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Photochemical *cis-trans* Isomerization of 2,4,5-Triphenylimidazolines[1]

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Irradiation of *cis*- (amarine; I) and *trans*- (isoamarine; II) 2,4,5-triphenylimidazolines in acetonitrile or benzene gave a photostationary mixture of *cis*- and *trans*-isomers, the latter predominating over the former. On irradiation in a dilute acetone solution under the conditions that acetone absorbed most of the incident light, *cis-trans* isomerization occurred only with isoamarine but not with amarine. In acetone, 2,4,5-triphenylimidazole (III) was also formed. Two kinds of intermediate species for the *cis-trans* isomerization were proposed; imidazolinyl radicals IV and/or V formed by hydrogen abstraction with the excited state of acetone (in acetone) and a biradical or a zwitterionic species VIa formed by cleavage from the excited state of I or II (in acetonitrile or benzene). Evidences for the intermediacy of VIa are presented.

In a previous paper,[2] it has been shown that imidazolines, on irradiation in acetone solutions, are dehydrogenated to give the corresponding imidazoles *via* imidazolinyl radicals which are formed by hydrogen abstraction with excited acetone. In the course of this investigation 2,4,5-triphenylimidazolines, amarine (I; *cis*) and isoamarine(II; *trans*), were found to undergo *cis-trans* isomerization simultaneously with dehydrogenation to 2,4,5-triphenylimidazole(III; lophine). Since such a type of *cis-trans* isomerization in heterocyclic systems appeared relatively rare,[3] the photochemical *cis-trans* isomerization of I and II was examined in some details.

Results and Discussion

cis-trans *Isomerization of I and II under Various Conditions.* Amarine(I) and isoamarine(II) were irradiated with a 100 W high-pressure mercury lamp (Pyrex) or a 10 W low-pressure mercury lamp (Vycor, mainly 2537 Å) under bubbling nitrogen in various solvents at different concentrations. The results are summarized in Table 1. The material balance of the photoreaction induced by Pyrex-filtered light was considerably good, and products other than I, II and lophine (III) were obtained only in small yields (*vide infra*).

In acetonitrile, no lophine (III) was formed and a photostationary mixture of I and II with predominance of the thermodynamically more stable isomer II was obtained from either I or II. Piperylene, a triplet quencher, failed to quench the *cis-trans* isomerization at various concentrations (Table 2), indicating that the excited state responsible for the isomerization may be singlet or short-lived triplet, provided that the triplet energies of I and II exceed that of piperylene.

In benzene, which is known as a triplet sensitizer except a few exceptional cases,[4] only a trace of III was detected and the photostationary mixture of I and II was obtained in the similar ratio to that in acetonitrile. Both I and II were found to isomerize at such a low concentration (0.17×10^{-2} M) that more than 99% of the incident light was absorbed by benzene. It was also found that the II/I ratio in the isomerization of I in benzene decreased with increase in the amount of added piperylene (Table 3), possibly due to partial quenching of the benzene triplet. These results suggest that the *cis-trans* isomerization of I and II may take place at least partly from their short-lived triplet state.

In acetone, lophine (III) was always formed to a

TABLE 1. PHOTOCHEMICAL *cis-trans* ISOMERIZATION OF AMARINE AND ISOAMARINE IN VARIOUS SOLVENTS

Solvent	Starting material	Concn ($\times10^2$ M)	Light source[a]	Irradn time (hr)	II/I ratio	Yield (%)	
						III	I+II
MeCN	I	3.14	B	24	1.8	0	61
	II	3.12	B	24	1.6	0	63
	I	1.77	A	8	2.3	0	96
	II	1.71	A	8	2.3	0	93
C_6H_6	I	3.45	A	15	1.6	trace	96
	I	0.172	B	3	1.6	trace	n. d.[b]
	II	0.168	B	3	1.4	trace	n. d.
Me_2CO	I	3.55	B	24	0.60	35	41
	I	3.27	A	15	0.46	21	74
	I	0.0282	A	1	0	29[c]	n. d.
	II	3.62	B	24	0.59	28	43
	II	0.0302	A	1	~0[d]	19[c]	n. d.
Me_2CHOH	I	3.54	A	15	3.0	0	95
Et_2O	I	1.36	A	15	1.8	trace	n. d.

a) A: high-pressure mercury lamp (Pyrex), B: low-pressure mercury lamp (2537 Å). b) Not determined. c) Determined after 30 min irradiation. d) II/I ratio is 0.43 after 0.5 hr, 0.083 after 1 hr.

Table 2. Quenching of excited I with piperylene in acetonitrile[a)]

Piperylene added(M)	0	0.0604	0.12	0.179	0.237	0.295	0.573
III/I ratio[b)]	0.24	0.31	0.33	0.30	0.27	0.26	0.27

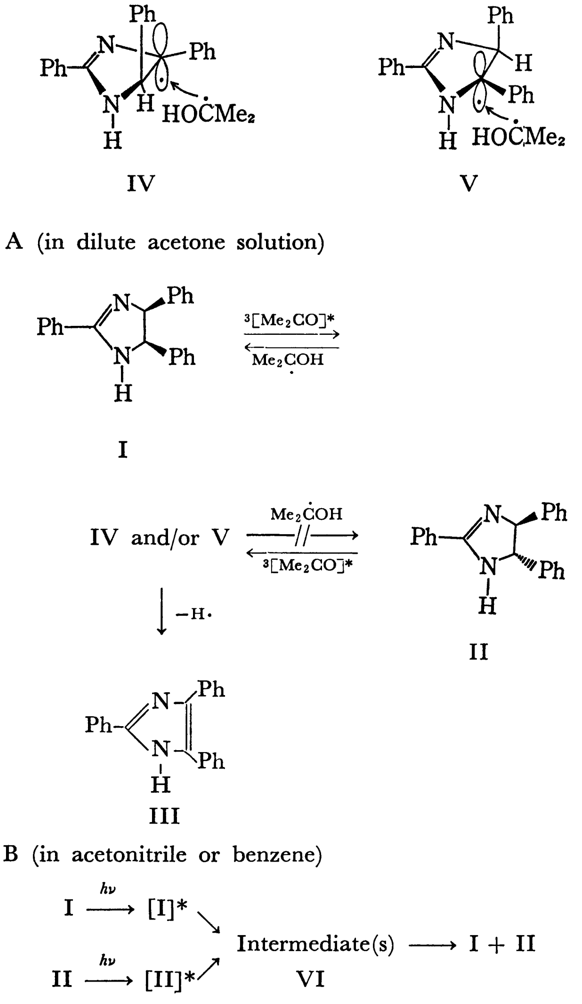
a) Initial concentration of I: 2.05×10^{-2} M. Light source, irradiation time, and temperature: 450-W high pressure mercury lamp (Pyrex), 3 hr, and 30±1 °C, respectively. b) Irradiation of I without piperylene showed that the value of II/I ratio increased almost linearly with increased irradiation time in the earlier stage of photolysis.

Table 3. Quenching experiment with piperylene in benezene[a)]

Initial concentrations[b)] of I ($\times10^3$ M)	1.71	1.87	1.72
Piperylene added(M)	0	0.0421	0.633
II/I ratio	1.6	1.4	0.8

a) Light source: 10-W low pressure mercury lamp (Vycor). Irradiation time: 3 hr b) At these concentrations of I, more than 99% of the incident light is absorbed by benzene.

considerable extent regardless of the light sources, and the *cis-trans* isomerization was found to be dependent on the initial concentration of I and II. At low concentrations (*ca.* 3×10^{-4} M), at which more than 99% of the incident light was absorbed by acetone, the isomerization occurred only from isoamarine(II) toward amarine(I) but not from I toward II. At high concentrations (*ca.* 3.5×10^{-2} M), at which about 50% of the incident light was absorbed by acetone, either I or II afforded a photostationary mixture of I and II with predominance of I over II in contrast to the case in acetonitrile and in benzene. These results obviously indicate that the mechanism of the *cis-trans* isomerization in acetone solution is different from that in acetonitrile or benzene solution.

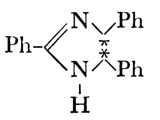


Scheme 1.

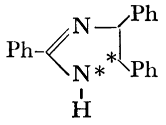
In the course of our study on the photochemical dehydrogenation of imidazolines to imidazoles in acetone,[2)] it has been shown that excited acetone can abstract a hydrogen atom at 4- or 5-position of imidazolines to yield imidazolinyl radicals IV and/or V and the acetone ketyl radical, and that the resultant imidazolinyl radical can be led either to the original imidazolines, a hydrogen atom being supplied by the acetone ketyl radical, or to the corresponding imidazoles. It is, therefore, quite reasonable to suppose that the photochemical *cis-trans* isomerization of I and II in dilute acetone solutions accompanied with dehydrogenation of both I and II to III proceeds through the imidazolinyl radicals IV and/or V as depicted in Scheme 1 (A).[2)] The completely stereoselective isomerization toward I in dilute acetone solutions must require that the hydrogen transfer from the acetone ketyl radical to the imidazolinyl radicals IV and/or V occurs only in the direction toward the thermodynamically less stable isomer I but not toward II. The result implies that the *cis-trans* isomerization of I or II from their excited states does not sensitized by acetone; in other words the acetone triplet acts only as a hydrogen transfer agent but not as a donor of excitation energy. The acetone ketyl radical may attack IV and/or V predominantly from the opposite side of a bulky phenyl group as shown below. At high concentrations of I and II in acetone, *cis-trans* isomerization through a common intermediate(s) (VI) from their excited states as in acetonitrile or benzene [Scheme 1 (B)] is possibly competing with *cis-trans* isomerization *via* the imidazolinyl radicals. Thus, it is reasonably explained that the II/I ratio observed at higher concentrations in acetone is smaller than that observed in acetonitrile or benzene. It should be noticed that these two processes shown in Scheme 1 provide a typical example of kinetically (A) and thermodynamically (B) controlled *cis-trans* isomerizations, and that reaction A provides an additional example of the so-called chemical sensitization.[4a)]

Irradiation of I in isopropyl alcohol or ether under the similar conditions also resulted in the *cis-trans* isomerization with predominance of II over I.

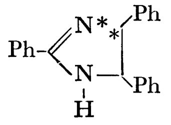
The Nature of the Intermediate VI. It seems reasonable to assume a homolytic or a heterolytic bond cleavage of ring bonds (VIa, VIb, VIc or VId) as the intermediate step of *cis-trans* isomerization in acetonitrile or benzene. Other pathways involving migration of 4-hydrogen (VIe or VIf[5)]) are also possible



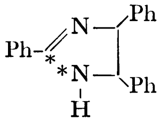
VIa



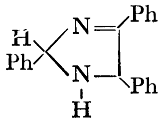
VIb



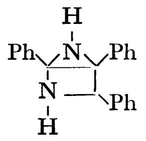
VIc



VId



VIe

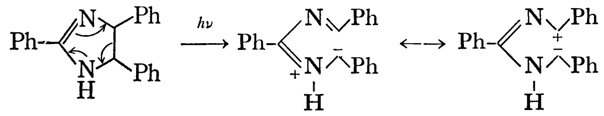


VIf

$* = \cdot$ or $+, -$

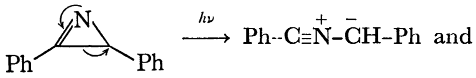
although less probable because of the following reasons. If 1,3-hydrogen shift occurs stepwise and homolytically in the process, I (or II)⇄VIe, the imidazolinyl radical IV must be transiently formed and consequently lophine (III) must be formed concurrently. Since III was unable to be detected among the products at least in acetonitrile, the 1,3-hydrogen shift, if it occurs, should proceed concertedly in a suprafacial manner[6] and should not result in *cis-trans* isomerization *via* the intermediary formation of VIe. The intermediate VIf also has the difficulty in explaining the results that deuterium incorporation is very inefficient during irradiation of I in acetonitrile–D_2O (below 1.9% after over the half of I employed isomerized into II).

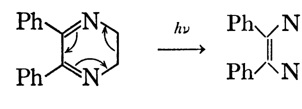
Among possible biradical or zwitterionic intermediates (VIa—VId), VIa is the most plausible one in view of bond dissociation energy data for similar types of bonds : $PhCH_2—CH_2Ph$ (45—48 kcal/mol)[7] and $PhCH_2—NHCH_3$ (58 kcal/mol).[8] The bond dissociation energy data for $-\overset{|}{C}{=}N{-}C\lessdot$ and $-\overset{|}{N}{-}\overset{|}{C}{=}N-$ bonds are not available, but they may have a higher value than those for other bonds in the imidazoline ring considering the less resonance-stabilized nature of $>C{=}N\cdot$ or $\cdot\overset{|}{C}{=}N-$ radical. The photochemical homolytic cleavage of C–C bonds has been recently reported.[3,9] Furthermore, the hetrolytic cleavage to generate VIa has some analogy to that of azirines[10] and 2,3-dihydropyrazines.[11]



I or II VIa

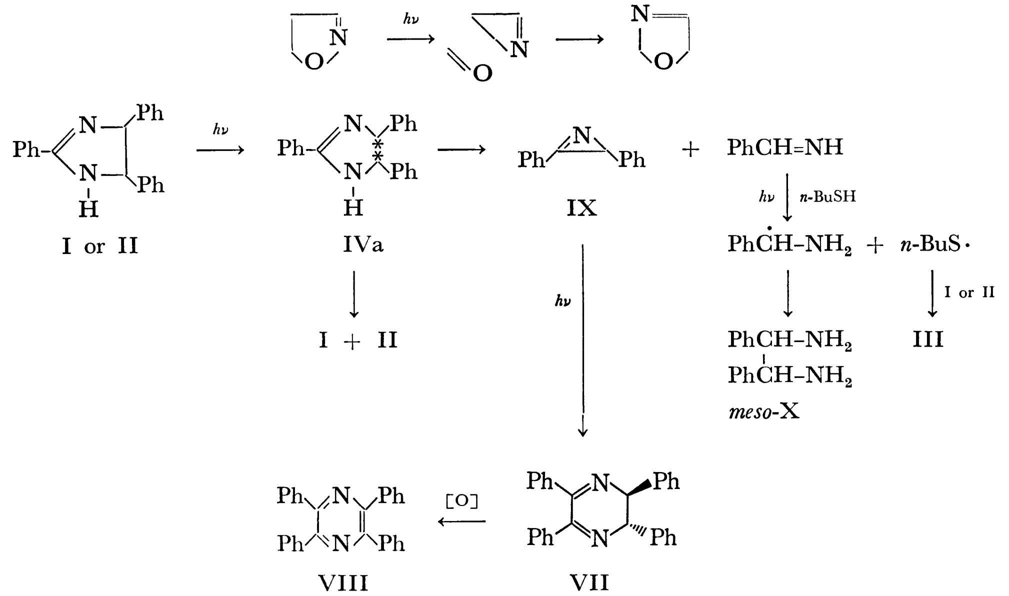
Compare with





In order to see whether the rupture of C_4–C_5 bond of I or II (VIa) occurs, it was attempted to isolate byproducts, which may be formed from the plausible intermediate VIa, and also to trap VIa by radical scavengers such as *n*-butyl mercaptan,[12] oxygen, and 2,2,6,6-tetramethylpiperidine-1-oxyl[13] and by the solvent isopropyl alcohol.[9a]

Amarine (I) was irradiated in acetonitrile with light through Pyrex to give a mixture of products from which *trans*-2,3,5,6-tetraphenyl-2,3-dihydropyrazine (VII, 2%) was isolated by chromatography. In addition, 2,3,5,6-tetraphenylpyrazine (VIII), which was probably formed by autoxidation of VII[14b] during work-up, was detected on tlc. A small amount (1—2%) of lophine (III) was also obtained in this case. Since VII and VIII are known to be formed photochemically from 2,3-diphenyl-2*H*-azirine (IX),[14] it is reasonably assumed that IX is an intermediate in the transformation of I into VII. The formation of IX can be rationalized by fragmentation of I or II through the intermediate

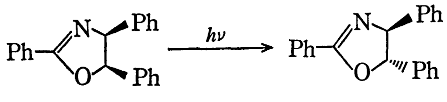


Scheme 2.

VIa (Scheme 2), similar to that of 2-isoxazolines to give an azirine and a carbonyl compound which recombine to form 3-oxazoline.[15]

Attempts for trapping VIa with 1-butanethiol (0.38 M in acetonitrile), 2,2,6,6-tetramethylpiperidine-1-oxyl (0.127 M in benzene), and the solvent isopropyl alcohol were unsuccessful. However, irradiation (Pyrex) of I in acetonitrile in the presence of 1-butanethiol afforded VII(2%), VIII (3%), III(48%), I(17%), II(9%) and *meso*-stilbenediamine (X, 2%). The last compound X appears to be a product derived from benzaldimine, the counterpart of IX (Scheme 2). Photoreductive dimerization of imines with a suitable hydrogen donor is well-known.[16] The formation of a large amount of III may be attributed at least partly to hydrogen abstraction with the 1-butanethiyl radical.[17]

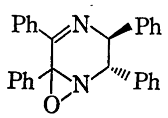
It is worthwhile to mention about the preliminary results of photolysis of *cis*-2,4,5-triphenyloxazoline(*cis*-XI). Upon photolysis (2537 Å) *cis*-XI afforded its *trans*-isomer (14%) and benzaldehyde. It should be noticed that this reaction is also explained by cleavage of the C_4–C_5 bond in the first step. If the O_1–C_2 bond is first broken, benzonitrile must be formed considering the photofragmentation of 2-isoxazolines.[15]



cis-XI *trans*-XI

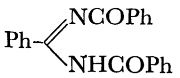
+ PhCHO + unidentified product(s)

The formation of VII may be rationalized by other mechanisms (Scheme 3). The pathways a and b were eliminated by the fact that photolysis of lophine(III) or a mixture of III and *dl*-stilbenediamine did not yield even a trace of VII and VIII. The pathway c, which must involve complex reactions, is also improbable, because the photolysis of I in acetonitrile in the presence of a small amount of benzaldehyde resulted in the decrease (less than 1%) of yields of VII and VIII. And a new product, which was assigned as oxaziridine XII (2% yield) on the basis of spectral data and an independent synthesis, was obtained in addition to I and II.

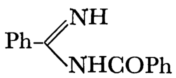


XII

Irradiation (Pyrex) of I in acetonitrile under bubbling oxygen gave *N*,*N*′-dibenzoylbenzamidine (XIII, 43%), *N*-benzoylbenzamidine (XIV), dibenzamide (XV) (the total yield of XIV and XV is 16%) and II (13%). At first glance, the oxidation of I to XIII appeared to proceed *via* trapping of the intermediate VIa by oxygen. It is, however, known[18,19] that the photochemical oxidation of III produces a lophine hydroperoxide (XVI), which decomposes gradually to XIII. In the present photooxidation of I, neither III nor XVI could be detected (tlc). But, at low temperature (−78 °C) at which the intermediate XVI is known to be stable and to be accumulated as the primary photooxidation product of III,[18] I resisted to photooxidation and only underwent *cis-trans* isomerization. Therefore, it can not be unambiguously known whether XIII, XIV, and XV were formed *via* VIa.



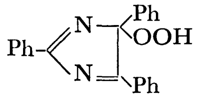
XIII



XIV

$(PhCO)_2NH$

XV

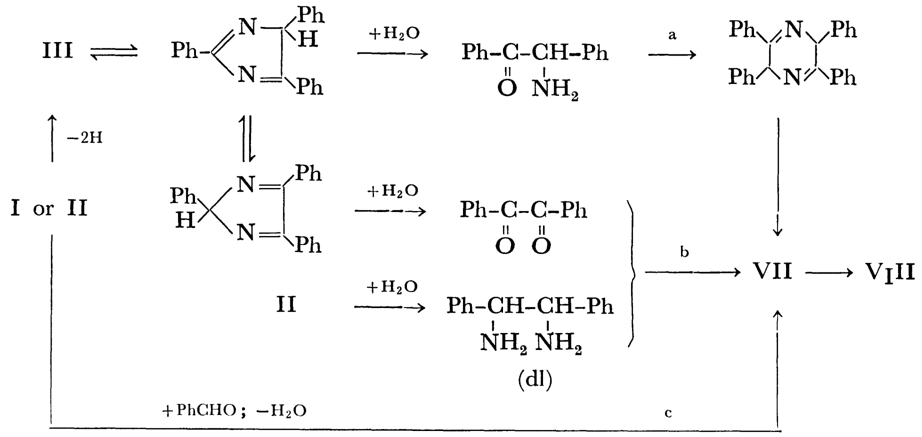


XVI

In conclusion, the *cis-trans* isomerization of I and II, the bond energy data, the isolation of VII and X, and the photoproducts of *cis*-XI are well accommodated by a mechanism involving the scission of C_4–C_5 bond. The result of photochemical oxidation of I is not inconsistent with this mechanism.

Experimental

All the melting points are uncorrected. NMR spectra were taken on an NEVA T-60 spectrometer with tetramethylsilane as the internal standard. IR and UV spectra were measured on a JASCO IRS spectrophotometer, and on a MODEL ORD/UV-5 Japan Spectrometer, respectively. Column chromatography was carried out with Mallinckrodt silica gel (100 mesh) as the adsorber. Thin layer chromatography (tlc) was carried out with Merck Kieselgel GF_{254} using UV



Scheme 3.

light and iodine for compound detection. Synthesis of amarine (I) and isoamarine (II) has been described.[2] All the solvents were distilled before use.

cis-trans *Isomerization of I and II under Various Conditions (Table 1).* A solution of I or II dissolved in a solvent, 110 ml when a 100-W highpressure mercury lamp (Pyrex filter) was used, 220 ml when a 10-W lowpressure mercury lamp (Vycor filter, mainly 2537 Å) was used, and 500 ml (acetone) for low concentration experiments, was irradiated several hours under bubbling nitrogen. After evaporation of the solvent under reduced pressure, the residue was subjected to NMR analysis (CCl_4–DMSO-d_6) and the II/I ratio was determined from the peak intensities of singlets at τ 4.55 for I and τ 5.10 for II. The yields of lophine (III) and recovered imidazolines (I+II) were determined by UV analysis (EtOH) and NMR analysis (CCl_4+DMSO-d_6; pinacol or 2-methylimidazoline as the internal standard), respectively. In solvents except acetone, none or a trace of III was detected by careful tlc analysis.

Quenching of the cis-trans *Isomerization of I.* Pyrex tubes (volume 20 ml) containing a fixed amount of I and freshly distilled piperylene (bp 45—47 °C) in acetonitrile were sealed after bubbling nitrogen through the solution and irradiated externally on a merry-go-round apparatus. After removing the solvent and the piperylene under reduced pressure, the II/I ratio was determined by NMR technique (Table 2).

The results of Table 3 were obtained by irradiating a fixed amount of I and piperylene in benzene (220 ml) under bubbling nitrogen and then by determining the II/I ratio by NMR spectroscopy.

Isolation of Byproducts and Experiments to Trap VIa in the cis-trans *Isomerization of I.* All irradiations were done with a 100-W high pressure mercury lamp (Pyrex filter) under bubbling nitrogen, unless otherwise specified. The photoproducts obtained after removing the solvent under reduced pressure were separated and characterized in the following way.

A) Isolation of Byproducts. The product mixture (after 17 hr irradiation)[20] from a solution of I (1.17 g) in acetonitrile (110 ml) was chromatographed on silica gel (40 g). Elution with 200 ml of 1 : 1 benzene–chloroform gave 12 mg of a solid which contained a trace of 2,3,5,6-tetraphenylpyrazine (VIII) (tlc). Further elution with 400 ml of the same solvent, followed by preparative tlc, afforded 35 mg (2%) of VII identified by IR, NMR, and tlc and 15 mg (1—2%) of III identified by IR and tlc. Further elution with the same solvent and finally with acetone gave 760 mg of II and 350 mg of I, respectively (total yield of I and II, 95%).

B) Irradiation of I with Trapping Reagents. *i) 1-Butanethiol*: A chloroform-insoluble part of the product mixture (after 15 hr irradiation) from a mixture of I (2.33 g; 0.035 M) and 1-butanethiol (9.0 ml; 0.38 M) in acetonitrile (220 ml) was recrystallized from acetone and 135 mg of III was obtained. The residue from the mother liquor was chromatographed on silica gel (70 g). Elution with 700 ml of chloroform afforded a yellow solid, which after preparative tlc (benzene) yielded 60 mg (3%) of 2,3,5,6-tetraphenylpyrazine (VIII) mp 260—261 °C (acetone-chloroform) (lit. mp 252 °C[21]) and 40 mg (2%) of *trans*-2,3,5,6-tetraphenyl-2,3-dihydropyrazine(VII), mp 205—206 °C (chloroform-ethanol) (lit. mp 199.5—200.5 °C[22]). The IR spectrum of VII were identical with that of an authentic sample.[22] The IR sepctrum of VIII was identical with that in the Sadtler Standard Spectra. Further elution with 800 ml of chloroform yielded 990 mg of III (the total yield of III, 48%). Further elution with chloroform and acetone, followed by preparative tlc (1 : 1 chloroform-acetone), yielded I (380 mg) and II (210 mg) and 40 mg (2%) of *meso*-stilbenediamine(X), mp 121—123 °C (ligroin-ether) (lit. mp 118—120 °C[23]) which was identical with an authentic sample.[24]

ii) Oxygen: The product mixture obtained from photolysis (15 hr) of a solution of I (1.07 g) in acetonitrile (110 ml) under bubbling oxygen instead of nitrogen was separated by preparative tlc (30—50 : 1 chloroform-acetone). Following products, in the order of increasing R_f values, were isolated: (1) *N,N′*-Dibenzoylbenzamidine(XIII); 460 mg (43%), which was unstable on silica gel (Kieselgel GF_{254}) or alumina (Aluminiumoxide GF_{254}) and decomposed to a mixture of XIII, XIV, and XV as reported earlier[18,19] but could be obtained in a sufficiently pure state for IR and NMR measurements. Its identity was confirmed by comparison with an authentic sample.[19] (2) *N*-Benzoylbenzamidine (XIV) and (3) dibenzamide(XV); combined yield, 165 mg (16%). These two compounds had the same R_f value of tlc ($CHCl_3$) and XIV decomposed on tlc to give XV. Recrystallization of the mixture from 3 : 1 ligroin-acetone, however, could yield pure XV, mp 152—154 °C (lit. mp 147—148 °C[25]) which was identified by NMR and IR spectra and had UV spectrum identical to the published data.[26] The residue from the mother liquor-consisted of mainly XIV, whose NMR and IR spectral data were in accord with those of an authentic sample.[19] (4) Isoamarine (II); 140 mg (13%). Amarine (I) was not detected. Low-temperature (−78 °C) oxidation of I was also carried out in the same manner and the reaction was followed by tlc, giving results that only I and II were detected, but III, XIII, XIV, XV and XVI[18] could not be detected.

iii) 2,2,6,6-Tetramethylpiperidine-1-oxyl.[27] A mixture of I (1.14 g, 0.0191 M) and this free radical (3.96 g, 0.127 M) in benzene (200 ml) was irradiated under nitrogen with light at 313 nm isolated from a 100-W mercury lamp with a chromate-carbonate filter.[28] The reaction was followed by tlc confirming the occurrence of ***cis-trans*** isomerization. In addition, a small amount of III was detected.[29] However, products expected from the trapping of VIa by the nitroxyl radical could not be observed until 52 hr of irradiation. At this point an aliquot of the photolysate was submitted to preparative tlc (30 : 1 chloroform–ethanol) and an almost equal amount of I and II and a small amount of III were isolated. The nitroxyl radical was fairly stable under these conditions and was largely recovered unchanged (*ca.* 72%).

iv) Isopropyl Alcohol. After 70 hr of irradiation, the photolysate from I (1.01 g) in isopropyl alcohol (100 ml) contained no significant product except I and II as the main product and traces of III, VII and VIII by tlc analysis.

Photolysis of I in the Presence of Benzaldehyde. The mixture obtained by the photolysis (15 hr) of a solution containing 1.01 g (3.41×10^{-2} M) of I and 50 µl (4.81×10^{-3} M) of benzaldehyde in acetonitrile (110 ml) with a 100-W high pressure mercury lamp (Pyrex) under bubbling nitrogen was evaporated and the residue was chromatographed on silica gel (30 g). Elution with chloroform, followed by preparative tlc (benzene or 20—50 : 1 chloroform–acetone) of the eluates, yielded 3 mg (<0.5%) of VIII, 5 mg (<0.5%) of VII, 20 mg (2%) of III and 23 mg (2%) of XII. Further elution with chloroform and acetone afforded 530 mg (52%) of II and 435 mg (43%) of I. The structure of XII, mp 184—185 °C (petroleum ether-methanol), was assigned from its spectral and analytical data; ν (film) 1665, 1325 cm^{-1}; τ (CCl_4) 2.17—3.17 (20H, m, arom), 4.88 (1H, d, J=3 Hz) and 4.98 (1H, d, J=3 Hz); λ_{max}(EtOH) 242 (ε 18400) nm.

Found: C, 83.48; H, 5.65; N, 6.82%. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.96%.

Synthesis of XII. To a solution of 90 mg (2.33×10^{-4} M) of VII in 1 ml of chloroform was added dropwise 450 mg (2.93×10^{-4} M) of perbenzoic acid (9% chloroform solution) with stirring. The mixture was stirred for further 1 hr at room temperature, and evaporated to dryness. The residue was separated by preparative tlc (chloroform) and 15 mg (23%) of XII was isolated as the main product which showed an IR spectrum identical with that of XII obtained photochemically. The method to prepare oxaziridines by the action of peracids or aerated aldehydes on Schiff's bases is well-known.[30]

Photolysis of III in the Presence or Absence of dl-*Stilbenediamine.* Two Pyrex tubes, each containing a solution of III (10 mg) in acetonitrile (20 ml) and a solution of III (11 mg) and *dl*-stilbenediamine (5 mg) in acetonitrile (20 ml), were irradiated externally with a 400-W high pressure mercury lamp (Pyrex) under bubbling nitrogen for 8 hr. By careful examination of the photolysate by tlc VII and VIII were not detected at all.

Deuterium Incorporation Experiment. A solution of 94 mg of I in a mixture of acetonitrile (15 ml) and D_2O (5 ml) placed in a Pyrex tube was sealed after bubbling nitrogen and irradiated externally with a 450-W high pressure mercury lamp for 16 hr. After evaporation of the photolysate under reduced pressure, the residue (II/I=1.2 by NMR) was dissolved in chloroform (20 ml) and washed four times with 20 ml of water to remove deuterium bound to nitrogen. The solution was evaporated after drying over Na_2SO_4 and was separated by preparative tlc (3 : 2 chloroform–acetone) to give I (25 mg) and II (34 mg). The latter was recrystallized from ether-ethanol and analyzed by mass spectroscopy (Hitachi RMU-6C) to determine deuterium content. It was estimated as less than 1.9% from comparison with the mass spectrum of the nondeuterated II.

Photolysis of cis-*2,4,5-Triphenyloxazoline (XI).* A solution of XI[31] (1.03 g) in acetonitrile (220 ml) was irradiated with a 10-W low pressure mercury lamp (Vycor) under bubbling nitrogen for 15 hr. After removing the solvent under reduced pressure, the residue (1.03 g) was chromatographed on silica gel (50 g). Elution with benzene (400 ml) afforded 35 mg of a yellow oil which contained *ca.* 1 mg of benzaldehyde (IR) by vpc analysis. Further elution with benzene (400 ml), followed by preparative tlc (2 : 1 chloroform–benzene), afforded 144 mg of *trans*-2,4,5-triphenyloxazoline, mp 86—87.5 °C (from petroleum ether) (lit. mp 83—85 °C[31]), which gave satisfactory spectral and analytical data. Further elution with benzene (1600 ml), followed by preparative tlc (5 : 1 chloroform–benzene), afforded a white solid (345 mg); mp 122—135 °C (from petroleum ether–acetone), which was unidentified.

References

1) Photoinduced Reactions. LXXXVIII. Part LXXXVII: I. Saito, Y. Chujo, H. Shimazu, M. Yamane, T. Matsuura, and H. J. Cahnmann, *J. Amer. Chem. Soc.*, **97**, 5272 (1975). A preliminary communication of the present paper appeared: T. Matsuura and Y. Ito, *Chem. Lett.*, **1972**, 431.

2) T. Matsuura, Y. Ito, and I. Saito, This Bulletin, **46**, 3805 (1973).

3) A photochemical *cis-trans* isomerization of *N*-substituted 2,3-diphenylaziridine *via* homolytic cleavage of C–C bond [A.G. Anastassiou and R. B. Hammer, *J. Amer. Chem. Soc.*, **94**, 303 (1972)] and a photochemical transformation of *trans*-2,3-dihydro-2,3,5,6-tetraphenylpyrazine to *cis*-isomer [A. Padwa and E. Glazer, *J. Amer. Chem. Soc.*, **94**, 7788 (1972)] have been reported.

4) a) P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971); b) J. P. Ferris and F. R. Antonucci, *J. Amer. Chem. Soc.*, **96**, 2014 (1974).

5) A similar rearrangement has been found with *N*-diphenylmethylidenediphenylmethylamine [K. N. Mehrotra and T. V. Singh, *Tetrahedron Lett.*, **1972**, 4949].

6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie GmbH, Academic Press, New York (1970).

7) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

8) J. A. Kerr, *ibid.*, **66**, 496 (1966).

9) a) M. H. Delton and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 2471 (1972). b) T. Shirafuji, Y. Yamamoto and H. Nozaki, This Bulletin, **45**, 2574 (1972).

10) A. Padwa and S. I. Wetmore, Jr., *J. Amer. Chem. Soc.*, **96**, 2414 (1974) and references cited therein.

11) P. Beck and J. L. Miesch, *J. Amer. Chem. Soc.*, **89**, 2375 (1967).

12) P. J. Wagner and R. G. Zepp, *ibid.*, **94**, 287 (1972).

13) W. K. Robbins and R. H. Eastmann, *ibid.*, **92**, 6077 (1970).

14) a) N. Gakis, M. Märky, H. -J. Hansen and H. Schmid, *Helv. Chim. Acta*, **55**, 748 (1972). b) A. Padwa, S. Clough, M. Dharan, J. Smolanoff and S. I. Wetmore, *J. Amer. Chem. Soc.*, **94**, 1395 (1972).

15) T. Matsuura and Y. Ito, *Tetrahedron Lett.*, **1973**, 2283; Y. Ito and T. Matsuura, *Tetrahedron*, **31**, 1373 (1975).

16) a) A. Padwa, W. Bergmark and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2654 (1969). b) N. Toshima, H. Hirai and S. Makishima, *Kogyo Kagaku Zashi*, **72**, 184 (1969).

17) S. G. Cohen and C. H. Wang, *J. Amer. Chem. Soc.*, **77**, 4435 (1955).

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

19) C. Dufraisse and J. Martel, *C. R. Acad. Sci. Paris*, **244**, 3106 (1957).

20) In this photoproduct a trace of III was detected by tlc, although it was not detected in the experiments in Table 1.

21) H. H. Strain, *J. Amer. Chem. Soc.*, **51**, 272 (1929).

22) T. Hayashi, *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), **39**, 89 (1941).

23) "Beilstein Handbuch der Organischen Chemie," E II, XIII, p. 114.

24) F. Feist, *Ber.*, **27**, 214 (1894). He isolated only *dl*-stilbenediamine, but in our case a mixture of *dl*- and *meso*-isomers was obtained (*dl*/*meso*=4.1/4.9 (NMR)). Each isomer was separated by preparative tlc (5 : 1 benzene–ethanol), and the reaction with benzyl according to the previous method[22] produced the corresponding dihydropyrazine.

25) "Beilsteins Handbuch der Organischen Chemie," EI, IX, p. 104.

26) "Organic Electronic Spectral Data," Volume II, Interscience Publishers, New York, London (1953—1955), p. 390.

27) R. Brière, H. Lemaire and A. Rassat, *Bull. Soc. Chim. Fr.*, **1965**, 3273.

28) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

29) A trace of III was also detected in the mixture kept in the dark.

30) "Advan. Heterocyclic Chem.", Vol. 2, ed. by A. R. Katritzky and A. J. Boulton, Academic Press, New York (1963), p. 85.

31) M. Svoboda, J. Sicher, J. Farkaš and M. Pánková, *Collect. Czech. Chem. Commun.*, **20**, 1426 (1955).