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PHOTOCHEMICAL SYNTHESIS OF 2-PHENYLPYRROLES BY THE CYCLIZATION OF β-AMINOVINYL KETONES[1]

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On irradiation, β-aminovinyl phenyl ketones (1) having such substituents as CH_3, OCH_3, and Cl on the phenyl ring cyclize to give pyrrole derivatives (2), except β-aminovinyl ρ-biphenyl ketone (1h). Also exocyclic β-aminovinyl ketone (3 and 4) are inert. The photochemical behavior of (1) is discussed in relation with that of aryl alkyl ketone.

In spite of the facts that the photochemical reactions of conjugated enones and dienones have extensively been investigated,[2] those of β-aminovinyl ketones have been little known.[3] Recently, we reported that β-N,N-dialkylaminovinyl phenyl ketones gave pyrrole derivatives via δ-hydrogen abstraction by an excited carbonyl on irradiation.[1] We now wish to report the photochemical reactions of some β-aminovinyl phenyl ketones (1) having various substituents on the phenyl ring and related compounds, (3 and 4) in order to provide the scope and limitation of this reaction.

In a typical experimental, a solution of (1b)[4] (400 mg) in dry benzene (40 ml) was irradiated in a Pyrex tube through a high pressure mercury lamp under nitrogen for 30 hr at room temperature. After removal of the solvent, the residual oil was chromatographed on a silica gel column. Elution with benzene yielded the pyrrole (2b)[5] (50 mg, 12.5%) [ν_{max}^{film} 3080, 1600, 1520, 820, and 750 cm^{-1}; $\delta(CDCl_3)$ 1.17 (t, 3H, $-CH_2C\underline{H}_3$), 2.28 (s, 3H, 5-$C\underline{H}_3$ or ρ-$C\underline{H}_3$), 2.38 (s, 3H, ρ-$C\underline{H}_3$ or 5-$C\underline{H}_3$), 3.38 (q, 2H, $-C\underline{H}_2CH_3$), 5.82 (d, 1H, J=2.5 Hz, H-3 or H-4), 5.96 (d, 1H, J=2.5 Hz, H-4 or H-3), and 7.13 (s, 4H, phenyl); m/e 199 (M^+)]. Likewise, the other β-aminovinyl phenyl ketones (1c-1f) gave the corresponding cyclized products (2c-2f). However, 1g and 1h did not afford the pyrroles and were recovered almost quantitatively. Exocyclic β-aminovinyl ketones (3 and 4) also did not give the cyclized products.[6] These results are summarized in Table 1

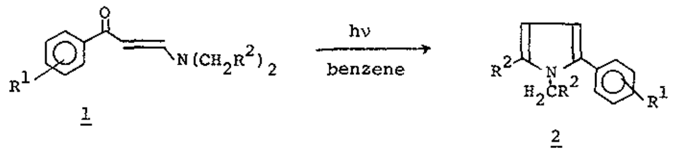
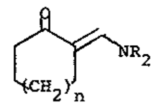


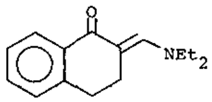
Table 1. Photoproducts from 1.

	R^1	R^2	Yield (%)
1a	H	Me	40
1b	ρ-Me	Me	12.5
1c	m-OMe	H	10
1d	m-OMe	Me	12.5
1e	ρ-OMe	Me	12
1f	ρ-Cl	Me	20
1g	ρ-OMe	H	-
1h*	ρ-Ph	Me	-

*1h was irradiated in benzene-methanol solution (3:2) because it was insoluble in benzene.



3 a n=0 R=Me
b n=1 R=Me
c n=1 R=Et



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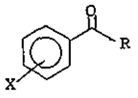
It is generally accepted that the Norrish type II reaction of aryl alkyl ketone (5) proceeds via the excited carbonyl followed by a biradical intermediates upon γ-hydrogen abstraction.[7] By analogy, the intermediacy of such a biradical (6) can be assumed also in the above reaction.



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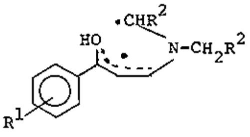

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The results from the photoreaction of β-aminovinyl phenyl ketones (1)[1,8] as shown in Table 1 seem to be compatible with this assumption because the substituent R^1 must have a direct effect on the excited carbonyl of 1.

It is well known that n,π^* triplet and π,π^* triplet states of aryl alkyl ketone lie close together and mix vibronically and that the relative energy levels of the two states are sensitive to the substituent X.[7] All these ketones with π,π^* lowest triplets show substantially reduced reactivity in intramolecular hydrogen abstraction. The inertness of 1h in the photocyclization can be explained in terms of the similar reasons, while that of 1g is not clear at present. The inertness of exocyclic β-aminovinyl ketones (3 and 4) is also explained by the differences of the excited states by analogy of those of the α,β-unsaturated ketones.[9] These photochemical reaction may be useful for the synthesis of 2-phenylpyrrole derivatives.

References and Footnotes

1. Part I of this series; H. Aoyama, T. Nishio, Y. Hirabayashi, T. Hasegawa, H. Noda, and N. Sugiyama, J. Chem. Soc. (Pekin I), 1975, 298.
2. A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry", Interscience, New York, 1969, p.232.
3. C. Kashima, M. Yamamoto, Y. Sato, and N. Sugiyama, Bull. Chem. Soc. Japan, 1969, **42**, 3596.
   K. Yamada, T. Konakahara, and H. Iida, ibid., 1973, **46**, 2504.
4. G. Jammaer, H. Martens, and G. Hoornaert, Tetrahedron, 1975, **31**, 2293.
5. No other products could be detected except stating material by tlc inspection.
6. The NMR spectrum of the photolysate of 3c in C_6D_6 (cyclohexane as internal standard) showed cis-trans isomerization on C=C double bond. Upon prolonged irradiation, polymerization of the products took place.

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A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashyan, *J. Amer. Chem. Soc.*, 1971, **93**, 6998.

8. The Mechanism for the formation of pyrrole (*2a*) from *1a* was explained in reference 1.

9. N. C. Yang and J. Jorgenson, *Tetrahedron letters*, 1964, 1203.

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