(24) A minor amount of absorption was present in the region of the lower field hydrogen for **2**-d_1, possibly derived from some 4-H present in the deuterated acetate. On the other hand, there was no evidence of the triplet associated with $=CH_2$ when the lower field hydrogen is present. 1-$AdCD_2NH_2$ was essentially 100% deuterated according to NMR. It was difficult to ascertain the purity, in relation to deuterium content, of the derived acetate partly because of the instability of the molecular ion in mass spectral analysis. A minor amount of 4-H may be present (possible exchange during diazotization). The presence of nondeuterated ester would increase the rate of elimination via path A, thus giving an increase in the value for path A/path B. Similarly, there would be a decrease in the value for the primary deuterium isotope effect.

Photochemical Rearrangements of Indazoles. Investigation of the Triplet Excited States of 1- and 2-Methylindazole[1]

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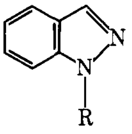
Abstract: The triplet states of 1-methylindazole (1-MI) and 2-methylindazole (2-MI) were studied by flash absorption and flash emission spectroscopy at room temperature and by emission spectroscopy and ESR spectroscopy at liquid-nitrogen temperatures. The triplet states exhibit similar absorption spectra with maxima at 420 and 405 nm, respectively. Comparable first-order rate constants of approximately 10^4 sec^{-1} for decay of the triplets of 1-MI and 2-MI were obtained by flash absorption and flash emission. Revised values of the triplet energies of 66.7 and 67.3 kcal were obtained for 1-MI and 2-MI, respectively. The triplets were quenched with oxygen and with piperylene. The photochemical rearrangements of 1-MI to *N*-methylanthranilonitrile and 2-MI to 1-methylbenzimidazole must proceed from the singlet excited states since they are not quenched by oxygen or dienes. High concentrations (10^{-1} *M*) of dienes react with the singlet state of 1-MI. Triplet energy transfer to cyclohexadiene (10^{-2} to 10^{-3} *M*), under conditions where no inhibition of product formations was observed, was established by the isolation of cyclohexadiene dimers. Radicals were detected by ESR spectra on irradiation of 1-MI and 2-MI. These may be formed by the cleavage of the N-N bonds in these compounds.

Detailed analyses have been carried out on the products of the photoisomerization of indazole and substituted indazoles.[2,3,4] Photolysis of the *N*(1)-alkylated indazoles (**1**) gives the corresponding alkylaminobenzonitriles (**4**) in 10–60% yield, while photolysis of *N*(2)-alkylated indazoles (**2**) proceeds rapidly and in high yield (~85%) to the *N*(1)-alkylated benzimidazoles (**3**). Indazoles without *N*-alkyl groups (**1**, R = H) give both benzimidazoles (**3**, R = H) and aminobenzonitriles (**4**, R = H) on irradiation.



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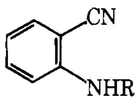

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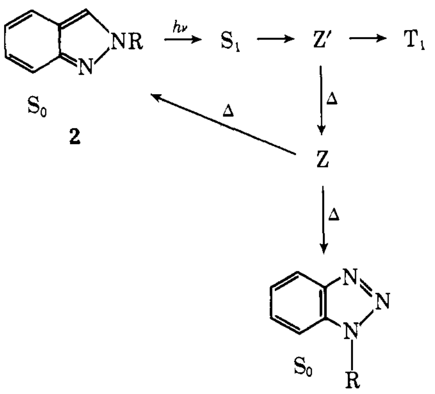
The photoisomerization of *N*(2)-alkylindazoles (**2**) is intramolecular and proceeds from the singlet excited state.[3] An intermediate having a lifetime of several seconds was detected by uv spectra. In addition, the decrease in the quantum yield of the photoisomerization with pH suggested the presence of an intermediate, the protonated form of which does not yield the benzimidazole product.[3] The yield of this intermediate (Z, Scheme I) was found to be independent of exciting wavelength and dependent on the temperature. This temperature dependence requires the presence of a second intermediate (Z′, Scheme I) which is stable at low temperatures. Labhart et al.[3] proposed the mechanistic pathway in Scheme I, the photoisomerization of 2-alkylindazoles (**2**) to 1-alkylbenzimidazoles (**3**). The exact nature of the two proposed intermediates Z and Z′ is not known.

The present work was carried out to obtain more information about the intermediate(s) involved in the photoisomerization of 1-MI and 2-MI and the multiplicity of the excited state from which they are derived.

Scheme I



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Experimental Section

Spectroquality solvents supplied by Matheson Coleman and Bell were used without further purification. Indazole was obtained from Aldrich Chemical Co. and was purified by vacuum sublimation (mp 147.5–148.5°). 1-MI and 2-MI were prepared by the methylation of indazole.[5] Twice-sublimed 1-MI (mp 60–61°) and twice-recrystallized 2-MI (mp 54.5–56.0°) were used in these studies. Degassing was done by three or four freeze-pump-thaw cycles. Uv spectra were run on a Unicam SP 800A spectrophotometer. A low-temperature cell developed by Richtol and Klappmeier[6] was used to measure the absorption spectra at low temperatures. The NMR spectra were recorded on a Varian T-60 spectrometer using Me_4Si as standard.

Flash Photolysis. Kinetics of transient(s) decay and transient absorption spectra were measured using the flash-photolysis apparatus described elsewhere.[7] Light from the flash lamp was filtered through CCl_4, and light from the continuous analyzing beam was filtered through plate glass. The rate constants for transient decay at room temperature were measured by flash-emission techniques using an FP-2R flash photolysis apparatus (Northern Precision

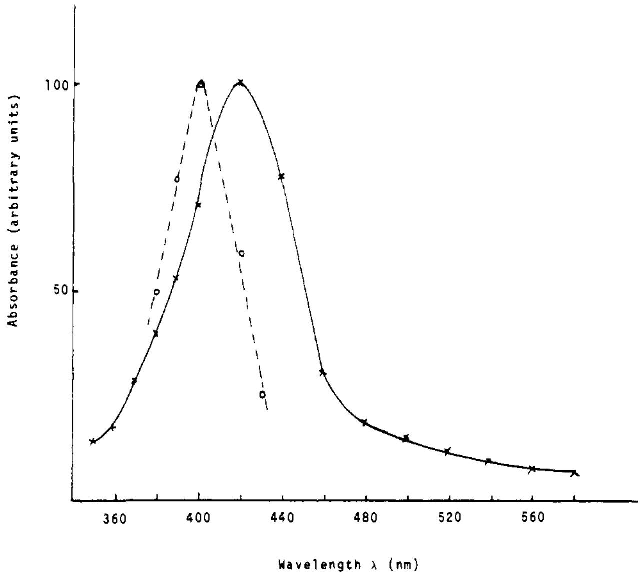


Figure 1. T-T absorption spectrum of 1-MI in MeOH at room temperature —. T-T absorption spectrum of 2-MI in MeOH at room temperature - - - -.

Company Ltd., London).[8] A solution of cobalt sulfate ($CoSO_4 \cdot 7H_2O$; 18.6g/100 ml) was used to filter the light from the flash lamp. The solvent and a solution of the indazole in the solvent were flashed, and the emission intensities were measured at the same time intervals after the flash. The difference between the intensities is the intensity of emission from the transients formed from the compound under study. The first-order decay constants for the transients were obtained from a plot of the log of emission intensity vs. time.

Electron Spin Resonance Spectra. Electron spin resonance experiments were carried out using a Varian E-12 spectrometer. The degassed samples ($\sim 10^{-3}$ *M*) were irradiated in a ethanol-methanol (4:1 v/v) glass in a quartz Dewar at ca. −160° using a 1-kW air-cooled mercury-xenon lamp. The beam was focused on the cavity using a quartz lens.[9]

Phosphorescence Emission. A Bausch and Lomb grating monochromator was used as the source of exciting light and a Jarrel-Ash scanning monochromator placed perpendicular to the exciting light beam was used to monitor the emission. The data from repeated scans were collected in a digital processor (Model 7010; Geoscience) connected to the scanning monochromator through a photomultiplier. The decay curve was then plotted on a recorder, and the first-order rate constant was determined from a plot of the log of the emission intensity vs. time. Approximately 10^{-3} *M* solutions (degassed) in ethanol-methanol (4:1 v/v) were used, and the measurements were made at liquid-nitrogen temperature.[9]

Quenching Studies. Photolyses were carried out in a Rayonet reactor with nondegassed solutions of indazoles ($\sim 10^{-4}$ *M* unless otherwise noted) using different concentrations of freshly distilled dienes and purified cyclohexene[10] as quenchers.

Results

Flash photolytic studies were made on 1-MI (**1**, R = CH_3), 2-MI (**2**, R = CH_3), and indazole (**1**, R = H) with the aim of detecting possible photochemical intermediates. Since 2-MI undergoes a very facile rearrangement to 1-methylbenzimidazole, care was taken to be sure very little isomerization took place during the course of the flash experiments. The decay kinetics were measured at several wavelengths, and the results are shown in Table I. The decay constants in Table I are in agreement within the experimental error. The error is greater in the decay constants for 1-MI above 480 nm since the extinction coefficient of the transient absorption is small at those wavelengths. The transient absorption spectra for 1-MI and 2-MI (Figure 1) are similar to the triplet absorption spectra of other 1- and 2-alkylated indazoles.[11] The transients were completely quenched in each case after the solution was thoroughly mixed with air, and transients from 1-MI were completely quenched in the presence of 10^{-3} *M trans*-piperylene.

Table I. First-Order Decay Constants of Indazole Transients in Methanol at Room Temperature

Wavelength, nm	$k \times 10^{-4}$, sec^{-1} Indazole[a]	1-MI	2-MI[b]
370	3.3	1.3	1.4
380		1.3	3.2
390	3.4	1.3	3.4
400		1.9	4.2
410		2.1	4.3
420	2.6	1.9	3.8
440		1.9	3.9 (at 430 nm)
460		1.5	
480		1.2	
500		1.0	
520		1.0	
540		0.9	
560		0.9	
580		0.7	

[a] The decay constant was only measured at three wavelengths for comparison with 1-MI and 2-MI. [b] The intensity of the transient was too weak at λ >430 nm to measure the decay constant accurately.

Table II. Transient First-Order Decay Constants

Compd	Monitoring wavelength, nm	$k_1 \times 10^{-4}$, sec^{-1} Flash absorption	Flash emission
1-MI	420	1.9	1.8
2-MI	420	3.8	2.6

The decay kinetics for the transients of 1-MI and 2-MI were also measured by the flash-emission technique. The first-order rate constants are comparable to those measured by flash absorption (Table II).

A long-lived transient exhibiting very weak absorption between 350-400 and 440-560 nm was detected by flash photolysis with both 1-MI and 2-MI. This species may also absorb in the 400-440 nm region, but it was not detected, because the intense absorption of the short-lived transient dictated the use of low detector amplification. This long-lived transient was detected by the observation that the decay curve of the short-lived transient did not return to the base line. The long-lived transient was quenched by oxygen and by *trans*-piperylene. Since the rearrangement proceeds from the singlet excited state, this long-lived transient cannot be due to a reaction intermediate.

We observed previously that the photochemical formation of anthranilonitriles from indazole and 1-MI was quenched to some extent by piperylene ($E_t \sim 60$ kcal[12]), cyclohexene (E_t = 70-75 kcal[13]), and biacetyl (E_t = 55 kcal[12]).[4] On the basis of these studies, it was suggested that the anthranilonitriles might be formed from the triplet state of the corresponding indazoles.[5] In most of the previous studies, a relatively high concentration of quencher (10^{-1} to 10^{-2} *M*) had been used. The possibility of singlet quenching and/or adduct formation between the quencher and the indazole also exists under these conditions. In the present study, solutions of 1-MI and 2-MI containing varying amounts of *trans*-piperylene or cyclohexene (10^{-3} to 3×10^{-2} *M*) were irradiated at 300 nm in quartz vessels. The rate of disappearance of 1-MI increased, and the yield of *N*-methylanthranilonitrile decreased as the concentration of the added olefins were increased. The relative quantum yields for the formation of *N*-methylanthranilonitrile were measured in the presence of *trans*-piperylene (Table III), and a curved Stern-Volmer plot was obtained. These data indicate that chemical reaction is taking place between the olefin and the excited 1-MI. However, the yield of 1-meth-

Table III. Variation in the Quantum Yield of *N*-Methylanthranilonitrile Formation with *trans*-Piperylene Concentration[a]

trans-Piperylene, *M*	Φ_0/Φ[b]
0	1.00
6.68×10^{-3}	1.21
1.34×10^{-2}	1.33
2.00×10^{-2}	1.38

[a] The concentration of *N*-methylanthranilonitrile was determined from the intensity of the uv absorption at 325 nm. [b] Φ_0 = quantum yield in the absence of diene; Φ = quantum yield in the presence of diene.

Table IV. Phosphorescence of 1-MI and 2-MI at −196° in EtOH–MeOH (4:1 v/v) Glass

Compd	Exciting λ, nm	0–0 band, nm	E_t, kcal/mol	τ, sec
1-MI	305	428.4	66.7	0.75[a]
1-MI	305	428.4	66.7	0.75[b]
2-MI	305	466.7	61.3	0.89[c]
2-MI	305	466.7	61.3	0.81[d]

[a] Decay at 429 nm. [b] Decay at 460 nm. [c] Decay at 510 nm. [d] Decay at 465 nm.

Table V. ESR Spectra of Irradiated 1-MI and 2-MI[a]

	1-MI	2-MI
H_{1z}	2225	2318
H_{1y}	2325	2621
H_{1x}	3172	2990
H_{2x}	Not observed	3680
H_{2y}	4370	4080
H_{2z}	4500	Not observed
$H_{\min}$	1605	1650

[a] Gauss.

ylbenzimidazole from 2-MI was not affected by up to 10^{-1} *M trans*-piperylene or 3.3×10^{-2} *M* cyclohexene. Obviously no quenching of any type is occurring with 2-MI.

When 2×10^{-3} *M* solutions of 1-MI and 2-MI were photolyzed in the presence of 1,3-cyclohexadiene with 300 or 360 nm light sources, cyclohexadiene dimers were formed as identified by GC comparison with authentic samples.[14] These dimers were not observed in controls where the 1-MI and 2-MI were omitted. These data establish that triplet energy transfer is taking place between 1-MI and 2-MI triplets and the 1,3-cyclohexadiene. The yield of cyclohexadiene dimers is significantly smaller when 2-MI is used as a sensitizer. Apparently intersystem crossing to the triplet state is more efficient in 1-MI than in 2-MI since the triplet energies of 1-MI and 2-MI are at least 9 kcal greater than that of 1,3-cyclohexadiene (see below), and therefore triplet quenching should be of equal (diffusion-controlled) efficiency.

The phosphorescence emission spectra of 1-MI and 2-MI were measured in ethanol–methanol (4:1 v/v) at −196°, and the triplet energies were calculated from the onset of the phosphorescence maximum (Table IV). In our previous emission measurements on these compounds, it was not possible to resolve the fluorescence and phosphorescence bands so the triplet energies were estimated from the high-energy end of the phosphorescence band.[4] Well-defined phosphorescence emission peaks were observed in this study. The reason for the difference is not clear, but it may be due to the enhanced resolution and/or slower scan rate on the different spectrofluorimeter used in the present work. It should be noted that the new values for the triplet energies of 1-MI and 2-MI in Table IV are comparable to the previously reported triplet energy of indazole (67.3 kcal).[4] The phosphorescence band of indazole is well resolved from the fluorescence band so that it was possible to accurately calculate the triplet energy of indazole in our previous studies.[4]

Signals which can be assigned to a radical ($g \sim 2.0$) and a triplet were observed when the ESR spectra of 1-MI and 2-MI were measured at −160° (Table V). The radical signal persisted when the light was cut off and disappeared only on warming. That portion of the ESR tube exposed to light turned yellow. This yellow color disappeared on warming. D/hc values of 0.102 ± 0.004 and 0.092 ± 0.004 cm^{-1} and E/hc values of 0.031 ± 0.001 and 0.014 ± 0.002 cm^{-1} were calculated for 1-MI and 2-MI, respectively.[15] The lower value of D for 2-MI suggests greater electron delocalization in the triplet state.

Discussion

The photochemical rearrangement of 2-substituted indazoles (**2**) to benzimidazoles (**3**) has been reported to proceed via two intermediates, Z′ and Z (Scheme I), which are formed from the singlet excited state.[3] Preliminary product-quenching data suggested that the photochemical rearrangement of 1-methylindazole (**1**, R = CH_3) to *N*-methylanthranilonitriles (**4**, R = CH_3) proceeds from the triplet excited state.[5] This appeared to be a reasonable postulate since the triplet excited state had been implicated in the related photochemical rearrangement of indoxazene to 2-cyanophenol.[4]

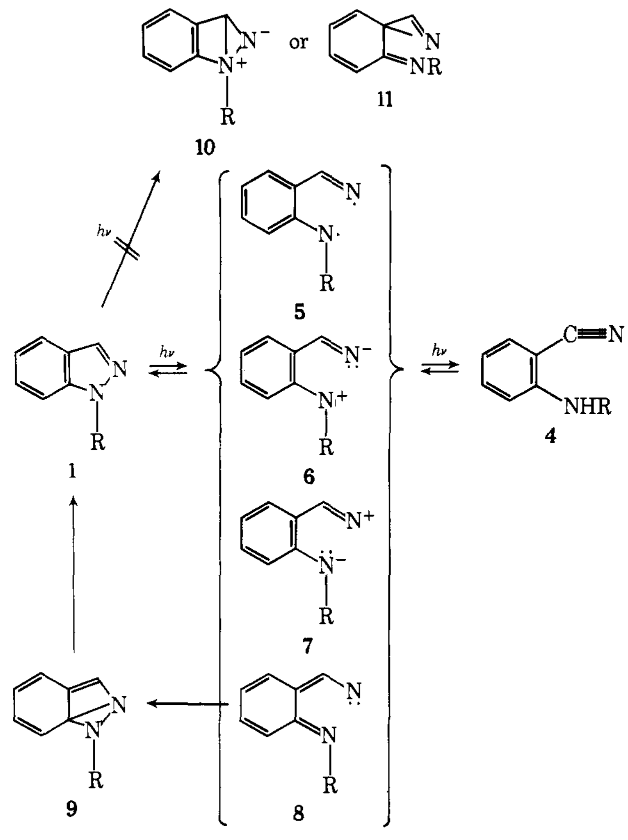
Although the flash absorption, flash emission, and ESR spectroscopy results reported here clearly show the triplet nature of the observed transients, the quenching studies have established that the photochemical rearrangements of 1-MI and 2-MI do not proceed from the triplet state. The reactions were not quenched by energy transfer to dienes (10^{-3} to 10^{-4} *M*) or oxygen, conditions leading to complete quenching of the transient triplet species. That triplet energy transfer was taking place under the preparative conditions was established by using 1,3-cyclohexadiene as a quencher. Product formation was not inhibited even though dimers of cyclohexadiene were observed.[14] We confirmed the observation that high concentrations (0.1 *M*) of dienes and cyclohexene depress the yields of **4**.[4,5] However, they also increase the rate of loss of 1-MI. Furthermore, a nonlinear Stern–Volmer plot was obtained using *trans*-piperylene as the quencher suggesting that chemical reaction with the diene and not triplet energy transfer was being observed. The quenching observed with high concentrations of cyclohexene is not due to triplet energy transfer, because the triplet energy of cyclohexene (72–75 kcal[13]) is greater than that of indazole and 1-MI (~67 kcal).

Our previous sensitization results, when considered together with the revised triplet energy of 1-MI, are completely consistent with singlet nature of the rearrangement.[4] Acetone ($E_s \approx 92$, E_t = 78–79 kcal)[16] does not sensitize the photoisomerization of indazole ($E_s = 94$, $E_t = 67.3$ kcal)[4] or 1-methylindazole ($E_s = 92$, $E_t = 66.7$ kcal). The singlet energy of acetone is close to that of the indazoles so that singlet sensitization is unlikely. However, the triplet energy of acetone is 10 kcal greater than that of the indazoles so that one would expect efficient triplet energy transfer. The absence of acetone-sensitized photoisomerization demonstrates the reaction does not proceed from the triplet excited state. The sensitization observed with benzene ($E_s = 109$, $E_t = 85$ kcal)[12] is undoubtedly due to singlet energy transfer in view of the absence of triplet sensitization by acetone. The benzene-sensitized rearrangement of indazoles yields anthranilonitrile in nonhydroxylic solvents and benzimidazole in hydroxylic solvents (1:1 benzene–ethanol).[17] These results are identical with those obtained on direct irradiation of indazole and are consistent with the singlet nature of the photoisomerization.

The possibility that the luminescence observed in the flash-emission studies was the result of delayed fluorescence,[18] or triplet-triplet annihilation[19] was eliminated by measurement of the luminescence spectrum. No fluorescence was observed for 1-MI and 2-MI at 420 nm, the wavelength chosen for the flash-emission studies.

Previous attempts to detect intermediates in the photochemical rearrangement of indazoles by low-temperature ir and uv techniques were not successful.[4,5] Radicals were detected in the present study by ESR when 1- and 2-MI were irradiated at -160°. Since it has been calculated that the N-N bond is the weakest in the ground and excited state of pyrazole,[3] it is possible that the radicals obtained from the methylindazoles are formed by N-N cleavage (e.g., **5** and **12** in Schemes II and III). It has been reported that the photochemical rearrangement of indazoles does not take place at temperatures below -100°.[11] If **5** and **12** are really the primary photoproducts, the subsequent intermediates would not be detectable by low-temperature techniques.

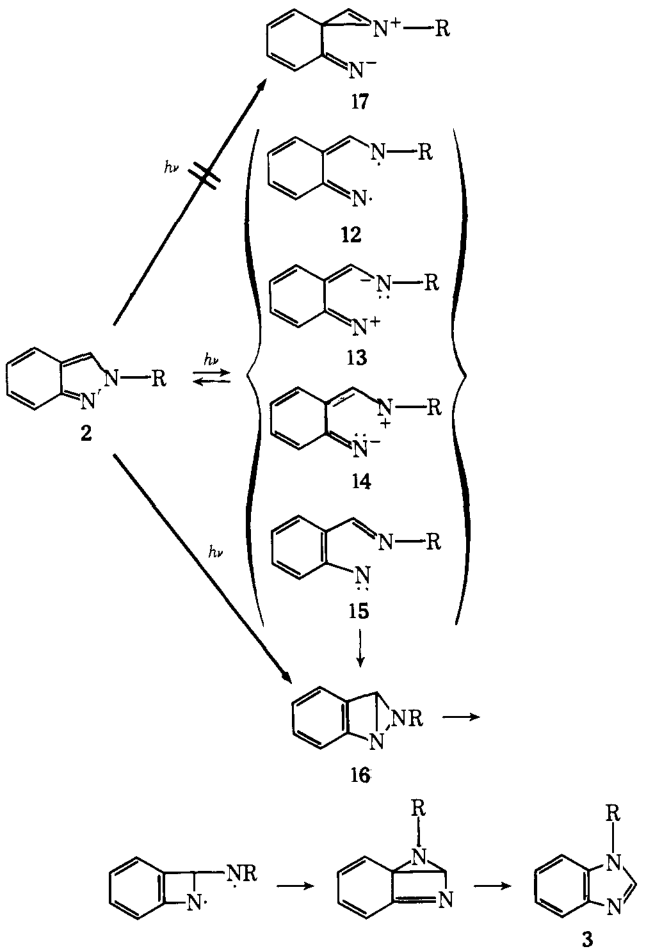
Scheme II



The similarities in energies, lifetimes, and spectra of the triplet states of 1-MI and 2-MI would intuitively suggest that the singlet excited states would also be similar. Consistent with this suggestion is the observation that the singlet energies differ by only 4 kcal.[4] In addition, the excited state π-bond orders and π-electron densities of 1-MI and 2-MI are similar.[20] However, quite different photoproducts are obtained from 1-MI and 2-MI, and the rate of photorearrangements of 2-MI is much greater than 1-MI.[4] It appears likely that the nature of the reaction product is governed by the subsequent reaction of an intermediate and not the initially formed excited state.

The N-N bond of the excited 1-MI could cleave either heterolytically or homolytically (Scheme II). The resulting cleavage products (**5-8**) could then lose a proton or hydrogen atom from the aldimine carbon atom to generate the nitrile grouping. The photochemical cyclization of *N*-methylanthranilonitrile to 1-MI could proceed via the same intermediates. The nitrene **8** could cyclize to the tricyclic derivative **9**; however, this would not be detected, because **9** would be expected to revert to 1-MI. Neither tricyclic structure **10** nor azirine **11** appears to be a likely intermediate since there is no direct way to generate *N*-methylanthranilonitrile from either of them.

Scheme III



The N-N bond of the excited 2-MI could also cleave heterolytically or homolytically (**12-15**, Scheme III). However, the subsequent proton or hydrogen atom loss is blocked by the *N*-alkyl group. The zwitterionic character of azirine **17** argues against it being a reaction intermediate. The tricyclic intermediate **16** formed directly from 2-MI or from nitrene **15** is the more likely intermediate. HMO calculations suggest that **16** would form readily from the excited state of 2-MI.[20] The rearrangement of **16** to 1-methylbenzimidazole follows a previously suggested pathway.[21]

Photolysis of indazole (**1**, R = H) yields both anthranilonitrile (**4**, R = H) and benzimidazole (**3**, R = H).[4] In nonpolar solvents, the reaction pathway is similar to that of 1-MI, and anthranilonitrile is obtained. In polar solvents, both anthranilonitrile and benzimidazole are obtained. The polar solvent facilitates proton shift between N-1 and N-2 so that photoproducts analogous to those from both 1-MI and 2-MI are observed.

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Purine *N*-Oxides. LX. The Photoreactions of 6-Methyl- and 6,9-Dimethylpurine 1-Oxides[1]

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Abstract: The photochemistry of 6-methyl- and 6,9-dimethylpurine 1-oxides was investigated to evaluate the role of tautomerism and the influence of reaction medium on the reaction pathways. Products resulting from rearrangement, reduction, and ring opening were identified. The extent of each type of reaction and the manner of ring opening varied with the photolysis conditions, but not in a uniform manner for both compounds. The data do not indicate a contribution by an *N*-hydroxy tautomer in the photochemistry of these compounds. The greatly enhanced extent of ring opening in acid media, which occurs at the expense of photorearrangement, indicates that protonation of an intermediate common to both processes increases the proportion that follows the former pathway. This is the first indication of the presence of an intermediate in the photorearrangement of aromatic amine *N*-oxides. A unifying mechanism is proposed for the formation of ureido- and nitrile-substituted imidazoles from purine 1-oxides. Studies with paramagnetic ionic triplet quenchers show that photoreduction of these purine *N*-oxides involves a triplet intermediate.

The facile photochemical formation of radicals in the solid state of *N*-hydroxypurines[2] and the possible association of radicals from such compounds with their oncogenic potential[3] encouraged a more detailed examination of the photochemistry of *N*-oxidized purines.[4,5] An earlier study examined the influence of tautomeric and ionic states on the photochemistry of *N*-hydroxyhypoxanthines,[4] which were selected as models of compounds whose neutral forms exist as the *N*-hydroxy tautomer. The similarity in behavior and structure of the anions of such compounds to aromatic *N*-oxides was noted[4] and we now report a study of the photochemistry of two purine *N*-oxides in which the *N*-oxide form should be the predominant or the exclusive tautomer.

Photolysis of 6-Methylpurine 1-Oxide (1) (Table I). The p*K*'s associated with protonation and ionization of **1**[6] are 1.18 and 7.51.[7] Irradiation of the neutral molecule (pH 3.0) produced 6-methylpurine (**3**, 5%), 6-methyl-2-hydroxypurine (**5**, 20%), and 4-amino-5-acetylimidazole (**7**, 32%) (Scheme I, Table I). Irradiation of the anion of **1** at pH 9.5 gave 5% of **3** and 31% of **5** but no **7**. From irradiations of **2** in CH_3OH or CH_3CN solution, the only uv-absorbing products detected were **3** and **5**, which were obtained in nearly equal amounts (9%).

Photolysis of 6,9-Dimethylpurine 1-Oxide (2). The p*K* of protonation of **2** was found to be 1.20 ± 0.06. Irradiation of **2** at pH's 3.0, 6.0, or 10 (Tables II and III) yielded approximately equal amounts (10-12%) of 6,9-dimethylpurine (**4**) and 6,9-dimethyl-2-hydroxypurine (**6**) as the major photoproducts. The latter has not previously been reported and its identity was confirmed by independent synthesis. In addition to **4** and **6**, 4-acetyl-5-amino-1-methylimidazole (**8**) was obtained from the irradiations of **2** at pH's 0 (3 *N* CF_3CO_2H) and 3.0. The *N*-oxide, **2**, was stable in these solvents at room temperature in the absence of light, but could be hydrolyzed to **8** under more vigorous conditions. In nonaqueous solvents the irradiation of **2** gave less than 1% of **4** and ca. 9% of **6**. When **2** was irradiated in methanol or ethanol solution, a new compound, 1-methyl-4-acetyl-5-ureidoimidazole (**9**) was obtained. The ureide undergoes rapid ring closure to **6** in alkaline solution, which complicated at-

Table I. Photolysis of 6-Methylpurine 1-Oxide[a]

Expt No.	Solvent	pH	Time[b]	3, %	5, %	7, %	1, %	Recovery, %[c]
1	H_2O	3.0	30	5	20	32		57
2	H_2O	9.5	30	5	31		15	51[d]
3	CH_3OH		15	9	7		6	22
4	CH_3CN		15	9	9			18

[a] Irradiations were performed under N_2 with a high pressure Hg lamp and a Pyrex filter. [b] Minutes. [c] Expressed as percent of starting material. [d] A small amount of a third, unidentified product could be detected.