

Photoinduced Reactions. LXVIII. Photochemical Dehydrogenation¹⁾ of Imidazolines to Imidazoles

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Imidazolines were found to be dehydrogenated to imidazoles by irradiation at 2537 Å or above 2900 Å in acetone. The n, π^* triplet acetone acts as a hydrogen-abstrating agent giving 4- and/or 5-imidazoliny radicals which in turn are transformed into imidazoles. This scheme is supported by the fact that the AIBN-initiated dehydrogenation of imidazolines gave corresponding imidazoles, that oxygen quenched the photochemical dehydrogenation, and that in some cases coupling products between the imidazoliny radical and the acetone ketyl radicals were formed. Various data indicate that the imidazoliny radical reverts to the parent imidazoline by hydrogen transfer from the acetone ketyl radical during the course of photolysis.

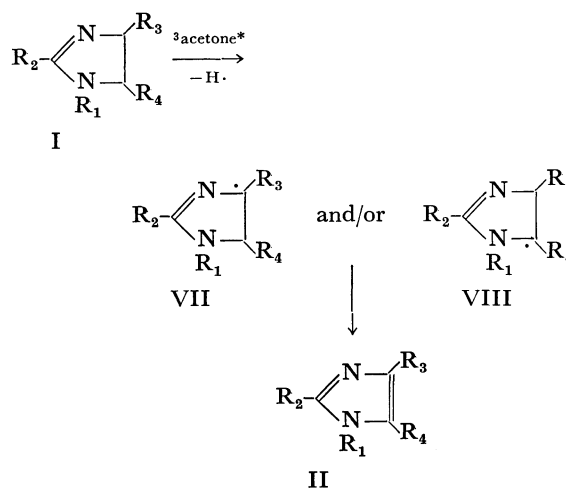
There are several reports on the methods of dehydrogenation of imidazolines leading to the corresponding imidazoles.²⁾ These methods involve dehydrogenation with catalysts such as nickel, iron, platinum, and palladium or with hydrogen acceptors such as sulfur and selenium. It is well-known that a variety of carbonyl compounds, in their excited states, can abstract hydrogen from various hydrogen-donating substrates.³⁾ However, examples of the photochemical dehydrogenation of hydroaromatic compounds to aromatic compounds are relatively few,⁴⁾ since simple carbonyl compounds often photochemically react with a hydrogen donor to form coupling products.⁵⁾ In the present paper we report a simple method for dehydrogenating imidazolines to imidazoles by irradiation in acetone.

Results and Discussion

Irradiation of an acetone solution of imidazolines (I) with a low-pressure mercury lamp (mainly 2537 Å) under nitrogen atmosphere followed by column chromatography of the reaction products gave corresponding imidazoles (II) in reasonable yields. The results are summarized in Table 1. 2-Methylimidazolines (Ia and Ib) gave dehydro-coupling products (III, IV and V) besides the corresponding imidazoles, but 2-hydroxyimidazoline (II) only a coupling product VI. It should be noted that both *cis*- (If; amarine) and *trans*- (Ig; isoamarine) 2,4,5-triphenylimidazolines underwent *cis*, *trans*-isomerization being accompanied by dehydrogenation to 2,4,5-triphenylimidazole (IIf; lophine). Acetone pinacol was isolated in low yield only in cases of Ia and Ib but not in all the other cases.

Oxygen was found to quench the formation of an

imidazole. Thus, irradiation of 2-methylimidazoline (Ia) under similar conditions except under bubbling oxygen instead of nitrogen gave 2-methylimidazolium acetate (12%) besides some recovered starting material (27%) but no 2-methylimidazole (IIa). Irradiation of an acetone solution of Ia, which had been degassed by four freeze-thaw cycles at 10^{-4} mm under cooling with liquid nitrogen, gave no effect on the reaction, and the IIa, IIIa, and pinacol were obtained in the same ratio as that under nitrogen. On irradiation in benzene or isopropyl alcohol under nitrogen, these imidazolines (Ib, Ic, Id, and Ie) were recovered unchanged except that *cis*, *trans*-isomerization was observed with amarine (If) and isoamarine (Ig).⁶⁾ Thus it is considered that the imidazoles were formed *via* 4-(VII) and/or 5-(VIII) imidazoliny radicals which were formed from the imidazolines by hydrogen abstraction with the n, π^* triplet state of acetone as shown in Scheme 1.



Scheme 1.

In order to confirm this scheme, hydrogen abstraction of 2-methylimidazoline (Ia), amarine (If), and isoamarine (Ig) by the 1-cyano-1-methylethyl radical generated by thermolysis of azobisisobutyronitrile (AIBN) was carried out. The corresponding imidazoles were obtained, their yields being dependent on the

1) Part LXVII: I. Saito, M. Imuta, and T. Matsuura, *Chem. Lett.*, **1972**, 1197.

2) a) L. P. Kyrides, F. B. Zienty, G. W. Steahly, and H. L. Morril, *J. Org. Chem.*, **12**, 577 (1947); b) H. H. Strain, *J. Amer. Chem. Soc.*, **49**, 1558 (1947); c) E. Fischer, *Ann.*, **211**, 217 (1882); d) British Patent 484862 (1938); *Chem. Abstr.*, **32**, 7679 (1938); e) R. E. Klem, H. F. Skinner, H. Balba, and R. W. Isensee, *J. Heterocycl. Chem.*, **7**, 403 (1970); f) T. Hayashi, M. Kuyama, E. Takizawa and M. Hata, *This Bulletin*, **37**, 1702 (1964).

3) D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publ. Co., New York, N. Y. (1967), p. 163.

4) A. Schönberg, G. O. Schenck, and O.-A. Neumüller, "Preparative Organic Photochemistry," Springer-Verlag New York Inc., New York, N. Y. (1968), p. 151.

5) Ref. 4, p. 198.

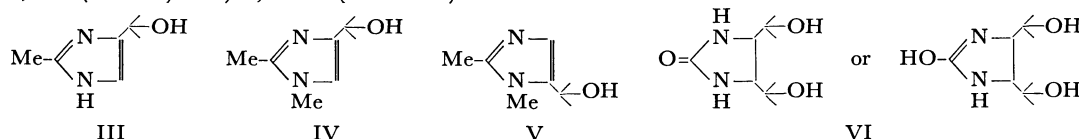
6) *cis,trans*-Isomerization of amarine and isoamarine, indeed takes place in various organic solvents.⁷⁾

7) T. Matsuura and Y. Ito, *Chem. Lett.*, **1972**, 431.

TABLE 1. PHOTOCHEMICAL DEHYDROGENATION OF IMIDAZOLINES I TO IMIDAZOLES II IN ACETONE

R ₁	I				Irradiation time (hr)	Recovered I (%)	Yield of II (%) ^{c)}	Other products (%) ^{c)}
	R ₁	R ₂	R ₃	R ₄				
Ia	H	Me	H	H	24	0	60	III (9)
Ib	Me	Me	H	H	24	0	22	IV (6)+V (5)
Ic	H	Ph	H	H	24	58	15	
					75	36	36	
Id	Me	Ph	H	H	24	26	18	
Ie	(CH ₂) ₂ OH	Ph	H	H	50	37	20	
If	H	Ph	Ph	Ph ^{a)}	24	25	35	Ig (16)
Ig	H	Ph	Ph	Ph ^{b)}	24	16	28	If (27)
Ih	H	SH	H	H	24	100	0	
Ii	H	OH	H	H	24	36	0	VI (20)

a) 4,5-*cis* (amarine). b) 4,5-*trans* (isoamarine)



c) Based on the starting imidazolines.

TABLE 2. AIBN-INITIATED DEHYDROGENATION OF IMIDAZOLINES^{a)}

Imidazoline	Concentration ($\times 10^{-2}$ M)		Molar ratio of AIBN/Imidazoline	Yield of imidazole (%) ^{b)}
	Imidazoline	AIBN		
2-Methyl- (Ia)	10.20	9.38	0.92	4.0
	9.60	4.69	0.49	0
<i>cis</i> -2,4,5-Triphenyl- (If)	2.72	3.70	1.36	26.0
	2.67	1.85	0.69	12.0
	2.71	0.37	0.14	4.5
<i>trans</i> -2,4,5-Triphenyl- (Ig)	2.68	8.66	3.24	3.2
	2.73	4.89	1.79	2.0

a) Reaction conditions: $68 \pm 1.5^\circ\text{C}$ in acetonitrile under nitrogen. b) Based on the starting imidazoline.

AIBN concentration and also on the structural feature of the imidazolines (Table 2). A difference between the reactivities of Ia and If may be due to the magnitude of the resonance stabilization of the intermediate radicals, VII and/or VIII: *i.e.*, radicals VIIf and VIIIf are obviously more stabilized by a phenyl group at positions 4 and 5, respectively. The slower dehydrogenation rate in Ig compared with If is probably due to a steric repulsion between a phenyl group at position 5 (or 4) and 1-cyano-1-methylethyl radical produced from AIBN in the abstraction of a hydrogen atom at position 4 (or 5).

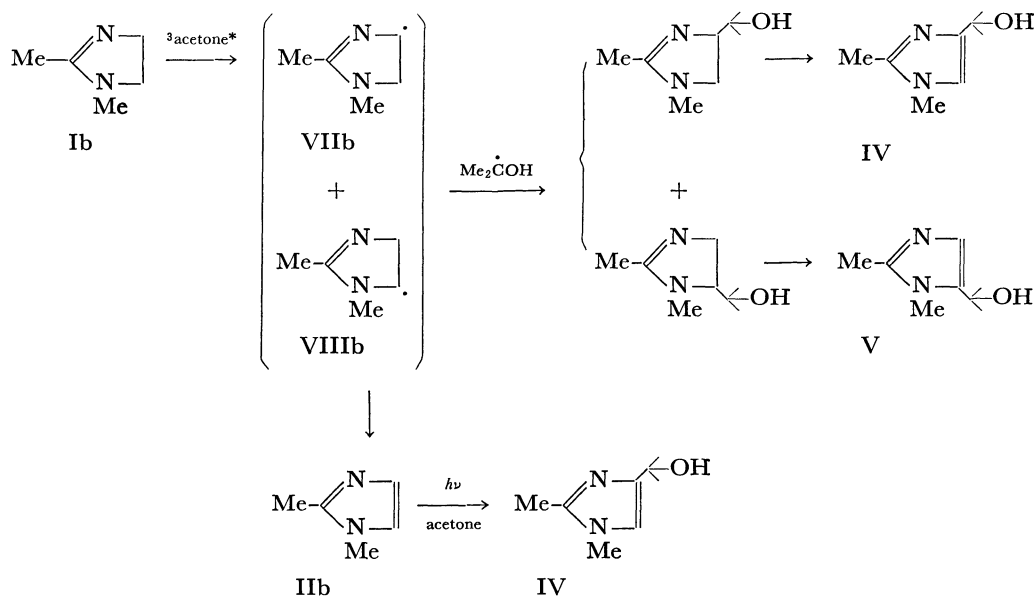
The mechanism of Scheme 1 involving the imidazolyl radical (VII or VIII), which is formed from the starting imidazoline by hydrogen abstraction with the n, π^* triplet state of acetone, is supported by the following facts. (1) Imidazoles are also formed by the hydrogen abstraction reaction initiated by AIBN (Table 2). (2) Oxygen, a triplet quencher,⁸⁾ inhibits the formation of 2-methylimidazole from 2-methylimidazoline. (3) In some cases coupling prod-

ucts such as III, IV, V, and VI are formed as byproducts, which obviously result from coupling between the acetone ketyl radical and the imidazolyl radical VII or VIII followed by dehydrogenation of the coupling products in cases of III, IV, and V. Matsuura *et al.* have found that irradiation of 1,2-dimethylimidazole (Iib) in acetone gives exclusively IV, which is formed *via* an unstable oxetane intermediate.⁹⁾ Thus the formation of an almost equal amount of IV and V from Ib should result from the coupling between the acetone ketyl radical and the imidazolyl radicals VIIb and VIIIb, although it is possible that a part of IV formed results from the photochemical addition of acetone to Iib (Scheme 2).

2-Methylimidazoline (Ia) is more susceptible to photochemical dehydrogenation than amarine (If) but less susceptible to the AIBN-initiated one (Tables 1

8) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

9) T. Matsuura, A. Banba, and K. Ogura, *Tetrahedron*, **27**, 1211 (1971).



and 2). The *cis,trans*-isomerization of amarine (If) and isoamarine (Ig), which is accompanied by dehydrogenation to lophine (IIIf), occurs only during irradiation in acetone but not during the AIBN-initiated free radical reaction. This can be interpreted by assuming that, in the case of photoreaction, free radical intermediates VII and/or VIII revert in part to the parent imidazoline by a hydrogen transfer from the acetone ketyl radical^{10,11} which is known to act as a hydrogen donor as seen in the photoreduction of benzophenone with isopropyl alcohol,¹⁴ and that, in the absence of such a hydrogen donor (AIBN-initiated reaction), the intermediate radicals VII and/or VIII are transformed to an imidazole II without reverting to the parent imidazoline I (Scheme 3). As regards the overall reaction from I to II, the imidazole-forming step (VII or VIII→II) may be more important in the photoreaction involving a reverse process from VII or VIII to I than in the AIBN-reaction without such a process. In contrast to this, the radical-forming step may be more important in the AIBN-reaction than in the photoreaction.¹⁵

10) In the cases of amarine (If) and isoamarine (Ig), it was shown that intermediate radicals VIIIf and/or VIIIIf revert only to amarine but not to isoamarine.⁷⁾ Formation of isoamarine (Ig) during the course of irradiation of amarine was found to arise from the excited state of amarine itself.^{6,7)}

11) The bond dissociation energy of the acetone ketyl radical ($\text{Me}_2\text{CO}\cdot\text{H}$) appears lower than that of $\text{Me}_2\text{C}(\text{CN})\cdot\text{H}$, since that of $\cdot\text{CH}_2\text{O}\cdot\text{H}$ (29 kcal/mol¹²⁾ is much lower than that of $\text{H}\cdot\text{CH}_2\text{CN}$ (ca. 86 kcal/mol¹³⁾).

12) M. K. Phibbs and B. deB. Darwent, *J. Chem. Phys.*, **18**, 495 (1950).

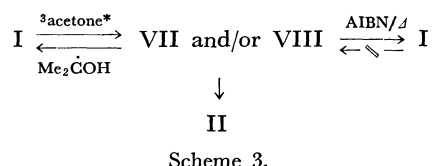
13) J. A. Kerr, *Chem. Rev.*, **66**, 496 (1966).

14) E. S. Huyser and D. C. Neckers, *J. Amer. Chem. Soc.*, **85**, 3641 (1963).

15) This is similar to the notion of a successive reaction:



If the process $B \rightarrow A$ is much faster than the process $B \rightarrow C$, the latter should be rate-determining (case 1). If on the contrary $B \rightarrow A$ is much slower than $B \rightarrow C$, the former process should be rate-determining (case 2). The photochemical reaction is similar to case 1 and the AIBN-initiated one to case 2.



For the sake of confirmation, the total π electron energies (E_π) of I, VII, and II were calculated by the HMO method.^{16,18)} It was assumed from the calculated E_π values for VII and VIII that VII contributes more than VIII to the free radical intermediate. Comparisons of the values of $\Delta E_{\pi_1} = E_\pi(\text{VII}) - E_\pi(\text{I})$ and $\Delta E_{\pi_2} = E_\pi(\text{II}) - E_\pi(\text{VII})$ with the yields of the imidazoles from the imidazolines I are given in Table 3. The yield of the photochemical conversion to imidazoles decreases in the order $\text{Ia} > \text{If} > \text{Ib} > \text{Ic}$. This is qualitatively correlated with ΔE_{π_2} but not with ΔE_{π_1} . A decrease in the yield of the photochemical conversion to imidazoles seems to be general for 1-alkylimidazolines as seen in the case of Ib, Id and Ie (Table 1). The yield of the AIBN-initiated conversion to imidazoles seems to be correlated with ΔE_{π_1} rather than ΔE_{π_2} . This led us to conclude that in the photochemical de-

16) Parameters were selected from those presented by Streitwieser^{17a)} except for parameters concerning sulfur bonds.^{17b)} The use of the E_π value for VIII for the following discussion does not alter the conclusion.

17) a) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley & Sons, Inc., New York, N. Y. (1961), p. 117. b) T. Yonezawa, N. Nagata, H. Kato, and A. Imamura, "Ryoshi-Kagaku Nyumon," Kagaku Dojin, Tokyo (1968), p. 56.

18) An attempt to correlate the relative rates of hydrogen abstraction from a series of arylmethanes by the trichloromethyl radical or bromine atom with the change in HMO ΔE_π value has been reported. [J. D. Unruh and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 2008 (1971); R. B. Roark, J. M. Roberts, D. W. Croom, and R. D. Gillion, *J. Org. Chem.*, **37**, 2042 (1972)].

19) When the twisted angle is assumed to be 25° , ΔE_{π_2} value is calculated to be 2.58445β . G. Rasch [*Z. Phys. Chem.*, **219**, 180 (1962)] assumed the twisted angle of phenyl groups of *cis*-stilbene as $26 \pm 4^\circ$.

TABLE 3. COMPARISON OF THE YIELD OF IMIDAZOLES (II) FROM IMIDAZOLINES (I) WITH ΔE_{π_2} AND ΔE_{π_1} VALUES

Imidazoline	Yield of imidazole (%)			$\Delta E_{\pi_2}(\beta)^d$	$\Delta E_{\pi_1}(\beta)^d$
	High concn ^{a)}	Photochemical Low concn ^{b)}	AIBN- initiated ^{c)}		
2-Methyl- (Ia)	60	20.0±0.5	6	2.58100	0.67520
1,2-Dimethyl- (Ib)	22	—	—	2.55070	0.69020
2-Phenyl- (Ic)	15	—	—	2.52744	0.73246
<i>cis</i> -2,4,5-Triphenyl- (If)	35	16.1±1.2	26	2.53995 ^{e)}	1.21005

a) Taken from the data of Table 1 (irradiation time, 24 hr). b) A *ca.* 10⁻³ M acetone solution was externally irradiated using a merry-go-round apparatus and the yields of imidazoles formed were determined by UV analysis. c) Taken from the data of Table 2. d) See text. e) Calculation was carried out by assuming that two phenyl groups at positions 4 and 5 are twisted 30° from the plane of the imidazole ring.¹⁹⁾

TABLE 4. DEUTERIUM INCORPORATION INTO 2-PHENYL-IMIDAZOLINE (Ic) DURING PHOTOLYSIS IN THE PRESENCE OF MeOD AND D₂O IN ACETONE

Concn of Ic (× 10 ⁻² M)	Solvent			Irradn. time (hr)	Ic-d ₁ ^{a)} (%)
	Acetone	MeOD	D ₂ O		
4.75	5	10	0	41 ^{b)}	0.2±0.1
3.63	5	10	5	163 ^{c)}	1.9±0.1
3.43	5	10	5	245 ^{c)}	1.6±0.2

a) Deuterium analysis was done by mass-spectrometry. c) Externally irradiated with a 100W high-pressure mercury lamp (Pyrex filter). c) Externally irradiated with a 450W high-pressure mercury lamp (Pyrex filter).

hydrogenation the resonance stabilization of the product imidazoles, represented by a higher ΔE_{π_2} value, is more important, and that in the AIBN-initiated dehydrogenation the resonance stabilization of the intermediate free radical VII, represented by a higher ΔE_{π_1} value, is more important. Accordingly, these calculated data are not inconsistent with the mechanism shown in Scheme 3.

For the sake of confirming the back reaction of the imidazolyl radicals VII or VIII to I by a hydrogen transfer from the acetone ketyl radical (Scheme 3), an acetone solution of 2-phenylimidazoline (Ic) was irradiated in the presence of MeOD and D₂O with different periods. The incorporation of deuterium into the recovered Ic obviously indicates that the back hydrogen transfer to VII or VIII by the acetone ketyl radical occurs in the photochemical reaction (Table 4). The deuterium incorporation into Ic was not so much as expected. This is probably due to a slower exchange reaction between the acetone ketyl radical and MeOD or D₂O than the back-transfer reaction.

Experimental

All the melting points are uncorrected. The NMR spectra were taken on an NEVA T-60 spectrometer using tetramethylsilane as an internal standard. The IR spectra were measured on a JASCO IRS spectrometer. The UV spectra were obtained with a JASCO ORD/UV-5 spectrometer. Vapor phase chromatography (vpc) was carried out with a Shimadzu GC-2C apparatus on Apiezon Grease L using helium as a carrier gas. Thin layer chromatography (tlc) was carried out with Merck "Kieselgel GF 254," "Aluminiumoxid GF 254" or Nagel "Cellulosepulver MN 300 G," using UV light and iodine vapor for compound detection. Column

chromatography was carried out with Mallinckrodt silicic acid (100 mesh).

Starting Materials. Commercial 2-Methylimidazoline (Ia) and 2-phenylimidazoline (Ic) were used after recrystallization from acetone. Commercial ethylenethiourea (Ih) and ethyleneurea (Ii) were used without further purification.

1,2-Dimethylimidazoline (Ib) was prepared by the method of King and McMillan.²⁰⁾ To 5 g of *N*-methylethylenediamine was added 7 g of acetic anhydride at room temperature and the mixture was heated at 170–190 °C for 1 hr. After cooling 3 g of magnesium powder was added. The mixture was heated at about 300 °C for 1 hr, then 1,2-dimethylimidazoline formed was distilled out. It was further refined by vacuum distillation to give pure Ib as a colorless liquid (3 g; 46%) which gave satisfactory spectral and analytical data; bp *ca.* 70 °C/14 mmHg (lit.²¹⁾ 60–62 °C/12 mmHg); n_D^{26} 1.4759 (lit.²¹⁾ n_D^{20} 1.4766); picrate, mp 137–138.5 °C (lit.²¹⁾ 145–147 °C).

1-Methyl-2-phenylimidazoline (Id) was prepared by the method of Hill and Aspinall.²²⁾ 18.4 g of benzoic acid was added to 11.2 g of *N*-methylethylenediamine and the mixture was heated at 150–170 °C for 1.5 hr, then at 200–220 °C for 2 hr. The product was refined by repeated vacuum distillation to give Id as colorless liquid (5 g; 21%); bp *ca.* 95 °C/4 mmHg; IR (neat 2850, 1605, 1270, 1065, 775, and 700 cm⁻¹; NMR (CDCl₃) τ 2.30–2.69 (m, 5H), 5.88–6.80 (m, 4H), and 7.20 (s, 3H); *m/e* 160 (M⁺). Found: C, 75.25; H, 7.79; N, 17.31%. Calcd for C₁₀H₁₂N₂: C, 74.96; H, 7.55; N, 17.49%. It gave a picrate, mp 121–123 °C.

1-(β -hydroxyethyl)-2-phenylimidazoline (Ie) was prepared analogously from *N*-(β -hydroxyethyl)ethylenediamine and benzoic acid, as colorless crystals; mp 103–104.5 °C; IR (Nujol) 3200, 1590, 1570, 1235, 765, and 685 cm⁻¹; NMR (CDCl₃) τ 2.33–2.72 (m, 5H), 5.90–7.00 (m, 8H), and 6.17 (s, 1H). Found: C, 69.68; H, 7.13; N, 14.81%. Calcd for C₁₁H₁₄ON₂: C, 69.50; H, 7.37; N, 14.71%.

Amarine (If) was prepared by the method of Strain²³⁾ and purified by repeated recrystallization from anhydrous ether. Isoamarine (Ig) was prepared by isomerizing amarine with sodium methoxide at 160–170 °C²⁴⁾ and purified by repeated recrystallization from ethanol.

General Procedure for Photodehydrogenation. The following procedure was used for experiments listed in Table 1. A solution of about 2 g of an imidazoline in 220 ml of acetone was irradiated with a 10 W low-pressure mercury lamp (Vycor

20) J. A. King and F. H. McMillan, *J. Amer. Chem. Soc.* **68**, 1774 (1946).

21) T. Tkaczynski, *Chem. Abstr.*, **64**, 587b (1966).

22) A. J. Hill and S. R. Aspinall, *J. Amer. Chem. Soc.*, **61**, 822 (1939).

23) H. H. Strain, *ibid.*, **49**, 1558 (1927).

24) E. H. Rodd, "Chemistry of Carbon Compounds," IVA, Elsevier Publ. Co., Amsterdam (1957), p. 304.

housing) under nitrogen at room temperature for 24 hr or more. After irradiation the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column. The yield of products was obtained by NMR or vpc analysis of the reaction mixture or by product isolation.

Isolation and Identification of Dehydrogenation Products.

2-Methylimidazoline (Ia): The residue obtained from 2.10 g of Ia was chromatographed on 70 g of silica gel. Elution with 100 ml of acetone yielded 350 mg of an oil which was again chromatographed to give 150 mg of pinacol (identified by IR and NMR). Further elution with 200 ml of acetone-ethanol (1 : 1) gave 1.18 g of a solid. Recrystallization from chloroform gave 400 mg of 4-(α -hydroxyisopropyl)-2-methylimidazole (III) as colorless crystals which were identical with an authentic sample⁹⁾ (IR, NMR, and mixed mp). Crystals obtained from the mother liquor were recrystallized from benzene to give 2-methylimidazole (IIa) as colorless crystals, identical with a commercial authentic sample (IR, NMR and mixed mp). Further elution of the chromatogram yielded 680 mg of a solid which was identified as IIa. The yields of the products were determined by NMR analysis of the product mixture with an internal standard (acenaphthene). The yield of pinacol was 6% assuming that 1 mol of Ia gives 1 mol of pinacol.

1,2-Dimethylimidazoline (Ib). The residue obtained from 1.85 g of Ib was chromatographed on 50 g of silica gel. Elution with 300 ml of chloroform and acetone (1 : 1) yielded 300 mg of an oil which was shown by IR and NMR to contain pinacol. Further elution with 300 ml of acetone yielded 110 mg of a solid which was recrystallized from acetone to give 10 mg of 1,2-dimethyl-5-(α -hydroxyisopropyl)imidazole (V) as colorless crystals; mp 179–181 °C; IR (Nujol) 3200, 1150, and 810 cm^{-1} ; NMR (CDCl_3) τ 3.33 (s, 1H), 6.25 (s, 3H), 6.79 (s, 1H), 7.67 (s, 3H), and 8.39 (s, 6H); mass spectrum, m/e 154 (M^+). The NMR and mass spectra are very similar to those of IV.⁹⁾

Found: C, 62.67; H, 9.23; N, 17.71%. Calcd for $\text{C}_8\text{H}_{14}\text{ON}_2$: C, 62.30; H, 9.15; N, 18.15%.

The mother liquor was shown by IR and NMR analyses to consist of 1,2-dimethylimidazole (IIb), 1,2-dimethyl-4-(α -hydroxyisopropyl)imidazole (IV) and V. Compound IIb was isolated by vpc and identified by comparison with an authentic sample⁹⁾ (IR). Compound IV was dehydrated during vpc to give 1,2-dimethyl-4-isopropenylimidazole,⁹⁾ which was identified by comparison with an authentic sample⁹⁾ (IR). Further elution of the chromatogram with acetone yielded a mixture of IIb, IV, and V, identified by tlc. The yields of these products were determined by vpc analysis with an internal standard (*p*-*t*-butylphenol). NMR analysis of the product mixture showed the formation of pinacol (0.3 mol/mol of IIb).

2-Phenylimidazoline (Ic). The residue obtained from 2.60 g of Ic was chromatographed on 60 g of silica gel. Elution with chloroform and ethanol (9 : 1) yield 2-phenylimidazole (IIc), identical with a commercial authentic sample (IR, NMR and mixed mp). The yield of IIc was determined by vpc analysis with an internal standard (diphenyl).

1-Methyl-2-phenylimidazoline (Id). The residue obtained from 2.03 g of Id was chromatographed on 60 g of silica gel. Elution with chloroform yielded 1-methyl-2-phenylimidazole (IID) as a liquid; bp 140–145 °C (bath temperature)/3 mmHg (lit,²⁴⁾ bp 175 °C/15 mmHg; IR (neat) 1500, 1480, 1410, 1270, 770, 715, and 700 cm^{-1} ; NMR (CDCl_3) τ 2.21–2.60 (m, 5H), 2.83 (d, 1H, $J=1$ Hz),

3.01 (d, 1H, $J=1$ Hz) and 6.25 (s, 3H). It gave satisfactory elemental analyses. The yield of IID shown in Table 1 is based on the product isolated. The recovered Id was analyzed by vpc.

Amarine (If) and Isoamarine (Ig). The residues obtained from 2.09 g of If and 2.02 g of Ig were chromatographed on 70 g of silica gel, respectively. Elution with chloroform successively gave lophine (IIf), Ig, and If, which were identical with authentic samples (IR and NMR). The yield of IIf was determined by UV analysis in ethanol and the recovered materials by NMR analysis with an internal standard, 2-methylimidazoline (in carbon tetrachloride-dimethylsulfoxide- d_6).

2-Hydroxyimidazoline (Ii). A suspension of Ii (1.63 g) was irradiated. The insoluble solid separated by filtration was found to be mainly the recovered Ii (IR and NMR). The residue from the filtrate was chromatographed on 60 g of silica gel. Elution with acetone yielded VI as colorless crystals; mp 198–201 °C; IR (Nujol) 3300, 1655, and 1175 cm^{-1} ; NMR ($\text{DMSO}-d_6$) τ 5.26 (s, 4H), 6.63 (s, 2H), and 8.86 (S, 12H).

Found: C, 53.48; H, 8.94; N, 13.75%. Calcd for $\text{C}_9\text{H}_{18}\text{N}_2\text{O}_3$: C, 53.44; H, 8.97; N, 13.85%.

The compound showed a UV maximum at 275 nm in ethanol identical with that of Ii. Further elution yielded additional Ii. The yields given in Table 1 are based on the product isolated.

Photoreaction of 2-Methylimidazoline (Ia) under Oxygen. A solution of 2.08 g of Ia in acetone was irradiated for 24 hr under similar conditions but with oxygen-bubbling instead of nitrogen. After removal of the solvent under reduced pressure, the residue was chromatographed on 60 g of cellulose powder (Whatman CF11). Elution with 1200 ml of benzene-chloroform (1 : 4) yielded 530 mg (27%) of Ia, identified by IR. Further elution with 1000 ml of acetone-ethanol (1 : 1) yielded 1.12 g of an oil. Vacuum distillation of the oil gave 400 mg (12%) of 2-methylimidazolium acetate, mp 95–96 °C (lit,²⁶⁾ mp 94.5–95.5 °C), which was identical with an authentic sample (IR and NMR).

Hydrogen Abstraction of Imidazolines Initiated with AIBN.

A given amount of each imidazoline was dissolved in 150 ml of acetonitrile. The solution was heated at 68 ± 1.5 °C under nitrogen, a given amount of azobisisobutyronitrile being added. After being left standing at the same temperature for 24 hr, the mixture was worked up in the same manner as in the photoreaction. The results are given in Table 2. 2-Methylimidazole was analyzed by NMR with an internal standard, pinacol, and lophine by UV in ethanol.

Deuterium Incorporation Experiment. A solution of ca. 100 mg of 2-phenylimidazoline (Ic) in a mixture of acetone and MeOD and D_2O placed in a Pyrex tube was sealed after bubbling nitrogen and irradiated externally. After evaporation of the mixture under reduced pressure, the residue was dissolved in chloroform and washed three times with 2 ml of water to remove any deuterium bound to nitrogen atom of Ic. The solution was evaporated after being dried with anhydrous sodium sulfate. The recovered Ic in the residue was isolated by preparative tlc (Al_2O_3 ; acetone-ethanol (3 : 1)) and recrystallized from benzene-petroleum ether. The pure Ic thus obtained was analyzed on a Hitachi VD-10001-A mass spectrometer. The molecular ion region was scanned several times for each sample. Deuterium contents were calculated by comparing peak heights with those of a non-deuterated sample of Ic.

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