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A NEW PHOTOCHEMICAL CLEAVAGE OF IMINES INTO NITRILES

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Irradiation of N-(1-phenyl-2-propylidene)-benzylamine in benzene, in contrast to the photochemically unreactive most acyclic simple imines, results in the cleavage into acetonitrile, dibenzyl, and toluene probably through the reaction of the excited state of the imine analogous to the Norrish type I cleavage of carbonyl compounds.

Recently active interests have been paid to photochemistry of carbon-nitrogen double bond.$^{1)}$ Compounds possessing carbon-nitrogen double bonds carrying adjacent hetero-atoms such as azines, oximes and their esters undergo decomposition through their excited states,$^{1)}$ however, for carbon-nitrogen double bonds without adjacent hetero-atoms, most of their excited states are recognized to be chemically unreactive and only a few compounds such as azirines which are highly strained,$^{2)}$ cyclic imines with conjugated carbonyl groups$^{3)}$ and imines with other suitably located functional groups$^{4)}$ are photochemically reactive. We now wish to report that even simple acyclic imines without any strain or conjugated groups, on being substituted with benzyl groups on their carbon and nitrogen atoms, become photochemically reactive to undergo cleavage into nitriles.

Irradiation of N-(1-phenyl-2-propylidene)-benzylamine (I) (6.95 mmol) in methanol (150 ml) under nitrogen with an immersion type 160 W low pressure mercury lamp for 30 hours afforded acetonitrile (59%), dibenzyl (14%) and toluene (9%) among the products. Similarly, N-(1,2-diphenylethylidene)-benzylamine, on irradiation in methanol, gave benzonitrile together with dibenzyl and toluene, although the cleavage proceeded more slowly than I.

Formation of the above products, for example, from imine (I) can be understood in terms that the excited state of the imine undergoes cleavage analogous to the Norrish type I reaction of the excited carbonyl compounds to give a benzyl radical (II) and an imidoyl radical (III) subsequently followed by facile decomposition of the latter radical$^{5)}$ into acetonitrile and a benzyl radical, which through dimerization or hydrogen atom transfer gives dibenzyl or toluene, respectively.

$$\mathrm{PhCH_2(CH_3)C{=}NCH_2Ph^*}\quad \mathrm{(I^*)} \longrightarrow \mathrm{PhCH_2\cdot}\ \mathrm{(II)} + \mathrm{CH_3\dot{C}{=}NCH_2Ph}\ \mathrm{(III)}$$

$$\mathrm{(III)} \longrightarrow \mathrm{CH_3CN} + \mathrm{PhCH_2\cdot}$$

An alternative pathway for the cleavage of the excited imine (I) into a benzyl radical and an imino radical, $\mathrm{PhCH_2(CH_3)C{=}N\cdot}$, and subsequent decomposition of the imino radical[6] into a benzyl radical and acetonitrile seems to be not effective in view of a finding that the irradiation of N-benzylidenebenzylamine in benzene did not show any evidence for the cleavage into an imino radical, $\mathrm{PhCH{=}N\cdot}$, and a benzyl radical.

The above result indicates that the excited states of the present imines undergo cleavage with rates enough to compete with the deactivation process whereas in the most imines their rates for the cleavage would be too low to compete with the deactivation. Thus, in the excited states of the present imines, the electronic excitation energy would be dissipated not only through the deactivation but also through the cleavage of the imidoyl linkage probably owing to their lower energies for dissociation of the imidoyl linkage to give stabilized benzyl radicals as compared with the unreactive imines.

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