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Effects of Substituents on the Smiles Rearrangement of *O-s*-Triazinyl-2-aminophenols

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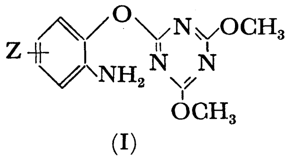
Several 4- or 5-substituted *O*-(*s*-triazinyl)-2-aminophenols were synthesized, and the kinetics of the Smiles rearrangement of these compounds have been studied spectrophotometrically in methanol, ethanol, and 2-propanol in order to make clear the effects of substituents on the rearrangement. Substituents in the *s*-triazine nucleus were found to affect the progress of the reaction to a great extent by changing the positive character of the triazine-ring carbon. On the other hand, a substituent in the aminophenol moiety affects both the nucleophilic reactivity of the attacking amino group and the stability of the leaving phenoxide anion or the reactivity of the *s*-triazinyl group, but the effect on the amino group was found to be predominant, the effect of a substituent in the aminophenol moiety was smaller than that of the substituents in the *s*-triazine nucleus.

In previous papers[1] we reported that *O*-*s*-triazinyl-2-aminophenols rearrange under various conditions, especially readily in the presence of acid, to give *N*-*s*-triazinyl-2-aminophenols. The migration of the triazinyl group was thought to proceed through an intramolecular nucleophilic attack by the amino group on the ring carbon of an *s*-triazinyl group, and substituents in *O*-*s*-triazinyl-2-aminophenol were found to affect the progress of the reaction to a great extent. The electronic effects of substituents on the Smiles rearrangement have already been studied, especially with the derivatives of *O*-nitrophenyl-2-aminophenols.[2] However, these studies have been limited to qualitative discussions and the details of the substituent effects have not been made clear. Therefore, it was of interest to study quantitatively the electronic effects of substituents upon the Smiles rearrangement with *O*-*s*-triazinyl-2-aminophenols.

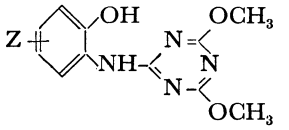
In preliminary experiments, it was found that solvents affect the progress of the rearrangement. *O*-*s*-Triazinyl-2-aminophenols are stable in aprotic solvents, such as cyclohexane, benzene, carbon tetrachloride, butyl ether, and acetone, but most of the *O*-*s*-triazinyl-2-aminophenols were found to rearrange readily to give *N*-*s*-triazinyl-2-aminophenols in protic solvents, such as water and lower alcohols. This paper will report the effects of substituents on the rearrangement with *O*-*s*-triazinyl-2-aminophenols in methanol, ethanol, and 2-propanol.

Results and Discussion

Syntheses of O-s-*triazinyl-2-aminophenols and* N-s-*triazinyl-2-aminophenols.* *O*-*s*-Triazinyl-2-aminophenols and *N*-*s*-triazinyl-2-aminophenols of the following general formulas—(I), (II), (III), and (IV)—were prepared according to Schemes 1 and 2:

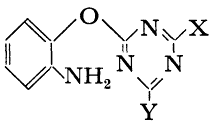


(I)

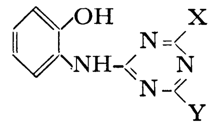


(III)

Z=H, 4-CH_3, 4-Cl, 4-OCH_3, 4-$COCH_3$, 5-CH_3, 5-Cl, 5-OCH_3

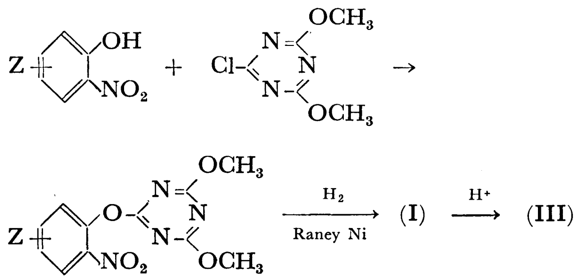


(II)



(IV)

(II-1), (IV-1), X=OCH_3, Y=$N(CH_3)_2$
(II-2), (IV-2), X=Y=$N(CH_3)_2$
(II-3), (IV-3), X=C_6H_5, Y=$N(CH_3)_2$
(II-4), (IV-4), X=NH_2, Y=OCH_3



Scheme 1.

The compounds (I) were prepared by the condensation of *o*-nitrophenol or substituted *o*-nitrophenols with chloro-dimethoxy-*s*-triazine, followed by catalytic hydrogenation in the presence of Raney nickel. On the other hand, *o*-nitrophenol was converted with 2,4-dichloro-6-methoxy-*s*-triazine or cyanuric chloride into 2-chloro-4-methoxy-6-(2-nitrophenoxy)-*s*-trizine or 2,4-dichloro-6-(2-nitrophenoxy)-*s*-triazine, which, with dimethylamine or ammonia, gave 2-dimethylamino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine, 2-amino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine, or 2,4-bis(dimethylamino)-6-(2-nitrophenoxy)-*s*-triazine. Compounds (II-1), (II-4), and (II-2) were obtained by the hydrogenation of 2-dimethylamino-4-methoxy-6-(2-ni-

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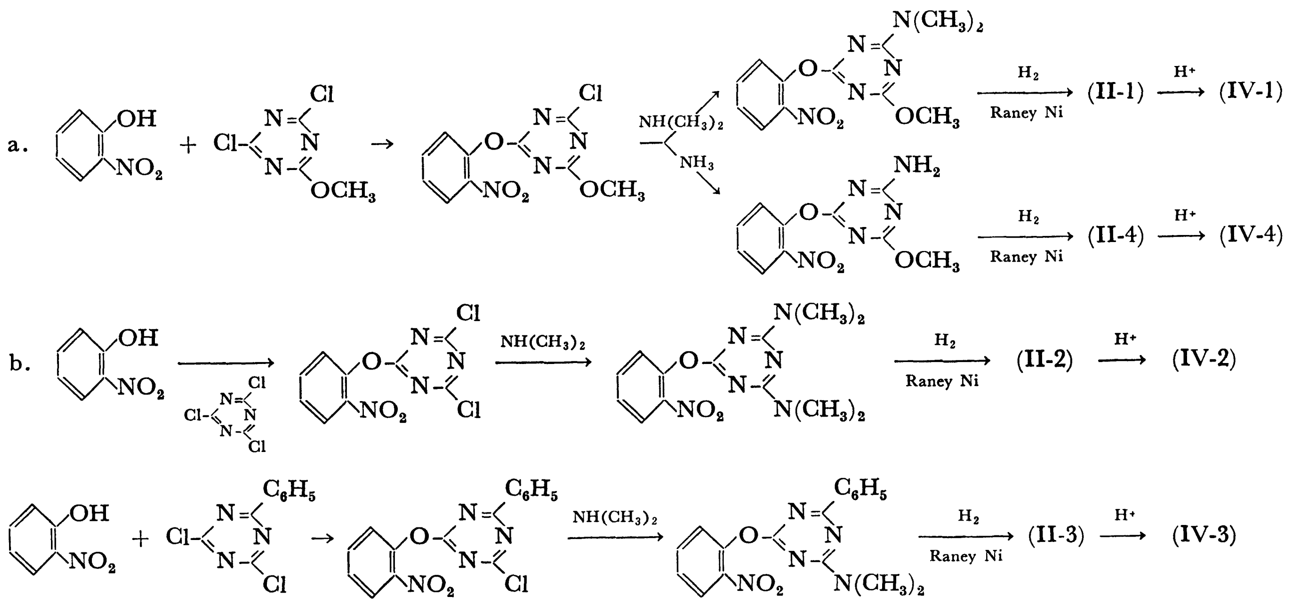
[1] T. Harayama, K. Okada, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 981 (1970); K. Matsui, N. Maeno, S. Suzuki, H. Shizuka and T. Morita, *Tetrahedron Lett.*, **1970**, 1467.

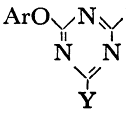
[2] W. E. Truce, E. M. Kreider and W. W. Brand, "The Smiles and Related Rearrangements of Aromatic Systems," Organic Reactions Vol. 18, p. 117 John Wiley & Sons, Inc. (1970); J. Bunnett, R. E. Zahler, *Chem. Rev.*, **49**, 362 (1951). A. A. Levi and S. Smiles, *J. Chem. Soc.*, **1932**, 1488; F. Galbraith and S. Smiles, *ibid.*, **1935**, 1234, B. A. Kent and S. Smiles, *ibid.*, **1934**, 422; W. J. Evans and S. Smiles, *ibid.*, **1935**, 181; K. C. Roberts et al., *ibid.*, **1935**, 196, K. C. Roberts and C. G. M. DeWorms, *ibid.*, **1935**, 1309; K. C. Roberts, J. A. Phys., *ibid.*, **1937**, 39; G. Pappalardo, *Gazz. Chim. Ital.*, **90**, 645 (1960).

trophenoxy)-*s*-triazine, 2-amino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine, and 2,4-bis(dimethylamino)-6-(2-nitrophenoxy)-*s*-triazine using Raney nickel as the catalyst. Compound (II–3) was obtained in a similar manner from *o*-nitrophenol and 2,4-dichloro-6-phenyl-*s*-triazine. The rearranged products of the general formulas of (III) and (IV) were obtained by treating the corresponding *O*-*s*-triazinyl-2-aminophenols with diluted hydrochloric acid. The intermediates, *O*-*s*-triazinyl-2-aminophenols and *N*-*s*-triazinyl-2-aminophenols, thus obtained are listed in Tables 1, 2, and 3.



Scheme 2.

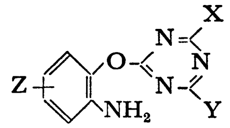
TABLE 1. ARYLOXY-*s*-TRIAZINES,



Ar	X	Y	Yield, %	Mp, °C	Solvent for recrystallization	Analysis, %		
							Found	Calcd
2-Nitrophenyl	-OCH_3	-OCH_3	88	137.5—138.5[a]	Benzene-Ligroin		—	—
4-Methyl-2-nitrophenyl	-OCH_3	-OCH_3	88	114.5[a]	Benzene-Ligroin		—	—
4-Methoxy-2-nitrophenyl	-OCH_3	-OCH_3	Quant.	120	Benzene-Ligroin	C H N	47.18 4.23 17.91	46.76 3.92 18.17
4-Chloro-2-nitrophenyl	-OCH_3	-OCH_3	77	119—120[a]	Benzene-Ligroin		—	—
4-Acetyl-2-nitrophenyl	-OCH_3	-OCH_3	50	122	Benzene-Ligroin	C H N	49.27 4.02 17.41	48.76 3.78 17.33
5-Methyl-2-nitrophenyl	-OCH_3	-OCH_3	Quant.	127—128	Benzene-Ligroin	C H N	50.00 4.50 19.17	49.32 4.14 19.23
5-Methoxy-2-nitrophenyl	-OCH_3	-OCH_3	Quant.	129	Benzene-Ligroin	C H N	47.22 4.18 18.07	46.76 3.92 18.17
5-Chloro-2-nitrophenyl	-OCH_3	-OCH_3	Quant.	123—124	Benzene-Ligroin	C H N	42.12 3.22 18.10	42.26 2.90 17.92
2-Nitrophenyl	-OCH_3	-$N(CH_3)_2$	Quant.	119.5—120.5	Benzene-Ligroin	C H	49.67 4.65	49.48 4.49
2-Nitrophenyl	-$N(CH_3)_2$	-$N(CH_3)_2$	88	169—170	Benzene-Ligroin	C H	51.30 5.20	51.31 5.29
2-Nitrophenyl	-C_6H_5	-$N(CH_3)_2$	Quant.	193—195	Benzene-Ligroin	C H	60.55 4.61	60.53 4.48
2-Nitrophenyl	-OCH_3	-NH_2	72	179—181	Benzene	C H	45.88 3.62	45.63 3.45

a) T. Harayama, K. Okada, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 981 (1970).

TABLE 2. *O*-*s*-TRIAZINYL-2-AMINOPHENOLS



Compound	X	Y	Z	Yield, %	Mp, °C	Solvent for recrystallization	Analysis, %	Found	Calcd
I-1	$-OCH_3$	$-OCH_3$	-H	60	91—92[a]	Petroleum ether		—	—
I-2	$-OCH_3$	$-OCH_3$	$4-CH_3$	89	123—124[a]	Benzene		—	—
I-3	$-OCH_3$	$-OCH_3$	$4-OCH_3$	69	121—122	Benzene	C H N	51.32 5.29 20.24	51.79 5.71 20.13
I-4	$-OCH_3$	$-OCH_3$	4-Cl	94	154—155[b]	Benzene		—	—
I-5	$-OCH_3$	$-OCH_3$	$4-COCH_3$	70	155	Benzene	C H N	53.75 5.10 19.44	53.79 4.86 19.30
I-6	$-OCH_3$	$-OCH_3$	$5-CH_3$	78	136—137	Benzene-Ligroin	C H N	54.88 5.22 20.84	54.96 5.38 21.36
I-7	$-OCH_3$	$-OCH_3$	$5-OCH_3$	43	137	Benzene-Ligroin	C H N	52.31 5.20 20.40	51.79 5.71 20.13
I-8	$-OCH_3$	$-OCH_3$	5-Cl	75	132	Benzene-Ligroin	C H N	46.41 4.08 20.17	46.74 3.92 19.81
II-1	$-OCH_3$	$-N(CH_3)_2$	-H	54	104—105	Benzene-Ligroin	C H	55.24 5.92	55.16 5.78
II-2	$-N(CH_3)_2$	$-N(CH_3)_2$	-H	75	134—135	Petroleum-ether-Benzene	C H	56.60 6.58	56.92 6.61
II-3	$-C_6H_5$	$-N(CH_3)_2$	-H	88	149—150	Benzene-Ligroin	C H	66.25 5.74	66.43 5.57
II-4	$-NH_2$	$-OCH_3$	-H	53	185—186	Benzene	C H	51.77 5.15	51.50 4.75

a) T. Harayama, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 975 (1970).
b) T. Harayama, K. Okada, S. Sekiguchi, and K. Matsui, *ibid.*, **7**, 981 (1970).

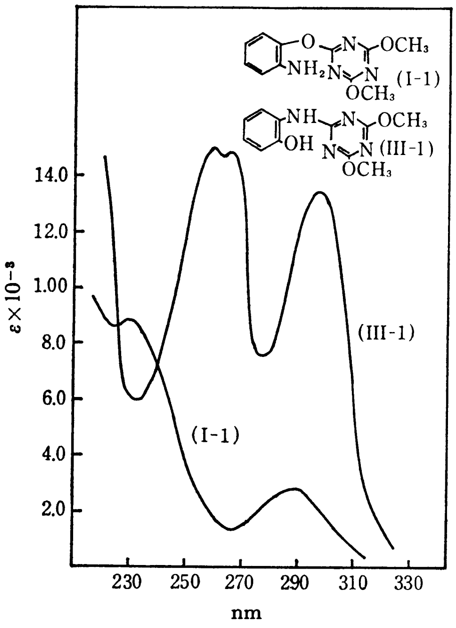


Fig. 1. Absorption spectra of *O*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminophenol (I-1) and *N*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminophenol (III-1) in methanol

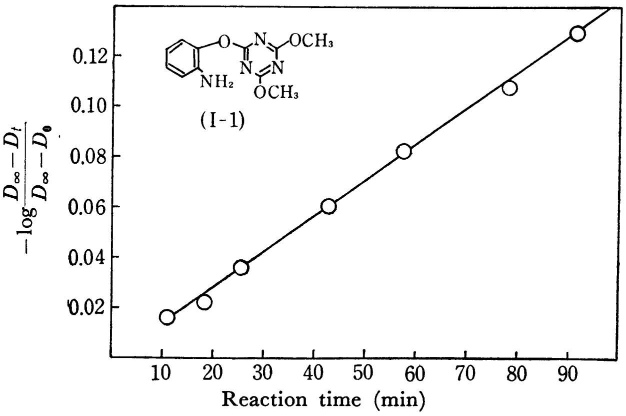
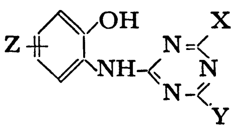


Fig. 2. The first order plot for the rearrangement of *O*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminophenol (I-1) in methanol at 30°C.

Rates of the Rearrangement of O-s-*triazinyl-2-aminophenols.* Both *O*-*s*-triazinyl-2-aminophenols and *N*-*s*-triazinyl-2-aminophenols have absorption maxima in the region from 290 to 310 nm, but in every case the molar extinction coefficient of the original compound is much smaller than that of the rearranged product, as is shown in Table 4 and Fig. 1. Therefore, the absorption in this region increases with the progress

TABLE 3. *N*-*s*-TRIAZINYL-2-AMINOPHENOLS,



Compound	X	Y	Z	Mp, °C	Solvent for crystallization	Analysis %	Found	Calcd
III-1	$-OCH_3$	$-OCH_3$	$-H$	172—173[a]	Benzene		—	—
III-2	$-OCH_3$	$-OCH_3$	$4-CH_3$	179—180[b]	Methanol		—	—
III-3	$-OCH_3$	$-OCH_3$	$4-OCH_3$	205	Methanol	C H N	52.04 5.56 20.46	51.79 5.71 20.13
III-4	$-OCH_3$	$-OCH_3$	4-Cl	211—212[b] (decomp.)	Methanol		—	—
III-5	$-OCH_3$	$-OCH_3$	$4-COCH_3$	178	Methanol	C H	53.25 5.30	53.79 4.86
III-6	$-OCH_3$	$-OCH_3$	$5-CH_3$	182—183	Methanol	C H	55.28 5.66	54.96 5.38
III-7	$-OCH_3$	$-OCH_3$	$5-OCH_3$	189	Methanol	C H N	51.79 5.64 20.23	51.79 5.71 20.13
III-8	$-OCH_3$	$-OCH_3$	5-Cl	210	Methanol	C H N	47.16 4.18 20.03	46.74 3.92 19.81
IV-1	$-OCH_3$	$-N(CH_3)_2$	$-H$	213—214	Ethanol	C H	55.27 5.89	55.16 5.78
IV-2	$-N(CH_3)_2$	$-N(CH_3)_2$	$-H$	185—186	Ethanol	C H	56.83 6.69	56.92 6.61
IV-3	$-C_6H_5$	$-N(CH_3)_2$	$-H$	159—160	Benzene-Ligroin	C H	66.56 5.66	66.43 5.57
IV-4	$-NH_2$	$-OCH_3$	$-H$	204—205	2-Propanol	C H	50.95 4.63	51.50 4.75

a) T. Harayama, S. Sekiguchi, and K. Matsui, *J. Heterocycl. Chem.*, **7**, 975 (1970).
b) T. Harayama, K. Okada, S. Sekiguchi and K. Matsui, *ibid.* **7**, 981 (1970).

TABLE 4. MOLAR EXTINCTION COEFFICIENTS OF *O*-*s*-TRIAZINYL-2-AMINOPHENOLS AND *N*-*s*-TRIAZINYL-2-AMINOPHENOLS IN ETHANOL

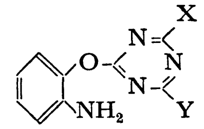
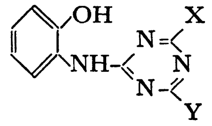
							
X	Y	λ_{max} (nm)	ε	X	Y	λ_{max} (nm)	ε
$-OCH_3$	$-OCH_3$	287	2400	$-OCH_3$	$-OCH_3$	295	13400
$-OCH_3$	$-N(CH_3)_2$	287	2800	$-OCH_3$	$-N(CH_3)_2$	292	12600
$-N(CH_3)_2$	$-N(CH_3)_2$	286	2900	$-N(CH_3)_2$	$-N(CH_3)_2$	290	11900

TABLE 5. RATE CONSTANTS FOR THE REARRANGEMENT OF *O*-*s*-TRIAZINYL-2-AMINOPHENOLS IN METHANOL

Compound	k_1 (min^{-1})					
	10°C	20°C	30°C	40°C	50°C	60°C
I-1	6.03×10^{-4}	1.43×10^{-3}	3.30×10^{-3}	6.50×10^{-3}	—	—
I-2	1.91×10^{-4}	5.24×10^{-4}	1.27×10^{-3}	2.72×10^{-3}	—	—
I-4	6.92×10^{-5}	1.83×10^{-4}	5.62×10^{-4}	1.26×10^{-3}	—	—
II-1	—	—	2.33×10^{-5}	5.85×10^{-5}	1.33×10^{-4}	2.91×10^{-4}
II-2*	—	—	—	—	—	—
II-3	—	—	1.08×10^{-5}	—	—	—
II-4	—	—	1.17×10^{-4}	—	—	—

* Rate constant was too slow to measure.

TABLE 6. RATE CONSTANTS FOR THE REARRANGEMENT OF *O*-*s*-TRIAZINYL-2-AMINOPHENOLS IN 2-PROPANOL

Compound	k_1 (min^{-1})					
	10°C	20°C	30°C	40°C	50°C	60°C
I-1	1.85×10^{-4}	5.21×10^{-4}	1.18×10^{-3}	2.36×10^{-3}	—	—
1-2	—	1.53×10^{-4}	3.85×10^{-4}	9.06×10^{-4}	1.89×10^{-3}	—
I-4	—	9.06×10^{-5}	2.29×10^{-4}	5.53×10^{-4}	1.31×10^{-3}	—
II-1	—	—	5.67×10^{-6}	1.38×10^{-5}	3.59×10^{-5}	9.66×10^{-5}

TABLE 7. ACTIVATION PARAMETERS FOR THE REARRANGEMENT OF *O*-*s*-TRIAZINYL-2-AMINOPHENOLS

Compound	2-PrOH		MeOH	
	E (kcal/mol)	$\Delta S^{\neq}$ (e.u.) (40°C)	E (kcal/mol)	$\Delta S^{\neq}$ (e.u.) (40°C)
I-1	15.4	−31.6	14.0	−34.0
I-2	16.5	−29.9	15.5	−31.0
1-4	17.4	−28.0	16.7	−28.7
II-1	19.0	−30.3	16.8	−34.4

of the rearrangement, and the rates of the rearrangement of *O*-*s*-triazinyl-2-aminophenols can be measured spectrophotometrically. For example, a plot of $-\log (D_\infty - D_t)/(D_\infty - D_0)$ against the reaction time, t, for the rearrangement of (I–1) in methanol gave a straight line, as is shown in Fig. 2.

Accordingly, the first-order rate constant for the rearrangement can be calculated using Eq. (1):

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

where D_0=initial optical density of a solution of *O*-*s*-triazinyl-2-aminophenol.
D_t=optical density of a solution at time t.
D_∞=optical density of a solution at an infinite time.

In Table 5 are listed the first-order rate constants for the rearrangements of (I–1), (I–2), (I–4), (II–1), (II–2), (II–3), and (II–4) at 10, 20, 40, 50, and 60°C in methanol, while in Table 6 are listed those in 2-propanol; the energies and entropies of activation thus obtained are listed in Table 7. Table 8 compares the rate constants of these compounds in methanol, ethanol, and 2-propanol.

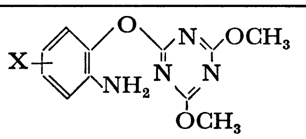
As is shown in Table 8, the rate of the rearrangement varied with the dielectric constant of the alcohol used, and in methanol the rearrangement took place most rapidly. However, no simple relation between the dielectric constant of the solvent and the rate constant has been observed. On the other hand, from a comparison of the rate constants, activation energies, and activation entropies in methanol and 2-propanol, it is apparent that, in the rearrangement of *O*-*s*-triazinyl-2-aminophenols, in spite of the counteracting change in the entropy of activation, the change in the activation energy dominates the rate change. These results can be explained as follows:[3] because the transition state of the reaction may be assumed to be more polar than the initial state, in a more polar solvent the rearrangement can be expected to proceed more rapidly by lowering activation energy under the formation of a stronger solvated transition state than in a less polar solvent.

TABLE 8. EFFECT OF SOLVENT ON THE RATE CONSTANT AT 30°C

Compound	k_1(min^{-1})		
	MeOH	EtOH	2-PrOH
I-1	3.30×10^{-3}	2.22×10^{-3}	1.18×10^{-3}
I-2	1.27×10^{-3}	7.22×10^{-4}	3.85×10^{-4}
I-4	5.62×10^{-4}	3.91×10^{-4}	2.29×10^{-4}
II-1	2.33×10^{-5}	1.49×10^{-5}	5.67×10^{-6}

Effects of Substituents on the Rearrangement. In Table 9, the rate constants for the rearrangement of 4- or 5-substituted *O*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminophenols in methanol at 20°C are listed. From Tables 5 and 9, it is apparent that the substituents in *O*-*s*-triazinyl-2-aminophenol affect the rate of the rearrangement to a great extent, and that the effects

TABLE 9. RATE CONSTANTS FOR THE REARRANGEMENT OF SUBSTITUTED *O*-(4,6-DIMETHOXY-*s*-TRIAZIN-2-YL)-2-AMINOPHENOLS IN METHANOL AT 20°C



Compound	Substituent X	k_1 (min^{-1})
I-1	H	1.43×10^{-3}
I-2	4-CH$_3$	5.24×10^{-4}
I-3	4-OCH$_3$	1.02×10^{-4}
I-4	4-Cl	1.83×10^{-4}
I-5	4-COCH$_3$	1.05×10^{-2}
I-6	5-CH$_3$	3.23×10^{-3}
I-7	5-OCH$_3$	2.43×10^{-2}
I-8	5-Cl	2.69×10^{-3}

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[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press. Itaca and London 2nd ed (1969) p. 457.

of substituents differ according to the nature and the position of substituents. The effect of the substituents in the triazine nucleus may become clear from a comparison of the rate constants of (I-1), (II-1), (II-2), (II-3), and (II-4). Although the rate of the rearrangement of (II-2) in methanol was too slow to measure, the facility of the rearrangement was found to vary in the following order:

$$\text{II-2} \ll \text{II-3} < \text{II-1} < \text{II-4} < \text{I-1}$$

In *s*-triazine compounds, it was found that the Hammett σ_m values of the benzene series are applicable in studying the effects of substituents and that the total effect of two substituents in the *s*-triazine ring on the reaction center is given by the summation of the two substituent constants, $\sum\sigma_m$.[4] Therefore, the sensitivity of the rearrangement towards the substituents in a triazine ring can be evaluated by a reaction constant which is calculated from the rate constants of (I-1), (II-1), (II-3), and (II-4) using the respective $\sum\sigma_m$ values. In the case studied, the reaction constant (ρ) thus obtained was 6.43, with a correlation coefficient of 0.987. As will be described later, this ρ value is considerably larger than those of the reactions attributable to the substituent in the aminophenol moiety.

Although it is yet uncertain whether this migration proceeds by the S_N2 mechanism or by the intermediate-complex mechanism, the effect of a substituent in the aminophenol moiety may reasonably be considered in view of the following two points: the influence of the substituent upon the nucleophilic reactivity of the attacking amino group, and the influence upon the reactivity of the migrating *s*-triazinyl group towards the amino group (the positive character of the ring carbon of the *s*-triazine nucleus) or the stability of the leaving phenoxide anion. In the former, an electron-releasing effect of a substituent favors the rearrangement, while an electron-attracting effect is favored in the latter. Therefore, the Hammett equation for reactions like this rearrangement may be expressed by Eq. 2, which consists of a sum of two terms.[5]

$$\log k/k_0 = \sigma\rho' + \sigma\rho'' \qquad (2)$$

where the reaction constants, ρ' and ρ'', are attributable to the effect of a substituent on the reactivity of the migrating triazine nucleus through the -O- bridge or the stability of the leaving phenoxide anion and the effect of a substituent on the nucleophilicity of the amino group respectively.

Using the rate constants (in the case of 4-COCH$_3$, the σ^- value was used), the ρ' and ρ'' values calculated by the method of least squares were:

$$\rho' = 2.86; \qquad \rho'' = -4.15$$

respectively, and the ρ''/ρ' ratio was -1.45. A Hammett plot of $\log k_1$ against $\sigma_m - 1.45\sigma_p$ when a substituent is in the 5-position or $\sigma_p - 1.45\sigma_m$ when a substituent is in the 4-position gave a straight line, with a correlation coefficient of 0.990, as is shown in Fig. 3.

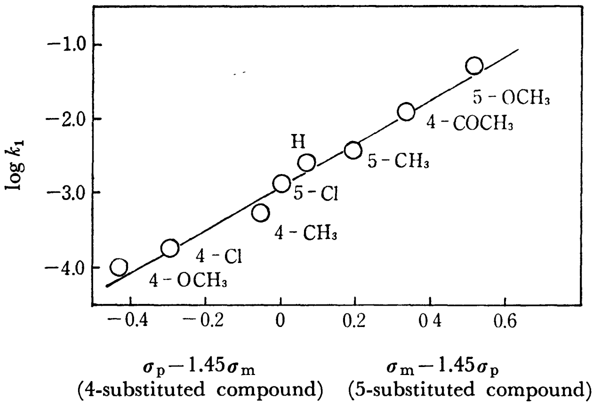

Fig. 3. Hammett plot for the rearrangement of 4- or 5-substituted *O*-(4,6-dimethoxy-*s*-triazin-2-yl)-2-aminophenols in methanol (20°C).

However, a linear relation between the substituent constants and log k_1 was not obtained by using a usual Hammett equation, involving only one term.

Therefore, a substituent in the 5-position affects the nucleophilic reactivity of the attacking amino group as a *para*-substituent and, simultaneously, the reactivity of the migrating *O*-*s*-triazinyl group as a *meta*-substituent. Such a situation holds for a substituent in the 4-position. As a result, the logarithm of the rate constants apparently depends upon a composite effect of these two. These results indicate that, in 4- or 5-substituted *O*-*s*-triazinyl-2-aminophenols, a substituent in the aminophenol moiety affects the nucleophilic reactivity of the free amino group more effectively than the reactivity of the *s*-triazinyl group or to stability of the leaving phenoxide anion. Moreover, as has been described previously, it has become apparent from a comparison of the value of ρ with those of ρ' and ρ'' that, in the Smiles rearrangement of *O*-*s*-triazinyl-2-aminophenols, the effect of the substituents in the *s*-triazine nucleus is larger than that of a substituent in the aminophenol moiety.

Experimental

All the melting points are uncorrected. The ultraviolet spectra were recorded on a Hitachi-124 UV-VIS spectrophotometer. The elemental analyses were performed in the Micro-analytical Center of the Gunma University.

Materials. *Aryloxy-4,6-dimethoxy-s-triazines*: A typical preparation is the case of 2,4-dimethoxy-6-(4-methoxy-2-nitrophenoxy)-*s*-triazine. Into a solution of 4.1 g (0.024 mol) of 2-nitro-4-methoxyphenol and 1.2 g(0.03 mol) of sodium hydroxide in 40 m*l* of acetone, we stirred, drop by drop, a solution of 5.0 g (0.028 mol) of 2-chloro-4,6-dimethoxy-*s*-triazine in 50 m*l* of acetone. After an additional 24 hrs' stirring at 40°C, the mixture was poured into 500 m*l* of ice water, filtered, and dried.

4- or 5-Substituted O-(4,6-dimethoxy-s-triazin-2-yl)-2-aminophenols (I). A typical run is shown in the case of *O*-(4,6-dimethoxy-*s*-triazin-2-yl)-4-methoxy-2-aminophenol. A mixture containing 50 m*l* of dioxane, 5.0 g (0.016 mol) of 2,4-dimethoxy-6-(4-methoxy-2-nitrophenoxy)-*s*-triazine, and 3 g of Raney nickel was stirred for 2 hr at room temperature under a pressure of 60 kg/cm^2 of hydrogen. After the

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[4] Y. Fukushima, N. Nohara, Y. Hashida, S. Sekiguchi, and K. Matsui, This Bulletin, **44**, 794 (1971).

[5] J. Tirouflet, *Bull. Soc. Chem. Fr.*, **1954**, 769.

catalyst had then been removed by filtration, the solution was poured into 500 m*l* of ice water containing a small amount of sodium hydroxide. The precipitate was filtered, washed with water, and dried.

O-*(4-Dimethylamino-6-methoxy-*s*-triazin-2-yl)-2-aminophenol (II-1).* *i) 2-Chloro-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine*: A solution of 139 g (1.0 mol) of *o*-nitrophenol and 45 g (1.1 mol) of sodium hydroxide in 500 m*l* of water was stirred, drop by drop, over 3-hr period and at 0—5°C, into a solution of 180 g (1.0 mol) of 2,4-dichloro-6-methoxy-*s*-triazine in 1 *l* of acetone. After an additional 2 hrs' stirring at room temperature, the mixture was poured into 2 *l* of ice water. The precipitate was then filtered and dried to give 270 g (quantitative) of crude 2-chloro-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine (mp 116—120°C). Recrystallization from benzene-ligroin gave an analytical sample; mp 122—123°C.

Found: C, 42.29; H, 2.47%; Calcd for $C_{10}H_7ClN_4O_4$: C, 42.49; H, 2.47%.

*ii) 2-Dimethylamino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine*: Into a solution of 230 g (0.84 mol) of 2-chloro-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine in 1 *l* of acetone, we stirred 190 m*l* of a 40% dimethylamine solution (1.7 mol) drop by drop over a 2-hr period at 10°C. Stirring was continued for 5 hr at 40°C; then the mixture was refluxed for 3 hr and poured into 2 *l* of ice water. The precipitate was filtered and dried to give 226 g (quantitative) of crude 2-dimethylamino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine; mp (116—120°C). Recrystallization from benzene-ligroin gave an analytical sample.

iii) O-*(4-Dimethylamino-6-methoxy-*s*-triazin-2-yl)-2-aminophenol (II-1)*: This was obtained in a 54% yield by the hydrogenation of 2-dimethylamino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine in dioxane in the presence of Raney nickel. Recrystallization from benzene-ligroin gave an analytical sample; mp 104—105°C.

O-*[4,6-Bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (II-1).* *i) 2,4-Dichloro-6-(2-nitrophenoxy)-*s*-triazine*: This compound was obtained in a 94% yield by the condensation of *o*-nitrophenol with cyanuric chloride in the presence of sodium hydroxide in acetone at 0—5°C. Recrystallization from benzene-ligroin gave an analytical sample; mp 136—137°C.

Found: C, 37.93; H, 1.51%; Calcd for $C_9H_4Cl_2N_4O_3$: C, 37.65; H, 1.40%.

*ii) 2,4-Bis(dimethylamino)-6-(2-nitrophenoxy)-*s*-triazine*: Into a solution of 75 g (0.26 mol) of 2,4-dichloro-6-(2-nitrophenoxy)-*s*-triazine in 300 ml of acetone, we stirred 130 ml of a 40% dimethylamine solution drop by drop over a 2-hr period at 10°C. The mixture was then processed according to the procedure used for 2-dimethylamino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine. Yield, 99%. Recrystallization from benzene-ligroin gave an analytical sample; mp 169—170°C.

iii) O-*[4,6-Bis(dimethylamino)-*s*-triazin-2-yl]-2-aminophenol (II-2)*: The compound (II-2) was obtained in a 75% yield by the catalytic reduction of 2,4-bis(dimethylamino)-6-(2-nitrophenoxy)-*s*-triazine, using Raney nickel as the catalyst in dioxane. Recrystallization from benzene gave an analytical sample of (II-2); mp 134—135°C.

O-*(4-Dimethylamino-6-phenyl-*s*-triazin-2-yl)-2-aminophenol (II-3).* 2-Chloro-4-phenyl-6-(2-nitrophenoxy)-*s*-triazine was obtained by treating *o*-nitrophenol with 2,4-dichloro-6-phenyl-*s*-triazine in acetone in the presence of sodium hydroxide; mp 152—153°C (benzene-ligroin)

Found: C, 54.75; H, 3.07%; Calcd for $C_{15}H_9ClN_4O_3$; C, 54.81; H, 2.76%.

it was then condensed with dimethylamine in acetone to give 2-dimethylamino-4-phenyl-6-(2-nitrophenoxy)-*s*-triazine; mp 193—195°C (benzene-ligroin). The compound (II-3) was obtained in an 88% yield by the catalytic hydrogenation of 2-dimethylamino-4-phenyl-6-(2-nitrophenoxy)-*s*-triazine in dioxane, using Raney nickel as the catalyst. Mp 149—150°C (benzene-ligroin).

O-*(4-Amino-6-methoxy-*s*-triazin-2-yl-2-aminophenol (II-4).* 2-Amino-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine obtained by treating 2-chloro-4-methoxy-6-(2-nitrophenoxy)-*s*-triazine with ammonia in acetone [mp 179—181°C (benzene)] was hydrogenated using Raney nickel as the catalyst in dioxane. Recrystallization from benzene then gave an analytical sample of (II-4); mp 185—186°C.

N-*(*s*-Triazinyl)-2-aminophenols (III, IV).* A typical run is the case of (IV-1). To a solution of 1.0 g (II-1) in 50 m*l* of acetone we added one drop of concentrated hydrochloric acid at room temperature, and then the mixture was stirred for 12 hr. After the mixture had been poured into 200 m*l* of ice water, the precipitate was filtered and dried to give 0.9 g of crude (IV-1) (mp 213—214°C).

Kinetic Measurements. Kinetic measurements were carried out spectrophotometrically by measuring the increase in the absorbance at 280—310 nm of an alcoholic solution of *O*-*s*-triazinyl-2-aminophenol at 10, 20, 30, 40, 50, and 60°C; the first-order rate constant for the rearrangement was calculated using Eq. 1.