Light-induced Reactions of 2-*N*-Alkyl-*N*-arylamino-cyclohexanones

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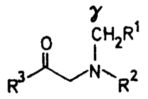
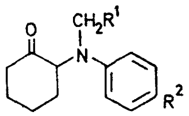
Summary Ultraviolet irradiation of 2-*N*-alkyl-*N*-arylamino-cyclohexanones yielded 1-arylcyclohexano[*b*]azetidin-3-ols (7-aryl-7-azabicyclo[4,2,0]octan-1-ols) as the major product.

α-DIALKYLAMINO-KETONES (I; R^2 = alkyl, R^3 = aryl) undergo type II fission on irradiation and it was suggested that the mechanism involved transfer of a non-bonding electron from nitrogen to oxygen.[1] The participation of such an electron transfer in the photoreduction of certain aryl ketones in the presence of amines was suggested earlier.[2] With less basic amino-ketone derivatives such as the ketosulphonamide[3] (I; R^2 = tosyl, R^3 = aryl) or an α-arylamino-ketone[4] (I; R^1 = alkyl or aryl, R^2 = aryl, R^3 = alkyl), transfer of a non-bonding electron from nitrogen is more difficult and in both cases different photochemical behaviour was observed. The ketosulphonamide underwent γ-hydrogen abstraction with subsequent cyclisation to an azetidinol whereas the arylamino-ketones gave products of fragmentation and rearrangement, although evidence for transient formation of azetidinols was presented.

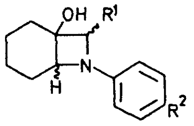
A further modification of photochemical behaviour was noted when alicyclic ketones were examined. A series of 2-*N*-alkyl-*N*-arylamino-cyclohexanones (IIa—e) and the 2-*N*-methylanilinocholestanone (V) were irradiated. In each case, the major reaction was formation of the corresponding cyclohexano[*b*]azetidinol (IIIa—e) and (VI), respectively (see Table). Direct fission of the α-carbon–nitrogen bond presumably occurs to a small extent since, in most cases, the secondary amine $p\text{-R}^2\text{C}_6\text{H}_4\text{NHCH}_2\text{R}^1$ was isolated in low yield. The tetrahydrocarbazoles (IV) which were also isolated ($\leqslant$10% yield) are probably photoproducts but in some cases they were also formed by cyclodehydration of the starting material (II) during work-up. A further product, 2-anilinocyclohexanol,† was obtained on irradiation of the *N*-ethyl- and *N*-2-phenylethyl-anilinocyclohexanones (IIc) and (IId), respectively (see Table). The structures of all products were consistent with their i.r., n.m.r., and mass spectra and satisfactory analyses were obtained for the azetidinols and other new compounds.



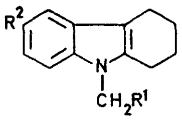
(I)



(II)

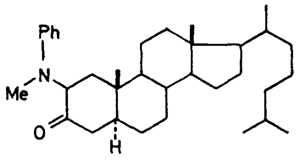


(III)

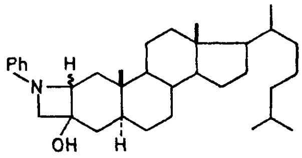


(IV)

(II)-(IV)
a ; R^1 = R^2 = H
b ; R^1 = H, R^2 = Me
c ; R^1 = Me, R^2 = H
d ; R^1 = PhCH_2, R^2 = H
e ; R^1 = Ph, R^2 = H



(V)



(VI)

TABLE

Arylaminoketone	Solvent	Reaction time (h)	Yield (%)[a] Azetidinol	2-Anilinocyclohexanol
(IIa)	MeOH	24	26 (38)	
(IIa)	Et_2O	20	33	
(IIb)	Et_2O	22	38 (58)	
(IIc)	Et_2O	22	18 (40)[b]	8 (18)
(IId)	MeOH	20	9 (39)[b]	5 (22)
(IIe)	Et_2O	19	30 (58)[b]	
(V)	Et_2O	4·7	38 (43)	

[a] Irradiation using a medium-pressure mercury-vapour lamp (type Q 81, Quarzlampen GMBH Hanau) and Pyrex filter. The yield based on the amount of starting material consumed is given in parentheses. [b] The product was obtained as an oil, presumably a mixture of diastereoisomers.

These results confirm the significance of the basicity of the amino group (or degree of delocalisation of the nitrogen non-bonding electron pair) in the photoreactions of α-amino-ketones and also show that the presence of the alicyclic ring has a marked influence on the course of the photoreaction of α-arylamino-ketones. The photoreaction of 2-arylamino-cyclohexanones is further of interest as a synthetic method as it provides a convenient route to systems containing an *N*-aryl-substituted azetidine ring. With the exception of β-lactams, *N*-arylazetidines are difficult to prepare in reasonable yield by other methods.

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† Evidence for the mode of formation of this product will be presented at a later date.

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