September, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 2711—2712 (1985)* 2711

Decarboxylative Photoaddition of 3-Butenoate Anion to 1-Methyl-2-phenyl-1-pyrrolinium Perchlorate *via* Electron-transfer Reaction

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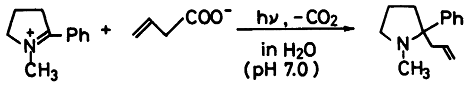
(Received April 11, 1985)

Synopsis. The photolysis of 1-methyl-2-phenyl-1-pyrrolinium perchlorate (**1**) with a 3-butenoate anion in an aqueous solution efficiently gives a 2-allylpyrrolidine adduct. Mechanistic studies demonstrate that the photoreaction is induced by a one-electron transfer from 3-butenoate to the singlet excited-state of **1**.

Photoinduced electron-transfer reactions of systems containing iminium cation chromophores have been extensively investigated in recent years with synthetic[1)] and biological[2)] interests. Mariano *et al.*[3–6)] have elucidated mechanistic details regarding photoreactions of pyrrolinium cations with a variety of electron donors such as olefins, allylsilanes, allenes, and arenes. In these, electron transfers to the excited singlet states of the cations take place to give 2-pyrrolidinyl radicals. Cation radical intermediates derived from the electron donors are transformed into neutral radicals by nucleophilic capture, deprotonation or desilylation followed by radical coupling with the pyrrolidinyl radicals leading to the production of photoadducts. In this note, we show that when a 3-butenoate anion is used as an electron donor in an aqueous solution, an allylic photoaddition to 1-methyl-2-phenyl-1-pyrrolinium perchlorate (**1**) occurs to give 1-methyl-2-phenyl-2-(2-propenyl)pyrrolidine (**2**) similar to a reaction in allylsilane systems.[4)]



1 2

Results and Discussion

1 was irradiated in an aqueous solution whose pH was adjusted to 7.0 with NaOH and contained 0.388 M (1 M=1 mol dm^{-3}) 3-butenoic acid to afford **2**. This was isolated after extraction with chloroform and was distilled under a reduced pressure in a 67.9% yield. The identification of **2** was made by a direct comparison of the ^{1}H NMR and IR spectra with those of an authentic sample[4)] prepared by the photoaddition of 3-(trimethylsilyl)propene to **1**. No dark reaction to produce **2** was observed and the fluorescence and absorption spectra of **1** in aqueous solutions containing the acid revealed the absence of an excited- and ground-state complex formation. When the solution pH was not neutralized and, thus, the carboxylic acid existed predominantly in an undissociated form, the yield of **2** was reduced to about one-fortieth. This suggested that the adduct was mainly produced by a photoreaction with the carboxylate anionic form.

One of the requirements for the feasibility of an electron-transfer-initiated photoaddition in the olefin-pyrrolinium cation pairs is an efficient quenching of the fluorescences of the cations by olefins.[3,4)] Certainly, the rate constant ($k_q=(3.08\pm0.08)\times10^9$ M^{-1} s^{-1}) of the fluorescence quenching of 2-phenyl-1-pyrrolinium perchlorate by the undissociated form in acetonitrile (obtained from the slope of a linear Stern-Volmer plot) was comparable to those for methyl 3-methyl-2-butenoate (3.7×10^9)[3)] and 3-(trimethylsilyl)propene (5.25×10^9 M^{-1} s^{-1})[4)] which are able to undergo photoaddition. Furthermore, it should be noted that quenching of the fluorescence of **1** by the anionic form ($k_q\tau=3.00\pm0.06$ M^{-1})[7)] in an aqueous solution was more efficient than that by the excellent olefin quencher, the undissociated form ($k_q\tau=1.84\pm0.03$ M^{-1}). Thus, the allylic photoaddition described above seems to be induced not only by an electron transfer from the vinyl group of the 3-butenoate anion to the singlet excited state of **1** ($\mathbf{1}^{S_1}$), but also by an electron transfer from the carboxylato group (Scheme 1). In fact, an acetate anion quenched the fluorescence of **1**,[8)] though the $k_q\tau$ value (1.14 ± 0.07 M^{-1}) was no more than *ca.* one-third the value for the butenoate and no more than *ca.* one-half the value for the butenoic free acid. The calculated free-energy change (−1.1 eV)[9)] using estimated one-electron oxidation potentials of carboxylates[10)] and the reduction potential (−0.95 V *vs.* SCE in an aqueous solution) and singlet energy (3.9 eV) of **1** also suggests that a one-electron transfer from the carboxylato group should be energetically feasible.

The steady-state analysis of a sequence, analogous to that for the allylsilane systems,[4)] shown in Scheme 1, gives $\phi_a^{-1}=\alpha_a^{-1}+(\alpha_a k_q\tau[\text{3-butenoate}])^{-1}$, where ϕ_a and α_a represent the quatum yield of the formation of **2** and the limiting ($[\text{3-butenoate}]\rightarrow\infty$)$\phi_a$, respectively. The ratio of the intercept to slope from a linear plot of ϕ_a^{-1} *vs.* $[\text{3-butenoate}]^{-1}$ shown in Fig. 1 was 2.6 ± 0.5 M^{-1} and closely agreed with the $k_q\tau$ value (3.00 M^{-1}) obtained from fluorescence quenching. This agreement of mathematically equivalent quantities obtained independently of one another suggests that the fluorescence quenching and photoaddition are kinetically coupled and, thus, that the photoaddition proceeds *via* the singlet excited state of **1**. In addition, the reciprocal of the intercept, α_a (0.33) and

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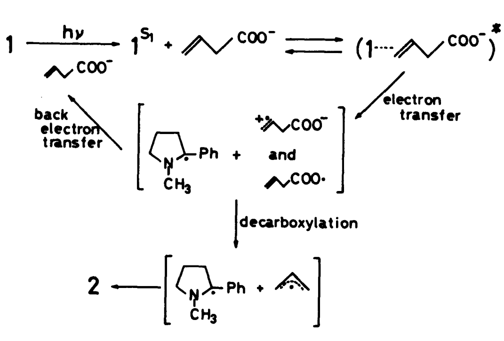

Scheme 1.

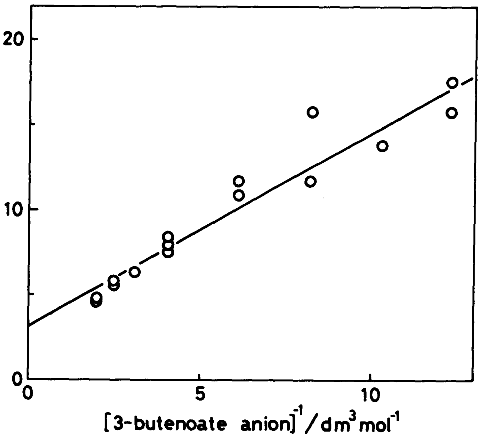

Fig. 1. Double reciprocal plot of the quantum yield for formation of **2** *vs*. the concentration of 3-butenoate anion.

the ratio (0.69) of ϕ_a (0.22±0.02) to the quantum yield for the disappearance of 1 (ϕ_{dis}=0.32±0.03) obtained at [3-butenoate] of 0.5 M had larger values than those regarding the photoaddition of 3-(trimethylsilyl)-propene (α_a=0.02 and ϕ_a/ϕ_{dis}=0.5).[4)] This indicates a higher efficiency of the adduct formation with a 3-butenoate anion.

Experimental

The ^{1}H NMR, UV, and IR spectra were recorded on a Hitachi R-24B, a Shimadzu UV 202, and a Hitachi 285, respectively. The fluorescence emission was measured using a Shimadzu RF-510 spectrometer. **1** was prepared and purified according to a method from the literature:[7b)] mp 117.5—119.0 °C (uncorrected). 3-Butenoic acid was commercially available and distilled *in vacuo* just before use.

Photolysis of 1 with 3-Butenoate Anion. In an aqueous solution (200 cm^3) containing 3-butenoic acid (6.67 g, 0.0776 mol) adjusted to pH 7.0 with NaOH, **1** (401 mg, 1.54 mmol) was dissolved and irradiated for 60 min. The irradiation was carried out using a 400-W high-pressure mercury lamp (Riko-Sha UVL-400HA) equipped with a Pyrex water-jacket under an atmosphere of argon. The photolysate was acidified (pH 1) with HCl and then concentrated to 5 cm^3 *in vacuo*. The acidic solution was made basic (pH 10) with NaOH, saturated with NaCl, and extracted with three 20-cm^3 portions of chloroform. The extract was dried over anhydrous Na_2SO_4 and then concentrated *in vacuo*. The resulting oily residue was purified by distillation under a reduced pressure to give 213 mg (67.9% yield) of a clear oily product **2**.

Fluorescence Quenching Experiments. The relative intensities of the fluorescence at 380 nm of **1** (1×10^{-3} M) were measured at 25±1 °C. The excitation wavelength was 305 nm and concentrations of the quenchers were in the 0.1—0.5 M ranges.

Quantum Yields. Quantum yields were measured using a linear optical-bench system equipped with a 500-W super-high-pressure mercury lamp (Ushio USH-500D) at 25±1 °C. The 280-nm band (1.54×10^{14} quanta s^{-1}) isolated with a monochrometer (Jarrel Ash JE-25E) was used to irradiate an argon-purged aqueous solution (pH 6.0, [**1**]=1.00×10^{-3} M, [3-butenoate]=0.5 M). Product analyses were performed by GLC (Shimadzu GC-3BF, 5% PEG 20M) for reaction mixtures worked up as in the preparative run. Biphenyl was used as an internal standard. The degrees of the disappearance of **1** were determined from the decrease of the absorbance at the λ_{max} of 258 nm. The conversions were not more than 10%. The relative quantum yields for the formation of **2** at different concentrations of 3-butenoate were obtained at 25±1 °C using a merry-go-round apparatus at the center of which was the 400-W high-pressure mercury lamp employed in the preparative run.

The authors wish to thank Professor Patrick S. Mariano of the University of Maryland for his helpful comments.

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