

Light-Induced Reactions of α -*N*-Alkylanilino-ketones: Formation of Di-indolylmethanes

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Irradiation of α -*N*-alkylanilino-ketones, $\text{PhN}(\text{CH}_2\text{R}^1)\cdot\text{CHR}^2\cdot\text{COMe}$ (R^1 and/or $\text{R}^2 = \text{H, Me, or Ph}$), in methanol, propan-2-ol, or benzene caused fission of the α -carbon–nitrogen bond to give a secondary amine ($\text{PhNH}\cdot\text{CH}_2\text{R}^1$), a ketone ($\text{R}^2\text{CH}_2\cdot\text{COMe}$), an α -[*p*-(alkylamino)phenyl] ketone formed by *para*-rearrangement, and a substituted 2-methylindole formed by *ortho*-rearrangement with subsequent cyclodehydration. *N*-Alkylanilinoacetones, $\text{PhN}\cdot\text{CH}_2\text{R}\cdot\text{CH}_2\cdot\text{COMe}$, also yielded a di-indol-3-ylmethane derived from the 2-methylindole. Di-indolylmethanes were also formed when anilino-ketones $\text{PhN}(\text{CH}_2\text{R}^1)\cdot\text{CHR}^2\cdot\text{COMe}$ were irradiated together with 1,2-dimethylindole. The mode of formation of di-indolylmethanes was studied and 1-phenylazetidins are suggested as labile intermediates. Other anilino-ketones $\text{PhNR}^1\cdot\text{CH}_2\cdot\text{COR}^2$ ($\text{R}^1 = \text{H, Me, or Bu}^t$; $\text{R}^2 = \text{Me, Et, Bu}^t, \text{ or Ph}$) were also irradiated.

IRRADIATION of α -*N*-alkylanilino-ketones (I) in methanol, benzene, or propan-2-ol, with a medium-pressure mercury-vapour lamp and a Pyrex filter, gave a mixture of products (see Table 1).[†] In all cases, the secondary amine (II) was formed, together with the indole (IV) and the amino-ketone (III) which are products of *ortho*- and *para*-rearrangement of the Hofmann–Martius type. The indole (IV) presumably results from cyclodehydration of the product (VIII) of *ortho*-rearrangement. A light-induced Hofmann–Martius rearrangement of *N*-benzylanilines was described recently.¹

The anilino-acetones (I; $\text{R}^2 = \text{H}$) yielded a further product, the di-indolylmethane (V), which is formed from the indole (IV). In these cases, the yield of indole

[†] For a preliminary report, see J. Hill and J. Townend, *Tetrahedron Letters*, 1970, 4607.

¹ Y. Ogata and K. Takagi, *J. Org. Chem.*, 1970, **35**, 1642.

was low compared with that from anilino-ketones (I; $\text{R}^2 = \text{Me or Ph}$) which cannot yield di-indolylmethanes.

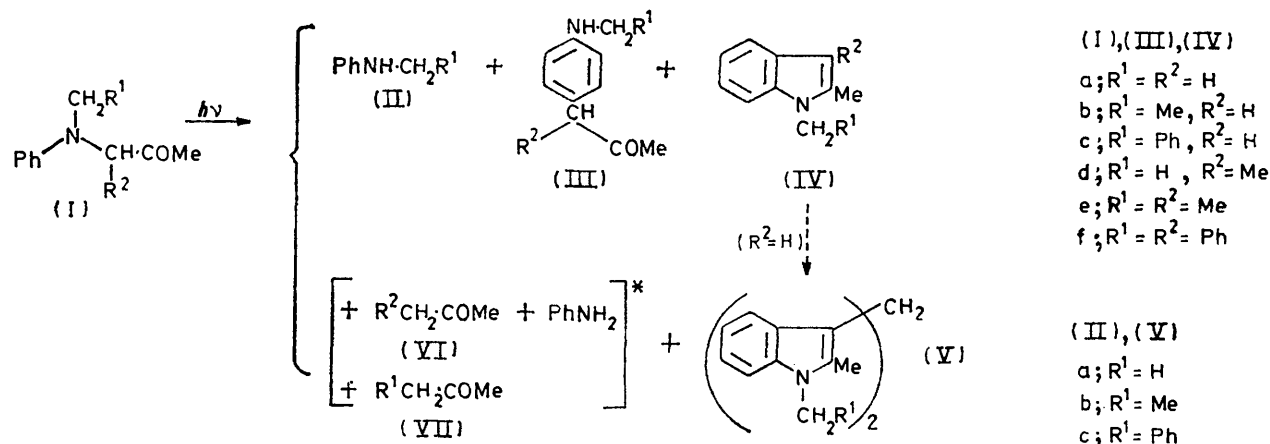
The volatile ketones (VI) and (VII) (the same compound, where $\text{R}^1 = \text{R}^2$) were normally lost during evaporation of the solvent, but their detection (g.l.c.) and/or isolation as 2,4-dinitrophenylhydrazones was carried out in specific experiments. Similarly, aniline was not detected during the usual work-up, but it was shown to be present (isolated as *sym*-diphenylthiourea) in two typical reactions.

Rearrangement of α -N-Alkylanilino-ketones.—Formation of products (II)–(VI) requires fission of the α -carbon–nitrogen bond of structure (I). This may occur as direct fission [path (i)] of an excited form of (I) to give species (IX) and (X), probably radicals ($\ast = \cdot$), which recombine to yield products (III) and (IV) or abstract hydrogen to yield (II) and (VI). Photorearrangement of

TABLE I
Irradiation of α -*N*-alkylanilino-ketones

Anilino-ketone	Solvent	Reaction time (h)	Yield (%) ^a				Other products ^b	
			<i>N</i> -Alkyl-aniline	<i>ortho</i> (indole)	<i>para</i>	Di-indolyl-methane		
(Ia)	MeOH	30	14.5 (IIa)	2 (IVa)	15 (IIIa)	11 (Va)	3 (PhNH ₂) 15 (VI; R ² = H) ^c	
(Ia)	Pr ⁱ OH	20	4.3 (IIa)	2.3 (IVa)	5 (IIIa)	15 (Va)		
(Ia)	Bu ^t OH	24	3 (IIa)	1 (IVa)	4 (IIIa)	11 (Va)		
(Ia)	PhH	24	15 (IIa)	1.8 (IVa)	7 (IIIa)	7 (Va)		
(Ia)	Et ₂ O	24	16 (IIa)	Trace (IVa)	2.5 (IIIa)	1.5 (Va)		
(Ia)	0.2% Et ₂ NH-MeOH	30	16 (IIa)	3 (IVa)	11 (IIIa)	12 (Va)		
(Ia)	0.2M-HCl-MeOH	24	27 (IIa)			70 (Ia)		
(Ib)	MeOH	24	11 (IIb)	4.7 (IVb)	16 (IIIb)	5 (Vb)		13 (VI; R ² = H), ^c 5 (VII; R ¹ = Me) ^e
(Ib)	Pr ⁱ OH	24	14 (IIb)	22 (IVb)	12 (IIIb)	5 (Vb)		
(Ib)	PhH	24	<i>d</i>	15 (IVb)	<i>d</i>	1.2 (Vb)		(VI; R ² = H), ^c (VII; R ¹ = Me), ^e 2.5 (PhNH ₂) ^c
(Ib)	0.2M-HCl-MeOH	24	29 (IIb)				65 (Ib), 24 (VI; R ² = H) ^c	
(Ic)	MeOH	24	14 (IIc)	6 (IVc)	9 (IIIc)	3.8 (Vc)	3.8 (VII; R ¹ = Ph) ^c	
(Id)	MeOH	24	4 (IIa)	41 (IVd)	24 (IIIId) ^f			
(Ie)	MeOH	24	14 (IIb)	44 (IVe)	27 (IIIe)			
(Ie)	Pr ⁱ OH	25	3.2 (IIb)	58 (IVe)	9 (IIIe)			
(If)	Pr ⁱ OH	28	25 (IIc)	15 (IVf)	12 (IIIf)			
(XIIb)	MeOH	24	4 (IIa)		5 (XVI)		70 (XIIb), 22 (XIV), 2.4 (XV)	
(XIIc)	MeOH	20	1.5 (IIa)	3 (XIIIa)			82 (XIIc), 5 (MeCOBu ^t) ^c	
(XIIc)	MeOH	46	3 (IIa)	6 (XIIIa)			71 (XIIc)	
(XIIId)	Pr ⁱ OH	24	1 (PhNHBu ^t)	5 (XIIIb)			85 (XIIId)	
(XIIe)	MeOH	30					70 (XIIe) + complex mixture	
(XIIIf)	MeOH	24	5 (IIa)				90 (XIIIf)	
(XIIg)	MeOH	24					75 (XIIg), 2 (PhNH ₂), 10 (XI; R ¹ = Ph)	

^a In all cases some starting material remained. Irradiation with a high-pressure mercury-vapour lamp and Pyrex filter. ^b Volatile products (ketones) not isolated in most experiments. ^c Isolated as the 2,4-dinitrophenylhydrazone. ^d Product not isolated. ^e G.l.c. analysis. ^f Evidence for structure from n.m.r. and i.r. spectra and t.l.c. only.



* Not isolated in all cases

related α -aryloxy-ketones² and similar aryl alkyl ethers,³ or of *N*-benzylanilines,¹ is believed to proceed *via* recombination of radical pairs, although in general the intermediacy of radicals does not appear to have been rigorously proven.

² J. R. Collier, M. K. M. Dirania, and J. Hill, *J. Chem. Soc. (C)*, 1970, 155; Y. Saburi, T. Yoshimoto, and K. Minami, *Nippon Kagaku Zasshi*, 1967, **88**, 1326; 1968, **89**, 1248.

³ D. P. Kelly, J. T. Pinhey, and R. D. G. Rigby, *Austral. J. Chem.*, 1969, **22**, 977, and references therein.

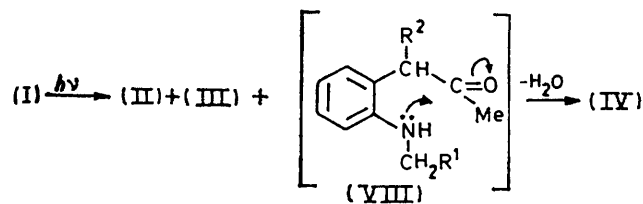
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An alternative mode for fission of structure (I) is type II cleavage [path (ii)], which is a typical reaction of ketones, particularly of aryl ketones.⁴ Type II cleavage was reported for ω -(dibenzylamino)acetophenones,⁵ and was also found to occur on irradiation of ω -(*N*-benzylanilino)acetophenone (XIIg), which gave acetophenone

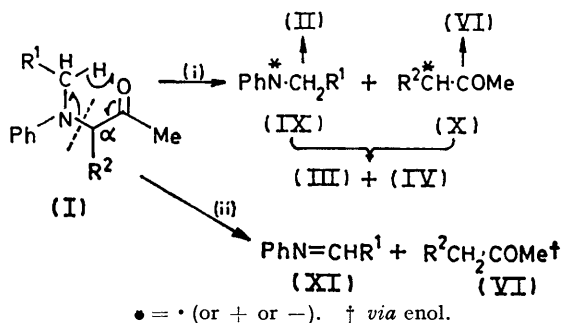
⁴ J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, p. 382.

⁵ A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, 1969, **91**, 1857.

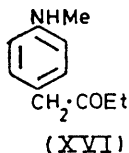
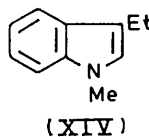
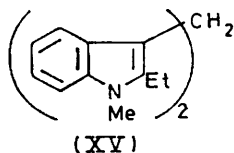
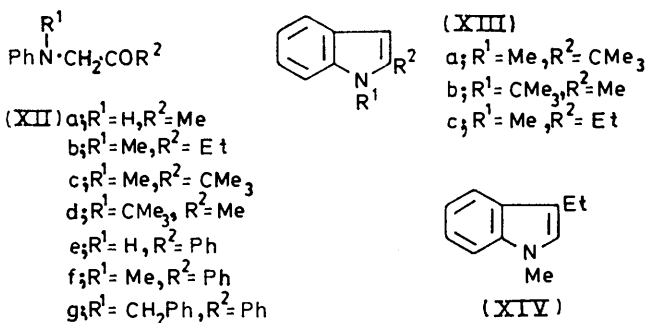
and benzylideneaniline (XI; $R^1 = \text{Ph}$) but no products of rearrangement. However, although photoreduction of anil (XI) to amine (II) appears feasible, cleavage



products (XI) and (VI) are not likely to recombine to form the products of rearrangement. As a test for such a possibility, benzylideneaniline (XI; $R^1 = \text{Ph}$) and



acetone (VI; $R^2 = \text{H}$), type II cleavage products of anilino-ketone (Ic), were irradiated in methanol. No change was observed other than slight decomposition of the anil with formation of aniline, which also occurred in the absence of light.



Although type II cleavage does not appear to play a significant part in the photoreactions of anilino-ketones (I), anilino-ketones (XIIa) and (XIIc), which cannot undergo such a process, are far more stable to irradiation. Anilinoacetone (XIIa) was recovered in almost quantitative yield after irradiation in methanol, propan-2-ol, or

benzene. Irradiation of *N*-*t*-butylanilinoacetone (XIIc) gave some (5%) product of *ortho*-rearrangement (XIIb) but again the starting material was recovered in high yield (87%).

A change of the α -methyl group in the anilino-ketone (I) to a different alkyl or to an aryl group [*i.e.* R^2 in (XII)] had a marked effect on the photoreaction. Whereas the methyl ketones (I) yield indoles (IV) formed by rearrangement, irradiation of the ethyl ketone (XIIb) gave the indole (XIV), which is the expected product of thermal cyclisation without rearrangement. However, the expected photoproduct, the indole (XIIIc), appears to have been formed to some extent during the photoreaction, since the di-indolylmethane (XV) derived from (XIIIc) was isolated in low yield.

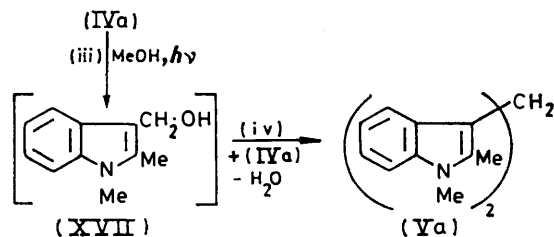
Only *N*-methylaniline (1.5%) and a small amount (3%) of the indole (XIIIa) were obtained on irradiation of the *t*-butyl ketone (XIIc). The phenyl ketones (XIIe) and (XII f) also behave differently to the methyl ketones (I) and no products, other than *N*-methylaniline from (XII f), could be isolated and characterised. ω -Anilinoacetophenone (XIIe) yielded a complex mixture and the *N*-methyl homologue (XII f) was largely unchanged after irradiation in methanol.

Normal behaviour was observed when the anilino-ketone (Ia) was irradiated in the presence of a stronger base (diethylamine). On irradiation of (Ia) in methanol containing enough hydrogen chloride to cause almost complete protonation (determined from u.v. spectrum), only *N*-methylaniline was isolated after evaporation of the solvent. Under similar acidic conditions, *N*-ethyl-anilinoacetone (Ib) yielded *N*-ethyl-aniline and acetone, whereas in the absence of acid, a further volatile product, butan-2-one, was also formed. Thus, in acid, the photoreaction appears to be restricted to simple cleavage.

Further aspects of the photorearrangement of anilino-ketones are being studied.

Di-indolylmethane Formation.—Anilino-ketones (Id—f; $R^2 \neq \text{H}$) cannot form di-indol-3-ylmethanes directly, since the indole photoproduct (IV) already possesses a 3-substituent. Thus, investigation of di-indolylmethane formation was carried out directly on the anilino-ketones (I; $R^2 = \text{H}$) and with indole (IVa) added to the reaction mixture in the case of the anilino-ketones (I; $R^2 \neq \text{H}$) (see Table 2).

Since the first observation of di-indolylmethane formation was made after the irradiation of anilino-ketone



(Ia) in methanol, the following reaction sequence was considered. A photoreaction (iii) of indole (IVa) with the solvent (methanol) yields the 3-hydroxymethylindole

(XVII), which then undergoes a dark reaction with a further molecule of (IVa) to give the di-indolylmethane (Va). The first stage (iii) is similar to the photo-hydroxyethylation of quinoline,⁶ and the second stage is a known reaction of 3-hydroxymethylindoles.⁷ However, irradiation of the indole (IVa) in methanol caused only

TABLE 2
Irradiation of 1,2-dimethylindole (IVa)^a
Yield (%)^b

Solvent	Reaction time (h)	Additive	Di-indolylmethane	Recovered indole (IVa)
MeOH	24		4.6 (Va)	93 ^c
MeOH	25	PhCOMe ^d	4.9 (Va)	90 ^c
MeOH	24	PhNMe ₂ ^d	4.6 (Va)	90 ^c
PhH	24			98
PrOH	24			97
MeOH	16	(Id)	88 (Va)	10
MeOH	24	(Id)	56 (Va) ^e	44 ^e
MeOH	24	(Ie)	20 (Va) ^f	75
PrOH	25	(Ie)	4 ^g	90
PrOH	28	(If)	90 (XXIb) ^h	5
PrOH	24	(XIIg)	70 (XXIb) ^h	18

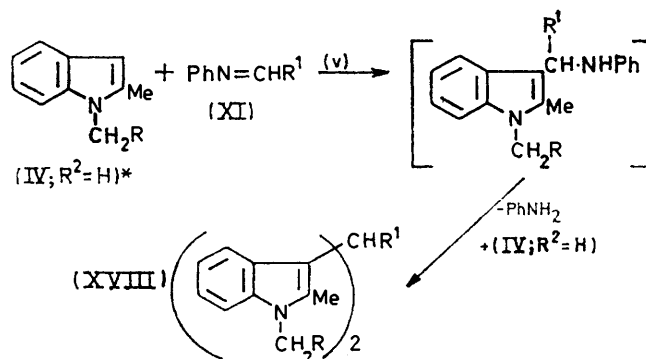
^a Indole (IVa) (100 mg) irradiated with solvent (70 ml) and anilino-ketone (1 g) (if any). ^b Yields based on the amount of indole used. ^c 1–2% of an unidentified indole dimer, *M* 304, isolated. ^d Equimolar amounts of indole and additive. ^e 200 mg of indole used. ^f Product possibly formed *via* solvent incorporation [reactions (iii) and (iv)]. ^g N.m.r. and mass spectra indicate product formed *via* incorporation of solvent but structure not confirmed. ^h (XXIb) ≡ (XVIII; R = H, R¹ = Ph).

low conversion into the di-indolylmethane (Va) and most of the indole was recovered. In contrast, most of the indole formed in the photoreaction of the anilino-ketones (I), or added to the reaction mixture, is converted into a di-indolylmethane (see Table 2). Irradiation of the indole (IVa) in the presence of possible sensitizers (acetophenone or *NN*-dimethylaniline) resulted in no increase in the yield of di-indolylmethane.

Photoreaction of the indole with solvent was shown to be, at most, a very minor reaction by irradiating the anilino-ketone (Ia) in propan-2-ol or in benzene. In both cases, the same di-indolylmethane (Va) was formed as was obtained with methanol as the solvent. No di-indolylmethane was formed on irradiating the indole (IVa) in benzene or in propan-2-ol.

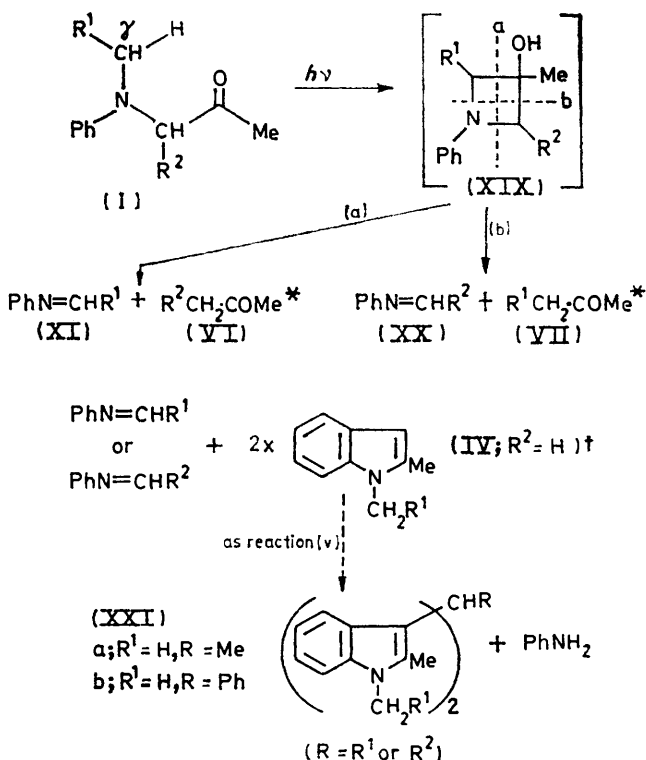
An alternative explanation for di-indolylmethane formation requires type II cleavage of anilino-ketone (I) [reaction (ii)] to give the anil (XI) which then reacts with indole (IV; R² = H) by a normal dark reaction (v). This can be discounted as a general reaction of the anilino-ketones (I) since ketones (Ib) and (Ic), where R¹ is not H, still yield di-indolylmethanes (XVIII; R¹ = H) with no substituent at the methylene bridge. The results obtained on irradiation of the deuteriated anilino-ketones (XXII) and (XXV) are similarly inconsistent with type II cleavage. The sole anilino-ketone studied, (XIIg), which underwent type II cleavage on irradiation

(see before) also appeared to give a di-indolylmethane by this process [reactions (ii) and (v)]. Irradiation of (XIIg) with indole (IVa) gave di-indolylmethane (XVIII; R = H, R¹ = Ph). Apart from this one case, all experimental results [*i.e.* from anilino-ketones (I) and (XIIb)]



* R = R¹ if the indole is formed by photorearrangement of (Ia–c), or R = H if indole (IVa) was added to reaction mixture.

regarding di-indolylmethane formation may be accounted for by the reaction sequence shown in Scheme 1.



* *via* enol. † Formed by photorearrangement of (I; R² = H), or added as (IVa).

SCHEME 1

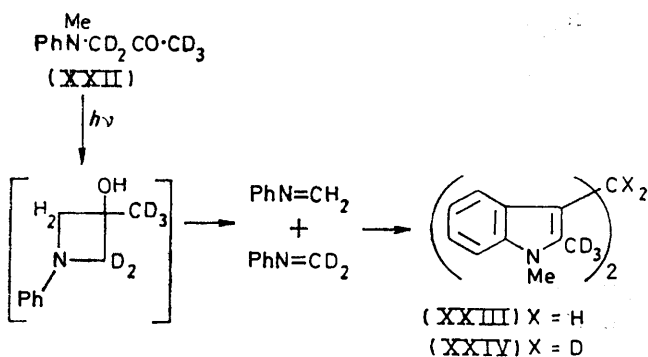
The first step involves formation of an azetidol (XIX), initiated by γ -hydrogen abstraction as in the well-known formation of cyclobutanols by irradiation of

⁶ F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Amer. Chem. Soc.*, 1970, **92**, 2745.

⁷ E. Leete, *J. Amer. Chem. Soc.*, 1959, **81**, 6023.

ketones.⁸ It is then suggested that the azetidinol fragments as shown [path (a) or (b)] by a thermal or photoreaction to give an anil (XI) or (XX) and a ketone (VI) or (VII). The observed preference for formation of di-indolylmethanes with no substituent at the methylene bridge (XXI; R = H) follows if the azetidinol (XIX) fragments with preferential fission of the carbon-nitrogen bond joining the nitrogen atom to that carbon atom which bears the substituent (assuming R¹ or R² = H). Thus, decomposition of the azetidinol (XIX; R¹ or R² = H) will always give formanil (PhN=CH₂). In the last step of the sequence, aniline is formed as a by-product. In two typical photoreactions, aniline was shown to be formed in small amounts by treating the acid-soluble products with isothiocyanatobenzene and subsequently isolating *sym*-diphenylthiourea [(PhNH)₂CS].

Experiments with deuteriated anilino-ketones, in which neither path (a) nor path (b) would be expected to be exclusive for fragmentation of the intermediate azetidinol, support the suggested scheme. Irradiation of the anilino-ketone (XXII; *ca.* 85% CD₂) in methanol or in benzene yielded a mixture of di-indolylmethanes (XXIII) and (XXIV). The approximate ratios of (XXIII) to (XXIV) were 4 : 1 (methanol as solvent) and 3 : 2 (benzene as solvent). These rather high ratios may



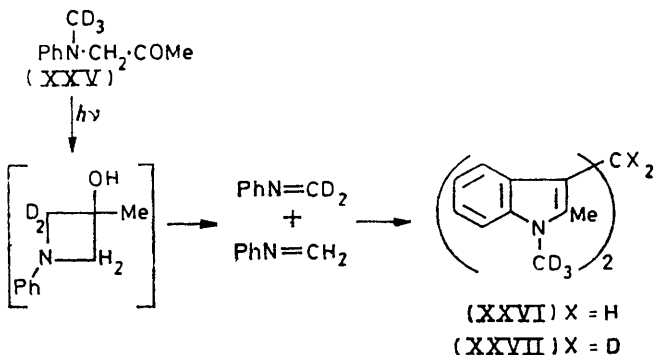
be largely accounted for by the deuterium exchange which occurs during the reaction, as evidenced by the considerably decreased deuterium content of the recovered anilino-ketone. With the anilino-ketone (XXV), deuterium exchange was not expected and the ratio of products (XXVI) and (XXVII) was *ca.* 1 : 1.

Irradiation of the disubstituted anilino-ketone (If) in the presence of the indole (IVa) yielded the substituted di-indolylmethane (XXIb)* in accordance with Scheme 1. Similarly, irradiation of (Ie) in the presence of the indole (IVa) was expected to give the di-indolylmethane (XXIa) but no such product was detected. However, this material (XXIa) was shown to decompose when passed down a column of silica gel and hence its isolation from the product mixture by column chromatography, the standard procedure, could not be expected.

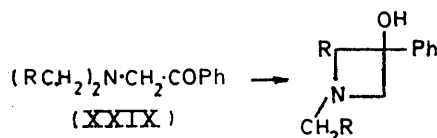
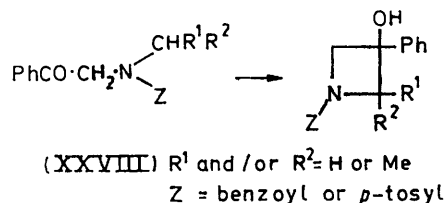
At present, more direct evidence for the formation of

* This compound was referred to previously as (XVIII; R = H, R¹ = Ph), the irradiation product from (XIIg) + (IVa).

azetidinols during the photoreaction is lacking. The light-induced formation of azetidinols from keto-amides



(XXVIII) has been described,⁹ and azetidinols were reported to be products of the irradiation of ω -(dialkyl-amino)acetophenones (XXIX).¹⁰ We were unable to repeat the preparation of an azetidinol from the amino-ketone (XXIX; R = H), and recent work by Gold⁹ casts doubt on this reaction.



Further indirect evidence for the intermediacy of azetidinols in the photoreaction was provided by the isolation of the ketones (VII; R¹ = Me) and (VII; R¹ = Ph) after irradiation of anilino-ketones (Ib) and (Ic), respectively. In each case, the expected ketone (VI; R² = H) was also isolated. The formation of ketones (VII) requires bonding between the carbon atom of the carbonyl group and the α -carbon atom of the *N*-alkyl group. This is satisfactorily explained by fragmentation [path (b)], in the preferential manner, of an intermediate azetidinol (XIX).

Dark Reaction of α -N-Alkylanilino-ketones.—All the α -N-alkylanilino-ketones (I) and (XII) were stable in solution (generally methanol) in the dark. 1,2-Dimethylindole (IVa) was also stable under these conditions. However, when a mixture of the indole (IVa) and an anilino-ketone, (Ia), (Ib), (Id), or (XIIb), was stored for several days (or weeks) in solution, partial conversion into the di-indolylmethane (Va) took place (Table 3).

⁸ A. Schonberg, 'Preparative Organic Photochemistry,' Springer-Verlag, 1968, p. 34.

⁹ E. H. Gold, *J. Amer. Chem. Soc.*, 1971, **93**, 2793.

¹⁰ R. A. Clasen and S. Searles, jun., *Chem. Comm.*, 1966, 289.

This reaction is considerably slower than the photo-reaction. For example, after irradiation of a mixture of (IVa) and (Id) for 16 h, only 10% of the indole (IVa) was recovered, whereas after the same mixture had stood for 84 days in the dark, 70% of the indole was recovered.

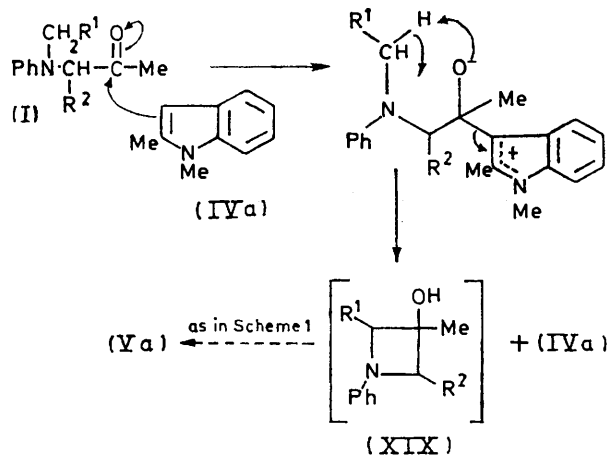
TABLE 3
Dark reactions of 1,2-dimethylindole (IVa) with
 α -N-alkylanilino-ketones

Anilino-ketone ^a	Amount (IVa) (mg)	Solvent	Time (days)	Di-indolyl-methane (Va)	Re-covered (IVa)
(Ia)	100	MeOH	5	20	80
(Ia)	200	EtOH	80	35	55
(Ia)	100	PrOH	93	9	90
(Ia)	100	PhH	93	9	90
(Ib)	200	MeOH	7	6	90
(Ib)	100	MeOH	38	15	78
(Ib)	400	MeOH	104	b	b, c
(Ic)	100	EtOH	130	25	70
(Id)	100	MeOH	84	20	70
(If)	100	PrOH	110	15	80
(XIIb)	200	MeOH	50	(XXIb) 45	55

^a 1 g anilino-ketone used. ^b Product not isolated.

^c Aniline (2.7%) isolated as (PhNH)₂CS.

Similarly, the *N*-benzylanilino-ketone (If) and indole (IVa) gave the substituted di-indolylmethane (XXIb) in 15% yield after 110 days and 80% of the indole was recovered. A mechanism (Scheme 2) similar to that suggested for the photoreaction may be operative. Indoles should be particularly capable of participating in such a reaction. The dark reactions of anilino-ketones with indoles and with other suitable compounds are being investigated further.

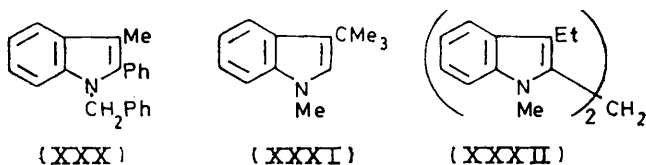


SCHEME 2

Preparation of α -N-Alkylanilino-ketones and Characterisation of the Photoproducts.— α -N-Alkylanilino-ketones (I), (XII), and (XXV) were prepared from the appropriate *N*-alkylanilines and α -chloro- or α -bromo-ketones. The deuteriated anilinoacetone (XXII; 87% CD₂, 84% CD₃) was formed on treating a solution of ketone (Ia) in deuterium oxide and methan[²H]ol with sodium deuterioxide.

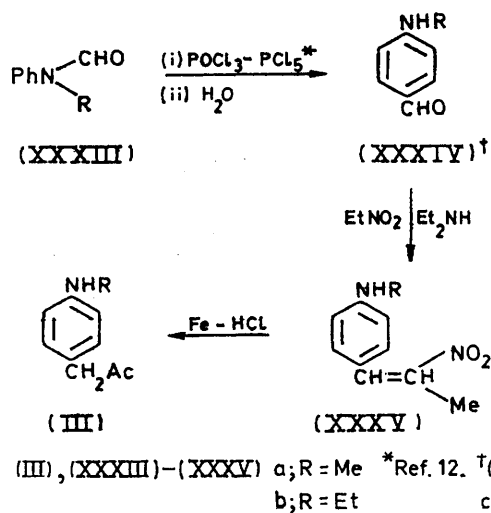
The indoles (IVa—e) and (XIV) were identical with authentic materials. The structures of the indoles (IVf), (XIIIa), and (XIIIb) were consistent with their n.m.r. spectra. The indoles (IVf) and (XIIIa) were also shown to be different from the isomeric indoles (XXX) and (XXXI) formed by thermal cyclodehydration of the anilino-ketones (If) and (XIIc), respectively.

The di-indolylmethanes (Va) and (Vc) were identical with authentic materials. The substituted di-indolylmethane (XXIa) was obtained when the indole (IVa) was stored for several days with acetaldehyde in the presence



of acetic acid. The di-indolylmethanes (Vb), (XV), and (XXIb) were readily prepared in high yield (ca. 90%) by the acid-catalysed reaction¹¹ of the corresponding indole with formaldehyde (or, in the latter case, with benzaldehyde). The di-indol-2-ylmethane (XXXII) was prepared similarly, but in low yield (25%) and with a much longer reaction time (4 days).

The products of *para*-rearrangement, *p*-(alkylamino)-phenylacetones (IIIa) and (IIIb), were identical with samples prepared from the respective *N*-alkylformanilides (XXXIIIa) and (XXXIIIb) as shown. The structures of all products of *para*-rearrangement were



consistent with their n.m.r. spectra and, in each case, characteristic t.l.c. behaviour was shown. Satisfactory analyses were obtained for (IIIa) and for the 2,4-dinitrophenylhydrazones of (IIIb), (IIIe), and (III f).

The structures of the deuteriated anilino-ketones (XXII) and (XXV) and di-indolylmethane mixtures

¹¹ S. Földeak, J. Czombos, and B. Matkovics, *Acta Univ. Szeged, Acta Phys. Chem.*, 1965, **11**, 115.

¹² A. Vilsmeier and A. Haack, *Ber.*, 1927, **60**, 119.

TABLE 4

N.m.r. spectra (CDCl ₃) (τ at 60 MHz; J in Hz) of indoles and di-indolylmethanes					
Indole	CH ₂	CMe	NMe	ArH	
(IVa)		7.6	6.38	2.33—3.03 (4H, m), 3.74 (1H)	
(IVb)	6.07(q, J 7)	7.7		2.33—3.12 (4H, m), 3.82 (1H)	
(IVc)	4.68	8.8(t, J 7)		2.2—3.17 (9H, m), 3.62 (1H)	
(IVd)		7.62	6.41	2.35—3.05 (4H)	
(IVe)	5.88(q, J 7.5)	7.7, 7.75		2.33—3.08 (4H, m)	
(IVf)	4.65	7.65, 7.73			
(XIIIa)		8.72(t, J 7.5)		2—3.15 (14H, m)	
(XIIIb)		7.6	6.15	2.3—3 (4H, m), 3.66 (1H)	
(XIIIc)	7.24(q, J 8)	8.6 (9H)		2.18—3.1 (4H, m), 3.82 (1H)	
(XIV)	7.2(q, J 7.5)	7.42, 8.22 (9H)		2.25—3.05 (4H, m), 3.67 (1H)	
1,3-Dimethylindole		8.66(t, J 8)	6.34	2.22—3.05 (4H, m), 3.2 (1H)	
(XXX)	4.78	8.7(t, J 7.5)	6.30	2.25—3.05 (4H, m), 3.18 (1H)	
(XXXI)		7.65		2.22—3.22 (14H, m)	
Di-indolylmethane		7.78	6.35	2.03—3.1 (4H, m), 3.22 (1H)	
(Va)	5.82	8.62 (9H)			
(Vb)	5.83	7.64	6.36	2.35—3.15 (8H, m)	
(Vc)	5.93(q, J 7)	8.72(t, J 7)		2.4—3.23 (8H, m)	
(XV)	4.65, 5.73	7.69		2.33—3.17 (8H, m)	
(XXXII)	7.22(q, J 8)	7.68	6.33	2.4—3.17 (8H, m)	
(XXIa)	5.63	8.95(t, J 8)		2.2—3.05 (8H, m)	
(XXIb)	7.22(q, J 7.5)	8.78(t, J 7.5)	6.53	2.22—3.25 (8H, m)	
(XXIc)	[5.22(q, J 7.5)] *	7.7	6.39	2.5—3.25 (13H, m)	
(XXId)	(3.87) *	8.01(d, J 7.5)			
(XXIe)		7.85	6.35		

* CH signal.

TABLE 5

N.m.r. spectra (CDCl ₃) (τ at 60 MHz; J in Hz) of α - <i>N</i> -alkylanilino-ketones					
Anilino-ketone	CH	CH ₂	CMe	NMe	ArH(m)
(Ia)		6.0	7.9	6.94	2.5—2.9 (2H), 3.05—3.45 (3H)
(Ib)		6.02	7.84		2.54—2.88 (2H), 3.05—3.45 (3H)
(Ic)		6.5(q, J 8)	8.8(t, J 8)		2.5—2.9 (7H), 3.05—3.45 (3H)
(Id)	5.65(q, J 7)	5.33, 5.92	7.87	7.21	2.5—2.83 (2H), 3.0—3.33 (3H)
(Ie)	5.79(q, J 7)	6.69(q, J 7)	8.69(d, J 7)		2.53—2.92 (2H), 3.05—3.4 (3H)
(If)	4.44	5.43 ^a	7.83		2.3—3.3 (15H)
(XIIb)		5.97	8.17(d, J 7)	6.93	2.53—2.86 (2H), 3.05—3.43 (3H)
(XIIc)		7.53(q, J 7.5)	8.8(t, J 7)		
(XIId)		5.76	7.83	7.17	2.6—2.97 (2H), 3.13—3.5 (3H)
(XIIe)		6.17	8.89 (9H)		2.62—3.4 (5H)
(XIIIf)		5.23, 5.33	7.88, 8.88 (9H)		1.9—3.48 (15H)
(XIIIg)		6.0 (0.25H) ^b	7.88 (0.45H) ^b	6.94	2.5—2.85 (2H), 3.07—3.45 (3H)
(XIIH)		6.0	7.9		2.5—2.9 (2H), 3—3.5 (3H)

^a Poorly defined AB system. ^b Remainder CD₂ (or CD₃).

TABLE 6

N.m.r. spectra (CDCl ₃) (τ at 60 MHz; J in Hz) of α -[<i>p</i> -(alkylamino)phenyl] ketones and synthetic precursors					
Compound	CH	CH ₂	NH(br)	Me	ArH ^a
(IIIa)		6.4	ca. 6.15	7.17, 7.88	3.16
(IIIb)		6.48		7.86	3.17
(IIIc)		6.8(q, J 7)		8.75(t, J 7)	3.15, 2.4—2.9 (5H, m)
(IIId)	6.36(q, J 7)	5.66, 6.42	ca. 6.8	7.87	3.25
(IIIe)	6.34(q, J 7)	6.81(q, J 7)	ca. 6.95	7.18, 7.98	
(IIIIf)				8.75(d, J 7)	3.24
(XVI)	4.8	5.64		7.97	
(XXIVa)		6.0		8.66(d, J 7)	2.2—3.6 (14H, m)
(XXIVb)		7.56(q, J 7)		8.75(t, J 7)	3.25
(XXIVc)	1.3		ca. 5.2	7.77	
(XXIVd)	1.88		ca. 5.6	6.97	
(XXIVe)	1.87	6.67(q, J 7)	ca. 5.85	8.94(t, J 7)	2.82
				7.13(d, J 4) ^b	2.95
				7.17, 7.5	2.97
				7.5	
				8.72(t, J 7)	

^a The single figure refers to centre of A₂B₂ multiplet (4H). ^b Signal collapses to a singlet in presence of D₂O.

(XXIII)—(XXIV) and (XXVI)—(XXVII) were determined from n.m.r. spectra and, in the case of (XXV) and (XXVI)—(XXVII), were confirmed by mass spectra.

TABLE 7
Mass spectra *

Anilino-ketone	M^+	Base peak	Major peaks
(Ia)	163(45)	120	121(30), 105(35), 104(30), 77(55)
(Ib)	177(25)	134	135(25), 106(85), 77(70)
(Id)	177(5)	134	120(20), 107(20), 106(30), 77(35)
(XIIb)	177(25)	120	121(25), 105(20), 77(35)
(XXV)	166(50)	123	138(75), 124(40), 108(85), 77(85)
Indole			
(IVa)	145(90)	144	130(25), 115(25), 103(15), 102(10), 77(30)
(IVf)	297(30)	144	145(90), 91(95)
Di-indolyl-methane			
(Va)	302(80)	157	145(40), 144(35)
(Vb)	330(75)	171	315(50), 144(25), 143(30)
(Vc)	454(50)	233	438(5), 364(5), 232(50), 91(70)
(XV)	330(40)	171	301(25), 172(35), 170(30)
(XXXII)	330(65)	171	315(20), 172(65), 170(40)
(XXIb)	378	378	363(95), 301(70), 233(90), 232(95)
(XXIa)	316(30)	300	301(25), 171(45), 170(25), 145(40)
(XXVI) + (XXVII)	310(60) } 308(60) }	162 } 160 }	148(35), 147(30)

* % of base peak in parentheses.

TABLE 8

U.v. spectra (methanol) of α -N-alkylanilino-ketones

Anilino-ketone	$\lambda_{\max.}/\text{nm}$ (log ϵ)
(Ia)	249(4.18), 294(3.32)
(Ib)	251.5(4.09), 295(3.36)
(Ic)	249.5(4.16), 294.5(3.33)
(Id)	248.5(4.04), 295(3.38)
(Ie)	254(4.09), 294(3.34)
(If)	248(4.09), 289sh (ca. 3.34)
(XIIa)	244(3.94), 290sh (ca. 3.29)
(XIIb)	249(4.18), 294.5(3.31)
(XIIc)	250(4.20), 291(3.35)
(XIId)	248(3.56), 284sh (ca. 2.63)
(XIIe)	245(4.43), 286(3.50)
(XII f)	249.5(4.44), 288.5(3.48)
(XII g)	248.5(4.47), 284(3.53)

EXPERIMENTAL

All irradiations were carried out with stirring, in dried and distilled solvents, under nitrogen at room temperature. The light source, a high-pressure mercury-vapour lamp (type Q81, Quarzlampen GMBH Hanau), was centrally situated in a water-cooled Pyrex cold-finger apparatus.

The silica gel used for column chromatography was Hopkin and Williams M.F.C.; for t.l.c. Merck Kieselgel G was used. Light petroleum had b.p. 60–80°. Where the same compound was obtained by different routes, identity was established by comparison of i.r. spectra.

Preparation of α -N-Alkylanilino-ketones (I) and (XII) — In general, the following procedure was used.

¹³ M. Julia and J. Lenzi, *Bull. Soc. chim. France*, 1962, 2263.

¹⁴ J. W. Magee and H. R. Henze, *J. Amer. Chem. Soc.*, 1940, **62**, 910.

¹⁵ E. F. J. Janetzky and P. E. Verkade, *Rec. Trav. chim.*, 1946, **65**, 691.

¹⁶ F. Wessely, H. Pawloy, and W. Rizzi, *Monatsh.*, 1955, **86**, 75.

¹⁷ N. J. Leonard and S. Gelfand, *J. Amer. Chem. Soc.*, 1955, **77**, 3272.

The appropriate α -halogeno-ketone (0.1 mol) (α -bromo-ketones except for chloroacetone and α -chloro- α -phenylacetone) and N-alkylaniline (0.1 mol) were heated under reflux for 18–24 h with sodium hydrogen carbonate (20 g) and ethanol (50 ml). After removal of solids and evaporation of the solvent, the crude product was obtained *via* extraction into 4N-hydrochloric acid with subsequent basification. Anilino-ketones (Ia),¹³ (Ib),¹³ (Ic),¹⁴ (Id),¹⁵ (Ie),¹⁵ (XIIa),¹⁶ and (XIIc)¹⁷ were purified by distillation under reduced pressure and (XIIe),¹⁸ (XII f),¹⁹ and (XII g)²⁰ were purified by crystallisation.

2-N-Benzylanilino-2-phenylpropan-2-one (If) had m.p. 105° (Found: C, 83.7; H, 6.7; N, 4.2. $C_{22}H_{21}NO$ requires C, 83.8; H, 6.7; N, 4.4%). $\nu_{\max.}$ (Nujol) 1715 cm^{-1} .

1-N-Methylanilinobutan-2-one (XIIb) had b.p. 108° at 1.5 mmHg (Found: C, 74.5; H, 8.5. $C_{11}H_{15}NO$ requires C, 74.5; H, 8.5%), $\nu_{\max.}$ (film) 1720 cm^{-1} .

N-t-Butylanilinoacetone (XIId) had b.p. 145–150° at 12 mmHg (Found: C, 76.2; H, 9.4. $C_{13}H_{19}NO$ requires C, 76.1; H, 9.3%), $\nu_{\max.}$ (film) 1720 cm^{-1} .

N-[²H₃]Methylanilinoacetone (XXV), prepared similarly from bromoacetone and N-[²H₃]methylaniline²¹ with a reaction time of 5 h, was purified by chromatography over silica gel, eluting with benzene-ethyl acetate. The product (62%) had b.p. 100–102° at 1 mmHg, $\nu_{\max.}$ (film) 1725 and 2060 cm^{-1} , M^+ 166.

N-[²H₃]Acetonyl-N-methylaniline (XXII).—N-Methylanilinoacetone (3 g), methan[²H]ol (2 g), and 30% sodium deuterioxide in deuterium oxide (3 g) were heated under reflux for 1 h. The mixture was extracted into ether, the dried extract was evaporated, and the residue was distilled under reduced pressure. The partly deuteriated anilino-ketone was treated again in a similar manner to give a final product (1.5 g) containing 87% CD₂ and 84% CD₃ (from n.m.r. spectrum).

Irradiation of α -N-Alkylanilino-ketones (I) and (XII) (see Table 1).—After irradiation of a ca. 2.5% solution of the anilino-ketone, the solvent was evaporated off and the products were isolated by column chromatography over silica gel, successively eluting with benzene-light petroleum, benzene, benzene-ethyl acetate, and ethyl acetate.

The formation of volatile ketones (VII) and/or (VI) during the photoreaction was demonstrated with anilino-ketones (Ia), (Ib), (Ic), and (XIIc). The solvent was carefully distilled off at atmospheric pressure and the distillate was treated with acidified 2,4-dinitrophenylhydrazine in ethanol to yield the corresponding 2,4-dinitrophenylhydrazones. Benzyl methyl ketone 2,4-dinitrophenylhydrazone was obtained from the neutral residue left after evaporation of the solvent. In one case, (Ib), the presence of acetone and butan-2-one in the distillate was confirmed by g.l.c. analysis.

Aniline was shown to be present after irradiation of (Ia) and (Ib) by treating the basic products with isothiocyanato-benzene and isolating *sym*-diphenylthiourea by column chromatography.

Irradiation of N-[²H₃]Methylanilinoacetone (XXV).—Irradiation of the ketone (XXV) (250 mg) for 18 h in methanol (70 ml) yielded, on evaporation, an oil which was

¹⁸ A. F. Crowther, F. G. Mann, and D. Purdie, *J. Chem. Soc.*, 1943, 58.

¹⁹ P. E. Verkade and E. F. J. Janetzky, *Rec. Trav. chim.*, 1943, **62**, 763.

²⁰ W. F. Cockburn, R. A. W. Johnstone, and T. S. Stevens, *J. Chem. Soc.*, 1960, 3340.

²¹ F. Dalton, R. D. Hill, and G. D. Meakins, *J. Chem. Soc.*, 1960, 2927.

chromatographed over silica gel. Elution with benzene-light petroleum gave a solid (8 mg), presumably [1-*Me*-²H₅]-1,2-dimethylindole, followed by a mixture (18 mg) of di-indolylmethanes (XXVI) and (XXVII). Subsequent elution with benzene-ethyl acetate gave *N*-trideuteriomethylaniline (15 mg), anilino-ketone (XXV) (150 mg), and finally an oil (15 mg) which was probably the product of *para*-rearrangement. The ratio (XXVI):(XXVII) was *ca.* 50:50 according to the n.m.r. and mass spectra (see Table 7) of the mixture.

Irradiation of N-[²H₅]Acetyl-*N*-methylaniline (XXII).—

(i) The anilino-ketone (XXII) (1 g) was irradiated for 24 h in methanol (70 ml). After evaporation of the solvent, the residue was chromatographed over silica gel. Elution with benzene-light petroleum yielded a solid (8 mg), presumably partly deuteriated 1,2-dimethylindole, and then a mixture (46 mg) of di-indolylmethanes (XXIII) and (XXIV). Further elution with benzene-ethyl acetate gave *N*-methylaniline (50 mg), the anilino-ketone (XXII) (470 mg), and an oil (90 mg), presumably the product of *para*-rearrangement. The n.m.r. spectrum of the di-indolylmethane mixture indicated that the ratio (XXIII):(XXIV) was *ca.* 4:1, with 75% CD₃ at the 2-position of the indolyl group. The recovered anilino-ketone (XXII) had 50% CD₂ and 70% CD₃.

(ii) Irradiation of compound (XXII) (500 mg) in benzene (70 ml) as in (i) yielded a mixture (30 mg) of di-indolylmethanes (XXIII) and (XXIV), and the anilino-ketone (XXII) (150 mg) was recovered. The n.m.r. spectra indicated that the ratio (XXIII):(XXIV) was *ca.* 3:2 with 50% CD₃ at the 2-position of the indolyl group, and that the recovered ketone (XXII) had 10% CD₂ and 60% CD₃.

Irradiation of 1,2-Dimethylindole (IVa) (see Table 2).—A 1% solution of indole (IVa) was used and the products were isolated by chromatography over silica gel. Elution with benzene-light petroleum (2:3) gave the indole (IVa) and elution with benzene-light petroleum (4:1) gave the di-indolylmethane (Va).

Irradiation of 1,2-Dimethylindole (IVa) in the Presence of α -N-Alkylanilino-ketones (see Table 2).—In general, the α -*N*-alkylanilino-ketone (1 g) and 1,2-dimethylindole (100 mg) were irradiated in the solvent (70 ml). The indole (IVa) and the di-indolylmethane (Va) or (XXIb) were isolated by column chromatography in the usual manner (see before).

Dark Reactions of 1,2-Dimethylindole (IVa) with α -N-Alkylanilino-ketones (see Table 3).—A solution of 1,2-dimethylindole (100–400 mg) and the anilino-ketone (1 g) in the solvent (70 ml) was stored for several days (or weeks) in the absence of light. Indole (IVa) and the di-indolylmethane (Va) or (XXIb) were isolated in the usual manner (see before).

Identification of the Photoproducts.—In general, the photoproducts were compared (i.r. spectra) with authentic samples or characterised by their i.r. and/or n.m.r. (see Tables) spectra and by elemental analysis.

The *N*-alkylanilines (IIa–c), *N*-*t*-butylaniline, and *N*-[²H₅]methylaniline²¹ and the 2,4-dinitrophenylhydrazones of acetone, butan-2-one, pinacolone, and benzyl methyl ketone were identical with authentic samples. Similarly, the indoles (IVa),²² (IVb),¹³ (IVc),²³ (IVd),¹³ (IVe),¹⁵ (XIIIc),²⁴ and (XIV),²⁵ and the di-indolylmethanes (Va)⁷

and (Vc)²³ were identical with samples prepared according to literature methods.

1-Benzyl-2-methyl-3-phenylindole (IVf) had m.p. 100° (Found: C, 88.4; H, 6.6; N, 4.7. C₂₂H₁₉N requires C, 88.8; H, 6.4; N, 4.7%).

2-*t*-Butyl-1-methylindole (XIIIa), obtained as an oil, gave a *picrate* m.p. 96–97° (Found: C, 54.7; H, 5.2; N, 13.2. C₁₉H₂₀N₄O₇ requires C, 54.8; H, 4.8; N, 13.5%).

1-*t*-Butyl-2-methylindole (XIIIb), obtained as an oil, gave a *picrate*, m.p. 110° (Found: C, 55.0; H, 5.0; N, 13.5. C₁₉H₂₀N₄O₇ requires C, 54.8; H, 4.8; N, 13.5%).

1-Benzyl-3-methyl-2-phenylindole (XXX).—The anilino-ketone (If) (1 g) was heated under reflux for 24 h in ethylene glycol (3 ml). The cooled mixture was diluted with 2*N*-hydrochloric acid (50 ml) and extracted with ether. The dried extract was evaporated and the residue was crystallised to give the indole (XXX) (26%), m.p. 112° (Found: C, 88.4; H, 6.7; N, 4.4. C₂₂H₁₉N requires C, 88.8; H, 6.4; N, 4.7%).

3-*t*-Butyl-1-methylindole (XXXI) was obtained similarly from the anilino-ketone (XIc) as an oil (12%), after chromatography over silica gel, and gave a *picrate*, m.p. 116° (Found: C, 54.6; H, 4.7; N, 13.3. C₁₉H₂₀N₄O₇ requires C, 54.8; H, 4.8; N, 13.5%).

1-[*p*-(Methylamino)phenyl]propan-2-one (IIIa).—Nitroethane (1.5 ml), diethylamine hydrochloride (250 mg), and potassium carbonate (150 mg) were added to *p*-(methylamino)benzaldehyde (5 g) (prepared¹² from *N*-methylformanilide) in ethanol (15 ml) and the mixture was stored at room temperature for 2 days. Water (30 ml) was added and the styryl compound (XXXVa) (5.3 g) was filtered off. Crystallisation from aqueous ethanol gave red needles, m.p. 116° (Found: C, 62.6; H, 6.2. C₁₀H₁₂N₂O₂ requires C, 62.5; H, 6.3%), ν_{\max} (Nujol) 3395 cm⁻¹.

Iron powder (2.5 g), iron(III) chloride (100 mg), and 12*N*-hydrochloric acid (1.25 ml) were added to a solution of compound (XXXVa) (1 g) in 25% aqueous ethanol (50 ml), and the mixture was heated under reflux for 0.5 h; the red colour had then been discharged. The mixture was made alkaline with aqueous 4*N*-sodium hydroxide and extracted into ether and the extract was dried and evaporated. Chromatography of the residue over silica gel, eluting with benzene-ethyl acetate (10:1), yielded 1-[*p*-(methylamino)phenyl]propan-2-one (0.4 g) as an oil (Found: C, 73.4; H, 7.8. C₁₀H₁₃NO requires C, 73.6; H, 8.0%), ν_{\max} (CHCl₃) 3450 and 1710 cm⁻¹.

1-[*p*-(Ethylamino)phenyl]propan-2-one (IIIb).—*N*-Ethylformanilide was converted into *p*-(ethylamino)benzaldehyde by the method¹² used for *p*-(methylamino)benzaldehyde. The crude aldehyde was similarly condensed with nitroethane to give the styryl compound (XXXVb), m.p. 81° (Found: C, 63.8; H, 6.7. C₁₁H₁₄N₂O₂ requires C, 64.0; H, 6.8%), ν_{\max} (CHCl₃) 3390 cm⁻¹.

Treatment of compound (XXXVb) with iron and hydrochloric acid, as before, gave 1-[*p*-(ethylamino)phenyl]propan-2-one as an oil, ν_{\max} (film) 3400 and 1710 cm⁻¹, which formed a 2,4-dinitrophenylhydrazone, m.p. 175° (Found: C, 56.9; H, 5.3. C₁₇H₁₉N₅O₄ requires C, 57.1; H, 5.4%).

3-[*p*-(Ethylamino)phenyl]butan-2-one (IIIe), ν_{\max} (film) 3400 and 1705 cm⁻¹, formed a 2,4-dinitrophenylhydrazone, m.p. 155–156° (Found: C, 57.9; H, 5.6. C₁₈H₂₁N₅O₄ requires C, 58.2; H, 5.7%).

²² G. Berti and A. Da Settimo, *Gazzetta*, 1960, **90**, 525.

²³ G. Ehrhart and I. Hennig, *Arch. Pharm.*, 1961, **294**, 550.

²⁴ L. A. Aksanova, N. F. Kucherova, and V. A. Zagorevskii, *Zhur. obshchei Khim.*, 1964, **34**, 1609.

²⁵ H. R. Snyder, E. L. Eliel, and R. E. Carnahan, *J. Amer. Chem. Soc.*, 1951, **73**, 970.

1- [*p*-(Benzylamino)phenyl]-1-phenylpropan-2-one (III_f), ν_{\max} (film) 3405 and 1700 cm^{-1} , formed a 2,4-dinitrophenylhydrazone, m.p. 185° (Found: C, 67.5; H, 5.6. $\text{C}_{28}\text{H}_{25}\text{N}_5\text{O}_4$ requires C, 67.9; H, 5.1%).

The structures of the remaining products of *para*-rearrangement: (III_c), ν_{\max} (film) 3400 and 1705 cm^{-1} ; (III_d), ν_{\max} (film) 3420 and 1705 cm^{-1} ; and (XVI), ν_{\max} (CHCl_3) 3450 and 1685 cm^{-1} , were consistent with their n.m.r. spectra (see Table 6).

Preparation of Di-indolylmethanes (Vb), (XV), (XXIb), and (XXXII).—*N*-Sulphuric acid (1.5 ml) and then aqueous 40% (w/v) formaldehyde (0.4 ml) [or benzaldehyde (0.006 mol) for (XIIb)] were added to a 2.5% solution of the appropriate indole (0.01 mol) in 50% aqueous ethanol and the mixture was heated under reflux for 4 h. Cooling and addition of water yielded the di-indolylmethane.

The di-indolylmethane (XXXII) required a reaction time of 4 days.

Bis-(1-ethyl-2-methylindol-3-yl)methane (Vb) (92%) had m.p. 161° (Found: C, 83.8; H, 7.7; N, 8.6. $\text{C}_{23}\text{H}_{26}\text{N}_2$ re-

quires C, 83.6; H, 7.9; N, 8.5%); *bis*-(1-methyl-2-ethylindol-3-yl)methane (XV) (99%) had m.p. 146° (Found: C, 83.9; H, 8.1; N, 8.6%); α -*bis*-(1,2-dimethylindol-3-yl)toluene (XXIb) (99%) had m.p. 204° (Found: C, 85.4; H, 7.1; N, 7.3. $\text{C}_{27}\text{H}_{26}\text{N}_2$ requires C, 85.7; H, 6.9; N, 7.4%); *bis*-(3-ethyl-1-methylindol-2-yl)methane (XXXII) (25%) had m.p. 163° (Found: C, 83.2; H, 7.6; N, 7.9%).

1,1-*Bis*-(1,2-dimethylindol-3-yl)ethane (XXIa).—A mixture of 1,2-dimethylindole (2.9 g), acetaldehyde (0.88 g), water (50 ml), and acetic acid (0.6 ml) was left with occasional shaking for 29 days at room temperature. The precipitate was filtered off and triturated with hot light petroleum to remove 1,2-dimethylindole. Crystallisation of the residue from aqueous acetone gave the *di*-indolyl-ethane (XXIa) (0.54 g), m.p. 152° (Found: C, 83.8; H, 7.5; N, 8.9. $\text{C}_{22}\text{H}_{24}\text{N}_2$ requires C, 83.5; H, 7.6; N, 8.9%).

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