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PHOTOLYSIS OF α-*N*-ALKYLANILINO-KETONES: FORMATION OF DI-INDOLYLMETHANES

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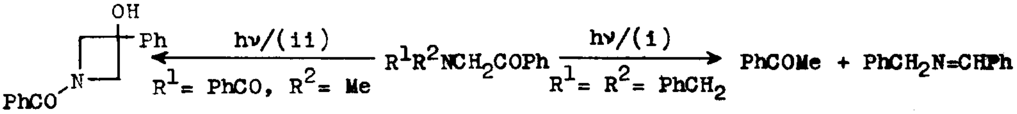
Ultraviolet irradiation of an α-*N*,*N*-dialkylamino-ketone resulted in Type II fission to yield an imine and a ketone [reaction (i)],[1] and an α-*N*-alkyl-*N*-acylamino-ketone was shown to yield an azetidinol [reaction (ii)].[2] With α-*N*-alkyl-*N*-arylamino-ketones (I), a Hofmann-Martius type rearrangement[3] is the major photoreaction. Experimental results also indicate the occurrence of a further photoreaction which may involve formation of an azetidinol.



Ultraviolet irradiation of *N*-alkylanilinoketones (Ia - c) in isopropanol, benzene, or methanol yielded the corresponding *N*-alkylaniline (IVa or b), and the products (IIa - c) and (IIIa - c) of a Hofmann-Martius type rearrangement. The latter, (III), are presumably formed by cyclodehydrogenation of the product of *ortho*-rearrangement.

Ketones (Ia) and (Ib) also gave di-indolylmethanes (Va) and (Vb) respectively. These products appear to be formed by a reaction of the indole (IIIa or b) with the corresponding ketone (Ia or b), the ketone being the source of the methylene bridge. Di-indolymethane (Va) was also formed when indole (IIIa) was irradiated in the presence of ketone (Ic). The experimental results are given in the Table.

Di-indolylmethane formation may be rationalised as shown in the scheme. Irradiation of ketone (I) leads to an azetidinol (VI) [path (a)] which, under the reaction conditions, undergoes ring-opening to give formaldehyde anil (VIII). This anil will be formed from each of the ketones (Ia - c) if bond fission always occurs between the nitrogen atom and that carbon atom which bears the substituent (if any).

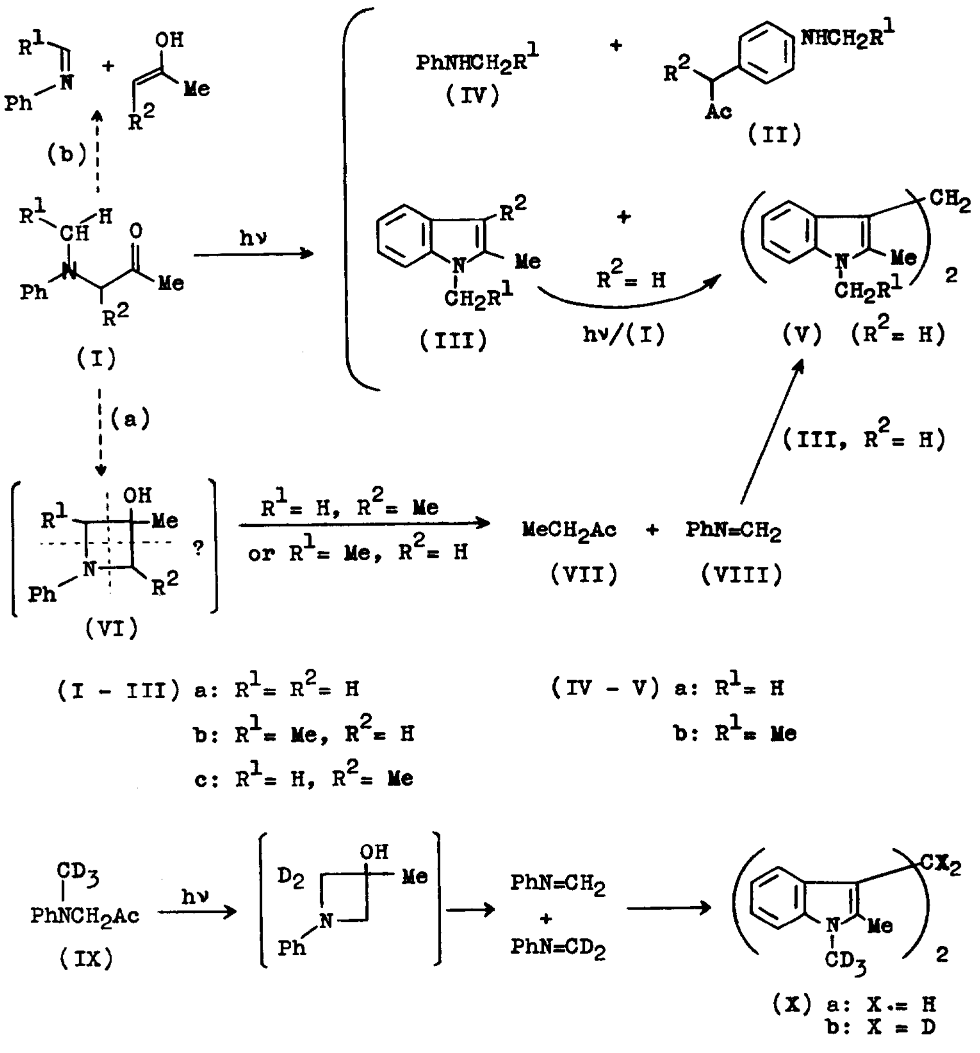
Table: Irradiation of α-N-Alkylanilino-ketones

Ketone	Reaction time (h)	Solvent	Products isolated, Yield (%)[a]
(Ia)	24	PhH	14.5 (IVa), 7 (IIa), 2 (IIIa), 7 (Va), 5 (AcMe)[b], 1.5 ($PhNH_2$)[c]
(Ib)	24	i-PrOH	13.5 (IVb), 19.5 (IIb), 22 (IIIb), 5 (Vb), 13 (AcMe)[b], 5.5 (VII)[b]
(Ib)	24	PhH	(IVb)[d], (IIb)[d], 15 (IIIb), 1.2 (Vb), 2.2 ($PhNH_2$)[c], 10 (AcMe)[e], 2 (VII)[e]
(Ic)	24	MeOH	4 (IVa), 24 (IIc), 41 (IIIc)
(Ic)	16	MeOH + (IIIa)[f]	(IVa)[d], (IIc)[d], 37 (IIIc), 90 (Va)[g]

[a] Irradiation of a ca. 1.5% solution of the ketone using a medium-pressure mercury-vapour lamp with pyrex filter. [b] Isolated as the 2,4-dinitrophenylhydrazone. [c] Isolated as s-diphenylthiourea. [d] Presence indicated by t.l.c., product not isolated. [e] Evidence and yield from g.l.c. of volatile products. [f] 0.1 g (IIIa) per 1 g (Ic). [g] Yield based on amount of (IIIa) used.

Reaction of indole (IIIa or b) with anil (VIII) should give the corresponding di-indolylmethane with aniline as a by-product. The related reaction of an indole with formaldehyde occurs readily.[4] Type II fission of ketones (Ia or c) [path (b)] would also yield anil (VIII), but

Scheme



(I - III) a: R^1= R^2= H
b: R^1= Me, R^2= H
c: R^1= H, R^2= Me

(IV - V) a: R^1= H
b: R^1= Me

similar fission of ketone (Ib) would yield the anil of acetaldehyde.

The isolation of 2-butanone (VII) and aniline, after irradiation of the anilinoacetone (Ib), lends support to the proposed reaction pathway. Further evidence was obtained by irradiating the deutero-ketone (IX). A mixture was formed of di-indolylmethanes (Xa) and (Xb) in the ratio (Xa)/(Xb) = ca. 55/45 [as shown from the mass spectrum of the product (X)], which is consistent with azetidinol formation and subsequent ring-opening [path (a)], but not with Type II fission [path (b)].

Anilinoketones (I) were prepared from the appropriate N-alkylaniline and α-bromoketone. All photoproducts were characterised satisfactorily.

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