**A PHOTOCHEMISTRY OF 1-(1-PHENYLVINYL)-3,4-DIHYDROISOQUINOLINE**

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**Abstract** — Irradiation of the 1-(1-phenylvinyl)-3,4-dihydroisoquinoline (2) in benzene in the presence of xanthone gave the spirobenzylisoquinoline (4) in low yield. On the other hand, irradiation of 2-hydrochloride in alcohol solvent (methanol, ethanol, and iso-propanol) afforded the hydroxyalkylated product (10), (13), and (14) in moderate yield, respectively.

In a previous paper, we reported preparation of the spirobenzylisoquinoline (2) from the 1-α-toluoyl-3,4-dihydroisoquinoline (1) by photochemical reaction. However, the isolated yield of 2 was low.\(^1\) The Norrish type II split of the photoproduct (2) may occur as a secondary reaction.\(^2,3\) We thought that the photochemical reaction of the 1-(1-phenylvinyl)-3,4-dihydroisoquinoline (2) might yield the spirobenzylisoquinoline (4) without the Norrish type II split. Then we examined the photochemical reaction of 2. We wish to describe the conversion of 2 to 4 and the preparation of the hydroxyalkylated products which were encountered during the course of our studies.

\[\text{MeO} \quad \text{MeO} \quad \text{X} = \text{O} \quad \text{MeO} \quad \text{MeO} \quad \text{X} = \text{CH}_2\]

\[\text{hv} \quad \rightarrow \quad \text{MeO} \quad \text{MeO} \quad \text{X} = \text{O} \quad \text{MeO} \quad \text{MeO} \quad \text{X} = \text{CH}_2\]

Scheme 1
The 1-(1-phenylvinyl)-3,4-dihydroisoquinoline (3) was prepared from the corresponding phenylacetic acid (5). Treatment of 5 with 2 equiv. of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) containing hexamethylphosphoric triamide (HMPA) followed by bubbling of formaldehyde gas gave the 2-(hydroxymethyl)phenylacetic acid (6) in 73% yield. Dehydration of 6 was effected by treatment with methanesulfonyl chloride in 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) to give the 2-(methylene)phenylacetic acid (7) in 52% yield. The acid (7) was converted to the corresponding amide (8) in 56% yield on treatment with oxalyl chloride followed by (3,4-dimethoxyphenyl)ethylamine. Cyclisation of 8 was carried out by heating with phosphorus oxychloride (2 equiv.) in benzene for 2 h to yield 3 as its hydrochloride in 86% yield.

![Scheme 2](image)

Irradiation of 3 with 200 watt high pressure mercury lamp using a vycol filter in benzene in the presence of xanthone at 10°C for 25 h gave the spirobenzylisoquinoline (4) in 6% yield und unknown reaction mixture. The structure of 4 was established by comparison with the spectral data of analogous compounds. Although the photochemical reaction of 3 was examined under many conditions, we could not get over 6% yield of 4. Next, the photochemical reaction of 3-hydrochloride in alcohol was carried out. Irradiation of 3-hydrochloride with the same mercury lamp in methanol at 10°C for 25 h gave the hydroxymethylated product (10) and the reduced product (9) in 29% and 6% yield, respectively. The starting material was recovered in 9% yield. The structure of 10 was identified by an alternative synthesis starting from the 1-benzylisoquinoline (11). 10 was converted to the
benzindolizine (12) as a stereoisomeric mixture in 72% yield by treatment of methanesulfonyl chloride in pyridine followed by sodium borohydride reduction. Furthermore, we undertook the photochemical reaction of 3-hydrochloride in ethanol and iso-propanol. Irradiation of 3-hydrochloride in ethanol for 25 h gave 13 and 9 in 20% and 8% yield, respectively. In iso-propanol, irradiation of 3-hydrochloride afforded 14 in 61% yield.

We are continuing to explore mechanistic details of this photoreaction and application to other simpler 1-aza-1,3-diene compounds.

REFERENCE AND NOTES

4. All new compounds gave satisfactory elemental analyses and mass spectroscopic data. Some selected characteristics are listed below.

\( \text{3-A} \)

- ir (Nujol) cm\(^{-1}\): 3400, 1655, 1605
- \(^{1}H\)-nmr (CDCl\(_{3}\)) \( \delta \): 2.11 (3H, s, ArCH\(_{3}\))
5.42 (1H, d, J=3 Hz, olefinic proton), 6.46 (1H, d, J=3 Hz, olefinic proton).

3: ir (CDCl₃) cm⁻¹ 1605; uv (MeOH) nm 315, 283; ¹H-nmr (CDCl₃) δ 2.21 (3H, s, ArCH₃), 2.65 (2H, t, J=7 Hz, C₄-H), 3.78 (2H, t, J=7 Hz, C₃-H), 5.61 (1H, d, J=2 Hz, olefinic proton), 5.87 (1H, d, J=2 Hz, olefinic proton).

4: ¹H-nmr (CDCl₃) δ 3.20 (3H, s, ArCH₂Cl), 4.80 (1H, s, olefinic proton), and 5.13 (1H, s, olefinic proton); 9: ir (CHCl₃) cm⁻¹ 1621; ¹H-nmr (CDCl₃) δ 1.46 (3H, d, J=7 Hz, CH₃CH₂Ar), 2.51 (3H, s, ArCH₃), 4.42 (1H, q, J=7 Hz, MeCH₂Ar).

11: ir (CHCl₃) cm⁻¹ 3200, 1622; ¹H-nmr (CDCl₃) δ 2.20 (2H, q, J=5 Hz, OCH₂CH₂-), 2.54 (3H, s, ArCH₃), 3.43-3.66 (2H, m, HOCH₂-), 4.68 (1H, t, J=5 Hz, methine proton).

12: ir (CHCl₃) cm⁻¹ 3200, 1620; ¹H-nmr (CDCl₃) δ 1.15 (3H, d, J=5 Hz, CH₂CH(OH)-), 2.56 (3H, s, ArCH₃), 3.68-3.80 (1H, m, MeCH₂OH), 4.80 (1H, t, J=4 Hz, CH₂CH₂Ar); 13: ir (CHCl₃) cm⁻¹ 3200, 1620; ¹H-nmr (CDCl₃) δ 1.27 and 1.30 (6H, each s, -CH₃), 2.53 (3H, s, CH₂Ar), 4.50 and 4.67 (1H, dd, J=3 and 7 Hz, methine proton).


6. Condensation of the 1-benzylisoquinoline (11) with 2-(2-bromoethoxy)tetrahydropyran using LDA in THF followed by acidic hydrolysis gave 10 in 90% yield.


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