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# Effects of *N*-Acyl- and *N*-*s*-Triazinyl Groups on the Rearrangement of *S*-(*s*-Triazinyl)-2-aminothiophenols and *O*-(*s*-Triazinyl)-2-aminophenols

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*S*-*s*-Triazinyl-2-aminothiophenols (I) containing methoxyl and/or dimethylamino groups in the *s*-triazine nucleus gave disulfides of *N*-*s*-triazinyl-2-aminothiophenols upon the S→N migration of the *s*-triazinyl group in the presence of acid; the rate of S→N migration was slow compared to that of the O→N migration of the corresponding *O*-*s*-triazinyl-2-aminophenol. On acylation or *s*-triazinylation, *S*-dimethoxy-*s*-triazinyl-2-aminothiophenol (I-1) and *O*-dimethoxy-*s*-triazinyl-2-aminophenol (II-1) gave *N*-acyl-*N*-*s*-triazinyl- or *N*,*N*-bis (*s*-triazinyl) derivatives upon the S→N or O→N migration of the *s*-triazinyl group. However, *S*-dimethylaminomethoxy-*s*-triazinyl-2-aminothiophenol (I-2), *S*-bis[(dimethylamino)-*s*-triazinyl]-2-aminothiophenol (I-3) and the corresponding derivatives of *o*-aminophenol gave *N*-acyl- or *N*-*s*-triazinyl derivatives, wihtout any migration of the *s*-triazinyl group, by acylation or *s*-triazinylation. The facility of the rearrangement of these *N*,*S*-bis-(*s*-triazinyl)-2-aminothiophenols and *N*,*O*-bis(*s*-triazinyl)-2-aminophenols depended not only upon the substituents in *S*- or *O*-*s*-triazine nucleus, but also upon the substituents in the *N*-*s*-triazine nucleus; the substituents in the *N*-*s*-triazine nucleus of strong electron-attracting and of strong electron-donating substances were not appropriate for the rearrangement in the presence of alkali to give disulfides of *N*-*s*-triazinyl-2-aminothiophenols (III-I) or *N*-*s*-triazinyl-2-aminophenols (III-II).

In previous papers,[1] we have reported that *O*-*s*-triazinyl-2-aminophenols rearrange in protic solvents or photochemically[2] to give the corresponding *N*-*s*-triazinyl-2-aminophenols.

It has been known that not only *O*-aryl-2-aminophenols, but also their *N*-acyl derivatives,[3] undergo the rearrangement of the *O*-aryl groups. Similarly, many *S*-aryl derivatives of *o*-aminothiophenol, their *N*-acyl derivatives,[4] and other related compounds, such as 2-acetamido-2′-nitrodiphenylsulfoxide,[5] 2-acetamido-2′-nitrodiphenylsulfone[4-1] or *o*-*N*-alkylamino sulfides, have been known to rearrange to yield the *N*-nitrophenyl derivatives or the derivatives of phenothiazine.[6] Recently, rearrangements of *s*-triazinyl groups have been reported in the reactions of 1-acylamino- or 1-*s*-triazinylamino-8-hydroxynaphthalene-3,6-disulfonic acid[7] and 3-hydroxy-2-naphthanilide with chloro-*s*-triazines.[8] However, in these papers the effect of *N*-acyl and *N*-triazinyl groups on the rearrangement of the *s*-triazinyl group, and their function in that rearrangement have not been mentioned. This paper will report on the S→N and O→N rearrangement of the *s*-triazinyl group of *S*-*s*-triazinyl-2-aminothiophenols, *N*-acyl, or *N*-*s*-triazinyl derivatives of *S*-*s*-triazinyl-2-aminothiophenols and *O*-*s*-triazinyl-2-aminophenols; the effects of *N*-acyl and *N*-*s*-triazinyl groups and their function in the rearrangement will also be discussed.

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).

2) K. Matsui, N. Maeno, S. Suzuki, H. Shizuka, and T. Morita, *Tetrahedron Lett.*, **1970**, 1467.

3) K. C. Roberts and C. G. M. deWorms, *J. Chem. Soc.*, **1934**, **727**; K. C. Roberts and C. G. M. deWorms, *ibid.*, **1935**, 1309.

4) a) W. J. Evans and S. Smiles, *ibid.*, **1935**, 181. b) K. J. Farrington and W. K. Warburton, *Aust. J. Chem.*, **9**, 480 (1956). c) C. F. Witht and S. Smiles, *J. Chem. Soc.*, **1935**, 340.

5) A. Levi, L. A. Warren, and S. Smiles, *ibid.*, **1933**, 1490.

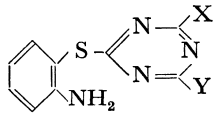
6) W. E. Truce, E. M. Kreider, and W. W. Brand, "The Smiles and Related Rearrangements of Aromatic Systems," Organic Reactions, Vol. 18, John Wiley & Sons, Inc., (1970) p. 117; K. Fujii, *J. Pharm. Soc. Jap.*, **77**, 3 (1957).

7) R. Budziarek, *Chem. Commun.*, **1968**, 1427; *J. Chem. Soc., C*, **1971**, 74.

8) R. Budziarek and P. Hampson, *ibid.*, **1971**, 1167.

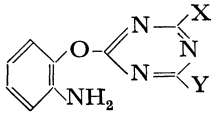
## Results and Discussion

*S-s*-Triazinyl-2-aminothiophenols and *O-s*-triazinyl-2-aminophenols[1b] of the following general formulas were synthesized for this work:



(I)

(1) X=Y=-$OCH_3$
(2) X=-$OCH_3$, Y=-$N(CH_3)_2$
(3) X=Y=-$N(CH_3)_2$

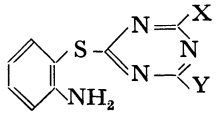


(II)

*S→N Rearrangement of the* s-*Triazinyl Group of* S-s-*Triazinyl-2-aminothiophenols (I-1∼3).* In contrast to the cases of *O-s*-triazinyl-2-aminophenols,[1] the (I) compounds could be easily prepared by treating *o*-aminothiophenol with the corresponding chloro-*s*-triazines in the presence of sodium hydroxide; the success in preparing the (I) compounds by this method is considered to be due to the facts that the nucleophilic reactivity of the thiophenoxide anion is much larger than that of the phenoxide anion[9] and that the rate of the rearrangement of *S-s*-triazinyl-2-aminothiophenols is much slower than that of *O-s*-triazinyl-2-aminophenols in an alkaline solution. Table 1 lists the compounds obtained.

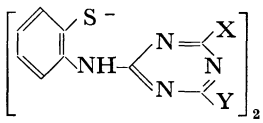
Generally, *S-s*-triazinyl-2-aminothiophenols are much more inactive to rearrangement than the corresponding *O-s*-triazinyl-2-aminophenols. For example, (I-1) could be stored for a long period and scarcely no rearrangement was observed even in an alkaline solution. However, (II-1) gave *N-s*-triazinyl-2-aminophenol upon storage in the laboratory in a solid state. This difference in the facility of the rearrangement agreed with the difference in mobility between –SAr and –OAr as leaving groups in the nucleophilic substitution reactions with amine; the mobility order is known as –OAr>–SAr.[10] However, (I-1) readily gave a disulfide of *N*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminothiophenol (III-I-1) when a dilute solution (0.5 g/100 ml acetone) was treated with a small amount of hydrochloric acid, while when a concentrated solution

Table 1. *S-s*-Triazinyl-2-aminothiophenols



| | X | Y | Yield (%) | Mp (°C) | Solvent for recrystallization | | Anal (%) Found | Anal (%) Calcd |
|---|---|---|---|---|---|---|---|---|
| (I-1) | $OCH_3$ | $OCH_3$ | 95 | 121—122 | Benzene-ligroin | C | 50.26 | 49.98 |
| | | | | | | H | 4.84 | 4.58 |
| (I-2) | $OCH_3$ | $N(CH_3)_2$ | 60 | 102—103 | Benzene-ligroin | C | 52.34 | 51.97 |
| | | | | | | H | 5.54 | 5.45 |
| (I-3) | $N(CH_3)_2$ | $N(CH_3)_2$ | 42 | 76.5—77.5 | Petroleum ether | C | 53.71 | 53.77 |
| | | | | | | H | 6.27 | 6.25 |

Table 2. Disulfides of *N-s*-triazinyl-2-aminothiophenols



| | X | Y | Yield (%) a) | Yield (%) b) | Mp (°C) | Solvent for recrystallization | M. W.c) Found | M. W.c) Calcd | | Anal (%) Found | Anal (%) Calcd |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (III-I-1) | $OCH_3$ | $OCH_3$ | 93 | — | 159—160 | Methanol | 540 | 527 | C | 50.54 | 50.18 |
| | | | | | | | | | H | 4.16 | 4.21 |
| (III-I-2) | $OCH_3$ | $N(CH_3)_2$ | 87 | 95 | 190—191 | Benzene-ligroin | — | — | C | 52.40 | 52.16 |
| | | | | | | | | | H | 5.47 | 5.11 |
| (III-I-3) | $N(CH_3)_2$ | $N(CH_3)_2$ | 80 | 95 | 184—185 | Benzene-ligroin | 587 | 579 | C | 54.14 | 53.96 |
| | | | | | | | | | H | 6.08 | 5.92 |

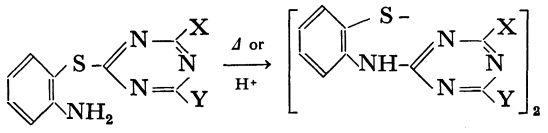
a) Yields of disulfides after standing for 24 hr in acetone in the presence of hydrochloric acid ($1\times10^{-2}$ mol/l) at room temperature.
b) Yields of disulfides after heating at 200 °C for 5 hr.
c) Measured by the method of Rast.

9) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1969); R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1968).

10) L. Bartolotti, and A. Cerniani, *Chem. Abstr.*, **50**, 15182e, (1956).

(20 g/100 ml) was used, (III-I-1), *N,N*-bis(*s*-triazinyl)-2-aminothiophenol (IV-I-1-8) and *o*-aminothiophenol were obtained, indicating that an intermolecular migration of the *s*-triazinyl group took place.

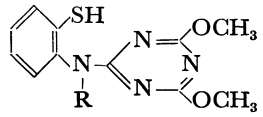
Compounds (I-2) and (I-3) are more inactive than (I-1) to the rearrangement, as may be expected; however, they also gave disulfides of the corresponding *N*-*s*-triazinyl-2-aminothiophenols when treated with an acid or when heated above their melting points. The disulfides of *N*-*s*-triazinyl-2-aminothiophenols thus obtained are listed in Table 2.

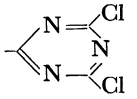
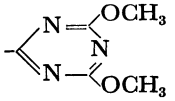
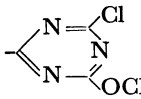
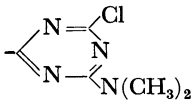


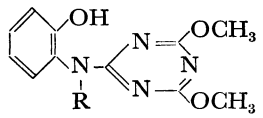
(I) (III-I)

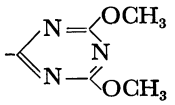
*Rearrangement of the* S- *or* O-s-*Triazinyl Group during the Reactions of* S-*Dimethoxy*-s-*triazinyl-2-aminothiophenol (I-1) and* O-*Dimethoxy*-s-*triazinyl-2-aminophenol (II-1) with Acylating or* s-*Triazinylating Reagents. (a) Reaction of* S-*(4,6-Dimethoxy*-s-*triazin-2-yl)-2-aminothiophenol (I-1)*: When I-1 was treated with 2-chloro-4,6-dimethoxy-*s*-triazine in acetone under nearly neutral conditions by adding sodium carbonate, *N,N*-bis(*s*-triazinyl)-2-aminothiophenol (IV-I-1-8) was obtained as the main product instead of the expected *N,S*-bis(*s*-triazinyl)-2-aminothiophenol. A similar migration of the *S*-*s*-triazinyl group during the reaction was observed when I-1 was treated with acetic anhydride, benzoyl chloride, cyanuric chloride, or ethyl chloroformate. I-1 reacted readily with phenyl isocyanate (at room temperature) or phenyl isothiocyanate (at 60 °C) in benzene to give *N*-*s*-triazinyl-*N*-phenyl-

Table 3. *N*-Acyl-*N*-*s*-triazinyl- and *N,N*-bis(*s*-triazinyl)-2-aminothiophenols and 2-aminophenols



| | R | Yield (%) | Mp (°C) | Solvent for recrystallization | | Anal (%) Found | Anal (%) Calcd |
|---|---|---|---|---|---|---|---|
| (IV-I-1-1) | $COCH_3$ | 85 | 137—138 | Benzene | C | 51.10 | 50.99 |
| | | | | | H | 4.32 | 4.57 |
| (IV-I-1-2) | $COC_6H_5$ | 87 | 138—139 | Benzene-ligroin | C | 58.23 | 58.68 |
| | | | | | H | 4.07 | 4.38 |
| (IV-I-1-3) | $CONHC_6H_5$ | 95 | 170—171 | Benzene | C | 56.50 | 56.24 |
| | | | | | H | 4.53 | 4.72 |
| (IV-I-1-4) | $CSNHC_6H_5$ | 95 | 167 | Benzene | C | 54.54 | 54.53 |
| | | | | | H | 4.25 | 4.32 |
| (IV-I-1-5) | $COCH_2COCH_3$ | 54 | 134—135 | Benzene-ligroin | C | 51.83 | 51.72 |
| | | | | | H | 4.72 | 4.64 |
| (IV-I-1-6) | $COOCH_2CH_3$ | 74 | 105—106 | Ethanol | C | 49.85 | 49.99 |
| | | | | | H | 4.55 | 4.79 |
| (IV-I-1-7) |  | 97 | 155—156 | Benzene | C | 40.75 | 41.03 |
| | | | | | H | 2.70 | 2.69 |
| (IV-I-1-8) |  | 82 | 175—176 | Benzene-ligroin | C | 47.92 | 47.63 |
| | | | | | H | 4.49 | 4.26 |
| (IV-I-1-9) |  | 75 | 146.5—147.0 | Benzene | N | 24:12 | 24:04 |
| (IV-I-1-10) |  | 90 | 168.5 | Benzene-ligroin | N | 26.76 | 26.62 |



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (IV-II-1-1) | $COCH_3$ | 70 | 133—134 | Ligroin | C | 54.06 | 53.79 |
| | | | | | H | 5.10 | 4.86 |
| (IV-II-1-2) |  | 81 | 132—133 | Benzene | C | 49.32 | 49.61 |
| | | | | | H | 4.46 | 4.39 |

carbamoyl- or *N-s*-triazinyl-*N*-phenylthiocarbamoyl-2-aminothiophenol in a good yield. I-1 also reacted with diketene upon heating under reflux in xylene to give *N*-acetoacetyl-*N*-dimethoxy-*s*-triazinyl-2-aminothiophenol. Thus, *N*-acyl- and *N-s*-triazinyl-*S*-dimethoxy-*s*-triazinyl-2-aminothiophenols were not obtained in these cases. However, in the reaction of I-1 with acrylonitrile (heated in dioxane in the presence of Triton B) or 2,4-dinitrofluorobenzene (in the presence of triethylamine), merely an *N*-substituted product (V-I-1-1～V-I-1-2) was obtained, without any rearrangement in any case.

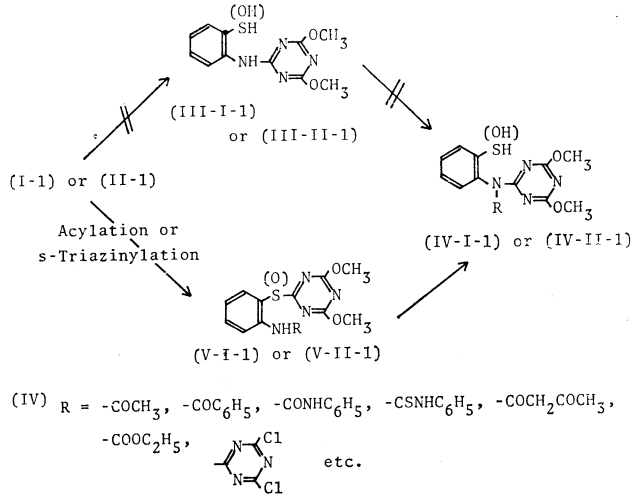
Table 3 lists the compounds thus obtained.

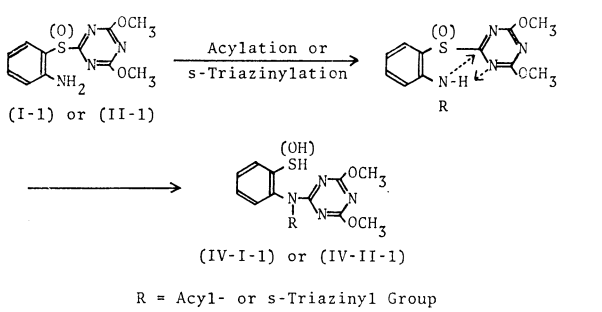
*(b) Reaction of O-(4,6-Dimethoxy-s-triazin-2-yl)-2-aminophenol (II-1)*: A similar rearrangement was observed in the reaction of II-1 with 2-chloro-4,6-dimethoxy-*s*-triazine or acetic anhydride, which gave *N,N*-bis(*s*-triazinyl)-2-aminophenol or *N*-acetyl-*N-s*-triazinyl-2-aminophenol.

In most of these cases (except the case of diketene), (I-1) and (II-1) are stable under the reaction conditions and scarcely no formation of the rearranged product [(III-I) or (III-II)] was observed when the acylating or *s*-triazinylating reagents were absent. From these results, a process involving the intermediary formation of *N-s*-triazinyl-2-aminothiophenol or *N-s*-triazinyl-2-aminophenol (III) is not considered for these reactions; the reactions are, assumed to proceed by means of a preferential acylation or *s*-triazinylation of the amino group, followed by a rearrangement giving the end products. This assumption is supported by thin-layer chromatograms of the reaction mixture; for example, in the reaction of II-1 with acetic anhydride in the presence of triethylamine, no spot of *N-s*-triazinyl-2-aminophenol (III-II-1) was observed at any time during the course of the reaction (developed on a silica gel layer; developing solvent, chloroform–benzene–ligroin–methanol=15 : 5 : 5 : 5 by volume). A short time after the reaction components were mixed, however, a new, unidentified spot appeared, followed by a spot of *N*-acetyl-*N-s*-triazinyl-2-aminophenol (IV-II-1-1). The latter increased gradually with the reaction time; however, the unidentified spot [probably attributable to *N*-acetyl-*O-s*-triazinyl-2-aminophenol (V-II-1-1)] was small and remained almost constant throughout the course of the reaction until it disappeared at last.

In contrast to the case of I-1, II-1 gave merely *N*-dimethoxy-*s*-triazinyl-2-aminophenol when heated with diketene in xylene or when heated with acrylonitrile. Because of the slow S→N migration, the reaction of (I-1) is assumed to proceed by means of a preferential reaction at the amino group, followed by the rearrangement giving the end product. On the other hand, (II-1) rearranges rapidly upon mere heating; therefore, in the case of II-1 the rearrangement is considered to take place in preference to the reaction of the amino group with the reagent, because the preformed *N-s*-triazinyl-2-aminophenol is inert to the attack by diketene or acrylonitrile under the present reaction conditions.

From the results, it is obvious that the introduction of the acyl or *s*-triazinyl group into the amino group very much facilitates the S→N or O→N migration of the *S*- or *O*-dimethoxy-*s*-triazinyl group. Generally, the nucleophilic reactivities of NH-*s*-triazinyl and NH-acyl groups are known to be low. Thus, the rate of the rearrangement of *N*-acyl-*O*-(2,4-dinitrophenyl)-2-aminophenols is much slower than that of the parent aminoether in the absence of alkali.[3] Therefore, it is unlikely that the ready rearrangement of intermediary *N*-acyl or *N-s*-triazinyl derivatives (V) merely proceeds by means of a general nucleophilic attack by the NH-acyl or NH-*s*-triazinyl group. However, a process involving the formation of a reactive anion by the abstraction of a proton from the NH-acyl- or NH-*s*-triazinyl group is also unlikely, for, in most of these cases, the acylation and *s*-triazinylation were carried out under nearly neutral conditions; in certain cases, as in the reaction of I-1 with phenyl isocyanate, even though the reactions were carried out without the addition of any base, the rearrangement took place very readily. Consequently, it may be considered that the presence of an acidic -NH- hydrogen atom resulting from the introduction of an acyl or *s*-triazinyl group is important for the ready rearrangement, and that the difference in effect of introducing an acyl group between the nitrophenyl (retardation) and *s*-triazinyl (acceleration) derivatives is attributable to the presence or absence of a ring nitrogen atom in the migrating aryl nucleus. From these considerations, it seems reasonable to assume that the ready rearrangement of *N*-acyl or *N-s*-triazinyl derivatives of I-1 and II-1 proceeds by intramolecular four-center electrophilic-nucleophilic processes, as is shown below:



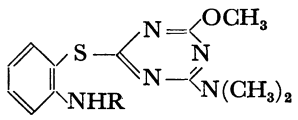



From the viewpoint of this assumption, it may be considered that the –NH– group of the 2,4-dinitrophenyl derivative is more favorable for the protonation-like process than are the ordinary NH-acyl groups; however, its nucleophilic reactivity is assumed to be too low to attack the *s*-triazine ring carbon. An opposite situation holds for the *N*-β-cyanoethyl derivative.

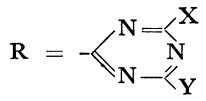
*Reactions of* S-*(2-Dimethylamino-4-methoxy-*s*-triazin-2-yl)-2-aminothiophenol (I-2),* O-*(2-Dimethylamino-4-methoxy-*s*-triazin-2-yl)-2-aminophenol (II-2),* S-[*2,4-Bis-(dimethylamino)-*s*-triazin-2-yl*]*-2-aminothiophenol (I-3), and* O-[*2,4-Bis(dimethylamino)-*s*-triazin-2-yl)-2-aminophenol (II-2) with Acylating or* s*-Triazinylating Reagents, and the Migration of the* s*-Triazinyl Group of* N,S-*Bis(*s*-triazinyl)-2-aminothiophenols and* N,O-*Bis(*s*-triazinyl)-2-aminophenols.* When I-2 or II-2 was treated with acetic anhydride, phenyl isocyanate, benzoyl chloride, ethyl chloroformate, cyanuric chloride, 2,4-dichloro-6-methoxy-*s*-triazine, or 2,4-dichloro-6-methyl-*s*-triazine in manners similar to those described above, an *N*-acyl- or *N-s*-triazinyl-derivative was obtained in every case, without any migration of the *S*- or *O*-triazinyl group. Tables 4 and 5 list the compounds, (V-I-2) and (V-II-2), thus obtained. Similar results were also obtained in the reactions of I-3 and II-3 with acylating or *s*-triazinylating reagents; Tables 6 and 7 list the compounds, (V-I-3) and (V-II-3), thus obtained.

When *N*-chloro-*s*-triazinyl-*O-s*-triazinyl-2-aminophenols [(V-II-2-5)～(V-II-2-7) and (V-II-3-8)～(V-II-3-10)] and *N*-chloro-*s*-triazinyl-*S-s*-triazinyl-2-aminothiophenols [(V-I-2-4)～(V-I-2-6) and (V-1-3-5)

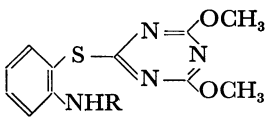
TABLE 4. *N*-ACYL-*S-s*-TRIAZINYL- AND *N,S*-BIS(*s*-TRIAZINYL)-2-AMINOTHIOPHENOLS (V-I-2)



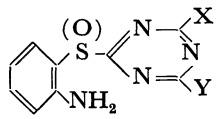
| | R | Yield (%) | Mp (°C) | Solvent for recrystallization | | Anal (%) Found | Calcd |
|---|---|---|---|---|---|---|---|
| (V-I-2-1) | $COCH_3$ | 91 | 146—146.5 | Benzene-ligroin | C | 52.34 | 52.65 |
| | | | | | H | 5.32 | 5.36 |
| (V-I-2-2) | $COC_6H_5$ | 84 | 147—148 | Benzene-ligroin | C | 60.21 | 59.83 |
| | | | | | H | 5.22 | 5.03 |
| (V-I-2-3) | $CONHC_6H_5$ | 84 | 201—220 | Dioxane | C | 57.27 | 57.57 |
| | | | | | H | 5.21 | 5.07 |

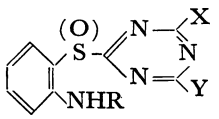
R = 

| | X | Y | | | | | |
|---|---|---|---|---|---|---|---|
| (V-I-2-4) | Cl | Cl | 95 | 176.5 | Benzene | C | 42.03 | 42.37 |
| | | | | | | H | 3.55 | 3.33 |
| (V-I-2-5) | Cl | $OCH_3$ | 90 | 144 | Benzene-ligroin | C | 46.01 | 45.67 |
| | | | | | | H | 4.37 | 4.07 |
| (V-I-2-6) | Cl | $CH_3$ | 95 | 158—159 | Benzene-ligroin | C | 47.12 | 47.46 |
| | | | | | | H | 4.08 | 4.23 |
| (V-I-2-7) | Cl | $N(CH_3)_2$ | 91 | 190—191 | Benzene | N | 29.14 | 28.84 |
| (V-I-2-8) | $CH_3$ | $OCH_3$ | 83 | 119—120 | Benzene-ligroin | N | 27.71 | 27.98 |
| (V-I-2-9) | $OCH_3$ | $N(CH_3)_2$ | 84 | 141—142 | Benzene-ligroin | C | 50.54 | 50.34 |
| | | | | | | H | 5.39 | 5.40 |
| (V-I-2-10) | $CH_3$ | $N(CH_3)_2$ | 97 | 167—168 | Benzene-ligroin | N | 30.15 | 30.48 |
| (V-I-2-11) | $N(CH_3)_2$ | $N(CH_3)_2$ | 93 | 148—149 | Benzene-ligroin | C | 51.49 | 51.57 |
| | | | | | | H | 6.29 | 5.92 |



| | R | | | | | |
|---|---|---|---|---|---|---|
| (V-I-1-1) | $C_6H_3(NO_2)_2$-(2,4-) | 30 | 231—232 | Monochlorobenzene | C | 47.60 | 47.44 |
| | | | | | H | 3.01 | 3.28 |
| (V-I-1-2) | $CH_2CH_2CN$ | 60 | 106—107 | Ethanol | C | 52.15 | 52.38 |
| | | | | | H | 5.04 | 4.76 |

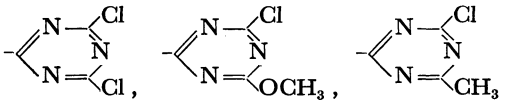

(I) or (II)


(V-I) or (V-II)

(V-I-2), (V-II-2), X=-$OCH_3$, Y=-$N(CH_3)_2$

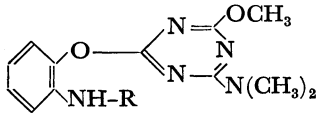
(V-I-3), (V-II-3), X=Y=-$N(CH_3)_2$

R=-$COCH_3$, -$COC_6H_5$, -$CONHC_6H_5$, -$COOC_2H_5$,

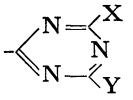


~(V-I-3-7)] were treated with dimethylamine, one or two chlorine atoms were replaced by a dimethylamino group, depending upon the amounts of dimethylamine used and the reaction temperature; the migration of the *O*- or *S*-*s*-triazinyl group was not observed in any case. However, in the reaction with sodium methoxide, not only the replacement of the chlorine atom, but also the migration of the *s*-triazinyl group, took place. For example, V-II-2-5 reacted with an equimolar amount of sodium methoxide to give V-II-2-6. However, with more than two equivalents of sodium methoxide V-II-2-5 gave *N*-(4-dimethylamino-6-methoxy-*s*-triazin-2-yl)-2-aminophenol (III-II-2) under the O→N

Table 5. *N*-Acyl-*O*-*s*-triazinyl- and *N*,*O*-bis(*s*-triazinyl)-2-aminophenols (V-II-2)



| | R | Yield (%) | Mp (°C) | Solvent for recrystallization | | Anal (%) Found | Calcd |
|---|---|---|---|---|---|---|---|
| (V-II-2-1) | $COCH_3$ | 76 | 175—176 | Benzene | C | 55.25 | 55.43 |
| | | | | | H | 5.78 | 5.65 |
| | | | | | N | 23.06 | 23.09 |
| (V-II-2-2) | $CONHC_6H_5$ | 92 | 168—169 | Benzene | C | 60.35 | 59.99 |
| | | | | | H | 5.51 | 5.30 |
| | | | | | N | 22.40 | 22.09 |
| (V-II-2-3) | $COC_6H_5$ | 63 | 110—111 | Benzene-ligroin | C | 62.79 | 62.45 |
| | | | | | H | 5.50 | 5.24 |
| | | | | | N | 19.30 | 19.16 |
| (V-II-2-4) | $COOC_2H_5$ | 88 | 88— 89 | Benzene-methanol | C | 53.85 | 54.04 |
| | | | | | H | 6.05 | 5.75 |
| | | | | | N | 21.04 | 21.00 |

R = 

| | X | Y | | | | | |
|---|---|---|---|---|---|---|---|
| (V-II-2-5) | Cl | Cl | 95 | 136—137 | Benzene-petroleum ether | C | 44.41 | 44.02 |
| | | | | | | H | 3.70 | 3.45 |
| | | | | | | N | 27.66 | 27.38 |
| (V-II-2-6) | Cl | $OCH_3$ | 75 | 99—100 | Methanol | C | 47.75 | 47.47 |
| | | | | | | H | 4.55 | 4.23 |
| | | | | | | N | 27.36 | 27.68 |
| (V-II-2-7) | Cl | $CH_3$ | 91 | 147—148 | Benzene | C | 49.07 | 49.43 |
| | | | | | | H | 4.63 | 4.41 |
| | | | | | | N | 28.57 | 28.82 |
| (V-II-2-8) | Cl | $N(CH_3)_2$ | 86 | 166—167 | Benzene-ligroin | C | 49.12 | 48.87 |
| | | | | | | H | 5.05 | 4.82 |
| | | | | | | N | 30.51 | 30.17 |
| (V-II-2-9) | $N(CH_3)_2$ | $N(CH_3)_2$ | 70 | 160—161 | Benzene | C | 53.88 | 53.51 |
| | | | | | | H | 6.45 | 6.14 |
| | | | | | | N | 32.87 | 32.49 |
| (V-II-2-10) | $OCH_3$ | $N(CH_3)_2$ | 95 | 142—143 | Benzene | C | 51.95 | 52.29 |
| | | | | | | H | 5.83 | 5.61 |
| | | | | | | N | 30.84 | 30.49 |
| (V-II-2-11) | $CH_3$ | $N(CH_3)_2$ | 95 | 165—166 | Acetone | C | 54.81 | 54.40 |
| | | | | | | H | 6.05 | 5.83 |
| | | | | | | N | 31.61 | 31.72 |

rearrangement and the cleavage of one of the *s*-triazinyl groups. III-II-2 was also obtained from V-II-2-7 when it was treated with more than one equivalent of sodium methoxide. Similarly, V-II-3-8 gave V-II-3-9 or III-II-3 when treated with one or more than two equivalents of sodium methoxide. However, when V-II-3-8 was treated with one and a half equivalents of sodium methoxide, even though the reaction mixture was slightly acidic at the end of the reaction, instead of an intermediary *N*-[bis(dimethylamino)-*s*-triazinyl]-*N*-(chloromethoxy-*s*-triazinyl)-2-aminophenol (IV-II-3)′ or *O*-[bis(dimethylamino)-*s*-triazinyl]-*N*-(dimethoxy-*s*-triazinyl)-2-aminophenol (V-II-3)′, the rearranged product of the latter (IV-II-3), which gave III-II-3 in the presence of alkali, was obtained, together with III-II-3. Thus, it is obvious that the reaction of V-II-2-5 or V-II-3-8 with sodium methoxide proceeds by means of a preferential replacement of the chlorine atoms by methoxyl groups, followed by the O→N migration of the *O*-*s*-triazinyl group to give IV-II-2 or IV-II-3, which gave the end product by a cleavage of the dimethoxy-*s*-triazinyl group, as is shown below.

Compound (V-II-3-10), however, unlike V-II-2-7 or V-II-3-9, gave only a replaced product when

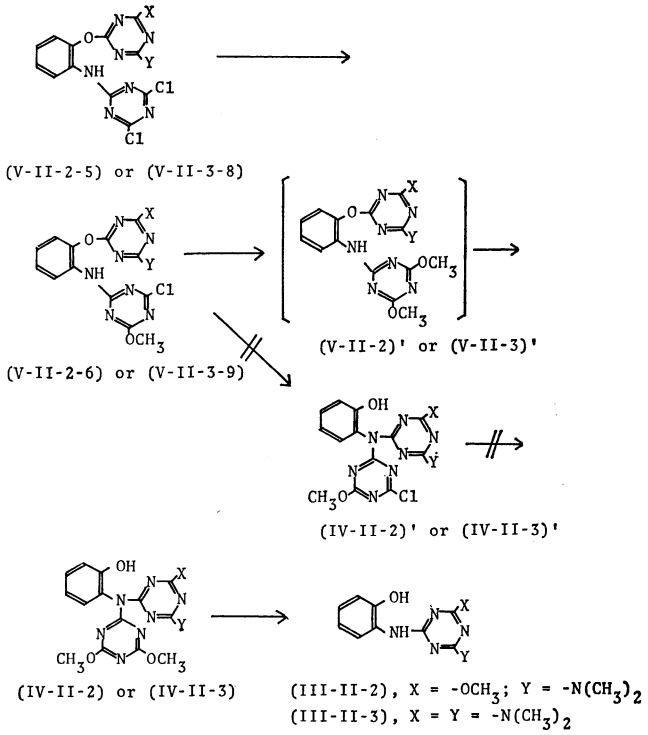
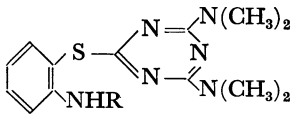
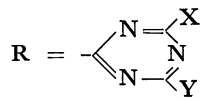



TABLE 6. *N*-ACYL-*S*-*s*-TRIAZINYL- AND *N*,*S*-BIS(*s*-TRIAZINYL)-2-AMINOTHIOPHENOLS (V-I-3)

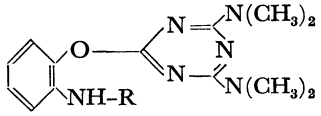


| | R | Yield (%) | Mp (°C) | Solvent for recrystallization | Anal (%) | Found | Calcd |
|---|---|---|---|---|---|---|---|
| (V-I-3-1) | $COCH_3$ | 72 | 138.5—139.5 | Ligroin | C | 54.22 | 54.20 |
| | | | | | H | 5.94 | 6.06 |
| (V-I-3-2) | $CONHC_6H_5$ | 95 | 186 | Benzene | C | 58.96 | 58.66 |
| | | | | | H | 5.85 | 5.66 |
| (V-I-3-3) | $CSNHC_6H_5$ | 62 | 170—170.5 | Benzene | C | 56.26 | 56.44 |
| | | | | | H | 5.52 | 5.45 |
| (V-I-3-4) | $C_6H_3(NO_2)_2$(2,4-) | 87 | 193.5—194.0 | Benzene | C | 50.24 | 49.99 |
| | | | | | H | 4.93 | 4.42 |

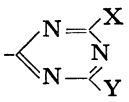
R = 

| | X | Y | | | | | |
|---|---|---|---|---|---|---|---|
| (V-I-3-5) | Cl | Cl | 95 | 170—171 | Benzene-ligroin | C | 44.33 | 44.38 |
| | | | | | | H | 4.02 | 3.96 |
| (V-I-3-6) | Cl | $OCH_3$ | — | 161.5 | Benzene-ligroin | C | 47.17 | 47.06 |
| | | | | | | H | 5.00 | 4.65 |
| (V-I-3-7) | Cl | $CH_3$ | — | 174.5 | Benzene-ligroin | C | 48.72 | 48.86 |
| | | | | | | H | 5.09 | 4.82 |
| (V-I-3-8) | $OCH_3$ | $OCH_3$ | 90 | 152—153.5 | Benzene-ligroin | N | 29.68 | 29.35 |
| (V-I-3-9) | Cl | $N(CH_3)_2$ | — | 195—196 | Benzene-ligroin | N | 31.36 | 31.33 |
| (V-I-3-10) | $CH_3$ | $OCH_3$ | — | 177—178 | Benzene-ligroin | N | 30.60 | 30.48 |
| (V-I-3-11) | $OCH_3$ | $N(CH_3)_2$ | — | 181—181.5 | Benzene-ligroin | C | 52.07 | 51.57 |
| | | | | | | H | 6.20 | 5.92 |
| (V-I-3-12) | $CH_3$ | $N(CH_3)_2$ | — | 172.5—173 | Benzene-ligroin | C | 53.18 | 53.50 |
| | | | | | | H | 5.26 | 4.98 |
| (V-I-3-13) | $N(CH_3)_2$ | $N(CH_3)_2$ | — | 169.5—170.5 | Benzene-ligroin | C | 52.35 | 52.72 |
| | | | | | | H | 6.23 | 6.42 |

Table 7. *N*-Acyl-*O*-*s*-triazinyl- and *N*,*O*-bis(*s*-triazinyl)-aminophenols (V-II-3)



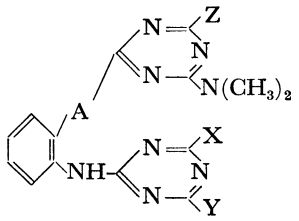
| | R | Yield (%) | Mp (°C) | Solvent for recrystallization | | Anal (%) Found | Calcd |
|---|---|---|---|---|---|---|---|
| (V-II-3-1) | $COCH_3$ | 95 | 203—204 | Benzene | C | 57.00 | 56.95 |
| | | | | | H | 6.70 | 6.37 |
| | | | | | N | 26.33 | 26.57 |
| (V-II-3-2) | $CONHC_6H_5$ | 93 | 218—219 | Dioxane | C | 60.90 | 61.05 |
| | | | | | H | 5.93 | 5.89 |
| | | | | | N | 24.75 | 24.92 |
| (V-II-3-3) | $COC_6H_5$ | 74 | 121—122 | Benzene-ligroin | C | 63.77 | 63.47 |
| | | | | | H | 6.05 | 5.86 |
| | | | | | N | 22.38 | 22.21 |
| (V-II-3-4) | $CSNHC_6H_5$ | 49 | 162 | Dioxane | C | 58.95 | 58.66 |
| | | | | | H | 5.93 | 5.66 |
| | | | | | N | 24.06 | 23.94 |
| (V-II-3-5) | $COOC_2H_5$ | 95 | 113—114 | Methanol | C | 55.80 | 55.48 |
| | | | | | H | 6.64 | 6.40 |
| | | | | | N | 24.06 | 24.26 |
| (V-II-3-6) | $C_6H_3(NO_2)_2$(2,4-) | 95 | 145—146 | Benzene-ligroin | N | 25.01 | 25.44 |
| (V-II-3-7) | $CH_2CH_2CN$ | 31 | 132—133 | Benzene-ligroin | C | 58.95 | 58.70 |
| | | | | | H | 6.58 | 6.47 |
| | | | | | N | 30.30 | 29.95 |

R = 

| | X | Y | | | | | |
|---|---|---|---|---|---|---|---|
| (V-II-3-8) | Cl | Cl | 95 | 164—165 | Benzene-ligroin | C | 45.89 | 45.52 |
| | | | | | | H | 4.16 | 4.06 |
| (V-II-3-9) | Cl | $OCH_3$ | 95 | 102—103 | Methanol | C | 48.87 | 48.87 |
| | | | | | | H | 4.64 | 4.82 |
| (V-II-3-10) | Cl | $CH_3$ | 95 | 103—104 | Methanol | C | 51.05 | 50.81 |
| | | | | | | H | 5.23 | 5.02 |
| (V-II-3-11) | $CH_3$ | $OCH_3$ | 88 | 134—135 | Benzene | C | 54.22 | 54.41 |
| | | | | | | H | 5.82 | 5.79 |
| (V-II-3-12) | Cl | $N(CH_3)_2$ | 95 | 187—188 | Benzene | C | 50.34 | 50.20 |
| | | | | | | H | 5.47 | 5.34 |
| (V-II-3-13) | $N(CH_3)_2$ | $N(CH_3)_2$ | 82 | 182—183 | Benzene | C | 54.61 | 54.65 |
| | | | | | | H | 6.85 | 6.60 |
| (V-II-3-14) | $OCH_3$ | $N(CH_3)_2$ | 95 | 142—143 | Benzene-ligroin | C | 53.75 | 53.51 |
| | | | | | | H | 6.30 | 6.14 |
| | | | | | | N | 32.80 | 32.84 |
| (V-II-3-15) | $CH_3$ | $N(CH_3)_2$ | 95 | 165—166 | Benzene | C | 55.71 | 55.61 |
| | | | | | | H | 6.26 | 6.34 |

treated with sodium methoxide. Similarly, III-I-2 was obtained in the reaction of V-I-2-4 with sodium methoxide; however, V-I-3-5 gave merely a replaced product upon treatment with an excess of sodium methoxide. Thus, although, because of the ready rearrangement *N*-dimethoxy-*s*-triazinyl derivatives of V-I-1～2 and V-II-1～3 types could not be obtained, *N*,*S*- and *N*,*O*-bis(*s*-triazinyl) derivatives of V-I-2～3 and V-II-2～3 types containing such substituents as –Cl, –Cl; –Cl, $-OCH_3$; –Cl, $-CH_3$; –Cl, $-N(CH_3)_2$; $-OCH_3$, $-CH_3$; $-OCH_3$, $-N(CH_3)_2$; $-N(CH_3)_2$, $-N(CH_3)_2$, and $-CH_3$, $-N(CH_3)_2$ in the *N*-*s*-triazine nucleus were prepared as fairly stable compounds, as Tables 4, 5, 6, and 7 show. From these results it has become clear that the facility of the rearrangement of *N*,*S*-bis(*s*-triazinyl)-2-aminothiophenols

TABLE 8. REARRANGEMENT OF *N,O*-BIS(*s*-TRIAZINYL)-2-AMINOPHENOLS AND *N,S*-BIS(*s*-TRIAZINYL)-2-AMINOTHIOPHENOLS IN THE PRESENCE OF SODIUM HYDROXIDE IN ACETONE



| X | Y | $\sigma_m X+\sigma_m Y$[a] | A = | -O- | | -S- | |
|---|---|---|---|---|---|---|---|
| | | | Z = | $-OCH_3$, | $-N(CH_3)_2$ | $-OCH_3$, | $-N(CH_3)_2$ |
| Cl | $OCH_3$ | +0.488 | | ×[1] | ×[2] | ×[3] | ×[3] |
| Cl | $CH_3$ | +0.304 | | ○ | ○ | × | × |
| $OCH_3$ | $OCH_3$ | +0.230 | | ● | ● | ● | ○ |
| Cl | $N(CH_3)_2$ | +0.162 | | ○ | — | ○ | ○ |
| $CH_3$ | $OCH_3$ | +0.049 | | ● | ○ | ○ | ○ |
| $OCH_3$ | $N(CH_3)_2$ | −0.096 | | × | ○ | × | × |
| $CH_3$ | $N(CH_3)_2$ | −0.280 | | × | × | × | × |
| $N(CH_3)_2$ | $N(CH_3)_2$ | −0.422 | | × | × | × | × |

a) Effect attributable to substituents in the *N-s*-triazine nucleus can be expressed by $\sigma_m X+\sigma_m Y$.[13]
1), 2) and 3); Results obtained after standing for 5 hr at room temperature, after standing for 24 hr at room temperature and after standing for 5 hr at 60°C, respectively.
○ indicates a formation of the rearranged product.
× indicates a failure of the rearrangement.
● indicates that the compound was not obtained owing to the rearrangement during the synthesis.

and *N,O*-bis(s-triazinyl)-2-aminophenols depends not only upon the substituents in the *S-* or *O-s*-triazine nucleus, but also upon the substituents in the *N-s*-triazine nucleus; however, no simple relation such as holds in the case of the substituents in the *O-s*-triazine nuclues[1b] was observed between the facility of the rearrangement and the substituents in the *N-s*-triazine nucleus. As will be mentioned later, some of the compounds, V-I-2∼3 and V-II-2∼3, rearrange in the presence of alkali (*cf.* Table 8). However, these results suggest that the ready rearrangement during the methoxydechlorination proceeds in a manner similar to that mentioned before by means of intramolecular four-center electrophilic-nucleophilic processes, and that, in these cases, the presence of alkali is necessary not for the rearrangement, but for the hydrolytic fission of the *s*-triazinyl group.

*Migration of the* S- *and* O-s-*Triazinyl Groups of* N-*Acyl*-S-s-*triazinyl*-, N,S-*Bis(*s-*triazinyl)-2-aminothiophenols, and* N-*Acyl*-O-s-*triazinyl*-, N,O-*Bis(*s-*triazinyl)-2-aminophenols in the Presence of Alkali.* The compounds listed in Tables 4∼7 are stable in a neutral or acidic solution. However, in the presence of sodium hydroxide some of these compounds give III-I or (III-II) upon the S→N or O→N migration of the *S-* or *O-s*-triazinyl group and the subsequent hydrolytic fission of the acyl group or one of the *s*-triazinyl groups, while *N*-2,4-dinitrophenyl and *N*-*β*-cyanoethyl derivatives of V-I-3 and V-II-3 types fail to give the rearranged products even in the presence of alkali. The results are shown in Table 8.

In the reaction of *N*-acyl derivatives of V-II-2 and (V-II-3) types in the presence of alkali, anions formed by the dissociation of the NH- groups were confirmed to be reactive species, as will be discussed in a subsequent paper;[11] similar reactive species may be assumed in the rearrangement of *N,O*-bis(*s*-triazinyl)-2-aminophenols and the corresponding derivatives of 2-aminothiophenol in the presence of alkali. It has been established, from the results on *N*-substituted *o*-amino sulfides and *o*-amino sulfones,[4a,5] that the proper balance of acidity and nucleophilicity of an attacking group is important for the rearrangement in the presence of alkali. However, in these cases it is assumed that a simple relation between acidity and nucleophilicity does not hold among the compounds used, because there is no similarity in the *N*-substituents. Therefore, it may be better to use as *N-s*-triazinyl groups a series of *N*-substituents of the same kind in order to make clear the importance of the proper balance mentioned above.

From Table 8 it is obvious that a good correlation holds between the substituents in the *N-s*-triazine nucleus ($\sigma_m X+\sigma_m Y$)[12] and the reactivity. Substituents in the *N-s*-triazine nucleus of strong electron-attracting or strong electron-donating substances were not appropriate for the rearrangement; this suggests that the balance between the acidity of the NH- group and the nucleophilicity of the anion is important. The failure of the rearrangement of derivatives containing strong electron-attracting substituents may be attributed to the low nuclepohilic reactivities of their anions, while the derivatives containing strong electron-donating substituents are assumed to be too weakly

11) T. Shiojima, Y. Hashida, and K. Matsui, submitted to this Bulletin.

12) Y. Fukushima, N. Nohara, Y. Hashida, S. Sekiguchi, and K. Matsui, This Bulletin, **44**, 794 (1971). Y. Fukushima, Y. Hashida, and K. Matsui, *Nippon Kagaku Kaishi*, **1972**, 629.

acidic to provide a sufficient concentration of reactive anions under the present reaction conditions.

## Experimental

All the melting points are uncorrected.

The infrared spectra were measured in potassium bromide discs on a Jasco D-301 spectrophotometer. The NMR spectra were recorded on a Varian A-60D spectrometer. The elemental analyses were performed in the Micro-analytical Center of Gunma University.

The identification of the reaction products was performed by means of their NMR and infrared spectra, by elemental analyses, by molecular-weight determinations, by studying the solubility in an alkaline solution, by the color reaction of the -SH or -OH group, and by mixed-melting-point tests with an authentic sample.

*Materials.* S-s-*Triazinyl-2-aminothiophenols (I-1~3).* S-*(4,6-Dimethoxy-s-triazin-2-yl)-2-aminothiophenol (I-1)*: A solution of 2.5 g (0.02 mol) of *o*-aminothiophenol in 10 ml of a 10% sodium hydroxide solution was stirred, drop by drop, into a solution of 3.5 g (0.02 mol) of 2-chloro-4,6-dimethoxy-*s*-triazine in 30 ml of acetone at room temperature. Stirring was continued for 2 hr at 30 °C, and then the solution was poured into 200 ml of ice water. The precipitate was then filtered and dried. IR (KBr) $cm^{-1}$, ($NH_2$) 3440, 3400; (*s*-triazine) 810. NMR ($CDCl_3$), $\delta$ 3.90 (s, 6H), 4.18 (s, 2H), 7.30 (m, 4H).

S-*(4-Dimethylamino-6-methoxy-s-triazin-2-yl)-2-aminothiophenol I-2*: The I-2 compound was prepared in a manner similar to that described above by treating *o*-aminothiophenol with 2,4-dichloro-6-methoxy-*s*-triazine, followed by treatment with dimethylamine. IR (KBr) $cm^{-1}$, ($NH_2$) 3300, 3190; (*s*-triazine) 790. NMR (DMSO-$d_6$), $\delta$ 2.95 (s, 6H), 3.90 (s, 3H), 5.00 (s, 2H), 7.03(m, 4H).

S-[*4,6-Bis(dimethylamino)-s-triazin-2-yl*]-*aminothiophenol (I-3)*: A solution of 5.0 g (0.04 mol) of *o*-aminothiophenol in 20 ml of a 10% sodium hydroxide solution was stirred, drop by drop, into a solution of 8.0 g (0.04 mol) of 2-chloro-4,6-bis(dimethylamino)-*s*-triazine in 30 ml of dioxane; then the mixture was refluxed with stirring for 12 hr and poured into 200 ml of ice water. The oily precipitate was extracted with benzene, the benzene layer was washed with a sodium hydroxide solution and evaporated *in vacuo*, and the residue was collected. IR (KBr) $cm^{-1}$, ($NH_2$), 3400, 3310, (*s*-triazine) 795. NMR (DMSO-$d_6$), $\delta$ 2.95 (s, 12H), 5.20 (s, 2H), 7.00 (m, 4H).

*Rearrangement of I in the Presence of Acid.* A typical run is the case of *S*-(dimethoxy-*s*-triazinyl)-2-aminothiophenol (I-1). To a solution of 0.5 g of I-1 in 100 ml of acetone, we added 3 drops of concd. hydrochloric acid at room temperature. After it had stood for 24 hr at room temperature, the mixture was poured into ice water and neutralized with sodium carbonate; the precipitate thus formed was filtered and dried. IR(KBr) $cm^{-1}$; (NH) 3380. NMR (DMSO-$d_6$), $\delta$ 3.85 (s, 6H), 7.60(m, 4H), 9.65 (s, 1H).

*Reactions of* S-s-*Triazinyl-2-aminothiophenols (I) or* O-s-*Triazinyl-2-aminophenols (II) with Acylating or* s-*Triazinylating Reagents.* Some typical runs are noted below.

*i) Reaction of I-1 with Acetic Anhydride to give* N-*(Acetyl)*-N-*(dimethoxy-s-triazinyl)-2-aminothiopheonl (IV-I-1-1).* To a stirred solution of 2.6 g (0.01 mol) of I-1 and 6 ml of triethylamine in 50 ml of acetone, we added 2.0 g (0.02 mol) of acetic anhydride at room temperature. After it had stood for 5 hr, the mixture was poured into 200 ml of ice water, and the precipitate thus formed was filtered and dried. NMR (DMSO-$d_6$), $\delta$ 2.04 (s, 3H), 3.85 (s, 6H), 7.50 (m, 4H), 9.38 (s, 1H).

*ii) Reaction of I-1 with Benzoyl Chloride to give* N-*(Benzoyl)*-N-*(dimethoxy-s-triazinyl)-2-aminothiophenol (IV-I-1-2).* To a stirred mixture of 2.6 g (0.10 mol) of I-1, 30 ml of acetone, and 1.7 g (0.01 mol) of benzoyl chloride, 12 ml of a 5% sodium hydroxide solution was added, drop by drop, while the reaction mixture was kept at a nearly neutral condition at room temperature. After stirring for 5 hr, the mixture was poured into 200 ml of ice water, and the precipitate thus obtained was filtered and dried. NMR (DMSO-$d_6$), $\delta$ 3.85 (s, 6H), 7.70 (m, 9H), 9.55 (s, 1H).

*iii) Reaction of I-1 with Cyanuric Chloride to give* N-*(Dichloro-s-triazinyl)*-N-*(dimethoxy-s-triazinyl)-2-aminothiophenol (IV-I-1-7).* To a stirred solution of 2.6 g (0.01 mol) of I-1 in 50 ml of acetone, we added 1.8 g (0.01 mol) of cyanuric chloride, a 10 ml portion of a 1 N solution of sodium carbonate was then added, drop by drop, at 0 °C. After it had been stirred for 1 hr, the reaction mixture was poured into 300 ml of ice water, and the precipitate thus formed was filtered and dried. NMR (DMSO-$d_6$), $\delta$ 3.75 (s, 6H), 7.55 (m, 4H), 10.87 (s, 1H).

*iv) Reaction of I-1 with Phenyl Isocyanate to give* N-*(Dimethoxy-s-triazinyl)*-N-*(phenylcarbamoyl)-2-aminothiophenol (IV-I-1-3).* To a stirred solution of 2.6 g (0.01 mol) of I-1 in 100 ml of benzene, we added 1.2 g (0.01 mol) of phenyl isocyanate at room temperature. After it had been stirred for 3 hr, the precipitate thus formed was filtered and dried. NMR (DMSO-$d_6$) $\delta$ 3.83 (s, 6H), 7.35 (m, 9H), 8.23 (s, 1H), 9.35 (s, 1H).

*v) Reaction of II-2 with Phenyl Isocyanate to give* N-*(Phenylcarbamoyl)*-O-*(4-dimethylamino-6-methoxy-s-triazin-2-yl)-2-aminophenol (V-II-2-1).* To a solution of 2.6 g (0.01 mol) of (II-2) in 50 ml of benzene, we added 1.2 g (0.01 mol) of phenyl isocyanate at room temperature. After the mixture had been stirred for 5 hr, the precipitate thus formed was filtered and dried. NMR (DMSO-$d_6$), $\delta$ 3.10 (d, 6H), 3.83 (s, 3H), 7.30 (m, 9H), 8.14 (s, 1H), 9.13 (s, 1H).

*vi) Reaction of II-2 with 2,4-Dichloro-6-methoxy-s-triazine to give* N-*(4-Chloro-6-methoxy-s-triazin-2-yl)*-O-*(4-dimethylamino-6-methoxy-s-triazin-2-yl)-2-aminophenol (V-II-2-6).* To a stirred solution of 2.6 g (0.01 mol) of II-2 and 1.8 g (0.01 mol) of 2,4-dichloro-6-methoxy-*s*-triazine in 100 ml of acetone, we added a solution of 1.0 g (0.012 mol) of sodium bicarbonate in 30 ml of water, drop by drop, at room temperature. After having been stirred for 2 hr, the reaction mixture was poured into 300 ml of ice water; the precipitate thus formed was then filtered and dried. NMR (DMSO-$d_6$), $\delta$ 3.10 (d, 6H), 3.85 (s, 3H), 3.90(s, 3H), 7.40(m, 4H), 10.10(s, 1H).

*vii) Reaction of II-3 with 2,4-Dinitrofluorobenzene to yield* N-*(Dinitrophenyl)*-O-*[4,6-bis(dimethylamino)-s-triazin-2-yl]-2-aminophenol (V-II-3-6).* To a stirred solution of 2.7 g (0.01 mol) of II-3 and 1.0 g (0.01 mol) of triethylamine in 100 ml of benzene, we added 1.8 g (0.01 mol) of 2,4-dinitrofluorobenzene at room temperature. After the mixture had been stirred at room temperature for 8 hr, the benzene was distilled off *in vacuo*; the residue was then washed with water and filtered. NMR (DMSO-$d_6$), $\delta$ 2.99 (s, 12H), 7.40 (m, 7H), 9.91 (s, 1H).

*viii) Reaction of II-3 with Ethyl Chloroformate to give* N-*Ethoxycarbonyl)*-O-*[4,6-bis(dimethylamino)-s-triazin-2-yl]-2-aminophenol (V-II-3-5).* To a mixture of 2.7 g (0.01 mol) (I-3), 1.5 g (0.018 mol) of sodium bicarbonate, and 30 ml of water in 100 ml of acetone, we added a solution of 2.0 g (0.018 mol) of ethyl chloroformate in 50 ml of acetone at room temperature. After having been stirred, for 5 hr at room temperature, the reaction mixture was poured into 500 ml of ice water, and the precipitate thus formed was

filtered and dried. NMR (DMSO-$d_6$), $\delta$ 1.19 (t, 3H), 2.99 (s, 12H), 4.09 (q, 2H), 7.15 (m, 4H), 8.60 (s, 1H).

*Reactions of* N-*(Chloro-*s*-triazinyl)*-S-*(*s*-triazinyl)-2-amino thiophenols and* N-*(Chloro-*s*-triazinyl)*-O-*(*s*-triazinyl)-2-aminophenols with Neucleophiles.* Some typical runs will be shown in the case of *N*-(4,6-dichloro-*s*-triazin-2-yl)-*O*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (V-II-3-8).

*i) Reaction of V-II-3-8 with Dimethylamine to give* N-*(4-Chloro-6-dimethylamino-*s*-triazin-2-yl)*-O-*[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophtnol (V-II-3-12).* To a solution of 2.1 g (0.005 mol) of V-II-3-8 in 100 ml of acetone, we added 1.2 ml (0.01 mol) of a 40% dimethylamine solution at 0 °C. After having been stirred for 3 hr at 0 °C, the reaction mixture was poured into 300 ml of ice water; the precipitate thus formed was then filtered and dried. NMR (DMSO-$d_6$), $\delta$ 2.98 (s, 18H), 7.30(m, 4H), 8.60(s, 1H). When the reaction was carried out using 2.5 ml of a 40% dimethylamine solution at 50 °C, the reaction product was V-II-3-13.

*ii) Reaction of V-II-3-8 with Sodium Methoxide. ii-a) Reaction of V-II-3-8 with Sodium Methoxide in a Molar Ratio of 1 : 1 to give* N-*(4-Chloro-6-methoxy-*s*-triazin-2-yl)*-O-*[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (V-II-3-9).* To a mixture of 2.1 g (0.005 ml) of V-II-3-8 in 100 ml of methanol, we added 5 ml of a 1 N methanolic sodium methoxide solution at 0 °C. After it had stood for 1 night, the reaction mixture was poured into 300 ml of ice water. The precipitate thus formed was filtered and dried. (This compound was also obtained by the condensation of I-3 with 2,4-dichloro-6-methoxy-*s*-triazine). NMR (DMSO-$d_6$), $\delta$ 2.85 (s, 12H), 3.85 (s, 3H), 7.40 (m, 4H), 10.10 (s, 1H).

*ii-b)* When the Above-mentioned reaction was carried out using 15 ml of a sodium methoxide solution, *N*-[4,6-bis-(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (mp 185—186 °C)[1b] (III-II-3) (yield, 95%) and dimethylcyanuric acid[13] (yield, 82%) were obtained. However, in the reaction of V-II-3-8 with sodium methoxide in a molar ratio of 1 : 1.5, two rearranged products were obtained. One was *N*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (yield, 33%), and the other was found to be *N*-(4,6-dimethoxy-*s*-triazin-2-yl)-*N*-[4,6-bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol. (Mp 95—97 °C, recrystallized from cyclohexane), (yield, 36%). Found: C, 52.66; H, 5.83; N, 30.32%. Calcd for $C_{18}H_{23}N_9O_3$: C, 52.29; H, 5.61; N, 30.49%. NMR (DMSO-$d_6$), $\delta$ 2.97 (s, 12H), 3.83 (s, 6H), 7.55 (m, 4H), 8.98 (s, 1H).

*Rearrangement of* N,S-*Bis(*s*-triazinyl)-2-aminothiophenols (V-I) and* N,O-*Bis(*s*-triazinyl)-2-aminophenols (V-II) in the Presence of Sodium Hydroxide.* To a solution of 0.2 g of a *N,S-* or *N,O*-bis(*s*-triazinyl) derivative in 30 ml of acetone, we added 3 ml of a 0.5 N sodium hydroxide solution. After having stood (at room temperature in the case of V-II, and at 60 °C in the case of V-I) the reaction mixture was developed on a silica gel layer, using a mixture of benzene and acetone (6 : 1 by volume) as the developing solvent. From the thin-layer chromatogram thus obtained, the rearranged product was eluted with ethanol and thus identified.

13) A. W. Hofmann, *Ber.*, **19**, 2067 (1886), K. H. Slotta, R. Tschesche, *ibid.*, **60**, 303 (1927).