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PHOTODECOMPOSITION OF 1-SUBSTITUTED 3,4-DIHYDROISOQUINOLINES[1]

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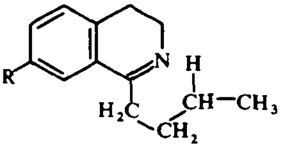
Abstract—Irradiation of 1-alkyl-3,4-dihydroisoquinolines(**Ia, b**) containing γ-hydrogen afforded 1-methyl-3,4-dihydroisoquinolines(**IIa, b**) in poor yields. The elimination is analogous to the type II cleavage of ketone. The similarity between this photoreaction and the electron-impact fragmentation was observed. Ethyl 3,4-dihydroisoquinoline-1-acetate(**Ic**) without γ-hydrogen is stable photochemically in an inert solvent, but it was readily photodecomposed to yield **IIa** in a good yield in excess HCl aq. **Ic** is stable in the dark at room temperature, but **Ic** decomposes quantitatively into **IIa** by refluxing 50% HCl aq. A reaction pathway is presented and discussed.

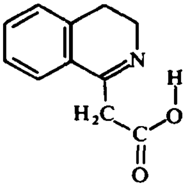
PHOTOREDUCTION of carbonyl compounds has been studied,[2] where the n-π^* excited CO group can abstract an H atom from hydrogen sources. In contrast, with few exceptions.[3-5] photoreduction of C=N double bond does not seem to involve its n-π^* excited state as a reactive intermediate which can abstract an H atom, but instead a ketyl radical, Ar$\dot{C}$(OH)R, which is derived from carbonyl compounds present as an impurity or as a photogenerated species.[6]

The only instance for the intramolecular photoreaction of C=N groups has been reported with heteroaromatics such as 2-substituted quinolines which is reduced to 2-methylquinoline *via* its excited n-π^* singlet state.[7] But in general, there is no strong evidence that excited azomethine can abstract an H atom, although the azomethine group resembles the CO group in its electronic characteristics. As pointed out by Hammond.[8] Cohen,[9] Pitts[10] and others, the hydrogen abstraction in carbonyl photochemistry is a useful tool for the elucidation of the excited state. Therefore, the photoreduction of C=N bonds may imply some information about their photoreactivity. In general, azomethine is susceptible to hydrolysis by even a trace amount of water giving the CO compound.

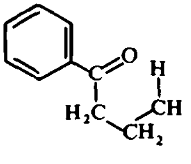
In order to avoid this difficulty, we chose 1-substituted 3,4-dihydroisoquinolines, which are stable against hydrolysis in the presence of a small amount of water. These azomethine compounds (**Ia. b** and **d**) have a structure similar to butyrophenone (**III**), which undergoes the typical Norrish type II elimination giving acetophenone and ethylene.



Ia,b



Id

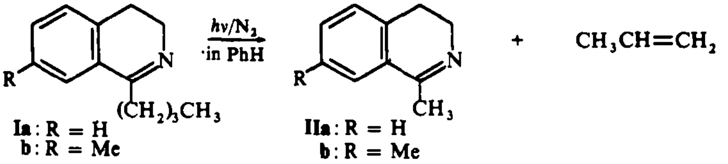


III

The present paper reports an example of an intramolecular hydrogen abstraction by n-π* excited azomethine. The parallelism between the photoelimination and the electron impact fragmentation reaction will be discussed. Also the decarboxylation of 3,4-dihydroisoquinoline-1-acetic acid (**Id**) which is formed on hydrolysis of ethyl 3,4-dihydroisoquinoline-1-acetate (**Ic**) will be presented and discussed.

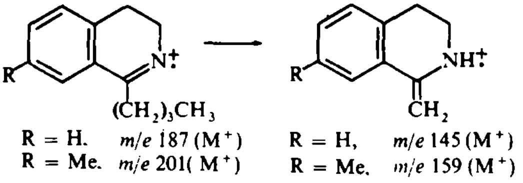
RESULTS AND DISCUSSION

Irradiation of $2{\cdot}7 \times 10^{-3}$ M 1-*n*-butyl-3,4-dihydroisoquinoline (**Ia**) in C_6H_6 under N_2 gas for 50 hr results in 1-methyl-3,4-dihydroisoquinoline (**IIa**, 4·4%). Similarly, photolysis of $3{\cdot}8 \times 10^{-3}$ M 1-*n*-butyl-3,4-dihydro-7-methylisoquinoline (**Ib**) in C_6H_6 for 38 hr gave the corresponding 1-methyl isomer (**IIb**, 1·0%). The products were identified by GLC.



(2)

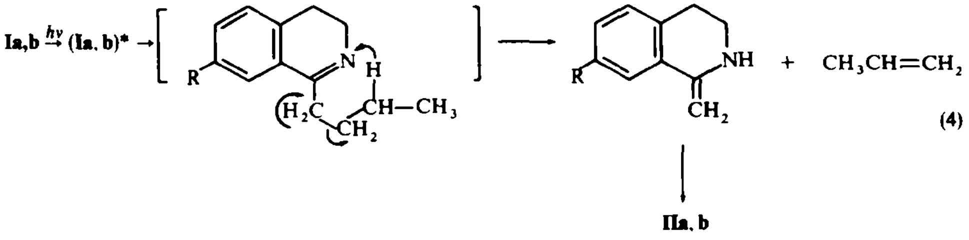
The electron impact fragmentation of **Ia** and **Ib** afforded mass spectra of products (Fig. 1), which were almost identical with that of 2-*n*-butylquinoline reported by Sample *et al.*[11] Stermitz *et al.*[7b] have observed a correlation between the McLafferty rearrangement and the photoconversion of 2-*n*-butylquinoline to 2-methylquinoline



(3)

as observed with carbonyl compounds which undergo the type II elimination reaction.

These results suggest that the photoreduction of **Ia** and **Ib** proceed *via* an intramolecular γ-hydrogen transfer to an N atom of excited azomethine followed by β-cleavage.



(4)

The azomethine seems to be excited to n-π*, because UV spectra of **Ia** shows a bathochromic shift at a longer-wave length band by a change of solvent from MeOH (λ_{max}, 249 nm (ε 8,360) and 280 nm (shoulder)) to non-polar cyclohexane (λ_{max}, 247 nm

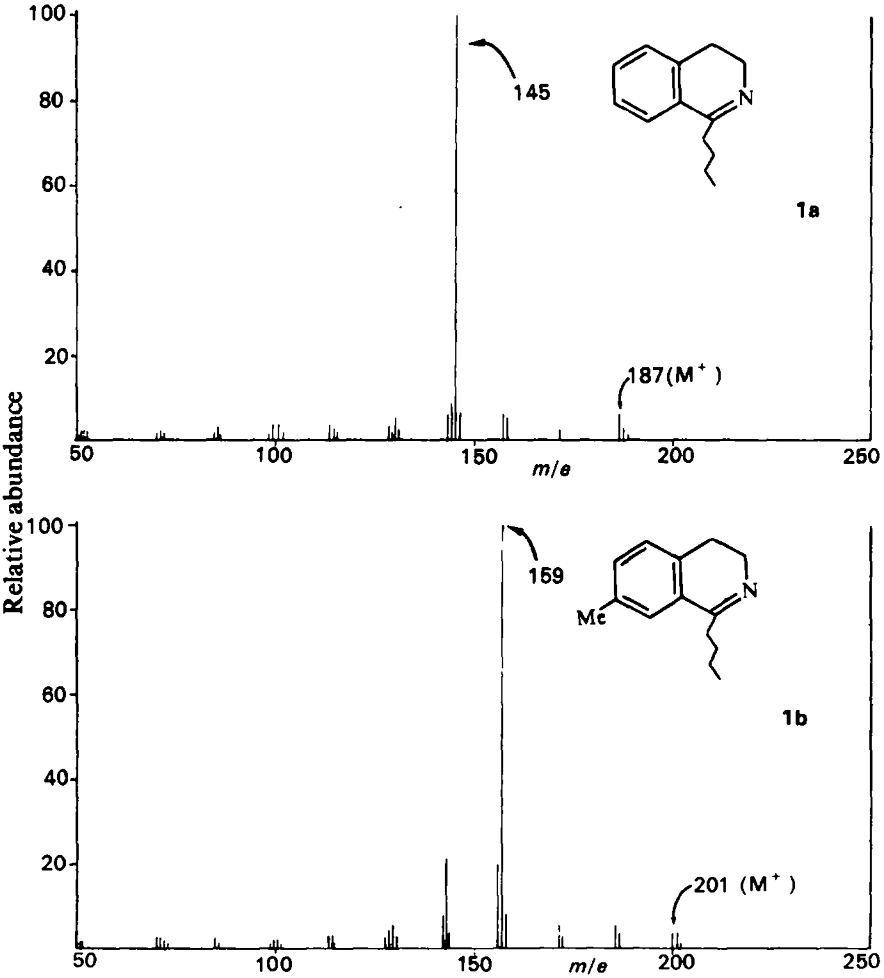
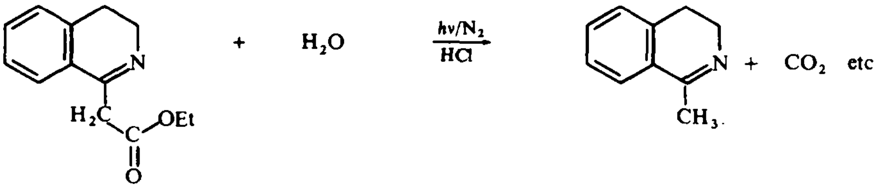


FIG 1. Mass spectra of 1-*n*-butyl-3,4-dihydroisoquinolines

and 282 nm). The similar phenomenon was observed with **Ib**; i.e. λ_{max} 252·5 nm (ε 7,500) and 288 nm (shoulder) in MeOH and λ_{max} 249 nm and 290 nm in cyclohexane. Generally, N-alkylimine does not show a distinct band of *n*-π^* transition, since it is often shielded by its intense π-π^* absorption,[6] but a tail at long wave length with conjugated imines such as benzalaniline may be due to n-π^* transition.

The analogy between electron impact fragmentation and photolysis of the azomethines is expected, since the electron bombardment of **Ia** and **b** may give radical cations by removing a non-bonding electron on a nitrogen atom, and the n-π^* excitation of **Ia** and **b** causes a non-bonding electron to flip up to upper π^* level to form $\underset{\cdot}{C}^{-}=\underset{\cdot}{N}^{+}$. Thus electron deficient nitrogen atom can abstract a γ-hydrogen atom.

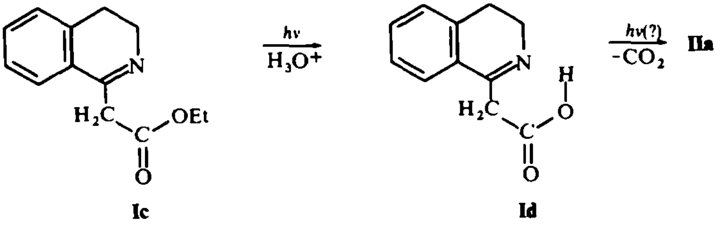
As an extension of this type of reaction, photochemical decarboxylation of ethyl 3,4-dihydroisoquinoline-1-acetate[12] in HCl aq has been attempted. A *n*-hexane solution (0·09 M) of **Ic** λ_{max}^{MeOH} 247 nm (ε 13,260) and 332 nm (ε 14,200) was photolysed for 34 hr in a degassed sealed quartz tube, but no reaction occurred. Whereas, irradiation of an aqueous solution (5·0 × 10^{-3} M) of **Ic** in *ca* two equivalents of HCl aq at room temperature yielded 1-methyl-3,4-dihydroisoquinoline (**IIa**, 37·2%), recovered **Ic** (54·8%) and CO_2 together with two other minor unknown products. Moreover, an excess of 50% HCl aq gave only 75% of **IIa** and 25% of **Ic**. Photoproduct, **IIa**, was identified by comparison of its IR, UV spectra and GLC retention times with those of an authentic sample. Carbon dioxide was trapped by $Ba(OH)_2$ aq.



(5)

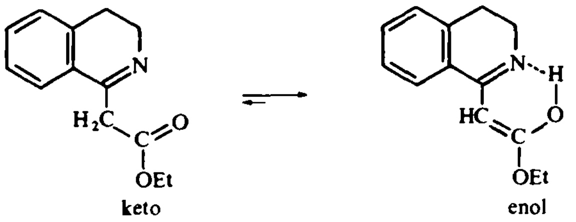
No decomposition of **Ic** occurred in the dark on treatment with an excess of 50% HCl aq at 40° for 24 hr, while **Ic** was quantitatively decomposed to afford **IIa** on reflux-in the dark. Irradiation of **Ic** hydrochloride in EtOH or H_2O gave no **IIa**, but other unknown products.

This facile photodecomposition of **Ic** giving **IIa** may be a sort of type II elimination of intermediary 3,4-dihydrosisoquinoline-1-acetic acid (**Id**) formed by hydrolysis of **Ic** which is promoted by UV irradiation. But in the presence of an excess amount of the strong acid, almost complete protonation of nitrogen atom may inhibit the n-π^* transition of C═N group. Therefore, it is less probable that the n-π^* excited group abstract a carboxylic γ-hydrogen atom. Since acid, **Id**, is unstable and readily decomposed to give **IIa** even in the dark, the acceleration of the reaction of ester **Ic**, may be the photochemical acceleration of hydrolysis.



(6)

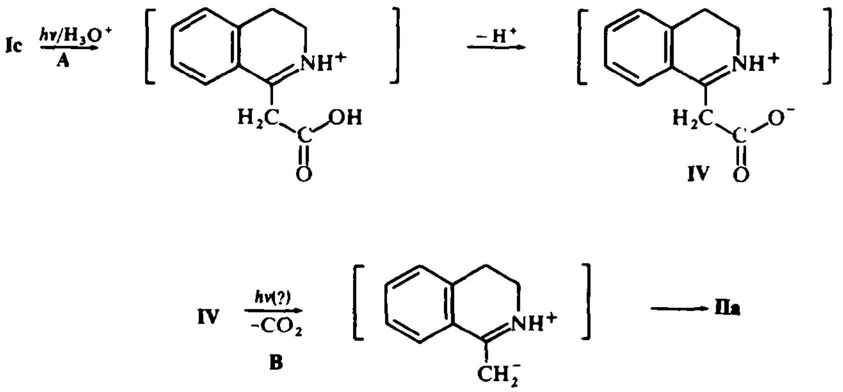
Ester, **Ic** forms an internal hydrogen bonding in neat or non-polar solvent in view of its IR peaks of 3280 cm^{-1} (C—OH), 1645 cm^{-1} (C═N) and 1735 cm^{-1} (C═O, shoulder). An increase of absorption intensity of ester carbonyl and a simultaneous decrease of that of hydroxyl was observed with increasing amount of added acid (HCl) which may prevent hydrogen bonding. The absorption assigned to C═N bond stretching also shifts to higher frequencies (1650 cm^{-1}) on addition of HCl.



(7)

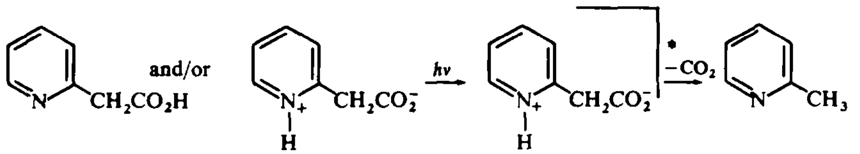
It is known that equilibrium 7 for β-diketones conjugated with an aryl group is on the enol side, e.g., 98% of α-acetylacetophenone exists as enol.[13] There is no report on the intramolecular photoreduction of β-diketones, where no n-π* transition is observed as a result of internal hydrogen bonding. This fact supports also the photochemical acceleration of acid-catalysed hydrolysis of **Ic**.

The following reaction mechanism may explain the present photoreaction as shown in Eq. 8. Protonated nitrogen interacts with carboxylate ion leading decarboxylation at the stage of step B.



(8)

The analogous photodecarboxylation of 2-, 3- and 4-pyridylacetic acids to the corresponding methylpyridines has been reported to be most efficient at their isoelectric points,[14] hence a scheme involving zwitterion has been presented.



(9)

However, we have no decisive data at present to decide whether the hydrolysis (step A) alone or the decarboxylation (step B) also is photo-excited.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer Model 337 and UV spectra by a Hitachi spectrophotometer. Electron impact fragmentations were carried out by a direct system technique using a Mattauchi-Herzog type (JMS-OSG) mass spectrometer.

1-n-Butyl-3.4-dihydroisoquinoline was prepared by the condensation of N-valerylphenethylamines with the freshly prepared polyphosphoric acid at 200° for 3·5 hr, b.p. 100–106°/0·6 mm, (lit[15], b.p. 87–93°/0·15 mm. characteristic IR spectrum (liquid film) 1630 cm^{-1} (C=N), λ_{max}^{MeOH} 249 nm (ε 8.360) and 280 nm (shoulder). Similar condensation of N-valeryl-(4-methyl)phenethylamine gave **Ib**, b.p. 93–97°/0·17 mm, characteristic IR spectrum (liquid film) 1620 cm^{-1} (C=N), λ_{max}^{MeOH} 252·5 nm (ε 7,500) and 288 nm (shoulder). Authentic **IIa** and **IIb** were prepared by the reaction of acetyl chloride with β-phenethylamine and β-(4-methyl)phenethylamine, followed by condensation in polyphosphoric acid, respectively; **IIa**, b.p. 76–80°/2–3 mm, (lit[15], b.p. 75–77°/1 mm), λ_{max}^{MeOH} 246 nm and 280 nm, and **IIb**, b.p. 72–75°/1 mm. Compound **Ic** was prepared by the reaction of ethyl cyanoacetate with β-chloroethylbenzene in anhyd. $SnCl_4$ at 110–115°. b.p. 123–126°/0·2 mm, (lit,[12] b.p. 156–158°/1 mm), n_D^{20} 1·610 (lit,[12] n_D^{20} 1·6035), characteristic IR spectrum, 3280 cm^{-1} (C—OH), 1735 cm^{-1} (C=O) and 1650 cm^{-1} (C=N), λ_{max}^{MeOH} 247 nm (ε 13,260) and 332 nm (ε 14,200).

Irradiation procedures. 0·003–0·1 M 1-substituted 3,4-dihydroisoquinolines were placed in a cylindrical quartz vessel and flushed with N_2 for 30 min prior to irradiation and the N_2 flow was continued throughout the irradiation. All experiments were carried out in either a cylindrical quartz vessel (20 × 150 mm) or an immersion type reactor (1 l.) equipped with a tube for introducing N_2 gas. A Halos high-press 300W Hg lamp with a water-cooling quartz jacket was used as a light source. The tests for comparison were run without light for all reactions and there was no change unless otherwise noted.

Identification and the estimation of product. The analysis of the products was done by means of GLC employing a Yanagimoto gas chromatograph with a flame ionization detector Model GCG-550F operated with a column (1·7 m × 2·5 mm) packed with PEG 20M (2·5 wt%) on Chamelite CS of 80–100 mesh using N_2 as a carrier gas at 130–230°. The similarity of the retention times of the peaks of the samples with those of the authentic samples established their identity. The yield of the products was also estimated by GLC under the same conditions. Furthermore, photoproduct IIa from Ic was identified with an authentic sample by means of comparison of their IR and UV spectra. Evolved CO_2 gas was carried by N_2 to a trap containing satd. $Ba(OH)_2$ to give $BaCO_3$. but no quantitative determination of $BaCO_3$ was done.

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REFERENCES

[1] Contribution No. 165

[2a] N. J. Turro. *Molecular Photochemistry*. Benjamin. New York. N.Y. (1965)

[b] R. O. Kan. *Organic Photochemistry*. McGraw-Hill Book. New York. N.Y. (1966)

[c] J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*. Wiley. New York. N.Y. (1966)

[d] D. C. Neckers. *Mechanistic Organic Photochemistry*. Rheinhold. New York. N.Y. (1967)

[3] M. Fisher. *Tetrahedron Letters* 5273 (1966); *Chem. Ber.* **100**. 3599 (1967)

[4] A. Kellman and J. T. Dubois. *J. Chem. Phys.* **42**. 2518 (1967)

[5] N. Toshima. H. Hirai and S. Makishima, *Kogyo Kogaku Zasshi* **72**, 184 (1969)

[6] A. Padwa. W. Bergmark and D. Pashayan. *J. Am. Chem. Soc.* **91**. 2653 (1969)

[7a] F. R. Stermitz and C. C. Wei. *Ibid.* **91**. 3103 (1969)

[b] F. R. Stermitz, C. C. Wei and C. M. O'Donnell. *Ibid.* **92**. 2745 (1970)

[8] W. H. Moore. G. S. Hammond and R. P. Foss. *Ibid.* **83**. 2789 (1961)

[9] S. G. Cohen and H. M. Chao. *Ibid.* **90**. 165 (1968)

[10] E. J. Baum, J. K. S. Wan and J. N. Pitts, Jr.. *Ibid.* **88**. 2652 (1966)

[11] S. D. Sample. D. A. Lightner. O. Buchardt and C. Djerassi. *J. Org. Chem.* **32**. 997 (1967)

[12] S. G. Agbalyan. A. O. Nshanyan and L. A. Nersesyan. *Izv. Akad. Nauk. Arm. SSSR Khim. Nauki.* **16**. 77 (1963); *Chem. Abstr.* **59**. 5132b (1963)

[13a] R. D. Cambell and H. M. Gilow, *J. Am. Chem. Soc.* **82**. 5429 (1960)

[b] B. Eistert and E. Merkel. *Chem. Ber.* **86**, 895 (1953)

[c] G. Allen and R. A. Dweck, *J. Chem. Soc.* (B) 161 (1966)

[14] F. R. Stermitz and W. H. Huang. *J. Am. Chem. Soc.* **92**. 1446 (1970)

[15] J. G. Cannon and G. L. Webster. *J. Am. Pharm. Associ. Ed.* **47**. 353 (1958); *Chem. Abstr.* **52**. 17273a (1958)