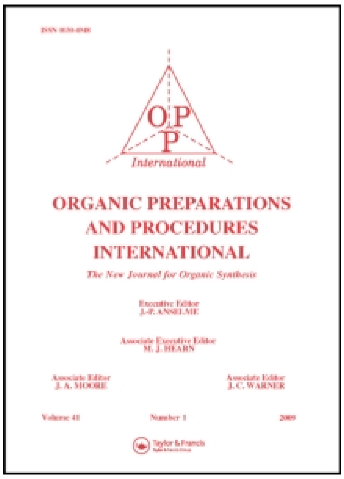

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COMPOUNDS RELATED TO ACRIDINE. IX.[1]

COPPER CATALYZED OXIDATION OF 9-ETHYNYLACRIDINE AND ITS REACTION WITH SECONDARY AMINES

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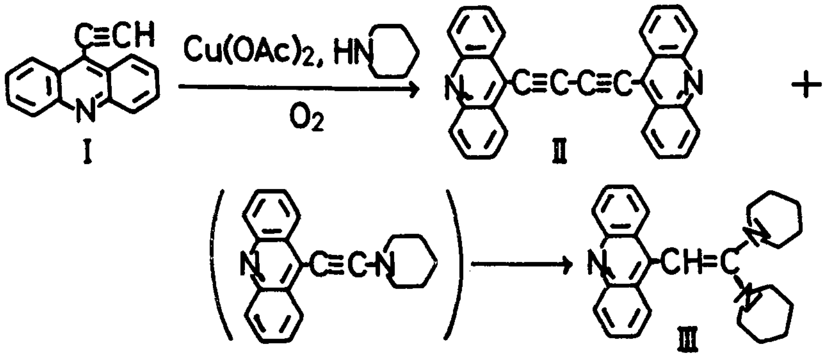
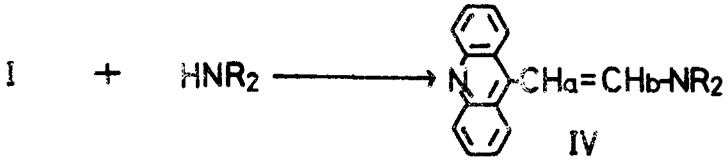
Little information is available about the preparation and the reactions of heteroaromatics having an ethynyl group. Recently, we have reported a convenient synthesis of 9-ethynylacridine (I).[3] We now describe the preparation of 1,4-di(9-acridinyl)butadiyne (II) and the reaction of I with secondary amines to yield enamines.

The oxidation of I with oxygen in the presence of cupric acetate and piperidine afforded the expected butadiyne II, mp 310° (dec.), in a 46% yield, accompanied by a small amount of 1-(9-acridinyl)-2,2-dipiperidinoethylene (III), mp 165°. The structures of II and III were confirmed by their spectral data as well as by their microanalyses. Recently, Peterson[4] found that the copper catalyzed oxidation of phenylacetylene in the presence of dimethylamine gave 1,4-diphenylbutadiyne and the ynamine, N,N-dimethyl-2-phenylethynylamine. Therefore, the formation of III can be viewed as proceeding by the initial formation of the corresponding ynamine, followed by the further addition of piperidine to the ynamine.



The addition of secondary amines to acetylenes, in particular to acetylenic esters and acetylenic sulfones,[5-8] is applicable to the preparation of conjugated acyclic enamines. The formation of III suggests that I, having the electron-attracting acridinyl group, could react easily with secondary amines to yield enamines. In fact, I reacted easily with secondary amines such as piperidine, morpholine and pyrrolidine at 0° to afford the corresponding <u>trans</u>-enamines (IV) in excellent yields.[9] The yields, physical properties and results of microanalyses of IV are summarized in Table 1.



a: R_2=piperidyl, b: R_2=morpholinyl, c: R_2=pyrrolidinyl

Table 1. Enamines IV[a)]

	Yield	Mp.	NMR(in $CDCl_3$)[b)]			Analysis, %			M^+
			Ha	Hb	Jab	Found(Calcd.)			
	%	°C	τ	τ	Hz	C	H	N	(m/e)
IVa	82	148-150	3.23	3.90	13	83.58 (83.29)	7.02 (6.99)	9.44 (9.71)	288
IVb	94	216-217	3.35	3.95	14	78.50 (78.59)	5.98 (6.25)	9.02 (9.05)	290
IVc	93	186-187	2.85	4.15	14	83.33 (83.17)	6.37 (6.61)	9.93 (10.21)	274

a) All IV are yellow prisms (from petroleum ether).
b) Both Ha and Hb appeared as doublets.

EXPERIMENTAL

All the melting points are uncorrected. The NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer using a direct inlet and an ionization energy at 70 eV. The IR spectra were measured as KBr pellets. The microanalyses were performed by Miss M. Akita of our laboratory.

Copper-catalyzed Oxidation of I in the presence of piperidine. -- A solution of 1.0 g (5 mmoles) of I in 10 ml of benzene was added dropwise over 30 min to a stirred solution of 0.2 g of cupric acetate monohydrate and 3.5 g of piperidine in 10 ml of benzene maintained at 5°. A stream of oxygen was passed continuously through the reaction mixture during the addition of I and then for another 1 hr. Filtration gave yellow crystals which on recrystallization from nitrobenzene afforded 0.46 g (46%) of II, mp 310° (dec.), as yellow needles.

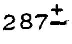
Anal. Calcd. for $C_{30}H_{16}N_2$: C, 89.09; H, 3.99; N, 6.93.
Found: C, 88.94; H, 3.96; N, 6.86.

Mass spectrum: m/e 404 (M^+, base peak), 202 (1/2 M^+).

The benzene filtrate was extracted with 30 ml of water and the organic layer was separated, dried over anhydrous sodium sulfate and then concentrated *in vacuo* to yield orange crystals. Recrystallization from benzene afforded 50 mg (3%) of III, mp 165°, as orange prisms.

Anal. Calcd. for $C_{25}H_{29}N_3 \cdot H_2O$: C, 77.08; H, 8.02; N, 10.79.
Found: C, 77.25; H, 7.94; N, 10.60.

NMR ($CDCl_3$): τ 8.6 (12H, m, $C\underline{H_2}$), 7.0 (8H, m, $C\underline{H_2}$), 4.8 (1H, s, =C$\underline{H}$), 2.3 (8H, m, aromatic protons).

Mass spectrum: m/e 371 (M^+), 287 (M^+- ), 203 (287^+- ), 178 (203^+- C≡CH).

Reaction of I with secondary amines.-- The general procedure is illustrated with the reaction with piperidine. A solution of 0.2 g (1 mmol) of I in 5 g of piperidine was stirred for 15 min at 0°. The reaction mixture was poured into 50 ml of ice-cooled water and the precipitated crystals were recrystallized from petroleum ether to give 0.19 g (82%) of enamine IVa. The results are given in Table 1.

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