line dimer, as well as that of a simple monomeric benzyliso-quinoline to an isoquinolone, is an intrinsic part of the general alkaloid catabolic process within *B. baluchistanica*.[7]

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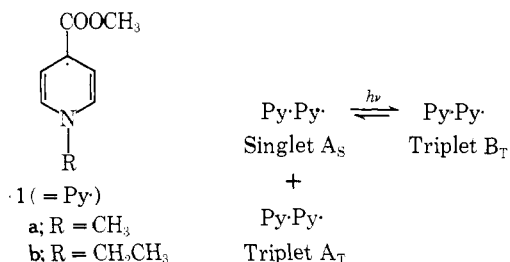
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Singlet–Triplet Transformation in the Dimeric Association of Pyridinyl Radicals

Sir:

Three kinds of radical pairs, A_S, A_T, and B_T, have been postulated for the association of pyridinyl radicals **1** in 2-methyltetrahydrofuran (MTHF) glass, and the generation of the triplet dimer B_T from the diamagnetic dimer A_S by light irradiation was demonstrated in a previous esr study.[1] A further study on the association has now revealed that the transformation of A_S into B_T occurred probably through the charge-transfer excitation of the diamagnetic dimer. The spectroscopic study will be reported.

$$Py \cdot Py \cdot \underset{}{\overset{h\nu}{\rightleftharpoons}} Py \cdot Py \cdot$$

Singlet A_S Triplet B_T

$+$

Py·Py·

Triplet A_T

$\cdot 1 (= Py \cdot)$
a; R = CH₃
b; R = CH₂CH₃

The esr study disclosed that the triplet B_T species can be generated by irradiating the radical solution at 77°K with the light of 420–500 nm, which was selected by the use of three Toshiba glass filters, VY-42, VY-50, and VV-44. However, the radical solution does not show any characteristic absorption band in this region at 77°K.[2] It was then thought that the specimen had been irradiated with the light enough to convert A_S into B_T. Thus, the following careful examination of the radical spectra was carried out.

1-Methyl-4-methoxycarbonylpyridinyl (**1a**) was purified by distillation under vacuum. The radical solution in MTHF at 77°K exhibited the spectrum shown in Figure 1 (b and c), which was taken before the solution at 77°K was exposed to any light except the dispersed light of a Cary 14 spectrophotometer for the measurement.[3] This spectrum has a significant absorption band at 437 nm. Irradiation of the solution with a light beam from the near-infrared source
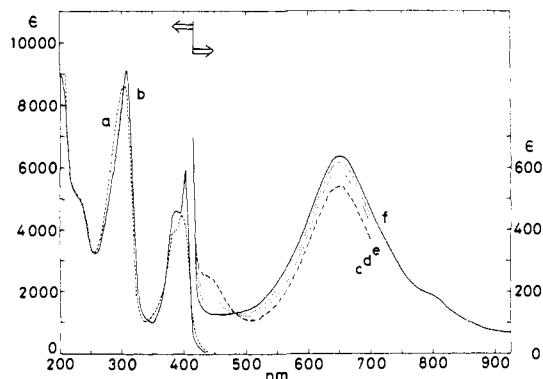

Figure 1. Absorption spectrum of 1-methyl-4-methoxycarbonylpyridinyl in MTHF: (a) 6.7×10^{-3} M, at room temperature; (b) 8.3×10^{-3} M, at 77°K; (c) 6.3×10^{-2} M, at 77°K before irradiation; (d) after 10-sec irradiation with a W-lamp; (e) after 20-sec irradiation; (f) after sufficient irradiation.
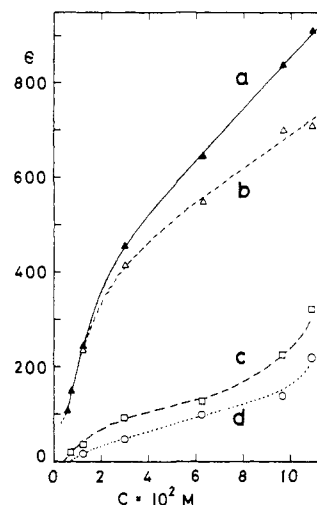

Figure 2. Concentration dependences of the absorption intensities of 1-methyl-4-methoxycarbonylpyridinyl at 77°K: (a) ϵ(653 nm) after irradiation; (b) ϵ(653 nm) before irradiation; (c) intensity increase at 675 nm with irradiation; (d) intensity decrease at 437 nm with irradiation.

(GE-CPR W-lamp) of the spectrometer for 10 sec changed the spectrum into that of Figure 1d. Further irradiation with the light for 10 sec gave the spectrum of Figure 1e, and then the spectrum of Figure 1f was finally shown after sufficient irradiation. It was thus clearly observed that the light irradiation causes the disappearance of the band at 437 nm, being accompanied by the increase of the broad absorption in 500–800 nm with the maximum increase at 675 nm. Wavelength specificity to the spectral change was the same as that shown in the esr study.[1] The change of the green color into a blue on irradiation was also seen. The spectral change is observed when the solution was moderately concentrated, implying that the change is directly related to the transformation in the radical associations. The concentration dependences of the intensity changes at two wavelengths are shown in Figure 2, together with the dependence of ϵ (at 653 nm) on the radical concentration.[4]

A similar phenomenon was observed for 1-ethyl-4-methoxycarbonylpyridinyl (**1b**) in MTHF glass. The spectrum is shown in Figure 3, in which the disappearance of the absorption at 440 nm on irradiation accompanied the spectral change in the region of 500–750 nm.

The absorption at around 440 nm coincides in wavelength with the light specific to the generation of the B_T species observed in the esr study. Since the intensity de-
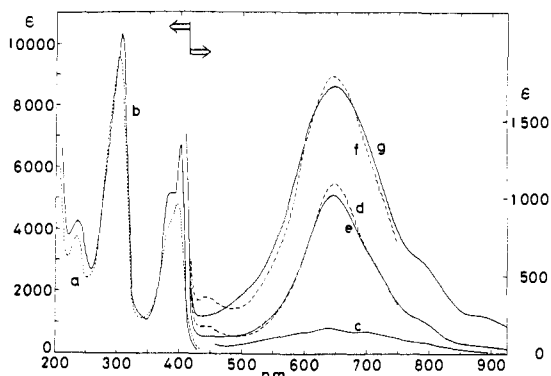
Figure 3. Absorption spectrum of 1-ethyl-4-methoxycarbonylpyridinyl in MTHF: (a) 5.5 × 10⁻³ M, at room temperature; (b, c) 6.9 × 10⁻³ M, at 77°K; (d) 2.9 × 10⁻² M, at 77°K before irradiation; (e) after sufficient irradiation of d with a W-lamp; (f) 6.0 × 10⁻² M, at 77°K before irradiation; (g) after irradiation of f.

pends on the radical concentration, the band is characteristic of the radical association and is presumably assigned to the second charge-transfer band in consideration of the appearance of two charge-transfer bands for some pyridinium salts.[5] The first band is almost certainly near 1.9 eV. It is thus assumed that the transformation of A_S into B_T occurred through the charge-transfer excitation of A_S, followed by the intersystem crossing to the triplet configuration. This sequence may include the dynamic reorientation of the radicals in a dimer to the positions capable of triplet transitions.

Spectral change seen in Figure 1 and the concentration dependences shown in Figure 2 may be explained by the transformation of A_S into B_T. However, the change in Figure 3 is different in intensity from that of Figure 1 for the region of 500–750 nm. This difference between two radicals will be caused by the fact that the absorptions in the 500–900-nm region originate in several kinds of species, such as radical monomer and singlet and triplet radical dimers. The monomer has an absorption due to the lowest excitation, $\Psi_g \rightarrow \Psi_1$,[2] in this region, which corresponds to the broad and weak absorption of the radical at room temperature.[6] The dimers would show the similar absorption due to the local excitation in a dimer. The radical association clearly leads to the appearance of other absorptions which are dependent on the radical concentration, as seen in Figure 2. It is thus difficult to interpret in detail the absorption intensity and the assignment for the 500–900-nm region. This region also bears relation to the π-mer formation[7] and the appearance of two charge-transfer bands demonstrated for some pyridinium salts.[5]

Further study on the transformation in the glassy state is in progress for the associations of analogous radicals.

References and Notes

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(3) A Dewar vessel with quartz windows was constructed for the measurement. The cell was immersed in liquid nitrogen.
(4) When the radical was purified carefully by distillation, cooling of the radical solution did not bring about the significant change of the spectrum for the region shorter than 400 nm (Figure 1a and 1b), and the absorption intensity in 650-nm region at 77°K is smaller than that reported previously.[2] Addition of a metal halide to the solution sometimes results in an increase of the intensity at around 610 nm with the spectral change in the shorter region. For example, λ_{max} (ε) for **1a** in MTHF with lithium iodide at 77°K is 618 nm (4800) at the concentration of 4.7 × 10⁻³ M. This is explained by the complex formation of **1a** with lithium iodide.[1]
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Reactions of Sodium Borohydride in Acidic Media. I. Reduction of Indoles and Alkylation of Aromatic Amines with Carboxylic Acids[1]

Sir:

We wish to report that sodium borohydride ($NaBH_4$) in neat carboxylic acids sequentially reduces the indole double bond and alkylates the nitrogen atom to give N-alkylindolines, e.g., **1 → 2**, and that this combination of reagents conveniently alkylates primary and secondary aromatic amines, e.g., **3 → 2** (Scheme I).

Scheme I. Transformations in Acetic Acid
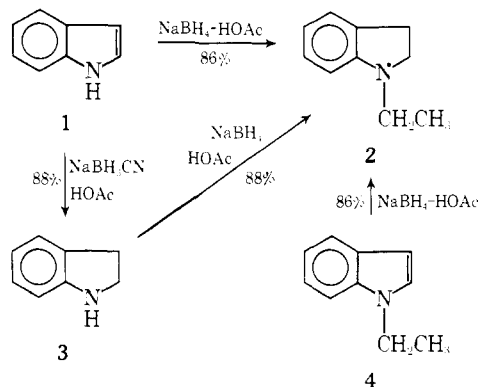
Although the reduction of indoles to indolines has received considerable attention,[2] there is no general, efficient procedure for this transformation. Encouraged by the tendency of the indole ring to protonate at the 3-position[3,4] and by the observations that enamines can be reduced by $NaBH_4$ in acetic acid-tetrahydrofuran (HOAc-THF)[5] and sodium cyanoborohydride ($NaBH_3CN$),[6] we have examined the behavior of indoles with $NaBH_4$ in neat carboxylic acids.

Quite unexpectedly, the reaction of indole (**1**) with $NaBH_4$ in glacial HOAc gives N-ethylindoline (**2**) in 86% yield. Likewise, the reactions of indoline (**3**) and N-ethylindole (**4**) with $NaBH_4$-HOAc give **2** in high yield.

This unprecedented reduction-alkylation of indoles and reduction of N-alkylindoles[7] with $NaBH_4$ in liquid carboxylic acids appears to be a general transformation (Table I). However, the stronger acid, formic, produces indole dimers and other products in addition to N-methylindoline. Interestingly, the reaction of **1** with $NaBH_4$ in trifluoroacetic acid (CF_3CO_2H) gives indoline (**3**), the product of reduction without alkylation, in low yield. The yield of **3** can be increased to 88% when **1** is treated with $NaBH_3CN$-HOAc (Table I). This latter reaction permits a very convenient synthesis of **3**.

We believe that the reaction of **1 → 2** involves 3-protonation of indole,[4] followed by reduction of the resulting indolenium ion to give **3**,[8] which is subsequently alkylated (*vide infra*). The reduction of the indoloquinolizidine alkaloid **5**