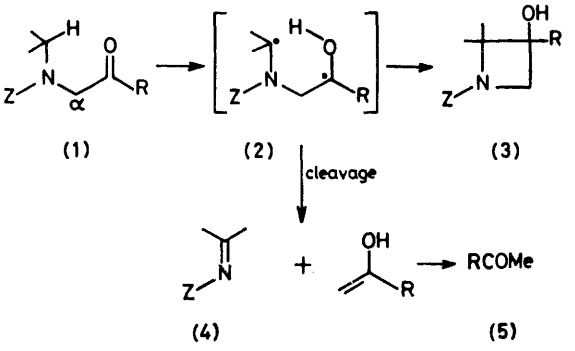
Light-induced Reactions of 2-(*N*-Alkyl-*N*-arylamino)acetophenones and Related Amino-ketones: Formation of 1,3-Diarylazetidin-3-ols

By **Keith L. Allworth, Ahmad A. El-Hamamy, Massoud M. Hesabi,** and **John Hill,*** The Ramage Laboratories, Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT

On irradiation in ether, 2-(*N*-methylanilino)acetophenones, $Ar^1NMe{\cdot}CH_2COAr^2$ (Ar^1, Ar^2 = Ph, Ph; Ph, *p*-MeO·C_6H_4; Ph, *p*-Ph·C_6H_4; *p*-Cl·C_6H_4, Ph; *p*-MeO·C_6H_4, Ph; and *p*-Me·C_6H_4, Ph), underwent type II cyclisation to isomeric 1,3-diarylazetidin-3-ols. A minor photoproduct was one of the two expected type II fission products, the corresponding aectophenone Ar^2COMe. The second type II fission product, imine $Ar^1N{=}CH_2$, was not detected, but in three cases a 1,3-diarylimidazolidine, probably derived from this imine, was isolated. Similar results were obtained on irradiation of the related amino-ketones, 2-(*N*-methylanilino)-2'-acetonaphthone and 2-(*N*-methylanilino)-1-tetralone. Direct fission of the C-2–N bond occurred on irradiation of 2-(*N*-methylanilino)indan-1-one and 2,2-dimethyl-2-(*N*-methylanilino)acetophenone. 2-(*N*-Alkylanilino)acetophenones, $PhNR{\cdot}CH_2COPh$ (R = Et, Me_2CH, and $PhCH_2$), yielded complex mixtures on irradiation.

A VARIETY of photochemical behaviour has been reported for β-ketoamines (1) during recent years (Scheme 1). With alkyl ketones (1; R = alkyl), direct fission of the N–C-α bond generally occurs,[1,2] in some cases [2] (1; Z = aryl) with subsequent recombination of the fragments in an alternative manner to give rearrangement products. The aryl ketones (1; R = aryl) undergo type II photoreactions. Those aryl ketones derived from aliphatic amines (1; R = aryl, Z = alkyl) cleave to a ketone (5) and an imine (4) (which may react further),[3-5] whereas the amido-ketones (1; R = aryl, Z = acyl or tosyl) cyclise to azetidinols (3) with some accompanying cleavage.[3,6] Both type II cleavage and cyclisation of ketones are believed to proceed through a common biradical intermediate [7] [*cf.* (2)] but the factors which influence its subsequent reaction, cleavage or cyclisation, are not fully understood. It has been suggested, in the case of amino-ketones, that the biradical (2) may be formed by an initial transfer of an electron from nitrogen to oxygen followed by transfer of a proton from carbon to oxygen.[3,8]



SCHEME 1

Azetidinols appear to be formed on irradiation of amino-ketones which are relatively weakly basic (where the nitrogen lone-pair is delocalised), for example from α-(*N*-acylamino)-*acetophenones* [3,6] and also from 2-*arylamino*-cyclohexanones.[9] It seemed likely therefore, that azetidinols would result from irradiation of aryl-aminoacetophenones. To investigate this possibility, and to obtain further information on the relationship between structure and photoreactivity of α-amino-ketones, a series of α-(*N*-alkyl-*N*-arylamino)-ketones was prepared and irradiated.

RESULTS

Irradiation of α-(N-*Alkyl*-N-*arylamino*)-*ketones* (6), (14), (17), (19), (25), *and* (26).—The products isolated after irradiation of these amino-ketones are shown in the Table.

With ether [or tetrahydrofuran for the less soluble (6c)] as the solvent, the 2-(*N*-methyl-*N*-arylamino)acetophenones (6a—c and e—g) gave the azetidinols (8) as the major photo-products (see Scheme 2). The reaction was sensitive to the solvent used, as the anilinoketone (6a) yielded the corresponding azetidinol (8a) in ether (48% yield) and in benzene (15.5% yield) but none when the solvent was methanol. Similarly, the yield of azetidinol (8c) from the anilino-ketone (6c) was high (70%) with tetrahydrofuran as

Irradiation of α-(*N*-alkyl-*N*-arylamino)-ketones

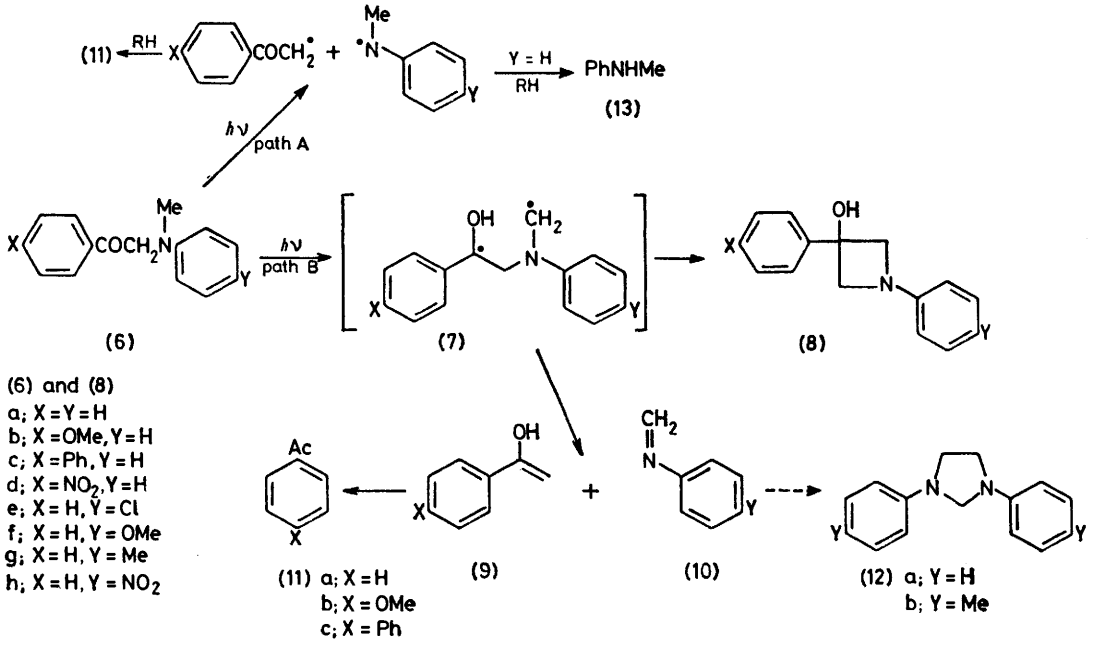
Amino-ketone	Solvent	Reaction time/h	Yield (%) [a] Azetidinol	Other products
(6a)	Et_2O [d]	11	48 (8a)	4 (11a),[b] 20 (12a) [e]
(6a)	MeOH [e]	22		5 (13), 90 (6a)
(6a)	PhH	13.5	15.5 (8a)	1 (11a),[b] 28 (6a)
(6b)	Et_2O	27	50 (8b)	17 (11b),[b] 6 (12a) [e]
(6c)	THF	6.75	70 (8c)	7 (11c)
(6c)	EtOH [d]	13	14 (8c)	7.5 (11c)
(6e)	Et_2O	10	28 (8e)	4 (11a),[b] 1.4 (6e)
(6f)	Et_2O	18	19 (8f)	4 (11a), 40 (6f)
(6g)	Et_2O [f]	5	27 (8g)	6 (11a), 17 (6g), 7 (12b) [e]
(14)	Et_2O	5	68 (15)	19 (16),[b] 26 (13)
(17)	Et_2O	1.5		25 (18),[b] 40 (13) [g]
(19)	Et_2O [f]	3	17 (20)	40 (13), 4 (24), 10 (21),[b] 2 (22), 3 (23)
(25)	Et_2O	5		39 (13) [g]
(25)	EtOH	27		21 (13),[g] 12 ($PhCO_2H$)
(26a)	Et_2O [f]	6.5	10 (27) [h]	30 (26a), trace (11a)

Products are shown in parentheses. [a] Using a 75 W high-pressure mercury-vapour lamp, unless otherwise stated. [b] Isolated as the 2,4-dinitrophenylhydrazone. [c] Assuming 3 mol of (6) yield 1 mol of (12). [d] Initially the amino-ketone was only partly in solution. [e] See ref. 2. [f] Using a 125 W high-pressure mercury-vapour lamp. [g] Isolated as the toluene-*p*-sulphonyl derivative. [h] A crude material for which structure (27) is consistent with spectroscopic data.

the solvent but low (14%) when the solvent was ethanol. In all cases, a minor photoproduct was the corresponding acetophenone (11). A further minor photoproduct was the 1,3-diarylimidazolidine (12a) or (12b) obtained on irradiation of anilino-ketones (6a) and (6b) or (6g) respectively. In one case, when the anilino-ketone (6a) was irradiated in methanol, *N*-methylaniline (13) was isolated in low yield. No products could be isolated after irradiation of the nitro-amino-ketones (6d) and (6h) which slowly yielded complex

Irradiation in ether of the αα-disubstituted α-anilinoacetophenone (25) slowly yielded a complex mixture from which only *N*-methylaniline (13) was isolated. With ethanol as the solvent, *N*-methylaniline and a little benzoic acid were obtained.

The effect of substitution in α-(*N*-methylanilino)-ketones at the *N*-methyl group was investigated by irradiating the *N*-alkylanilinoacetophenones (26a—c) in ether. In all three cases, complex mixtures were produced, and isolation of

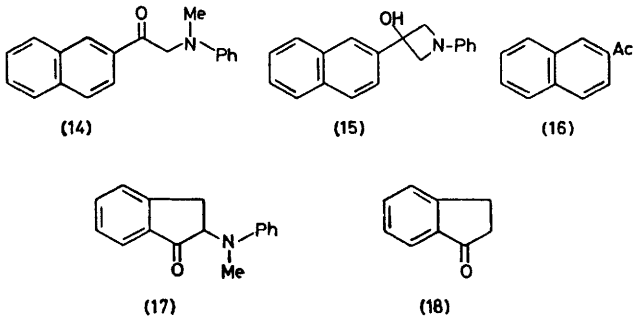


SCHEME 2

mixtures, probably resulting mainly from photoreactions of the nitro-group rather than of the carbonyl group.

Irradiation of the naphthyl ketoamine (14) gave the azetidinol (15) in good yield together with the naphthylketone (16). In this case, *N*-methylaniline (13) was also a significant photoproduct.

The photoreactions of two cyclic ketones (17) and (19)



were investigated. No azetidinol was produced from the anilinoindanone (17), the products being the indanone (18) and *N*-methylaniline (13). Irradiation of the anilinotetralone (19) (Scheme 3) yielded the corresponding azetidinol (20) along with *N*-methylaniline (13), the major product, and low yields of 1-tetralone (21), 1-naphthol (22), 2-(*N*-methylanilino)-1-naphthol (23), and the benzocarbazole (24).

products was hindered by the decomposition of some of them during the subsequent attempted chromatographic separation. The mixture from the photolysis of the *N*-ethylanilino-ketone (26a) contained a material which appeared, from its spectral properties, to be the azetidinol (27), but attempts to obtain a pure sample were unsuccessful (see Experimental section).

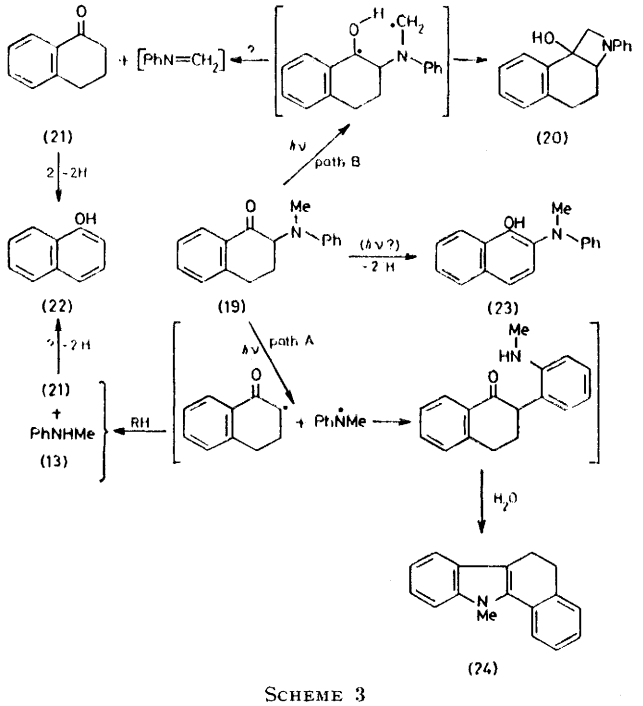
Irradiation of Ketones (28a), (28b), *and* (21).—In an investigation into the mode of formation of the imidazolidine (12a), a photoproduct from the anilino-ketones (6a) and (6b), *N*-methylaniline was irradiated in the presence of an aromatic ketone. With acetophenone (28a) and ether as the solvent, a trace (*ca.* 1%) of the imidazolidine (12a) was produced, the major product being the pinacol (29a). Only benzpinacol (29b) was isolated after irradiation of *N*-methylaniline with benzophenone (28b) in benzene, and no significant reaction occurred when benzophenone was irradiated in benzene in the absence of *N*-methylaniline.

1-Tetralone (21) was irradiated in ether in order to determine the extent to which dehydrogenation to 1-naphthol (22) would take place. A little (2%) 1-naphthol was produced together with the pinacol (30) and unidentified products derived from interaction of tetralone with the solvent.

Preparation of α-(N-*Alkylarylamino*)-*ketones*.—In general, the aminoketones were prepared according to the method of Brown and Mann,[10] whereby the appropriate α-bromoketone was treated with an excess of the appropriate *N*-

alkylaniline in ethanol. The hindered bromo-ketone (31) did not react under these conditions but formed the desired amino-ketone (25) on treatment with lithium *N*-methylanilide. The nitroanilinoacetophenone (6h) was prepared by nitration of the amino-ketone (6a) as no reaction occurred between *N*-methyl-*p*-nitroaniline and phenacyl bromide.

Characterisation of the Photoproducts.—The azetidinols were characterised by their i.r. (ν_{OH} at 3 200—3 330 cm^{-1}; no carbonyl absorption), n.m.r., and mass spectra. The main feature of the n.m.r. spectra of the azetidinols (8) and (15) was the double doublet for the ring methylene groups which replaces the $COCH_2$ and *N*-Me singlets of the original amino-ketones. The azetidine ring methylene group in the azetidinol (20) appeared as a sharp singlet which changed to a double doublet on treating with $Eu(fod)_3$ shift reagent, whereas the ring methylene groups in the azetidinols (8f) and (8g) appear as double doublets which collapse to a singlet on adding deuterium oxide. The mass spectra of the azetidinols are also characteristic and the main fragmentation pathways of many of the azetidinols described here have previously been reported.[11]

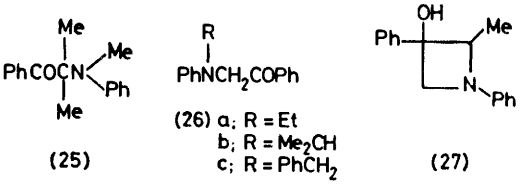


SCHEME 3

The crude azetidinol (27) may be a mixture of geometrical isomers, although only one signal for the methyl group was observed in the n.m.r. spectrum which was similar to other azetidinol spectra apart from the additional coupling involving the methyl group. The i.r. spectrum showed no carbonyl absorption and had ν_{OH} at 3 200 cm^{-1}. In its mass spectrum, the majority of significant peaks may be attributed to ions formed by fragmentation typical [11] of a 1,3-diarylazetidin-3-ol.

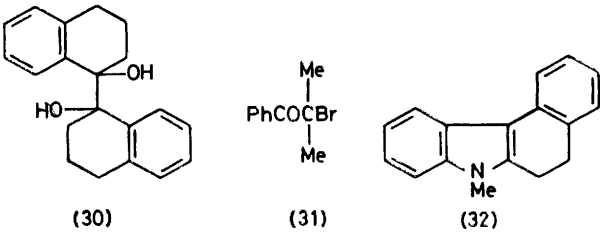
The ketones (11), (18), and (21) were compared with authentic samples (generally as their 2,4-dinitrophenylhydrazones) as were *N*-methylaniline, benzoic acid, 1-naphthol, and the imidazolidines (12a) [12] and (12b).[13]

The dihydrobenzocarbazole (24) was identical with a sample [14] prepared from 1-tetralone and 1-methyl-1-phenylhydrazine. As 2-(*N*-alkylanilino)cyclohexanones readily cyclise (on silica gel, with acid, or on heating) to tetrahydrocarbazoles,[9] it was thought possible that the dihydrobenzocarbazole (32), isomeric with (24), might be formed during the irradiation (or subsequent work-up) of the *N*-methylanilinotetralone (19). To prepare a sample for comparison, the amino-ketone (19) was heated in glacial acetic acid.



(25) (26) a; R = Et b; R = Me_2CH c; R = $PhCH_2$ (27)

Instead of cyclodehydration, dehydrogenation occurred and a product was isolated (42% yield) which appeared to be the aminonaphthol (23). Its n.m.r. spectrum contains no signals for aliphatic protons other than that for *N*-Me and the i.r. spectrum shows a broad peak (OH) at 3 430 cm^{-1} and no carbonyl absorption. The base peak in the mass spectrum is the molecular ion (*m/e* 249) and the major fragment corresponds to loss of the methyl group. The dehydrogenation product was identical with the material (23) formed in low yield on irradiation of the amino-ketone (19). When the amino-ketone (19) was heated in acetic acid under nitrogen, a lower yield (20%) of (23) was obtained along with a trace (0.6%) of the benzo[*c*]carbazole (32). An authentic sample [15] of the latter was prepared from 2-tetralone and 1-methyl-1-phenylhydrazine.

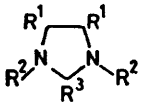


(30) (31) (32)

DISCUSSION

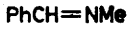
Irradiation of α-(N-Alkyl-N-arylamino)-ketones (6a—c *and* e—g) *and* (14).—The major photoproduct, with ether or tetrahydrofuran as the solvent, was the corresponding azetidinol formed by type II cyclisation (see Scheme 2). In this, the arylamino-ketones (6) and (14) show similar photochemical behaviour to the above-mentioned α-(*N*-acylamino)acetophenones [3,6] and 2-arylaminocyclohexanones.[9] However, unlike the arylaminocyclohexanones, little if any azetidinol was produced [from the amino-ketones (6a) and (6c) [6]] when a hydroxylic solvent was used. On irradiation of (6a) in methanol only limited photoreaction occurred and this was presumably direct homolysis (see below) rather than type II cleavage of the N–C-α bond, a low yield of *N*-methylaniline being obtained. In contrast, the quantum yields for type II reactions of some alkyl phenyl ketones were higher in a hydroxylic solvent than in an aprotic solvent such as benzene. This was attributed to hydrogen bonding of solvent molecules with the biradical intermediate which favours reaction by suppressing disproportionation to the starting ketone.[7]

A minor photoproduct from the ketones (6) and (14) was the corresponding acetophenone (11) or naphthyl ketone (16) respectively. This ketone could be formed *via* direct fission (path A) or by type II fission (path B) (Scheme 2). Since the major product is formed by type II cyclisation and since no *N*-methylaniline, a probable direct fission product, was produced, it is likely that the



(33)

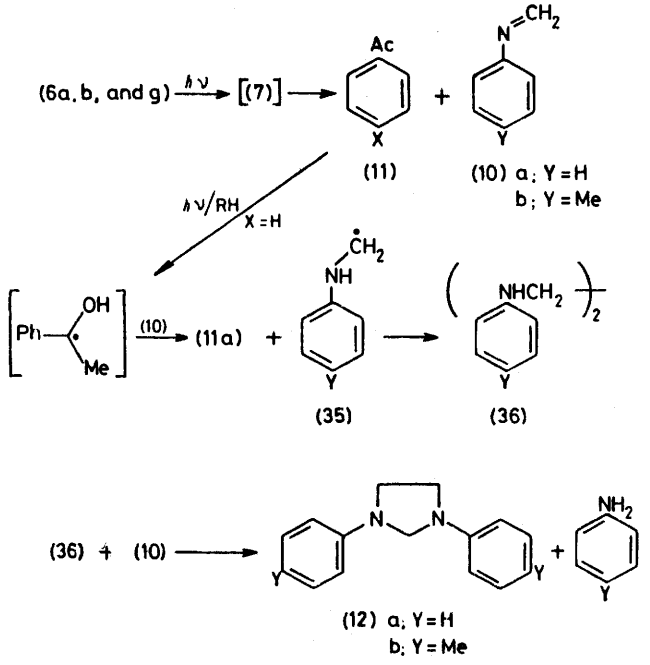
a; R^1=Ph, R^2= Me, R^3=H
b; R^1=R^3=Me, R^2=Et



(34)

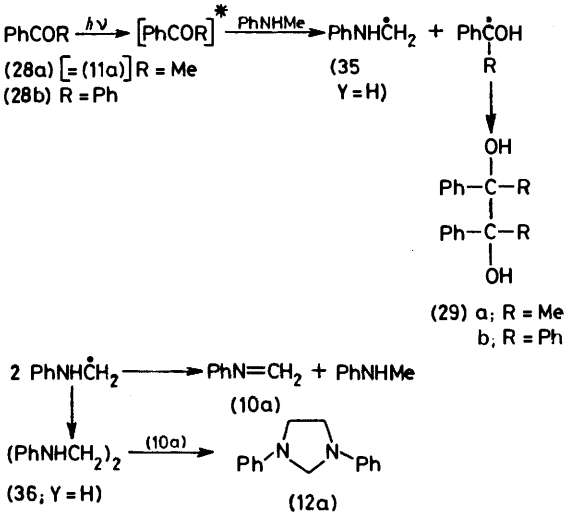
ketones (11) and (16) are mainly formed by type II fission. The formation of the corresponding secondary amine on irradiation of an α-amino-ketone has been cited as evidence for direct fission to radicals rather than for type II fission,[1] although on present knowledge, formation of a secondary amine *via* the type II cleavage product (4) cannot be discounted. *N*-Methylaniline was a significant photoproduct from the naphthyl ketoamine (14) which suggests that direct fission (path A, Scheme 2) may have occurred along with type II photoreaction.

The remaining minor photoproduct, imidazolidine (12) formed from anilinoacetophenones (6a), (6b), and (6g), may also result from type II cleavage *via* the inter-



SCHEME 4

mediacy of the imine (10). The formation of an imidazolidine, (33a), on irradiation of an imine, *N*-methylbenzalimine (34), has been described.[16] A mechanism was proposed by Padwa in which the reactive species was a ' ketyl ' radical produced on irradiation of a carbonyl compound present in the reaction mixture.[17] Based on this proposal we suggest the mechanism outlined in Scheme 4 to account for the formation of the imidazolidine (12). The production of an imidazolidine, (12a), on irradiation of a 1,2-dianilinoethane (36; Y = H) in methanol has been reported.[18] In our case, the conversion of the diamine (36) into the imidazolidine (12) is probably effected by the imine (10) as indicated in Scheme 4. A similar conversion of a diamine into an imidazolidine was proposed by Allan and Swan as the last step in the sequence of reactions by which the imidazolidine (33b) was produced on irradiation of diethylamine.[19] A test for the reaction pathway in Scheme 4 would be to irradiate the imine (10a) in the presence of acetophenone (11a). However, the reaction of aniline with formaldehyde leads to a triazine (37) and not to the imine (10a). An attempt was made to



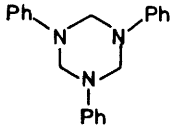
SCHEME 5

prepare the imine (10a) together with the amine radical (35; Y = H) by the photoreaction of *N*-methylaniline with an excited ketone, and then to observe the subsequent reactions of the species present. The formation of the imidazoline (12a), for which the reaction sequence in Scheme 5 is suggested, would be consistent with the mechanism outlined in Scheme 4. Reactions similar to those in Scheme 5 are the production of the *NN'*-dimethyl homologue of the diamine (36; Y = H) by irradiation of *NN*-dimethylaniline in the presence of benzophenone,[20] and the photodehydrogenation of certain amines to imines [21] in the presence of aromatic ketones.

Irradiation of acetophenone (28a) [= (11a)] with *N*-methylaniline produced, however, only a low yield (1%) of the imidazolidine (12a) and no imidazolidine resulted when *N*-methylaniline was irradiated with benzophenone (28b) in benzene. Since benzpinacol (29b) is formed in the latter reaction but not when benzophenone is irradiated in benzene alone, it appears that excited benzophenone must have abstracted hydrogen from *N*-methylaniline in forming benzpinacol (as in Scheme 5).

The fact that the resulting amine radical (35; Y = H) did not react further to give imidazolidine (12a) to any appreciable extent may be due to lack of dimerisation of the radical to the diamine (36; Y = H) and/or lack of disproportionation to the imine (10a) and *N*-methylaniline.

An alternative pathway to the imidazolidine (12a) might be from the stable trimer (37) of the imine (10a) by further photoreaction. The conversion of (37) into



(37)

PhN=CHPh

(38)

(12a) on heating with activated zinc has been described.[22] This route is unlikely since no triazine (37) was detected as a photoproduct on irradiation of the amino-ketones (6a) and (6b), and irradiation of (37) in ether, with or without acetophenone as a sensitiser, resulted in no significant change.

Irradiation of Cyclic Ketones (17) *and* (19).—The presence of the extra ring in these two ketones increases the strain in the transition state for type II photoreaction, and *N*-methylaniline (13), presumably formed by direct N-C-α bond fission, was in each case the major photoproduct. With the aminoindanone (17) no type II cyclisation occurred, the only other product being the indanone (18) which could have arisen by type II or direct fission. In the case of the aminotetralone (19), the strain in the transition state leading to an azetidinol is less than that for the five-membered ring ketone (17), and the azetidinol (20) was produced (Scheme 3). Of the minor photoproducts, 1-tetralone (21) may be formed either by direct fission (path A) or by type II fission (path B). In this case, no product derived from the other type II fission product ($PhN{=}CH_2$) was detected. Further evidence that direct fission to radicals occurs in the reaction was furnished by the isolation of the benzo[*a*]carbazole (24), which results from recombination of the radicals in an alternative manner followed by cyclodehydration. A similar rearrangement is a typical photoreaction of many α-(*N*-alkylanilino)ketones derived from aliphatic ketones.[2]

The naphthols (22) and (23) may be formed in the photoreaction of (19) by dehydrogenation of the tetralones (21) and (19), respectively, by a photochemical or non-photochemical route. Irradiation of 1-tetralone (21) in ether gave 1-naphthol in a yield (2%) similar to that obtained in the photoreaction of aminotetralone (19). An alternative route to both 1-naphthol and 1-tetralone is disproportionation of the ketone radical produced on direct fission. The aminonaphthol (23) was also produced by the action of acetic acid on the amino-ketone (19) (see above).

Irradiation of α-(N-*Alkylanilino*)-*ketones* (25) *and* (26).—Lewis and his co-workers have shown that the ratio of cyclisation : fission in type II photoreactions of alkyl phenyl ketones [23] and bicycloalkyl phenyl ketones [24] was increased when α-methyl substituents were present. To investigate the effect of α-substitution on the photoreactivity of an anilinoacetophenone, the αα-dimethyl-substituted amino-ketone (25) was irradiated. In contrast to the previously mentioned alkyl phenyl ketones, no type II photoreaction was observed. The products, *N*-methylaniline and benzoic acid probably result from direct fission and α-cleavage respectively. Benzoic acid would be formed on oxidation of the α-cleavage product, benzaldehyde, a known photoproduct from phenyl t-alkyl ketones.[25]

The effect of substitution in *N*-methylanilinoacetophenones at the *N*-methyl group, analogous to the γ-position in alkyl phenyl ketones, was also investigated by irradiating the anilinoacetophenones (26). In alkyl phenyl ketones, γ-substituents affect the extent to which the biradical [*cf.* (2)] disproportionates but have little effect on the cyclisation : fission ratio.[7] Irradiation of the amino-ketones (26) gave in each case complex mixtures, some of the products undergoing decomposition during attempted chromatographic separation. Possible unstable products would be the imines formed by type II fission. The imine (38) was isolated in low yield after irradiation of (26c) in methanol.[2] Products were isolated only from 2-(*N*-ethylanilino)acetophenone (26a). These were a trace of acetophenone (11a) and material which resisted purification and appeared to consist mainly of the type II cyclisation product (27). It appears that substitution at the *N*-methyl group (γ-substitution) hinders type II cyclisation and increases the complexity of the photoreaction. This type of substituent effect was not observed with 2-(*N*-alkylarylamino)cyclohexanones.[9]

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 (generally a 75 W type Q81, Quarzlampen GMBH Hanau or, where specified, a 125 W Thorn Electric Kolorlux MBF with the outer glass envelope removed), was centrally situated in a water-cooled Pyrex cold finger. Silica gel used for column 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 and n.m.r. spectra were recorded with deuteriochloroform as the solvent unless otherwise stated.

Preparation of α-N-*Alkylanilinoketones* (6), (14), (17), (19), (25), *and* (26).—In general, the procedure of Brown and Mann [10] was used, whereby the appropriate α-bromoketone was heated under reflux in ethanol with 2.0—2.5 mol. equiv. of the *N*-alkylaniline for 1—5 h (time and yield given below). A little water (less than 10% of the volume of ethanol) was added, the mixture was cooled and the product was filtered off, washed with water, dried, and crystallised. By this method were prepared 2-N-*methylanilino*-4′-*methoxyacetophenone* (6b), 2 h (55%), m.p. 112—113 °C (from ethanol) (Found: C, 75.4; H, 6.9; N, 5.2. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}$ l 685 cm^{-1}; τ 1.8—3.4 (m, ArH), 5.28 (s, CH_2), 6.14 (s, OMe), and 6.9 (s,

NMe); *m/e* 255 (M^+, 10%), 135 (4), 121 (13), 120 (100), 105 (8), 104 (6), and 77 (13); 2-(4-*chloro*-N-*methylanilino*)-*acetophenone* (6e), 3 h (65%), m.p. 114 °C (from ethanol) (Found: C, 69.2; H, 5.4; N, 5.2. $C_{15}H_{14}ClNO$ requires C, 69.4; H, 5.4; N, 5.4%); $\nu_{max.}$ 1 705 cm^{-1}; τ 2—3.6 (m, ArH), 5.32 (s, CH_2), and 6.97 (s, NMe); *m/e* 259 (M^+, 10%), 156 (100), 139 (57), 119 (33), 105 (15), 91 (15), and 77 (51); 2-(4-*methoxy*-N-*methylanilino*)*acetophenone* (6f), 1 h (84%), m.p. 86—88 °C (from ethanol) (Found: C, 75.0; H, 6.65; N, 5.4. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}$ 1 700 cm^{-1}; τ 1.95—3.3 (m, ArH), 5.35 (s, CH_2), 6.25 (s, OMe), and 6.93 (s, NMe); *m/e* 255 (M^+, 20%), 150 (100) 135 (98), 120 (96), 105 (28) 92 (42), and 77 (66); 2-(N-*methylanilino*)-2′-*acetonaphthone* (14), 1 h (84%), m.p. 112—113 °C (from ethanol) (Found: C, 82.7; H, 6.0; N, 5.3. $C_{19}H_{17}NO$ requires C, 82.9; H, 6.2; N, 5.1%); $\nu_{max.}$ 1 695 cm^{-1}; τ 2—3.3 (m, ArH), 5.16 (s, CH_2), and 6.9 (s, NMe); *m/e* 275 (M^+, 88%), 155 (22), 127 (45), 121 (100), 120 (45), 105 (59), 104 (45), 91 (22), and 77 (68); 2-(N-*methylanilino*)*indan*-1-*one* (17), 2 h (53%), purified by column chromatography over silica gel, eluting with 1% ethyl acetate–toluene, m.p. 77—78° (light petroleum containing a little ethanol) (Found: C, 80.1; H, 6.4; N, 5.9. $C_{16}H_{15}NO$ requires C, 81.0; H, 6.4; N, 5.9%); $\nu_{max.}$ 1 710 cm^{-1}; τ 2.1—3.4 (m, ArH), 5.32 (dd, *J* 6 and 8 Hz, 2-H), 6.52 (dd, *J* 8 and 17 Hz, 3-H), 6.93 (dd, *J* 6 and 17 Hz, 3-H), and 7.19 (NMe); *m/e* 237 (M^+, 40%), 208 (77), 194 (52), 132 (36), 106 (100), 91 (72), and 77 (94); 2-(N-*methylanilino*)-1-*tetralone* (19), 3.5 h (40%), the crude product being extracted into ether, the ethereal solution washed (3×) with 0.3N-hydrochloric acid to remove *N*-methylaniline and then extracted into 4N-hydrochloric acid; basification and ether extraction yielded the crude product which on extraction several times with hot light petroleum followed by evaporation yielded the aminoketone (19), m.p. 70 °C (from ethanol containing a little light petroleum) (Found: C, 81.2; H, 7.1; N, 5.7. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); $\nu_{max.}$ 1 682 cm^{-1}; τ 1.9—2 (m, 1 ArH) and 2.3—3.4 (m, ArH), 5.44 (dd, *J* 7 and 11 Hz, 2-H], 6.1—8.2 (m, 2 × CH_2), and 7.17 (s, NMe); *m/e* 251 (M^+, 35%), 146 (72), 117 (100), 115 (45), 107 (92), 106 (100), 91 (48), and 77 (59); and 2-(N-*isopropylanilino*)*acetophenone* (26b), 5 h (95%), m.p. 113 °C (from light petroleum) (Found: C, 80.0; H, 7.1; N, 5.8. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.6; N, 5.5%); $\nu_{max.}$ 1 685 cm^{-1}; τ (CCl_4) 1.8—3.5 (m, ArH), 5.43 (s, CH_2), 5.81 (septet, *J* 7 Hz, CH), and 8.82 (d, *J* 7 Hz, 2 × Me); *m/e* 253 (M^+, 8%), 149 (16), 148 (100), 135 (13), 107 (16), 106 (100), 105 (16), 104 (16), 91 (12), and 77 (75) (Litvinenko *et al.*[26] report the preparation of this compound but quote m.p. 170—175 °C and elemental analysis C, 81.15; H, 6.25; N, 4.5%).

The following anilinoacetophenones, which were prepared in a similar manner, have been described previously; (6a),[27] (6c),[10] (6d),[28] (6g),[26] (26a),[29] and (26c).[30]

2-(N-*Methyl*-4-*nitroanilino*)*acetophenone* (6h).—A solution of concentrated nitric acid (0.33 g) in glacial acetic acid (2 ml) was added dropwise, with stirring, to 2-(*N*-methylanilino)acetophenone (6a) (1.5 g) in warm glacial acetic acid (9 ml) at a temperature high enough to prevent crystallisation of the anilinoacetophenone. The mixture was heated at 70 °C for 20 min, cooled, and poured into ice-water, and the resulting solid purified by column chromatography over silica gel. Elution with 5% ethyl acetate–toluene and crystallisation from ethanol gave 2-(N-*methyl*-4-*nitroanilino*)*acetophenone* (6h) (0.19 g, 16%), m.p. 130—132 °C (Found: C, 66.9; H, 5.2; N, 10.4. $C_{15}H_{14}N_2O_3$ requires C, 66.6; H, 5.2; N, 10.4%); $\nu_{max.}$ 1 690 cm^{-1}; τ 1.9—2.6 (m, Ph), 1.8 and 3.38 (doublets with slight further splitting, *J ca.* 9 Hz, ArH, A_2B_2 system), 5.08 (s, CH_2), and 6.8 (s, NMe); *m/e* 270 (M^+, 20%), 166 (22), 165 (100), 149 (10), 120 (84), 91 (10), and 77 (20).

2,2-*Dimethyl*-2-(N-*methylanilino*)*acetophenone* (25).—A solution of n-butyl-lithium (0.02 mol) in hexane was added dropwise during 10 min, under nitrogen, to a stirred solution of freshly distilled *N*-methylaniline (2.14 g) in dry ether (20 ml) with ice-bath cooling and the mixture was then allowed to warm to room temperature. 2-Bromoisobutyrophenone (4.3 g) in dry ether (20 ml) was slowly added to the above solution which was stirred for 4 h and then water (2 ml) was added. The mixture was extracted into ether and the ethereal solution was washed with 2N-aqueous sodium hydroxide, dried, and evaporated to give an oil (4.1 g) which formed crystals (from ethanol) of the *anilinoacetophenone* (25) (3.2 g, 63%), m.p. 51—53 °C (Found: C, 81.1; H, 7.2; N, 5.3. $C_{17}H_{19}NO$ requires C, 80.6; H, 7.6; N, 5.5%); $\nu_{max.}$ 1 675 cm^{-1}; τ 1.5—3 (m, ArH), 7.03 (s, NMe), and 8.53 (s, 2 × Me); *m/e* 253 (M^+, 2%), 149 (63), 148 (100), 133 (23), 118 (100), 106 (21), 105 (35), 91 (17), and 77 (100).

Apart from commercially available materials, the following α-bromo-ketones and *N*-alkylanilines were prepared according to literature methods: 2-bromo-4′-methoxyacetophenone,[31] 2-bromoacetylnaphthalene,[32] 2-bromoindan-1-one,[33] 2-bromo-1-tetralone,[34] *p*-chloro-*N*-methylaniline,[35] and *p*-methoxy-*N*-methylaniline.[36]

Irradiation of α-(N-*Alkylanilino*)*ketones* (6), (14), (17), (19), (25), *and* (26a).—A 1—2% solution of the amino-ketone was irradiated, the solvent evaporated, and the residue chromatographed over silica gel (60—100 g for each g of photoproduct). In a few cases, the solution was extracted with alkali and/or acid before evaporation (see below). Reaction times, solvent used, and yields are given in the Table. Generally toluene and then toluene containing ethyl acetate in progressively increasing amounts were used as eluant.

The ketones (11) and (21) were eluted with 1—2% ethyl acetate–toluene and the ketones (16) and (18) with toluene. Usually the impure ketonic fraction was extracted into hot light petroleum and the extract, after evaporation, was treated with 2,4-dinitrophenylhydrazine and concentrated hydrochloric acid in ethanol to yield the ketone 2,4-dinitrophenylhydrazone. The azetidinols (15) and (20) were eluted with 1—2% ethyl acetate–toluene and the azetidinols (8) and (27) with 3—5% ethyl acetate–toluene. The azetidinol (20) crystallised from a mixture containing the ketone (21) on trituration with light petroleum.

The imidazolidines (12) were eluted with toluene. Benzocarbazole (24) was the first product obtained by elution with light petroleum–toluene (50 : 50) of the products from photolysis of the amino-ketone (19). The amino-ketones (6) and (26a) were recovered unchanged on eluting with 1—2% ethyl acetate–toluene.

N-Methylaniline (13) was either eluted with toluene [irradiation of (6g) and (17)] or separated by extraction into dilute hydrochloric acid [irradiation of (25)]. After irradiation of the amino-ketone (19) the solution was extracted first with 0.5N-hydrochloric acid to obtain (13) on basification and then with 2N-aqueous sodium hydroxide to give, after acidification, crude 1-naphthol (22) which was purified by extraction into hot light petroleum. The

remaining material was chromatographed in the usual manner. The aminonaphthol (23) did not extract into alkali but was obtained on elution with toluene. Generally, extraction with dilute hydrochloric acid is not advisable as the azetidinols are usually only partly extracted, even with 4N-acid.

Benzoic acid, from irradiation of (25), was isolated by extraction into 4N-aqueous sodium carbonate.

After irradiation of the amino-ketone (6c) the solution was evaporated and the residue was extracted into hot light petroleum (b.p. 100—120 °C). Cooling gave (8c) (63%). Evaporation of the filtrate and chromatography of the residue yielded the remaining photoproducts including the remainder (7%) of (8c).

Identification of Photoproducts.—The photoproducts were compared (i.r. spectra) with authentic samples or characterised by their i.r., n.m.r., and mass spectra. Analytical and spectroscopic data for the azetidinols are given below. Mass spectral information is not included where this has already been fully described.[11] *1,3-Diphenylazetidin-3-ol* (8a) had m.p. 86 °C (from light petroleum) (Found: C, 79.9; H, 7.0; N, 5.9. $C_{15}H_{15}NO$ requires C, 80.0; H, 6.7; N, 6.2%); $\nu_{max.}$ 3 290 cm^{-1}; τ 2.4—3.8 (m, ArH), 5.9 (d, *J* 8 Hz) and 6.08 (d, *J* 8 Hz) (2 × CH_2), and 7.3 (s, OH). *3-(p-Methoxyphenyl)-1-phenylazetidin-3-ol* (8b) had m.p. 82—83 °C (from ether–light petroleum) (Found: C, 74.9; H, 6.1; N, 5.2. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}$ 3 300 cm^{-1}; τ 2.4—3.7 (m, ArH), 5.95 (d, *J* 8 Hz) and 6.12 (d, *J* 8 Hz) (2 × CH_2), 6.27 (s, OMe), and 6.6 (s, OH). *3-(p-Biphenylyl)-1-phenylazetidin-3-ol* (8c) had m.p. 140—145 °C (from light petroleum) (Found: C, 83.3; H, 6.7; N, 4.6. $C_{21}H_{19}NO$ requires C, 83.8; H, 6.4; N, 4.6%); $\nu_{max.}$ 3 240 cm^{-1}; τ 2.2—3.6 (m, ArH), and 5.69 (d, *J* 7.5 Hz) and 5.88 (d, *J* 7.5 Hz) (2 × CH_2). *1-(p-Chlorophenyl)-3-phenylazetidin-3-ol* (8e) had m.p. 118—120 °C (from light petroleum) (Found: C, 69.7; H, 5.2; N, 4.9. $C_{15}H_{14}ClNO$ requires C, 69.4; H, 5.4; N, 5.4%); $\nu_{max.}$ 3 320 cm^{-1}; τ 2.3—2.9 (m, Ph), 2.9 and 3.7 (2 d, *J ca.* 9 Hz with slight further splitting, ArH, A_2B_2 system), 5.92 (d, *J* 8 Hz) and 6.07 (d, *J* 8 Hz) (2 × CH_2), and 6.7 (OH). *1-(p-Methoxyphenyl)-3-phenylazetidin-3-ol* (8f) had m.p. 96—98 °C (from light petroleum) (Found: C, 75.0; H, 6.75; N, 5.2. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); $\nu_{max.}$ 3 260 cm^{-1}; τ 2.3—3 (m, Ph), 3.2 and 3.56 (2 d, *J ca.* 9 Hz with slight further splitting, ArH, A_2B_2 system), 5.89 (d, *J* 8 Hz) and 6.05 (d, *J* 8 Hz) (2 × CH_2, collapses to a singlet at τ 5.8 on addition of D_2O), and 6.28 (s, OMe). *3-Phenyl-1-(p-tolyl)azetidin-3-ol* (8g) had m.p. 71—72 °C (from light petroleum) (Found: C, 80.4; H, 7.4; N, 5.7. $C_{16}H_{17}NO$ requires C, 80.3; H, 7.2; N, 5.9%); $\nu_{max.}$ 3 280 cm^{-1}; τ 2.4—3 (m, Ph), 3.03 and 3.62 (2 d, *J ca.* 8 Hz with slight further splitting, ArH, A_2B_2 system), 5.88 (d, *J* 8 Hz) and 6.05 (d, *J* 8 Hz) (2 × CH_2, collapses to a singlet at τ 5.77 on addition of D_2O), 6.9 (OH), and 7.74 (Me). *3-(2-Naphthyl)-1-phenylazetidin-3-ol* (15) had m.p. 122—123° (from ethanol) (Found: C, 82.9; H, 6.2; N, 5.1. $C_{19}H_{17}NO$ requires C, 82.9; H, 6.2; N, 5.1%); $\nu_{max.}$ 3 300 cm^{-1}; τ [$CDCl_3$ + $(CD_3)_2SO$] 1.8—3.6 (m, ArH), and 5.87 (d, *J* 8 Hz) and 5.93 (d, *J* 8 Hz) (2 × CH_2); *m/e* 275 (M^+, 6%), 170 (66), 155 (28), 141 (28), 128 (100), 127 (59), 106 (47), 105 (57), 104 (47), 115 (22), 91 (19), and 77 (88). *2-Phenyl-1,2,2a-3,4,8b-hexahydronaphth[2,1-b]azet-8b-ol* (20) had m.p. 116 °C [from light petroleum (b.p. 100—120 °C)] (Found: C, 81.2; H, 7.1; N, 5.5. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%); $\nu_{max.}$ 3 330 cm^{-1}; τ 2.3—3.6 (m, ArH), 5.6—5.75 (m, 2a-H], 6.12 [s, 1-H_2, changes to 5.86 (d, *J* 7.5 Hz) and 5.98 (d, *J* 7.5 Hz) on addition of Eu(fod)$_3$ shift reagent], 6.7—8.6 (m, 3-H_2 and 4-H_2), and 7.56 (OH); *m/e* 251 (M^+, 26%), 146 (100), 145 (37), 131 (38), 117 (12), 115 (15), 107 (20), 106 (98), 105 (27), 91 (12), and 77 (36). The photoproduct obtained as an oil from the amino-ketone (26a) appeared to be crude 2-methyl-1,3-diphenylazetidin-3-ol (27). $\nu_{max.}$ 3 200 cm^{-1}; τ 1.8—3.6 (m, ArH), 5.66 (q, *J ca.* 7 Hz, 2-H), 5.84 (d, *J ca.* 9 Hz) and 5.94 (d, *J ca.* 9 Hz) (4-H_2), and 8.45 (d, *J ca.* 7 Hz, Me); *m/e* 239 (M^+, 9%), 134 (10), 133 (10), 120 (43), 119 (60), 106 (35), 105 (60), 104 (45), 91 (16), and 77 (100). Benzoic acid, 1-naphthol (22), and *N*-methylaniline (13) [in some cases isolated as its toluene-*p*-sulphonyl derivative (see Table)] were identical with authentic samples. The ketones (11a—c), (16), (18), and (21) were isolated and/or characterised as their 2,4-dinitrophenylhydrazones. The imidazolidines (12a) [12] and (12b) [13] and the benzo[*a*]carbazole (24) [14] were identical with samples prepared by literature methods. *2-(N-Methylanilino)-1-naphthol* (23) had m.p. 95—96 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 81.8; H, 6.3; N, 5.6. $C_{17}H_{15}NO$ requires C, 81.9; H, 6.1; N, 5.6%); $\nu_{max.}$ 3 430 cm^{-1}; τ 1.5—3.5 (m, ArH) and 6.83 (s, NMe); *m/e* 249 (M^+, 100%), 234 (M^+ — 15, 70), 172 (13), 115 (11), 104 (11), 91 (8), and 77 (19).

Irradiation of N-Methylaniline in the Presence of Acetophenone or Benzophenone.—(i) *N*-Methylaniline (1.5 g) and acetophenone (3.36 g) in ether were irradiated for 11 h using a 125 W lamp and the solution was extracted with 4N-hydrochloric acid. Basification of the extract yielded *N*-methylaniline (0.58 g) after purification by chromatography over silica gel. Chromatography of the remaining material, eluting with light petroleum, gave a little imidazolidine (12a) (*ca.* 1%) and further elution with 10% ethyl acetate–toluene gave 1,2-diphenylethane-1,2-diol [37] (29a) (0.76 g), m.p. 120—121 °C (ethanol), identical with an authentic sample.

(ii) *N*-Methylaniline (1.5 g) and benzophenone (5.1 g) in benzene (140 ml) were irradiated for 3 h using a 125 W lamp. Evaporation yielded a solid which crystallised from ethanol to give benzpinacol [37] (29b) (2.5 g), identical with an authentic sample. No further products were isolated from the photolysis mixture.

No significant reaction was observed after irradiation of benzophenone in benzene with a 125 W lamp for 19 h in the absence of *N*-methylaniline.

Irradiation of the Triazine (37).—(i) The triazine (37) [38] (0.5 g) was irradiated for 5.5 h in ether. Little change was observed (t.l.c.).

(ii) The above irradiation was repeated with acetophenone (0.2 ml) present. No significant change was observed after 6.5 h and the presence of imidazolidine (12a) was not detected.

Irradiation of the Tetralone (21).—1-Tetralone (1.1 g) was irradiated in ether (100 ml) for 6 h using a 125 W lamp. The product was extracted with 2N-aqueous sodium hydroxide and, after acidification, crude 1-naphthol (0.018 g) was obtained. The neutral material was dissolved in hot light petroleum from which, on standing, pinacol (30) [39] (0.12 g) crystallised, m.p. 186—189 °C (from ethanol); $\nu_{max.}$ 3 560, 3 535, and 1 453 cm^{-1}. Distillation of the residue from the mother-liquor gave fractions containing (t.l.c., i.r., and n.m.r.) 1-tetralone and a product (or products) from interaction of 1-tetralone with ether (*cf.* photoproduct from interaction of 1-tetralone with methanol [39]).

Action of Acetic Acid on the Aminotetralone (19).—(i) The aminotetralone (19) (0.31 g) in glacial acetic acid (3 ml) was heated on the water-bath for 3 h under nitrogen. The mixture was evaporated and the residue was chromatographed over silica gel. Elution with toluene–light petroleum (1 : 1) gave a trace (0.6%) of the benzo[*c*]-carbazole (32), identical with an authentic sample (see below). Further elution gave 2-(*N*-methylanilino)-1-naphthol (23) (0.061 g), identical with the material isolated after irradiation of (19).

(ii) The aminotetralone (19) (0.3 g) was heated, as above, in acetic acid but not under nitrogen. No benzocarbazole (32) was formed and the aminonaphthol (23) was obtained in higher yield (42%).

5,6-Dihydro-7-methyl-7H-benzo[c]*carbazole* (32).—2-Tetralone (0.44 g) and 1-methyl-1-phenylhydrazine (0.38 g) were heated in glacial acetic acid (5 ml) for 0.5 h on a water-bath. Addition of water to the cold solution gave the benzocarbazole (32) (0.4 g), m.p. 134—135 °C (from light petroleum) (lit.,[15] 132—134 °C).

We thank the S.R.C. for a Research Studentship (to K. L. A.).

[9/1213 *Received*, 1*st August*, 1979]

REFERENCES

[1] J. J. Hlavka and P. Bitha, *Tetrahedron Letters*, 1966, 3843.
[2] J. Hill and J. Townend, *J.C.S. Perkin I*, 1972, 1210.
[3] A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, 1971, **93**, 6998.
[4] P. J. Wagner, A. E. Kemppainen, and T. Jellinek, *J. Amer. Chem. Soc.*, 1972, **94**, 7512.
[5] J. A. Hyatt, *J. Org. Chem.*, 1972, **37**, 1254.
[6] E. H. Gold, *J. Amer. Chem. Soc.*, 1971, **93**, 2793.
[7] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.
[8] S. G. Cohen, A. Parola, and G. H. Parsons, jun., *Chem. Rev.*, 1973, **73**, 141.
[9] J. Hill and J. Townend, *J.C.S. Chem. Comm.*, 1972, 1108.
[10] F. Brown and F. G. Mann, *J. Chem. Soc.*, 1948, 847.
[11] J. Clark and J. Hill, *J.C.S. Perkin II*, 1976, 1514.
[12] H.-W. Wanzlick and W. Löchel, *Chem. Ber.*, 1953, **86**, 1463.
[13] M. Scholtz and K. Jaross, *Ber.*, 1901, **34**, 1504.
[14] Ng. Ph. Buu-Hoi and P. Jacquignon, *J. Chem. Soc.*, 1956, 1515.
[15] P. Schiess and A. Grieder, *Helv. Chim. Acta*, 1974, **57**, 2643.
[16] P. Cerutti and H. Schmid, *Helv. Chim. Acta*, 1964, **47**, 203.
[17] A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, 1969, **91**, 2653.
[18] P. Cerutti and H. Schmid, *Helv. Chim. Acta*, 1962, **45**, 1992.
[19] L. T. Allan and G. A. Swan, *J. Chem. Soc.*, 1965, 4822.
[20] R. S. Davidson, P. F. Lambeth, and M. Santhanam, *J.C.S. Perkin II*, 1972, 2351.
[21] S. G. Cohen and R. J. Baumgarten, *J. Amer. Chem. Soc.*, 1967, **89**, 3471.
[22] J. Nosek and J. Gasparič, *Coll. Czech. Chem. Comm.*, 1967, **32**, 2028.
[23] F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, 1972, **94**, 3852.
[24] F. D. Lewis, R. W. Johnson, and R. A. Ruden, *J. Amer. Chem. Soc.*, 1972, **94**, 4292.
[25] F. D. Lewis and J. G. Magyar, *J. Org. Chem.*, 1972, **37**, 2102; H.-G. Heine, *Tetrahedron Letters*, 1972, 3411.
[26] L. M. Litvinenko, L. A. Perel'man, A. F. Popov, and L. I. Voroshilova, *J. Org. Chem.* (*U.S.S.R.*), 1970, **6**, 2096.
[27] P. E. Verkade and E. F. J. Janetzky, *Rec. Trav. chim.*, 1943, **62**, 763.
[28] G. Pifferi, G. Cignarella, and E. Testa, *Ann. Chim.* (*Italy*), 1962, **52**, 59 (*Chem. Abs.*, 1962, **57**, 631).
[29] A. F. Crowther, F. G. Mann, and D. Purdie, *J. Chem. Soc.*, 1943, 58.
[30] W. F. Cockburn, R. A. W. Johnstone, and T. S. Stevens, *J. Chem. Soc.*, 1960, 3340.
[31] K. Kindler and L. Blaas, *Ber.*, 1944, **77**, 585.
[32] T. Immediata and A. R. Day, *J. Org. Chem.*, 1940, **5**, 512.
[33] C. L. Arcus and G. C. Barrett, *J. Chem. Soc.*, 1958, 2740.
[34] J. Cymerman Craig, D. M. Temple, and B. Moore, *Austral. J. Chem.*, 1961, **14**, 84.
[35] R. M. Roberts and P. J. Vogt, *J. Amer. Chem. Soc.*, 1956, **78**, 4778.
[36] H. King and I. M. Tonkin, *J. Chem. Soc.*, 1946, 1063.
[37] G. Ciamician and P. Silber, *Ber.*, 1900, **33**, 2911.
[38] L. Zalukajevs, *Latv. PSR Zināt. Akad. Vēstis*, 1952, **55**, 136 (*Chem. Abs.*, 1954, **48**, 3921).
[39] H. Göth, P. Cerutti, and H. Schmid, *Helv. Chim. Acta*, 1965, **48**, 1395.