphenylthio*)-1,3,5-*triazine* (10·9 g.), m. p. 103—108°, raised to 112—113° by crystallisation from light petroleum (b. p. 80—100°) (Found: C, 44·4; H, 2·7; Cl, 26·0; N, 15·8; S, 11·6. $C_{10}H_7Cl_2N_3S$ requires C, 44·1; H, 2·55; Cl, 26·1; N, 15·45; S, 11·75%).

Similar condensations of cyanuric chloride with thiophenol ,4-chlorothiophenol, 2,5-dichlorothiophenol, 4-chloro-2-methylthiophenol, and 4-hydroxythiophenol, gave mixtures, analysis of which indicated a preponderance of dichlorotriazine in each instance; the dichlorotriazines were not obtained pure by repeated recrystallisation of these mixtures.

2-*Chloro*-4,6-*bis*-(4-*nitrophenylthio*)-1,3,5-*triazine*.—4-Nitrothiophenol (8·9 g.; sodium salt) in water (500 c.c.) was added dropwise to a stirred suspension of cyanuric chloride (9·3 g.) in acetone (50 c.c.), water (400 c.c.), and ice (100 g.) at 0—5° during 2 hr. After a further 2 hr. at 0—5°, the product was collected and dried. Recrystallised from toluene, the *compound* had m. p. 213—214° (Found: Cl, 8·7; N, 16·6. $C_{15}H_8ClN_5O_4S_2$ requires Cl, 8·5; N, 16·6%).

*Condensation of Cyanuric Chloride with Thiophenol*-3-*Sulphonic Acid*.—Cyanuric chloride (9·3 g.) suspended in water (500 c.c.) and acetone (50 c.c.) was condensed at 0—5° with thiophenol-3-sulphonic acid (0·05 g. mol.; sodium salt) in water (500 c.c.) under neutral conditions, after which the solution was heated at 95—100° for 4 hr. with diethylamine (25 c.c.). The solution was evaporated to dryness and the residue was extracted with acetone. The extract was evaporated, the residual oil was dissolved in an equal volume of water, and the solution was strongly acidified with concentrated hydrochloric acid and cooled in ice. The product was collected, dissolved in dilute aqueous sodium hydroxide, and excess of diethylamine was removed with steam. Acidification of the solution gave 2,4-*bisdiethylamino*-6-(3-*sulphophenylthio*)-1,3,5-*triazine* (7·2 g.), which was purified by crystallisation from water (Found: C, 47·2; H, 6·4; N, 16·5; S, 14·6. $C_{17}H_{25}N_5O_3S_2,H_2O$ requires C, 47·55; H, 6·3; N, 16·3; S, 14·9%).

4,6-*Dichloro*-1,3,5-*triazin*-2-*yl* NN-*Diethyldithiocarbamate*.—Cyanuric chloride (9·3 g.) in acetone (100 c.c.) was stirred at −15° during the addition of sodium diethyldithiocarbamate (8·6 g.) in acetone (100 c.c.) over 20 min. After a further 10 min. at −10°, the mixture was diluted with ice-cold water (800 c.c.) and the product (11·5 g.) was collected and dried. Recrystallised from light petroleum (b. p. 60—80°, the *compound* had m. p. 69—70° (Found: Cl, 24·3; N, 19·4; S, 22·1. $C_8H_{10}Cl_2N_4S_2$ requires Cl, 23·9; N, 18·9; S, 21·6%).

4-*Chloro*-6-*methoxy*-1,3,5-*triazin*-2-*yl* NN-*Diethyldithiocarbamate*.—A stirred suspension of 2,4-dichloro-6-methoxy-1,3,5-triazine (45 g.) in acetone (250 c.c.) and water (2 l.) at 20° was treated with sodium diethyldithiocarbamate (42 g.) in water (1 l.) during 15 min. After 1 hr. at 25°, the product (62 g.) was collected and dried. Twice recrystallised from light petroleum (b. p. 60—80°), the *compound* (27 g.) had m. p. 78—79° (Found: Cl, 12·6. $C_9H_{13}ClN_4OS_2$ requires Cl, 12·15%).

4-*Chloro*-6-*phenyl*-1,3,5-*triazin*-2-*yl* NN-*Diethyldithiocarbamate*.—2,4-Dichloro-6-phenyl-1,3,5-triazine (5·6 g.) suspended in acetone (30 c.c.) and water (200 c.c.) at 15° was treated with sodium diethyldithiocarbamate (4·2 g.) in water (100 c.c.) during 1 hr. After a further 1 hr. at 15°, the product was collected and dried. Twice recrystallised from light petroleum (b. p. 60—80°), the *compound* (7·5 g.) had m. p. 67—68° (Found: C, 49·6; H, 4·7; Cl, 11·0; N, 16·6; S, 18·5. $C_{14}H_{15}ClN_4S_2$ requires C, 49·6; H, 4·45; Cl, 10·5; N, 16·55; S, 18·9%).

S-(4-*Chloro*-6-*phenyl*-1,3,5-*triazin*-2-*yl*) O-*Ethylxanthate*.—2,4-Dichloro-6-phenyl-1,3,5-triazine (5·5 g.) suspended in acetone (30 c.c.) and water (200 c.c.) was treated at 20° during 1 hr. with potassium ethylxanthate (4·0 g.) in water (50 c.c.). The solution was brought to pH 8·0 by addition of 2N-sodium hydroxide and stirred at 30—35° for a further 3 hr., after which the pH was 7·4. The product (8 g.) was collected, dried and recrystallised from ethanol, after which the *compound* had m. p. 63—64° (Found: C, 46·6; H, 3·4; Cl, 11·9. $C_{12}H_{10}ClN_3OS_2$ requires C, 46·25; H, 3·2; Cl, 11·4%).

4-*Chloro*-6-*phenyl*-1,3,5-*triazin*-2-*yl Ethyl Trithiocarbonate*.—2,4-Dichloro-6-phenyl-1,3,5-triazine (2·75 g.) in acetone (50 c.c.) was heated under reflux with potassium ethyl trithiocarbonate (2·2 g.) for 4 hr. The solution was filtered and the filtrate was evaporated to dryness. Recrystallised from ethanol, the *compound* (2·4 g.) had m. p. 94—95° (Found: C, 44·2; H, 3·2; Cl, 10·4; N, 12·3; S, 29·5.

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[7] C. Grundmann and A. Kreutzberger, *J. Amer. Chem. Soc.*, 1955, **77**, 44.

$C_{12}H_{10}ClN_3S_3$ requires C, 44·0; H, 3·05; Cl, 10·85; N, 12·8; S, 29·3%).

*Condensation of Cyanuric Chloride with* 2-*Mercaptobenzothiazole*.—(*a*) Cyanuric chloride (9·3 g.) suspended in acetone (50 c.c.), water (500 c.c.), and ice (100 g.), and treated at 0—5° during 2 hr. with 2-mercaptobenzothiazole (8·4 g.) in sodium hydroxide (2·0 g.) and water (500 c.c.), gave 2,4,6-*tris*(*benzothiazol*-2-*ylthio*)-1,3,5-*triazine*, m. p. (from toluene) 209—210° (Found: N, 14·4. $C_{24}H_{12}N_6S_6$ requires N, 14·6%).

(*b*) Cyanuric chloride (18·5 g.) in acetone (150 c.c.) was treated with 2-mercaptobenzothiazole (16·7 g.) and *NN*-dimethylaniline (14 c.c.) in acetone (100 c.c.) at −25°. After being stirred for 1 hr. at −10°, the solution was diluted with ice-cold water (500 c.c.) and the product (23·5 g.) was collected and dried; it had m. p. 136—142°, and consisted predominantly of dichlorotriazine mixed with some monochlorotriazine. Recrystallisation from methylcyclohexane raised the m. p. to 140—142°, giving a product which was still somewhat low in nitrogen for the pure dichloro-compound (Found: N, 17·0. $C_{10}H_4Cl_2N_4S_2$ requires N, 17·8%).

2-(*Benzothiazol*-2-*ylthio*)-4-*chloro*-6-*methoxy*-1,3,5-*triazine*.—A stirred suspension of 2,4-dichloro-6-methoxy-1,3,5-triazine (45 g.) in acetone (200 c.c.) and water (2 l.) was treated gradually at 10 ± 3° during 45 min. with 2-mercaptobenzothiazole (42 g.) in water (1 l.) and sodium hydroxide (10 g.). After a further 5 min. the product (48·6 g.) was collected, dried, and crystallised from methylcyclohexane to give the *compound*, m. p. 144° (Found: Cl, 11·5. $C_{11}H_7ClN_4OS_2$ requires Cl, 11·45%).

2-(*Benzothiazol*-2-*ylthio*)-4-*chloro*-6-*phenyl*-1,3,5-*triazine*.—A stirred suspension of 2,4-dichloro-6-phenyl-1,3,5-triazine (5·6 g.) in acetone (30 c.c.) and water (200 c.c.) was treated gradually at 10° during 1 hr. with 2-mercaptobenzothiazole (4·2 g.) in water (100 c.c.) and sodium hydroxide (1·0 g.). After a further 1·5 hr. at 20°, the product was collected, dried, and recrystallised from methylcyclohexane, when the *compound* had m. p. 138° ± 0·5° (Found: Cl, 10·0; S, 18·2. $C_{16}H_9ClN_4S_2$ requires Cl, 9·95; S, 17·95%).

2-(*Benzothiazol*-2-*ylthio*)-4-*chloro*-6-o-*chloroanilino*-1,3,5-*triazine*.—A suspension of 2,4-dichloro-6-*o*-chloroanilino-1,3,5-triazine (6·9 g.) in acetone (30 c.c.) and water (100 c.c.) was treated gradually with 2-mercaptobenzothiazole (4·2 g.) in water (50 c.c.) and sodium hydroxide (1·0 g.) during 3 hr. at 45—50° and at pH <8. After a further 1 hr. at 50—55°, the *compound* was collected, dried, and recrystallised from benzene; m. p. 196° (Found: C, 47·8; H, 2·3; Cl, 17·9; N, 16·9; S, 15·4. $C_{16}H_9Cl_2N_5S_2$ requires C, 47·3; H, 2·2; Cl, 17·5; N, 17·25; S, 15·75%).

2-(*Benzothiazol*-2-*ylthio*)-4-*chloro*-6-*diethylamino*-1,3,5-*triazine*.—A suspension of 2,4-dichloro-6-diethylamino-1,3,5-triazine (5·5 g.) in acetone (30 c.c.) and water (200 c.c.) was treated with 2-mercaptobenzothiazole (4·2 g.) in water (60 c.c.) and sodium hydroxide (1·0 g.) at 50—60° for 10 hr., and the product (5·7 g.) was recrystallised from benzene to give the *compound*, m. p. 164° (Found: N, 19·7; S, 18·4. $C_{14}H_{14}ClN_5S_2$ requires N, 19·9; S, 18·2%).

2-(*Benzothiazol*-2-*ylthio*)-4-*chloro*-m-*sulphoanilino*-1,3,5-*triazine*.—A suspension of cyanuric chloride (18·5 g.) in acetone (120 c.c.), water (300 c.c.), and ice (300 g.) was treated with a neutral solution of metanilic acid (20 g.) in water (300 c.c.) and sodium hydroxide during 25 min., and 2N-sodium carbonate was added portionwise during 15 min. to maintain a pH of 6·5—7·0. To this solution at 0—5° was added during 30 min., 2-mercaptobenzothiazole (16·7 g.) in water (400 c.c.) and sodium hydroxide (4·0 g.). The solution was stirred for 1 hr. at 30° and for a further 1 hr. at 40°, after which it was treated with sodium chloride (1 g./10 c.c.) and the product (46·5 g.) collected. The *compound* was purified by crystallisation from water (Found: Cl, 7·0; S, 19·5; Na, 4·9. $C_{16}H_9ClN_5NaO_3S_3,H_2O$ requires Cl, 7·25; S, 19·55; Na, 4·7%).

2-(*Benzoxazol*-2-*ylthio*)-4-*chloro*-6-*phenyl*-1,3,5-*triazine*.—A suspension of 2,4-dichloro-6-phenyl-1,3,5-triazine (5·6 g.) in acetone (30 c.c.) and water (200 c.c.) was treated with 2-mercaptobenzoxazole (3·3 g.) in water (100 c.c.) and sodium hydroxide (1·0 g.) during 2 hr. at 15—20° and the solution was stirred for a further 2 hr. at 20°. The product (7·4 g.) was recrystallised from methylcyclohexane, after which the *compound* had m. p. 157° (Found: Cl, 10·9; N, 15·9; S, 9·9. $C_{16}H_9ClN_4OS$ requires Cl, 10·4; N, 16·4; S, 9·4%).

2-(*Benzimidazol*-2-*ylthio*)-4-*chloro*-6-*diethylamino*-1,3,5-*triazine*.—A suspension of 2,4-dichloro-6-diethylamino-1,3,5-triazine (11·06 g.) in acetone (40 c.c.) and water (400 c.c.) was stirred with 2-mercaptobenzimidazole (7·5 g.) in water (100 c.c.), acetone (20 c.c.), and sodium hydroxide (2 g.) for 12 hr. at 50—60°. The product (14·6 g.), m. p. 151—154° was collected and recrystallised from benzene, after which the *compound* (9·8 g.) had m. p. 155—156° (Found: C, 50·3; H, 4·8; S, 10·0. $C_{14}H_{15}ClN_6S$ requires C, 50·25; H, 4·5; S, 9·6%).

2-(*Benzimidazol*-2-*ylthio*)-4-*chloro*-6-*phenyl*-1,3,5-*triazine*.—A suspension of 2,4-dichloro-6-phenyl-1,3,5-triazine (11·2 g.) in acetone (50 c.c.) and water (500 c.c.) was treated with 2-mercaptobenzimidazole (7·6 g.) in water (100 c.c.), acetone (40 c.c.), and sodium hydroxide (2·0 g.) during 2 hr. at 20°, and for a further 30 min. at 20—25°. After recrystallisation from benzene, the *compound* (14 g.) had m. p. 175° (decomp.) (Found: Cl, 11·0; S, 9·3. $C_{16}H_{10}ClN_5S$ requires Cl, 10·5; S, 9·4%).

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