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ON THE UNREACTIVE NATURE OF THE EXCITED IMINES IN HYDROGEN ATOM ABSTRACTION

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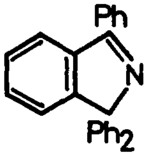
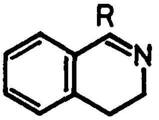
Photochemically excited carbonyl compounds are well known to undergo various types of reactions. On the contrary, for the carbon-nitrogen double bonds (imines) isoelectronic to the carbonyl group, in spite of recent active efforts of investigation, very few reactions and no emission have been recognized occurring certainly from their excited states, (1,2) although heteroaromatic compounds possessing carbon-nitrogen double bonds often appear photochemically reactive and emissive. (3) The unreactive nature of the excited imines are often supposed to result from their facile radiationless deactivation to their ground states accompanied by their syn-anti isomerization like the triplet olefines. (1,2)

We have attempted to investigate the behaviours of the excited states of imines whose carbon-nitrogen double bonds are restricted in cyclic systems prevented from syn-anti isomerization, and now report that they are still unreactive towards hydrogen atom abstraction and it is attributable to the high π,π^* character of their triplet states on the basis of the first successful observation of the emission from the excited states of imines.

1,3,3-Triphenylisoindolenine(I), 1-methyl(IIa)-, 1-benzyl(IIb)-, and 1-phenyl(IIc)-3,4-dihydroisoquinoline were found to be quite stable upon irradiation in 2-propanol, methanol, ether or toluene under nitrogen with a high or low pressure mercury lamp; no isolable amount of products were obtained and the starting materials were nearly quantitatively recovered.(4) It is remarkable, however, that the phosphorescence of the imines was observed in EPA and in methylcyclohexane at 77K as summarized in the table. Their fluorescence was not detected at room temperature, but at 77K only I exhibited fluorescence (maximum wavelength of 385 nm).(5)



I



II
a R : CH_3
b R : $PhCH_2$
c R : Ph

Table. Phosphorescence of Imines at 77 K. Maximum wavelength, λ_{max}, in nm, the corresponding triplet energy, E_T, in kcal mol $^{-1}$, and the triplet lifetime, τ_T, in second.

Rigid Solvent		I			II_a	II_b	II_c
EPA	λ_{max}	465,	495,	525	510	540	530
	E_T	61.5,	57.8	54.5	56.1	53.0	54.0
	τ_T		0.8		0.12	0.3	0.6
Methylcyclohexane	λ_{max}		495		520	510	500
	E_T		57.8		55.0	56.1	57.2
	τ_T		0.2		0.08	0.18	0.6

The table indicates that the triplet states of the imines examined lie 53-61 kcal mol $^{-1}$ above their ground states with lifetimes ranging from 0.1 to 0.8 s. It is noticeable that their triplet energies are much lower and their triplet lifetimes are remarkably longer than those for the n,π* triplet states of aromatic ketones such as benzophenone (triplet energy: 69 kcal mol $^{-1}$; triplet lifetime: 0.008 s(6)) which is isoelectronic to I or IIc in the structure containing two phenyl groups substituted on the carbon atom of the unsaturated bonds. The above fact undoubtedly indicates that the emissive triplet states of the imines are abundant in π,π* rather than n,π* character. The triplet lifetimes of the imines II increase as the substituent changes from methyl, benzyl to phenyl in each rigid solvent employed, showing that contribution of π,π* character to the emissive state increases in the same order.(7) For the most imines examined, their triplet lifetimes are longer in EPA than in methylcyclohexane, which is understood in terms that polar solvent, EPA, through stabilization of π,π^* electronic configuration, enhances the degree of its contribution to the emissive state leading to the increase in the triplet lifetimes.(7,8)

Finally, an attempt was made to employ the imine as a sensitizer for the isomerization of 1,3-pentadiene. For example, trans-1,3-pentadiene(0.1 M) was irradiated in methanol in the presence of I with 313 nm light from a high pressure mercury lamp to result in a photostationary mixture of trans- and cis-pentadiene with a ratio of 3.5 determined by vpc. Comparison of this ratio with Hammond and his coworkers' result concerning the variation of the isomer ratio upon the triplet energies of the sensitizers employed (9) suggests that the triplet energy of I lies in the range of 55-58 kcal mol^{-1}, which is in satisfactory agreement with that determined by phosphorescence.

The above facts indicates that, for the cyclic imines examined, their triplet states undoubtedly result from the intersystem crossing from their singlet states and they exhibit phosphorescence and are capable of undergoing triplet energy transfer to 1,3-pentadiene resulting in its geomerical isomerization but not capable of abstracting hydrogen atom from alcoholic solvents. In view that the reactivity of the triplet carbonyl compounds for hydrogen atom abstraction decreases with the increase of π,π^* character at the expense of n,π^* character in their triplet states, (7) it is reasonable to conclude that the unreactive nature of the excited imines is attributable to their high π,π^* character of their triplet states as well as to low bond energy of N-H bond which would result from hydrogen atom transfer to imines.

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4. For example, I, 0.69 g (2.28 mmol) in freshly distilled methanol, 200 ml, was irradiated with an immersion-type 160 W low pressure mercury lamp for 95 hrs. After the evaporation of the solvent, I was recovered in 94% yield.
5. Possibility that the observed emission would result from impurities is excluded since attempted acid hydrolysis of the imines gave no emissive product and any material used for their preparation were not emissive and the phosphorescence of II was different from the isoquinolines.
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