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PHOTOREARRANGEMENTS OF SOME N-METHYL DIAZOLES

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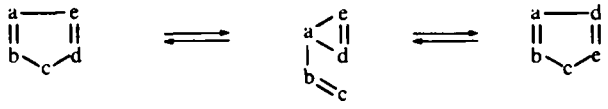
Abstract—The photointerconversion of 1,4-dimethylimidazole and 1,2-dimethylimidazole and the photorearrangements of 1,4,5-trimethylimidazole to 1,2,5-trimethylimidazole and of 1,3,5-trimethylpyrazole to 1,2,4- and 1,2,5-trimethylimidazole are reported. The pathway proposed for the formal interchange of the 2 and 4 positions is supported by the positionally specific photorearrangement of 1,4-dimethylimidazole-2*d*.

Photorearrangements of aromatic compounds are of synthetic and mechanistic interest. The photointerchange of contiguous atoms, the most generally observed process, may be accounted for by a series of valence isomerizations[1] or by a ring-contraction ring-expansion sequence.[2] The photoisomerization of many different 5-membered nitrogen heteroaromatics appears to proceed by the latter route *via* formation of an azirine intermediate and interchange of adjacent ring atoms on re-formation of a 5-membered ring.



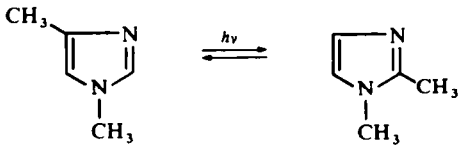
This process has been thoroughly documented by Singh and Ullman for the photorearrangement of 3,5-diarylisoxazoles to 2,5-diaryloxazoles *via* 3-aryol-2-aryl-1-azirines. Analogous pathways can account for the major products in the photoisomerizations of other isoxazoles to oxazoles[3] and of pyrazoles and their derivatives to imidazoles and their derivatives.[4,5] Similar photo-reactions are observed for the furans[6] and thiophenes.[7]

This report describes some photoisomerizations of N-methylimidazoles which do not appear to follow a ring-contraction ring-expansion sequence.[8] An alternative pathway for the photorearrangement of five-membered heteroaromatics is proposed.

RESULTS AND DISCUSSION

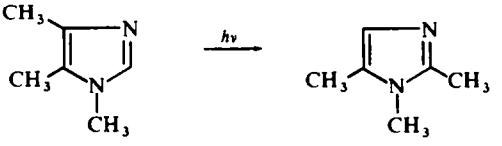
Irradiation of 1,4-dimethylimidazole (**1**) in t-butyl alcohol for 41 hr with a high-pressure mercury resonance lamp gives 1,2-dimethylimidazole (**2**) in 40% conversion (25% yield). Under the same conditions **2** is converted to **1** with 50% conversion (30% yield) after 30·5 hr. The products were identified in each case by GLPC, preparation of the picrates and comparison with authentic material by IR and m.p. criteria.

Photolysis of 1,4,5-trimethylimidazole (**3**) in ethanol with a low-pressure mercury lamp gives ca. 40% 1,2,5-trimethylimidazole (**4**). The product **4** was also identified as a product of the photolysis of 2,3-dihydro-5,6-dimethyl-pyrazine in 22% yield; in this



1 2

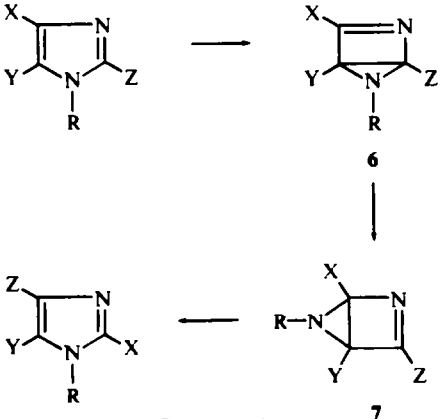
case it arises from rearrangementof the initially formed **3**.[9] Separation of **4** is achieved by GLPC or preparative TLC, and comparison of the picrate with authentic material by mass spectral, IR and melting point criteria established identity. The photoconversion of **3** to **4** proceeds in t-butyl alcohol or cyclohexane with the low- or high-pressure lamps. The latter and cyclohexane give, after 31 hr of irradiation, a 61% conversion (35% yield) of **3** to **4**. Irradiation of 1.2.5-trimethylimidazole in cyclohexane led to



3 4

destruction of 70% of the **4** initially present, with less than 5% of **3** formed. Photolysis of 1,2,4-trimethylimidazole (**5**), a possible isomeric product, in t-butyl alcohol gives less than 10% disappearance of starting material after 28 hr. In cyclohexane, **5** is photoreactive but the unidentified products are not the isomeric trimethylimidazoles. Photolysis of 4,5-diphenyl-1-methylimidazole for 47·5 hr in ethanol with the low-pressure lamps gave no reaction.

The photorearrangements of **1**, **2** and **3** to isomeric imidazoles may be viewed as a formal interchange of the 1,5 or the 2,4 carbons. That these results cannot be accommodated by a ring-contraction ring-expansion sequence which allows interhange of only the 2,3 or 4,5 positions is apparent. Pathway A, which involves an initial disrotatory formation of a bicyclic isomer **6** followed by a 1,3-sigmatropic shift to a second bicyclic isomer **7** which undergoes a disrotatory ring opening to the product can be envisioned. These transformations are allowed as concerted photochemical proesses in

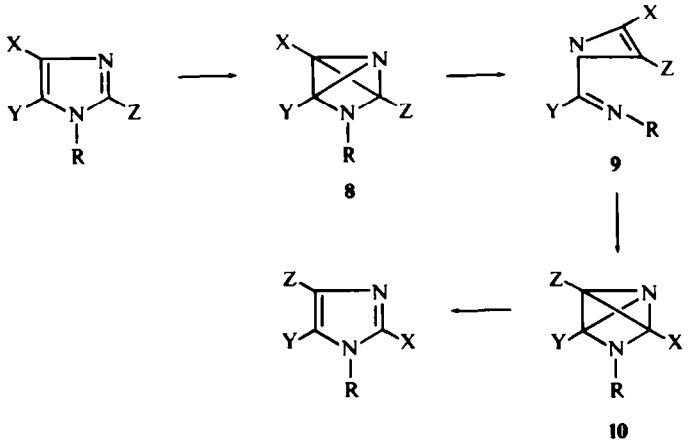


6

7

PATHWAY A

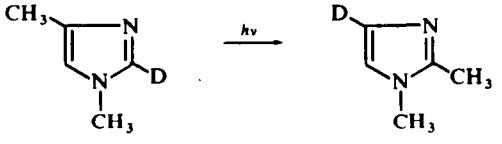
systems having appropriate symmetry according to the Woodward–Hoffmann rules.[10] Analogies for this sequence may be found in the photochemistry of 3-phenylthiophene benzene,[1] pyrazolenines,[11] cyclopentadiene,[12] and other carbocycles.[13] An alternative pathway (B) involving **8**, **9**, and **10** in a new form of a ring-contraction ring-expansion sequence can also be envisaged and also has analogy in the photoisomerizations of the benzenes[1] and thiophenes.[7] The sequence shown leads to one of several conceivable products. A difference between these processes lies in the symmetry of **8** in which the



PATHWAY B

original 2 and 5 positions become equivalent when Y and Z are equivalent. The intermediates in pathway A do not allow equivalence of the 1 and 5 positions.

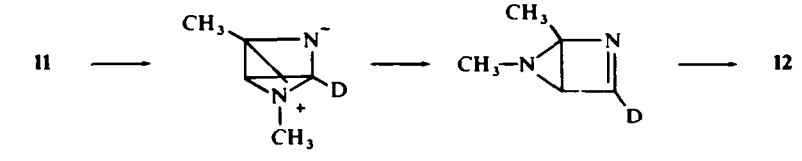
Experimental distinction between pathways A and B may be seen in the photorearrangement of 1,4-dimethylimidazole-2*d* (**11**). If path A is followed, the expected product is 1,2-dimethylimidazole-4*d* (**12**); if path B is followed, the expected product would be an equal mixture of **12** and 1,2-dimethylimidazole-5*d*. Irradiation of **11**, having 85% 2*d* and 30% 5*d* in an isotopic mixture, in cyclohexane gives **12**, having



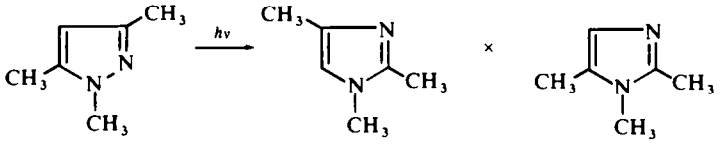
11 **12**

76% 4*d* and 21% 5*d*, as shown by NMR in accord with pathway A for at least 90% of the rearrangement.*

* Paths A and B do not exhaust the conceivable routes for rearrangement. For example, the labelling results cannot rule out a rearrangement *via* i or elaborate schemes of sequential rearrangements.



Pyrazoles are conceivable products of the photorearrangements of imidazoles. To establish the photochemical relationship between these isomers[4] in the present instance, the irradiation of 1,3,5-trimethylpyrazole (**13**) was investigated. Irradiation of **13** in ethanol for 3 hr with a high-pressure lamp gives 1,2,4-trimethylimidazole (**4**) and 1,2,5-trimethylimidazole (**5**) in 7 and 2% yields, respectively. Identification of **4** and **5** is based on NMR and GLPC comparison with authentic material and comparison of the picrate of **4** with authentic material by mass spectral, infrared, and melting point criteria. The photorearrangement of **13** in cyclohexane gives 33% conversion to **5** (26% yield) and 13% conversion to **4** (10% yield) after 12 hr. The



13 **5** **4**

reaction proceeds in t-butyl alcohol and cyclohexane with the high- and low-pressure lamps. Separate photolyses in cyclohexane showed that **4** and **5** are not appreciably interconverted under the reaction conditions. The formation of **4** from **13** is consistent with a ring-contraction ring-expansion sequence while the conversion of **13** to **5** may be rationalized by two such sequences with 1,3,4-trimethylpyrazole as an intermediate or by a process analogous to pathway A.

No emission was observed in attempts to measure the phosphorescence spectrum of **3** in a 1:1 ethanol–ether glass.* Attempts to photosensitize the photorearrangements with acetophenone and benzophenone were unsuccessful, in contrast to the sensitization previously observed in the photorearrangement of some pyrazoles to imidazoles.[4] Attempts to gain information about reaction intermediates by an isosbestic study were frustrated by the formation of unidentified light-absorbing products.

EXPERIMENTAL

The m.ps were determined with a Buchi Capillary apparatus or Reichert Hot Stage apparatus and are uncorrected. The b.ps are uncorrected. The IR spectra were determined on a Perkin-Elmer 137 NaCl Spectrophotometer. The UV spectra were measured on a Cary Model 14m spectrophotometer and a Perkin-Elmer 202 UV-Visible spectrometer. The PMR were obtained on Varian Associates Model A-60, A-60A, A-56/60, and HA-100 spectrometers with 10–30% $CHCl_3$-*d* solns, unless otherwise noted, and are reported in σ, ppm relative to the internal standard, TMS. The mass spectra were determined by Mr. J. Wrona on an Atlas CH4 mass spectrometer with a vacuum lock inlet system. GLC chromatographic analyses were carried out on an Aerograph A-90-P and A-90-P3. The microanalyses were performed by Mr. Joseph Nemeth and his associates.

Light sources. The light sources used for photolysis were an Hanovia Type L 450-watt high-press quartz Hg-vapor immersion lamp, an Hanovia 23-watt Type SC-2537 low-press Vycor Hg-vapor immersion lamp, and a Rayonet Srinivasan-Griffin Photochemical Reactor with RPR-2537A lamps. The high-press lamp provides a continuous spectrum of radiation from 220 mμ when used in the water-cooled quartz immersion well. A 7740 Pyrex glass filter sleeve was used to prevent portions of the radiated energy from reaching the reacting material. This filter transmits 0% of the incident light at 260 mμ, 1% at

* We are grateful to Dr. Bruce Monroe of California Institute of Technology for these measurements.

280 mμ, 30% at 300 mμ, 71% at 320 mμ, and 87% at 340 mμ. The low-press Hg-vapor lamp emits 96·5% of its radiation at 253·7 mμ. The balance of UV emission is scattered over other weak lines between 220 and 400 mμ. The RPR-2537A lamps emit 85·4% of their radiation at 253·7 mμ, with the remainder being scattered over other weak lines between 265·2 and 578·0 mμ.

1,4-*Dimethylimidazole* (**1**) was prepared from acetonyl acetate, methylamine hydrochloride, formaldehyde, and ammonium hydroxide by the method of McLean and Muir[14] b.p. 97–98° (14 mm) (lit.[14] 197–198°). Purification was achieved by preparative GLPC with a 1 m 25% FS 1265 Silicone Fluid on Chromosorb W column at 125°. The NMR, σ 2·07 (3H s, C$\underline{H}_3$C), 3·48 (3H s, C$\underline{H}_3$N), 6·67 (1H broad s, C$\underline{H}$CCH$_3$), 7·38 (1H broad s, C$\underline{H}$N), and IR spectra are consistent with the established structure.

The picrate salt was prepared and recrystallized from water to give fine yellow needles m.p 164·5–167° (lit.[14] 167–168°).

2-*Deutero*-1,4-*dimethylimidazole* (**11**). A soln of 88 mg of 1,4-dimethylimidazole in 0·5 ml of D_2O (Columbia Organic Chemicals, 99·5% pure) was allowed to stand for 4 days. The NMR spectrum of the soln indicated 0·15 and 0·70 protons remaining in the peaks at σ 7·38 (C–2$\underline{H}$) and 6·67 (C–5$\underline{H}$) ppm, respectively.[15] The soln was made basic with NaOD-D_2O soln and continuously extracted with CH_2Cl_2.

After drying over Na_2SO_4 and filtration, the solvent was removed under reduced press to give 90 mg of material. The NMR spectrum was consistent with the above assignment.

1,2-*Dimethylimidazole* (**2**) was obtained from K and K Laboratories, Inc. It was purified by GLPC on the FS 1265 column at 125° before photolysis. The NMR, σ 2·28 (3H s, C$\underline{H}_3$C), 3·48 (3H s, C$\underline{H}_3$N), 6·83 (1H d, J=1·5 Hz. C$\underline{H}_3$=CH), 6·93 (1H d. J=1·5 Hz, CH=C$\underline{H}_4$), and IR spectra were consistent with the established structure.

The picrate salt 1,2-dimethylimidazole was prepared and the yellow plates had mp 178–180° (lit.[16] 178–180°).

1,4,5-*Trimethylimidazole* (**3**) was prepared from 4,5-dimethylimidazole[17] by methylation with Me_2SO_4 bp 118° (13 mm) (lit.[18] 117° (20 mm)). 1,4,5-Trimethylimidazole was also prepared from 2,3-dihydro-5,6-dimethylpyrazine by the method of Beak and Miesel[9] bp 108–109° (11 mm). The NMR spectrum in benzene showed the resonances of the Me groups at σ 2·80, 2·22, and 1·73 ppm, comparing reasonably well with the reported values of 2·63, 2·21, and 1·65 ppm.[19] The UV spectrum of 1,4,5-trimethylimidazole showed λ_{max} 226 mμ (ε 4650) (EtOH and t-BuOH) and $\lambda_{max}^{cyclohexane}$ 234 mμ (ε 5300), and 213 mμ (ε 4600).

The picrate salt of 1,4,5-trimethylimidazole was prepared and recrystallized from water to give fine yellow needles m.p. 218–220·5° (lit.[20] 218–219°). The IR and mass spectra were consistent with the established structure.

1,2,5-*Trimethylimidazole* (**4**). A soln of 4·0 g of 1,2-dimethyl-imidazole and 14·0 g of a 37% soln of formaldehyde was heated in a sealed tube at 135° for 6 hr.[20,21] After dilution with water and basification with NaOHaq the aqueous soln was continuously extracted with CH_2Cl_2. The CH_2Cl_2 extracts were dried over Na_2SO_4 and filtered, and the solvent was removed under reduced press. Trituration with acetone gave a 4·6% yield of white crystals which could be recrystallized from acetone to give material with m.p. 161–165°. The NMR spectrum, σ 2·32 (3H s, C$\underline{H}_3$C), 3·55 (3H s, C$\underline{H}_3$N), 4·42 (2H s, OC$\underline{H}_2$), and 6·88 (1H s, C$\underline{H}$N), was consistent with the assigned structure as 1,2-dimethyl-5-hydroxymethylimidazole. Found: C, 56·88; H, 8·24; N, 21·51. Calc. for $C_6H_{10}N_2O$: C, 57·12; H, 7·99; N, 22·20.

To 73 mg of 1,2-dimethyl-5-hydroxymethylimidazole covered with 1·5 ml benzene was added 0·1 ml thionyl chloride. After the mixture had been heated on a steam bath for 15 min and was allowed to stand at room temp for 12 hr, the solvent was removed on a steam bath. The resulting thick residue, presumed to contain 1,2-dimethyl-5-chloromethylimidazole, was used without further purification.

To a soln of 1,2-dimethyl-5-chloromethylimidazole in 3 ml AcOH was added 0·15 g Zn dust. The mixture was heated at 110° for 5 hr and the solvent was removed by distillation to give a thick residue which was dissolved in 3 ml water, filtered, basified with NaOH and continuously extracted with CH_2Cl_2. The CH_2Cl_2 extracts were dried over Na_2SO_4, filtered, and evaporated to dryness under reduced press. The benzene-soluble portion of the resulting material was separated by filtration and evaporated under reduced press to give 16 mg (25% yield from 1,2-dimethyl-5-hydroxymethylimidazole) yellow oil.

The NMR spectrum in benzene showed peaks at σ 1·73, 2·03, and 2.47 ppm, in good agreement with the values of σ 1·74, 2·04, and 2·53 ppm reported for 1,2,5-trimethylimidazole.[19]

The picrate salt of 1,2,5-trimethylimidazole was prepared and recrystallized from water to give yellow plates m.p. 197–206° (lit.[20] 208–209°). The IR and mass spectra were consistent with the established structure.

1,2,4-*Trimethylimidazole* (**5**) was prepared by methylation of 2,4(5)-dimethylimidazole[22] by the method of Ochiai and Sibata[23] bp 108–110° (14 mm). The material solidified during the distillation. The NMR spectrum in benzene showed the Me group resonances at σ 2·00, 2·25, and 2·82 ppm. in reasonable agreement with the reported values of σ 1·95, 2·29, and 2·62 ppm.[19] Smaller peaks at σ 1·82, 2·07, and 2·70 ppm indicated the presence of ca. 20% 1,2,5-trimethylimidazole.

The picrate salt of 1,2,4-trimethylimidazole was prepared and recrystallized from water to give fine yellow needles, m.p. 145–154° in 51% yield. After resolidification it had m.p. 154–157° (lit.[20] 152–154°). The IR and mass spectra were consistent with the established structure and, along with the NMR, served to distinguish this compound from the 1,2,5-isomer.

The assignment of structures to **4** and **5** had been previously made on the basis of their syntheses. Condensation of 1,5-dimethylimidazole with formaldehyde and subsequent reduction with P and HI gives a trimethylimidazole which is different from that obtained upon methylation of 4,5-dimethylimidazole and is thus assigned as 1,2,5-trimethylimidazole.[20] The structure of 1,5-dimethylimidazole follows from its formation from the condensation product of α-methylaminopropionacetal and thiocyanic acid.[24] 1,2,4-Trimethylimidazole has been formed in a sealed tube reaction between methylamine and 2,4-dimethyl-5-oxazolecarboxylic acid.[19] The m.ps. of the picrates of 1,2,5-trimethylimidazole, 208–209°,[20] and 1,2,4-trimethylimidazole, 152–154°,[19] are quite different as are the Me resonances in benzene: 1.74, 2·04, and 2·53 ppm for (**4**) and 1·95, 2·29, and 2·62 ppm for (**5**).[19]

1,3,5-*Trimethylpyrazole* (**13**) was prepared by methylation of 3,5-dimethylpyrazole by the method of Grandberg and Kost[25] b.p. 107° (65 mm) (lit. [25] 165–167° (741 mm)). The NMR spectrum in benzene showed the Me peak resonances at σ 1·82, 2·20, and 3·28 ppm, in reasonable agreement with the reported values of σ 1·68, 2·26, and 3·17 ppm.[26] Other NMR spectra showed the ring proton at σ 5·81 ppm, in good agreement with the reported value of σ 5·83 ppm.[26] The IR and UV (λ_{max}^{EtOH} 221 mμ (ε 4650) λ_{max}^{EtOH} 210 mμ (ε 3800)) spectra are consistent with the established structure.

General procedures for photolysis. The solns were irradiated in a Pyrex container into which the high-press Hg-vapor lamp and filter in a quartz immersion well or the low-press Hg-vapor lamp had been placed. Before the photolysis was started, the soln was deaerated for a minimum of 30 min by a stream of O_2-free dry N_2 which was maintained during the course of the photolysis. The N_2 was purified by passage through two traps of Fieser solution,[27] a lead acetate soln trap, a H_2SO_4 trap, and a drying tower of mixed Molecular Sieve and indicating Drierite. Smaller amounts of material were irradiated in solns in quartz or Pyrex test tubes or in Beckman 10 mm silica UV cells.

Photolysis of 1,4-*dimethylimidazole* (**1**). A soln of 60 mg of 1,4-dimethylimidazole in 10 ml of t-BuOH in quartz test tubes was irradiated with a high-press Hg-vapor lamp. After 41 hr, GLPC analysis on the FS 1265 column at 125° indicated that approximately 40% of **1** remained, and a photoproduct with a retention time identical to that of 1,2-dimethylimidazole was present in about 25% yield. The starting material and photoproduct were separated by preparative GLPC.

The IR spectrum of the photoproduct was identical to that of 1,2-dimethylimidazole. The picrate salt of the photoproduct had m.p. 178–180·5° (lit.[16] 178–180°) and m.m.p. with authentic 1,2-dimethylimidazole picrate was undepressed.

The recovered 1,4-dimethylimidazole was identified by its IR and preparation of the picrate.

Photolysis of 2-*deutero*-1,4-*dimethylimidazole* (**11**). A soln of 66 mg of 2-deutero-1,4-dimethylimidazole in 20 ml cyclohexane was irradiated in quartz test tubes with a high-press Hg-vapor lamp. GLPC analysis indicated approximately 10% 1,2-dimethylimidazole after 18 hr.

Preparative GLPC gave 1,2-dimethylimidazole. A computer time-averaged NMR spectrum of this product showed singlets at σ 2·32, 3·53, 6·74, and 6·84 ppm with relative areas of 3·0, 2·9, 0·76, and 0·21, respectively. Addition of 1,2-dimethylimidazole to this soln resulted in the increase of these peaks, confirming the assignments.

Photolysis of 1,2-*dimethylimidazole* (**2**). A soln of 49 mg of 1,2-dimethylimidazole in 10 ml of t-BuOH in quartz test tubes was irradiated with a high-press Hg-vapor lamp. GLPC analysis, after 30·5 hr, showed that ca. 40% **2** was present and a photoproduct with a retention time identical to that of 1,4-dimethylimidazole was present in ca. 30% yield. The photoproduct was separated by preparative GLPC.

The IR spectrum of the photoproduct was identical to that of 1,4-dimethylimidazole. The picrate salt

of the photoproduct had m.p. 162–166° (lit.[14] 167–168°). A m.m.p. with authentic 1,4-dimethylimidazole picrate was undepressed.

The recovered 1,2-dimethylimidazole was identified by IR and preparation of the picrate.

Photolysis of 1,4,5-*trimethylimidazole* (**3**). A soln of 1·118 g of 1,4,5-trimethylimidazole in 365 ml abs EtOH was photolyzed with a low-press Hg-vapor lamp. After 42 hr the UV spectrum and TLC analysis on silica gel with a $CHCl_3$–MeOH–NH_4OH (80:25:0·1) solvent system[28] indicated that most of the starting material was gone and gave a spot with an R_f identical to that of 1,2,5-trimethylimidazole. The solvent was removed under reduced press and the residue was distilled to give 541 mg clear liquid b.p. 118–119° (13 mm) which crystallized during the distillation. The NMR spectrum in benzene showed Me resonances of equal areas at σ 1·83, 2·07, and 2·78 ppm, with smaller peaks at σ 1·77, 2·18, and 2·90 ppm, indicating a 5:1 ratio of photoproduct to 1,4,5-trimethylimidazole. GLPC analysis confirmed this assignment.

For preparative purposes the 1,4,5-trimethylimidazole was produced *in situ* by photorearrangement of 2,3-dihydro-5,6-dimethylpyrazine.[9] A soln of 1·337 g 2,3-dihydro-5,6-dimethylpyrazine in 250 ml absEtOH was photolyzed with a low-press Hg-vapor lamp. After 80 hr most of the solvent was removed under reduced press. The residue was distilled to give a fraction b.p. 130–134° (31 mm) containing 650 mg of faintly yellow liquid. The NMR spectrum indicated a mixture containing 50% 1,2,5-trimethylimidazole (peaks of equal area at σ 1·77, 2·03, and 2·67 ppm) and 20% 1,4,5-trimethylimidazole (peaks of equal area at σ 1.70, 2·13, and 2·80 ppm).

Preparative TLC of 68 mg of this material was carried out with a 2000-μ layer of Merck Silica Gel PF_{254}. Development 3 times with MeOH gave a satisfactory separation as shown by spraying a strip with an I_2 in $CHCl_3$ soln. The band containing the photoproduct was removed and extracted with MeOH. Evaporation of the solvent and preparation of the picrate gave 47 mg (22%) of yellow crystals mp 204·5–205·5°. The m.m.p. of this picrate and 1,2,5-trimethylimidazole picrate was undepressed. The IR and mass spectra were virtually identical to those of 1,2,5-trimethylimidazole picrate.

GLPC separation of a sample of the photomixture was carried out on the FS 1265 column at 125°. Preparation of the picrate gave fine yellow needles m.p. 202·5–208° (lit.[20] 208–209°).

The photorearrangement could also be achieved with the low- and high-press lamps in t-BuOH and cyclohexane. Conversion appeared to be fastest with cyclohexane solns and the high-press lamp; a 61% conversion (corrected for 43% unreacted starting material) of 1,2,5-trimethylimidazole from 1,4,5-trimethylimidazole was determined by GLPC after 31 hr irradiation. Irradiation of 1,4,5-trimethylimidazole in acetone with the low-press lamp or in AcOH with the high-press lamp gave disappearance of starting material but less than a few per cent conversion to 1,2,5-trimethylimidazole.

Attempts to sensitize the photorearrangement in t-BuOH or cyclohexane with acetophenone (E_t = 76·3 kcal/mole in hydrocarbon solvents[29]) or benzophenone (E_t = 68·5 kcal/mole in hydrocarbon solvents[29]) were not successful. Photolysis in benzene (E_t = 85 kcal/mole)[29] did not produce rearrangement. Attempts to carry out an isosbestic study of the rearrangement were not successful apparently due to the formation of other absorbing species.

Photolysis of 1,2,5-*trimethylimidazole* (**4**). A soln of 1,2,5-trimethylimidazole in cyclohexane was irradiated in an UV cell with a high-press Hg-vapor lamp for 4 hr. Analysis of the soln at intervals by GLPC on the FS 1265 column at 125° showed that the amount of 1,2,5-trimethylimidazole present decreased 70% while less than 5% 1,4,5-trimethylimidazole was observed.

Photolysis of 1,2,4-*trimethylimidazole* (**5**). A soln of 1,2,4-trimethylimidazole in 5 ml of t-BuOH was irradiated with a high-press Hg-vapor lamp. GLPC analysis at intervals on the FS 1265 column at 125° showed no formation of photoproducts or disappearance of starting material after 28 hr of photolysis.

Photolysis of 1,3,5-*trimethylpyrazole* (**13**). A soln of 992 mg of 1,3,5-trimethylpyrazole in 400 ml absEtOH was photolyzed with a high-press Hg-vapor lamp. After 3 hr the solvent was removed under reduced press and the brown residue was distilled to give 148 mg of faintly yellow liquid which solidified upon cooling. The NMR spectrum of this material in benzene was consistent with that of a mixture of 1,2,4-trimethylimidazole (peaks at σ 1·97, 2·22, and 2·72 ppm), 1,3,5-trimethylpyrazole (peaks at σ 1·76, 2·22, and 3·13 ppm), and 1,2,5-trimethylimidazole (peaks at σ 1·76, 2·02, and 2·57 ppm), with the relative amounts ca. 3:2:1, respectively.

Column chromatography of this material on 10·5 g of BDH Reagent silica gel gave 24 mg of yellow oil on elution with $CHCl_3$—MeOH. The NMR spectrum in benzene showed signals at σ 1·98, 2·19, and 2·73 ppm which are in reasonable agreement with the values reported for the Me resonances of 1,2,4-trimethylimidazole of σ 1·95, 2·29, and 2·62 ppm.[19]

The picrate prepared from this material has m.p. 148–153° and m.p. 152–155° (lit.[19] m.p. 152–154°) after it has resolidified. A m.m.p. determination with authentic 1,2,4-trimethylimidazole picrate showed the same behavior. The IR and mass spectra were virtually identical to those of 1,2,4-trimethylimidazole picrate.

The minor photoproduct was identified as 1,2,5-trimethylimidazole by the NMR spectrum of the mixture and its GLPC retention time on the FS 1265 column.

Photorearrangement of 1,3,5-trimethylpyrazole proceeded in t-BuOH and cyclohexane with the high-press lamp. The conversions were determined in cyclohexane after 12 hr of irradiation by GLPC to be 33% 1,2,4-trimethylimidazole and 13% 1,2,5-trimethylimidazole (based on 78% of 1,3,5-trimethylpyrazole reacted). Attempts to sensitize the rearrangement with acetophenone or benzophenone in t-BuOH or cyclohexane were not successful.

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