Light-induced Reactions of 2-(*N*-Alkyl-*N*-arylamino)cyclohexanones and Related Amino-cycloalkanones: Formation of 7-Azabicyclo[4.2.0]octan-1-ols [1]

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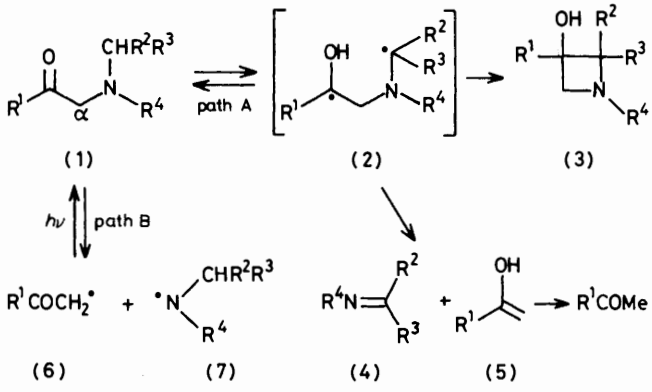
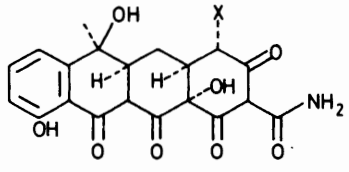
On irradiation, 2-(*N*-alkyl-*N*-arylamino)cyclohexanones (aryl = Ph; alkyl = Me, benzyl, allyl, Et, CH_2CH_2Ph, or CH_2CF_3; or aryl = *p*-tolyl; alkyl = Me) (10) or (20), 4,4-dimethyl-2-(*N*-methylanilino)-cyclohexanone (24), and 2-(*N*-methylanilino)-5α-cholestan-3-one (26) underwent type-II cyclisation to afford azetidinol (7-azabicyclo[4.2.0]octan-1-ol) derivatives. In general, fission to give the corresponding *N*-alkyl-*N*-arylamine and ketone was a minor photoreaction. When the alkyl group of the 2-(*N*-alkylanilino)cyclohexanone had the structure $-CH(R)CH_2R'$, a double 1,5-hydrogen transfer occurred leading to a low yield of a 2-anilinocyclohexanol (31a). Photolysis of 2-anilinocyclohexanone (32a) gave a little of the direct-fission product aniline (17a), and the alkylamino-ketones 2-(*NN*-diethylamino)- (32b) and 2-(*N*-pyrrolidino)-cyclohexanone (32c) underwent no significant photoreaction in methanol. The isolation of indan-1-one and *N*-trideuteriomethylaniline on irradiation of 2-(*N*-trideuteriomethylanilino)-indan-1-one (33b) in diethyl ether indicated that the photoreaction was a direct C_α–N bond fission and not a type-II fission.

α-Amino-ketones (1; R^1 = aryl or heteroaryl [2]) derived from aryl or heteroaryl ketones undergo a type-II photoreaction *via* the biradical (2) (path A, Scheme 1). When the substituent R^4 is an aryl group,[3] or when NR^4 is part of an amide [4,5] or lactam [6] system, cyclisation to an azetidinol (3) predominates, whereas fission to an imine (4) and an enol (5) is the main photoreaction [5,7,8] when R^4 is an alkyl group. With most *aryl* ketones (1; R^1 = aryl), direct cleavage of the N–C_α bond (path B) is generally unimportant. In contrast, cleavage to give radicals (6) and (7) is the major photoreaction of α-arylamino *alkyl* ketones (1; R^1 = alkyl, R^4 = aryl).[9] Direct cleavage is also believed to be the mechanism by which tetracycline (8) is deaminated to give the product (9),[10] but it is at most a minor photoreaction of 2-arylamino-cyclohexanones (10). The major photoreaction of these amino-ketones [1] is type-II cyclisation (path A, Scheme 2) to afford the isomeric azetidinol (12) *via* the biradical (11).†

The results obtained on irradiating a series of 2-(*N*-alkyl-*N*-arylamino)cyclohexanones and related amino-ketones are described below.



Scheme 1



(8) X = NMe_2
(9) X = H

Results

Irradiation of the 2-(N-*Methyl*-N-*arylamino*)*cyclohexanones* (10a), (20), (24), *and* 2-(N-*Methylanilino*)-5α-*cholestan*-3-*one* (26).—The products isolated after irradiation of these amino-ketones, generally in diethyl ether or in methanol, are given in the Table. In each case, the major photoproduct, obtained as a crystalline solid, was the corresponding azetidinol (or 7-azabicyclo[4.2.0]octan-1-ol derivative) (12a), (21), (25), and (27), respectively. *N*-Methylaniline (17a) was a minor photoproduct from the (*N*-methylanilino)cyclohexanones (10a) and (24), and *N*-methyl-*p*-toluidine (23) was similarly obtained from the aminocyclohexanone (20). The tetrahydrocarbazoles (19a) and (22) were also minor photoproducts, and were produced from the aminocyclohexanones (10a) and (20), respectively.

Irradiation of the 2-(N-*Alkylanilino*)*cyclohexanones* (10b—g) *and* (28).—As with the above group of amino-ketones, the major photoproduct from the (*N*-alkylanilino)cyclohexanones (10b—f), in which the *N*-alkyl group RCH_2 is not methyl, is the corresponding azetidinol (12b—f). However, unlike the azetidinols formed from (*N*-methylanilino)cyclohexanones, the products (12b—f) were obtained as oils which would not solidify. Minor photoproducts were the *N*-alkylaniline (17b—f) and the tetrahydrocarbazole (19b—f). Irradiation of the isopropylanilinocyclohexanone (28) also yielded an amine (29) and a tetrahydrocarbazole (30) but no azetidinol was formed.

The (*N*-alkylanilino)cyclohexanones (10d), (10e), and (28), in which the *N*-alkyl substituent is ethyl or a monosubstituted ethyl group, yielded a further photoproduct, 2-anilinocyclo-

† For a more detailed summary of the photoreactions of α-amino-ketones, see ref. 3.

Table. Irradiation of 2-(*N*-alkyl-*N*-arylamino)cycloalkanones *

Amino-cycloalkanone	Solvent	Reaction time (h)	Yield (%) [a] Recovered amino-ketone	Azetidinol	Tetrahydro-carbazole	Arylamine	Other products
(10a)	MeOH	24	32	26 (12a)	10 (19a)	7 (17a)	
(10a)	Et_2O	20		33 (12a)	(19a) [b]	(17a) [b]	
(10b)	Et_2O	19	48	26 (12b)	6 (19b)	2.5 (17b)	
(10c)	Et_2O	24		48 (12c)	6 (19c)	(17c) [b]	
(10d)	MeOH	24	30	15 (12d) [c]	10 (19d)	4 (17d)	6 (31a)
(10d)	Et_2O	22	55	18 (12d) [c]	7 (19d)	5 (17d)	8 (31a)
(10e)	MeOH	20	78	9 (12e) [c]	2 (19e)	6 (17e)	5 (31a)
(10f)	Et_2O	18	40	10 (12f) [c]	10 (19f)	9 (17f)	
(10g)	MeOH	32	72	5 (12g) [c]	7 (19g) [c]		Trace (31b) [d]
(20)	Tetrahydrofuran	23	41	25 (21)	5 (22)	(23) [b]	
(20)	Pr^iOH	20	30	26 (21)	10 (22)	2 (23)	
(20)	Et_2O	22	34	38 (21)	8 (22)	2.5 (23)	
(20)	Hexane	21	85	8 (21)	5 (22)	(23) [b]	
(24)	MeOH	35		37 (25)		24 (17a)	
(26)	Et_2O	4.7	12	38 (27)			
(28)	Et_2O	50	37		3.5 (30)	7.5 (29)	5 (31a)
(28)	Et_2O–H_2O	70	(28) [b]		(30) [b]	(29) [b]	(31a),[b] 4 (MeCHO), +6 (Me_2CO) [e]

* Products are shown in parentheses.

[a] Irradiation using a 75-W high-pressure mercury vapour lamp. [b] Presence indicated by t.l.c. [c] Structure consistent with the spectral data. [d] Evidence for this compound comes from the mass spectrum. [e] Isolated as a mixture of 2,4-dinitrophenylhydrazones; yields calculated from the n.m.r. spectrum.

hexanol (31a). When the trideuterioethylanilinocyclohexanone (10g) was irradiated in methanol, the reaction was slower than that of the non-deuterio-analogue (10d). Starting material (70%) was isolated along with low yields of the expected products (identified by their i.r. and n.m.r. spectra) and only a trace of a product with a mass spectrum consistent with the structure (31b). The isopropylanilinocyclohexanone (28) was irradiated in diethyl ether saturated with water and the volatile photoproducts were treated with 2,4-dinitrophenylhydrazine to yield a mixture of acetaldehyde- and acetone-2,4-dinitrophenylhydrazone.

Irradiation of the Amino-ketones (32) *and the* 2-(N-*Methylanilino*)*indanones* (33).—Little reaction occurred when the aminocyclohexanones (32) were irradiated in methanol. A low yield of aniline was obtained from anilinocyclohexanone (32a).

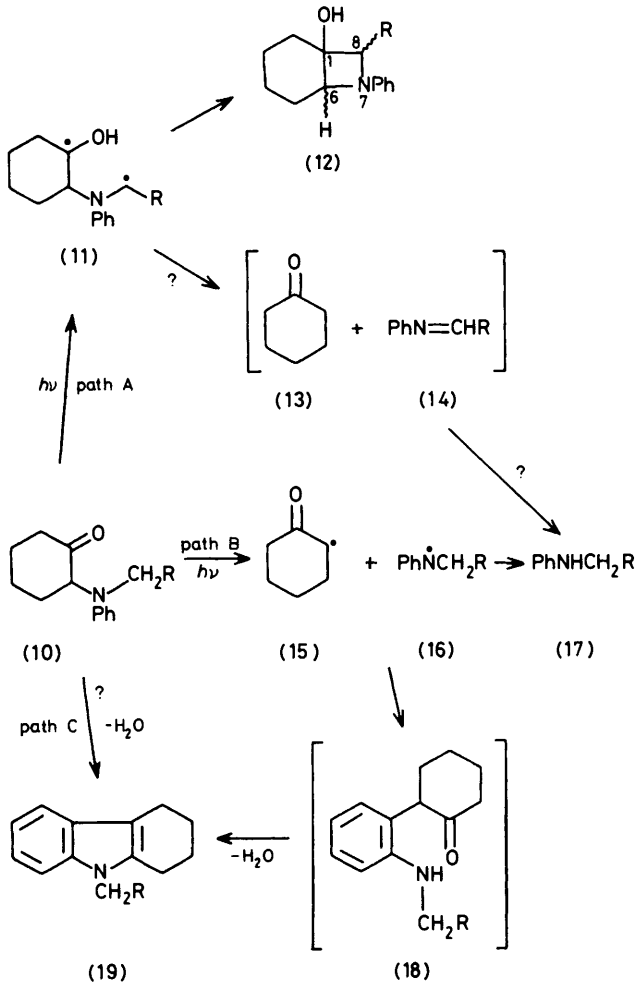
As part of an investigation into the mode of formation of amines $R^2R^3CHNHR^4$ from amino-ketones (1), the trideuteriomethylanilinoindanone (33b) was irradiated in diethyl ether. The main photoproducts were trideuteriomethylaniline $PhNHCD_3$ (36%) and indan-1-one (13%). Irradiation of the aminoindanone (33a) in benzene, a poor hydrogen donor, yielded *N*-methylaniline (17a) (38%) and indan-1-one (15%), a result similar to that obtained when diethyl ether [3] was the solvent.

Preparation of Amino-ketones.—All the amino-ketones were synthesised from the appropriate α-halogeno-ketone and amine. In general, the method of Campaigne and Lake [11] was used. Work-up, in the case of the anilinocyclohexanones (10), (20), and (28), was complicated by their ready cyclodehydration to give tetrahydrocarbazoles, either on heating or during column chromatography over silica gel. To minimise this side-reaction, chromatography was performed rapidly, or the excess of amine was removed by washing the product with 0.1—0.25M-hydrochloric acid and the less basic amino-ketone was then isolated *via* extraction into 4M-hydrochloric acid. *N*-(2,2,2-Trideuterioethyl)aniline (17g) was prepared by reduction of *N*-trideuterioacetylaniline with lithium aluminium hydride. All other amines and the α-halogenoketones were commercially available or prepared according to literature methods (see Experimental section).

Characterisation of the Photoproducts.—The 7-azabicyclo-[4.2.0]octan-1-ol derivatives were characterised by their i.r. (ν_{OH} *ca.* 3 400 cm^{-1}), n.m.r., and mass spectra. Compounds (12b—f) containing a substituent R in the azetidine ring were all produced as oils which would not solidify. Presumably they are each mixtures of two diastereoisomers in which the group R is *cis* or *trans* to the hydroxy-group. This is consistent with the n.m.r. spectrum of compound (12d) in which two doublets (τ 8.6 and 8.82, *J ca.* 7 Hz) are seen for the methyl group. The mass spectra are characteristic and the fragmentation of compounds (12a) and (21) has already been described.[12] In an attempt to synthesise compound (12a) by an alternative route, the epoxide (34) was kept at room temperature, or heated, in acetonitrile, dimethylformamide, hexamethylphosphoric triamide, polyphosphoric acid, acetic acid, or boron trifluoride–diethyl ether. In no case was compound (12a) detected (t.l.c.) amongst the reaction products in any significant amount. The epoxide was prepared by heating 2-anilinocyclohexanone with dimethyl sulphoxonium methylide.

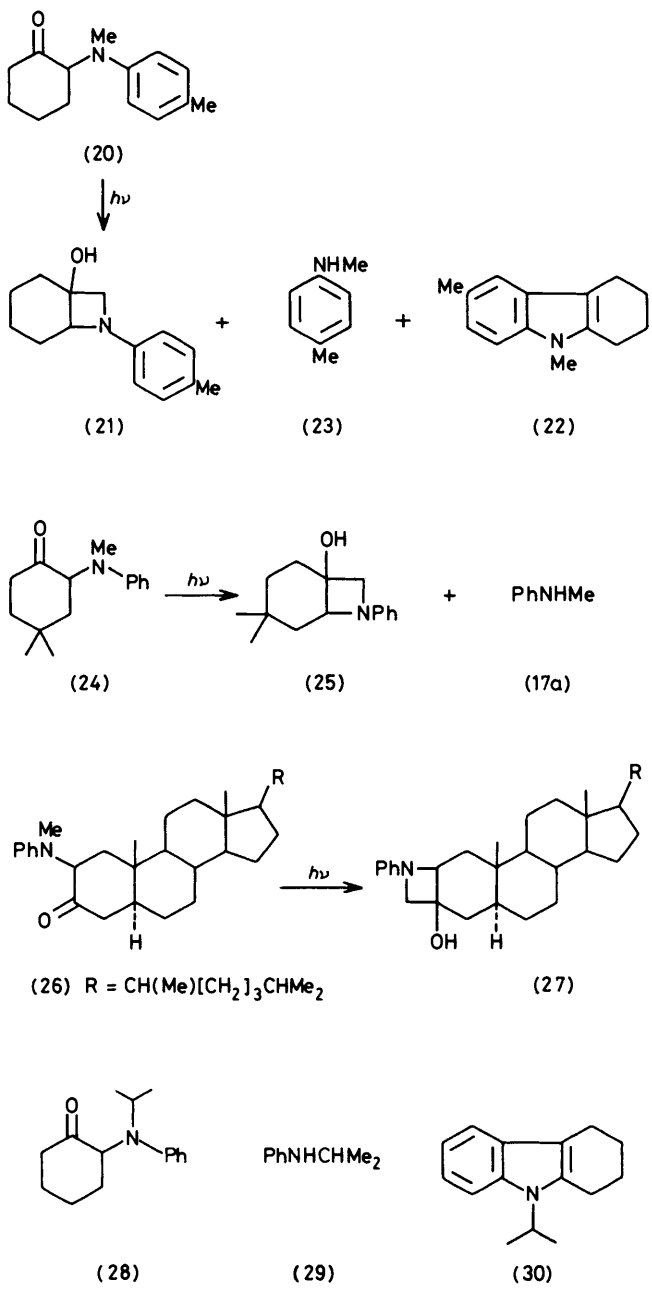
2-Anilinocyclohexanol (31a) was obtained as an oil whose i.r. spectrum was almost identical with that of a sample obtained on reduction of 2-anilinocyclohexanone with lithium aluminium hydride. In both cases the products are likely to be mixtures of *cis*- and *trans*-isomers. The product (31a) from the photolysis of the amino-ketone (28) partially solidified on being kept cold and this solid was used as a seed to initiate crystallisation of the reduction product. Repeated recrystallisation yielded a solid, m.p. 58—59 °C, which is presumably the *trans*-isomer since a sample, m.p. 58 °C, was prepared from cyclohexene oxide and aniline.[13] A second isomer of 2-anilinocyclohexanol, m.p. 72—74 °C, has also been reported.[14]

The tetrahydrocarbazoles (19), (22), and (30) isolated from the photoreaction mixtures were identical with samples



(10), (12), (17) and (19) a; R = H
b; R = Ph
c; R = CH=CH$_2$
d; R = Me
e; R = CH$_2$Ph
f; R = CF$_3$
g; R = CD$_3$

Scheme 2

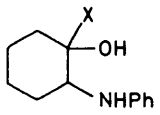


obtained by cyclodehydration of the corresponding amino-cyclohexanones in ethylene glycol or in glacial acetic acid. The basic product from the irradiation of 2-(*N*-trideuteriomethylanilino)indan-1-one (33b) appeared to be largely trideuteriomethylaniline PhNHCD$_3$, and not PhNHCD$_2$H, by comparison of its i.r. spectrum with that of an authentic sample and from its mass spectrum [*m*/*z* 110 (93, PhNHCD$_3$$^+$) 109 (22), and 108 (100%)]. All other photoproducts were identical with authentic samples.

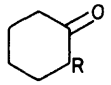
Discussion

Irradiation of the 2-(N-*Methylarylamino*)*cycloalkanones* (10a), (20), (24), *and* (26).—The major photoreaction of the aminocyclohexanone (10a) is type-II cyclisation to give the azetidinol (12a) *via* the biradical (11a), with the amine (17a) and the tetrahydrocarbazole (19a) being minor products. A similar result was obtained with the amino-ketone (20), and in both cases the reaction was not significantly affected by the nature of the solvent, except that the rate of conversion of compound (20) was appreciably lower in hexane. This result contrasts with the photoreactivity of 2-(*N*-alkylarylamino)-acetophenones (1; R^1 = R^4 = aryl) which also form azetidinols as the major product in aprotic solvents, but only in low yield or not at all in hydroxylic solvents.[3]

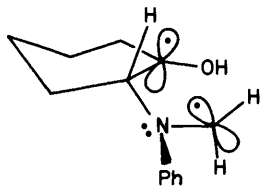
As the azetidinols (12a), (21), and (27) are crystalline solids it is likely that the cyclisation is stereoselective and leads to one geometrical isomer (*cis* or *trans* ring-junction) only. A *cis* ring-junction is more likely as indicated by the europium-induced increases in the chemical shifts of the OH, 6- 8-, and 8′-H protons in the n.m.r. spectrum of compound (12a) [see Experimental section]. Examination of molecular models does not allow a clear-cut decision between the two orientations to be made. The initially formed biradical (35) from the amino-ketone (10a) (radical centres with planar geometry)



(31) a; X = H
b; X = D



(32) a; R = NHPh
b; R = NEt_2
c; R = *N*-pyrrolidino



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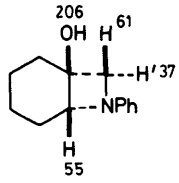
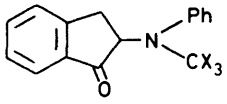
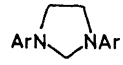


(12a - *cis*)

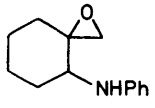
Europium-induced shifts in Hz



(33) a; X = H
b; X = D



(36)



(34)

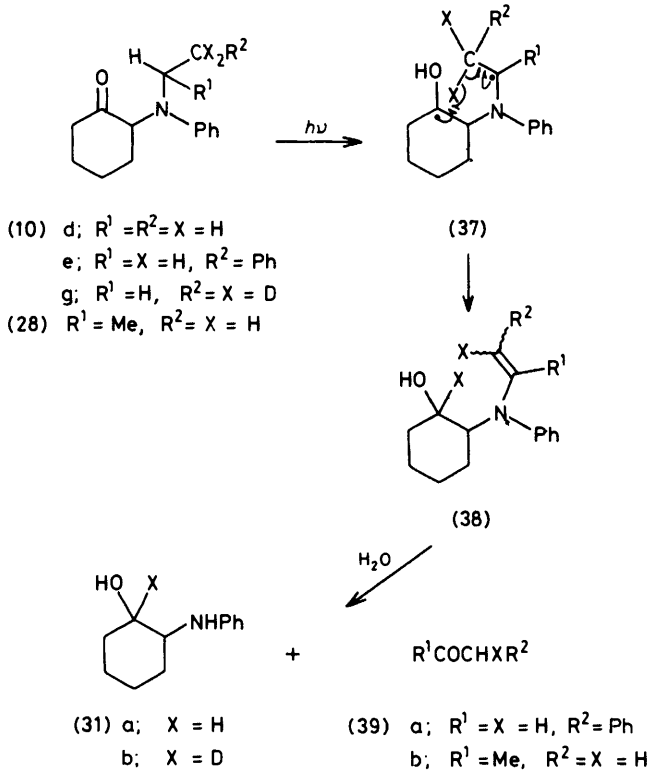
can assume a conformation with reasonable overlap of orbitals leading to a *cis* ring-junction but where overlap leading to the *trans*-isomer is poor. On the other hand, if the radical centres have a tetrahedral or pyramidal geometry, there is little difference between the overlaps leading to either the *cis*- or the *trans*-isomer. Cyclisation is hindered by the developing 1,3-diaxial interactions in both cases.

The tetrahydrocarbazole (19a) could arise by two routes (Scheme 2); (i) direct cyclodehydration (path C) or (*ii*) *via* homolytic fission (path B) and recombination of the radicals (15) and (16) to give the intermediate (18); such homolytic fission is a major photoreaction [9] of the amino-ketones (1; R^1 = alkyl, R^4 = aryl). Since the amino-ketones (10) readily cyclise to give tetrahydrocarbazoles during chromatography over silica gel (the method used for separation of the photoproducts) path C is probably responsible for most if not all of the tetrahydrocarbazole obtained. Two amino-ketones, (24) and (26), were irradiated under conditions in which paths B and C would lead to different tetrahydrocarbazoles. However, in both cases, the amount of carbazole formed was negligible and the main product was again an azetidinol. Since both these amino-ketones do not readily undergo thermal cyclodehydration, lack of tetrahydrocarbazole formation in their photoreactions is consistent with path C being the main route to tetrahydrocarbazoles during the irradiation of 2-arylaminocyclohexanones. 2-(*N*-Methylanilino)-1,2,3,4-tetrahydronaphthalen-1-one, which undergoes thermal cyclodehydration less readily than do the aminocyclohexanones (10), does form a tetrahydrocarbazole derivative *via* homolytic fission (*cf.* path B) on photolysis.[3]

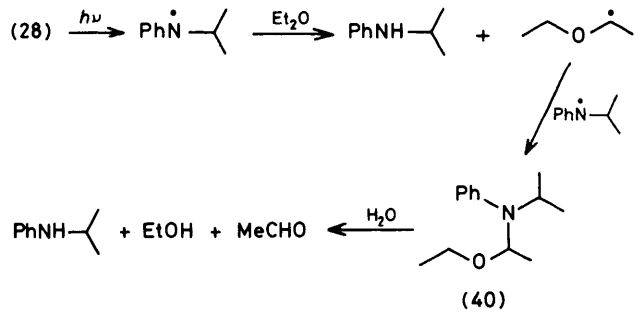
Another minor photoproduct formed from the 2-(*N*-methylarylamino)cyclohexanones (10a), (20), and (24) is the corresponding *N*-methylarylamine. Amines $PhNHCH_2R$ were similarly obtained from other aminocyclohexanones (10) and (28). The two routes most likely for the formation of the *N*-alkylanilines (17) are (i) reduction of the imine (14), believed to be produced along with cyclohexanone (13) *via* path A, and (ii) hydrogen abstraction by the radical (16) formed *via* path B (Scheme 2). As the most common fate of the unstable imines $ArN{=}CH_2$ [formed on irradiation of amino-ketones $ArN(Me)CH_2COAr'$] is further photoreaction to yield an imidazolidine (36),[3] the lack of such a photoproduct from the aminocyclohexanones (10) suggests that type-II fission to give the imines (14) is not significant. Formation of *N*-trideuteriomethylaniline *via* homolytic fission (*cf.* path B) on irradiation of 2-(*N*-trideuteriomethylanilino)indan-1-one (33b) was demonstrated by the isolation of $PhNHCD_3$, and not $PhNHCD_2H$ which would have been formed if the imine $PhN{=}CD_2$ had been an intermediate.

Irradiation of the 2-(N-*Alkylanilino*)*cyclohexanones* (10b—g) *and* (28).—The azetidinols (12b—g) were also the major photoproducts from the (*N*-alkylanilino)cyclohexanones (10b—g) in which the *N*-alkyl group is not methyl. This contrasts with the behaviour of the (*N*-alkylanilino)acetophenones, $ArCOCH_2N(Ph)CH_2R$, which undergo type-II cyclisation only when R is hydrogen. This result may parallel the tendency of biradicals formed from 2-alkylcyclohexanones [15] to have a higher cyclisation : cleavage ratio than do the biradicals formed from alkyl aryl ketones, where cleavage usually predominates.[16]

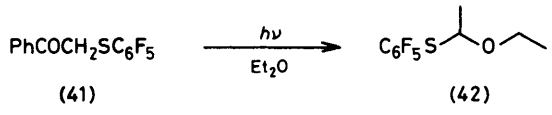
As with the amino-ketones described in the previous section, the amines (17) and the tetrahydrocarbazoles (19) were minor photoproducts, but in the case of the amino-ketones (10d), (10e), and (28) a further photoproduct, 2-anilinocyclohexanol (31a), was obtained. The proposed mechanism for its formation, shown in Scheme 3, involves a 1,5-hydrogen transfer in the biradical (37) to yield the enamine (38) which subsequently decomposes to give the product (31a) and an aldehyde or ketone (39). The presence of a hydrogen atom on C-2 of the *N*-alkyl group is necessary for this reaction since only amino-ketones possessing this feature (10 or 28; X = H) produce 2-anilinocyclohexanol as a photoproduct. To confirm this mechanism, the deuterioethylanilinocyclohexanone (10g) was irradiated in methanol. The expected photoproducts were isolated, except that only a trace of a compound corresponding (t.l.c.) to 2-anilinocyclohexanol was obtained. Its mass spectrum was consistent with structure (31b). A deuterium isotope effect which lowers the rate of the conversion of the biradical (37) into compound (38), and makes this reaction less competitive with the other photoreactions, probably accounts for the low yield of the deuteriocompound (31b). Attempts were made to isolate the carbonyl compound (39) which would be formed on hydrolysis of the enamine (38). Phenylacetaldehyde (39a) was not detected after irradiation of the amino-ketone (10e); this may be due to reaction of the aldehyde by photodegradation. However, irradiation of isopropylanilinocyclohexanone (28) in diethyl ether, with water added to aid hydrolysis of any intermediate enamine, did yield a volatile carbonyl product. Treatment of the volatile products with 2,4-dinitrophenylhydrazine gave a derivative which was a mixture of acetone- (39b) and acet-



Scheme 3



Scheme 4



aldehyde-2,4-dinitrophenylhydrazone in the ratio *ca.* 6% : 4% (analysis of the n.m.r. spectrum). Isolation of acetone is consistent with the reaction pathway proposed in Scheme 3. Acetaldehyde may arise by interaction of a photochemically generated amine radical with the solvent (diethyl ether) as shown in Scheme 4. The formation of the unstable amino-ether (40) is similar to the production of the more stable monothioacetal (42) on irradiation of the keto-sulphide (41) in diethyl ether.[17]

Irradiation of the Amino-ketones (32).—2-Anilinocyclohexanone (32a), which cannot undergo a type-II photoreaction, is less reactive than the aminocyclohexanones (10) and cleaves on irradiation to give a low yield of aniline. Whereas alkylaminoketones (1; R^4 = alkyl) undergo type-II fission but not cyclisation, the alkylaminocyclohexanones (32b and c) were almost totally unreactive to irradiation in methanol.

Experimental

All irradiations were carried out on stirred solutions under nitrogen. The light source, a 75-W type Q81 Quarzlampen GMBH Hanau (unless otherwise stated), was centrally situated in a water-cooled Pyrex cold finger. Silica gel used for chromatography was Hopkin and Williams M.F.C. Light petroleum had b.p. 60—80 °C. I.r. spectra were recorded as Nujol mulls (for solids) or liquid films; ^{1}H n.m.r. spectra (data in τ values) were recorded in $CDCl_3$ with $SiMe_4$ as internal standard; u.v. spectra were determined in MeOH with $\log_{10}$ ε values quoted in parentheses.

Preparation of 2-(N-*Alkyl*-N-*arylamino*)*cycloalkanones* (10), (20), (24), (26), *and* (28).—The method of Campaigne and Lake [11] was used, whereby the appropriate α-halogeno-ketone (0.1 mol) and *N*-alkyl-*N*-arylamine (0.1 mol) were heated under reflux for 0.75 h in 2-methoxyethanol (75 ml) in the presence of quinoline (0.01 mol) and anhydrous sodium carbonate (15 g). The mixture was cooled, filtered, and the filtrate was evaporated. Purification of the residue was by crystallisation (method A), rapid chromatography over silica gel using gradient elution with 2—5% ethyl acetate in toluene (or benzene) as eluant (method B), or by removal of the excess of *N*-alkyl-*N*-arylamine by washing an ethereal solution of the residue with 0.1—0.25M-hydrochloric acid, extraction of the amino-ketone into 4M-hydrochloric acid, and basification (method C). Amino-ketones prepared in this way were 2-(N-*methylanilino*)*cyclohexanone* (10a), (52%, method B), obtained as an oil (Found: C, 76.6; H, 8.3. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4%); $\nu_{max.}$ 1 720 cm^{-1}; $\lambda_{max.}$ 251 (4.04) and 294.5 nm (3.27); τ 2.52—2.94 (m, 2 × ArH), 3.07—3.42 (m, 3 × ArH), 5.45—5.8 (m, CH), 7.1 (s, NMe), and 7.35—8.35 (8 H, m, 4 × CH_2); *m/z* 203 (M^+, 5%), 146 (50), 107 (100), 106 (75), and 77 (75); 2-(N-*benzylanilino*)*cyclohexanone* (10b), (56%, method A), m.p. 110—111 °C (from ethanol) (Found: C, 81.4; H, 7.5; N, 4.9. $C_{19}H_{21}NO$ requires C, 81.7; H, 7.6; N, 5.0%); $\nu_{max.}$ 1 718 cm^{-1}; τ 2.5—3.5 (m, Ph), 2.65 (s, Ph), 5.33 (d, *J* 19 Hz, NC*H*Ph), 5.5 (d, *J* 19 Hz, NC*H*Ph), 5.4—5.75 (m, CH), and 7.3—8.7 (8 H, m, 4 × CH_2); *m/z* 279 (M^+, 12%), 251 (36), 222 (65), 188 (11), 160 (12), 132 (7), 104 (18), 91 (100), and 77 (30); 2-(N-*allylanilino*)*cyclohexanone* (10c), (65%, method C), m.p. 60—61 °C (from light petroleum containing a little ethanol) (Found: C, 78.2; H, 8.0; N, 5.9. $C_{15}H_{19}NO$ requires C, 78.6; H, 8.4; N, 6.1%); $\nu_{max.}$ 1 722 cm^{-1}; τ 2.6—3.5 (m, Ph), 3.68—4.36 (1 H, m, 1 vinyl H), 4.53—5.02 (2 H, m, 2 vinyl H), 5.43—5.87 (m, CH), 5.92—6.2 (m, NCH_2), and 7.2—8.8 (8 H, m, 4 × CH_2); *m/z* 229 (M^+, 27%), 201 (50), 172 (97), 160 (43), 159 (39), 144 (47), 132 (68), 104 (54), and 77 (100); 2-(N-*phenylethylanilino*)*cyclohexanone* (10e), (12%, method B), m.p. 115 °C (from ethanol–light petroleum) (Found: C, 81.5; H, 8.1; N, 4.5. $C_{20}H_{23}NO$ requires C, 81.9; H, 7.9; N, 4.8%); $\nu_{max.}$ 1 720 cm^{-1}; $\lambda_{max.}$ 254 (4.21) and 291 nm (3.31); τ 2.3—3.3 (10 H, m, 2 × Ph), 5.5—5.85 (m, CH), and 6.3—8.4 (12 H, m, 6 × CH_2); 2-[N-(2,2,2-*trifluoroethyl*)*anilino*]*cyclohexanone* (10f), (22%, method B), obtained as an oil, $\nu_{max.}$ 1 720 cm^{-1}; $\lambda_{max.}$ 243 (4.01) and 283.5 nm (3.27); τ 2.5—3.3 (m, Ph), 5.5—5.85 (m, CH), 6.04 (q, *J* 9 Hz, NCH_2), and 7.2—8.5 (8 H, m, 4 × CH_2); the 2,4-dinitrophenylhydrazone (Found: C, 53.1; H, 4.3; N, 16.0. $C_{20}H_{20}F_3N_5O_4$ requires C, 53.2; H, 4.5; N, 15.5%); 2-[N-(2,2,2-*trideuterioethyl*)*anilino*]*cyclohexanone* (10g), (43%, method C), m.p. 57—58 °C (from light petro-

leum); $\nu_{max.}$ 2 270, 2 170 (w), 2 120 (w), and 1 720 cm^{-1}; τ 2.5—3.6 (m, Ph), 5.5—5.95 (m, CH), 6.75 (m, CH_2), and 7.0—9.0 (8 H, m, 4 × CH_2); *m/z* 220 (M^+, 22%), 192 (40), 174 (33), 164 (64), 163 (100), 106 (47), 105 (25), 104 (40), and 77 (54); 2-(N-*methyl*-p-*toluidino*)*cyclohexanone* (20), (47%, method B), obtained as an oil (Found: C, 77.2; H, 8.7. $C_{14}H_{19}NO$ requires C, 77.4; H, 8.8%); $\nu_{max.}$ 1 720 cm^{-1}; $\lambda_{max.}$ 238 (4.05), 252 (4.08), and 300 nm (3.49); τ 2.8—3.6 (4 H, A_2B_2 m, ArH), 5.6—5.9 (m, CH), 7.1 (s, NMe), 7.3—8.6 (8 H, m, 4 × CH_2), and 7.73 (s, Me); 4,4-*dimethyl*-2-(N-*methylanilino*)*cyclohexanone* (24), (69%, method C), obtained as an oil which decomposed on attempted purification (Found: M^+, 231.1623. $C_{15}H_{21}NO$ requires *M*, 231.1623); $\nu_{max.}$ 1 725 cm^{-1}; τ 2.6—3.4 (m, Ph), 5.5 (dd, *J* 8 and 12 Hz, CH), 7.15 (s, NMe), 7.3—8.6 (6 H, m, 3 × CH_2), 8.71 (s, Me), and 8.91 (s, Me); *m/z* 231 (M^+, 39%), 214 (78), 174 (66), 146 (100), 107 (33), 91 (18), and 77 (54); 2-(N-*methylanilino*)-5α-*cholestan*-3-*one* (26), (9%, method B), m.p. 151—152 °C (from ethanol) (Found: C, 82.8; H, 10.8; N, 2.8. $C_{34}H_{53}NO$ requires C, 83.0; H, 10.9; N, 2.8%); $\nu_{max.}$ 1 720 cm^{-1}; τ 2.6—3.7 (m, Ph), 5.5—6.0 (m, CH), 7.19 (s, NMe), and 7.3—9.6 (total 44 H, m, remainder); *m/z* 491 (M^+, 21%), 463 (27), 147 (43), 146 (100), 132 (15), 120 (40), 107 (23), 106 (15), and 77 (7); 2-(N-*isopropylanilino*)*cyclohexanone* (28), (31%, method C), m.p. 61—62 °C (from light petroleum containing a little ethanol) (Found: C, 78.1; H, 8.9; N, 6.3. $C_{15}H_{21}NO$ requires C, 77.9; H, 9.2; N, 6.1%); $\nu_{max.}$ 1 715 cm^{-1}; τ 2.5—3.3 (m, Ph), 5.8—6.3 (m, NCH), 6.18 (1 H, septet, *J* 7 Hz, C*H*Me_2), 7.0—8.6 (8 H, m, 4 × CH_2), and 8.82 (6 H, d, *J* 7 Hz, 2 × Me); *m/z* 231 (M^+, 28%), 203 (38), 188 (100), 174 (60), 160 (21), 146 (5), 132 (40), 120 (92), 104 (33), 91 (11), and 77 (54).

2-(*N*-Ethylanilino)cyclohexanone (10d) [11] was prepared in a similar manner.

2-(N-*Trideuteriomethylanilino*)*indan*-1-*one* (33b).—2-Bromoindan-1-one (1.05 g) and *N*-trideuteriomethylaniline (1.15 g) were heated under reflux in ethanol (15 ml) for 2.5 h. Considerable darkening of the solution occurred. After evaporation of the ethanol, the residue was extracted into diethyl ether and the ethereal solution was washed with a little 0.1M-hydrochloric acid and was then extracted into 4M-hydrochloric acid. Basification of the acid extract yielded a dark oil which was extracted several times with light petroleum. The petroleum extracts were reduced in volume to 30 ml, a few drops of ethanol were added, and the solution was cooled. Recrystallisation of the resulting solid from light petroleum gave 2-(*N*-trideuteriomethylanilino)indan-1-one (33b) (0.22 g), m.p. 79—79.5 °C; $\nu_{max.}$ 2 100 and 1 720 cm^{-1}; τ 2.0—3.5 (9 H, m, ArH), 5.33 (dd, *J* 6 and 8 Hz, CH), and 6.2—7.25 (m, CH_2); *m/z* 240 (M^+, 78%), 238 (32), 212 (20), 211 (98), 195 (30), 194 (48), 178 (20), 109 (100), 105 (22), 91 (36), and 77 (36).

2-Anilinocyclohexanone,[11] 2-diethylaminocyclohexanone,[18] and 2-(*N*-piperidino)cyclohexanone [18] were prepared according to literature procedures.

N-(2,2,2-*Trideuterioethyl*)*aniline* (17g).—Lithium aluminium hydride (1.5 g) was added in portions to a cooled solution of *N*-trideuterioacetylaniline [19] (4 g) in dry diethyl ether (50 ml). The mixture was heated for 1 h under reflux, cold water was then added, and the mixture was extracted into diethyl ether. After being washed with dilute aqueous sodium hydroxide, the extracts were dried and evaporated and the residue was distilled to give N-(2,2,2-*trideuterioethyl*)*aniline* (17g) (2.96 g), b.p. 201—203 °C; $\nu_{max.}$ 3 410, 2 260, and 2 155 (w) cm^{-1}; τ(CCl_4) 2.7—3.8 (m, Ph), 6.76 (s, NH), and 6.97 (s, CH_2); *m/z* 124 (M^+, 12%), 106 (52), 94 (100), and 77 (20).

Apart from commercially available materials, the following α-halogenoketones and *N*-alkylarylamines were prepared according to literature methods; 2-chloro-4,4-dimethylcyclohexanone,[20] 2-bromocholestan-3-one,[21] 2-bromoindan-1-one,[22] *N*-allylaniline (17c),[23] *N*-phenethylaniline (17e),[24] *N*-(2,2,2-trifluoroethyl)aniline (17f),[25] *N*-methyl-*p*-toluidine (23),[26] *N*-isopropylaniline (29),[27] and *N*-trideuteriomethylaniline.[28]

Irradiation of the α-Amino-ketones (10), (20), (24), (26), *and* (28).—A 1—2% solution of the amino-ketone was irradiated, the solvent was evaporated off, and the residue was chromatographed over silica gel (60—100 g for each gram of the photoproduct) with benzene (or toluene)–light petroleum (1 : 1), benzene (or toluene), and benzene (or toluene) containing ethyl acetate in progressively increasing amounts as the eluant. In two cases [reactants (10b) and (28)] most of the unchanged amino-ketone was removed as a solid on trituration with light petroleum and the soluble material was chromatographed. Reaction times, solvent used, and yields are given in the Table.

The tetrahydrocarbazoles (19) and (22) were eluted with benzene (or toluene)–light petroleum (1 : 1) and with benzene (or toluene) and, in general, the remaining products were eluted with 1—6% ethyl acetate in benzene (or toluene) in the order amine and/or starting material, azetidinol, and 2-anilinocyclohexanol [from (10d, e, and g) and (28)].

The mixture of acetone- and acetaldehyde-2,4-dinitrophenylhydrazone prepared from the amino-ketone (28) was obtained by distilling the solvent (after irradiation) into a solution of acidified ethanolic 2,4-dinitrophenylhydrazine.

Irradiation of 2-*Anilinocyclohexanone* (32a).—A solution of the amino-ketone (0.7 g) in methanol (70 ml) was irradiated for 24 h and the solvent was evaporated off. Elution of the residue over silica gel using gradient elution with 2—5% ethyl acetate in benzene as the eluant yielded the starting material (0.56 g) and aniline (42 mg).

Irradiation of 2-(N-*Methylanilino*)*indan*-1-*one* (33a).—A solution of the amino-ketone (1 g) in benzene (80 ml) was irradiated for 1 h. Diethyl ether was added and the insoluble material was filtered off. Extraction of the filtrate with 0.1M-hydrochloric acid, followed by basification, gave *N*-methylaniline (17a) (0.17 g, 38%) (characterised as its picrate). The residual ethereal solution was evaporated to dryness and the residue was treated with acidified 2,4-dinitrophenylhydrazine to yield indan-1-one 2,4-dinitrophenylhydrazone (0.1 g, 15%), m.p. 252—254 °C.

Irradiation of 2-(N-*Trideuteriomethylanilino*)*indan*-1-*one* (33b).—A solution of the amino-ketone (0.2 g) in diethyl ether (70 ml) was irradiated for 1 h using a 125-W high-pressure mercury vapour lamp (Thorn Electric Kolorlux MBF with the outer glass envelope removed). After filtration the filtrate was evaporated to dryness and the residue was chromatographed over Merck Kieselgel 60H, type 7736 (12 g). Elution with toluene gave first, *N*-trideuteriomethylaniline (33 mg, 36%) and then crude indan-1-one which was isolated as its 2,4-dinitrophenylhydrazone (35 mg, 13%).

Identification of the Photoproducts.—The photoproducts were compared (i.r. spectra) with authentic samples, or were characterised by their i.r., n.m.r., and mass spectra. Spectroscopic and analytical [except for mixtures (12d—f)] data for the azetidinols (7-azabicyclo[4.2.0]octan-1-ols) are given

below. The mass spectra of the azetidinols (12a) and (21) have already been described.[12] *7-Phenyl-7-azabicyclo*[4.2.0]*octan-1-ol* (12a) had m.p. 70 °C (from light petroleum) (Found: C, 76.3; H, 8.5; N, 6.8. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4; N, 6.9%); $\nu_{max.}$ 3 380br cm^{-1}; τ 2.65—3.6 (m, Ph), *ca.* 6.2—6.32 (m, 6-H), 6.24 and 6.7 (both doublets, *J* 7 Hz, together 8-H_2), 7.5 (s, OH), and 7.9—8.7 (8 H, m, 4 × CH_2); τ[$CDCl_3$ + Eu(fod)$_3$*] 2.65—3.5 (m, Ph), 5.22 (s, OH), 5.56—5.75 (m, 6-H), 5.84 and 6.02 (both doublets, *J* 7 Hz, together 8-H_2), and 7.6—8.5 (8 H, m, 4 × CH_2).

7,8-*Diphenyl-7-azabicyclo*[4.2.0]*octan-1-ol* (12b) was a mixture of isomers obtained as an oil and was purified by rechromatography over silica gel (Found: C, 81.5; H, 7.7; N, 4.8. $C_{19}H_{21}NO$ requires C, 81.7; H, 7.6; N, 5.0%); $\nu_{max.}$ 3 410br cm^{-1}; τ 2.4—3.6 (m, Ph), 2.6br (s, Ph), 5.32 (s, 8-H; signal split into two lines, separation 1.5 Hz, on adding D_2O), 6.05—6.3 (m, 6-H), 7.6—9.5 (8 H, m, 4 × CH_2), and 7.9br (s, OH); *m/z* 279 (M^+, 10%), 181 (80), 180 (100), 179 (70), 132 (13), 104 (30), 91 (30), and 77 (90).

7-Phenyl-8-vinyl-7-azabicyclo[4.2.0]*octan-1-ol* (12c) was a mixture of isomers obtained as an oil (Found: C, 78.65; H, 8.2; N, 5.9. $C_{15}H_{19}NO$ requires C, 78.6; H, 8.4; N, 6.1%); $\nu_{max.}$ 3 410br cm^{-1}; τ 2.5—3.65 (m, Ph), 3.65—4.85 (3 H, m, vinyl), 5.5br and 5.6br (2 × s, 8-H), 5.95—6.12 (m, 6-H), 7.7br (s, OH), and 7.7—9.2 (8 H, m, 4 × CH_2); *m/z* 229 (M^+, 7%), 132 (70), 131 (36), 130 (80), 104 (36), and 77 (100).

8-Methyl-7-phenyl-7-azabicyclo[4.2.0]octan-1-ol (12d) was a mixture of isomers obtained as an oil; $\nu_{max.}$ 3 400br cm^{-1}; τ 2.5—3.6 (m, Ph), 5.7—6.6 (total 2 H, m, 6- and 8-H), 7.5—9.3 (8 H, m, 4 × CH_2), 7.68br (s, OH), and 8.6 and 8.82 (2 × d, each *J ca.* 7 Hz, Me groups in each isomer); *m/z* 217 (M^+, 21%), 132 (17), 120 (100), 119 (84), 118 (27), 104 (53), 98 (39), 86 (18), 84 (53), and 77 (43).

8-Benzyl-7-phenyl-7-azabicyclo[4.2.0]octan-1-ol (12e) was a mixture of isomers obtained as an oil; $\nu_{max.}$ 3 410br cm^{-1}; τ 2.3—3.5 (m, Ph), 2.67 (s, Ph), 5.5—6.2 (total 2 H, m, 6- and 8-H), 6.65—7.05 (m, CH_2Ph), and 7.5—9.3 (8 H, m, 4 × CH_2); *m/z* 293 (M^+, 3%), 202 (25), 149 (18), 106 (100), 105 (38), 104 (30), 91 (35), and 77 (45).

7-Phenyl-8-trifluoromethyl-7-azabicyclo[4.2.0]octan-1-ol (12f) was a mixture of isomers obtained as an oil; $\nu_{max.}$ 3 390br cm^{-1}; τ 2.5—3.5 (m, Ph), 5.5—6.5 (total 2 H, m, 6- and 8-H), 7.3—9.2 (8 H, m, 4 × CH_2), and 7.68br (s, OH); *m/z* 271 (M^+, 56%), 174 (31), 132 (23), 119 (54), 104 (46), 98 (100), and 77 (67).

7-p-*Tolyl-7-azabicyclo*[4.2.0]*octan-1-ol* (21) had m.p. 77 °C (from light petroleum) (Found: C, 77.4; H, 8.8; N, 6.4. $C_{14}H_{19}NO$ requires C, 77.4; H, 8.8; N, 6.4%); $\nu_{max.}$ 3 400br cm^{-1}; τ 2.92 and 3.43 (total 4 H, A_2B_2 m, *J ca.* 8.5 Hz, ArH), 6.1—6.4 (m, 6-H), 6.15 and 6.65 (total 2 H, 2 × d, each *J* 7 Hz, together 8-H_2), 7.5—9.0 (8 H, m, 4 × CH_2), 7.73 (s, Me), and 8.1br (s, OH).

4,4-*Dimethyl-7-phenyl-7-azabicyclo*[4.2.0]*octan-1-ol* (25) was obtained as an oil which decomposed on heating (Found: C, 78.2; H, 8.9; N, 5.9. $C_{15}H_{21}NO$ requires C, 77.9; H, 9.2; N, 6.1%); $\nu_{max.}$ 3 340br cm^{-1}; τ 2.7—3.6 (m, Ph), *ca.* 6.13 (m, 6-H), 6.1 and 6.51 (total 2 H, 2 × d, each *J* 8 Hz, together 8-H_2), *ca.* 7.5—9.0 (6 H, m, 3 × CH_2), 8.95 (s, Me), and 9.0 (s, Me); *m/z* 231 (M^+, 25%), 166 (12), 119 (15), 106 (100), 105 (10), and 77 (12).

The *cholestano-azetidinol* (27) had m.p. 117—119 °C (from ethanol) (Found: C, 82.6; H, 10.8; N, 2.4. $C_{34}H_{53}NO$ requires C, 83.0; H, 10.9; N, 2.8%); $\nu_{max.}$ ($CHCl_3$) 3 400br cm^{-1}; τ 2.5—3.7 (m, Ph), 5.9 and 6.53 (total 2 H, 2 × d, each *J* 8 Hz, together NCH_2), 6.1—6.5 (m, CH), 7.5—9.7 (total 44 H, m, remaining CH), and 7.93br (s, OH); *m/z* 491 (M^+, 14%), 178 (25), 136 (21), 135 (33), 132 (12), 106 (100), 97 (25), 95 (27), 93 (19), 91 (25), 87 (25), 85 (27), 83 (27), 81 (28), and 77 (18).

The tetrahydrocarbazoles (19), (22), and (30), and 2-anilinocyclohexanol (31a) were compared with authentic samples (see below). Crude 2-anilino-1-deuteriocyclohexanol (31b), obtained in trace amounts on irradiation of the amino-ketone (10g), showed signals in its mass spectrum at *m/z* 192 (M^+, 48%), 149 (17), 133 (70), and 132 (100).

The *N*-alkylarylamines (17), (23), and (29) were identical with the samples used for the synthesis of the corresponding 2-(*N*-alkylarylamino)cyclohexanones. The basic product obtained on irradiation of the anilinoindanone (33b) appeared to be *N*-trideuteriomethylaniline (comparison of i.r. spectrum with that of an authentic sample); *m/z* 110 (M^+, 93%), 109 (22), 108 (PhNHCD_2^+, 100), 105 (20), 85 (32), and 77 (30).

Cyclodehydration of the 2-(N-*Alkylarylamino*)*cyclohexanones* (10), (20), *and* (28) *to give the* 9-*Substituted* 1,2,3,4-*tetrahydrocarbazoles*.—(i) The 2-(*N*-alkylarylamino)cyclohexanone (1 g) was heated under reflux in ethylene glycol (3 ml) for 24 h. After the solution had cooled, 2M-hydrochloric acid (50 ml) was added and the mixture was extracted into diethyl ether. Evaporation of the extract and crystallisation of the residue yielded the tetrahydrocarbazole. Thus prepared were *9-phenylethyl-1,2,3,4-tetrahydrocarbazole* (19e) (78%), m.p. 64 °C (Found: C, 86.9; H, 7.7; N, 4.8. $C_{20}H_{21}N$ requires C, 87.2; H, 7.7; N, 5.1%); τ 2.2—3.05 (9 H, m, ArH), 5.8 (t, *J* 7.5 Hz, NCH_2), 7.03 (t, *J* 7.5 Hz, CH_2Ph), 7.1—7.85 (4 H, m, 2 × CH_2), and 8.0—8.45 (4 H, m, 2 × CH_2), and 9-(2,2,2-*trifluoroethyl*)-1,2,3,4-*tetrahydrocarbazole* (19f) (56%), m.p. 88 °C (Found: C, 66.0; H, 5.7; N, 5.2. $C_{14}H_{14}F_3N$ requires C, 66.4; H, 5.6; N, 5.5%); τ 2.35—3.0 (m, ArH), 5.5 (q, *J* 9 Hz, NCH_2), 7.08—7.53 (4 H, m, 2 × CH_2), and 7.83—8.28 (4 H, m, 2 × CH_2).

The tetrahydrocarbazoles (19a),[29] (19c) (as the picrate),[30] (19d) (as the picrate),[29] and (22) [31] were prepared in a similar manner.

(ii) The tetrahydrocarbazole (19b) [30] was prepared by heating the amino-ketone (10b) in glacial acetic acid for 1 h.

(iii) 9-*Isopropyl*-1,2,3,4-*tetrahydrocarbazole* (30), isolated in 10% yield as the neutral by-product from the preparation of the amino-ketone (28) (see above), had m.p. 59 °C (from methanol) (Found: C, 83.9; H, 8.9; N, 6.4. $C_{15}H_{19}N$ requires C, 84.5; H, 9.0; N, 6.6%); τ 2.3—3.1 (m, ArH), 5.47 (1 H, septet, *J* 7 Hz, C*H*Me_2), 7.0—7.6 (4 H, m, 2 × CH_2), 7.8—8.4 (4 H, m, 2 × CH_2), and 8.43 (d, *J* 7 Hz, 2 × Me).

2-Anilinocyclohexanol (31a).—2-Anilinocyclohexanone (32a) [11] (1 g) was heated under reflux in dry diethyl ether (20 ml) in the presence of lithium aluminium hydride (0.3 g). Diethyl ether was then added, the excess of hydride was destroyed by addition of water, and the ethereal layer was washed with dilute aqueous sodium hydroxide. Evaporation of the dried ethereal solution yielded an oil which was presumably a mixture of *cis*- and *trans*-2-anilinocyclohexanols. A crystal of the 2-anilinocyclohexanol obtained on irradiation of the amino-ketone (28) was added to the oil which was kept for 18 h at 4 °C. Trituration of the resulting semi-solid mass with a little light petroleum gave a solid (0.74 g), m.p. 39—49 °C which, on repeated recrystallisation from light petroleum containing a little ethanol, yielded trans-2-*anilinocyclohexanol*, m.p. 58—59 °C. This structure assignment follows from a comparison of the m.p. with that (m.p. 58 °C) of the product of the reaction of aniline with cyclohexene oxide (originally described as the *cis*-isomer).[13]

* Eu(fod)$_3$ = Europium tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate).

2-Anilinocyclohexane-1-spiro-2'-oxiran (34).[32]—A solution of dimethylsulphoxonium methylide,[33] prepared from trimethylsulphoxonium iodide (2.58 g) and sodium hydride (0.28 g) in dry dimethyl sulphoxide (25 ml), was stirred for 6 h at 65 °C under nitrogen with 2-anilinocyclohexanone [11] (2 g). The product was then poured into stirred water (60 ml) and the mixture was rendered just acid (litmus) with 2M-hydrochloric acid. Extraction with diethyl ether gave an oil which solidified with time. Crystallisation (twice) from ethanol yielded 2-anilinocyclohexane-1-spiro-2'-oxiran (34) (0.54 g), m.p. 82—92 °C (Found: C, 76.5; H, 8.4; N, 6.7. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4; N, 6.9%); $\nu_{max.}$ 3 370 cm^{-1}; τ 2.6—3.6 (m, Ph), 6.1—6.6 (total 2 H, m, NCH and NH, intensity halved on adding D_2O), 7.02 and 7.5 (total 2 H, 2 × d, each *J* 5 Hz, together oxiran CH_2), and 7.3—9.0 (8 H, m, 4 × CH_2).

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