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PHOTOCHEMICAL REACTIONS OF β,γ-UNSATURATED AROMATIC AMINES[1]

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Abstract—Exposure of a dilute solution of N-allylaniline (**1**) in EtOH to UV light under N_2 gave mainly aniline (57%), accompanied by *o*-allylaniline (**2**, 6·8%) and *p*-allylaniline (**3**, 11·7%) etc. Irradiation of **1** in the presence of an oxidising agent such as $FeCl_3 \cdot 6H_2O$ gave different products, quinoline (**4**) in a low yield (2·6%), together with benzene, aniline and an unknown product. No reaction of **1** with $FeCl_3 \cdot 6H_2O$ to yield **4** occurred in the dark at room temperature. Similarly, N-allyl-α-naphthylamine (**5**) is photo-oxidised with $FeCl_3 \cdot 6H_2O$ to benzo[*h*]quinoline (**6**, 2·4%). Further, irradiation of N-cinnamylaniline (**8**) in the presence of an oxidising agent gave 2-phenylquinoline (**9**, 5%) instead of the expected 4-phenylquinoline (**10**). The 2-phenyl isomer (**9**), but not **10**, was obtained in a good yield on photolysis of N-cinnamylideneaniline (**11**), which is expected in the $FeCl_3 \cdot 6H_2O$ oxidation of **8**. Probable reaction pathways are discussed.

UV IRRADIATION of N-alkylanilines gives mainly *o*- and *p*-alkylanilines.[2] The acid-catalysed rearrangement of N-alkylanilines in the dark, known as the Hofmann-Martius reaction, proceeds via an intermolecular attack of alkyl carbonium ion to phenyl carbon.[3]

On the other hand, there is evidence of an intramolecular photochemical rearrangement of the same substrates.[2] This rearrangement may proceed via a triplet state in view of the quenching study, and a plot of the σ value for a substituent in the migrating benzyl group *vs* the logarithm of relative rate which gives a positive ρ value with various quantum yields for intersystem crossing.[4]

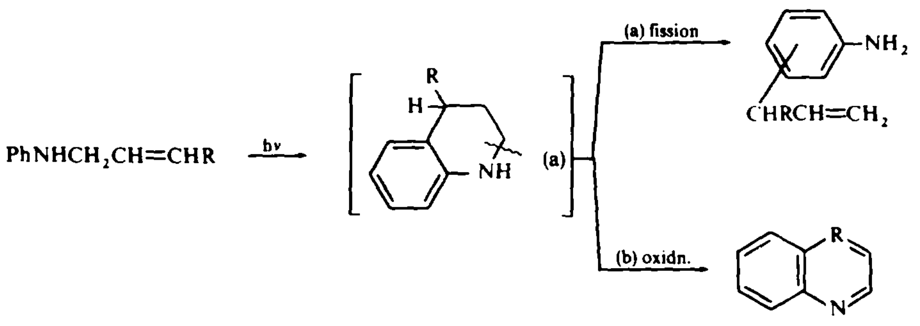
As an extension of the photochemical reaction of N-alkylanilines, the authors attempted the photolysis of β,γ-unsaturated aromatic amines, which on irradiation, may undergo alkyl migration from nitrogen to the ring carbon via either recombination of formed radical fragments or a 6-membered cyclic transition state.

The pyrolysis of N-allylaniline(**1**) up to 700° gives only fission products, i.e., propylene and aniline, instead of *o*-allylaniline(**2**),[5] which is expected from the behaviour of allyl phenyl ethers. Marcinkiewicz *et al.*[6] suggested that more energy is required to bring about the necessary coplanarity in aromatic allylamines with a pyramidal N atom than in allyl ethers.

However, the *ortho*-rearranged product (but not the *p*-isomer) has been obtained in the decomposition of N-allylanilines in the presence of $ZnCl_2$.[7] Hurd *et al.*[7] have reported that N-cinnamylaniline(**8**) with $ZnCl_2$ gave 2-phenylquinoline(**9**) together with *o*-cinnamylaniline in good yields.

The authors report the photolytic behaviour of β,γ-unsaturated aromatic amines including N-allylaniline(**1**), N-allyl-α-naphthylamine(**5**), N-pent-2-enylaniline(**7**) and

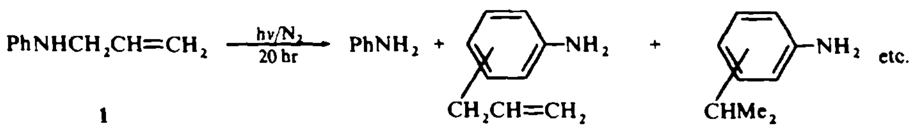
N-cinnamylaniline(8) together with the photolysis in the presence of $FeCl_3 \cdot 6H_2O$ as an oxidising agent. The photolysis gives quinolines via cyclic transition states.



(1)

RESULTS

Direct irradiation of β,γ-*unsaturated aromatic amines.* An ethanol solution of N-allylaniline(1) when irradiated under N_2 yielded a mixture containing aniline (57%) and rearranged products [*o*-allylaniline(2), 6·8% and *p*-allylaniline(3), 11·7%]



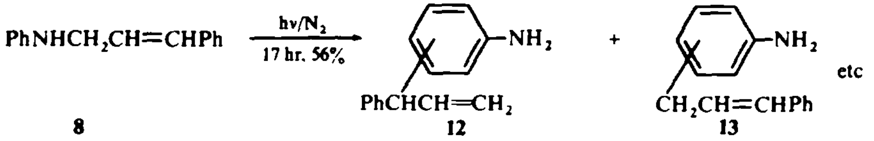
(2)

together with *o*- and *p*-isopropylanilines. The identification and estimation of the products was carried out by means of GLC in comparison with the authentic samples.

Similar irradiation of N-allyl-α-naphthylamine(5) gave only 14% of α-naphthylamine and a trace of 2-allyl-α-naphthylamine(6). In contrast to the photolysis, thermal rearrangement of 5 at 230° resulted in formation of a dark brown oil, which contained *o*-allyl-α-naphthylamine(6) in a yield of 10%. The photolysis of N-pent-2-enylaniline(7) in *t*-butyl alcohol gave only aniline.

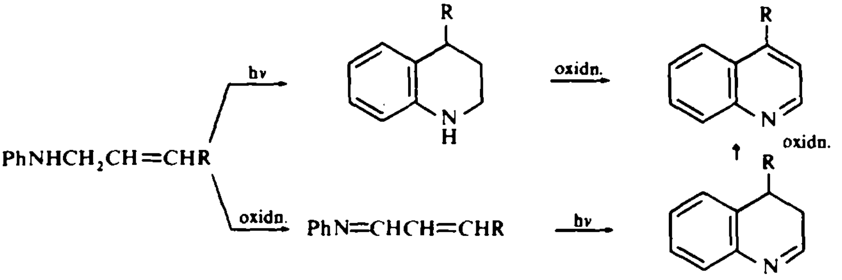
These results show that the photolysis of β,γ-unsaturated aromatic amines leads generally to aliphatic C—N bond fission, but their recombination to *o*- and *p*-isomers is unfavourable; this is in contrast to N-benzyl- or α-phenethylanilines. A cyclic transition state formed by the interaction between terminal vinyl carbon and ortho carbon appears less favourable in the photolysis of the substrates, because C—N bond fission is a main primary process, and because *o*- and *p*-isopropylanilines were detected in the photolysis of 1. The results correspond to the Hoffman-Woodward law that [3,3] sigmatropic migration is permitted in thermal reactions and forbidden in photo-excited ones (see Discussion).

Further, N-cinnamylaniline(8) on UV irradiation in ethanol, rapidly turned brown. The products, after separation, afforded a mixture of (3-aminophenyl-3′-phenyl-propene-1(12) and cinnamylaniline(13), identified by IR spectra which were similar to those of *o*- and *p*-allylanilines.



(3)

Irradiation of β, γ-unsaturated aromatic amines with $FeCl_3 \cdot 6H_2O$. N-Allylaniline (**1**) and N-benzylaniline were easily oxidised to the corresponding imines by $FeCl_3 \cdot 6H_2O$.[8] If the resulting α,β-unsaturated imine is susceptible to the electrocyclic reaction of a six π-electron system, a heteroaromatic would be found. Alternatively, the starting amine could cyclise initially to a 6-membered intermediate, followed by oxidation to a N-heteroaromatic as shown in Eq. 4.



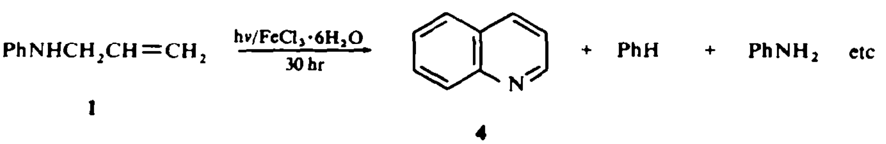
(4)

A methanol–ether solution of N-allylaniline (**1**) with an equimolar amount of $FeCl_3 \cdot 6H_2O$ was irradiated, and the product shown to contain aniline, benzene, quinoline(**4**) and an unknown compound (Table 1). After 30 hr's irradiation, the starting N-allylaniline(**1**) and the subsequent imine was almost consumed to yield 2·6% of quinoline(**4**). Another "unknown product" was not identified.

TABLE 1. PHOTOLYSIS OF N-ALLYLANILINE (1) WITH $FeCl_3 \cdot 6H_2O$[a]

Time (hr)	1 (%)	Aniline (%)	Quinoline (4) (%)	Unknown product (%)
10	excess	4	0·4	14
20	28·5	4	0·5	9
30	trace	1·3	2·6	4·6

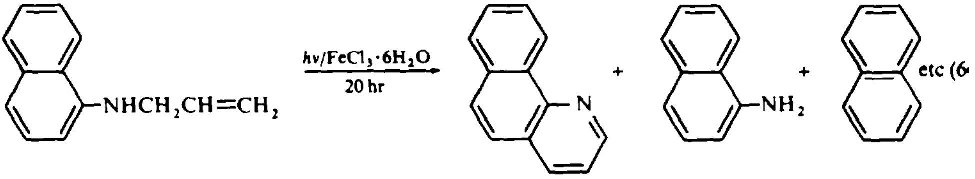
[a] Yields are calculated on the basis of used N-allylaniline (1)



(5)

A similar reaction of **1** in the dark at room temperature gave no quinoline(**4**), which indicates the cyclisation to be a photochemical process.

Irradiation of an equimolar mixture of N-allyl-α-naphthylamine(**5**) and $FeCl_3 \cdot 6H_2O$ in ethanol gave benzo[*h*]quinoline(**6**, 2·4%), α-naphthylamine (31%) and a trace of naphthalene.



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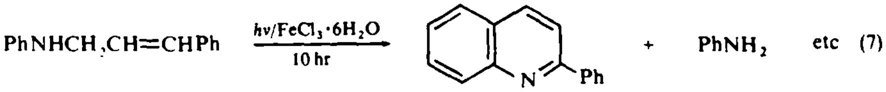
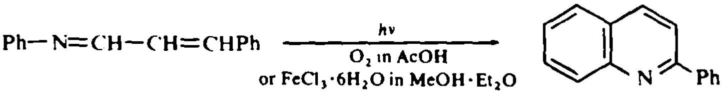
The photolysis of N-cinnamylaniline(**8**) with $FeCl_3 \cdot 6H_2O$ for 10 hr yielded 2-phenylquinoline(**9**, 5%).



8

9

Formation of **9** instead of 4-phenylquinoline(**10**) was unexpected and implies an abnormal cyclisation pathway. Consequently, N-cinnamylideneaniline(**11**) was prepared[9] and irradiated with $FeCl_3 \cdot 6H_2O$. The only product isolated was the same 2-phenylquinoline(**9**, 25%), but not the 4-phenyl-isomer(**10**).



(8)

11

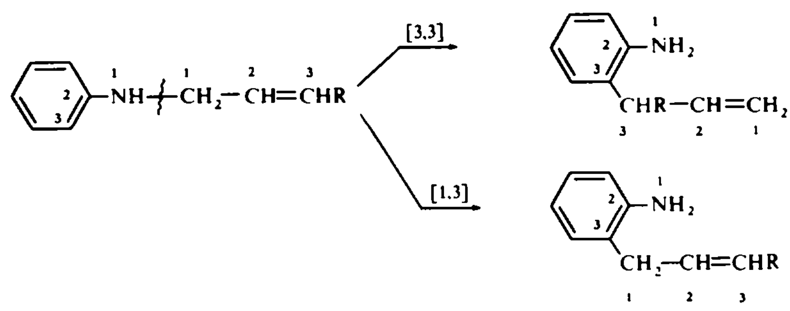
9

Hence, β,γ-unsaturated aromatic amines are initially oxidised to α,β-unsaturated imines (e.g., **11**) and then cyclised to the corresponding quinolines.

DISCUSSION

The above data show that irradiation of β,γ-unsaturated aromatic amines do not give a 6-membered cyclic complex, but aniline by fission of C—N bond, and that in the presence of an oxidising agent e.g., $FeCl_3 \cdot 6H_2O$, they are oxidised to α,β-unsaturated imines followed by cyclisation to quinoline derivatives.

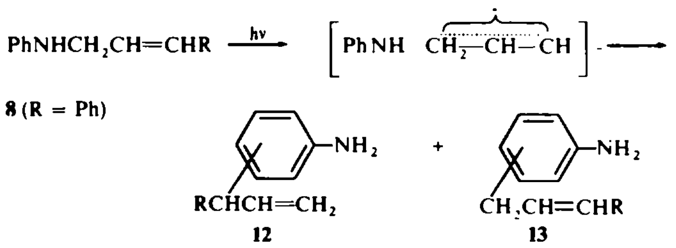
This is in accordance with the Hoffman-Woodward law for an excited reaction, [3,3] sigmatropic migration is forbidden, but [1,3] sigmatropic migration is permitted.



(9)

A few examples of photochemical [1,3] sigmatropic migrations are known. Thus, the thermal reaction of allyl phenyl ether proceeds to the *o*-isomer through a 6-membered cyclic transition state, while the photolysis goes through radical fission and recombination.[10] Another example is the photochemical rearrangement of *p*-ditolyl ether, which results in 2-(*p*-tolyl)-4-methylphenol instead of 2-(*m*-tolyl)-4-methylphenol.[11]

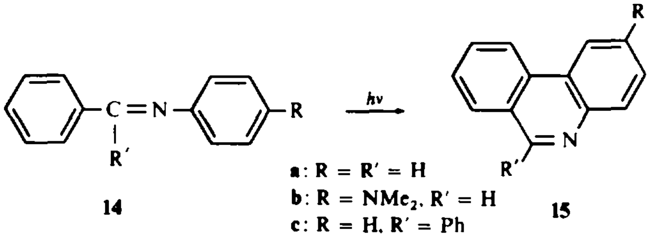
N-Cinnamylaniline(**8**) is photolysed into anilino and cinnamyl radicals. The cinnamyl radical is stabilised by the delocalisation of an odd electron to the phenyl group and then it couples with an anilino radical either at its α-position carbon forming **12** or at its γ-position carbon forming **13**. The photochemical rearrangement of β,γ-unsaturated aromatic amines may be explained as follows.



(10)

Therefore, the photochemical reaction of β,γ-unsaturated aromatic amines in the presence of $FeCl_3 \cdot 6H_2O$ is an electrocyclic reaction of α,β-unsaturated aromatic imines formed by dehydrogenation of the amines.

In general, benzylideneanilines(**14**)[12] cannot cyclise on irradiation in the presence of oxygen or iodine to phenanthridines(**15**) except for a few examples in contrast to photocyclisation of stilbenes or azobenzenes. This may be because the *cis*-isomer of the anil, precursor of cyclisation to dihydrophenanthridine, can not populate on account of slow rate of photochemical *cis-trans* isomerisation, since the lowest excited state of *trans*-isomer is n–π^* but not π–π^*.[13] An electron-releasing group on the anilino ring of benzylideneaniline seems to make the energy of π–π^* transition lower than n–π^*,[14] since **14b** with an NMe_2 group can cyclise to the corresponding phenanthridine(**15b**).[15] Photocyclisation was also observed with benzophenone anil(**14c**) without *cis-trans* isomerisation.[14] It is known that irradiation of **14a** in conc. H_2SO_4 can give **15a**,[16] because strong H-bonding of conc H_2SO_4 to nitrogen makes n-π^* excitation less favourable.

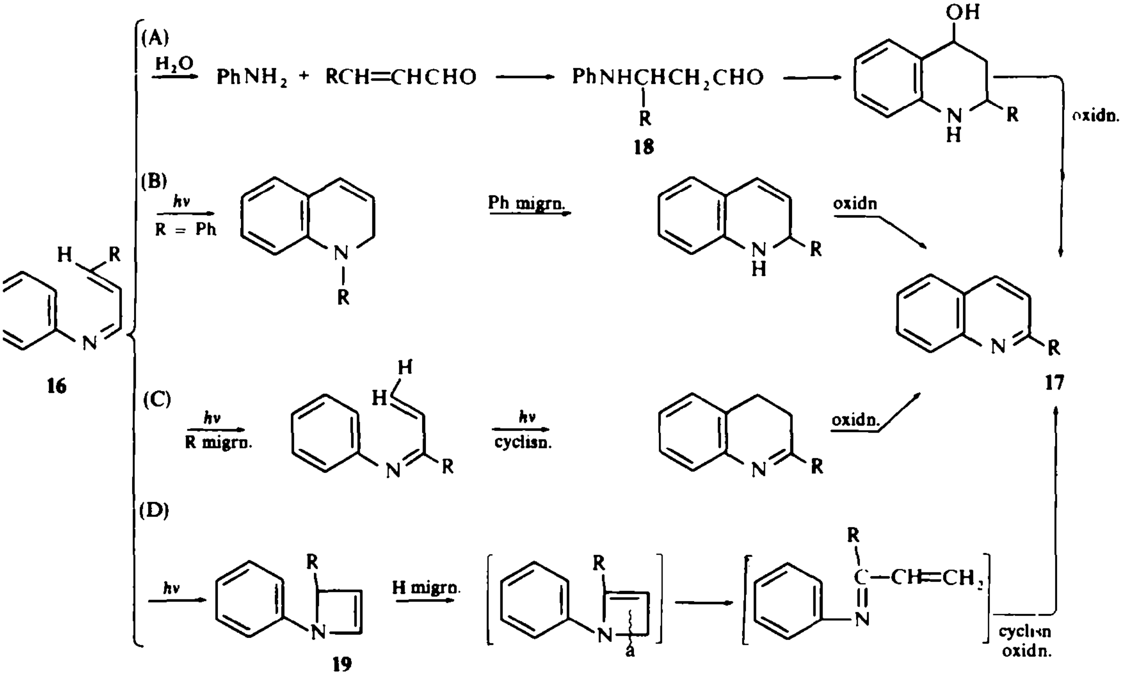


14 **15**

(11)

There is no evidence that irradiation of α,β-unsaturated aromatic imines results in quinoline derivatives in the presence of an oxidising agent. Independently, irradiation of N-cinnamylideneaniline(11) gives 2-phenyldihydroquinoline in a good yield, but the product was not isolated.[17]

There is a possible explanation for the photolysis of **11** with $FeCl_3 \cdot 6H_2O$ to yield **9** but not the expected 4-phenyl-isomer(**10**) (Eq. 7), following four pathways of α,β-unsaturated aromatic imines(**16**) to quinoline derivatives(**17**).

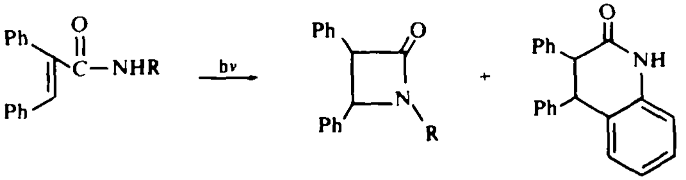


In case A, **11**(**16**, R = Ph) is hydrolysed by a trace of water in the system to aniline and cinnamaldehyde, both of which further give adduct, **18**, which can cyclise in the dark (Doebner-Miller reaction[18]). However, no reaction of N-allylaniline(**1**) with

$FeCl_3 \cdot 6H_2O$ occurred, and therefore path A is improbable. In B, with N-cinnamylideneaniline(**11**) the imino nitrogen may add to the *ortho* position of the cinnamyl group followed by the phenyl shift giving 2-phenylquinoline(**9**) (**17**, R = Ph). But for **1** or **5** without phenyl substituent, this pathway cannot explain the product. Pathway C or D may be possible as a reaction scheme involving apparent alkyl migration. Although there is no conclusive evidence, the pathway C via a simple 1,3-alkyl migration seems less probable, since it involves the C-alkyl bond fission. In pathway D, the α,β-unsaturated imine(**16**) initially gives the unsaturated 4-membered cyclic system (azetine, **19**), followed by ring expansion to a 6-membered N-heterocyclic system by C—N bond fission at "a". Steric hindrance between terminal alkyl group, R, and phenyl group may facilitate the approach of the α-phenyl carbon to the anilino *ortho* position more difficult.

Irradiation of carbonyl homologs similar to α,β-unsaturated imines gave a fairly stable oxetene, although there is no report on photochemical formation of azetidine by addition of imine to olefin. Thus, irradiation of 3,4-dimethylpent-3-en-2-one afforded the oxetene (50%).[19]

Substituted acrylamides give on irradiation β-lactams(**21**) and/or dihydrocarbostyryls(**22**).[20]

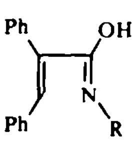


R = H, Ph

21 (major)

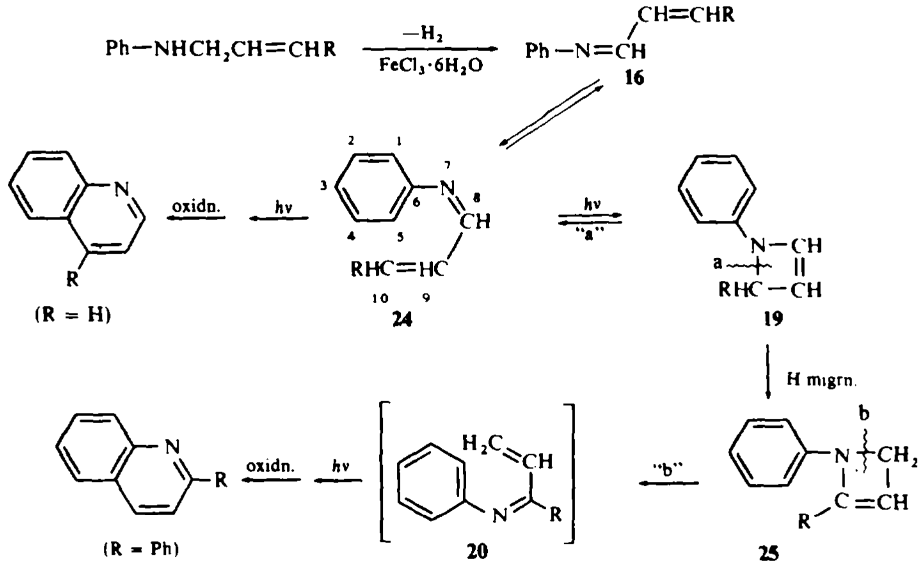
22 (minor)

The amides may be photochemically excited to the enol form(**23**) and then cyclise to β-lactams(**21**).



23

Tentatively, a probable scheme for the photochemical cyclisation of β,γ-unsaturated aromatic imines may be as follows. A starting amine is initially oxidised to a α,β-unsaturated imine by $FeCl_3 \cdot 6H_2O$, followed by photo-isomerisation to the s-*cis* form(**24**), which is either cyclised to 4-alkyldihydroquinoline or to a 4-membered N-heterocycle(**19**). Fission of **19** at bond "a" regenerates the starting β,γ-unsaturated imine or fission of **25** at bond "b" yields **20**, which subsequently cyclises to 2-alkyldihydroquinoline under irradiation.



In addition, MO calculation[17] predicts the bond formation between 7 and 10 position or 1 and 10 positions in s-*cis* form(**24**).

EXPERIMENTAL

A Perkin-Elmer grating IR spectrophotometer, Model 337 and a Shimadzu UV spectrophotometer, Model SV-50A or a Hitachi spectrophotometer, Model 124 were used for the corresponding spectral analyses. GLC analysis was carried out by a Yanagimoto gas chromatograph with FID, Model GCG-550F, employing a 1·7 m × 2·5 mm column packed with PEG 20M (2·5 wt%) on Chamelite CS of 80–100 mesh using N_2 as a carrier gas at 100 to 250°.

Materials. Most of materials used were purified by column chromatography, their purity being confirmed by GLC. N-Allylaniline(**1**) was prepared (28%) by stirring alkyl chloride, aniline and Na in toluene below 25° for 10 hr and then refluxing for 7 hr, b.p. 92–93°/8 mm (lit.[21] 68–70°/1·3 mm). The crude product, contaminated by aniline, was purified by *p*-toluenesulfonylation and then hydrolysis (HCl) to yield a pale yellow oil **1**; λ_{max}^{MeOH} nm (log ε), 246 (3·88) and 296 (3·17). A mixture of *o*-(**2**) and p-allylanilines(**3**) was prepared from allylbenzene, by nitration with HNO_3 fum. -AcOH at 5–10° followed by $FeSO_4$ reduction under reflux, b.p. 88–90°/5 mm (lit.[7] 99–100°/8 mm), n_D^{19} 1·5672 (lit.[7] **2**, 1·5661; **3**, 1·5668). IR spectrum showed their characteristic absorption, i.e., 3440 and 3350 (—NH_2), 1270 (C_{arom}—N), 3080, 990 and 910 (CH_2=CH—), 820 (2H) and 750 (4H). The column chromatography of the mixture with silica gel eluted two isomers with benzene (250 ml) as an eluent; **2**, fr. 19–25, λ_{max}^{MeOH} nm (log ε), 243 (3·72) and 286 (3·19), and **3**, fr. 29–35, λ_{max}^{MeOH} nm (log ε), 238·5 (3·84) and 289·5 (3·06). The purity of the isomer was confirmed by GLC. N-allyl-α-naphthylamine(**5**) was prepared from α-naphthylamine and allyl bromide in ethanol in the presence of Na_2CO_3 for 6 hr, b.p. 105–109°/~0·5 mm, and was purified by chromatography (Silica gel–benzene). N-Pent-2-enylaniline(**7**) was prepared from aniline and 3-chloropent-1-ene with sodium carbonate at 100° for 5 hr, b.p. 105–111°/4·5 mm (38%). Benzo[*h*]quinoline(**6**) was prepared by the condensation of α-naphthylamine with acrolein diacetate and $FeCl_3 \cdot 6H_2O$ followed by neutralisation with KOH, and then steam-distillation, m.p. 47–49° (lit.[22] 50–52°, λ_{max}^{MeOH} (nm), 265, 315, 330 and 345 (lit.[23] λ_{max}^{EtOH} (nm), 260, 320, 330 and 350). N-Cinnamylaniline(**8**) was prepared by the condensation of cinnamyl bromide with aniline in ether at room temp, b.p. 170°/2–3 mm (lit.[7] 159–160°/1·2 mm), and was purified by column chromatography (silica gel) using benzene, λ_{max}^{MeOH} nm (log ε), 251 (4·41), 283 (3·54) and 292 (3·45). N-Cinnamylideneaniline(**11**) was prepared from benzylideneaniline and cinnamaldehyde,[9] recrystallised from MeOH, m.p. 109–110° (lit.[9] 109°), λ_{max}^{MeOH} nm (log ε), 228 (4·08) and 307 (4·42). 2-Phenylquinoline(**9**) was prepared from quinoline N-oxide and PhMgBr in ether at 0° and recrystallised from EtOH[24], m.p. 84·5–85·0° (lit.[24] 84–85°), $\lambda_{\max}^{\mathrm{MeOH}}$ (nm), 255 and 320. 4-Phenylquinoline(**10**) was prepared by the condensation of β-chloropropiophenone, aniline, aniline hydrochloride and $FeCl_3 \cdot 6H_2O$ in EtOH at 93° for 1 hr, b.p. 70–110°/8 mm (lit.[25] 160–195°/3 mm), and was purified through column (silica gel-benzene), $\lambda_{\max}^{\mathrm{MeOH}}$ (nm), 228 and 293.

General procedure of irradiation. All experiments were carried out in a cylindrical quartz vessel (20 × 150 mm) under N_2 except when an oxidising agent was used. A Halos high press 300 W Hg lamp (HIP 300) with a water cooling quartz jacket was used as a light source.

Typical photo-rearrangement of **8**. An EtOH soln (0·013 M) of **8** was irradiated for 17 hr. The resulting soln was condensed *in vacuo*, and chromatographed using benzene as an eluent to give fr. 1–14 (unknown products), fr. 16–24 (recovered **8**, 123 mg) and 30–56 (a pale yellow oil, 202 mg, 57%), $\lambda_{\max}^{\mathrm{MeOH}}$ (nm), 220 and 240. The last fraction was identified with a mixture of two rearranged products, **12** (major, R_f 0·31) and **13** (minor, R_f 0·35) from GLC, TLC and IR spectra, 3350 and 3200 (—NH_2), 3080 and 2975 (CH_2=CH—), 3050 and 3020 (C_{arom}—H), 2920 and 2850 (– CH_2—), 1275 (C_{arom}—N), 990 and 910 (CH_2=CH– –), 965 (*trans*), 830 (2H), 750 and 690 (5H), and the absence of $C_{\mathrm{aliph.}}$—N stretching vibration absorption.

Typical irradiation of **11**. An acetic acid soln (0·015 M) of **11** in the presence of O_2 was irradiated for 29 hr. The condensed reaction mixture, after treatment with KOHaq followed by acetylation, was KOHaq, the condensed mixture was separated by a column packed with silica gel using benzene as an eluent, fr. 29–40 (16 mg, 5%), was identified as **9** by GLC, TLC and UV spectrum ($\lambda_{\max}^{\mathrm{MeOH}}$ 255 nm) in comparison with the authentic sample.

Typical irradiation of **11**. An acetic acid soln (0·015 M) of **11** in the presence of O_2 was irradiated for 29 hr. The condensed reaction mixture, after treatment with KOHaq followed by acetylation, was extracted with HCl aq, after neutralisation with conc KOH aq, and then extracted with ether. The extract was dried over KOH, and evaporated to yield a pale yellow solid (25%), which was crystallised from EtOH to give 2-phenylquinoline, m.p. 84·5–85·0°, m.m.p., 84·5–85·0°.

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