

PHOTOINDUCED REACTIONS—XLV

PHOTOADDITION OF KETONES TO METHYLIMIDAZOLES¹

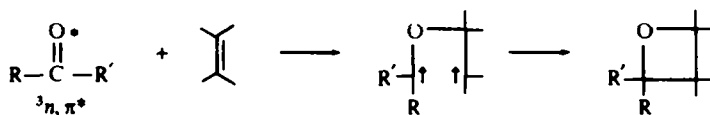
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Abstract—The photoaddition of acetone to 2-methyl- (Ia), 1,2-dimethyl- (Ib) and 1-methyl-imidazole (Ic) and the photoaddition of benzophenone and acetophenone to 1,2-dimethylimidazole have been investigated. The products were not oxetanes, usually obtained on photoaddition of carbonyl compounds to olefins, but α -hydroxyalkylimidazoles (II, V, VI and VII). A mechanism involving an oxetane intermediate was proposed. The selective attack of the excited carbonyl oxygen to the 4-position of N-methylimidazoles is in accord with results of simple Hückel calculations on N-methylimidazoles.

THERE have been a great many examples of the photocycloaddition of carbonyl compounds to olefins giving oxetanes. It is generally accepted that, when an olefin is not electron deficient and the energy of the n, π^* triplet state of a carbonyl compound is lower than that of the π, π^* triplet state of an olefin, the addition proceeds *via* a more stable biradical intermediate caused by attack of the oxygen atom of the excited carbonyl on an olefin in the ground state.²



The oxetane formation with a carbon-carbon double bond in heteroaromatic systems is known only for furans.³ The present report describes the photoaddition of ketones to some methylated imidazoles (Ia, Ib and Ic) giving α -hydroxyalkylimidazoles (II, V, VI and VII) which are, most probably, formed *via* an oxetane intermediate.

Irradiation of an acetone solution of 1,2-dimethylimidazole (Ib) with a low-pressure mercury lamp (mainly 2537 Å) gave a 1 : 1 adduct (IIb). The NMR spectrum (CDCl₃) exhibits two Me signals at τ 6.50 and 7.65 which are almost unshifted from those of Ib, two equivalent Me signal at τ 8.47, a hydroxyl proton signal at τ 7.27, and an aromatic proton signal at τ 3.35. The mass spectrum of IIb shows a fragmentation pattern similar to that of imidazoles reported by Hodges and Grimmett.⁴ From these spectral data, it can be suggested that IIb is not an oxetane but an imidazole derivative having an α -hydroxyisopropyl group at the 4 or 5-position of Ib. Treatment of IIb with dry HCl in acetic anhydride or pyrolysis at 150° gave a dehydrated

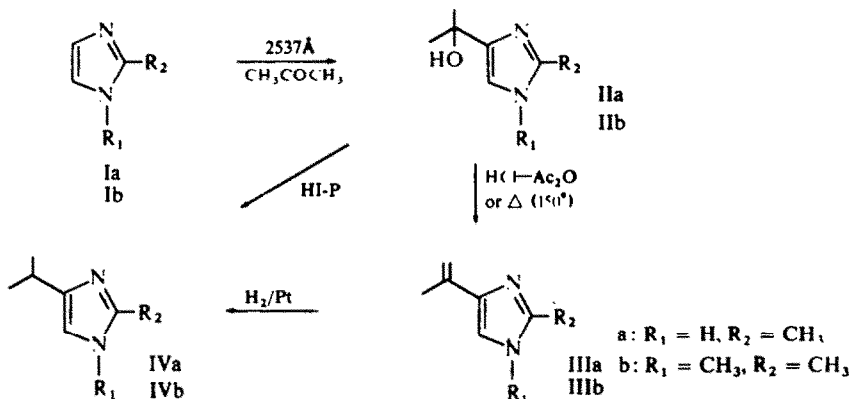
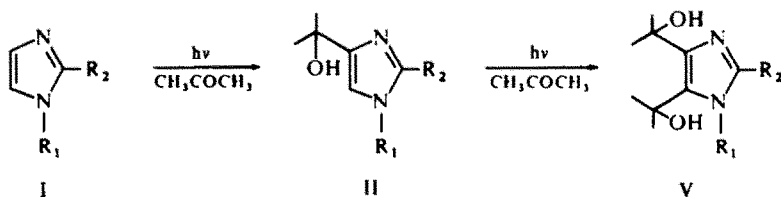


TABLE I. PHOTOADDITION OF ACETONE TO IMIDAZOLES

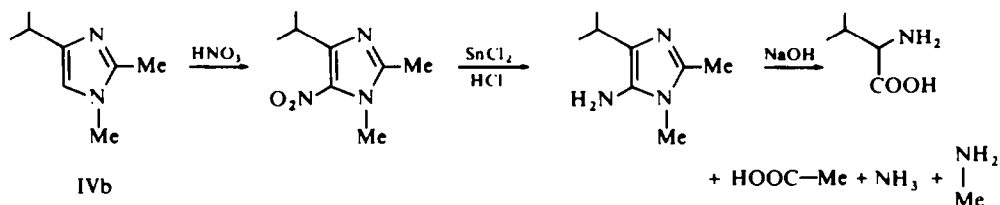
I	conc	irradn time	Yield of adduct	Recovered I
R_1 R_2	(mmol/l)	(h)	(%)	(%)
a H CH_3	95	132	IIa 8 V 14.5	10
b CH_3 CH_3	90	93	IIb 70	17
c CH_3 H	75	370	IIc 9.1	18
d H H	180	207	—	62



product IIIb which was considered to be 4- or 5-isopropenyl-1,2-dimethylimidazole from its NMR, IR and UV spectra. The product was hydrogenated over Pt-black catalyst to give an isopropyl derivative IVb which was also obtained by the direct reduction of IIb with red phosphorus and hydriodic acid. These results confirm the structure of IIb to be that of an α -hydroxyisopropyl-1,2-dimethylimidazole, although the position (4 or 5) of the α -hydroxyisopropyl group is unknown.

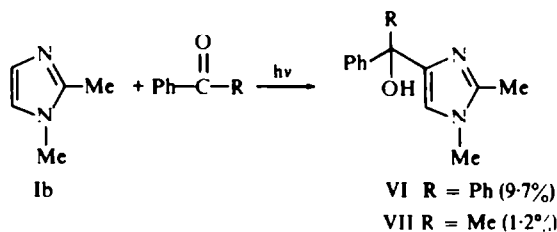
There have been several reports of methods for determining the position of a substituent on N-methylimidazoles.⁵⁻⁸ Among them the method established by Pyman⁵ and by Sawa *et al.*⁸ seemed to be most reliable and useful. According to their reports, 5-amino-1,4-dimethylimidazole, resulting from the reduction of 5-nitro-1,4-dimethylimidazole, decomposes on alkali hydrolysis to give DL-alanine, methylamine and ammonia, while 4-amino-1,5-dimethylimidazole gives DL-N-methylalanine and ammonia. Therefore, if IVb is 4-isopropyl-1,2-dimethylimidazole, its 5-amino derivative will give DL-valine, methylamine and ammonia. This method

was applied to a mononitro derivative of IVb. The products were found to be DL-valine and methylamine, but no DL-N-methylvaline was detected which would be expected to be formed from 5-isopropyl-1,2-dimethylimidazole. Thus the structure of IIb was established as 4-(α -hydroxyisopropyl)-1,2-dimethylimidazole.



Irradiation of an acetone solution of 1-methylimidazole (Ic) also gave a 1:1 adduct (IIc). The structure of IIc was obtained from the spectral data analogous to those of IIb. Irradiation of 2-methylimidazole (Ia) in acetone gave a 1:1 adduct (IIa) and a 2:1 adduct (V). Irradiation of IIa in acetone gave V. Dehydration of IIa followed by hydrogenation gave IVa and methylation of IIa with methyl iodide gave IIb. Therefore the structure of IIa was that of 4- (or 5-) (α -hydroxyisopropyl)-2-methylimidazole, and the structure of V of 4,5-di-(α -hydroxyisopropyl)-2-methylimidazole. Irradiation of imidazole (Id) in acetone did not give any isolable products and a large amount of Id was recovered. These reactions are summarized in Table 1. As can be seen from Table 1, the more methylated imidazoles, which are considered to be more electron-rich, give the adduct in higher yield.

Irradiation of benzophenone or acetophenone and 1,2-dimethylimidazole (Ib) in *t*-butyl alcohol with a high-pressure mercury lamp through Pyrex ($>2800 \text{ \AA}$) gave a 1:1 adduct (VI or VII) albeit in poor yield. The structures of the products were assigned from their spectral data which are analogous to those of IIb.



Up to the present, there has been no experimental data on the triplet energy of imidazoles. However, from the facts that this photoaddition did occur even in the case of benzophenone whose triplet energy is rather low (68.5 kcal/mole) and the quantum yield of whose triplet state formation is nearly unity,⁹ and that imidazoles used in the present photoreaction show no evident absorption in the region of the n, π^* absorption of the ketones used, it is reasonable to suggest that the reactive

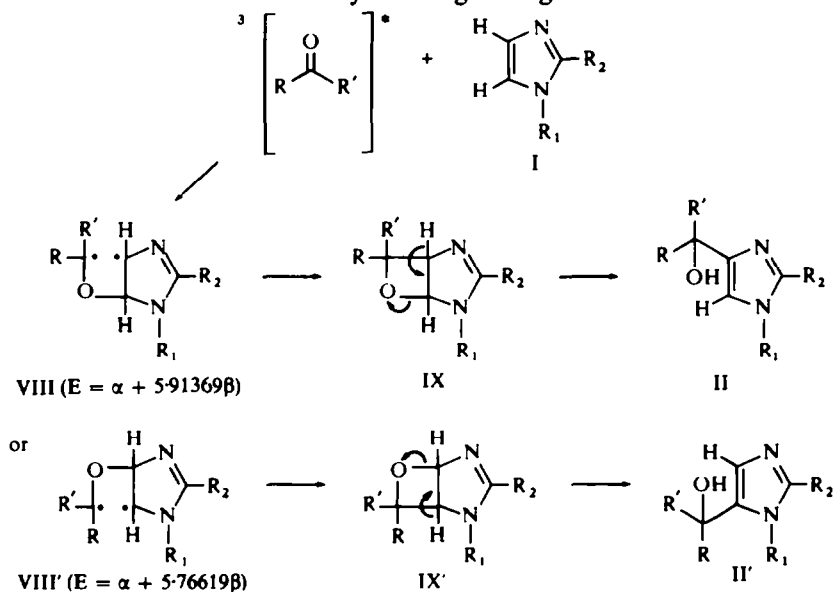
species responsible for the photoaddition are not excited imidazoles but excited ketones in the n, π^* triplet state.

In the first place, in order to distinguish between the possible reactive species, the concentration dependence of acetone in the reaction with 1,2-dimethylimidazole (Ib) was examined. In this experiment, acetone was used in excess, so that the incident light would be completely absorbed only by acetone. Within the range of acetone concentrations in which the concentration of the n, π^* excited acetone could be kept constant, the concentration of acetone was varied. Under these conditions the concentration of the excited imidazole, which might be formed by energy transfer from the excited acetone or by any other process, would be also kept constant, and the concentration of acetone would be independent of irradiation time in the earlier stages of the reaction. Plotting the yields of the adduct (IIb) based on the used Ib against concentrations of acetone gave a linear relation as shown in Fig 1.

If the only process for giving IIb was reaction of the excited Ib with acetone in the ground state, the yields of IIb would be in direct proportion to concentration of acetone, while if the excited acetone reacted with Ib in the ground state, the yields would be independent of acetone concentration. The plot shows that the predominant reaction is that of excited acetone with Ib in the ground state.

Next, in order to discover the multiplicity of the n, π^* state of acetone, a quenching experiment using oxygen as a triplet quencher was carried out. The result showed that oxygen, to some extent, quenched the n, π^* triplet state of acetone which is considered to be the main reactive species.

On the basis of the results described above, we propose a mechanism, shown in Scheme 1, for the photoaddition of ketones to imidazoles. The oxygen atom of a ketone in the n, π^* triplet excited state attacks the carbon atom at 5-position of an imidazole (I) giving a biradical intermediate VIII which cyclizes to give an oxetane derivative IX. The oxetane IX finally rearranges to give the adduct II.



SCHEME I

Although only 4-(α -hydroxyalkyl)imidazoles (II) were obtained from N-methylimidazoles, it is possible at least formally to consider that the carbonyl oxygen atom attacks the carbon atom at 4-position giving another biradical VIII' which leads to II' via an oxetane IX'. The experimental results indicate that a difference between reactivities at 4- and 5-positions of I and a difference between stabilities of the

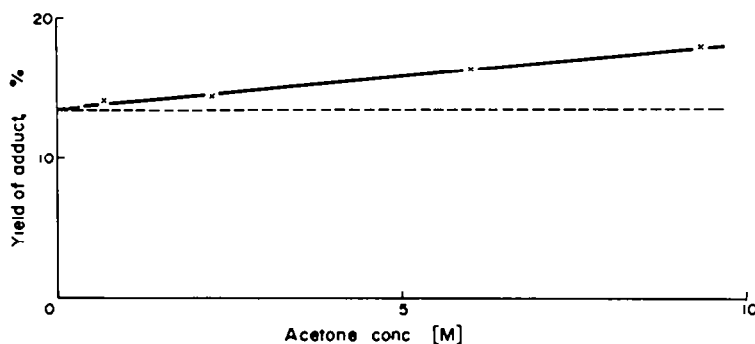


FIG 1

biradical intermediates VIII and VIII' may cause the selective addition of the ketones to give only 4-(α -hydroxyalkyl)imidazoles. Therefore, radical reactivity indices were calculated for the carbons at 4- and 5-positions of 1,2-dimethylimidazole (Ib), using the simple Hückel method, including (A) the hyperconjugation of two methyl groups in the π -system and (B) considering only their inductive effect. The results, listed in Table 2, show that the carbon atom at the 5-position of Ib is more reactive than that at the 4-position. Similar results were obtained from the calculations for 1-methylimidazole (Ic). The energies of the two biradical intermediates VIIIb and VIIIb' which can result from 1,2-dimethylimidazole were also calculated by a localization method, using simple Hückel calculations. The result that VIIIb is more stable than VIIIb' is again in accord with the experimental results.

TABLE 2. RADICAL REACTIVITY INDICES FOR 4- AND 5-POSITIONS OF 1,2-DIMETHYLIMIDAZOLES (Ib)

	A		B	
	Position		Position	
	4	5	4	5
Free Valence	0.43489	0.44915	0.42187	0.43366
Frontier Electron Density	0.28864	0.42817	0.27839	0.45239
Superdelocalizability	0.93362	0.93482	0.87393	0.89818

The 1:1 adduct IIa from acetone and 2-methylimidazole (Ia) has at least two tautomeric forms, both of which can give the same 2:1 adduct V. Finally the question arises, if the oxetane derivatives were formed, why were they not isolated from these

photoaddition reactions as in the case of furans.³ According to Orgel *et al.*¹⁰ imidazole has a larger delocalization energy than furan by about 0.8 β . If this holds true also in the case of methylimidazoles, it may be the driving force for the rearrangement of oxetanes IX to the adducts II. Furthermore, an alternative mechanism of adduct formation involving the attack of a ketyl radical, which may be formed by hydrogen abstraction from the n, π^* triplet of ketones can be excluded, because, according to this mechanism, 5-(α -hydroxyalkyl)imidazoles must be the predominant product over 4-(α -hydroxyalkyl)imidazoles as would be shown by the results of the above calculations.

EXPERIMENTAL

1,2-Dimethylimidazole (Ib) and 1-methylimidazole (Ic) were prepared according to the method of Matsuura and Ikari.¹¹ 2-Methylimidazole (Ia) and imidazole were available commercially.

Photoaddition of acetone to 1,2-dimethylimidazole (Ib)

Isolation of the reaction products. A soln containing 1.395 g of Ib in acetone (230 ml) was irradiated with a 10-W low-pressure mercury arc lamp (Vycor) for 48 hr under bubbling N₂ and external cooling with tap water. After removal of acetone under reduced pressure, the residue was chromatographed on 70 g of silica gel. Elution with 1450 ml of acetone gave 219 mg of a mixture of unknown products which were not further investigated. Further elution with 2850 ml of acetone yielded 1.1 g (50%) of yellow crystals. Recrystallization from Et₂O-light petroleum afforded colorless crystals (IIb), m.p. 94–95°; ν_{\max}^{KBr} 3200 cm⁻¹; UV spectrum, no maximum above 210 m μ ; mass spectrum, m/e 136 (base peak 100%), 135 (37), 121 (30), 94 (30), 80 (14), 42 (39), 41 (9), 39 (16). (Found: C, 62.23; H, 9.10; N, 18.05. Calc for C₈H₁₄ON₂: C, 62.30; H, 9.15; N, 18.15%). Further elution with 2000 ml of MeOH gave 222 mg of a brown oil which contained mainly Ib (by IR).

Quantitative analysis of the product. A soln containing 5.188 g of Ib in acetone (600 ml) was irradiated with a 40-W low-pressure mercury arc lamp (Quartz) for 93 hr under bubbling N₂ and external cooling with tap water. The solvent was evaporated under reduced pressure to give a pale brown oil. VPC (silicone DC 550; column length 1.5 m; carrier gas, H₂; 0.8 kg/cm² gauge; column temp, 145°) of this oil showed that the yield of IIb was 70% and the recovery of Ib 17%. The yield of the product was determined by calibration with an authentic mixture (internal standard: 2,4,6-tri-*t*-butylphenol).

Dehydration of IIb

(a) *With HCl.* A soln containing 2.42 g of Ib in acetone (230 ml) was irradiated with a 10-W low-pressure mercury arc lamp (Vycor) for 78 hr under similar conditions. The solvent was evaporated under reduced pressure to give 4.2 g of a pale brown oil. Dry HCl was bubbled through a soln of this oil in 15 ml of Ac₂O under cooling with water for 15 min, the mixture was allowed to stand overnight at room temp. The mixture was added to ice water, made alkaline with K₂CO₃ and extracted with 3 \times 100 ml portions of Et₂O. Evaporation of Et₂O gave 1.42 g (40% on Ib) of an oil (IIIb) which showed almost one spot by TLC (silica gel, EtOH). The oil was purified by molecular distillation: ν_{\max}^{KBr} 890 cm⁻¹; $\lambda_{\max}^{\text{EtOH}}$ 247 m μ (ϵ 8700) and 251 m μ (shoulder, ϵ 7900); NMR spectrum (CDCl₃): τ 3.26 (1H, s), 4.30–4.45 (1H, m), 5.05–5.25 (1H, m), 6.49 (3H, s, methyl), 7.65 (3H, s, methyl), 7.95–8.05 (3H, m, methyl). The picrate of IIIb was recrystallized from EtOH, m.p. 149°. (Found: C, 46.02; H, 4.04; N, 19.02. Calc for C₁₄H₁₃O₇N₅: C, 46.03; H, 4.14; N, 19.17%).

(b) *By pyrolysis.* A soln containing IIIb in acetone was passed through a VPC column (column temp, 170°). The substance recovered (clear oil) was collected in a glass tube. This was identified as IIIb by IR (almost quantitative yield).

Preparation of IVb

(a) *By hydrogenation of IIIb.* A soln containing 7 g of IIIb in AcOH (30 ml) was hydrogenated on 370 mg of Pt-black catalyst at room temp (4 h). The catalyst was filtered off and the filtrate diluted with 50 ml of water, made alkaline with Na₂CO₃ and extracted with Et₂O. The extract gave 4 g of an oil on evaporation, distillation of which gave 1.6 g of IVb as an oil, b.p. 84–90°/10 mm. UV spectrum: no maximum above

210 μ . The picrate of this oil was recrystallized from EtOH, bright yellow needles, m.p. 100–101°; NMR spectrum (CDCl_3): 1.57 (2H, s), 3.26 (1H, s), 6.23 (3H, s methyl), 6.87 (1H, septet, $J = 9.6$ cps), 7.30 (3H, s, methyl) and 8.77 (6H, d, $J = 9.6$ cps, two Me groups). (Found: C, 45.57; H, 4.55; N, 18.88. Calc for $\text{C}_{14}\text{H}_{17}\text{O}_7\text{N}_3$: C, 45.77; H, 4.67; N, 19.07%.)

(b) *By direct reduction of IIb.* A mixture of 6.62 g of IIb, 2.43 g of red P and 20 ml of HI ($d = 1.70$) was heated at 110–120° for 7 hr. The mixture was poured into 100 ml of water, made alkaline with Na_2CO_3 and extracted with 3×50 ml portions of CHCl_3 . The residue, left on evaporation, was distilled under reduced pressure to give 1.97 g (34%) of an oil, b.p. 47–51°/5 mm, which was identified IVb (by NMR and mixed m.p. of the picrate).

Nitration of IVb

To 1.74 g of IVb, 3.82 g of HNO_3 ($d = 1.42$) and then 7.33 g of conc H_2SO_4 were added in small portions under cooling with water. The mixture was heated at 160–180° for 1.5 hr and after cooling poured into 100 ml of water, made alkaline with Na_2CO_3 and extracted with 4×50 ml portions of benzene. After evaporation, the extract was distilled to give 1.29 g (58%) of a yellow oil, b.p. $\sim 70^\circ/5$ mm. $\nu_{\text{max}}^{\text{IR}}$ 1550 and 1360 cm^{-1} ; NMR spectrum (CDCl_3): τ 6.11 (3H, s, methyl), 6.31 (1H, septet, $J = 7.7$ c/s), 7.51 (3H, s, methyl) and 8.69 (6H, d, $J = 7.7$ c/s, two Me groups). The picrate was recrystallized from EtOH, m.p. 179.5–180.5°. (Found: C, 40.84; H, 3.89; N, 20.54. Calc for $\text{C}_{14}\text{H}_{16}\text{O}_9\text{N}_6$: C, 40.78; H, 3.91; N, 20.38%.)

Reduction of nitro-derivative of IVb and hydrolysis of product

A mixture of 1.14 g of the nitro-derivative of IVb, 4.95 g of SnCl_2 and 18.7 ml of conc HCl was shaken at room temp for 4 hr and kept overnight. A solid mass (3.7 g) separated and was collected by filtration. Concentration of the filtrate gave another crop of the solid. The combined solid was treated with water and neutralized with aq NaOH, then filtered, the crystals deposited on concentration of the filtrate being filtered off. To the final filtrate (~ 10 ml) was added 4 ml of water and 1 g of NaOH and the mixture was refluxed for 42 h. During this time, the liberated gas was absorbed by dil HCl. Then the soln was diluted with water and the pH brought to the isoelectric point of valine (5.96–6.00) with HCl; the solid precipitated was filtered off. The mother liquor was concentrated and filtered three times to remove inorganic salts. The final mother liquor was concentrated and the residue was dried under reduced pressure. The TLC (silica gel) of the aq soln of the residue showed a spot identical with that of authentic DL-valine but not with authentic DL-N-methylvaline in two solvent systems, $n\text{BuOH}:\text{H}_2\text{O}:\text{AcOH} = 6:2:2$ (v/v), pH = 2.1 and $\text{M}/10 \text{NH}_4\text{OH}:\text{M}/10 \text{NH}_4\text{Cl} = 9:7:0.3$ (v/v), pH = 11.0. Paper chromatography showed a spot identical with authentic DL-valine but not with authentic DL-N-methylvaline in two solvent systems, $n\text{BuOH}:\text{H}_2\text{O}:\text{AcOH} = 6:2:2$ (v/v), pH = 2.1 (R_f of DL-valine = 0.55, R_f of the sample = 0.55, R_f of DL-N-methylvaline = 0.65) and $n\text{PrOH}:\text{28\% NH}_4\text{OH} = 7:5:2.5$ (v/v) (R_f of DL-valine = 0.56, R_f of sample = 0.58, R_f of DL-N-methylvaline = 0.66). The IR spectrum of crystals sublimated from the residue (200–230°/5 mm) was identical with that of authentic DL-valine. The dil HCl used to absorb liberated gas was concentrated and its residue was found by TLC to contain CH_3NH_2 , HCl and NH_4Cl .

Concentration dependence of the photoaddition of acetone to 1,2-dimethylimidazole (Ib)

Four samples of 48.9 mg of Ib and acetone (0.5, 1.5, 4.5 and 7.0 ml) were diluted with $t\text{BuOH}$ to 10 ml and placed in quartz tubes. The UV spectrum of the soln was ascertained to be off-scale in the region of the n, π^* band of acetone. These samples were irradiated under N_2 for 32 hr with a 10-W low-pressure mercury arc lamp (Vycor) using a merry-go-round apparatus.

The yield of IIb in each sample was determined by VPC analysis. The results are shown in Fig 1.

Quenching experiment

Two samples of quartz tubes each containing 45.3 mg of 1,2-dimethylimidazole (Ib) in 10 ml of acetone were prepared; one was placed under O_2 and the other under N_2 . These samples were irradiated for 66 hr with a 10-W low-pressure mercury arc lamp (Vycor) using a merry-go-round apparatus. The yield of IIb and the recovery of Ib were determined by VPC analysis. The yields of IIb under O_2 and N_2 were 4.0 and 13.6% respectively and the recovery of Ib was 73.6 and 55.4% respectively.

Photoaddition of acetone to 1-methylimidazole (Ic)

A soln containing 1.230 g of Ic in acetone (200 ml) was irradiated with a 10-W low-pressure mercury arc lamp (Vycor) for 370 hr under N_2 and external cooling with tap water. After removal of acetone under

reduced pressure the residue was chromatographed on 70 g of silica gel. Elution with 1200 ml of CHCl_3 -acetone (9:1-1:4), 1200 ml of acetone and 200 ml of acetone-MeOH (1:4) gave 2.14 g of a mixture of unknown products which were not further investigated. Further elution with 200 ml of acetone-MeOH (1:4) yield 204 mg of an oil (IIc). TLC (silica gel; EtOH) gave just a single spot. The picrate of this oil was recrystallized from EtOH, m.p. 203-204° (decomp); NMR spectrum (CD_3SOCD_3): τ 1.07 (1H, s, disappeared on addition of D_2O), 1.42 (2H, s), 2.30 (1H, diffused s, became doublet by addition of D_2O , $J = 1.3$ c/s), 2.53 (1H, slightly broad, became doublet on addition of D_2O , $J = 1.3$ c/s), 6.17 (3H, s, methyl), 8.52 (6H, s, two Me groups). (Found: C, 42.36; H, 4.02; N, 19.07. Calc for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_8$: C, 42.28; H, 4.09; N, 18.97%). Continuing elution with 1300 ml of MeOH-acetone (1:1) gave 290 mg of a mixture containing Ic (by VPC). The yield of the product was determined by VPC. The yield of IIc; 9.1% and the recovery of Ic; 18%.

Photoaddition of acetone to 2-methylimidazole (Ia)

A soln containing 4.690 g of Ia in acetone (600 ml) was irradiated with a 40-W low-pressure mercury arc lamp (quartz) for 132 hr under N_2 and external cooling with tap water. After removal of the solvent under reduced pressure, the residue was recrystallized from MeOH-acetone (1:1) to give 643 mg (8%) of IIa as colorless crystals, m.p. 162-163°; $\nu_{\text{max}}^{\text{KBr}}$ 3100 cm^{-1} ; UV spectrum: no maximum above 210 μm ; NMR spectrum (CD_3SOCD_3): τ 3.45 (1H, s), 7.81 (3H, s, methyl), 8.16 (6H, s, two Me groups), OH and NH protons did not appear. (Found: C, 59.70; H, 8.69; N, 19.87. Calc for $\text{C}_7\text{H}_{12}\text{ON}_2$: C, 59.97; H, 8.63; N, 19.99%). The mother liquor was chromatographed on 150 g of silica gel. Elution with 730 ml of acetone gave 1.587 g of a mixture of unknown products which were not further investigated. Further elution with 1550 ml of acetone yielded 1.781 g (14.5%) of V. This was recrystallized from acetone and dried *in vacuo* at 50° for 20 h, then again recrystallized from abs EtOH- CHCl_3 to give colorless needles, m.p. 173-174°; $\nu_{\text{max}}^{\text{KBr}}$ 3500 and 3250 cm^{-1} ; UV spectrum: no maximum above 210 μm ; NMR spectrum (CD_3SOCD_3): τ 3.62 (2H, broad s, disappeared on addition of D_2O), 7.82 (3H, s, methyl), 8.55 (12H, s, four Me groups), NH protons did not appear. (Found: C, 60.69; H, 9.13; N, 13.84. Calc for $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_2$: C, 60.58; H, 9.15; N, 14.13%). Further elution with 800 ml of MeOH gave 447 mg (10%) of the recovered Ia (by IR).

Dehydration of IIa

A soln of 413 mg of IIa in 10 ml of Ac_2O was refluxed for 4 hr. After cooling, the mixture was poured into 50 ml of ice water, made alkaline with K_2CO_3 and extracted with 3 \times 50 ml portions of ether. Evaporation of the ethereal layer gave 400 mg of an oil (IIIa) which showed just a single spot on TLC, $\nu_{\text{max}}^{\text{KBr}}$ 890 cm^{-1} ; λ_{max} 254 μm (ϵ 4500). The picrate of this oil was recrystallized from EtOH, m.p. 175-176°; NMR spectrum (CD_3SOCD_3): τ 1.41 (2H, s), 2.41 (1H, s), 4.40-4.50 (1H, m), 4.75-4.85 (1H, m), 7.43 (3H, s, methyl) and 7.92-8.02 (3H, m, methyl). (Found: C, 44.44; H, 3.90; N, 19.61. Calc for $\text{C}_{13}\text{H}_{13}\text{O}_7\text{N}_3$: C, 44.45; H, 3.73; N, 19.94%).

Hydrogenation of IIIa

A soln of 323 mg of IIIa in AcOH (6 ml) was hydrogenated on 17 mg of Pt-black catalyst at room temp (6 h). The catalyst was filtered off and the filtrate diluted with 20 ml of water, made alkaline with Na_2CO_3 and extracted with 4 \times 30 ml portions of Et_2O . Evaporation of the extract gave 187 mg of IVa as an oil. The picrate of this oil was recrystallized from EtOH, m.p. 142-143°; NMR spectrum (CD_3SOCD_3): 4.43-3.13 (2H, broad, disappeared on addition of D_2O), 1.42 (2H, s), 2.76 (1H, s), 7.05 (1H, septet, $J = 7.2$ c/s), 7.46 (3H, s, methyl) and 8.77 (6H, d, $J = 7.2$, two methyl groups). (Found: C, 44.45; H, 4.27; N, 20.11. Calc for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_7$: C, 44.19; H, 4.28; N, 19.83%).

Photoaddition of acetone to IIa

A soln containing 531 mg of IIa in acetone (200 ml) was irradiated with a 10-W low-pressure mercury arc lamp (Vycor) for 70 hr under N_2 and external cooling with tap water. After removal of acetone under reduced pressure, the residue was chromatographed on 30 g of silica gel. Elution with 200 ml of acetone gave 172 mg of a mixture of unknown products which were not further investigated. Further elution with 370 ml of acetone gave 243 mg (30%) of V (by IR and mixed m.p.). Further elution with 100 ml of EtOH gave 283 mg (~50%) of IIa (by TLC and IR).

N-Methylation of IIa

To a soln of 96 mg of Na metal and 380 mg of IIa in abs EtOH (2.6 ml) was added an excess (~2 ml)

of MeI, and the mixture was kept for 15 hr. After removal of the solvent and MeI under reduced pressure, the residue was poured into 30 ml of water and extracted with 3 × 20 ml portions of CCl₄. The extract gave 110 mg (26%) of IIb m.p. 72–75° (by IR, VPC, TLC and mixed m.p.).

Irradiation of acetone solution of imidazole (Id)

A soln containing 2.80 g of Id in acetone (230 ml) was irradiated with a 10-W low-pressure mercury arc lamp (Vycor) for 207 hr under N₂ and external cooling with tap water. TLC (silica gel, EtOH) and VPC of the product showed that 62% of Id was recovered.

Photoaddition of benzophenone to 1,2-dimethylimidazole (Ib)

A soln of 4.504 g of benzophenone and 2.273 g of Ib in tBuOH (230 ml) was irradiated for 29 hr with a 100-W high-pressure mercury arc lamp (Ushio UM 100) surrounded by a Pyrex cooling jacket under N₂; the vessel was immersed in water kept at 30–40°. After removal of the solvent under reduced pressure, the residue was recrystallized from acetone to give 637 mg (9.7%) of VI, m.p. 175–177° $\nu_{\text{max}}^{\text{KBr}}$ 3250 cm⁻¹, 1600 cm⁻¹, 1500 cm⁻¹ and 703 cm⁻¹; NMR spectrum (CDCl₃) τ 2.30–3.10 (10H, m), 3.79 (1H, s), 5.93 (1H, s, disappeared on addition of D₂O), 6.52 (3H, s, methyl) and 7.63 (3H, s, methyl). (Found: C, 77.89; H, 6.42; N, 10.12. Calc for C₁₈H₁₈ON₂: C, 77.67; H, 6.52; N, 10.07%). The mother liquor was chromatographed on 70 g of silica gel. Elution with 1750 ml of CHCl₃ gave 2.37 g (55%) benzophenone; further elution with 500 ml of MeOH gave 3.32 g of a mixture which contained Ib (<40%). The mixture was not further investigated.

Photoaddition of acetophenone to 1,2-dimethylimidazole (Ib)

A soln of 3.234 g of acetophenone and 2.086 g of Ib in tBuOH (205 ml) was irradiated for 69 hr under the same conditions as above. After removal of the solvent, the residue was chromatographed on 53 g of silica gel. Elution with 150 ml of CHCl₃ gave 3 g (~90%) of acetophenone, further elution with 200 ml of acetone gave 722 mg of an oil. This oil was further chromatographed on 25 g of silica gel. After elution with 300 ml of CHCl₃, the column was cut into eight pieces. From two of them 55 mg (1.2%) of impure VII were obtained by washing with MeOH. The picrate was prepared and recrystallized from EtOH, m.p. 205–206°; NMR spectrum (CD₃SOCD₃): τ 2.40 (2H, s), 2.4–2.7 (5H, m), 2.47 (1H, s), 6.46 (3H, s, methyl), 7.47 (3H, s, methyl) and 8.39 (3H, s, methyl), OH proton did not appear. (Found: C, 51.44; H, 4.60; N, 15.51. Calc for C₁₉H₁₉O₈N₃: C, 51.23; H, 4.30; N, 15.73%). Other pieces gave 194 mg of a mixture of acetophenone and VII. Further elution of the original chromatograph with 300 ml of acetone gave 188 mg of an oil which was a mixture of Ib and VII and further elution with 400 ml of acetone and 500 ml of MeOH gave ~1.5 g (75%) of Ib.

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