The *N*→*O* and *N*→*S* Migrations of the *s*-Triazinyl Groups of *N*,*N*-Di-*s*-triazinyl Derivatives of *o*-Aminophenol and *o*-Aminothiophenol

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N,*N*-Bis(dichloro-*s*-triazinyl)-2-aminophenol reacted with an excess of dimethylamine or methylamine to give *N*,*O*-bis(*s*-triazinyl)-2-aminophenol and *N*-*s*-triazinyl-2-aminophenol upon the aminodechlorination, *N*→*O* migration, and cleavage of the *s*-triazinyl group. However, *N*-(dimethoxy-*s*-triazinyl)-*N*-(dichloro-*s*-triazinyl)-2-aminothiophenol reacted with an excess of dimethylamine to give merely a disulfide of *N*-*s*-triazinyl-2-aminothiophenol upon the aminodechlorination and cleavage of the dimethoxy-*s*-triazine nucleus. On the other hand, *N*,*N*-bis(*s*-triazinyl)-arylamines containing no *ortho*-OH or -SH group were stable to the attack by amines, while phenoxy-dimethoxy-*s*-triazine or phenylthio-dimethoxy-*s*-triazine reacted readily with dimethylamine to give dimethylamino-dimethoxy-*s*-triazine upon the fission of phenol or thiophenol. From these resutls, the reactions of the *N*,*N*-bis(*s*-triazinyl) derivatives of both *o*-aminophenol and *o*-aminothiophenol with amines to give the corresponding *N*-*s*-triazinyl derivatives are considered to proceed by means of an intramolecular nucleophilic attack by the phenoxide or thiophenoxide anion on the *s*-triazine ring carbon to give the *N*,*O*- or *N*,*S*-bis(*s*-triazinyl) derivative upon the *N*→*O* or *N*→*S* migration of the *s*-triazinyl group, followed by the cleavage of the *O*- or *S*-*s*-triazinyl group to give the final product. However, when the intermediary derivative is stable to amine, the intermediate is obtained as the major final product.

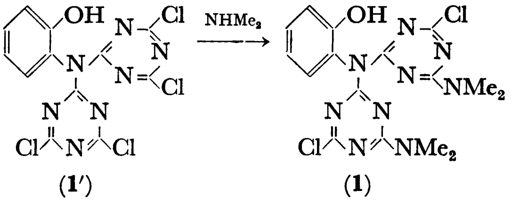
In previous papers we reported that *O*-*s*-triazinyl-2-aminophenols and *S*-*s*-triazinyl-2-aminothiophenols rearrange to give the corresponding *N*-*s*-triazinyl derivatives in protic solvents, especially readily in the presence of acid[1] or photochemically,[2] and that *O*-(dimethoxy-*s*-triazinyl)-2-aminophenol and *S*-(dimethoxy-*s*-triazinyl)-2-aminothiophenol give *N*-(acyl)-*N*-(*s*-triazinyl)- or *N*,*N*-bis(*s*-triazinyl) derivatives upon the *O*→*N* or *S*→*N* migration of the *s*-triazinyl group on acylation or *s*-triazinylation.[3] In addition, the *O*-*s*-triazinyl groups of *N*-(dichloro-*s*-triazinyl)-*O*-(*s*-triazinyl)-2-aminophenols migrate to give *N*,*N*-bis(*s*-triazinyl)-2-aminophenols on the methoxydechlorination[3] of the active chlorine atoms in the *N*-*s*-triazine nucleus.

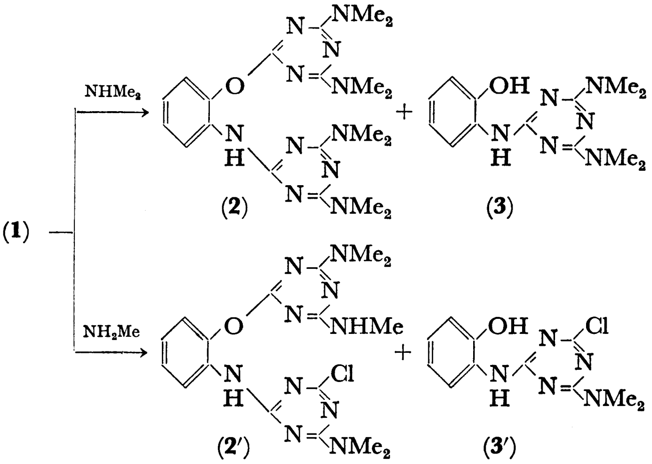
In these ways, in the ordinary Smiles rearrangements of *s*-triazinyl derivatives of *o*-aminophenol and *o*-aminothiophenol, the *s*-triazinyl group migrates from the oxygen or sulfur atom to the amino nitrogen atom, as in the rearrangements of nitrophenyl derivatives of *o*-aminophenol.[4] However, on the contrary, we have found that some *N*,*N*-bis(*s*-triazinyl) derivatives of *o*-aminophenol and *o*-aminothiophenol rearrange to give *N*,*O*-bis(*s*-triazinyl)- or *N*,*S*-bis(*s*-triazinyl) derivatives or/and their cleaved products upon treatment with amines.

This paper will report on reverse Smiles rearrangements involving the *N*→*O* and *N*→*S* migrations of aromatic systems with *N*,*N*-bis(*s*-triazinyl) derivatives of *o*-aminophenol and *o*-aminothiophenol, in which rearrangements the *s*-triazinyl group migrates as an aromatic system.

Results and Discussion

N→O *Migration of the* s-*Triazinyl Group of* N,N-*Bis(*s-*triazinyl)-2-aminophenols in the Reaction with Amines.* In the reaction of *N*,*N*-bis(dichloro-*s*-triazinyl)-2-amino phenol (**1′**)[5] with dimethylamine in a molar ratio of 1:4, two chlorine atoms were replaced to give *N*,*N*-bis(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-2-aminophenol (**1**). However, when (**1′**) was treated with





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[1] a) T. Harayama, K. Okada, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 981 (1970); b) N. Maeno, T. Itagaki, S. Uno, and K. Matsui, This Bulletin, **45**, 3133 (1972); c) T. Shiojima, Y. Hashida, and K. Matsui, *ibid.*, in press.

[2] K. Matsui, N. Maeno, H. Shizuka, and T. Morita, *Tetrahedron Lett.*, **1970**, 1467; H. Shizuka, N. Maeno, and K. Matsui, *Mol. Photochem.*, **4**, 335 (1972).

[3] T. Shiojima, T. Kuroda, S. Ohkawa, Y. Hasegawa, and K. Matsui, This Bulletin, **46**, 2549 (1973).

[4] W. E. Truce, E. M. Krider, and W. W. Brand, "The Smiles and Related Rearrangements of Aromatic Systems," Organic Reactions Vol. 18, John-Wiley & Sons. Inc., (1970), p. 116.

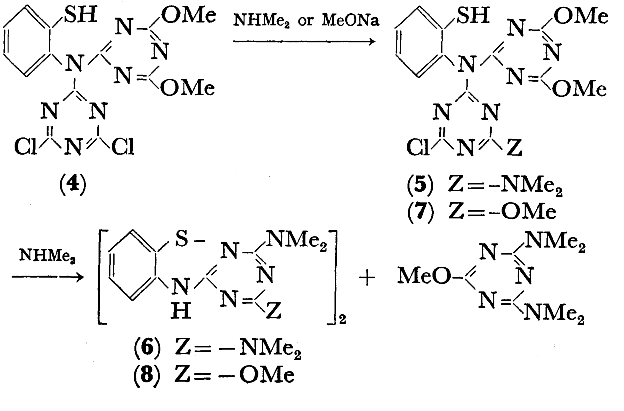
[5] T. Harayama, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 975 (1970).

an excess of dimethylamine at room temperature in acetone, *N,O*-bis[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (**2**) was obtained as the main product, along with a small amount of *N*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (**3**).

Apparently, the formation of **2** results from the *N*→*O* migration of the *s*-triazinyl group and the replacement of the chlorine atoms by dimethylamino groups. However, it is uncertain whether **3** results from a cleavage of the *s*-triazinyl group from **1** or from *N,O*-bis(*s*-triazinyl)-2-aminophenol (**2**). A similar rearrangement was observed when **1** was treated with methylamine; in this case, however, *N*-(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-2-aminophenol (**3′**) and *N,O*-bis(*s*-triazinyl)-2-aminophenol containing one residual chlorine atom were obtained. The latter is considered to be *N*-(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-*O*-(4-dimethylamino-6-methylamino-*s*-triazin-2-yl)-2-aminophenol (**2′**) from the facts that **3′** was obtained in this reaction and that an active chlorine atom in the *O*-*s*-triazinyl nucleus is more reactive towards nucleophiles than that in the *N*-*s*-triazinyl nucleus. The results suggest that the *N*→*O* migration of the *s*-triazinyl group took place prior to the replacement of the chlorine atom by the methylamino group. When pyridine was used as a base, only unchanged **1** was recovered under similar reaction conditions. On the other hand, in the reaction of **1** with an excess of sodium methoxide only *N*-(4-dimethylamino-6-methoxy-*s*-triazin-2-yl)-2-aminophenol was obtained upon the fission of one of the *s*-triazinyl groups.

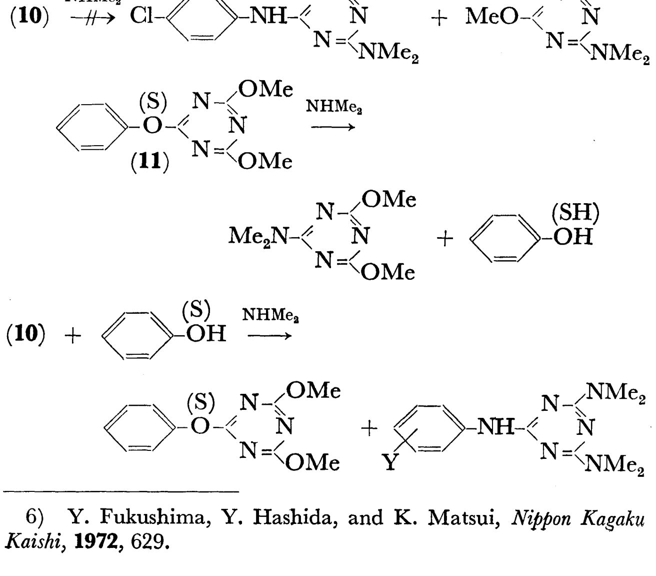
N→S *Migration of the* s-*Triazinyl Group in the Reaction of* N,N-*Bis(*s*-triazinyl)-2-aminothiophenols with Dimethylamine.* When *N*-(dichloro-*s*-triazinyl)-*N*-(dimethoxy-*s*-triazinyl)-2-aminothiophenol (**4**)[3] was treated with dimethylamine in a molar ratio of 1 : 2, a replaced product of one chlorine atom (**5**) was obtained. However, with an excess of dimethylamine (**4**) gave a disulfide of *N*-[bis(dimethylamino)-*s*-triazinyl]-2-aminothiophenol (**6**) and 2-dimethylamino-4,6-dimethoxy-*s*-triazine[5] upon the cleavage of the dimethoxy-*s*-triazinyl group; *N,S*-bis(*s*-triazinyl)-2-aminothiophenol was not obtained in this case. A similar result was also obtained when *N*-(4-chloro-6-methoxy-*s*-triazin-2-yl)-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminothiophenol (**7**) was treated with an excess of dimethylamine.

Generally, *N*-(acyl)-*N*-(*s*-triazinyl)- or *N,N*-bis(*s*-triazinyl)-arylamines are readily decomposed to give *N*-acyl- or *N*-*s*-triazinylarylamines upon the cleavage of the acyl or one of the *s*-triazinyl groups by sodium hydroxide or sodium methoxide, even in the absence of an *ortho*-OH or -SH group. Therefore, in the reaction of **1** with sodium methoxide to give *N*-*s*-triazinyl-2-aminophenol, a process involving the intermediary formation of *N,O*-bis(*s*-triazinyl)-2-aminophenol is unlikely. However, *N,N*-bis(*s*-triazinyl)-arylamines are fairly stable to amines when an *ortho*-OH or -SH group is absent; therefore, *N,N*-bis(*s*-triazinyl)-arylamine containing active chlorine atoms undergo merely a replacement of the chlorine atoms upon treatment with amines.



Thus, *N*-(4,6-dichloro-*s*-triazin-2-yl)-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-4-chloroaniline (**9**), whose triazinyl groups are expected to be somewhat more reactive towards nucleophiles than those of **5** and **7** because of the presence of the *p*-chloro substituent, reacted with an excess of dimethylamine to give merely a replaced product (**10**), without any cleavage of the *s*-triazinyl group, under similar reaction conditions. On the other hand, 2,4-dimethoxy-6-phenoxy-*s*-triazine and 2,4-dimethoxy-6-phenylthio-*s*-triazine gave 2-dimethylamino-4,6-dimethoxy-*s*-triazine[6] upon treatment with an excess of dimethylamine. Similarly, **2** gave **3** and tris(dimethylamino)-*s*-triazine when treated with dimethylamine, although the reaction took place very slowly. In addition, **10** did not react with phenol or thiophenol in the presence of dimethylamine to give a derivative of phenoxy-*s*-triazine or phenylthio-*s*-triazine under similar reaction conditions.

From these results, it may be considered that the reaction of **5** or **7** with dimethylamine to give **6** or **8**, and the formation of **3** in the reaction of **1** with di-



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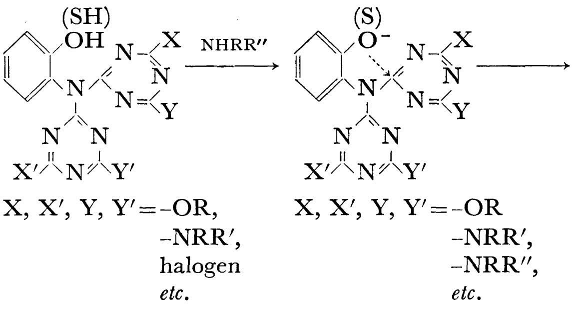
[6] Y. Fukushima, Y. Hashida, and K. Matsui, *Nippon Kagaku Kaishi*, **1972**, 629.

methylamine, does not proceed by means of a direct attack by dimethylamine on the *s*-triazine ring carbon of the *N*,*N*-bis(*s*-triazinyl) derivatives; the presence of the *ortho*-OH or -SH group is assumed to play an important role in the cleavage of the *s*-triazinyl group in these reactions.

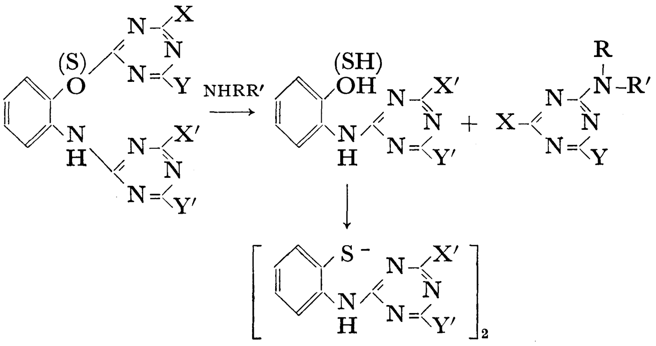
The participation of the neighboring –OH or –SH group may be explained reasonably by means of an intramolecular nucleophilic attack on the *s*-triazine nucleus by the phenoxide or thiophenoxide anion formed in the presence of amine; this assumption may be supported by the fact that, for instance, the peak of the hydroxy proton of **1** (δ 8.40) almost disappears on the addition of amine in acetone. When two *s*-triazinyl groups of different kinds are present, the nucleophilic attack may be anticipated to take place preferentially upon the more electron-deficient ring carbon, as in Reactions (**5**) and (**7**). The fact that, in the reaction of **1** with methylamine, the *N*→*O* migration of the *s*-triazinyl group took place prior to the replacement may be explained by a similar reason; the reactivity of the *s*-triazine nucleus of **1** towards the intramolecular nucleophilic attack by the phenoxide anion is assumed to be greater than that of the replaced product. Thus, in the reaction of *N*,*N*-bis(*s*-triazinyl)-2-aminophenol or 2-aminothiophenol containing an active chlorine atom with amines, the replacement and rearrangement are considered to take place competitively. When the chlorine atom is reactive enough, the replacement may occur preferentially; however, when the chlorine is not so reactive, the rearrangement may take place prior to the replacement. The intermediary *N*,*O*- or *N*,*S*-bis(*s*-triazinyl) derivative thus formed may react with amine to give the *N*-*s*-triazinyl derivative upon the cleavage of the *O*- or *S*-*s*-triazinyl group. When the *O*-*s*-triazinyl group is reactive enough towards amines, only the *N*-*s*-triazinyl derivative may be obtained as the final product, as in the cases of **5** and **7**. However, when the intermediary compound is not so reactive towards amines, the *N*,*O*- or *N*,*S*-bis(*s*-triazinyl) derivative can be expected to be obtained as the final product, as in the case of **1**.

From these results, it can be said that, in the reactions of *N*,*N*-bis(*s*-triazinyl) derivatives of *o*-aminophenol or *o*-aminothiophenol with bases, the processes of the reactions and reaction products vary depending upon the basicities and nucleophilic reactivities of the bases employed. In a reaction with a base of a high nucleophilic reactivity such as sodium methoxide, the reaction proceeds by means of a direct nucleophilic attack at the *N*-*s*-triazine nucleus to give the *N*-*s*-triazinyl derivative. However, in a reaction with amines, the nucleophilic attack at the *s*-triazine nucleus takes place indirectly by means of the phenoxide or thiophenoxide anion upon the *N*→*O* or *N*→*S* migration of the *s*-triazinyl group. However, when the amine is a weak base, as in the case of pyridine, the rearrangement does not take place.

Therefore, the reactions of **1**, **5**, and **7** with amines to give not only the *N*,*O*-bis(*s*-triazinyl) derivatives, but also the corresponding *N*-*s*-triazinyl derivatives, are considered to involve the *N*→*O* and *N*→*S* migrations of *s*-triazinyl groups; these migrations can be regarded as examples of the reverse Smiles rearrangement.



R = lower alkyl group
R', R'' = lower alkyl group or -H



Experimental

All the melting points are uncorrected. The NMR spectra were taken on a Varian A-60D spectrometer, using tetramethylsilane as the internal standard. The elemental analyses were performed in the Micro-analytical Center of Gunma University. The reaction products were identified by means of a study of their NMR spectra, by elemental analyses, by studying their solubility in an alakline solution, and by mixed-melting-point tests with authentic samples.

Materials. The *N*,*N*-bis(dichloro-*s*-triazinyl)-2-aminophenol (**1'**),[5] *N*-(dichloro-*s*-triazinyl)-*N*-(dimethoxy-*s*-triazinyl)-2-aimnothiophenol (**4**),[3] and *N*-(dichloro-*s*-triazinyl)-*N*-(dimethoxy-*s*-triazinyl)-*p*-chloroaniline (**9**)[7] were prepared by the methods already described.

*2,4-Dimethoxy-6-phenoxy-*s*-triazine* To a solution of 53 g (0.30 mol) of 2-chloro-4,6-dimethoxy-*s*-triazine in 200 ml of chloroform, we added an aqueous solution of 31 g (0.33 mol) of phenol and 13.5 g (0.34 mol) of sodium hydroxide in 200 ml of water. After 6 hrs' stirring at 60 °C, the solvent was evaporated. The recrystallization of the residue from ligroin yielded 2,4-dimethoxy-6-phenoxy-*s*-triazine in an almost quantitative yield. (Mp 102—102.5 °C. Found: C, 56.55; H, 5.01%. Calcd for $C_{11}H_{11}N_3O_3$: C, 56.65; H, 4.75%.)

A similar method was adopted for the preparation of 2,4-dimethoxy-6-phenylthio-*s*-triazine. (Mp 69—69.5 °C, recrystallized from ligroin. Found: C, 54.44; H, 4.45%. Calcd for $C_{11}H_{11}N_3O_2S$: C, 54.00; H, 4.45%.)

(i) Reaction of N,N-*bis(dichloro-*s*-triazinyl)-2-aminophenol (**1'**) with dimethylamine in a molar ratio of 1: 4.* To a stirred solution of 3.4 g (0.0084 mol) of **1'** in 100 ml of acetone, 4.0 g (0.034 mol) of a 40% dimethylamine solution was added, drop by

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[7] N. Nohara, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 519 (1970).

drop, at 0 °C. After 3 hrs' stirring, the mixture was poured into 300 ml of ice–water. The precipitate thus formed was filtered, dried, and recrystallized from ethylbenzene to afford *N,N*-bis(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-2-aminophenol (1) in an almost quantitative yield. (Mp 187—188 °C. Found: C, 45.79; H, 4.16%. Calcd for $C_{16}H_{17}Cl_2N_9O$: C, 45.49; H, 4.06%. NMR (CD_3Cl) δ 8.40 (broad, 1H), 7.26 (m, 4H), 3.17 (s, 9H), 3.01 (s, 3H.)

(ii) Reaction of **1′** *with an Excess of Dimethylamine.* To a stirred solution of 1.04 g (0.0025 mol) of **1′** in 150 ml of acetone, 13 g (0.012 mol) of a 4% dimethylamine solution was added, drop by drop, at 20 °C, after which the mixture left overnight at room temperature. The subsequent evaporation of the acetone gave a residue which, on recrystallization from acetone, yielded *N,O*-bis[bis(dimethylamino)-*s*-triazinyl]-*o*-aminophenol (**2**) (mp 184.5—185.5 °C)[3] in an almost quantitative yield. The thin-layer chromatogram (developed on a silica gel layer; developing solvent, acetone: benzene= 1: 10 by volume) of the reaction mixture showed the presence of *N*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (**3**).[1b]

(iii) Reaction of **1** *with methylamine.* Into a stirred solution of 1.03 g (0.0024 mol) of **1** in 150 ml of acetone, we stirred 8.9 g (0.01 mol) of a 4% methylamine solution, drop by drop. After 48 hrs' stirring at 50 °C, the solvent was evaporated. The residue was purified by column chromatography on silica gel, using a mixture of benzene and acetone (10: 1 by volume) as the developing solvent; this yielded 0.27 g (26.7%) of *N*-(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-*o*-(4-dimethylamino-6-methylamino-*s*-triazin-2-yl)-2-aminophenol (**2′**) and 0.015 g (2.25%) of **3′**. **2′**; [mp 209—210 °C, recrystallized from benzene. Found: C, 48.54; H, 4.97%. Calcd for $C_{17}H_{21}ClN_{10}O$; C, 48.98; H, 5.07%. NMR (DMSO-d_6) δ 8.90 (broad, 1H), 7.76 (broad, 1H), 7.25 (m, 4H), 3.03 (s, 12H), 2.73 (s, 3H).] The structure of Compound **3′** was confirmed by a mixed-melting-point test with an authentic sample prepared by a method to be described below. Into a stirred solution of 15.5 g (0.06 mol) of *N*-(dichloro-*s*-triazinyl)-2-aminophenol[5] in 200 ml of acetone, 14.4 g (0.12 mol) of a 40% dimethylamine solution was added, drop by drop, at 0 °C. After standing for 5 hr at room temperature, the reaction mixture was poured into 500 ml of ice–water. The precipitate thus formed was filtered, dried, and recrystallized from benzene to give *N*-(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-2-aminophenol (**3′**) in a 91% yield. [Mp 222—223 °C. Found: C, 49.98, H, 4.60%. Calcd for $C_{11}H_{12}ClN_5O$; C, 49.69; H, 4.55%. NMR (DMSO-d_6) δ 8.51 (broad, 1H), 7.76 (broad, 1H), 6.81 (m, 4H), 3.08 (s, 6H).]

(iv) Reaction of N-*(dichloro-*s*-triazinyl)*-N-*(dimethoxy-*s*-triazinyl)-2-aminothiophenol (4) with dimethylamine.* Into a solution of 4.2 g (0.01 mol) of **4** in 100 ml of acetone, we stirred, drop by drop, 2.3 g (0.02 mol) of a 40% solution of dimethylamine at 5 °C. After 1 hr's stirring at 10 °C, the mixture was poured into 300 ml of ice–water; the precipitate thus formed was filtered and dried. Recrystallization from benzene–ligroin gave an analytical sample of *N*-(4,6-dimethoxy-*s*-triazin-2-yl)-*N*-(4-chloro-6-dimethylamino-*s*-triazin-2-yl)-2-aminothiophenol (**5**) in an almost quantitative yield. Mp 168.5 °C. Found: N, 26.76%. Calcd for $C_{16}H_{17}ClN_8O_2S$; N, 26.62%.

(v) Reaction of **5** *with an excess of dimethylamine.* A procedure similar to that described above was employed using 5.0 g of a 40% solution of dimethylamine. After 10 hrs' stirring at room temperature, the mixture was poured into 300 ml of ice–water, and the precipitate thus formed was filtered and dried. Recrystallization from benzene–ligroin yielded a disulfide of *N*-[bis(dimethylamino)-*s*-triazinyl]-2-aminothiophenol (**6**). [Mp 184—185 °C, in an 85% yield. Found: C, 54.14; H, 6.08%. Calcd for $C_{26}H_{34}N_{12}S_2$: C, 53.96; H, 5.92%. NMR (DMSO-d_6), δ 8.60 (s, 1H), 7.65 (m, 4H), 3.00 (s, 12H).] The thin-layer chromatogram of the reaction mixture proved the presence of 2-dimethylamino-4,6-dimethoxy-*s*-triazine.[5]

(vi) Reaction of **4** *with Sodium Methoxide.* Into a solution of 4.2 g (0.01 mol) of Compound **4** in 100 ml of dioxane, we stirred, drop by drop, an equimolar methanolic solution of sodium methoxide at 0 °C. After 1 hr's stirring at 0 °C, the mixture was poured into 300 ml of ice–water; the precipitate thus formed was then filtered and dried. Recrystallization from benzene–ligroin yielded *N*-(4-chloro-6-methoxy-*s*-triazin-2-yl)-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminothiophenol (**7**) in an 80% yield. (Mp 146.5—147 °C. Found: C, 44.45; H, 3.68; N, 24.12%. Calcd for $C_{15}H_{14}ClN_7O_3S$: C, 44.18; H, 3.46; N, 24.04%.)

(vii) Reaction of **7** *with an Excess of Dimethylamine.* Compound **7** was treated with an excess of dimethylamine by a method similar to that described in (v). The crude product was purified by recrystallization from benzene–ligroin to give a disulfide of *N*-(4-dimethylamino-6-methoxy-*s*-triazinyl)-2-aminothiophenol (**8**) in a 70% yield. Mp 190—191 °C. Found: C, 52.30; H, 5.27%. Calcd for $C_{24}H_{28}N_{10}O_2S_2$: C, 52.16; H, 5.11%. NMR (DMSO-d_6) δ 8.98 (s, 1H), 7.0 (m, 4H), 3.80 (s, 3H), 3.03 (s, 6H). A thin-layer chromatogram of the reaction mixture showed the presence of 2-dimethylamino-4,6-dimethoxy-*s*-triazine.

(viii) Reaction of N-*(dichloro-*s*-triazinyl)*-N-*(dimethoxy-*s*-triazinyl)*-p-*chloroaniline (9) with dimethylamine.* To a stirred solution of 4.1 g (0.01 mol) of **9** in 100 ml of acetone, 4.0 g (0.1 mol) of a 40% dimethylamine solution was added, drop by drop, at room temperature. After 5 hrs' stirring, the mixture was poured into 300 ml of ice–water; the precipitate was filtered and dried. Recrystallization from acetone yielded *N*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-*p*-chloroaniline (**10**) in an almost quantitative yield: mp 172—173 °C. Found: N, 29.26%. Calcd for $C_{18}H_{22}ClN_9O_2$: N, 29.18%. In a thin-layer chromatogram of the reaction mixture, no spots of *N*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-4-chloroaniline and 2-dimethylamino-4,6-dimethoxy-*s*-triazine were observed.

(ix) Reaction of **2**, *2,4-dimethoxy-6-phenoxy-*s*-triazine and 2,4-dimethoxy-6-phenylthio-*s*-triazine with dimethylamine.* A typical run is shown in the case of 2,4-dimethoxy-6-phenoxy-*s*-triazine. 5 g of a 4% solution of dimethylamine was stirred, drop by drop, into a solution of 0.2 g of 2,4-dimethoxy-6-phenoxy-*s*-triazine in 30 ml of acetone. Stirring was continued for 10 hr at 25 °C, and then the mixture was poured into 100 ml of ice–water. The precipitate was filtered and dried. The product was purified by column chromatography to give 0.035 g of 2,4-dimethoxy-dimethylamino-*s*-triazine. A thin–layer chromatogram of the reaction mixture showed the presence of phenol.