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PHOTOCHEMISTRY OF HETEROCYCLIC COMPOUNDS. III.[1] PHOTOCHEMICAL REACTION OF O-ACETYLINDOXYL

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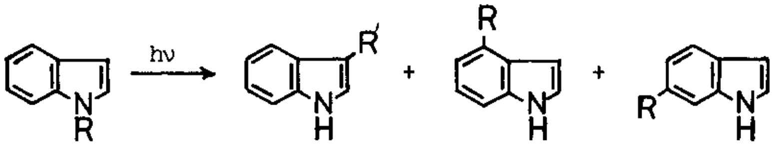
Irradiation of O-acetylindoxyl (I) in benzene solution by a high-pressure mercury lamp afforded indigo (II) and diacetyl (III), and no photo-Fries rearranged products were formed. Upon irradiation of I in the presence of excess benzophenone (IV), however, 2-diphenylmethyleneindolin-3-one (Va) was obtained as a predominant product. The pathways for the formation of II, III, and Va are discussed.

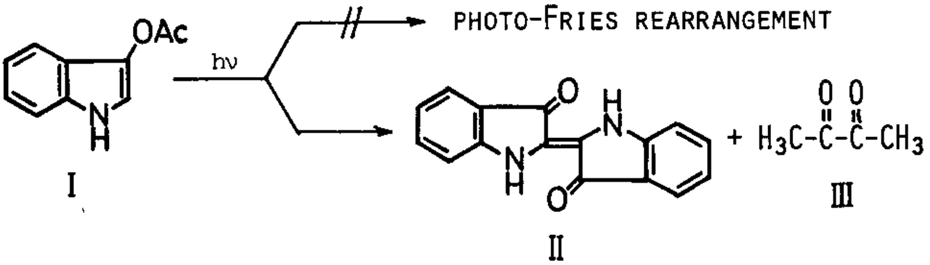
Since it has been reported by Anderson and Reese[2] as well as by Kobsa[3] that phenolate esters rearrange photochemically to yield a mixture of o- and p-hydroxyarylketones, a variety of aryl esters of carboxylic acids, vinyl esters, and N-arylamides were found to undergo analogous photo-Fries rearrangements.[4,5] However, little attention has been paid to the photo-Fries rearrangement of heteroaromatic esters of the type Het-OCOR (Het: heteroaromatic group). Recently, Somei and Natsume[6] reported the facile direct introduction of various kinds of side chain units into the 3-, 4-, and 6-positions of the indole ring by photo-Fries type rearrangement of 1-substituted indoles.



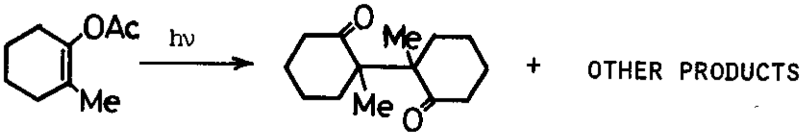
R=COOEt, COMe, CH_2Ph, $SO_2C_6H_4Me(p)$, OMe, OEt

We have undertaken an investigation of the photolysis of O-acetylindoxyl (I), analogous acetyl migration being expected to occur. In the present paper novel findings concerning photochemical reaction of I are described.

When a benzene solution of I (1.14×10^{-2} M/l) stirred by a stream of nitrogen, was irradiated by 300W high-pressure mercury lamp with a Pyrex filter for 2 h, indigo (II) and diacetyl (III) were formed in 25.4 and 23.3% yields along with resinous materials. The structure of II was confirmed by comparison of the spectral data with an authentic sample, and III was identified as its disemicarbazone. Upon irradiation of I in ethanol under similar conditions, however, resinous materials only formed. Thus, irradiation of I gave no photo-Fries rearranged products.

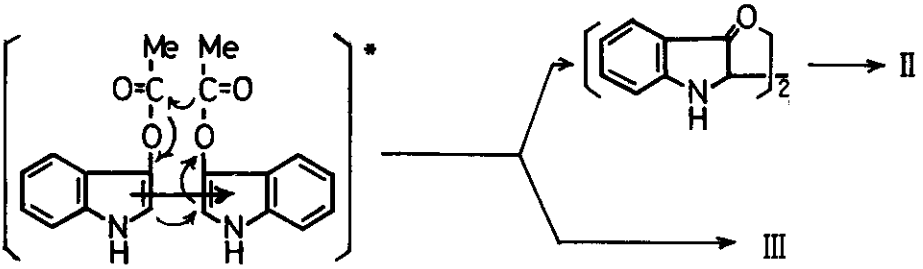


It has been reported that the photo-Fries rearrangement of aryl esters involves initial light-induced fission of the acyl-oxygen bond of the ester into a pair of acyl and phenoxy radicals in the solvent cage, which recombine to form the rearranged products.[3] In general, the phenoxy radical diffused from the cage abstracts hydrogen from the solvent to form a phenol, but the fate of the free acyl radical is not known. Yogev et al.[7] found that irradiation of 2-methylcyclohexenyl acetate afforded the dimeric ketone arising from the dimerization of free enolate radicals, in addition to the rearranged product and 2-methylcyclohexanone.



The formation of diacetyl (III) in the present photolysis is particularly noteworthy. On the basis of the view of Yogev et al.,[7] in the photolysis of I indigo (II) might be produced from leucoindigo which would be formed by the dimerization of free indoxyl radicals, but the formation of III could not be understood in terms of the dimerization of free acetyl radicals.[8]

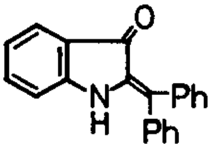
Although the exact pathway for the present photolysis is not clear, we postulate a possible one as follows: the reaction starts with the formation of an excimer, followed by a concerted dimerization-elimination process [$\pi2 + \pi2 + \sigma2 + \sigma2$] to yield leucoindigo which is easily transformed into indigo (II), and diacetyl (III). The postulated pathway seemed to be supported by the formation of II and III with almost equal yields.



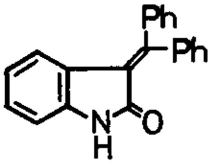
We found that I reacted with benzophenone (IV) upon irradiation. Irradiation of equimolar quantities of I and IV in benzene solution furnished a new product V [mp 196-197°C, red crystals] in 8% yield in addition to II (15% yield) and III (10% yield). When IV was employed in excess (I/IV =1/5 M/M), the compound V was obtained in 23.5% yield along with traces of II and III. The presence of IV seemed to suppress the formation of excimer.

The molecular formula of V agreed with that of a compound arising from a 1:1 adduct of I and IV by the elimination of acetic acid. The spectral data of V are as follows: ν_{max}^{KBr} 3300 (NH), 1670 (C=O), 1620 cm^{-1} (C=C); $\delta_{ppm}^{CDCl_3}$ 6.7 (1H, broad, N<u>H</u>, exchanged with D_2O), 6.8-7.7 (14H, m, aromatic protons); M^+ m/e 297. Treatment of V with 30% aqueous hydrogen peroxide in 10% ethanolic potassium hydroxide solution at room temperature afforded benzophenone in 90% yield; this indicates the presence of diphenylmethylene group in V.

On the basis of the above observations, either of two compounds, 2-diphenylmethyleneindolin-3-one (Va) or 3-diphenylmethyleneoxindole (Vb), is thought possible for the structure of V. However, the compound Vb could be excluded from the possible structure of V, because the compound V was different from the authentic sample of Vb [mp 240°C, yellow crystals].[9]

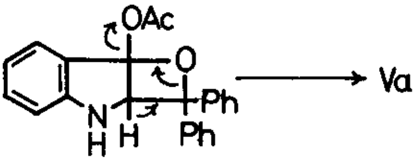


Va

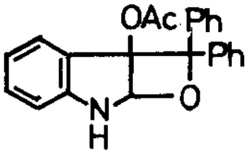


Vb

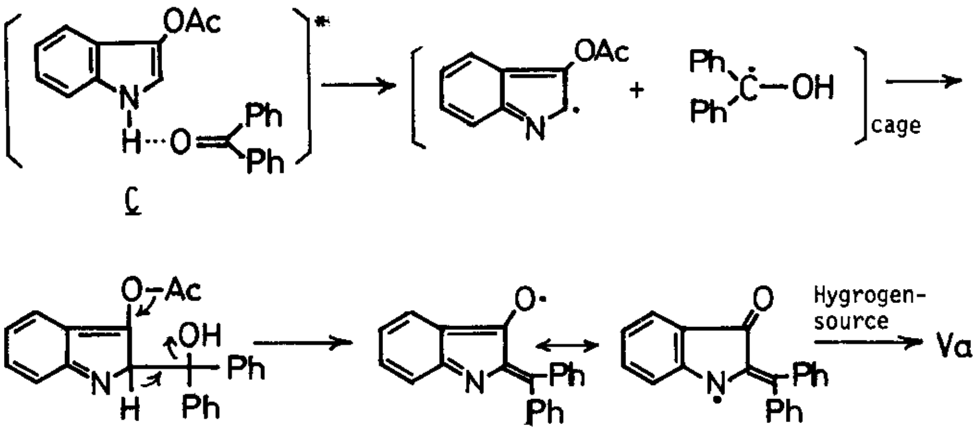
Recently, Julian and Tringham[10] reported that irradiation of IV in the presence of N-acylindoles afforded the corresponding tetrahydro-oxeto[2,3-b]-indoles, while indole did not react with IV upon irradiation. The lack of reactivity of indole may be caused by a quenching effect on the excited ketone by the non-bonded electrons on the nitrogen atom. Even if the pathway for giving Va proceeded <u>via</u> formation of an oxetane intermediate, the intermediate would be the oxeto[3,2-b]indole <u>A</u>, but not oxeto[2,3-b]indole <u>B</u>, and then Va would be given from A with the elimination of acetic acid. However, attempts to detect the formation of acetic acid were unsuccessful.



A



B



C

The mechanisms reported for novel photo-induced C-alkylations of heterocyclic compounds with alcohols[11] and alkanoic acids[12] seemed to be very informative for the present photochemical reaction. Although further study is under progress, we tentatively propose a potential pathway for the formation of Va proceeding via initial formation of an exciplex C, followed by formation of a pair of radicals in the solvent cage, as shown in the above scheme.

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8 It is known that oxidation of O-acetylindoxyl (I) with oxygen in basic solution affords indigo (II) *via* leucoindigo. However, leucoindigo is formed by the coupling reaction between indoxyl radical and indoxyl anion, but not by the coupling of indoxyl radicals. The formation of diacetyl (III) did not detect (G. A. Russell and G. Kaupp, *J. Amer. Chem. Soc.*, 1969, **91**, 3851).

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