The Photo-Fries Rearrangement of Aryloxy-1,3,5-triazines

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Aryloxy-*s*-triazines gave *o*- and/or *p*-hydroxyaryl-*s*-triazines upon irradiation; however, from arylamino- and arylthio-*s*-triazines, no photo-rearrangement product was obtained. The *p*-CH_3, *p*-Cl, and *p*-OCH_3 groups in the phenoxy moiety did not prevent the photoreaction of aryloxy-*s*-triazines; however, the *p*-CHO, *p*-$COCH_3$, *p*-$COOC_2H_5$, and *p*-NO_2 groups prevented the photoreaction. As to substituents in the *s*-triazine moiety, such groups as –Cl, –OCH_3, –OC_6H_5, and –CH_3 did not prevent the photoreaction; however, C_6H_5 and amino groups prevented the reaction. In the photolysis of 2,4-dimethoxy-6-(1-naphthyloxy)-*s*-triazine, 1-hydroxy-2-naphthyl- and 4-hydroxy-1-naphthyl-*s*-triazines were obtained, with the preferential formation of the former. On the other hand, from 2,4-dimethoxy-6-(2-naphthyloxy)-*s*-triazine, 2-hydroxy-1-naphthyl-*s*-triazine was obtained upon irradiation. In a similar manner, 2- and 4-acetyl-1-naphthols were obtained from 1-naphthyl acetate, and 1-acetyl-2-naphthol was isolated from 2-naphthyl acetate.

The photo-Fries rearrangement has been extensively investigated; the mechanism of the reaction and some of the substituent effects have been revealed with the reactions of *O*-acyl-phenols and *N*-acyl-anilines.

Recently, we have reported that aryloxy-dimethoxy-*s*-triazines rearrange photochemically to give the corresponding *o*-, and/or *p*-hydroxyaryl-*s*-triazines.[1] The reaction had been found to proceed *via* a radical process. However, the characteristics of the *s*-triazinyl moiety as a migrating group and the relations between the chemical constitutions and the photoreactivities have not been revealed. In addition, aryloxy-*s*-triazines containing various substituents in the aryloxy and *s*-triazine moieties are readily available by the condensation of aryloxy-halo-*s*-triazines with nucleophiles or by the reaction of halo-*s*-triazines with phenolates. Therefore, if the photo-Fries rearrangement of aryloxy-*s*-triazines takes place regardless of substituents in the aryloxy and *s*-triazine moieties, this photoreaction may provide a useful and convenient route for the syntheses of various hydroxyaryl-*s*-triazines. This paper will report the substituent effects on the photo-Fries rearrangement of phenoxy-*s*-traizines and naphthyloxy-*s*-triazines; the function of the *s*-triazinyl group for the reaction will also be discussed.

Experimental

Materials. Aryloxy-*s*-triazines were prepared by the condensation of phenolates with cyanuric chloride in the usual way,[2] followed by treatment with nucleophiles. The compounds thus obtained are listed in Table 1.

The experimental procedure and solvents were almost the same as those previously described.[1] A low-pressure mercury lamp was used as the 254 nm radiation source. After long irradiation at 254 nm, the reaction mixture was concentrated and the photo-products were separated and purified by column chromatography.

The identification of the photo-products was performed by means of their NMR, IR, UV, and MS spectra, by elemental analyses, and by studying the solubility in an alkaline solution.

Results and Discussion

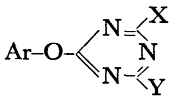
Scope of the Photo-Fries Rearrangement of s-*Triazine Derivatives.* It is well known that not only *O*-acyl-phenols,[3] but also *N*-acyl-anilines,[4] rearrange photochemically to yield the corresponding ketones. Thus, in the cases of *s*-triazine derivatives, the photolysis was investigated not only with aryloxy-*s*-triazines, but also with arylamino- and arylthio-*s*-triazines. However, such an attempt with arylamino-*s*-triazines was unsuccessful, regardless of the substituents in the *s*-triazine and aniline moieties; ordinary arylamino-*s*-triazines are stable on irradiation with UV light. On the other hand, dimethoxy-phenylthio-*s*-triazine showed a complex spectral change on irradiation, and it had no isosbestic point. Thus, it may be said that, among the arylamino-, aryloxy-, and arylthio-*s*-triazines, the aryloxy derivative is the sole *s*-triazine compound capable of yielding photo-rearrangement products.

*Effects of Substituents on the Photo-Fries Rearrangement of Phenoxy-*s*-triazines.* As preliminary experiments, the reactivities for the photoreaction of all the phenoxy-*s*-triazines listed in Table 1 were checked by measuring their spectral change with the lapse of time at 254 nm in cyclohexane and ethanol. As a result, the progress of the photoreaction of aryloxy-*s*-triazines was found to depend significantly upon the substituents in the aryloxy and *s*-triazinyl groups.[5] The *p*-CH_3, *p*-Cl, and *p*-OCH_3 groups in the phenoxy moiety did not prevent the progress of the photoreaction; however, when electron-withdrawing groups such as *p*-CHO, *p*-$COCH_3$, *p*-$COOC_2H_5$, and *p*-NO_2 were introduced into the phenoxy moiety, the photoreaction did not take place.

As for substituents in the *s*-triazine nucleus, although the overall effect varied with the combination of two substituents, such substituents as –Cl, –OCH_3, –OC_6H_5, and –CH_3 did not prevent the photoreaction. Thus, any aryloxy-*s*-triazines containing any two of these substituents underwent the photo-rearrangement readily. It is known[6] that the derivatives of halo-*s*-triazine dissociate into the halogen atom and the *s*-triazinyl radical in benzene to give *s*-triazinylbenzene on irradiation. However, *s*-triazine derivatives containing both chloro and aryloxy substituents are preferentially rearranged photochemically to give hydroxyaryl-chloro-*s*-triazines. On the other hand, the phenyl group and such substituents as –NH_2, –$NHCH_3$, –$N(CH_3)_2$, and –NHC_6H_5 prevented the reaction very much.

In order to make clear the effects of the substituents

TABLE 1. ARYLOXY-*s*-TRIAZINES

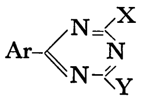


No.	Ar	X	Y	Mp (°C)	Solvent for recrystallization	Analysis (%) Found C	Found H	Calcd C	Calcd H
1	Phenyl	$-OCH_3$	$-OCH_3$	102—102.5[a]	Ligroin	——			
2	*o*-Tolyl	$-OCH_3$	$-OCH_3$	87.5—88.5	Ligroin	58.52	5.39	58.29	5.30
3	*p*-Tolyl	$-OCH_3$	$-OCH_3$	89—90.5[a]	Ligroin	——			
4	*p*-Chlorophenyl	$-OCH_3$	$-OCH_3$	86—87.5[a]	Ligroin	——			
5	*p*-Methoxyphenyl	$-OCH_3$	$-OCH_3$	80—81[a]	Ligroin	——			
6	*p*-Formylphenyl	$-OCH_3$	$-OCH_3$	146—147	Benzene	55.39	4.29	55.17	4.24
7	*p*-Acetylphenyl	$-OCH_3$	$-OCH_3$	119—120	Benzene	56.78	4.62	56.72	4.76
8	*p*-Ethoxycarbonylphenyl	$-OCH_3$	$-OCH_3$	122.6—123	Benzene	54.91	5.00	55.08	4.97
9	*p*-Nitrophenyl	$-OCH_3$	$-OCH_3$	136—136.5[b]	Benzene	——			
10	*α*-Naphthyl	$-OCH_3$	$-OCH_3$	87.5—88.5	Ligroin	58.62	5.39	58.29	5.30
11	*β*-Naphthyl	$-OCH_3$	$-OCH_3$	117—118	Benzene	63.54	4.57	63.60	4.63
12	1-Methyl-2-naphthyl	$-OCH_3$	$-OCH_3$	114—115	Ligroin	64.78	5.17	64.64	5.09
13	Phenyl	$-OCH_3$	$-Cl$	128—129	Ligroin	50.21	3.37	50.54	3.49
14	Phenyl	$-OCH_3$	$-OC_6H_5$	150—151	Benzene–Ligroin	63.78	4.76	63.60	4.63
15	Phenyl	$-OCH_3$	$-SCH_3$	112—114	Ligroin	52.89	4.36	53.21	4.47
16	Phenyl	$-OCH_3$	$-NH_2$	225—226	Benzene	55.24	4.68	55.04	4.62
17	Phenyl	$-OCH_3$	$-NHCH_3$	140.5—141.5	Benzene–Ligroin	58.88	5.52	58.53	5.72
18	Phenyl	$-OCH_3$	$-N(CH_3)_2$	94—95	Ligroin	60.03	6.01	60.46	5.46
19	Phenyl	$-OCH_3$	$-NHC_6H_5$	133—134	Benzene–Ligroin	58.18	5.52	58.53	5.73
20	Phenyl	$-OC_6H_5$	$-C_6H_5$	114—115	Ligroin	73.55	4.35	73.88	4.42
21	Phenyl	$-OC_6H_5$	$-OC_6H_5$	235—236[c]	Benzene	——			
22	Phenyl	$-OC_6H_5$	$-N(CH_3)_2$	145—146	Benzene	66.54	5.07	66.22	5.23
23	Phenyl	$-SCH_3$	$-Cl$	80.5—82.5	Ligroin	47.58	3.16	47.34	3.58
24	Phenyl	$-SCH_3$	$-SCH_3$	93—94	Ligroin	49.58	4.15	49.79	4.17
25	Phenyl	$-SCH_3$	$-N(CH_3)_2$	66—67	Ligroin	55.35	5.65	54.94	5.37
26	Phenyl	$-Cl$	$-Cl$	112—113[d]	Ligroin	——			
27	Phenyl	$-Cl$	$-NH_2$	231—232	Methanol	48.85	2.87	48.55	3.17
28	Phenyl	$-Cl$	$-NHCH_3$	148—149	Methanol–H_2O	50.35	3.85	50.75	3.83
29	Phenyl	$-Cl$	$-N(CH_3)_2$	139.5—140	Benzene–Ligroin	52.41	4.29	52.66	4.42
30	Phenyl	$-Cl$	$-NHC_6H_5$	102—104	Benzene–Ligroin	60.43	4.02	60.31	3.71
31	Phenyl	$-NHCH_3$	$-N(CH_3)_2$	136—137	Methanol–H_2O	56.90	5.54	57.13	5.66
32	Phenyl	$-N(CH_3)_2$	$-N(CH_3)_2$	106—107	Ligroin	60.49	6.54	60.22	6.60
33	Phenyl	$-NHC_6H_5$	$-NHC_6H_5$	185.5—187	Benzene	70.57	4.67	70.91	4.81
34	*p*-Tolyl	$-OCH_3$	$-OC_6H_4CH_3(p)$	96—97	Ligroin	67.06	5.51	66.86	5.30
35	*p*-Tolyl	$-OCH_3$	$-N(CH_3)_2$	87—88	Ligroin	60.34	6.50	59.97	6.20
36	*p*-Tolyl	$-Cl$	$-Cl$	90—91	Ligroin	47.27	2.90	46.90	2.75
37	*p*-Tolyl	$-OC_6H_4CH_3(p)$	$-OC_6H_4CH_3(p)$	216—217	Benzene	72.45	4.96	72.17	5.30
38	*p*-Tolyl	$-N(CH_3)_2$	$-N(CH_3)_2$	109—110	Ligroin	61.74	7.27	61.52	7.01
39	Phenylthio*	$-OCH_3$	$-OCH_3$	69—69.5	Ligroin	54.44	4.45	54.00	4.45
40	Anilino*	$-OCH_3$	$-OCH_3$	128—129[e]	Ligroin	——			
41	Anilino*	$-Cl$	$-Cl$	135.5—136.5[f]	Benzene	——			
42	Anilino*	$-N(C_2H_5)_2$	$-N(C_2H_5)_2$	87—89[g]	Ligroin	——			
43	*p*-Chloroanilino*	$-N(C_2H_5)_2$	$-N(C_2H_5)_2$	134—135[g]	Ligroin	——			
44	*N*-methylanilino*	$-OCH_3$	$-OCH_3$	51—52[h]	Aq. Methanol	——			

* Indicates that the substituent combines with the *s*-triazine nucleus in place of aryloxy group.

a) H. Shizuka, K. Matsui, *et al.*, *Tetrahedron*, **27**, 4021 (1971). b) T. Harayama, K. Matsui, *et al.*, *J. Heterocycl. Chem.*, **7**, 981 (1970). c) A. Hofmann, *Ber.*, **19**, 2063 (1886). d) R. Hirt and H. Nidecker, *Helv. Chim. Acta*, **33**, 1365 (1950). e) A. F. Crowther and F. H. S. Curd, *J. Chem. Soc.*, **1948**, 1636. f) J. T. Thurston *et al.*, *J. Amer. Chem. Soc.*, **73**, 2981 (1951). g) D. Walker, Y. L'Italien, W. Pearlman, and C. Banks, *J. Amer. Pharm. Assoc.*, **39**, 383 (1950). h) J. R. Dudley, J. T. Thurston *et al.*, *J. Amer. Chem. Soc.*, **73**, 2986 (1951).

TABLE 2. MOLAR EXTINCTION COEFFICIENTS AND QUANTUM YIELDS FOR THE PRODUCT FORMATION AT 254 nm IN CYCLOHEXANE



Ar	X	Y	λmax (nm)	ε	Φ	∑Φ	$\sigma_m X+\sigma_m Y$
HO-C_6H_4-(*o*)	-OC_6H_5	-OC_6H_5	270	2.25×10^4	0.21_1		
HO-C_6H_4-(*p*)	-OC_6H_5	-OC_6H_5	288	2.03×10^4	0.16_6	0.37_7	+0.504
HO-C_6H_4-(*o*)	-OC_6H_5	-OCH_3	268	1.95×10^4	0.17_3		
HO-C_6H_4-(*p*)	-OC_6H_5	-OCH_3	287	1.90×10^4	0.13_0	0.30_3	+0.367
HO-C_6H_4-(*o*)	-OCH_3	-OCH_3	267	1.67×10^4	0.14_6		
HO-C_6H_4-(*p*)	-OCH_3	-OCH_3	282	2.28×10^4	0.12_0	0.26_6	+0.230
HO-C_6H_4-(*o*)	-OC_6H_5	-$N(CH_3)_2$	261	1.69×10^4			
HO-C_6H_4-(*p*)	-OC_6H_5	-$N(CH_3)_2$	278	2.22×10^4			+0.041
HO-C_6H_4-(*o*)	-$N(CH_3)_2$	-$N(CH_3)_2$	256	1.85×10^4	0.002		
HO-C_6H_4-(*p*)	-$N(CH_3)_2$	-$N(CH_3)_2$	264	2.39×10^4	0.001	0.003	−0.422
(HO-)(CH_3-)C_6H_3-(2,5-)	-OCH_3	-OCH_3	268	1.85×10^4	0.13_4		+0.230
(HO-)(CH_3-)C_6H_3-(2,5-)	-OCH_3	-$N(CH_3)_2$	262	1.90×10^4	0.097		−0.096
(HO-)(CH_3-)C_6H_3-(2,5-)	-$N(CH_3)_2$	-$N(CH_3)_2$	257	2.18×10^4	0.002		−0.422
(HO-)(CH_3-)C_6H_3-(2,5-)	-OC_6H_4-CH_3(*p*)	-OCH_3	271	2.11×10^4	0.20_7		——
(HO-)(CH_3-)C_6H_3-(2,5-)		-OC_6H_4-CH_3(*p*)	273	2.29×10^4	0.23_5		——

in the *s*-triazine nucleus quantitatively, the quantum yields for the product formation were measured with several aryloxy-*s*-triazines. The results are shown in Table 2. From Table 2 it is obvious that the introduction of amino groups into the *s*-triazine nucleus hinders the photoreaction; in the experimental results it can be seen that, regardless of the substituents, the more positive the $\sigma_m X+\sigma_m Y$ value in Table 2 becomes, the larger the quantum yield for the product formation becomes. These facts indicate that the progress of the photo-rearrangement depends mainly upon the electron-attracting ability of the *s*-triazine moiety. However, this apparent relation does not hold in every case; aryloxy-phenyl-*s*-triazine did not rearrange photochemically even though the phenyl group ($\sigma_m=+0.06$) is an electron-attractive substituent. If the reaction mechanism of the photo-Fries rearrangement is kept in mind, the question of the substituent effects may be solved. In general, the photo-Fries rearrangement occurs *via* the predissociation originated from $S_1(\pi\pi^*)$ $^1B_2$ (or ^1L_b), involving the *β*-bond fission of benzene derivatives.[1,7] The photochemical primary process of aryloxy-*s*-triazine originates from the lowest excited singlet state, $^1B_2$, which corresponds to the $^1B_{2u}$ state of benzene.[1] The reactivity in the photo-Fries rearrangement is dependent upon the electronic character of the lowest excited singlet state in a benzene derivative. The absorption spectrum of aryloxy-phenyl-*s*-triazine is very close to that of 2,4-dimethoxy-6-phenyl-*s*-triazine. Thus, the lowest absorption band of the molecule may be assigned to $^1L_a\leftarrow{}^1A$ (not to $^1L_b\leftarrow{}^1A$), considering the structureless band at 255 nm with $\varepsilon=2.25\times10^4$, just like that of biphenyl.[8] This band ($^1L_a\leftarrow{}^1A$) masks the photoreactive band ($^1B_2\leftarrow{}^1A_1$), and the $^1B_2$ state is not the lowest $\pi\rightarrow\pi^*$ singlet state, resulting in the significant decrease in the *β*-bond fission.

The introduction of electron-donating substituents such as amino groups into the *s*-triazine nucleus results in a bathochromic shift of the $\pi\rightarrow\pi^*$ band in *s*-triazine and a slight hypsochromic shift of the $n\rightarrow\pi^*$ band.[9a] The amino substituent increases the intensity of the lowest singlet $\pi\rightarrow\pi^*$ band in *s*-triazine, whose transition is symmetry-forbidden.[9b] Furthermore, the $^1A_1\leftarrow{}^1A_1$ band in aryloxy-*s*-triazine, with an amino group in the *s*-triazine nucleus, is assumed to be large enough to overlap the $^1B_2\leftarrow{}^1A_1$ band of the aryloxy group.[5] In fact, the vibrational structure in the $^1B_2\leftarrow{}^1A_1$ band disappears, in contrast to that of 2,4-dimethoxy-6-

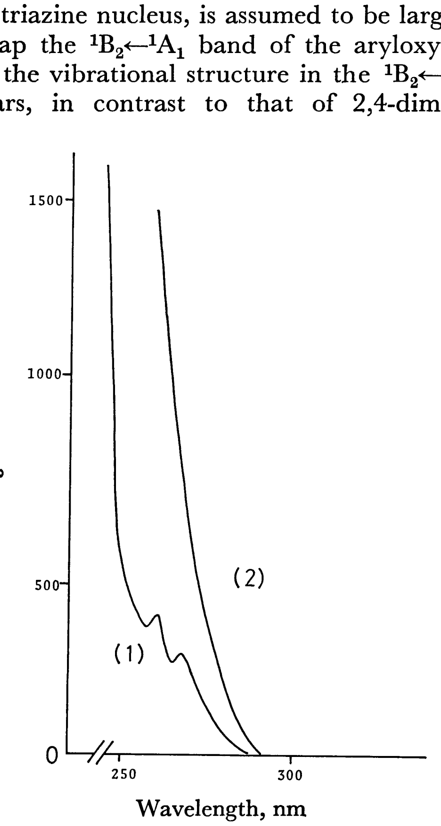


Fig. 1. UV spectra of 2,4-dimethoxy-6-phenoxy-*s*-triazine (1) and 2,4-bis(dimethylamine)-6-phenoxy-*s*-triazine (2).

phenoxy-*s*-triazine, as is shown in Fig. 1. Thus, the amino substituent in the *s*-triazine nucleus considerably lowers the quantum yield, as is shown in Table 2.

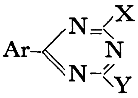
As has been mentioned above, the presence of an electron-withdrawing group such as *p*-NO_2, *p*-$COCH_3$, *p*-CHO, or *p*-$COOC_2H_5$, in the phenoxy moiety prevented the photo-rearrangement almost completely; it may be said that the predissociation at a β-band is difficult, because the $n\pi^*$ singlet state, which corresponds to the excitation from the non-bonding orbital in these substituents to the π^* molecular orbital, is the lowest excited singlet state in these cases (except for *p*-$COOC_2H_5$).

When more than two aryloxy groups are present in an *s*-triazine nucleus, the reaction stops at the stage of the rearrangement of one of the aryloxy groups, as in the photoreaction of tris(*p*-tolyloxy)-*s*-triazine to give 2-(5-methyl-2-hydroxyphenyl)-4,6-bis(*p*-tolyloxy)-*s*-triazine; *o*-hydroxyaryl-*s*-triazines are generally very stable on irradiation,[10] and *s*-triazine derivatives containing more than two *o*-hydroxyaryl groups could not be obtained by this photo-reaction.

Since *o*- and/or *p*-hydroxyaryl-chloro-*s*-triazines can be obtained in good yields by the photolysis of aryloxy-chloro-*s*-triazines, from these compounds a number of *o*- and *p*-hydroxyaryl-*s*-triazines including compounds which can not be obtained by the direct photolysis of the corresponding aryloxy-*s*-triazines were prepared by treatment with nucleophiles. There are several methods for the preparation of *o*- and *p*-hydroxyaryl-*s*-triazines.[10] Among these methods, the Friedel-Crafts *s*-triazinylation of phenols is assumed to be the most convenient; however, there are some limitations. For example, by the reaction with halo-*s*-triazines in the presence of aluminium chloride, only phenols with high reactivities towards electrophiles condense to give the desired products.[11] Therefore, the photo-Fries rearrangement of aryloxy-chloro-*s*-triazines, followed by treatment with nucleophiles, may be a novel and general convenient method for the preparation of various hydroxyaryl-*s*-triazines. Table 3 lists the *o*- and *p*-hydroxyaryl-*s*-triazines prepared directly or indirectly by the photo-Fries rearrangement.

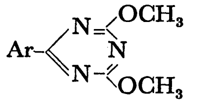
*Photo-rearrangements of Naphthyloxy-*s*-triazines.* From the standpoint of studying the effect of the aryloxy moiety on the photo-rearrangement of aryloxy-*s*-triazines, some photo-reactions of naphthyloxy-*s*-triazines have been carried out. There have been many studies

Table 3. 2- and 4-hydroxyaryl-*s*-triazines



Ar	X	Y	Mp (°C)	Solvent for recrystallization	Anal. (%)			
					Found		Calcd	
					C	H	C	H
HO-C_6H_4-(*o*)	-OC_6H_5	-OC_6H_5	164—165	Ligroin	70.64	4.42	70.58	4.23
HO-C_6H_4-(*p*)	-OC_6H_5	-OC_6H_5	237—238	Acetone	70.25	4.02	70.58	4.23
HO-C_6H_4-(*o*)	-OCH_3	-OC_6H_5	150—151	Ligroin	63.48	4.43	63.60	4.63
HO-C_6H_4-(*p*)	-OCH_3	-OC_6H_5	235—236	Acetone	63.78	4.51	63.60	4.63
HO-C_6H_4-(*o*)	-$N(CH_3)_2$	-OC_6H_5	147—148	Ligroin	65.88	4.96	66.22	5.23
HO-C_6H_4-(*p*)	-$N(CH_3)_2$	-OC_6H_5	238—239	Acetone	66.62	5.54	66.22	5.23
HO-C_6H_4-(*o*)	-$N(CH_3)_2$	-$N(CH_3)_2$	145—146	Ligroin	60.48	6.92	60.22	6.60
HO-C_6H_4-(*p*)	-$N(CH_3)_2$	-$N(CH_3)_2$	213—214	Acetone	60.58	6.98	60.22	6.60
(HO-)(CH_3-)C_6H_3-(2,5-)	-OCH_3	-$N(CH_3)_2$	137—138	Ligroin	60.28	6.47	59.97	6.20
(HO-)(CH_3-)C_6H_3-(2,5-)	-$N(CH_3)_2$	-$N(CH_3)_2$	162—163	Ligroin	61.74	7.09	61.52	7.01
(HO-)(CH_3-)C_6H_3-(2,5-)	-OCH_3	-OC_6H_4-CH_3(*p*)	131—132	Ligroin	66.50	5.49	66.86	5.30
(HO-)(CH_3-)C_6H_3-(2,5-)	-OC_6H_4-CH_3(*p*)	-OC_6H_4-CH_3(*p*)	158—159	Ligroin	71.89	5.50	72.17	5.30

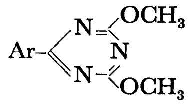
Table 4. Photo-products of naphthyloxy-*s*-triazines and quantum yields for the product formation at 254 nm



Ar	Yield[a] (%)	*o*/*p*	λmax (ε)[b] (nm)	Φ[b,c]
1-Hydroxy-2-naphthyl-(*o*-)	48	1.8	248(1.85×10^4), 325(1.07×10^4), 365(1.07×10^4)	0.12
4-Hydroxy-1-naphthyl-(*p*-)	27		236(1.21×10^4), 329(5.21×10^3)	0.09
(1-Naphthol)	18			—
2-Hydroxy-1-naphthyl-	67		301(1.67×10^4), 369(1.16×10^4)	0.17
(2-Naphthol)	17			—

a) Chemical yield in ethanol after irradiation with a 10-W low-pressure mercury lamp for 70 hr.
b) Measured in cyclohexane. c) Quantum yield for the product formation.

Table 5. Photo-products of 2,4-dimethoxy-6-naphthyloxy-*s*-triazines



Ar	Mp °C	Solvent for recrystallization	Anal. %			
			Found		Calcd	
			C	H	C	H
HO-$C_{10}H_6$-(1,2-)	189—190	Ligroin	63.28	4.45	63.60	4.63
HO-$C_{10}H_6$-(4,1-)	203.5—204.5	Benzene	63.73	4.35	63.60	4.63
HO-$C_{10}H_6$-(2,1-)	147—148	Ligroin	63.52	4.86	63.60	4.63

of the Fries-rearrangement of *O*-acyl-naphthols;12) however, little is known about their photo-reactions. Recently, the photolysis of 2-naphthyl ester with a high-pressure mercury lamp to give 2-naphthol13) and the γ-radiolysis of 2-naphthyl acetate to give 1-, 6-, and 8-acetyl-2-naphthols and 2-naphthol14) have been reported. However, no photo-Fries rearrangement of *O*-*s*-triazinyl-naphthols has been reported.

In the photolysis of 2,4-dimethoxy-6-(1-naphthyloxy)-*s*-triazine at 254 nm in ethanol, 2,4-dimethoxy-6-(1-hydroxy-2-naphthyl)-*s*-triazine, 2,4-dimethoxy-6-(4-hydroxy-1-naphthyl)-*s*-triazine, and α-naphthol were obtained, while only 2,4-dimethoxy-6-(2-hydroxy-1-naphthyl)-*s*-triazine was obtained as a rearrangement product, together with β-naphthol, from 2,4-dimethoxy-6-(2-naphthyloxy)-*s*-triazine, as is shown in Tables 4 and 5.

As has been mentioned in a previous paper,1) in the photo-Fries rearrangement of 2,4-dimethoxy-6-phenoxy-*s*-triazine the quantum yields for the product formation are parallel to the odd π electron densities of the phenoxy radical, as is shown below, where Φ_O and Φ_P denote the quantum yields for the formation of *o*- and *p*-hydroxyphenyl derivatives and where ρ_O and ρ_P denote the odd π electron densities on the *ortho* and *para* positions in the phenoxy radical

$$0.5\Phi_o/\Phi_p = \rho_o/\rho_p \approx 0.5$$

The values of ρ_P and ρ_O are 0.125 and 0.25 respectively, as reported by Muller *et al.*15)

In Fig. 2 are shown the calculated values of the odd π electron densities of the 1- and 2-naphthyloxy radicals obtained using the semi-empirical SCF-MO method.16) From these values, the formation of 2-, 4-, and 5-*s*-triazinyl derivatives from 1-naphthyloxy-*s*-triazine and the formation of 1-, 6-, and 8-*s*-triazinyl derivatives from 2-naphthyloxy-*s*-triazine may be expected. However, the photoproducts from 1-naphthyloxy-*s*-triazine were the 2- and 4-*s*-triazinyl derivatives, while in the case of the 2-naphthyloxy derivative, 1-*s*-triazinyl derivative was obtained as the sole photo-rearrangement product. The result of these reactions tempted us to check the photoreaction of ordinary naphthyl esters. In a similar manner, in the photoreactions of 1-naphthyl acetate, 2- and 4-acetyl-1-naphthols were obtained, while 1-acetyl-2-naphthol was isolated from 2-naphthyl acetate. Thus, in the cases of naphthyloxy-*s*-triazines and naphthyl esters, the experimental results on isomer distribution did not agree with the calculated values of the odd π electron densities of naphthyloxy radicals; in addition, no acyl or *s*-triazinyl derivative of the adjacent aromatic nucleus was obtained, unlike the case of the ordinary Fries rearrangement of *O*-acetyl-2-naphthol to give 1- and 6-acetyl-2-naphthols.17) When the 1-position of *O*-*s*-triazinyl-2-naphthol was occupied by another substituent, such as the methyl group, only a small amount of 1-methyl-2-naphthol was formed upon irradiation; most of the starting material was recovered, in spite of the expectation that *s*-triazinylated products at remote positions of high odd π electron densities of 2-naphthol would be formed.

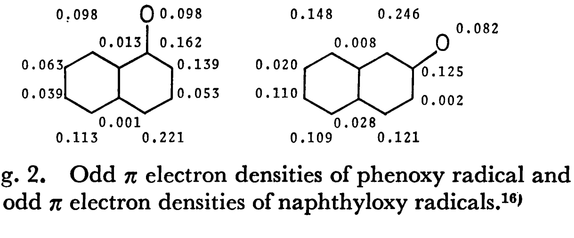


Fig. 2. Odd π electron densities of phenoxy radical and odd π electron densities of naphthyloxy radicals.16)

Table 6. Yields of photo-products on irradiation of ethanol solutions of naphthyl acetates with a 10-W low-pressure mercury lamp for 25 hr

	Yield %	*o*/*p*
1-Naphthyl acetate	—	
1-Hydroxy-2-acetylnaphthalene (*o*-)	41	1.5
4-Hydroxy-1-acetylnaphthalene (*p*-)	27	
(1-Naphthol)	18	
2-Naphthyl acetate	—	
2-Hydroxy-1-acetylnaphthalene	67	
(2-Naphtol)	20	

In Table 4 the quantum yields for the product formation in the reactions of naphthyloxy-*s*-triazines are listed. From these results, it is obvious that, in the photoreaction of 1-naphthyloxy-*s*-triazine, the ratio of the quantum yields for the *ortho* and *para* rearrangements [Φ_O/Φ_P (1.3)] differs considerably from that of the odd π electron densities of the 1-naphthyloxy radical [ρ_O/ρ_P (0.63)]; in the case of the 1-naphthyloxy radical, even though the calculated value of the odd π electron density at the 4-position is larger than that at the 2-position, the quantum yield for the rearrangement to the latter was larger than that to the former. A similar relation was also observed in the photoreaction of *O*-acetyl-1-naphthol, suggesting that the preferential formation of the *ortho* isomer generally holds in the photo-rearrangement of derivatives of the *O*-acyl-1-naphthol type. The preferential formation of the *ortho* isomer in these cases is of interest from the viewpoint of the synthesis of the 2-isomer, because, in the ordinary electrophilic reactions of 1-naphthol in the dark, the formation of the 4-isomer always predominates and the yield of the 2-isomer is quite low.

Thus, in the photo-rearrangement of *O*-acyl or *O*-*s*-triazinyl-naphthols the distance of the migration is considered to be also important, although the acyl or *s*-triazinyl group migrated to the positions of the high odd π electron densities; the migration of the acyl or *s*-triazinyl group to an adjacent position occurred readily, as in the cases of phenol derivatives, but it was difficult for any migration to a remote position to take place. These facts are consistent with the findings that the viscosity of a solvent scarcely affects the *ortho*-rearrangement, but does affect the *para*-rearrangement considerably.[1] A similar difficulty of the rearrangement to a remote position is also observed in the ordinary Fries rearrangement of *O*-acyl-1-naphthols. In this case, with an increase in the size of the acyl group, the rate of the formation of the 4-acyl-1-naphthols falls off to such an extent that the method is of little value in their preparation.[18] Generally, *s*-triazinyl group is a bulky substituent; therfore, in the cases of *O*-*s*-triazinyl-1-naphthols, the steric hindrance caused by the adjacent benzene nucleus, which is assumed to be the reason for the difficulty of the rearrangement to the 4-position, may be more significant than in the cases of ordinary acyl derivatives. However, the difference in steric hindrance between the *s*-triazinyl and acetyl groups seems to be small, as may be seen from a comparison of the values of the *o*/*p* ratio in these cases. On the other hand, in the photoreactions of naphthol derivatives, the formation of considerable quantities of naphthols was observed as compared with the cases of phenol derivatives. This difference between phenol and naphthol derivatives may be explained by a difference in the odd π electron densities at the oxygen atoms of the phenoxy and naphthyloxy radicals. Because of the low odd π electron densities at the oxygen atoms of naphthyloxy radicals, the probabilities of the back reactions with *s*-triazinyl radical to give the starting materials may be low, and naphthyloxy radicals are assumed to escape relatively readily from the solvent cage and to abstract a hydrogen atom from the solvent molecule to yield the respective naphthols in fairly good yields.

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