The $N^1 \rightarrow N^2$ Migration of the *s*-Triazinyl Group of 4-Substituted N^1,N^1-Bis-(*s*-triazinyl)-*o*-phenylenediamines

Kenji NAKAMURA, Noboru NOHARA, and Kohji MATSUI

Department of Chemistry, Faculty of Engineering, Gunma University, Tenjincho, Kiryu, Gunma

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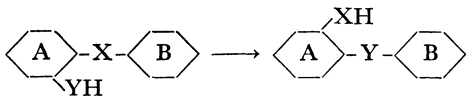
Several 4-substituted N^1-[bis-(diethylamino)-*s*-triazinyl]-N^1-(dimethoxy-*s*-triazinyl)-*o*-phenylenediamines were synthesized, and the migrations of the *s*-triazinyl group were investigated in these compounds. In methanol, every 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine gave only 4-substituted N^1-[bis-(diethylamino)-*s*-triazinyl]-N^2-(dimethoxy-*s*-triazinyl)-*o*-phenylenediamine by the migration of the dimethoxy-*s*-triazinyl group; the rearrangement was assumed to proceed through an intramolecular nucleophilic attack by the *ortho* amino group upon the ring carbon of the dimethoxy-*s*-triazinyl group. However, in the presence of a small amount of acid, the $N^1 \rightarrow N^2$ migration of the bis(diethylamino)-*s*-triazinyl group occurred preferentially, and two kinds of rearranged products were obtained. The kinetics of the rearrangement have also been studied spectrophotometrically in methanol, and the effects of the substituents on the rearrangement have been discussed.

Rearrangements involving intramolecular nucleophilic substitutions as are shown in Eq (1) are well known as Smiles rearrangements:[1]



(1)

(I) (II)

where X=O, S, CO_2, SO_2, *etc.*

YH=–OH, $–NH_2$, $–CONH_2$, –NH–Acyl, and –SH

A=substituted phenyl or other aromatic group

B=substituted phenyl or nitrogen heteroaromatic group

As for the Smiles rearrangement involving aryl migrations between two functional groups of the same kind, several examples of an oxygen-oxygen displacement have been reported.[2]

Recently, $N^1 \rightarrow N^2$ migrations of the aryl group have been observed in the reactions of *N*-phenyl derivatives of *o*-phenylenediamine or hydrazine[3] with alkyllithium and α-bromoacetanilides with amines.[4] However, little is known about the Smiles rearrangement of the nitrogen-nitrogen type. It was, therefore, of interest to study the $N^1 \rightarrow N^2$ migration of an aromatic system with *s*-triazinyl derivatives of *o*-phenylenediamine or other diamines in which the *s*-triazinyl group migrates as an aromatic system. For this purpose, 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamines were found to be suitable substrates; the present work will report the $N^1 \rightarrow N^2$ migration of the *s*-triazinyl group and the effect of substituents on the rearrangement with these compounds.

1) For example, 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. 99; T. Harayama, K. Okada, S. Sekiguchi, and K. Matsui *J. Heterocycl. Chem.*, **7**, 981 (1970).

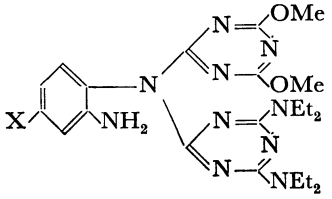
2) J. D. Loudon, J. R. Robertson, J. N. Watson, and S. D. Aiton, *J. Chem. Soc.*, **1950**, 55; J. D. Loudon and J. A. Scott, *ibid.*, **1953**, 265; W. Mayer and H. Csheuermann, *Angew. Chem.*, **71**, 382 (1959).

3) R. West and H. F. Stewart, *J. Amer. Chem. Soc.*, **92**, 853 (1970).

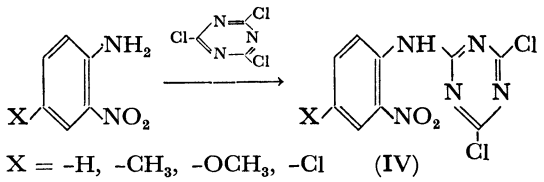
4) N. W. Gilman, P. Levitan, and L. H. Sternbach, *Tetrahedron Lett.*, **1970**, 4121.

Results and Discussion

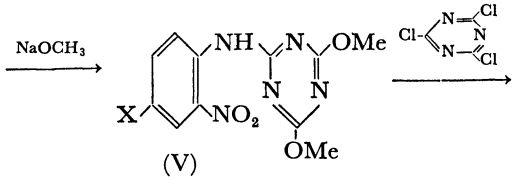
Syntheses of 4-substituted N^1,N^1-bis-(*s*-triazinyl)-*o*-phenylenediamines of the following general formula (III) were synthesized from 4-substituted 2-nitroanilines as follows:



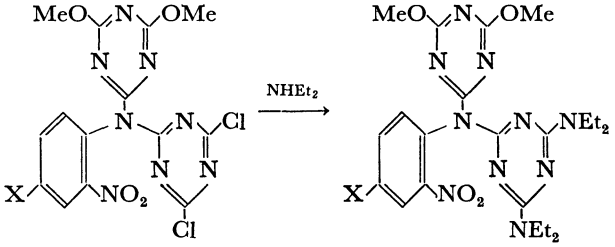
(III) X=-H, $-CH_3$, $-OCH_3$, -Cl



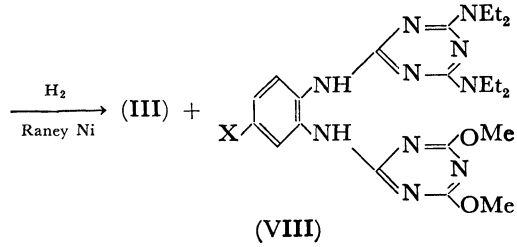
X = -H, $-CH_3$, $-OCH_3$, -Cl (IV)



(V)



(VI) (VII)



(VIII)

TABLE 1. 2-ARYLAMINO-4,6-DICHLORO-*s*-TRIAZINES (IV)

No.	Aryl	Yield (%)	Mp (°C)	Recrystn. solvent	Anal. (%) Found C	Found H	Calcd C	Calcd H
IV-1	2-Nitrophenyl-	70	196.5—197[a)]	Benzene	——		——	
IV-2	4-Methyl-2-nitrophenyl-	71	173—174	Benzene	40.35	2.46	39.98	2.33
IV-3	4-Methoxy-2-nitrophenyl-	95	168—168.5	Benzene	38.45	2.41	37.99	2.23
IV-4	4-Chloro-2-nitrophenyl-	88	144.5—146	Beuzene	33.65	1.39	33.72	1.25

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

TABLE 2. 2-ARYLAMINO-4,6-DIMETHOXY-*s*-TRIAZINES (V)

No.	Aryl	Yield (%)	Mp (°C)	Recrystn. solvent	Anal. (%) Found C	Found H	Calcd C	Calcd H
V-1	2-Nitrophenyl-	Quant.	174—176[a)]	Benzene	——		——	
V-2	4-Methyl-2-nitrophenyl-	Quant.	188—188.5	Benzene	49.29	4.27	49.46	4.46
V-3	4-Methoxy-2-nitrophenyl-	Quant.	192—193	Benzene	47.35	4.57	46.91	4.26
V-4	4-Chloro-2-nitrophenyl-	Quant.	207—207.5	Benzene	41.87	3.20	42.38	3.23

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

TABLE 3. *N*-(4,6-DICHLORO-*s*-TRIAZIN-2-YL)-*N*-(4,6-DIMETHOXY-*s*-TRIAZIN-2-YL)-ARYLAMINES (VI)

No.	Aryl	Yield (%)	Mp (°C)	Recrystn. Solvent		Anal. (%) Found	Calcd
VI-1	2-Nitrophenyl-	94	164.5—166.5[a)]	Chloroform		—	—
VI-2	4-Methyl-2-nitrophenyl-	74	155—156	Ligroin–Benzene	C	40.80	41.01
					H	2.90	2.75
VI-3	4-Methoxy-2-nitrophenyl-	70	158—159	Ligroin–Benzene	C	39.98	39.57
					H	2.93	2.65
					N	24.57	24.61
VI-4	4-Chloro-2-nitrophenyl-	76	165.5—166.5	Ligroin–Benzene	C	37.01	36.58
					H	2.02	1.97

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

TABLE 4. *N*-[4,6-BIS(DIETHYLAMINO)-*s*-TRIAZIN-2-YL]-*N*-(4,6-DIMETHOXY-*s*-TRIAZIN-2-YL)-ARYLAMINES (VII)

No.	Aryl	Yield (%)	Mp (°C)	Recrystn. solvent		Anal. (%) Found	Calcd
VII-1	2-Nitrophenyl-	—	115—116	Methanol	C	53.25	53.00
					H	6.47	6.07
					N	28.35	28.15
VII-2	4-Methyl-2-nitrophenyl-	71	104—105	Methanol	C	53.65	53.89
					H	6.23	6.29
VII-3	4-Methoxy-2-nitrophenyl-	85	115.5—116.5	Methanol	C	52.47	52.26
					H	6.07	6.10
VII-4	4-Chloro-2-nitrophenyl-	76	89— 91	Methanol	C	49.13	49.58
					H	5.69	5.48
					N	26.27	26.19

4-Substituted 2-nitroanilines were converted with cyanuric chloride into 2,4-dichloro-6-(4-substituted 2-nitrophenylamino)-*s*-triazines (IV), which, with sodium methoxide, then gave 2,4-dimethoxy-6-(4-substituted 2-nitrophenylamino)-*s*-triazines (V). The substances (V) were converted with cyanuric chloride into 4-substituted *N*-(4,6-dichloro-*s*-triazin-2-yl)-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-nitroanilines(VI), which, with diethylamine, then gave 4-substituted *N*-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-nitroanilines (VII); 4-substituted N^1-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-N^1-(4,6-dimethoxy-*s*-triazin-2-yl)-*o*-phenylenediamines (III) were obtained by the hydrogenation of VII, using

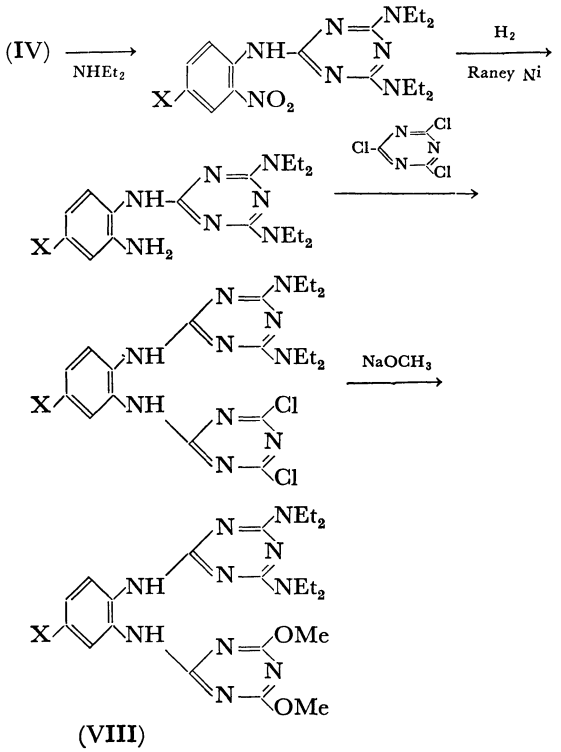
Table 5. 4-Substituted N^1-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-N^1-(4,6-dimethoxy-*s*-triazin-2-yl)-*o*-phenylenediamines (III)

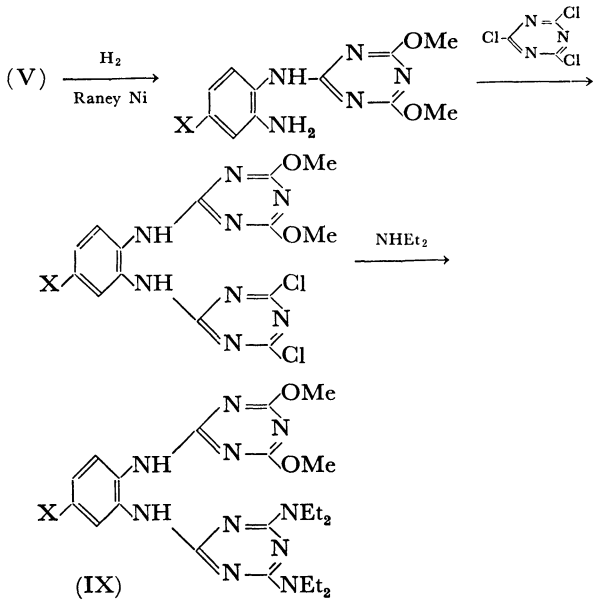
No.	Substituent	Yield (%)	Mp (°C)	Recrystn. Solvent	Anal. (%) Found C	Found H	Calcd C	Calcd H
III-1	H	98	141.5—142.5	Ligroin	56.60	6.98	56.51	6.68
III-2	CH_3-	85	100—101	Petroleum ether	57.31	7.22	57.24	7.10
III-3	CH_3O-	94	124—125	Ligroin	54.99	6.86	55.40	6.87
III-4	Cl-	88	113—114	Petroleum ether	51.94	6.12	52.53	6.21

Raney nickel as the catalyst. However, in the case of every hydrogenated product, the presence of N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamine (VIII), which is assumed to be produced by a rearrangement of preformed N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine (III), was observed. The formation of N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamine (VIII) during the hydrogenation shows that the rearrangement of N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine (III) occurred fairly readily.

The intermediates IV, V, VI, VII, and N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamines (III) thus obtained are listed in Tables 1, 2, 3, 4, and 5.

Rearrangement of N^1,N^1-*Bis(*s*-triazinyl)-*o*-phenylenediamines.* Because of the presence of two different *s*-triazinyl groups in these 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamines (III), it is assumed that each compound may rearrange to give two kinds of 4-substituted N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamines, depending upon whether the migrating group is the dimethoxy-*s*-triazinyl or bis(diethylamino)-*s*-triazinyl group. Authentic samples of these rearranged compounds were synthesized from IV or V as follows:





The N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamines (VIII and IX) thus obtained are listed in Tables 6 and 7.

In preliminary experiments, it was found that the compounds III are stable in such aprotic solvents as benzene, cyclohexane, carbon tetrachloride, and acetone, but that they rearrange to give N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamines (VIII) in methanol and ethanol, and somewhat more readily in the presence of sodium hydroxide in these protic solvents, as will be described kinetically later. However, an intermolecular reaction between III-1 and aniline to give 2,4-dimethoxy-6-anilino-*s*-triazine or 2,4-bis(diethylamino)-6-anilino-*s*-triazine did not take place. Moreover, *N*-[bis(diethylamino)-*s*-triazinyl]-*N*-(dimethoxy-*s*-triazinyl)-2-nitroaniline (VII-1), whose *s*-triazinyl groups are expected to be more reactive towards a nucleophilic reagent than those of III-1 because of the presence of a nitro group, did not react with aniline or *p*-anisidine under similar reaction conditions. From these results, it is obvious that the rearrangement of N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine (III) is intramolecular.

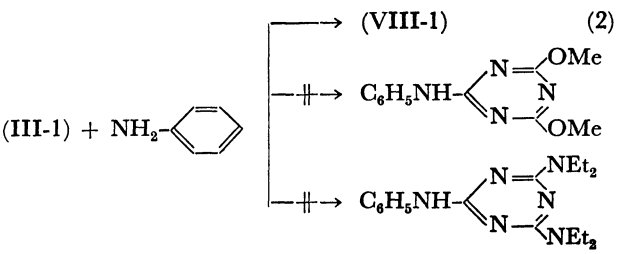
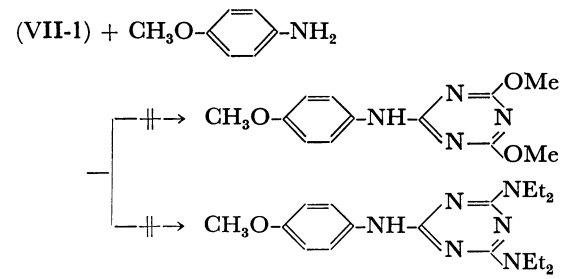


TABLE 6. 4-SUBSTITUTED N^1-[4,6-BIS(DIETHYLAMINO)-*s*-TRIAZIN-2-YL]-N^2-(4,6-DIMETHOXY-*s*-TRIAZIN-2-YL)-*o*-PHENYLENEDIAMINES (VIII)

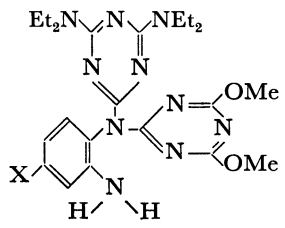
No.	Substituent	Mp (°C)	Recrystn. Solvent	Anal. (%) Found C	Found H	Calcd C	Calcd H
VIII-1	H	127.5—128.5	Methanol	56.43	7.05	56.51	6.68
VIII-2	CH_3-	155—155.5	Methanol	57.45	7.13	57.24	7.10
VIII-3	CH_3O-	106—107	Methanol	55.19	7.04	55.40	6.87
VIII-4	Cl-	161—162	Methanol	52.76	6.11	52.53	6.21

TABLE 7. 4-SUBSTITUTED N^1-(4,6-DIMETHOXY-*s*-TRIAZIN-2-YL)-N^2-[4,6-BIS(DIETHYLAMINO)-*s*-TRIAZIN-2-YL]-*o*-PHENYLENEDIAMINES (IX)

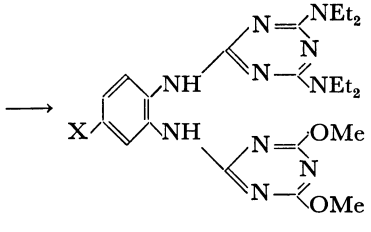
No.	Substituent	Mp (°C)	Recrystn. Solvent	Anal. (%)	Found	Calcd
IX-2	CH_3-	130—131	Methanol	C	57.03	57.24
				H	7.22	7.10
				N	29.13	29.02
IX-3	CH_3O-	103.5—104.5	Methanol	C	54.99	55.40
				H	6.97	6.87
				N	28.01	28.09
IX-4	Cl-	140—141	Methanol	C	53.00	52.53
				H	6.71	6.21
				N	27.54	27.85



When 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine was heated in methanol in either the presence or absence of sodium hydroxide, only one kind of 4-substituted N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamine was obtained, regardless of the substituent in the 4-position; in every case the rearranged product was proved to be 4-substituted N^1-[bis(diethylamino)-*s*-triazinyl]-N^2-(dimethoxy-*s*-triazinyl)-*o*-phenylenediamine (VIII) by a mixed-melting-point test with an authentic sample. These results show that, in these 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamines, a migration of the dimethoxy-*s*-triazinyl group occurs under these reaction conditions.



(III)



(VIII)

X = -H, -CH_3, -OCH_3, -Cl

Effects of Substituents on the Rearrangement of 4-Substituted N^1,N^1-*bis(s-triazinyl)-o-phenylenediamines.* Table 8 lists the yields of the rearranged products of several 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamines when they are heated at 50°C for 50 hrs in methanol in the presence of a small amount of sodium hydroxide. From these figures, it is apparent that the facility of the rearrangement varies with the substituent according to the following order:

$$H > CH_3 > Cl > OCH_3$$

TABLE 8. YIELDS OF REARRANGED PRODUCTS OF 4-SUBSTITUTED N^1-[4,6-BIS(DIETHYLAMINO)-*s*-TRIAZIN-2-YL]-N^1-(4,6-DIMETHOXY-*s*-TRIAZIN-2-YL)-*o*-PHENYLENEDIAMINES (III) IN METHANOL IN THE PRESENCE OF SODIUM HYDROXIDE (50°C)

Substituent	H	CH_3	Cl	CH_3O
Yield (%)	53	48	25	21

As has been described above, the compounds III gave 4-substituted N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamines in alcohols. In methanol, both N^1,N^1-bis(*s*-triazinyl)- and N^1,N^2-bis(*s*-triazinyl)-*o*-phenylenediamines have absorption maxima at about 270 nm, but in every case the molar extinction coefficient of the original substance is much smaller than that of the rearranged product, as Table 9 shows. Therefore, the absorption in this region increases with the progress of the rearrangement, and the rate of the rearrangement can be measured spectrophotometrically. Since a plot of $-\log (D_\infty - D_t)/(D_\infty - D_0)$ against the reaction time, t, was found to give a straight line, as is shown in Fig. 1, the first-order rate constant for the rearrangement can be calculated using Eq. 6. (See Experimental section). Table 10 lists the first-order rate constants

TABLE 9. MOLAR EXTINCTION COEFFICIENTS OF 4-SUBSTITUTED N^1-[BIS-(DIETHYLAMINO)-*s*-TRIAZINYL]-N^1-(DIMETHOXY-*s*-TRIAZINYL)-*o*-PHENYLENEDIAMINES (III) AND 4-SUBSTITUTED N^1-[BIS(DIETHYLAMINO)-*s*-TRIAZINYL]-N^2-(DIMETHOXY-*s*-TRIAZINYL)-*o*-PHENYLENEDIAMINES (VIII) AT 270 nm

III			VIII		
No.	Substituent	ε at 270 nm	No.	Substituent	ε at 270 nm
III-1	H-	7340	VIII-1	H-	23700
III-2	CH_3-	7160	VIII-2	CH_3-	22400
III-3	CH_3O	7120	VIII-3	CH_3O-	21000
III-4	Cl-	8200	VIII-4	Cl-	18700

Solvent; methanol

TABLE 10. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REARRANGEMENT OF 4-SUBSTITUTED N^1,N^1-BIS(*s*-TRIAZINYL)-*o*-PHENYLENEDIAMINES (III) IN METHANOL

No.	Substituent	Rate constant (min^{-1})			Activation parameter	
		40°C	45°C	50°C	E (kcal/mol)	$\Delta S^{\neq}$ (e. u.)
III-1	H-	1.36×10^{-4}	2.08×10^{-4}	2.78×10^{-4}	15.0	−38.4 (40°C)
III-2	CH_3-	9.08×10^{-5}	1.41×10^{-4}	1.88×10^{-4}	15.0	−39.2 (40°C)
III-3	CH_3O-	1.49×10^{-5}	——	——	——	——
III-4	Cl-	2.36×10^{-5}	——	——	——	——

The rate constants and activation parameters for the rearrangement of 4-substituted *O*-(dimethoxy-*s*-triazinyl)-2-aminophenols in methanol are as follows.[a)]

Substituent	Rate constant (min^{-1})			Activation parameters	
	20°C	30°C	40°C	E (kcal/mol)	$\Delta S^{\neq}$ (e. u.)
H	1.43×10^{-3}	3.30×10^{-3}	6.50×10^{-3}	14.0	−34.0 (40°C)
4-CH_3	5.24×10^{-4}	1.27×10^{-3}	2.72×10^{-3}	15.5	−31.0 (40°C)

a) See Ref. 5.

TABLE 11. EFFECT OF SODIUM METHOXIDE ON THE RATE OF THE REARRANGEMENT OF N^1-[BIS(DIETHYLAMINO)-*s*-TRIAZINYL]-N^1-(DIMETHOXY-*s*-TRIAZINYL)-*o*-PHENYLENEDIAMINE IN METHANOL (40°C)

Solvent	Rate constant (min^{-1})
Methanol	1.36×10^{-4}
Methanol-water (96.2 : 3.8 by volume)	1.34×10^{-4}
CH_3ONa methanolic solution (1.5×10^{-3} mol/*l*)	2.42×10^{-4}

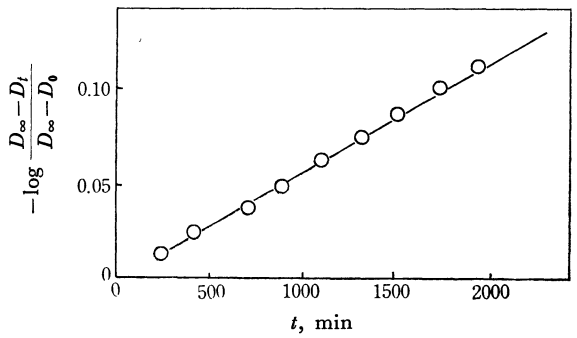


Fig. 1. First-order rate plot for the rearrangement of N^1-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-N^1-(4,6-dimethoxy-*s*-triazin-2-yl)-*o*-phenylenediamine (III-1) in methanol at 40°C.

and activation parameters for the rearrangements of III in methanol. From a comparison of these figures with those of the rearrangement of 4-substituted *O*-(dimethoxy-*s*-triazinyl)-2-aminophenols,[5)] it is apparent that these reactions proceed somewhat more slowly than those of the corresponding 4-substituted *O*-(dimethoxy-*s*-triazinyl)-2-aminophenols in methanol. However, *O*-(*s*-triazinyl)-2-aminophenols are also stable in aprotic solvents and rearrange readily in protic solvents, and the rearrangement is catalyzed by bases[6)] in a manner similar to that in the case of III. As an example, a catalytic effect of sodium methoxide on the rearrangement of III-1 in methanol is shown in Table 11. Moreover, both these reactions are intramolecular, and the activation energies and activation entropies of the rearrangements of III in methanol are close in magnitude to those of the rearrangement of *O*-(*s*-triazinyl)-2-aminophenols. Therefore, it may be assumed that the process of the rearrangement of N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenedi-

5) N. Maeno, T. Itagaki, S. Uno, and K. Matsui, submitted to This Bulletin.

6) T. Shiojima, Y. Hashida, and K. Matsui, details will be published elsewhere.

amines is very similar to that of *O*-(*s*-triazinyl)-2-aminophenols, involving an intramolecular nucleophilic attack by the *ortho* amino group upon the ring carbon of one of the *N*-*s*-triazinyl groups.

It can be seen from Table 10 that the substituents in N^1,N^1-(bis-*s*-triazinyl)-*o*-phenylenediamines affect the progress of the rearrangement to a great extent, but the effect of substituents differs according to the nature and the position of substituents. With respect to the substituents in the triazine nucleus, it is expected that an electron-withdrawing substituent will favor the nucleophilic attack by the amino group by lowering the electron density of triazine carbon atoms. In the cases studied, the dimethoxy-*s*-triazinyl group is anticipated to be more reactive towards nucleophiles than the bis(diethylamino)-*s*-triazinyl group. In fact, the formation of VIII from III indicates that, under the reaction conditions described above, the nucleophilic attack by the *ortho* amino group takes place preferentially upon the more electron-deficient ring carbon of the dimethoxy-*s*-triazinyl group.

Although it is still uncertain whether this migration proceeds by the S_N2 mechanism or by the intermediate-complex mechanism, the effect of a substituent in the *o*-phenylenediamine moiety may be considered from two points of view. One is the influence of the substituent upon the nucleophilic reactivity of the attacking amino group, and the other is the influence upon the reactivity of the migrating triazine nucleus through the nitrogen atom or the stability of the leaving amide anion. In the former, an electron-releasing effect of a substituent favors the rearrangement, while an electron-attracting effect favors the latter. In the cases studied, the position of the substituent was *meta* to the free amino and *para* to the bis-*s*-triazinylamino group, and it can be assumed that the more the σ_m value of a substituent becomes negative, and the more the σ_p value becomes positive, the more readily does the rearrangement occur. Therefore, the Hammett equation for reactions like this rearrangement may be expressed by Eq. (4), which consists of a sum of two terms:[7]

$$\log k/k_0 = \sigma_p\rho + \sigma_m\rho' \qquad (\rho \neq \rho') \qquad (4)$$

where the reaction constants ρ and ρ' are attributable to the effect of a substituent on the reactivity of the migrating triazine ring or on the stability of the leaving amide anion, and to the effect of a substituent on the nucleophilicity of the amino group, respectively. Using the rate constants at 40°C and the Hammett substituent constants, the ρ and ρ' values calculated by the method of least squares were found to be:

$$\rho = 2.20, \qquad \rho' = -3.35$$

respectively; the ratio ρ'/ρ was −1.52, and a Hammett plot of log k_1 against $\sigma_p - 1.52\,\sigma_m$ gave a straight line, with a correlation coefficient of 0.993, as is shown in Fig. 2.

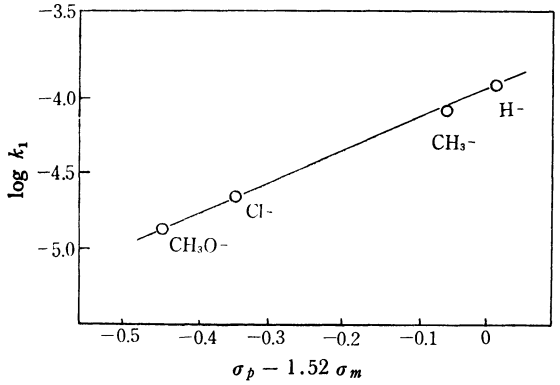


Fig. 2. Plot of log k_1 against $(\sigma_p - 1.52\,\sigma_m)$ for the rearrangement of 4-substituted N^1,N^1-Bis-(*s*-triazinyl)-*o*-phenylenediamines (III) in methanol. (40°C).

Thus, in this reaction, it became clear that, by using Eq. (4) instead of the usual Hammett equation, involving only one term, a good linear relationship is obtained between the substituent constants and the logarithm of the rate constants. These figures show that, in the rearrangement of 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamines (III), the substituent affects the nucleophilic reactivity of the the free amino group more than the stability of the leaving amide anion or the reactivity of the triazinyl group.

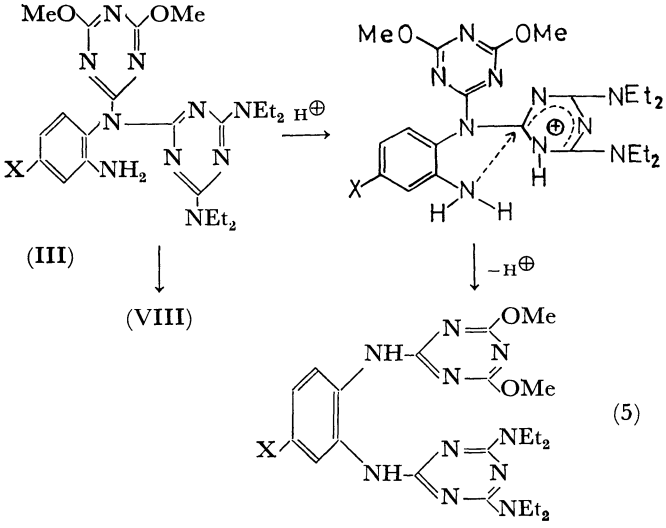
Rearrangement of N¹,N¹-*Bis(s-triazinyl)-o-phenylenediamines in the Presence of Acid.* As has been mentioned in the preceding paragraph, 4-substituted N^1 - [bis(diethylamino) - *s* - triazinyl] - N^1 - (dimethoxy-*s*-triazinyl)-*o*-phenylenediamines (III) gave, in methanol, only 4-substituted N^1-[bis(diethylamino)-*s*-triazinyl]-N^2-(dimethoxy-*s*-triazinyl)-*o*-phenylenediamines (VIII). In the presence of sodium hydroxide, the rearrangement was found to proceed more readily, as has been described above, but the compound VIII was the only product obtained in this case. However, in methanol in the presence of a small amount of hydrochloric acid (5×10^{-3} mol/*l*), 4-substituted N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine (III) (7×10^{-3} mol/*l*) gave two kinds of rearranged products, regardless of the substituent in the 4-position. One was 4-substituted N^1-[bis(diethylamino)-*s*-triazinyl]-N^2-(dimethoxy-*s*-triazinyl)-*o*-phenylenediamine (VIII), while the other was proved to be 4-substituted N^1-(dimethoxy-*s*-triazinyl)-N^2-[bis(diethylamino)-*s*-triazinyl]-*o*-phenylenediamine (IX), which is obviously produced by the migration of the bis(diethylamino)-triazinyl group. Under the present reaction conditions, the ratios of the yields of the two isomers (IX/VIII) were found to vary depending upon the substituentt in the 4-position; they were 1.1 when the substituent was the methoxyl group and 1.7 when the substituent was chlorine. Thus, in every case the major product was a compound of the IX type. These results indicate that the presence of acid accelerates the migration of the bis(diethylamino)-*s*-triazinyl group, and it can be assumed that the predominant rearrangement of the bis(diethylamino)-*s*-triazinyl group proceeds as follows. The initial stage of this reaction is a preferential lowering of the electron density of ring carbon atoms of the bis-diethylamino-*s*-triazinyl group by a protonation at the ring nitrogen atom[8] of this

7) J. Tirouflet, *Bull. Soc. Chim. Fr.*, **1954**, 769.

8) G. Morimoto, *Nippon Kagaku Zasshi*, **87**, 790 (1966), T. Tashiro and M. Yasuda, *Kobunshi Kagaku*, **26**, 853 (1969).

more basic *s*-triazine nucleus; the next step of the reaction is a nucleophilic attack by the *ortho* amino group upon the ring carbon of the activated triazine nucleus by protonation. A compound of the VIII type is anticipated to be produced by a non-catalytic process under the reaction conditions described above.

A study concerning the influences of solvents and bases on the rearrangement is in progress; it will be reported in the near future.



Experimental

All the melting points are uncorrected.

The ultraviolet spectra were recorded on a Hitachi-124 UV-VIS 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.

Materials. *2-Arylamino-4,6-dichloro-s-triazines (IV)*: 2-Arylamino-4,6-dichloro-*s*-triazines were prepared by treating 4-substituted 2-nitroanilines with cyanuric chloride, as has been described in the case of 2-(*o*-carbomethoxyanilino)-4,6-dichloro-*s*-triazine.[9]

2-Arylamino-4,6-dimethoxy-s-triazines (V): 2-Arylamino-4,6-dimethoxy-*s*-triazines were prepared by treating 2-arylamino-4,6-dichloro-*s*-triazines with sodium methoxide in methanol, as has been described in the case of 2,4-dimethoxy-6-(2-nitroanilino)-*s*-triazine (V-1).[9]

N-(4,6-Dichloro-s-triazin-2-yl)-N-(4,6-dimethoxy-s-triazin-2-yl)-arylamines (VI): These compounds were prepared by treating 2-arylamino-4,6-dimethoxy-*s*-triazines (V) with cyanuric chloride under conditions similar to those used in the preparation of *N,N*-bis(4,6-dichloro-*s*-triazin-2-yl)-arylamines[9] from IV.

N-[4,6-Bis(diethylamino)-s-triazin-2-yl]-N-(4,6-dimethoxy-2-s-triazin-2-yl)-arylamines (VII): A typical preparation is shown below in the case of *N*-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-4-methoxy-2-nitroaniline (VII-3). A solution of 8.8 g (0.12 mol) of diethylamine in 50 m*l* of acetone was stirred drop by drop into a solution of 13.7 g (0.03 mol) of *N*-(4,6-dichloro-*s*-triazin-2-yl)-*N*-(4,6-dimethoxy-*s*-triazin-2-yl)-4-methoxynitroaniline (VI-3) in 200 m*l* of acetone at 0—5°C. Stirring was continued for 8 hr at 35—40°C, and then the mixture was refluxed for 2 hr and poured into 500 m*l* of ice-water. The oily precipitate was extracted with chloroform and the chloroform layer was dried and evaporated and the residue was collected (VII-3).

4-Substituted N¹-[4,6-bis(diethylamino)-s-triazin-2-yl]-N¹-(4,6-dimethoxy-s-triazin-2-yl)-o-phenylenediamines (III): A typical run is noted in the case of N^1-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-N^1-(4,6-dimethoxy-*s*-triazin-2-yl)-4-chloro-*o*-phenylenediamine (III-4). A mixture containing 30 m*l* of dioxane, 5.4 g (0.01 mol) of VII-4, and 3 g of Raney nickel was stirred for 5 hr at room temperature under a pressure of 100 kg/cm² of hydrogen. After the catalyst had then been removed by filtration, the solution was poured into 500 m*l* of ice water. The precipitate was then filtered and dried. The recrystallization of the product from benzene-ligroin gave 3.5 g (88%) of III-4. NMR (DMSO-d_6) δ 1.10 (t, 12H), 3.48 (q, 8H), 3.80 (s, 6H), 5.24 (s, 2H), 6.84 (m, 3H).

4-Substituted N¹-[4,6-bis(diethylamino)-s-triazin-2-yl]-N²-(4,6-dimethoxy-s-triazin-2-yl)-o-phenylenediamines (VIII). *i)* *N¹-[4,6-Bis(diethylamino)-s-triazin-2-yl]-N²-(4,6-dimethoxy-s-triazin-2-yl)-o-phenylenediamine (VIII-1)*. A mixture containing 5.6 g (0.02 mol) of V-1, 40 m*l* of dioxane, and 3 g of Raney nickel was stirred for 7 hr at 50°C under a pressure of 60 kg/cm² of hydrogen. The mixture was processed according to the procedure for III-4 to give 4.8 g (97%) of crude *N*-(4,6-dimethoxy-*s*-triazin-2-yl)-*o*-phenylenediamine. Recrystallization from benzene gave an analytical sample. Mp 150—151°C. Found: C, 53.72; H, 5.20%. Calcd for $C_{11}H_{13}N_5O_2$: C, 53.43; H, 5.30%.

Compound VIII-1 was prepared by treating the *N*-(4,6-dimethoxy-*s*-triazin-2-yl)-*o*-phenylenediamine thus obtained with cyanuric chloride, followed by treatment with diethylamine according to the procedures used in the preparation of VII-3. Recrystallization from methanol gave an analytical sample. Mp 127.5—128.5°C. NMR (DMSO-d_6) δ 1.09 (t, 12H), 3.51 (q, 8H), 3.83 (s, 6H), 7.48 (m, 4H), 8.31 (s, 1H), 9.66 (s, 1H).

ii) *N¹-[4,6-Bis(diethylamino)-s-triazin-2-yl]-N²-(4,6-dimethoxy-s-triazin-2-yl)-4-methyl-o-phenylenediamine (VIII-2)*. Compound VIII-2 was prepared in a manner similar to that to be described below, the preparation of VIII-3 from IV-2 without any purification of the intermediates. Mp 155—155.5°C. NMR (DMSO-d_6), δ 1.10 (t, 12H), 2.31 (s, 3H), 3.52 (q, 8H), 3.87 (s, 6H), 7.29 (m, 3H), 8.31 (s, 1H), 9.60 (s, 1H).

iii) *N¹-[4,6-Bis(diethylamino)-s-triazin-2-yl]-N²-(4,6-dimethoxy-s-triazin-2-yl)-4-methoxy-o-phenylenediamine (VIII-3)*. 2,4-Bis(diethylamino)-6-(4-methoxy-2-nitroanilino)-*s*-triazine obtained by treating IV-3 with an excess of diethylamine [mp 95.5—96°C (ethanol), Found: C, 55.54; H, 7.32%. Calcd for $C_{18}H_{27}N_7O_3$: C, 55.51; H, 6.98%] was hydrogenated in dioxane in the presence of Raney nickel. The resulting oily product [crude 2,4-bis(diethylamino)-6-(2-amino-4-methoxyanilino)-*s*-triazine] was treated with cyanuric chloride and then with sodium methoxide in methanol. Recrystallization from methanol gave an analytical sample of VIII-3. Mp 106—107°C, NMR (DMSO-d_6) δ 1.08 (t, 12H), 3.50 (q, 8H), 3.76 (s, 3H), 3.87 (s, 6H), 7.15 (m, 3H), 8.32 (s, 1H), 9.58 (s, 1H).

iv) *N¹-[4,6-Bis(diethylamino)-s-triazin-2-yl]-N²-(4,6-dimethoxy-s-triazin-2-yl)-4-chloro-o-phenylenediamine (VIII-4)*. 2,4-Bis(diethylamino)-6-(4-chloro-2-nitroanilino)-*s*-triazine obtained by treating IV-4 with an excess of diethylamine in acetone [mp 128—129°C (benzene) Found: C, 51.50; H, 5.80%, Calcd for $C_{17}H_{24}ClN_7O_2$: C, 51.84: H, 6.14%] was hydrogenated in dioxane in the presence of Raney nickel to give 2,4-bis(diethylamino)-6-(2-amino-4-chloroanilino)-

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

s-triazine [mp 122—122.5°C (methanol)]. Found: C, 55.80; H, 7.02%. Calcd for $C_{17}H_{26}ClN_7$: C, 56.11; H, 7.20%.

The 2,4-bis(diethylamino)-6-(2-amino-4-chloroanilino)-*s*-triazine thus obtained was treated with cyanuric chloride and then with sodium methoxide in methanol. The recrystallization of the reaction product from methanol gave an analytical sample of VIII-4; mp 161—162°C. NMR (DMSO-d_6)δ 1.09 (t, 12H), 3.51 (q, 8H), 3.86 (s, 6H), 7.33 (m, 3H), 8.41 (s, 1H), 9.70 (S, 1H).

4-Substituted N¹-*(4,6-Dimethoxy-*s*-triazin-2-yl)*-N²-*[4,6-bis-(diethylamino)-*s*-triazin-2-yl]-*o*-phenlyenediamines (IX).* A typical run, that in the case of N^1-(4,6-dimethoxy-*s*-triazin-2-yl)-N^2-[4,6-bis(diethylamino)-*s*-triazin-2-yl]-4-methyl-*o*-phenylenediamine (IX-2), will be described. A mixture containing 3.5 g (0.012 mol) of V-2, 30 m*l* of dioxane, and 3 g of Raney nickel was stirred for 5hr at 60—70°C under a pressure of 100 kg/cm² of hydrogen. After the catalyst had then been removed by filtration, the solution was evaporated *in vacuo*. The residue was, without purification, treated with cyanuric chloride and then with diethylamine. The subsequent recrystallization of the product from methanol gave an analytical sample of IX-2. Mp 130—131°C. NMR (DMSO-d_6),δ 1.12 (t, 12H), 2.30 (s, 3H), 3.49 (q, 8H), 3.85 (s, 6H), 7.29 (m, 3H), 8.18 (s, 1H), 9.56 (s, 1H).

Identification and Quantitative Determination of Rearranged Products. A typical example is shown below in the case of III-3. A solution of III-3 in methanol (0.1009 g/30 m*l* $=2\times10^{-4}$ mol/30 m*l*) containing a small amount of sodium hydroxide (1×10^{-4} mol/30 m*l*) was warmed for 20 hr at 50°C. To the mixture, 0.0498 g (2.89×10^{-4} mol) of 4-chloro-2-nitroaniline was added as an internal standard, after which the mixture was developed on a silica-gel layer, using a mixture of benzene and acetone (40 : 3 by volume) as the developing solvent. From the thin-layer chromatogram thus obtained, the original substance, a rearranged product, and the internal standard were eluted with ethanol separately and afterward diluted to a constant volume, the concentration of each solution being determined by measuring the absorbance at 280 nm (original substance), 270 nm (rearranged product), and 410 nm (4-chloro-2-nitroaniline). The rearranged product was identified by a mixed-melting-point test with an authenitc sample after the rearranged product had been separated from the original and other substances by tlc and purified by recrystallization.

Kinetic Measurements. The kinetic measurements were carried out spectrophotometrically by measuring the increase in the absorbance at 270 nm of a methanolic solution of III (*ca.* 10^{-4} mol/l) at 40, 45, and 50°C; the first-order rate constant for the rearrangement was calculated using Eq. 6:

$$k_1 = -2.303\,\frac{1}{t}\log\frac{D_\infty - D_t}{D_\infty - D_0} \qquad (6)$$

where D_0=initial optical density of a solution of N^1,N^1-bis(*s*-triazinyl)-*o*-phenylenediamine (III) in methanol.

D_t=optical density of a solution at time t.

D_∞=optical density of a solution at an infinite time.