

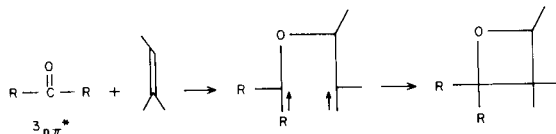
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Imidazole itself did not undergo photoaddition reactions with ketones. However, irradiation of 1-acetyl and 1-benzoylimidazole, and 1,1'-carbonyldiimidazole with benzophenone yielded oxetanes. On irradiation with carbonyl compounds, 1,2-dimethylimidazole and 1-benzylimidazole did not give oxetanes but a hydroxyaryl or hydroxyalkyl derivative. Thiazole itself did not yield any photoaddition product, but 2,4-dimethylthiazole afforded oxetanes on irradiation with benzophenone and with 3-benzoylpyridine. Irradiation of 2,4-dimethylthiazole with acetophenone led to the formation of a dimeric material. On irradiation with benzophenone, 4-methylisothiazole did not yield an oxetane but rather a hydroxyphenyl derivative. 3,5-Dimethylisoxazole on irradiation with benzophenone and with 3-benzoylpyridine gave oxetanes. Irradiation of 4,5-dimethylisoxazole yielded similarly an oxetane with benzophenone

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The formation of oxetanes by photocycloaddition of ketones to olefins was first studied by Paterno and Büchi (1). This reaction involves the addition of an excited ketone to an olefin to form an oxetane. The major mode of addition can be predicted by assuming that the radical-like oxygen atom of the $n\pi^*$ triplet ketone adds to the olefin to give preferentially the most stable biradical intermediate (2). Although the oxetane formation with a carbon-carbon double bond in heterocyclic system is known for furans (3) and thiophenes (4), the synthesis of the oxetanes of imidazoles (5), thiazoles, isothiazoles and isoxazoles (6) has not been reported previously.



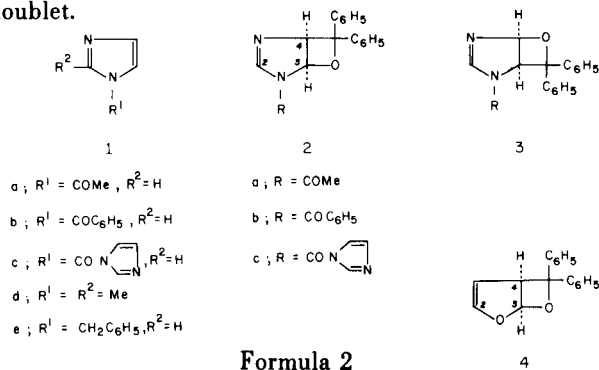
Formula 1

Results and Discussion.

We have previously studied the photoaddition of benzophenone to pyrrole (7) and 7-azaindole (8) and found that they themselves did not form oxetanes; in order to prepare their oxetanes it was essential to protect the NH groups in their molecules with an electron-withdrawing group, such as acetyl, benzoyl, etc. The reason for this was assumed to be due to greater electron density in the heterocyclic π -system or a quenching effect on the excited ketone by the non-bonded electrons on the nitrogen atom (9).

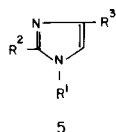
Imidazole itself behaved similarly and did not form an oxetane. In order to prepare an oxetane it was necessary to protect its NH group by acylation. When 1-acetyl (1a) and 1-benzoylimidazole (1b), and 1,1'-carbonyldiimidazole (1c) were irradiated in the presence of benzophenone in benzene, the oxetanes were obtained (50% yield in 1a;

34% yield in 1b; 51% yield in 1c). These oxetanes were assigned structures 2a, 2b and 2c, respectively. For these oxetanes the alternative structures 3a, 3b and 3c were also possible, but they were excluded on the basis of the following nmr evidence. We have previously noted in the oxetanes (4) from furans (10), that the proton at C-4 couples with the proton at C-2 with $J = 1.2$ Hz (allylic coupling), but the proton at C-5 does not couple to a detectable degree with the proton at C-2 ('W' path coupling). In the nmr spectra of the oxetanes 2a, 2b and 2c, the protons at C-5 appear at 6.63 (d), 6.46 (d), and 6.71 (d), respectively. These protons resonate at lower field than the protons at C-4, due to the proximity to both nitrogen and oxygen atoms. They only couple with the proton at C-4, and do not couple with the proton at C-2, thus occurring as a doublet ($J = 4.5$ Hz). However, the protons at C-4 at higher field (5.68, dd in 2a; 5.83, dd in 2b; 5.78, dd in 2c) couple not only with the proton at C-5 ($J = 4.5$ Hz) but also with the proton at C-2 ($J = 1.5$ Hz), and thus appear as a quartet. If the oxetanes were postulated to have structures 3, then the proton at C-4, which would resonate at lower field, would have to occur as a quartet, and the proton at C-5, which would resonate at higher field, would have to exhibit a doublet.



Formula 2

In the case of 1,2-dimethylimidazole and 1-benzylimidazole, no oxetane formation was observed, but a hydroxyalkyl or hydroxyphenyl derivative was obtained. Irradiation of 1,2-dimethylimidazole with benzophenone gave an alcohol (4% yield). The structure **5a** for this alcohol was readily deduced from the nmr spectrum. The spectrum exhibited a 1-methyl signal at 3.33 (s) which was almost unshifted from that of 1,2-dimethylimidazole, a methylene signal at 3.53 (s) (in place of a 2-methyl signal), an olefinic proton at 6.66 (d, $J = 1.2$ Hz) and 6.88 (d, $J = 1.2$ Hz), and aromatic ring protons at 7.30 (10H, m). This addition product has proved to be identical with the compound synthesized from 1,2-dimethylimidazole by reaction with *n*-butyllithium and benzophenone.



- a, $R^1 = \text{Me}$, $R^2 = \text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{OH}$, $R^3 = \text{H}$
 b, $R^1 = \text{Me}$, $R^2 = \text{Me}$, $R^3 = \text{C}(\text{CH}_3)_2\text{OH}$
 c, $R^1 = \text{CH}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)_2\text{OH}$, $R^2 = R^3 = \text{H}$

Formula 3

On irradiation with acetone 1,2-dimethylimidazole also yielded an alcohol (30% yield). The structure **5b** of this compound was assigned from its nmr data. The spectrum had a six-proton signal at 1.53 (s, $(\text{CH}_3)_2\text{-C}$), a 2-methyl signal at 2.33, a 1-methyl signal at 3.50, and an olefinic proton at 6.63 (s). The site of addition at the 4-position (not at C-5) of the imidazole nucleus was deduced by analogy with a similar work (11). The formation of this product may involve an oxetane such as **2** as an intermediate and a subsequent rearrangement of the expectedly unstable amino ether linkage.

Irradiation of 1-benzylimidazole with benzophenone in *t*-butyl alcohol similarly yielded an alcohol (20% yield). The structure **5c** of this addition product was readily assigned from the nmr spectrum which showed a benzylic proton at 6.31 (s), an olefinic proton at 6.98 (t) and 7.20 (t), benzenoid protons at 7.45 (15H, m), and an olefinic proton at 7.73 (t, 2-H). These photoaddition reactions probably proceed *via* transition of the π^* singlet to the triplet of the carbonyl compounds, the oxygen atom of which abstracts either the allylic, benzylic, or the imidazole ring hydrogen to form radicals that subsequently couple (12).

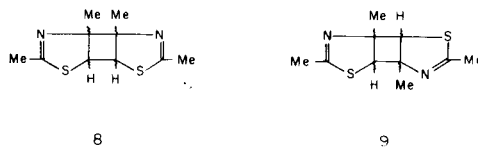
Thiazole itself did not give an oxetane nor an adduct with benzophenone on irradiation (13). 2,4-Dimethylthiazole, however, yielded oxetanes with either benzophenone or 3-benzoylpyridine (14). Evidence for the structure **6** rather than **7** for these oxetanes came from the following nmr spectra. In the spectra of the oxetanes from furans (10) and imidazoles (*vide ante*), the proton at C-5, which is

adjacent to two heteroatoms, resonates at a low field of 6.1-6.5. The oxetane (25% yield) from benzophenone showed the spectrum which contained two three-proton singlets at 1.30 (4- CH_3) and 2.10 (2- CH_3), a one-proton singlet at 6.50 (5-H), and a ten-proton multiplet (aromatic ring protons) at 7.30. The nmr spectrum of the oxetane (40% yield) from 3-benzoylpyridine exhibited a close similarity. It has three singlets at 1.40 (4- CH_3), 2.20 (2- CH_3), and 6.53 (5-H), and two multiplets at 7.50 (7H) and 8.70 (2H) (benzenoid and pyridyl protons). The occurrence of the signal of the 5-proton at the low field of 6.50-6.53 in these cases is compatible with structures **6a** and **6b** for the oxetanes from benzophenone and 3-benzoylpyridine, respectively. On irradiation with acetophenone, 2,4-dimethylthiazole, however, did not afford an oxetane nor an adduct, but rather a dimeric material (15). The yield of this dimer varied dependent upon the solvent used (60% without solvent, 10% in benzene and 30% in acetonitrile). The nmr spectrum showed the presence of two quaternary methyl groups at 1.36 as a six-proton singlet, two methyl groups on the double bond at 2.29 as a six-proton singlet, and two olefinic protons at 3.65 as a two-proton singlet. This dimer was formulated as either **8** or **9**, but the differentiation between these two structures could not be made.



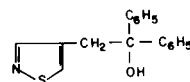
- a, $R = \text{C}_6\text{H}_5$
 b, $R = \text{C}_5\text{H}_4\text{N}$

Formula 4



Formula 5

Irradiation of 4-methylisothiazole with benzophenone did not yield an oxetane but a hydroxyphenyl derivative (33% yield). It was formulated as **10** since the nmr spectrum showed two two-proton singlets at 3.71 ($\text{CH}_2\text{-C}$) and 8.05 (3- and 5-H), and a multiplet (10H, aromatic ring protons) at 7.33.

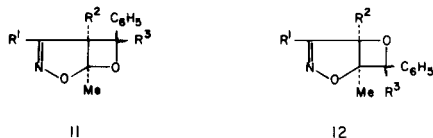


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Formula 6

On irradiation with benzophenone, 3,5-dimethylisoxazole gave an oxetane (40% yield). Its structure (**11a**) was deduc-

ed from the nmr spectral evidence. The spectrum showed two three-proton singlets at 1.36 (3-CH₃) and 1.60 (5-CH₃), a one-proton singlet at 4.43 (4-H), and a multiplet at 7.50 (10H, aromatic ring protons). It has been our experience that in the oxetanes from furans and thiophenes (10), the oxygen atom of benzophenone invariably adds to the carbon which is connected to the furan or thiophene heteroatom. In the spectra of these oxetanes (16), the methyl group attached to the carbon between two oxygen atoms or between oxygen and sulfur atoms presented chemical shifts at fairly low field of 1.35-1.81. The downfield shift (1.60) of the 5-methyl resonance in the oxetane from 3,5-dimethylisoxazole excluded the alternative structure (12). Irradiation of 3,5-dimethylisoxazole with 3-benzoylpyridine yielded the corresponding oxetane (11b) (24% yield). In this case, the product consisted of a 1:1.4 mixture of two oxetanes isomeric at C-7, as demonstrated by the nmr spectrum, and attempts to separate from each other were unsuccessful. In the spectrum, while the proton at C-4 and the methyl group at C-5 appeared as a singlet at 4.42 and 1.58, respectively, the singlet signal corresponding to the methyl group at C-3 displayed two separate peaks at 1.37 and 1.47 in an integral ratio of 1:1.4, respectively. Furthermore, benzenoid protons were also observed as two separate singlets at 7.36 and 7.50 and pyridyl protons as two separate multiplets at 7.73 and 8.60, whose integral ratios in both cases are 1:1.4, respectively.



- a ; R¹ = Me, R² = H, R³ = C₆H₅
 b ; R¹ = Me, R² = H, R³ = C₆H₄N
 c ; R¹ = H, R² = Me, R³ = C₆H₅

Formula 7

Finally, irradiation of 4,5-dimethylisoxazole with benzophenone afforded an oxetane (65% yield) whose structure was readily determined as 11c by the nmr spectrum. The spectrum showed 4- and 5-methyl signals at 1.20 and 1.56, respectively, a one-proton singlet at 7.35 (3-H), and a ten-proton multiplet (aromatic ring protons) at 7.16 (17).

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Ir spectra were recorded for potassium bromide discs with a Perkin-Elmer 337 spectrometer. Unless otherwise stated, nmr spectra were obtained for solutions in deuteriochloroform on a Varian A-60 or a Bruker WP-60 instrument and chemical shifts are reported in parts per million downfield from TMS (δ scale, abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). Mass spectra were recorded on a DuPont 21-492B (Data System 21-094B) or a Hitachi-Perkin-Elmer RMU 6H spectrometer at 70 eV using a direct inlet

system. For column chromatography, silica gel 60 (Merck, 35-70 or 70-230 mesh) was used. Thin layer chromatograms were prepared on silica gel G or silica gel GF₂₅₄60 (Merck) and the spots were observed by exposure to iodine vapor or uv light. Microanalyses were carried out by A. Bernhardt microanalytical laboratory, 5251 Elbach über Engelskirchen, West Germany.

All irradiations were carried out on a vessel or spiral tube into which a quartz immersion well containing a Pyrex filter sleeve and a Hanovia 450W medium pressure mercury lamp was fitted. The double-walled immersion well containing the light source was cooled at -25° and the solution was irradiated while nitrogen was bubbled through the solution before and during the irradiation. The reaction was monitored by tlc. Imidazole, 1,1'-carbonyldiimidazole, 1,2-dimethylimidazole, 1-benzylimidazole, thiazole, 2,4-dimethylthiazole, 4-methylisothiazole, 3,5-dimethylisoxazole, 4,5-dimethylisoxazole, and 3-benzoylpyridine were purchased from Aldrich Chemical Company.

Irradiation of 1-Acetylimidazole (1a).

1-Acetylimidazole (1a) (1.0 g., 0.0091 mole) in benzene (100 ml.) was irradiated with benzophenone (3.3 g., 0.0182 mole) for 12 hours. Removal of the solvent under reduced pressure left a crystalline oxetane (2a) which was treated with ether to show m.p. 137° (1.3 g.); nmr (acetone-d₆): 2.31 (3H, s, CH₃CO), 5.68 (1H, q, J_{4,5} = 4.5 Hz, J_{4,6} = 1.5 Hz, 4-H), 6.63 (1H, d, J_{5,4} = 4.5 Hz, 5-H), 7.18-7.90 (10H, m, benzenoid protons), and 7.98 (1H, d, J_{2,4} = 1.5 Hz, 2-H); ms: m/e 292 (M⁺).

Anal. Calcd. for C₁₁H₁₆N₂O₂: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.76; H, 5.26; N, 9.34.

Irradiation of 1-Benzoylimidazole (1b).

1-Benzoylimidazole (1b) (1.0 g., 0.0058 mole) in benzene (100 ml.) was irradiated with benzophenone (2.1 g., 0.0116 mole) for 7.5 hours. The solvent was removed under reduced pressure. The oxetane (2b) crystallized upon addition of ether to show m.p. 138-140° (0.69 g.); nmr: 5.83 (1H, q, J_{4,5} = 4.5 Hz, J_{4,6} = 1.0 Hz, 4-H), 6.46 (1H, d, J_{5,4} = 4.5 Hz, 5-H), 7.40-8.25 (15H, m, benzenoid protons), and 8.30 (1H, d, J_{2,4} = 1.0 Hz, 2-H); ms: m/e 354 (M⁺).

Anal. Calcd. for C₂₂H₁₈N₂O₂: C, 77.95; H, 5.12; N, 7.91. Found: C, 77.67; H, 4.89; N, 7.72.

Irradiation of 1,1'-Carbonyldiimidazole (1c).

1,1'-Carbonyldiimidazole (1c) (1.0 g., 0.0061 mole) in benzene (100 ml.) was irradiated with benzophenone (3.3 g., 0.0183 mole) for 21 hours. Removal of the solvent and crystallization of the residue from chloroform yielded the oxetane (2c), m.p. 265-268° (0.93 g.); nmr: 5.78 (1H, q, J_{4,5} = 4.5 Hz, J_{4,6} = 1.5 Hz, 4H), 6.71 (1H, d, J_{5,4} = 4.5 Hz, 5-H), 7.32-7.99 (13H, m, benzenoid protons and 2',4', and 5'-H), and 8.05 (1H, d, J_{2,4} = 1.5 Hz, 2-H); ms: m/e 344 (M⁺).

Anal. Calcd. for C₂₀H₁₆N₄O₂: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.56; H, 4.46; N, 16.06.

Irradiation of 1,2-Dimethylimidazole (1d) with Benzophenone.

1,2-Dimethylimidazole (1d) (2.3 g.) in *t*-butyl alcohol (150 ml.) was irradiated with benzophenone (4.5 g.) for 17 hours. The solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with benzene-chloroform (1:1) yielded the hydroxyphenyl derivative (5a) as a white solid, m.p. 187-188° (yield, 4%); 3.33 (3H, s, 1-CH₃), 3.53 (2H, s, 2-CH₃), 6.66 (1H, d, J_{4,5} = 1.2 Hz, 4(5)-H), 6.88 (1H, d, J_{5,4} = 1.2 Hz, 5(4)-H), and 7.30 (10H, m, benzenoid protons); ms: m/e 278 (M⁺).

Anal. Calcd. for C₁₂H₁₈N₂O: C, 77.67; H, 6.52; N, 10.07. Found: C, 77.46; H, 6.26; N, 9.86.

This compound has proved to be identical (m.p. and ir spectrum) with the compound synthesized from 1,2-dimethylimidazole by reaction of *n*-butyllithium and benzophenone according to the method reported (20).

Irradiation of 1,2-Dimethylimidazole (1d) with Acetone.

1,2-Dimethylimidazole (1d) (1.4 g.) in acetone (150 ml.) was irradiated for 3 hours. After removal of the solvent the residue was chromato-

graphed over silica gel. Elution with chloroform yielded the hydroxyalkyl derivative (**5b**) as a yellow solid, m.p. 95-96° (yield, 30%); nmr: 1.53 (6H, s, 3-C(CH₃)₂), 2.33 (3H, s, 2-CH₃), 3.50 (3H, s, 1-CH₃), and 6.63 (1H, s, 5-H); ms: m/e 154 (M⁺).

Anal. Calcd. for C₆H₁₄N₂O: C, 62.30; H, 9.15; N, 18.17. Found: C, 62.11; H, 8.92; N, 17.96.

Irradiation of 1-Benzylimidazole (**1e**) with Benzophenone.

1-Benzylimidazole (**1e**) (2.0 g.) in benzene (150 ml.) was irradiated with benzophenone (5.0 g.) for 24 hours. The solvent was removed under reduced pressure. The product (**5c**) crystallized as a yellow solid upon addition of hexane, which after recrystallization from benzene-chloroform showed m.p. 220-221° (yield, 20%); nmr: 6.31 (1H, s, 1-CHC₆H₅), 6.98 (1H, t, 4(5)-H), 7.20 (1H, t, 5(4)-H), 7.45 (15H, m, benzenoid protons), and 7.73 (1H, t, 2-H); ms: m/e 340 (M⁺).

Anal. Calcd. for C₂₅H₂₀N₂O: C, 81.15; H, 5.92; N, 8.23. Found: C, 80.96; H, 5.75; N, 8.01.

Irradiation of 2,4-Dimethylthiazole, 4-Methylisothiazole, 3,5-Dimethylisoxazole, and 4,5-Dimethylisoxazole.

In each case a mixture of the heterocyclic compound (10 g.) and the ketone (0.4-0.6 g.) was irradiated in a spiral tube for 24 hours. The yield of the product was calculated on the basis of the quantity of the ketone employed.

(a) Reaction of 2,4-Dimethylthiazole with Benzophenone.

The excess 2,4-dimethylthiazole was removed by distillation under reduced pressure. The residue crystallized on addition of ether. The crude oxetane was chromatographed over silica gel and elution with benzene-chloroform yielded the pure oxetane (**6a**), m.p. 97° (yield, 25%); ms: m/e 295 (M⁺).

Anal. Calcd. for C₁₈H₁₇NOS: C, 73.20; H, 5.80; N, 4.74. Found: C, 72.95; H, 5.65; N, 4.62.

(b) Reaction of 2,4-Dimethylthiazole with 3-Benzoylpyridine.

Unreacted 2,4-dimethylthiazole was removed under reduced pressure. Upon addition of a mixture of methanol and ether, the crude oxetane crystallized, which was further chromatographed over silica gel. Elution with benzene-chloroform yielded the oxetane (**6b**), m.p. 83° (yield, 40%); ms: m/e 296 (M⁺).

Anal. Calcd. for C₁₇H₁₆N₂OS: C, 68.90; H, 5.44; N, 9.45. Found: C, 68.76; H, 5.21; N, 9.26.

(c) Reaction of 2,4-Dimethylthiazole with Acetophenone.

(i) Without Solvent.

The excess 2,4-dimethylthiazole was removed under reduced pressure and the residue was treated with a mixture of methanol and ether. The crude product was obtained as a solid, which was chromatographed over silica gel. Elution with benzene-chloroform gave a dimer **8** or **9**, m.p. 59° (yield, 60%); ms: m/e 226 (M⁺).

Anal. Calcd. for C₁₀H₁₄N₂S₂: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.86; H, 6.01; N, 12.15.

(ii) In Benzene (70 ml.).

After removal of benzene, the product was purified as above. The compound **8** or **9** showed m.p. 59-60° (yield, 10%) and was found to be identical (ir spectrum) with the product in (i).

(iii) In Acetonitrile (70 ml.).

The product (yield, 30%), isolated as above, was found to be identical (m.p. and ir spectrum) with the product in (i) and (ii).

(d) Reaction of 4-Methylisoxazole with Benzophenone.

The excess of 4-methylisoxazole was removed by distillation under reduced pressure and the crystalline residue was chromatographed over silica gel. Elution with benzene-chloroform yielded the hydroxyphenyl derivative (**10**), m.p. 78° (yield, 33%); ms: m/e 281 (M⁺).

Anal. Calcd. for C₁₇H₁₅NOS: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.36; H, 5.20; N, 4.69.

(e) Reaction of 3,5-Dimethylisoxazole with Benzophenone.

The excess 3,5-dimethylisoxazole was removed under reduced pressure, and the residue was treated with ether. The oxetane (**11a**) was

obtained as a white solid, m.p. 163° (yield, 40%); ms: m/e 279 (M⁺).

Anal. Calcd. for C₁₈H₁₇NO₂: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.05; H, 5.96; N, 4.86.

(f) Reaction of 3,5-Dimethylisoxazole with 3-Benzoylpyridine.

After irradiation the product was isolated as above and chromatographed over silica gel. Elution with benzene-chloroform (6:4) yielded the oxetane (**11b**), m.p. 188° (yield, 24%); ms: m/e 280 (M⁺).

Anal. Calcd. for C₁₇H₁₆N₂O₂: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.57; H, 5.56; N, 9.65.

(g) Reaction of 4,5-Dimethylisoxazole with Benzophenone.

The product was isolated as above and chromatographed over silica gel. Elution with hexane-benzene (1:3) yielded the oxetane (**11c**), m.p. 137° (yield, 65%); ms: m/e 279 (M⁺).

Anal. Calcd. for C₁₈H₁₇NO₂: C, 77.39; H, 6.13; N, 5.01. Found: C, 77.21; H, 5.86; N, 4.85.

Acknowledgment.

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- (13) In this series of heterocyclic compounds including furans and thiophenes, methyl-substituted nuclei, which are considered to be more electron-rich, were found to be more susceptible to photoaddition reactions.
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- (15) Ketones, such as acetophenone, which have higher $n\pi^*$ triplet energies than benzophenone, would be expected to transfer energy rather than add to this imidazole, and quenching by ground state imidazole would occur.
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