Photochemical Reactions of Phenyl β-Aminovinyl Ketones

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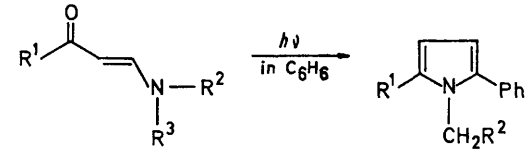
Summary Photochemical cyclization of phenyl β-dialkylaminovinyl ketones (Ia—d) to pyrroles (IIa—e), and related reactions are reported.

PHOTOCHEMICAL reactions of conjugated enones have been widely studied.[1] However, those of β-aminovinyl ketones have received little attention.[2] We report here on photochemical reactions of phenyl β-aminovinyl ketones (Ia—g) and related compounds.

When a benzene solution of (Ia) was irradiated in a Pyrex vessel with a high-pressure mercury lamp, 1-methyl-2-phenylpyrrole (IIa) was obtained (37%). Irradiation of (Ib) and (Ic) under the same conditions gave the corresponding pyrroles (IIb) (40%) and (IIc) (41%), respectively,

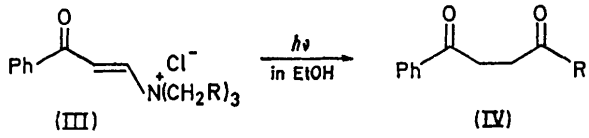


(I) (II)

a; R^1=Ph, R^2=R^3=Me
b; R^1=Ph, R^2=R^3=Et
c; R^1=Ph, R^2=R^3=Pr^n
d; R^1=Ph, R^2=Me, R^3=Et
e; R^1=Ph, R^2, R^3=$-[CH_2]_4-$
f; R^1=Ph, R^2, R^3=$-[CH_2]_2-O-[CH_2]_2-$
g; R^1=Ph, R^2=R^3=CH_2Ph
h R^1=Me, R^2=R^3=Et

a; R^1=R^2=H
b; R^1=R^2=Me
c; R^1=R^2=Et
d; R^1=H, R^2=Me
e; R^1=Me, R^2=H

while (Id) gave a 3:1 mixture of (IId) and (IIe) (combined yield 27%). On the other hand, (Ie—h) did not yield the corresponding pyrroles under the same conditions.

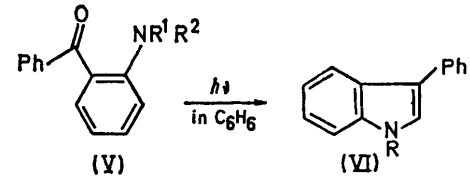


(III) (IV)

a; R = Me a; R = Me
b; R = Et b; R = Et

Irradiation of the quaternary ammonium salts (IIIa) and (IIIb) gave the 1,4-diketones (IVa) (10%) and (IVb) (11%), respectively.

Photochemical reactions of *o*-dimethylaminobenzophenone (Va) and *o*-methylethylaminobenzophenone (Vb) were studied in relation to those of (Ia—d).[3] Irradiation of (Va) yielded 1-methyl-3-phenylindole (VIa) (10%) and *o*-methylaminobenzophenone (a dealkylation product) (5%). Irradiation of (Vb) gave 1-ethyl-3-phenylindole (VIb) (4%), *o*-methylaminobenzophenone (13%), and *o*-ethylaminobenzophenone (11%).



(V) (VI)

+

dealkylation products

a; R^1 = R^2 = Me a; R = Me
b; R^1 = Et, R^2 = Me b; R = Et

The structures of (IIa),[4] (IVa),[5] and (VIa)[6] were confirmed by direct comparison with authentic samples and those of the other photo-products were elucidated using spectral data (i.r. and n.m.r.) and elemental analyses.

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