

PHOTOEXCITED BEHAVIOR OF NITROGEN HETEROAROMATICS (I).
PHOTOESTERIFICATION OF PHENANTHRIDINE IN CARBOXYLIC ACID.

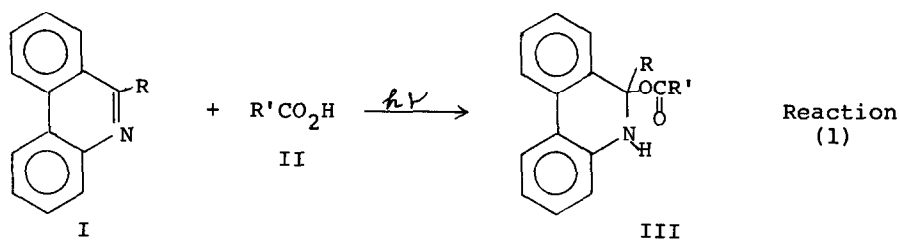
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Summary: Photoirradiation of phenanthridine (I) derivatives in carboxylic acid caused esterification of (I). Different reactivity from those of other heteroaromatics is discussed.

Considerable number of studies on the nature of photoexcited nitrogen heteroaromatics have been studied¹⁻⁷. The typical reaction feature would be classified as follows; (1) photochemical alkylation by carboxylic acid¹⁻⁴, (2) solvent incorporation in acidified media^{5,6}, (3) reductive dimerization of the substrate^{4b,7}. General mechanisms which involve free radical and free radical cation intermediates of the substrate have been postulated as well as molecular orbital calculations⁵. We now wish to report a new reaction which is the photoesterification of phenanthridine derivatives in carboxylic acid.

Irradiation of 6-methylphenanthridine (Ia) in dichloroacetic acid with high pressure mercury arc through pyrex wall for 2.5 hr and the subsequent chromatographic separation afforded 5-hydro-6-methyl-6-phenanthridyl dichloroacetate in 53% yield based on the initial concentration. Likewise, phenanthridine derivatives Ia-c were also photoesterified and the gas chromatographic analysis revealed that the photoalkylated products were scarcely formed making contrast with the reaction of the other nitrogen heteroaromatics⁴.



a R = CH ₃	a R' = CH ₃	aa R = CH ₃ R' = CH ₃
b Ph	b CHCl ₂	ab CH ₃ CHCl ₂
c PhCH ₂	c C ₂ H ₅	ba Ph CH ₃
		bb Ph CHCl ₂
		bc Ph C ₂ H ₅
		ca PhCH ₂ CH ₃

It was also found that the salt (IV) between phenanthridine and carboxylic acid resulted into the same ester (III) upon irradiation in acetonitrile, suggesting (IV) could be the precursor of the products. Table 1 shows the summary of the reaction 1.

Table 1 Yields and Spectroscopic Data of 6-Phenanthridyl Esters

Ester III	Irrad. Time (hr)	Yield (%)	IR (cm ⁻¹)				NMR (ppm)			
			√N-H	√C=O	√C-O	R	R'	N-H	Aromatic H	
IIIa	56	50 ^a	3350	1735	1239	2.96	2.56	2.77	7.33-8.68	
IIIab	1.5	53 ^b	3300	1743	1164	3.39	5.94	5.94	7.80-8.84	
IIIba	4.0	20 ^a	3360	1737	1229		1.69	2.42	7.30-8.50	
IIIbb	24	100 ^a	3540	1777	1156		5.94	6.06	7.39-8.61	
IIIbc	5.0	85 ^a	3370	1730	1169		0.91, 2.18 (-CH ₃) (-CH ₂ -)	4.34	6.54-7.95	
IIIca	5.8	29 ^a	3290	1740	1236	4.69 (Ph-CH ₂ -)	2.96	4.36	6.35-8.80	

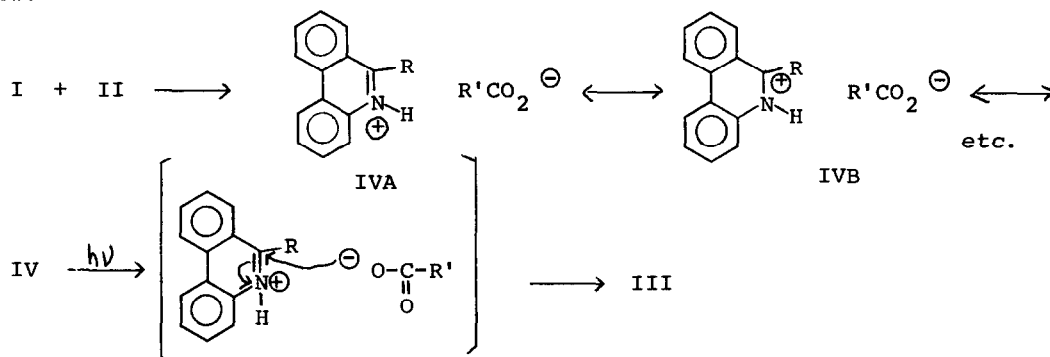
a) Determined by NMR

b) Isolated Yield

In order to gain more informations on the reaction, effects of additives were investigated using IVca⁸ in acetonitrile. It was found that neither

trans-1,3-pentadiene (triplet quencher, $E_T=59.2$ kcal/mol⁹), nor 2,6-di-*t*-butyl-4-methyl-phenol as radical scavenger did not affect the conversion appreciably, indicating the excited singlet state and the ionic channel was responsible for the reaction. Furthermore, the reaction was suppressed by trans-anethole completely. Since the fluorescence of phenanthridine is known to be quenched by various electron donating molecules¹⁰, the results support that the reaction proceeds from the excited singlet state of I.

Relative rate of disappearance of I was found to be $\text{PhCH}_2 > \text{Me} > \text{Ph}$, which would be the order of attacking susceptibility of carboxylate ion at 6 position in the canonical form IVB. A plausible reaction scheme is shown below.



The ionic pair complex (salt IV) was also postulated for other nitrogen heterocycles, and subsequent decarboxylation afforded the high yield of alkylated products⁴. Although we have to await further knowledge to get insight into the different reactivity of I from those of other nitrogen heterocycles, it may be ascribable to the following accounts. (1) 5,6 Bond of phenanthridine is of more double bonded character than the other compounds¹², (2) excited singlet energy of IV is 72-75 kcal/mol, and is considerably lower than quinoline (91 kcal/mol)¹⁴, therefore, decarboxylation may be slow for IV.

Acknowledgment: One of the authors (H.O.) is grateful to the Kawakami Foundation for financial support.

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8. Salt between 6-benzylphenanthridine and acetic acid. Salt was purified by recrystallization from acetone.
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10. Phenanthridine fluorescence was quenched by trans-anethole affording Stern-Volmer constant $k_{sv} = 18 \text{ M}^{-1}$ for Ia in ethanol. Fluorescence lifetime of Ia is not known, but it would be around 5 ns, which allows quenching rate is almost diffusion controlled.
11. Reinvestigation of the previous report⁴ confirmed that the photoesterification did not occur in those systems.
12. Phenanthrene, which is isoelectronic to phenanthridine is known to react like olefins¹³.
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(Received in Japan 26 July 1979)