PHOTODEHYDROXYLATION OF SOME 3-HYDROXYOXINDOLES[1]

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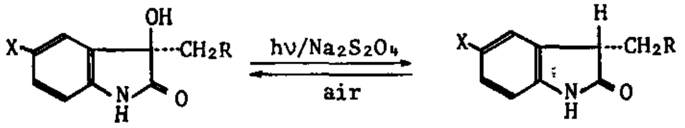
Photoreduction of 3-substituted 3-hydroxyoxindoles I-IV in the presence of sodium hydrosulfite led to loss of the 3-hydroxyl group. Irradiation at longer wavelengths (λ > 3000 Å) did not cause this photodehydroxylation.

While reduction of simple 3-hydroxyoxindoles usually gave the corresponding xindoles, 3-alkyl-3-hydroxyoxindoles sometimes produced the 3-alkylindoles together with the oxindoles.[2] Generalization on the reduction of the 3-hydroxyoxindoles was so far unknown. We now wish to report that irradiation of some 3-substituted 3-hydroxyoxindoles I-IV in aqueous solution in the presence of sodium hydrosulfite resulted in dehydroxylation of the 3-hydroxyl group (Scheme 1).

Scheme 1.

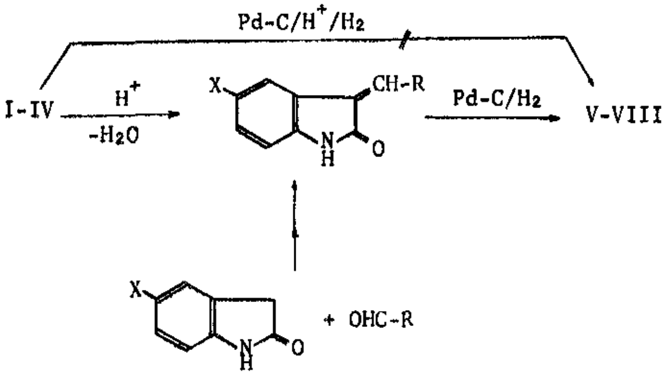


I: $R=COCH_3$, X=H
II: $R=C(NOH)CH_3$, X=H
III: R=Py, X=H
IV: R=Py, X=Cl

V: $R=COCH_3$, X=H
VI: $R=C(NOH)CH_3$, X=H
VII: R=Py, X=H
VIII: R=Py, X=Cl

In a typical run, a 10^{-2} M aqueous solution of 3-substituted 3-hydroxyoxindole in the presence of 10^{-1} M sodium hydrosulfite was irradiated at ambient temperature with a 450 W medium-pressure lamp (Ushio UM-452, 1.9 W at 2894 Å) equipped with a Vycor filter. After irradiation for 10 h, most of the starting material disappeared by monitoring silica gel thin-layer chromatography. Isolation by column chromatography gave a major photoproduct[3] (25-43% yield) which was confirmed to be 3-substituted oxindole (V-VIII) by direct comparison with an independently prepared sample in the following manner (Scheme 2).

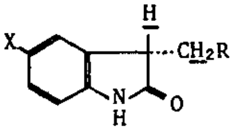
Scheme 2



Irradiation with light above 3000 Å did not cause dehydroxylation. Nmr data and melting points of these products were shown in Table I. The oxindole (V-VIII) was converted to the corresponding 3-hydroxyoxindole by aerial oxidation.[4] When sodium borohydride[5] was used in the place of sodium hydrosulfite, irradiation of the 3-hydroxyoxindole (I-IV) produced a mixture of several unidentified substances.

Addition of the low energy triplet-quencher such as biacetyl[6] gave no apparent effect on this photodehydration. A reasonable mechanism involve a reduced intermediate X *via* zwitterion IX as shown in Scheme 3.

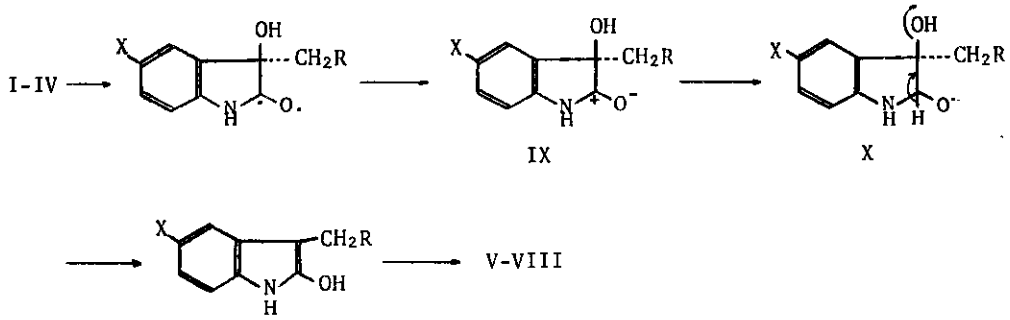
Table I*



	mp	δ_{CH}	$\delta_{C\underline{H}H}$	$\delta_{CH\underline{H}}$
V	99-101°	3.86 (q, J_1=4.2 Hz, J_2=8.2 Hz)	2.83 (q, J_1=8.2 Hz, J_2=17.5 Hz)	3.27 (q, J_1=4.2 Hz, J_2=17.5 Hz)
VI	175°(decomp.)	3.69 (q, J_1=4.7 Hz, J_2=8 Hz)	2.43 (q, J_1=8 Hz, J_2=15.3 Hz)	2.87 (q, J_1=4.7 Hz, J_2=15.3 Hz)
VII	130°	4.16 (q, J_1=5.2 Hz, J_2=9 Hz)	3.12 (q, J_1=9 Hz, J_2=15 Hz)	3.64 (q, J_1=5.2 Hz, J_2=15 Hz)
VIII	170-172°	4.15 (q, J_1=5 Hz, J_2=8.7 Hz)	3.08 (q, J_1=8.7 Hz, J_2=15 Hz)	3.60 (q, J_1=5 Hz, J_2=15 Hz)

* Nmr spectra were recorded on a Hitachi R-20 spectrometer (60 MHz) and the chemical shifts are in ppm from TMS.

Scheme 3



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3 All compounds gave satisfactory elemental analyses.

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