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THE PHOTOCHEMICAL REACTIONS OF SOME ARYLOXY-*s*-TRIAZINES IN SOLUTION

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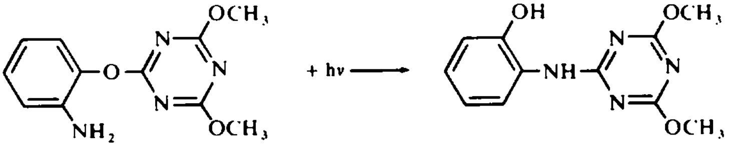
Abstract—The photochemical reactions of some aryloxy-*s*-triazines have been studied. It was found that aryloxy-*s*-triazines undergo two types of photoisomerizations: the photo-Smiles-rearrangement and the photo-Fries-rearrangement depending upon the presence or absence of an adjacent amino group on the aryloxy group.

The photoproducts obtained by the latter were assigned to *ortho*- and *para*-hydroxyaryl-*s*-triazines, the characteristic data of these new products are listed.

On the basis of quantum yields for the product formations, the reaction mechanism of the photo-Fries-rearrangements of some aryloxy-*s*-triazines has been discussed.

INTRODUCTION

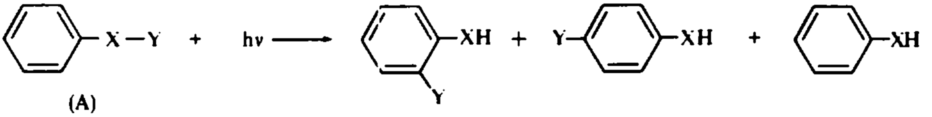
In a previous paper,[1] we reported that some aryloxy-*s*-triazine derivatives *e.g.* *R*(*O*-(4.6-dimethoxy-*s*-triazin-2-yl)-2-aminophenol(I) undergo photochemical rearrangement similar to the Smiles reaction. as shown in Eq. (1), now termed the photo-Smiles-rearrangement.



(I)

(1)

It is also known that compounds of the general formula (A)[2–17] rearrange to yield *ortho*- and *para*-substituted benzene derivatives by irradiation with UV light. indicated by Eq. (2).



(2)

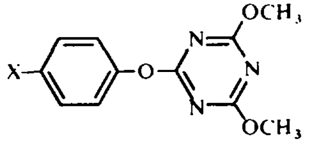
(A)

X: O, NH. Y: COR. C_6H_5 etc.

In the studies of the photochemical reactions of acetanilide. phenyl acetate. and *N*-acetyl diphenylamine, it has been shown that, in the liquid phase. the photo-Fries-rearrangement occurs via the predissociative intersystem crossing $^3\sigma_0(\text{N-C}) \leftarrow S_1(\pi\pi^*)$ or $^3\sigma_0(\text{O-C}) \leftarrow S_1(\pi\pi^*)$ forming pair radicals which recombine efficiently in a solvent cage into the original substance, *ortho*- and *para*-isomers.[9–14] The photochemical reactions of acetanilide[12] and phenyl acetate[18] in the vapour phase have also been studied. No photochemical rearrangement was observed, but photochemical decomposition occurred in either case.

In the absence of 2-amino group in I. the structure of aryloxy-*s*-triazine is similar to that of A. Therefore, the photochemical reaction similar to the photo-Fries-rearrangement may be expected in the case of 2,4-dimethoxy-6-phenoxy-s-triazine(II-1).

This paper reports the photochemical reactions of some aryloxy-*s*-triazines(II).



(II)

X: H, CH_3, Cl, OCH_3

RESULTS AND DISCUSSION

Reaction products. After long irradiation at 2537 Å of a highly concentrated solution of (II) the photoproducts were separated from unchanged material by column chromatography and crystallized. In the case of 2,4-dimethoxy-6-phenoxy-s-triazine-(II-1) two main products were found by tlc with a small amount of by-product. By means of NMR, IR, UV, pK_a, elemental analyses and mass spectral MW, the main photoproducts from II-1 were assigned to 2,4-dimethoxy-6-(2-hydroxyphenyl)-*s*-triazine (OII-1) and 2,4-di-methoxy-6-(4-hydroxyphenyl)-*s*-triazine (PII-1) to be described later. A small amount of phenol was also detected. Figure 1(a) shows the spectral change of the cyclohexane solution of II-1 during photolysis at 2537 Å.

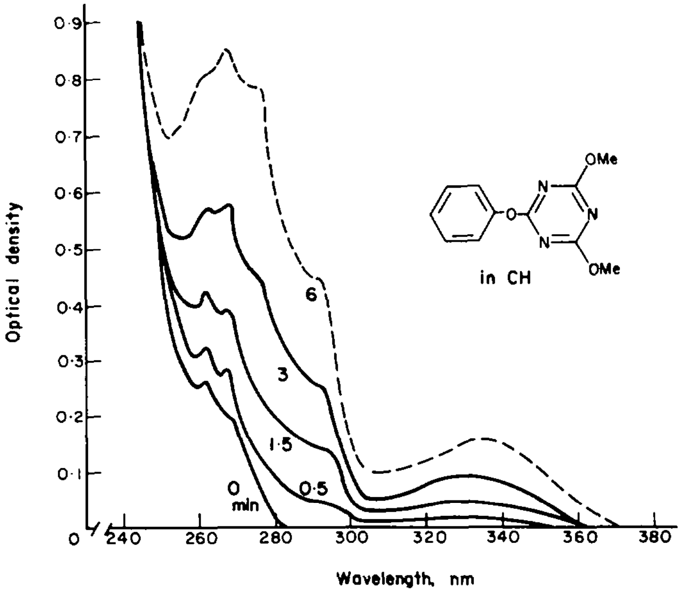


FIG 1(a). Spectral change of cyclohexane solution of 2,4-dimethoxy-6-phenoxy-*s*-triazine (II-1) with lapse of time at 2537 Å. Numbers refer to time at measurement in min

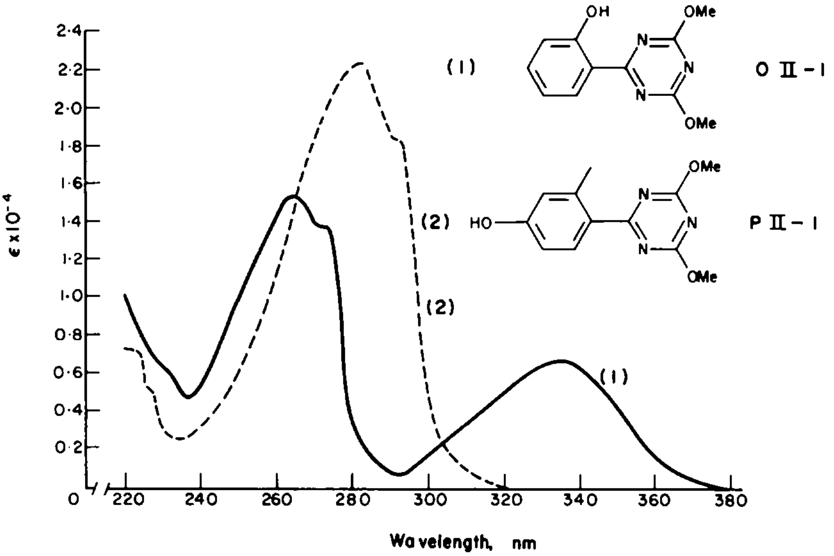


FIG 1(b). UV absorption spectra of 2,4-dimethoxy-6-(2-hydroxyphenyl)-s-triazine(1) and 2,4-dimethoxy-6-(4-hydroxyphenyl)-s-triazine(2)

This change indicates that the reaction products were *ortho-* and *para*-isomers as shown Fig. 1(b).

In the cases of 2,4-dimethoxy-s-(p-tolyloxy)-s-triazine (II-2), 2,4-dimethoxy-6-(p-chlorophenoxy)-s-triazine (II-3) and 2,4-dimethoxy-6-(p-methoxyphenoxy)-s-triazine (II-4) the products were assigned by the same procedure as for II-1. The photoproducts from II-2, II-3, and II-4 were assigned 2,4-dimethoxy-6-(2-hydroxy-5-methylphenyl)-s-triazine (OII-2), 2,4-dimethoxy-6-(2-hydroxy-5-chlorophenyl)-s- triazine (OII-3) and 2,4-dimethoxy-6-(2-hydroxy-5-methoxyphenyl)-s-triazine (OII-4) respectively, with small amount of phenol.

The spectrum of the cyclohexane solution of II-2 changed by irradiation with 2537 Å light as shown in Fig. 2.

The spectral change in II-2 (Fig. 2) shows the main product was only *ortho*-hydroxytolyl-s-triazine. Similar changes of II-3 and II-4 were also observed. The absorption spectra of II-3, OII-3, II-4 and OII-4 are shown in Fig. 3.

The characteristic data of the photoproducts from these aryloxy-s-triazines are summarized in Table 2.

The MS and elemental analyses (Table 2) show that the photoproducts were isomers of starting materials. They were soluble in an alkaline solution, and the presence of a phenolic OH group was confirmed by the coloration test using the mixed solution of $K_3Fe(CN)_6$ and $FeCl_3$. The compounds OII-1, OII-2, OII-3 and OII-4 had larger pK_a values, weaker and broader absorption bands of the OH group in the 2700–2900 cm^{-1} region, and the phenolic proton peaks in lower magnetic field in comparison with those of PII-1. These results may indicate that the OH group of OII-1, OII-2, OII-3 and OII-4 is in the *ortho* position and an intramolecular chelate formation between OH and ring nitrogen of triazinyl group in the products (OII-1–OII-4) takes place. It can be said that the photoproduct PII-1 has a free OH group

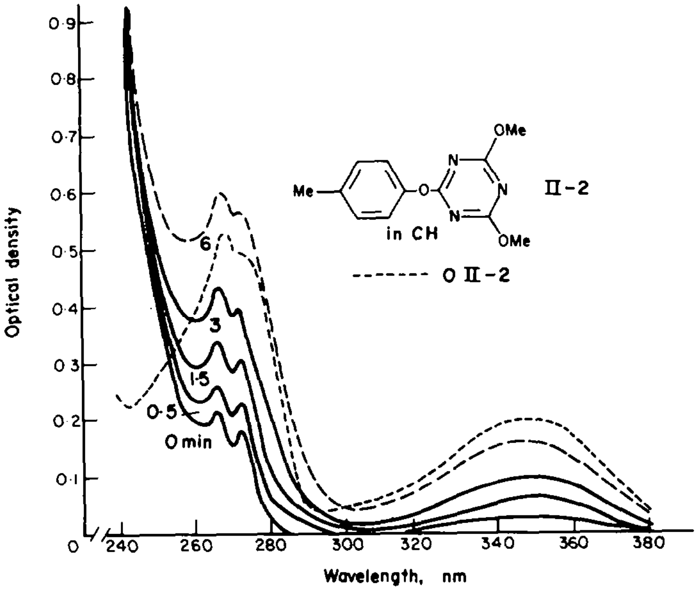


FIG 2. Spectral change of cyclohexane solution of 2,4-dimethoxy-6-(*p*-tolyloxy)-*s*-triazine at 2537 Å. Dotted line denotes the UV spectrum of 2,4-dimethoxy-6-(2-hydroxy-5-methylphenyl)-s-triazine(OII-2)

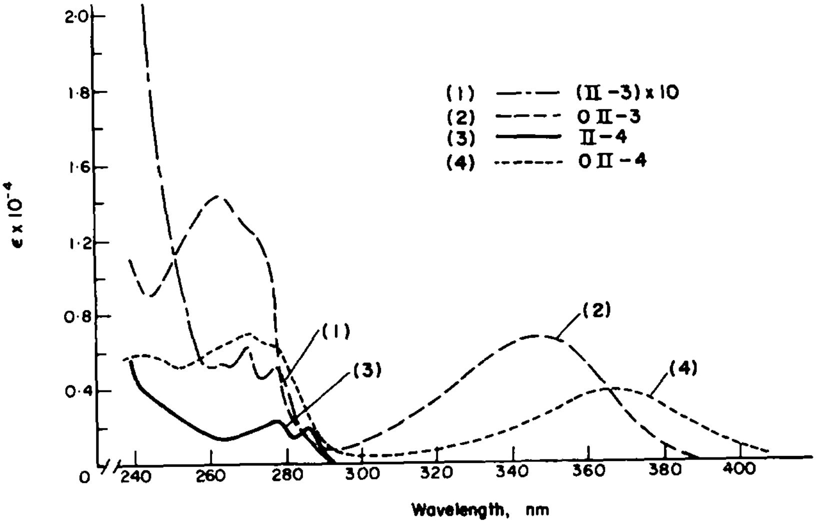
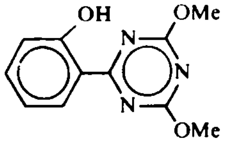
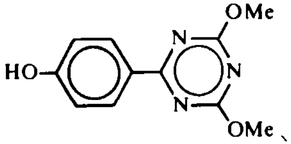
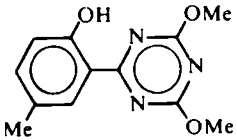
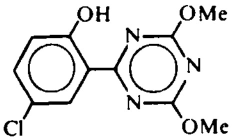
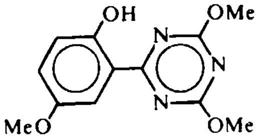


FIG 3. UV spectra of 2,4-dimethoxy-6-(*p*-chlorophenoxy)-*s*-triazine(1), 2,4-dimethoxy-6-(2-hydroxy-5-chlorophenyl)-*s*-triazine(2), 2,4-dimethoxy-6-(*p*-methoxyphenoxy)-*s*-triazine(3), and 2,4-dimethoxy-6-(2-hydroxy-5-methoxyphenyl)-s-triazine(4)

TABLE 2. THE CHARACTERISTIC DATA OF THE PHOTOPRODUCTS IN SOLUTION

No.	Compound	m.p.	Analyses % calc.	Analyses % found	MS m/e	I.R.[a] ν_{OH} cm^{-1}	NMR[b] τ(OH)	pK_a[c]
O-I		112–113	C 56·65 H 4·75 N 18·02	57·08 5·01 18·12	233	~2700	−2·52	11·17
P-I		239	C 56·65 H 4·75 N 18·02	56·46 5·14 17·94	233	3120	−0·18	8·46
O-II		134–135	C 58·29 H 5·30 N 17·00	58·68 5·57 17·08	247	~2760	−2.31	11.71
O-III		142–144	C 49·36 H 3·77	49·55 3·78	267	~2720	−2·64	10·39
O-IV		135–136	C 54·75 H 4.98	54·49 5·12	363	~2840	−2.10	11·97

[a] KBr discs.

[b] measured in DMSO-d_6.

[c] measured spectrophotometrically at 25°.

which is in the *para* position of the phenyl group from the results of IR. NMR. and UV spectra. The pK_a value of PII-1 is smaller than that of phenol (pK_a = 9·98). because of substitution of the electron-withdrawing group (2,4-dimethoxy-*s*-triazinyl group) on the *para* position in phenol.

The UV spectra of the products are consistent with those of *ortho*- or *para*-disubstituted benzene derivatives. The bathochromic shift of the ^1L_a benzene band in *para*-disubstituted benzene which is disubstituted by an electron-withdrawing group and an electron-releasing group in *para* positions to each other has been pointed out by Doub and Vandenbelt.[21] On the other hand, Nagakura *et al.*[22] have proposed the intramolecular charge transfer theory which elucidates the UV absorption spectra in substituted benzene derivatives: the CT band ($^1A_1 \leftarrow {}^1A_1$) appears in the near UV wavelength range in addition to the ^1L_b band ($^1B_2 \leftarrow {}^1A_1$) and masks the ^1L_b band in the cases of *para*-disubstituted benzenes described above. The *para*-isomer (PII-1) is to be the case: triazinyl and OH groups are an electron-withdrawing and an electron-releasing groups respectively. The CT band (^1L_a band) and PII-1 was observed at 282 nm. The red-shift of the CT band was measured in EtOH (Table 3). When groups of opposite character are substituted *ortho* to each other. the effects of the displacement on the ^1L_a and ^1L_b bands of benzene are almost the same as those caused by similar *para* substitution. Thus, the UV spectra in *ortho*-isomers show two absorption bands corresponding to ^1L_a and ^1L_b bands of benzene in near UV wavelength range as shown in Fig. 1(b) and Fig. 3. and Table 3.

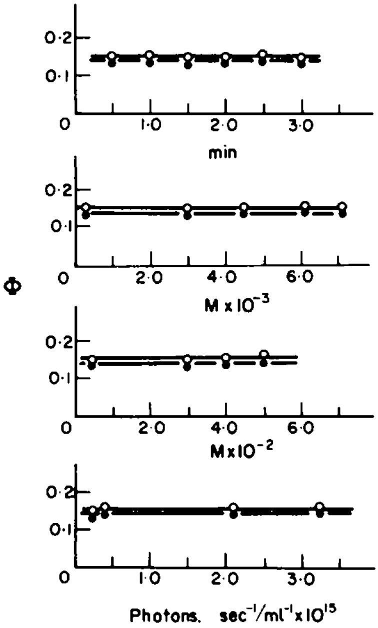
TABLE 3. MOLAR EXTINCTION COEFFICIENTS AND QUANTUM YIELDS FOR THE PRODUCT FORMATIONS AT 2537 Å

Substance No	Solvent	λ_{max} nm	ε $M^{-1}cm^{-1}$	Band Assignment	Φ
II-1	CH	261	4·0 × 10^2	$^1B_2$ (^1L_b)	
	EtOH	260	4·0 × 10^2	$^1B_2$ (^1L_b)	
OII-1	CH	267	1·67 × 10^4	(^1L_a)	0·146
		336	6·77 × 10^3	(^1L_b)	
	EtOH	265	1·74 × 10^4	(^1L_a)	0·12
		331	6·54 × 10^3	(^1L_b)	
PII-1	CH	282	2·28 × 10^4	^{1}CT (^1L_a)	0·15
	EtOH	299	2·50 × 10^4	^{1}CT (^1L_a)	0·09
II-2	CH	267	7·0 × 10^2	$^1B_2$ (^1L_b)	
	EtOH	266	7·0 × 10^2	$^1B_2$ (^1L_b)	
OII-2	CH	268	1·85 × 10^4	(^1L_a)	0·134
		347	7·16 × 10^3	(^1L_b)	
II-3	CH	270	6·3 × 10^2	$^1B_2$ (^1L_b)	
OII-3	CH	263	1·56 × 10^4	(^1L_a)	0·20
		347	6·72 × 10^3	(^1L_b)	
II-4	CH	279	2·25 × 10^3	——	
OII-4	CH	269	7·04 × 10^3	——	0·13
		369	3·29 × 10^3	——	

CH: cyclohexane
EtOH: EtOH
Me: CH_3
Φ: Quantum yield

The quantum yields for the product formation were measured spectrophotometrically. The molar extinction coefficients of the original compounds and the photoproducts are listed in Table 3.

Quantum yields for the product formation. The quantum yields were measured under various condition: the results are in Fig. 4 and Table 3. Quantum yields for the product formation from II-1 at 2537 Å did not change with variation in the II-1 concentration ($< \sim 7 \times 10^{-3}$M) as shown in Fig. 4(b). The photo-Fries-rearrangement of II-1 is an intramolecular reaction, as has been proposed by several workers.[2,9,11,13] The addition of piperylene as triplet quencher ($E_T = 2{\cdot}48$ eV) did not effect the quantum yield for this isomerization in the concentration range from 10^{-4} to 5×10^{-2}M as shown in Fig. 4(c). Dissolved oxygen had scarcely any effect on the quantum yield. Similar results were obtained regarding the quantum yields for the product formations from II-2, II-3, and II-4.



(a) on irradiation time with initial concentration of $5{\cdot}1 \times 10^{-3}$M

(b) on concentration

(c) on addition of piperylene

(d) on light intensity

○: Φ of 2,4-dimethoxy-6-(4-hydroxyphenyl)-*s*-triazine

●: Φ of 2,4-dimethoxy-6-(2-hydroxyphenyl)-*s*-triazine

FIG 4. Dependence of quantum yields in cyclohexane at 2537 Å and 20°

The photochemical primary process of the photo-Fries-rearrangement occurs via the lowest excited singlet state ($^1B_2$), as has been shown by Shizuka and Tanaka.[9] The features of the lowest excited singlet states in the aryloxy-*s*-triazines are very close to those of phenyl acetates,[13] considering their UV absorption spectra and molar extinction coefficients. Therefore, the symmetry for the lowest excited states in the starting materials may be assigned to $^1B_2$. It is of interest to note that the electron-withdrawing character of the triazinyl group is almost equivalent to that of the acyl group.

Of course, the UV absorption band of the local excitation in the 2,4-dimethoxy-*s*-triazinyl group should exist at shorter wavelength than ~2600 Å, judging from the

UV spectrum in 2,4-dimethoxy-6-hydroxy-*s*-triazine. It seems that the nπ* transition energy in II is larger than that of $^1B_2 \leftarrow {}^1A_1$, since the blue-shift of the nπ* transition[10, 23] may be caused by electron donating groups (phenoxy and methoxy) conjugated with an adjacent triazinyl group. Thus, in the cases of the aryloxy-*s*-triazines used, the photochemical primary processes are the same as those described before[9–14] because there is no dependence of the rearrangement quantum yields on piperylene and dissolved oxygen which are triplet quenchers. It can be assumed that the reaction mechanism of the aryloxy-*s*-triazines involves the predissociation, forming pair radicals which recombine efficiently in a solvent cage into the *ortho*- and *para*-isomers as has been studied by Shizuka *et al.*[9–14] In general, the predissociative intersystem crossing of benzene derivatives *via* the $^1B_2$ state occurs at a β-bond, as previously reported.[24]

The quantum yields for the product formation in the photo-Fries-rearrangement are parallel to the odd π electron densities (ρ) as shown in previous papers.[11, 13, 14] In the present work similar results were obtained as follows:

$$\frac{0{\cdot}5\,\Phi_0}{\Phi_p} = \frac{\rho_0}{\rho_p} \approx 0{\cdot}5 \tag{3}$$

where Φ_o and Φ_p denote the quantum yields for the OII-1 and PII-1 formations, and ρ_o and ρ_p donote the odd π electron densities on *ortho*- and *para*-positions in a phenoxy radical. The values of ρ_o and ρ_p are 0·125 and 0·25 respectively, as reported by Muller *et al.*[25] These facts show that the secondary processes in the photo-Fries-rearrangement involve the radical mechanism. No intermediate absorption was observed by means of the μ second flash technique. The absorptions of the products appeared immediately after the flash. No fluorescence and very weak phosphorescence were observed. Therefore, the predissociation and the radiationless deactivation *via* the $^1B_2$ state are the main processes in the photochemical reaction of II. The

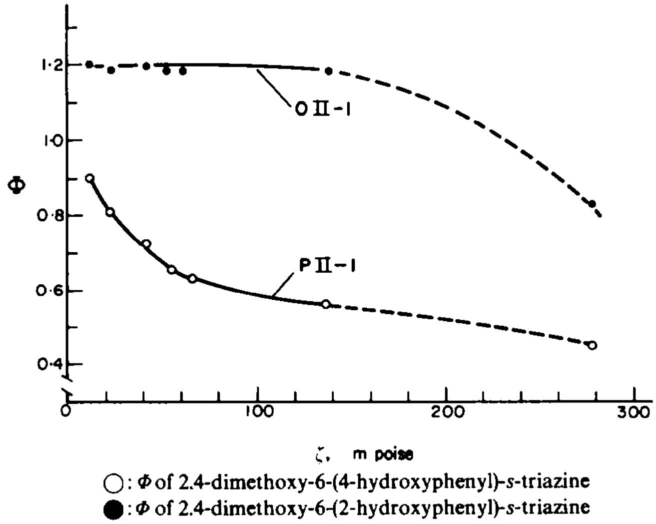


FIG 5. Dependence of quantum yields on viscosity(ζ) of solvent. Viscosity of the mixed solution of EtOH and glycerin measured by Ostwald viscometer

occurrence of large radiationless transition may be due to the hidden $n\pi^*$ states in the triazine derivatives. Similar phenomena of diazines[26] and stilbazoles[27] have been reported.

The effects of the quantum yields for product formation on viscosity of solvent were examined in the mixed solvent, EtOH/glycerin. Figure 5 shows the dependence of quantum yields on the solvent viscosity.

Viscosity scarcely affected the *ortho*-rearrangement, but considerably the *para*-rearrangement. A similar effect has been observed in the photochemical isomerization of acetanilide in PVA film.[12] These results indicate that the dependence of the *para*-rearrangement on the stiffness of the solvent cage is larger than that of the *ortho*-rearrangemnt because in a stiff solvent cage the *para*-position of the phenoxy radical and the triazinyl radical are separated by a longer path.

Thus, the reaction schemes in the photo-Fries-reactions of the aryloxy-*s*-triazines in solution at 2537 Å can be represented as follows:

$S_0 + h\nu \rightarrow S_1(^1B_2)$ excitation (4)
$S_1 \rightarrow S_0$ radiationless deactivation (5)
$S_1 \rightarrow PhO\cdot + \cdot Y$ predissociation (6)
$PhO\cdot + \cdot Y \quad S_0$ back reaction (7)
$PhO\cdot + \cdot Y$ *o*-isomer *o*-rearrangement (8)
$PhO\cdot + \cdot Y$ *p*-isomer *p*-rearrangement (9)
$PhO\cdot + RH \rightarrow PhOH + R$ hydrogen abstraction (10)

where S_0, S_1, T_1, denote the ground state, the lowest excited singlet state, and the lowest triplet state of the aryloxy-*s*-triazine, respectively, and PO·, Y·, RH and PhOH denote phenoxy radical, triazinyl radical, solvent and phenol respectively.

Finally, it can be said that the photochemical reactions of aryloxy-*s*-triazine derivatives undergo two different isomerizations: the photo-Smiles rearrangement[1] and the photo-Fries rearrangement occur with and without a 2-amino group on the aryloxy group respectively.

EXPERIMENTAL

Experimental procedure and solvents are almost the same as those previously described.[9,19] The aryloxy-*s*-triazines used were synthesized by treating 2-chloro-4,6-di-methoxy-*s*-triazine with phenol, *p*-cresol, *p*-chlorophenol, and *p*-methoxyphenol in the presence of alkali respectively, and purified by repeated recrystallization. Aryloxy-*s*-triazines thus obtained are listed in Table 1.

TABLE 1. THE DATA OF 2-ARYLOXY-4,6-DIMETHOXY-*s*-TRIAZINES

No	Aryl group	Yield %	m.p.	Recrystn. solvent	Calcd. %	Found %
II-1	Phenyl	92	102–102·5	ligroin	C 56·65 H 4·75	56·55 5·01
II-2	*p*-Tolyl	72	89–90·5	ligroin	C 58·29 H 5·30	57·83 5·06
II-3	*p*-Chlorophenyl	69	86–87·5	ligroin	C 49·36 H 3·77	49·50 3·96
II-4	*p*-Methoxyphenyl	84	75–76	ligroin	C 54·75 H 4·98	54·51 5·09

Irradiated solutions were concentrated and crystallized products separated and purified by column chromatography. Assignments of photoproducts were performed by means of NMR, IR, UV, MS, pK_a, and elemental analyses. A low pressure mercury lamp was used as the 2537 Å radiation source with a Vycor glass filter. Actinometry was carried out using a ferric oxalate solution,[20] thoroughly degassed on a high vacuum line by the freeze-pump-thaw method.

REFERENCES

[1] K. Matsui, N. Maeno, S. Suzuki, H. Shizuka and T. Morita, *Tetrahedron Letters* 1467 (1970)
[2] J. C. Anderson and C. B. Reese, *Proc. Chem. Soc.* 217 (1960); *J. Chem. Soc.* 1781 (1963)
[3] H. Kobsa, *J. Org. Chem.* **27**, 2293 (1962)
[4] D. Elad, D. V. Rao and V. I. Stenberg, *Ibid.* **30**, 3252 (1965)
[5] R. A. Finnegan and J. J. Matice, *Tetrahedron* **21**, 1015 (1965)
R. A. Finnegan and A. W. Hagen, *Tetrahedron Letters* 365 (1963)
[6] G. M. Coppinger and E. R. Bell, *J. Phys. Chem.* **70**, 3479 (1966)
[7] D. Bellus, P. Hrdlovic and P. Slama, *Collection Czech. Chem. Comm.* **33**, 2646 (1968)
P. Slama, D. Bellus and P. Hrdlovic, *Ibid.* **33**, 3752 (1968)
[8] M. R. Sandner, E. Hedaya and D. J. Trecker, *J. Am. Chem. Soc.* **90**, 7249 (1968)
[9] H. Shizuka and I. Tanaka, *Bull. Chem. Soc. Japan* **41**, 2343 (1968)
[10] H. Shizuka, *Ibid.* **42**, 52 (1969)
[11] H. Shizuka, *Ibid.* **42**, 57 (1969)
[12] H. Shizuka and I. Tanaka, *Ibid.* **42**, 909 (1969)
[13] H. Shizuka, T. Morita, Y. Mori and I. Tanaka, *Ibid.* **42**, 1831 (1969)
[14] H. Shizuka, M. Kato, T. Ochiai, K. Matsui and T. Morita, *Ibid.* **43**, 67 (1970)
[15] D. P. Kelly, J. T. Pinhey and R. D. G. Rigby, *Aust. J. Chem.* **22**, 977 (1969)
[16] H. J. Hageman, *Tetrahedron* **25**, 6015 (1969)
H. J. Hageman, H. L. Louwerse and W. J. Mus, *Ibid.* **26**, 2045 (1970)
[17] Y. Ogata, K. Takagi and I. Ishino, *Ibid.* **26**, 2703 (1970)
[18] J. W. Meyer and G. S. Hammond, *J. Am. Chem. Soc.* **92**, 2187 (1970)
[19] H. Shizuka, Y. Takayama, I. Tanaka and T. Morita, *Ibid.* **92**, 7270 (1970)
[20] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (*London*) **A235**, 518 (1956)
[21] L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.* **71**, 2414 (1949)
[22] S. Nagakura and I. Tanaka, *J. Chem. Phys.* **22**, 236 (1954)
S. Nagakura and S. Kuboyama, *J. Am. Chem. Soc.* **76**, 1003 (1954)
S. Nagakura, *J. Chem. Phys.* **23**, 1441 (1955)
[23] H. Baba, *Nippon Kagaku Zasshi* **72**, 74, 341 (1951)
[24] H. Shizuka, H. Kayoiji and T. Morita, *Mol. Photochem.* **2**, 165 (1970)
[25] E. Muller, A. Rieker and K. Scheffer, *Liebigs Ann.* **645**, 92 (1961)
[26] B. J. Cohen and L. Goodman, *J. Chem. Phys.* **46**, 713 (1967)
[27] D. G. Whitten and M. T. McCall, *J. Am. Chem. Soc.* **91**, 5097 (1969)
D. G. Whitten and Y. J. Lee, *Ibid.* **92**, 415 (1970)