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PHOTOINDUCED REACTIONS. LXI. PHOTOCHEMICAL cis,trans-ISOMERIZATION OF 2,4,5-TRIPHENYLIMIDAZOLES[1)]

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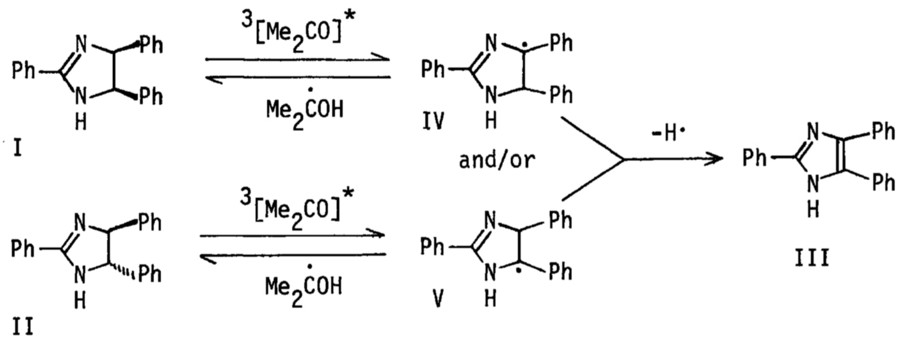
Irradiation of cis- (amarine) and trans- (isoamarine) 2,4,5-triphenylimidazolines in acetonitrile or benzene gave a photostationary mixture of cis- and trans-isomers. On irradiation in a dilute acetone solution, cis,trans-isomerization occurred only with isoamarine but not with amarine. In acetone, 2,4,5-triphenylimidazole was also formed. Two modes of mechanisms are proposed.

It has recently been shown by us that certain imidazolines, on irradiation (2537Å) in acetone solutions ($>3\times10^{-2}$M), are dehydrogenated to give corresponding imidazoles.[2)] During this study it was also found that 2,4,5-triphenylimidazolines, amarine (I, cis) and isoamarine (II, trans), undergo cis,trans-isomerization in addition to dehydrogenation to 2,4,5-triphenylimidazole (III, lophine) under the conditions. For the isomerization, we proposed a tentative mechanism involving hydrogen transfer from the acetone ketyl radical to intermediate imidazolinyl radicals, IV and/or V, which are formed from I and II by hydrogen abstraction with the n,π^* triplet of acetone as shown in Scheme 1.[2)]

Scheme 1



However, since both amarine and isoamarine also absorbed the incident light to some extent under the conditions employed, direct cis,trans-isomerization from their own excited states was also considered to be a possible process. The present investigation was undertaken in order to see whether this is the case.

TABLE 1. PHOTOCHEMICAL cis,trans-ISOMERIZATION OF AMARINE (I) AND ISOAMARINE (II) IN VARIOUS SOLVENTS.

Solvent	Starting material	Concentration ($\times10^{-2}$M)	Light source[a)]	Irradiation time (hr)	II/I ratio	Yield of III (%)
MeCN	I	3.14	B	24	1.77	none
	II	3.12	B	24	1.62	none
C_6H_6	I	3.45	A	15	1.60	trace
	I	0.172	B	3	1.55	trace
	II	0.168	B	3	1.41	trace
Me_2CO	I	3.55	B	24	0.60	35
	I	3.27	A	15	0.46	21
	I	0.0282	A	1	0	29[b)]
	II	3.62	B	24	0.59	28
	II	0.0302	A	1	0	19[b)]

a) A: high-pressure mercury lamp (>2800Å). B: low-pressure mercury lamp (2537Å).

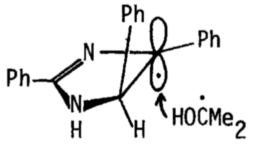
b) Determined after 30 min irradiation.

Amarine (I) and isoamarine (II) were irradiated with light from a 100W high-pressure mercury lamp through Pyrex glass (>2800Å) or with light from a 10W low-pressure mercury lamp through Vycor glass (mainly 2537Å) at various concentrations in acetonitrile, benzene or acetone. The results are summarized in Table 1. In all cases no appreciable product other than I, II,and III was detected.

In acetonitrile, no lophine (III) was detected and either I or II gave almost the same photostationary mixture of I and II with light at 2537Å. The product ratio shows that a thermodynamically more stable isomer II is predominant. The photochemical isomerization of I was not appreciably quenched by piperylene, a triplet quencher, at various quencher concentrations (0.06-0.57M) indicating that the excited state responsible for the isomerization may be singlet or short-lived triplet.

In benzene, which is known as a triplet sensitizer except a few exceptional cases,[3)] only a trace of lophine (III) was detected and the photostationary mixture of I and II was obtained in the similar ratio to that in acetonitrile. The ratio (II/I) was found to be independent on the initial concentrations of the starting material and on the wave-length of the incident light. The results suggest that the cis,trans-isomerization of the triphenylimidazolines I and II in benzene may occur from their triplet state.[4)]

In acetone, different results were obtained at high and low concentrations of triphenylimidazolines. In both cases lophine (III) was formed to a considerable extent regardless of the light sources, indicating that the imidazolinyl radicals IV and/or V should be formed. At low concentrations ($\sim 3\times10^{-4}$M), at which more than 99% of the incident light was absorbed by acetone, isomerization occurred only from isoamarine (II) toward amarine (I) but not from I toward II. In sharp contrast, at high concentrations ($\sim 3.5\times10^{-2}$M), at which about 50% of the incident light was absorbed by acetone, either I or II afforded a mixture of I and II. The photoreaction of I and II in dilute acetone solutions can be well rationalized by a modified mechanism of Scheme 1, by which hydrogen transfer from the acetone ketyl radical to the imidazolinyl radicals IV and/or V occurs only in the direction toward I but not toward II (See Scheme 2).[5)] The ketyl radical may attack IV and/or V predominantly from the opposite side of a bulky phenyl group as shown below. At high



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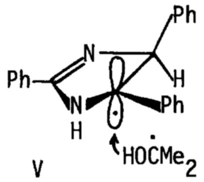


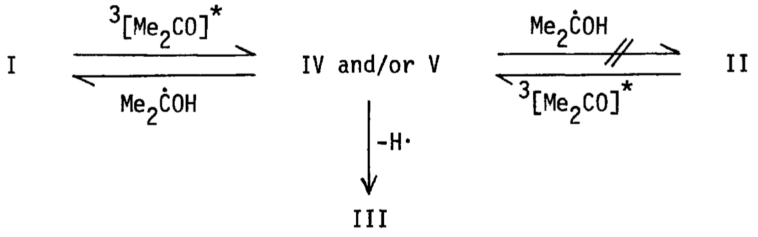
V

concentrations of I and II, cis,trans-isomerization from their excited state as in acetonitrile or benzene may compete with cis,trans-isomerization via the imidazolinyl radicals.

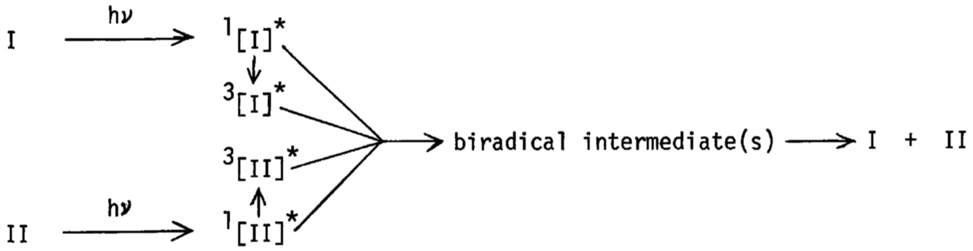
Scheme 2 summarizes two modes of mechanisms for the cis,trans-isomerization of amarine (I) and isoamarine (II), in addition to the dehydrogenation to lophine (III). It is noticed that the present photoreactions provide typical examples of kinetically (A) and thermodynamically (B) controlled isomerizations.

Scheme 2

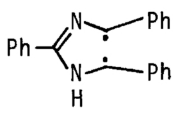
A [in acetone (low concn.)]:



B [in acetonitrile or benzene]:



The nature of the biradical intermediate(s) remains to be elucidated. However, it may be reasonable to assume that, among possible biradical intermediates VI, VII, and VIII, VI 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)$^{6)}$ and $PhCH_2$—$NHCH_3$ (58 kcal/mol).$^{7,8,9,10)}$



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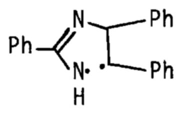
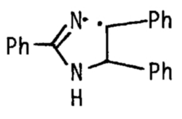


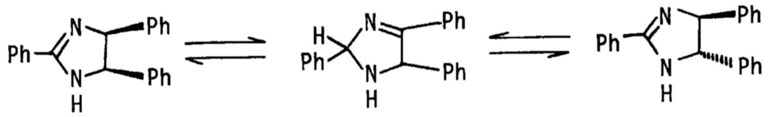
VII



VIII

REFERENCES AND FOOTNOTES

1) Part LX: I. Saito, M. Imuta, and T. Matsuura, submitted to Tetrahedron.
2) T. Matsuura and Y. Ito, "Symposium on Organic Free Radical Reactions", Abstracts of Papers, p. 60, Nagoya, October, 1971.
3) P. S. Engel and B. M. Monroe, Advan. Photochem., 8, 245 (1971).
4) This is strongly supported by the fact that I and II isomerized under conditions that more than 99% of the incident light was absorbed by benzene. Under such circumstance benzene should act as a triplet sensitizer. It was also found that the II/I ratio in the isomerization of amarine (I) in benzene ($\sim 1.7 \times 10^{-3}$M; at 2537Å) decreased with increased amount of piperylene (up to 0.63M).
5) A process involving energy transfer from the n,π^* excited state of acetone can be ruled out, since such a process should give a mixture of I and II from either I or II.
6) M. Szwarc, Chem. Revs., 47, 75 (1950).
7) J. A. Kerr, Chem. Revs., 66, 496 (1966).
8) The bond dissociation energy data for $>$C=N—C$<$ bond are not available, but it may have a higher value than the others considering the less resonance-stabilized nature of $>$C=N· radical.
9) A similar type of photochemical homolytic cleavage has been recently observed with benzpinacol diacetate. [T. Shirafuji, Y. Yamamoto, and H. Nozaki, 26th Meeting of the Chemical Society of Japan, Abstracts of Papers, III-p. 1089, Tokyo, April, 1972.]
10) An alternative mechanism involving 1,3-hydrogen shift may not be eliminated although less possible. The authors thank to a referee for this suggestion.



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