The Formation of Triaryl-*s*-triazine in the Chemiluminescence Reaction of Triarylimidazole and in the Photo-oxygenation of Triarylimidazole in the Presence of Ammonia[1]

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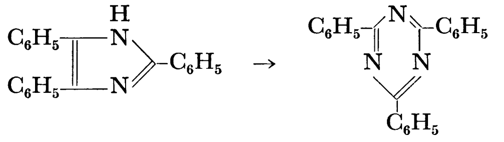
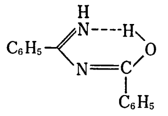
2,4,6-Triphenyl-*s*-triazine (II) is formed either in the chemiluminescence reaction of 2,4,5-triphenylimidazole (I) in the presence of oxygen and a strong base or in the photolysis of I in alcohol in the presence of ammonia and oxygen. II is also formed in the sensitized photo-oxygenation of I in alcohol containing ammonia. It was found that II was produced by the reaction between the lophyl hydroperoxide (V), which was prepared from I and was known to be one of the intermediates in chemiluminescence reaction of I, and ammonia. Chemical and spectroscopic evidence that II is produced from V and not *via* the dioxetane-type peroxide (VI) nor *N,N'*-dibenzoylbenzamidine (IV), is given. II and several other 2,4,6-triaryl-*s*-triazines were found to be easily prepared from the corresponding triarylimidazoles by the sensitized photo-oxygenation in methanol in the presence of ammonium acetate and this provides a new method for the synthesis of triaryl-*s*-triazine.

We found[2] that after the chemiluminescence of 2,4,5-triphenylimidazole (I) was exhibited by oxygen for about 1 day in 1 N ethanolic solution of potassium hydroxide at room temperature, a small amount (lower than 5%) of 2,4,6-triphenyl-*s*-triazine (II) was isolated as alkali-insoluble fine crystals, besides the major products, benzoic acid and ammonia.[3] Formation of II was also found to occur in a photolysis of I in alcohols in the presence of oxygen and ammonia at room temperature (16% yield) and in a sensitized photo-oxygenation of I in the presence of ammonia at about 0°C (22% yield). In this paper we will report the results of the study on the species involved in the transformation of I into II which led to a new synthetic method of triaryl-*s*-triazine.


I II

Results and Discussion

Compound II obtained in the chemiluminescence reaction of I was considered to be formed by the ring expansion of I by insertion of one nitrogen atom between C-4 and C-5 of the imidazole ring. The yield of II decreases with rise of the reaction temperature and increases slightly by addition of ammonia to the solution. These facts suggested that the inserted nitrogen atom is supplied by ammonia which is one of the major products of the chemiluminescence reaction of I. Therefore, the photolysis of I in the presence of ammonia was investigated in some detail. When a methanolic solution of I containing ammonia was irradiated by a high-pressure mercury lamp under bubbling of oxygen, II separated from the solution in 16% yield, and from the filtrate 4,5-(9',10'-phenanthryl)-imidazole (9%), benzamide (25%) and *N*-benzoylbenzamidine (III) (45%) were isolated. When the photo-oxygenation of I was carried out in a methanolic solution of ammonia containing methylene blue as sensitizer at about 0°C by an incandescent lamp, a considerable change in UV absorption of the solution was observed and after the irradiation was shut off II gradually separated from the solution in 22% yield. From the filtrate, III (33%) and benzamide (12%) were obtained. 4,5-(9',10'-Phenanthryl)imidazole could not be detected in this case. White and Harding[4] isolated III and IV from the reaction products of the chemiluminescence reaction of I and found that the observed luminescence is the fluorescence emission of IV which was suggested to be formed from the anion of lophyl hydroperoxide (V) through the anion of the dioxetane-type peroxide (VI). In view of their work and our present results, we assumed that IV, V or VI and ammonia were involved in the formation of triphenyl-*s*-triazine.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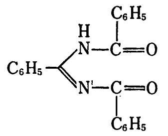
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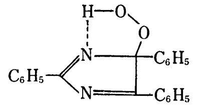
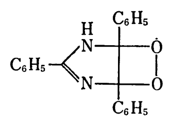

V


VI

In order to clarify the mechanism involved in the ring expansion, reactions of IV and V with ammonia were investigated. When V which was prepared[5] by the photo-oxygenation of I was dissolved in a metha-

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[1] Presented in part at the Symposium on Photochemistry, Tokyo, October, 1969.

[2] T. Hayashi and K. Maeda, Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

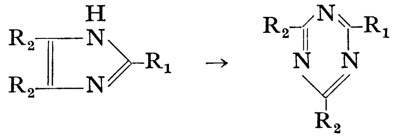
[3] B. Radziszewski, *Ber.*, **10**, 70 (1877).

[4] E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965).

[5] J. Sonnenberg and D. M. White, *J. Amer. Chem. Soc.*, **86**, 5685 (1964).

nolic solution of ammonia at room temperature, II separated from the solution within about 15 min (20% yield based on V) and from the filtrate I (13%), a small amount of III, and benzamide (65%) were isolated. II was also obtained by dissolving V in solutions of ammonia in ethanol, 2-propanol or dimethyl sulfoxide when the yield of II was lower than that obtained in alcoholic solutions. When V was dissolved in ether, acetone or benzene containing ammonia, II was not isolated. On the other hand, when IV was dissolved in a methanolic solution of ammonia at room temperature, II was not obtained, but III and benzamide were isolated. These facts showed that the ring expansion proceeds through V (probably its anion) and IV is not involved in the reaction. In order to elucidate whether VI is involved in the ring expansion or not, the following experiments were carried out. When V (0.026 g) was dissolved in a methanolic solution of potassium hydroxide (1 N, 20 m*l*), the solution exhibited chemiluminescence and showed an absorption band (λ_{max} 245 nm) coinciding with that of IV. The band disappeared within about 20 min with appearance of absorption bands (λ_{max} 247, 279 nm) which coincided with those of III and gradually changed to that of benzamide (λ_{max} 225 nm). On the other hand, when V (0.026 g) was dissolved in a methanolic solution of ammonia (0.45 g in 20 m*l*), the solution did not exhibit chemiluminescence and an absorption spectrum gradually changed to that of III without appearance of the absorption

TABLE 1. 2,4,6-TRIARYL-*s*-TRIAZINE OBTAINED FROM 2,4,5-TRIARYLIMIDAZOLE AND AMMONIUM ACETATE



Triaryl-*s*-triazine		Mp (°C) (lit.)	λ_{max}^{EtOH} (nm) ($\varepsilon \times 10^{-3}$)			Yield (%)
R_1	R_2					
p-$(CH_3)_2N$-C_6H_4-	C_6H_5-[a]	225—226		263 (18)	369 (15.5)	49
p-CH_3O-C_6H_4-	C_6H_5-*	161—162 (157.5—158.5)[6]	228 (sh)	270 (8)	300 (sh)	39
p-OH-C_6H_4-	C_6H_5-[b]	291—291.5	231 (sh)	268 (10)	303 (7)	30
o-OH-C_6H_4-	C_6H_5-*	257—257.5 (245)[7]	213 (sh)	273 (60)	340 (9.5)	56
p-CH_3-C_6H_4-	C_6H_5-*	206—208 (182—183)[8]	212 (sh)	272 (50)		33
o-CH_3-C_6H_4-	C_6H_5-[c]	121—122		268 (19.5)		25
$3',4'$-$CH_2\langle{}^{O}_{O}\rangle C_6H_3$-	C_6H_5-[d]	184—185	246	269 (9)	328 (4)	30
p-Cl-C_6H_4-	C_6H_5-*	200—201 (197.2—197.8)[9]	211 (11)	272 (30)		47
p-Br-C_6H_4-	C_6H_5-[e]	204—205	212 (sh)	275 (14)		28
C_6H_5-	C_6H_5-*	238—239 (232)[9]		268 (41)		35
C_6H_5-	$3',4'$-$CH_2\langle{}^{O}_{O}\rangle C_6H_3$[f]	195—196	240 (28)	277 (22)	330 (25)	33
p-CH_3-C_6H_4-	p-CH_3-C_6H_4-*	285—286 (280—281)[10]	214 (18)	283 (46.5)		30
p-Cl-C_6H_4-	p-Cl-C_6H_4-*	336—337 (335)[10]	216 (5)	283 (14)		32

* Satisfactory C, H, and N analyses were obtained for the corresponding formulas. sh: shoulder

a) Found: C; 78.38, H; 5.65, N; 15.93%. Calcd for $C_{23}H_{20}N_4$: C; 78.40, H; 5.68, N; 15.90%.

b) Found: C; 77.31, H; 4.62, N; 12.72%. Calcd for $C_{21}H_{15}N_3O$: C; 77.54, H; 4.62, N; 12.92%.

c) Found: C; 81.48, H; 5.18, N; 12.78%. Calcd for $C_{22}H_{17}N_3$: C; 81.78, H; 5.26; N; 13.00%.

d) Found: C; 74.68, H; 4.28, N; 11.70%. Calcd for $C_{22}H_{15}N_3O_2$: C; 74.78, H; 4.25, N; 11.89%.

e) Found: C; 65.18, H; 3.60, N; 10.68, Br; 20.60%. Calcd for $C_{21}H_{14}N_3Br$: C; 64.96, H; 3.60, N; 11.08, Br; 20.60%.

f) Found: C; 69.32, H; 3.83, N; 10.41%. Calcd for $C_{23}H_{15}N_3O_4$: C; 69.52, H; 3.70, N; 10.57%.

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[6] E. F. Silversmith, *J. Org. Chem.*, **28**, 3568 (1963).

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[8] M. Kung, K. Koherle, and E. Berthold, US 1989042 (1932).

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[10] D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).

band of IV, and then gradually changed to that of benzamide. Considering these facts together with the conclusion of White and Harding[4] it seems that in a methanolic solution of ammonia, II is formed directly from V and ammonia and VI is not involved in the ring expansion.

When ammonium salts (acetate, chloride, and carbamate) were used in place of ammonia, it was found that II was obtained from V in yields higher than those in the case of ammonia. When V was dissolved in a methanolic solution of ammonium acetate at room temperature, II precipitated in 35% yield after a few minutes. From the filtrate, a large amount of I (64%) was recovered, but III, IV, and benzamide were not obtained.

2-*p*-Chlorophenyl-4,6-diphenyl-*s*-triazine was obtained by the reaction of hydroperoxide of the corresponding imidazole with ammonia or ammonium acetate in methanol at room temperature. 2-*m*-Nitrophenyl-4,5-diphenylimidazole which did not give a hydroperoxide by the sensitized photo-oxygenation did not produce the corresponding *s*-triazine in the presence of oxygen and ammonia. The results are compatible with our finding that lophyl hydroperoxide is an immediate precursor in the ring expansion.

II was also obtained in relatively high yield (35%) by a sensitized photo-oxygenation of I in a methanolic solution of ammonium salts. Other substituted triphenyl-*s*-triazines shown in Table 1, were obtained from the corresponding substituted triphenylimidazole by the similar method. This is a new synthetic method of triaryl-*s*-triazine. This method has an advantage over other procedures since the triazines are obtained in an almost pure state even without recrystallization.

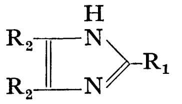
Experimental

Materials. Triarylimidazoles shown in Table 2 were prepared according either to the method of Davidson, Weiss, and Jelling[10] or that of Cook and Jones.[11]

Hydroperoxides of triarylimidazole were prepared according to the method of Sonnenberg and White.[5] A chloroform solution of triarylimidazole (0.20 g and 100 m*l*) containing methylene blue (0.015 g) as sensitizer was irradiated by an incandescent lamp (300 W) for 20 min under cooling with ice-water until an absorption spectrum of the hydroperoxide was observed. After methanol was removed under reduced pressure at room temperature, the residue was dissolved in ether to remove methylene blue. After removal of ether under reduced ressure, the hydroperoxide was obtained as an oily product which was crystallized from methanol.

2,4,5-Triphenyl-4-hydroxy-4*H*-isoimidazole (V) decomposed at 235—245°C, producing I. $\lambda_{\max}^{\mathrm{EtOH}}$: 225 nm ($\varepsilon$: 1.5×10^4), 280 nm (ε: 1.6×10^4). IR (KBr and $CHCl_3$): 2820, 1620, and 850 cm^{-1}. NMR ($CDCl_3$): Signals were observed at 7—9 ppm, but no signal was observed at 10—15

TABLE 2.



Triarylimidazole[a]		Mp (°C) (lit.)	Method of preparation
R_1	R_2		
p-$(CH_3)_2N$-C_6H_4-	C_6H_5-	261—262 (259.5—260[12])	10
p-CH_3O-C_6H_4-	C_6H_5-	238—239 (233.7—233.9[12])	10
p-OH-C_6H_4-	C_6H_5-	270—271 (268—268.5[12])	10
o-OH-C_6H_4-	C_6H_5-	214—215 (214—215[12])	10
p-CH_3-C_6H_4-	C_6H_5-	239—240 (237—237.5[12])	10
o-CH_3-C_6H_4-	C_6H_5-	249—250 (244—246[13])	10
3′,4′-$CH_2\langle{}^{O}_{O}\rangle C_6H_3$-	C_6H_5-	262—263.5 (246—247[13])	10
p-Cl-C_6H_4	C_6H_5-	261—262 (284—286 (d)[14] 256—257[12])	10
p-Br-C_6H_4-	C_6H_5-	268—269 (260—261 (d)[14] 253—254[13])	10
C_6H_5-	C_6H_5-	286—287 (273.5—274[4])	10
C_6H_5-	3′,4′-$CH_2\langle{}^{O}_{O}\rangle C_6H_3$-	269—270 (monohydrate)[b]	10
p-CH_3-C_6H_4-	*p*-CH_3-C_6H_4-	285—286 (280—281[11])	11
p-Cl-C_6H_4-	*p*-Cl-C_6H_4-	336—337 (335[11])	11

a) Satisfactory C, H, and N analyses were obtained for the corresponding formulas

b) Found: C; 68.46, H; 4.94, N; 6.76%. Calcd for $C_{23}H_{18}N_2O_5$: C; 68.66, H; 4.48, N; 6.96%.

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[11] A. H. Cook and D. G. Jones, *J. Chem. Soc.*, **1941**, 278.

[12] D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).

[13] S. Kori and S. Narisawa, *Asahi Garasu Kenkyu Hokoku*, **12**, 55 (1962).

[14] G. E. Philbrock, M. A. Maxwell, R. E. Taylor, and J. R. Totter, *Photochem. Photobiol.*, **4**, 1175 (1965).

ppm.

Found: C, 76.80; H, 4.91; N, 8.53%. Calcd for $C_{21}H_{16}N_2O_2$: C, 76.82; H, 4.48; N, 8.53%.

2-*p*-Chlorophenyl-4,5-diphenyl-4-hydroxy-4*H*-isoimidazole decomposed at 235—245°C, producing 2-*p*-chlorophenyl-4,5-diphenylimidazole. λ_{max}^{EtOH}: 230 nm (ε: 1.5×10^4), 290 nm (ε: 1.7×10^4). IR (KBr): 2810, 1620, 840 cm^{-1}.

Found: C, 69.83; H, 4.70; N, 7.51; Cl, 9.83%. Calcd for $C_{21}H_{15}N_2O_2Cl$: C, 69.52; H, 4.13; N, 7.72; Cl, 9.79%.

N,N'-Dibenzoylbenzamidine (IV) was prepared according to the method of Dufraisse and Martel,[15] mp 141.5—142.5°C. Satisfactory C, H, and N analyses were obtained for $C_{21}H_{16}N_2O_2$.

Photolysis of I in Methanol in the Presence of Oxygen and Ammonia. A methanolic solution of I (0.5 g in 500 m*l*) containing ammonia (0.5 g) was irradiated at room temperature by a 100 W high-pressure mercury lamp under bubbling of oxygen, until a crystalline precipitate of II began to separate after about 2 hr. Absorption spectrum and thin-layer chromatogram of the solution showed the absence of I and suggested the presence of 4,5-(9',10'-phenanthryl)imidazole, III, and benzamide in the solution. II (mp 238—239°C) was collected by filtration (0.083 g 16%) which was proved to be identical with an authentic sample. The filtrate was evaporated to leave a yellow oil which deposited a white crystalline precipitate upon standing overnight. A small amount of benzene was added and the crystalline precipitate (about 0.15 g) was filtered. The precipitate (A) was shown to consist of benzamide and III by thin-layer chromatography and UV spectrum. An oily residue obtained by evaporation of the solvent from the yellow filtrate was dissolved in methanol and a small amount of water was added to produce a crystalline precipitate, The precipitate collected was identified to be 4,5-(9',10'-phenanthryl)imidazole (0.050 g, 9%) by mixed-melting with an authentic sample. After removal of the solvent, the oily residue was shown to contain III and benzamide by thin-layer chromatography and UV spectrum. The oily residue and the precipitate (A) were dissolved in benzene-acetone (4 : 1) and chromatographed on a column of alumina (20 g), using the same solvent system for elution. The early fractions collected were evaporated and the oily residue obtained was crystallized from *n*-hexane to give colorless crystals of III (0.181 g, 45%) which was proved to be identical with an authentic sample. From the later fractions collected benzamide (mp 124—125°C, 0.190 g, 25%) was obtained by evaporation of the solvent.

Sensitized Photo-oxygenation of I in Methanol in the Presence of Ammonia. A methanolic solution of I (0.10 g in 100 m*l*) containing ammonia (0.1 g) and methylene blue (0.015 g) was irradiated by a 300 W incandescent lamp for 15 min under bubbling of oxygen at about 0°C. Thin-layer chromatogram and UV spectrum of the resultant solution showed the absence of I and formation of lophyl hydroperoxide (V). When the solution was allowed to stand at room temperature for about 1 hr, a crystalline precipitate of II separated from the solution. II (mp 238—239°C) was collected by filtration (0.023 g, 22%). The filtrate was evaporated to dryness, and the residue was dissolved in ether to remove methylene blue. The yellow filtrate was evaporated to obtain a yellow residue (about 0.05 g) showing the presence of III and benzamide by UV spectrum and thin-layer chromatography. A benzene-acetone (4 : 1) solution of the residue was chromatographed on a column of alumina (5 g) using the same solvent system for elution. III (0.024 g, 33%) and benzamide (0.010 g, 12%) were obtained from the early and later fractions, respectively.

Reaction of V with Ammonium Acetate in Methanol. When V (0.20 g) was dissolved in a methanolic solution of ammonium acetate (1.0 g in 10 m*l*) at room temperature, a crystalline precipitate appeared within about 5 min. It was proved to be identical with an authentic sample of II. After the solution was allowed to stand overnight at room temperature, the precipitate of II (mp 238—239°C) was collected by filtration (0.066 g, 35%). The filtrate was shown by thin-layer chromatography and UV spectrum to consist largely of I. After the filtrate was concentrated to about one-half, water was added to yield a precipitate of I. The precipitate of I collected was washed with water and recrystallized from ethanol (mp 272—273°C, 0.107 g, 64%).

Preparation of II by Sensitized Photo-oxygenation of I in a Methanolic Solution of Ammonium Acetate. A methanolic solution of I (0.20 g in 100 m*l*) containing ammonium acetate (5.0 g) and methylene blue (0.015 g) was irradiated by a 300 W incandescent lamp at about 0°C under bubbling of oxygen. On irradiation for 10—20 min, the absorption spectrum of I changed to that of V and only a spot of V on a thin-layer chromatogram was obtained. After shutting off the irradiation the solution was heated (about 50°C) until the absorption band of II appeared with diminishing of that of V (about 3 hr). When the solution was allowed to stand at room temperature, II gradually separated from the solution. II (mp 238—239°C) was collected by filtration (0.073 g, 35%). The filtrate was shown to consist largely of I by thin-layer chromatography and UV spectrum. The filtrate was concentrated by evaporation and water was added to the residue to give a precipitate of I and to remove methylene blue. The precipitate of I collected was washed with water and recrystallized from ethanol (mp 272—273°C, 0.10 g, 50%). The yield of II did not increase when the solution was allowed to stand at room temperature or lower after shutting off the irradiation.

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[15] C. Dufraisse and J. Martel, *Compt. Rend.*, **244**, 3106 (1957).