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Photoinduced Alkoxylation of 2-Vinylpyridinium Ion

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Synopsis. Photoirradiation of 2-vinylpyridine in acidic methanol afforded methyl 2-(2-pyridyl)ethyl ether in a high yield. Reactions in acidic ethanol and 2-propanol also provided the corresponding alkoxyl derivatives along with a considerable amount of 2-ethylpyridine. It was suggested that photoinduced intramolecular charge-shift from the pyridinium ion moiety into the vinyl group initiates the regioselective nucleophilic addition of alcohol.

It is well-known that photoirradiation of alkene in alcohol frequently results in alkoxylation. When a direct photoexcitation[1)] or sensitization reaction[2)] induces the generation of positive charge on the alkene moiety, a nucleophilic addition of alcohol to afford alkoxylation products is expected. In this paper, we report photochemical regioselective alkoxylation of 2-vinylpyridine in acidic alcohols. The key step of the reaction was supposed to be a photoinduced intramolecular charge-transfer in the 2-vinylpyridinium ion.

Experimental

2-Vinylpyridine was obtained from Aldrich, Co. and purified by distillation. All solvents were distilled from CaH_2 before use. A sample solution was saturated with argon or with air by bubbling and sealed in a Pyrex cell, which was irradiated by a 350 W high-pressure mercury lamp at room temperature. Product yields were determined by GLC (PEG-HT, 1 m) with an internal standard after neutralization. The structures of the products (**2a**–**c**) were determined by GC-MS, MS, ^1H and ^{13}C NMR after isolation by a medium-pressure liquid chromatograph (column, silica-gel; eluent, *n*-hexane and ether).

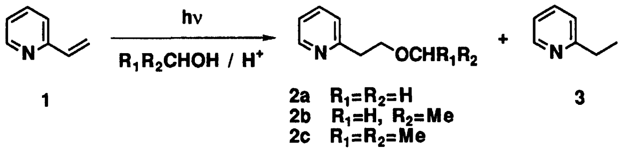
2a; ^1H NMR ($CDCl_3$) $\delta=3.13$ (2H, t, $J=6.6$ Hz), 3.35 (3H, s), 3.79 (2H, t, $J=6.6$ Hz), 7.22—8.57 (4H, m); ^{13}C NMR ($CDCl_3$) $\delta=37.7$ (t), 58.7 (q), 71.6 (t), 121.9 (d), 124.3 (d), 137.7 (d), 147.9 (d), 158.7 (s); MS m/z (rel intensity) 136 (M^++1, 3), 122 (100), 106 (29), 93 (31), 79 (13), 65 (10), 51 (11).

2b; ^1H NMR ($CDCl_3$) $\delta=1.17$ (3H, t, $J=7.1$ Hz), 3.06 (2H, t, $J=6.8$ Hz), 3.49 (2H, q, $J=7.0$ Hz), 3.80 (2H, t, $J=7.1$ Hz), 7.08—8.52 (4H, m); ^{13}C NMR $\delta=14.8$ (q), 38.4 (t), 65.8 (t), 69.5 (t), 120.9 (d), 123.2 (d), 135.9 (d), 148.9 (d), 159.0 (s); MS m/z (rel intensity) 152 (M^++1, 0.3), 150 (1.5) 122 (100), 106 (19), 93 (33), 78 (12), 65 (7), 59 (12), 51 (8).

2c; ^1H NMR ($CDCl_3$) $\delta=1.12$ (6H, d, $J=5.9$ Hz), 3.05 (2H, t, $J=7.1$ Hz), 3.57 (1H, q, $J=6.1$ Hz), 3.79 (2H, t, $J=7.1$ Hz), 7.08—8.53 (4H, m); ^{13}C NMR $\delta=21.9$ (q), 38.9 (t), 67.3 (t), 71.3 (d), 121.0 (d), 123.4 (d), 135.9 (d), 148.9 (d), 159.3 (s); MS m/z (rel intensity) 166 (M^++1, 0.5), 150 (0.2), 134 (1), 122 (100), 106 (43), 93 (65), 78 (17), 66 (6), 51 (7).

Results and Discussion

Photoirradiation of a methanol solution of 2-vinylpyridine (**1**, 20 mmol dm^{-3}) and hydrochloric acid (10 mmol dm^{-3}) under argon atmosphere afforded methyl 2-(2-pyridyl)ethyl ether (**2a**) in a high yield. Photoirradiation of **1** in ethanol or 2-propanol also afforded the corresponding alkoxyl derivatives, **2b** and **2c**, along with a considerable amount of 2-ethylpyridine (**3**) (Eq. 1). In the absence of hydrochloric acid, **1** was recovered unchanged after 2 h irradiation. Addition of hydrochloric acid is essential for these reactions. Photoirradiation of 4-vinylpyridine under similar conditions gave no reaction products and 4-vinylpyridine was recovered unchanged. The results obtained under various reaction conditions are summarized in Table 1.



(1)

In order to clarify the effect of hydrochloric acid on the photochemical reaction of **1**, 'titration' experiments were carried out. Upon photoirradiation of **1** in methanol, the conversion of **1** and the yield of **2a** both increased with the increasing concentration of hydrochloric acid up to the equivalent amount to that of **1** as shown in Fig. 1. The result suggests that the formation of 2-vinylpyridinium chloride is essential for the photoinduced reaction, which was further confirmed by

Table 1. Photochemical Reaction of 2-Vinylpyridine in Alcohols[a)]

Solvent	Additive		Conv.	Product yield/%[b)]	
	mmol dm^{-3}		%	**2**	**3**
MeOH	HCl	10	74	**2a**; 89	0
	H_2SO_4	5	57	**2a**; 97	0
	CH_3COOH	10	4	**2a**; 0	0
	None		0	**2a**; 0	0
EtOH	HCl	10	75	**2b**; 46	16
	None		0	**2b**; 0	0
i-PrOH	HCl	10	66	**2c**; 14	29
	None		0	**2c**; 0	0

a) Reaction conditions; [**1**]=20 mmol dm^{-3}, 350 W high-pressure mercury lamp through a Pyrex filter, 2 h irradiation at room temperature under argon atmosphere.
b) Yields are based on the amount of **1** consumed.

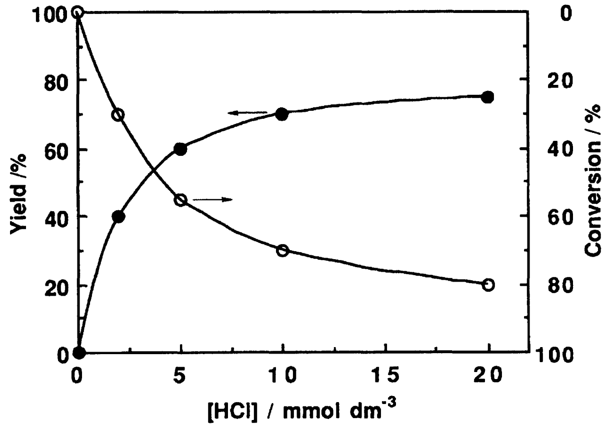


Fig. 1. Effect of hydrochloric acid on the photochemical reaction of 2-vinylpyridine (**1**) in methanol; the conversion of 2-vinylpyridine (**1**), (○) and the yield of the methanol adduct (**2a**), (●) are plotted against the concentration of hydrochloric acid; reaction conditions are as follows, $[\mathbf{1}]=20$ mmol dm^{-3}, 350 W high-mercury lamp through a Pyrex filter, 2 h irradiation at room temperature under argon atmosphere.

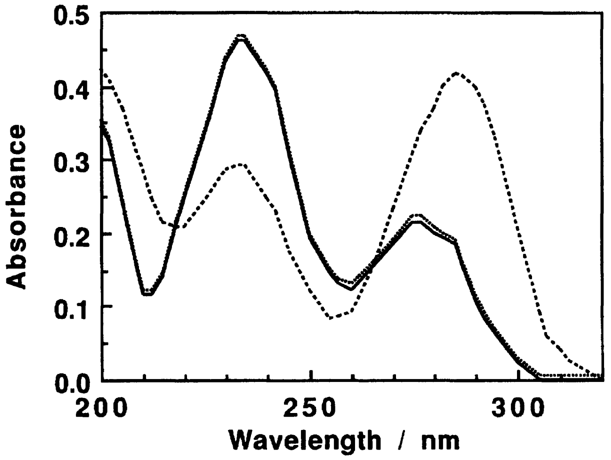
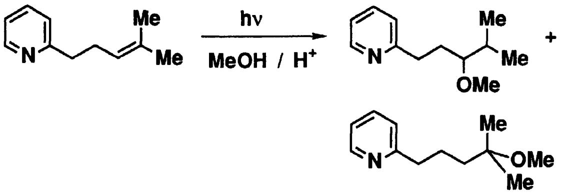


Fig. 2. Absorption spectra of 0.04 mmol dm^{-3} methanol solutions of 2-vinylpyridine observed in the absence of acid, —; in the presence of 0.4 mmol dm^{-3} hydrochloric acid, - - -; and in the presence of 0.4 mmol dm^{-3} acetic acid, ····.

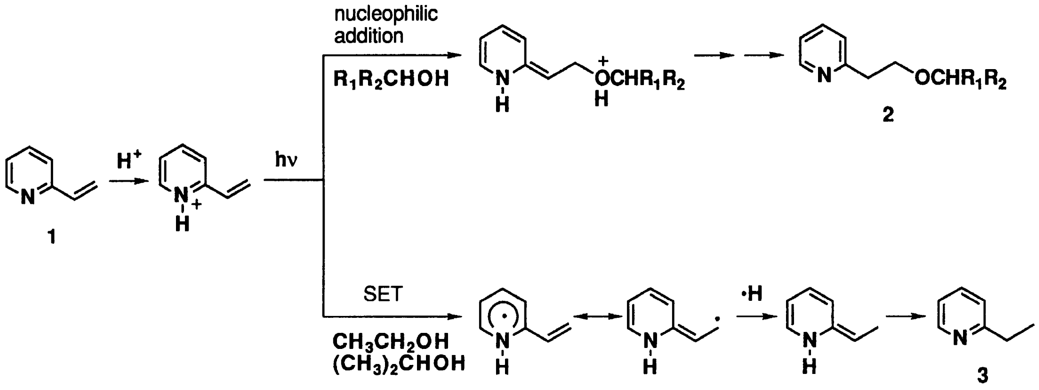
the absorption spectra as shown in Fig. 2. A methanol solution of **1** showed two absorption bands with λ_{max} at 244 nm and 277 nm.[3] Addition of hydrochloric acid induced obvious change of the absorption spectrum which suggests the formation of the pyridinium chloride. Sulfuric acid also induced a similar spectral change. On the contrary, no spectral change was observed in the case of acetic acid probably due to the high pK_a which is insufficient for the formation of the pyridinium salt. The effect of acids on the absorption spectrum was consistent with the results of the photochemical reactions as shown in Table 1. Thus, it is clear that the methoxylation takes place only in the presence of an acid which can produce the pyridinium salt.

The regioselective alkoxylation of **1** suggests the effective localization of the positive charge at the 2-position of the vinyl group of 2-vinylpyridinium upon photoexcitation. It has been reported that quinoline and pyridine derivatives show an electron deficient property upon protonation. Thus, in acidic media, pyridine and quinoline derivatives are expected to react with some nucleophilic reagents.[4] Mariano et al. reported that photoexcitation of pyridiniums induces SET (single electron transfer) from some electron donating molecules,[5—7] and the fact indicates that the electron accepting property of pyridiniums considerably increases upon photoexcitation. When an alkene moiety is attached to the pyridinium by a non-conjugated methylene chain, the photoexcitation induces an intramolecular SET from the alkene to the pyridinium. In other words, it is positive-charge transfer from the pyridinium to the alkene moiety. The resulting radical cation of alkene efficiently suffers a nucleophilic attack by alcohol. The positive charge may be distributed on the two vinyl carbons to a similar extent, since the regioselectivity of the reaction is low (Eq. 2).[5] In the present reaction system, photoexcitation of 2-vinylpyridinium is supposed to induce intramolecular charge shift, by which the positive charge is localized at the terminal vinyl carbon, leading to the regioselective addition of alcohol. In contrast, no reactivity of 4-vinylpyridinium may be due to the insufficient charge shift to the vinyl group in the photoexcited state.

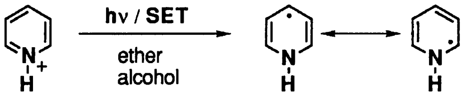


(2)

As described above, 2-ethylpyridine (**3**) was formed in a fairly high yield in ethanol and became the major product in the case of a 2-propanol solution. The formation of **3** was not observed in the absence of hydrochloric acid. The time course experiments in ethanol and 2-propanol indicated that both **2** and **3** are primary products. These facts suggest that not only **2** but also **3** are the photochemical primary products of 2-vinylpyridinium. It has been reported that the photoexcited pyridinium ion is quenched by methanol and ether via SET leading to the formation of a semiquinone-type radical (Eq. 3).[8] It is reasonable to consider the similar SET from alcohol for the photoexcited 2-vinylpyridinium, which leads to hydrogen abstraction by the vinyl group as shown in Scheme 1. However, in the case of 2-vinylpyridinium, the SET of the photoexcited state from alcohol competes with the nucleophilic addition of alcohol due to the considerable localization of the positive charge on the vinyl group.



Scheme 1.



(3)

It is well-known that the efficiency of SET mainly depends upon the free energy change (ΔG_{SET}) calculated by Weller's relationship.[9] Mariano et al. reported that the fluorescence of 2-phenyl-1-pyrrolinium perchlorate was quenched by alcohols via SET, and the rate constants of SET (k_{SET}) from 2-propanol and ethanol are one-order larger than that from methanol.[6,10] They concluded that the k_{SET} depends upon the ΔG_{SET} calculated on the basis of the oxidation potential of the alcohol which was estimated by Miller's relationship.[11] In the present results, the tendency for the formation of **3** ($\mathrm{MeOH} \ll \mathrm{EtOH} < i\text{-}\mathrm{PrOH}$) is inversely consistent with the magnitude of the ionization potentials of each alcohols (MeOH, 10.84 eV; EtOH, 10.49 eV; *i*-PrOH, 10.15 eV).[12] Thus, we presume that the ratio of the two products is determined by both the nucleophilicity and the ionization potential of the alcohol.

As an alternative reaction pathway leading to the reduction product, **3**, a direct hydrogen abstraction of photoexcited pyridinium from alcohol might be possible. Sugimori et al. reported photochemical substitution of 2-pyridinecarbonitrile hydrochloride,[13] in which the photoexcited state directly abstracts a hydrogen atom from alcohol, leading to an unstable hydroxyalkyl adduct. Unfortunately, pyridinium salts usually show no or very weak fluorescence, and it is difficult to distinguish the direct hydrogen abstraction from the SET pathway by a fluorescence quenching study.

In the present photochemical reaction system, it was concluded that photoexcitation of 2-vinylpyridinium ion competitively resulted in two kinds of reaction pathways; one is the intramolecular charge transfer which leads to the nucleophilic addition of alcohol and the other is the SET from alcohol which leads to the hydrogenation of the vinyl group in the cases of ethanol and 2-propanol.

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