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Photochemistry of 3-Amino-2-alkenimines: Synthesis of Substituted Quinolines

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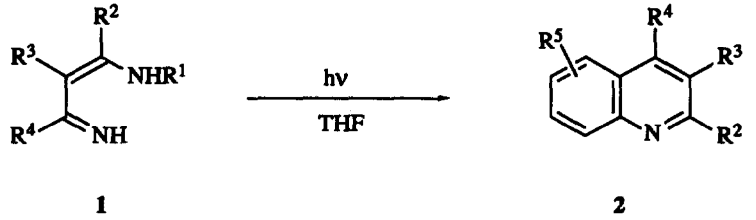
Abstract: The 3-amino-2-alkenimines **1** are photochemically reactives. Their irradiation in solution (tetrahydrofuran, methanol, diethyl ether, toluene) produces substituted quinolines **2** in good to acceptable yields. A six electon electrocyclic process is proposed.

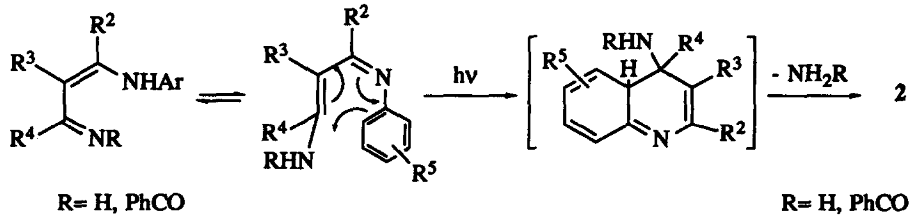
There is not any systematic study about the photochemistry of 1-azadienes and only a few particular reactions are known. Thus 1-azadienes which are part of six or higher-membered rings undergo the classical four electrons electrocyclic closure under irradiation,[1] and, among the few cases with acyclic 1-azadienes are found *cis-trans* or *syn-anti* isomerizations,[2] and three examples of the photo-cyclization of derivatives (N-hydroxy,[3] N-acyloxy[4] and N-acyl[5]). In addition, despite the high versatility of 3-amino-2-alkenimines **1** in synthetic procedures,[6] their photochemical behavior has not been investigated. These facts prompted us to study the photochemistry of **1**.

We have found that compounds **1** are photochemically actives and yield substituted quinolines **2** under irradiation (Scheme 1). Based on ultraviolet absorption data (tetrahydrofuran: λ=190–220 nm, and 340-360 nm: $\varepsilon \approx 50000$, and 15000, respectively), irradiation of a 10^{-2} M solution of **1** using a medium-pressure mercury lamp without filter (through quartz) leads to the formation of **2** as elucidated from their spectroscopic data (^{1}H and ^{13}C NMR, and IR) and mass spectrometry. Table 1 shows the synthesized substituted quinolines **2**.



Scheme 1

Ultraviolet irradiation through Pyrex glass (which removes λ radiation under 300 nm) gives the same results but with increased reaction times due to energy loss because of glass absorption. So, the active band in the photochemically induced cyclization is a $\pi \rightarrow \pi^*$ electronic transition (λ≈350 nm). Furthermore, if we take into account that the results are regardless of the solvent (methanol, diethyl ether, toluene) it can be proposed that reaction occurs through a six-electron electrocyclic process as shown in scheme 2. This mechanism is related to other electrocyclizations of imines described in the literature.[7] In order to confirm this mechanism, we have acylated the **1a** imine group with benzoyl chloride in pyridine,[8] and essayed its photochemistry. Irradiation of N-benzoylated **1a** yields quinoline **2a** and benzamide, the latter as a result of the aromatization (scheme 2).



Scheme 2

On the other hand, despite the large number of syntheses of quinoline derivatives which are reported,[9] because of their pharmacological properties,[10] except for two compounds, **2a** and **2b**,[11] none of the quinolines synthesized in this work were previously described. This means that our methodology allows to obtain unusal substituted derivatives. Special attention must be paid to compounds bearing an unsaturated group, **2h** and **2i**, where the mildness of the reaction conditions makes possible the presence of different functionalities.

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Table 1. Quinolines **2** Obtained from Azadienes **1** in THF

Azadiene[a] 1	R^1	R^2	R^3	R^4	t (h)[b]	R^5	Quinoline 2	Yield (%)[c]
1a	4-CH_3-C_6H_4	C_6H_5	CH_3	C_6H_5	52	6-CH_3	**2a**	91
1b	4-CH_3-C_6H_4	C_6H_5	CH_3	4-CH_3-C_6H_4	58	6-CH_3	**2b**	74
1c	C_6H_5	C_6H_5	CH_3	4-Cl-C_6H_4	40	H	**2c**	89
1d	C_6H_5	4-Cl-C_6H_5	CH_3	C_6H_5	38	H	**2d**	82
1e	2-CH_3-C_6H_4	C_6H_5	CH_3	C_6H_5	32	8-CH_3	**2e**	95
1f	3-CH_3-C_6H_4	C_6H_5	CH_3	C_6H_5	30	7-/5-CH_3	**2f/2f'**	94(15/1)[d]
1g	4-CH_3-C_6H_4	C_6H_5	C_2H_5	*c*-C_6H_{11}	58	6-CH_3	**2g**	39
1h	4-CH_3-C_6H_4	C_6H_5	CH_2=CH-CH_2	C_6H_5	48	6-CH_3	**2h**	36
1i	4-CH_3-C_6H_4	C_6H_5	HC≡C-CH_2	C_6H_5	45	6-CH_3	**2i**	32
1j	4-CH_3-C_6H_4	C_6H_5	C_6H_5-CH_2	C_6H_5	40	6-CH_3	**2j**	33

a. **1a**-**1g** synthesized according to reference 12, and **1h**-**1j** according to reference 8.

b. Irradiation time through quartz, for 1 mmol of azadiene **1**.

c. Yield of isolated products, relative to starting **1** and not optimized. The products were purified by column chromatography (silica, hexane-ether 3:1) and recrystallized (hexane-THF 5:1).

d. Isomers ratios, determined by ^1H NMR spectra of the crude reaction.

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13. Typical experimental procedure.

    A solution of 3-amino-2-alkenimine **1** (1 mmol) in anhydrous tetrahydrofurane (50 ml) was irradiated, at room temperature under argon atmosphere, using a medium-pressure mercury lamp (125 w) until the complete extinction of starting product (followed by ^{1}H NMR, see Table 1). The solution was evaporated under reduced pressure and the resulting quinoline **2** was purified by column chromatography (silica, hexane-ether 3:1) and recrystallized (hexane-THF 5:1).

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