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PHOTOCHEMISTRY OF SOME AROMATIC SCHIFF'S BASES AND NMR SPECTRA OF SOME BENZO[f]QUINOLINES

P. J. Collin, J. S. Shannon, H. Silberman, S. Sternhell* and G. Sugowdz
Division of Coal Research, C.S.I.R.O., P.O. Box 175,
Chatswood, New South Wales 2067, Australia

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Abstract— The principal products (up to 70% of theoretical yield) of the UV irradiation of Schiff's bases derived from β-naphthylamine in several primary alcohols are benzo[f]quinolines, i.e. the reaction involes the incorporation of moieties derived from the solvents. The effect of the nature of the substrate and solvent and of experimental conditions on the yields of these and other products was investigated.

NMR data for 9 substituted benzo[f]quinolines are tabulated and the stereochemistry of some dimers derived from Schiff's bases was investigated by NMR spectroscopy.

INTRODUCTION

Reports of oxidative photocyclizations of stilbenes to phenanthrenes[1,2] and of azobenzenes to benzo[c]cinnolines[3] have prompted us to investigate some aspects of the photochemistry of a number of Schiff's bases, although it had been previously found[4] that the irradiation of benazalaniline in the presence of air failed to yield any of the expected phenanthridine.

In preliminary publications[5,6] we have reported some unexpected products of UV irradiation of Schiff's bases derived from β-naphthylamine and aromatic aldehydes in some primary alcohols. This paper gives details of these experiments and some extensions. Since the inception of our work, three independent reports have appeared[7-9] describing the photooxidative cyclization of other aromatic Schiff's bases to phenanthridines.

The reasons for differences in behaviour between stilbenes and Schiff's bases in photochemical cyclization reactions have been discussed.[1]

RESULTS AND DISCUSSION

The results obtained in the course of 16 typical runs are summarized in Table 1 and Scheme 1. Further details of the procedures adopted are given in the experimental section.

Structure of products. A number of products encountered in this work have been reported previously and were identified by a comparison of their m.ps. New analytical data, mol. wt determinations (by mass spectrometry) as well as NMR and Mass Spectra (see below) were found to be in accord with their structures. The properties of compounds are given in Table 2, and some NMR and mass spectral data are discussed below.

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* Present address: Dept. of Organic Chemistry, The University of Sydney, Sydney, Australia.

The assignment of structures to new compounds was often simplified by their close analogy to compounds with established structures. The largest and most important group comprises a number of novel benzo[f]quinoline derivatives. The NMR spectra of this series of compounds are worthy of some attention: the data for aromatic protons summarized in Table 3 show a number of examples of downfield shifts due to "proximity" interactions[25] of aromatic protons H-1 and H-10. The data for non-aromatic protons are as follows:

2-Methyl-3-phenylbenzo[f]quinoline (III; R = C_6H_5, R' = Me): d, separation 0·8 c/s, 154 c/s, intensity 3H (benzylic Me).

3-*p*-Methoxyphenylbenzo[f]quinoline (III; R = *p*-OMe—C_6H_4, R' = H): s, 232 c/s, intensity 3H (OMe).

2-Ethyl-3-propylbenzo[f]quinoline (III; R = n-Pr, R' = Et): t, 64 c/s, intensity 3H (Me of the n-Pr group); t, 80 c/s, intensity 3H (Me of Et group); sextet, 112 c/s, intensity 2H (β methylene of n-Pr group); q, 171 c/s, intensity 2H (methylene of Et group); t, 180 c/s, intensity 2H (α methylene of n-Pr group).

2-Isopropyl-3-phenylbenzo[f]quinoline (III; R = Ph, R' = $CHMe_2$): d, 80 c/s, intensity 6H (Me's of the i-Pr group); septet, 204 c/s, intensity 1H (methine of the i-Pr group).

2-Butyl-3-phenylbenzo[f]quinoline (IV; R' = Bu): m, 60 c/s, intensity 6H (overlapping terminal Me groups); m, 175 c/s, intensity 4H (α methylene groups); complex multiplet in the range 70–120 c/s, intensity 8H (remaining methylene groups).

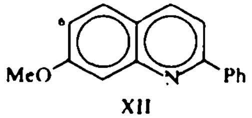
3-Methylbenzo[f]quinoline (IV; R' = H): s, 167 c/s, W_H = 0·95 c/s at a resolution at which W_H TMS = 0·55 c/s, intensity 3H (benzylic Me).

2-Isopropyl-3-isobutylbenzo[f]quinoline (IV; R' = $CHMe_2$): d, 62 c/s, intensity 6H (Me groups of C_3 Bu group); d, 83 c/s, intensity 6H (Me groups of C_2 i-Pr group); m, 141 c/s, intensity 1H (methine proton of the Bu group); septet, 205 c/s, intensity 1H (methine proton of the i-Pr group).

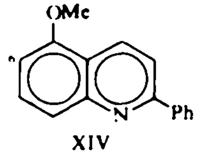
2-Butyl-3-phenylbenzo[f]quinoline (III; R = Ph, R' = Bu): t, 55 c/s, intensity 3H (Me); t, 175 c/s, intensity 2H (α methylene group); m, 65–115 c/s, intensity 4H (other methylene groups).

The splitting (or width at half-height) of the benzylic Me groups in compounds III, R = Ph, R' = Me and IV, R' = H correlates well with the expected bond-order of the adjacent aromatic bond.[26, 27] All vicinal, *ortho* and *meta* splittings were of the expected magnitude.

Irradiation of Schiff's base from *m*-anisidine and benzaldehyde (XI) in ethanol gave a product XII whose mol. wt was correct for a methoxyphenylquinoline (c.f. Table 2). The NMR spectrum showed a 3 proton singlet at 234·5 c/s (methoxyl Me) a doublet of doublets with the total spacing (equiv to $J_{AX} + J_{BX}$) of 11·4 c/s and of intensity corresponding to one proton at 427 c/s and a complex multiplet (9 protons) in the region 440–495 c/s. This spectrum is consistent with the structure XII *2-phenyl-7-methoxyquinoline* or XIV, the two most likely products:



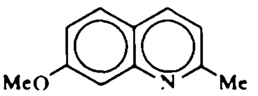
XII



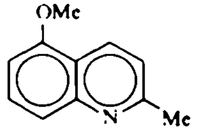
XIV

Assigning the doublet of doublets at 427 c/s to either H-6 in XII or in XIV we obtain from the usual ABX relation that either $J_{5,6} + J_{6,8}$ in XII or $J_{6,7} + J_{6,8}$ in XIV = 11·4 c/s. Now a study of monosubstituted quinolines[28] indicates that $J_{6,7} + J_{6,8}$ is in the range of 8–8·5 c/s while $J_{5,6} + J_{6,8}$ is in the range 9·4–11 c/s, which is clearly an example of the commonly observed[29] relation between J_{ortho} and the bond order of the adjacent double bond. We therefore suggest that the product has the structure XII rather than XIV.

The NMR spectrum of the second product 2-methyl-7-methoxyquinoline (XIII) isolated from the same reaction, whose mol wt corresponded to a methylmethoxyquinoline (see Table 2) showed the following signals which could be satisfactorily interpreted on the basis of the structure XIII but not on the basis of the alternative likely structure XV: singlet, 3 proton intensity at 162 c/s (C-2 Me); singlet, 3 proton intensity, at 235 c/s (OMe); doublet, 1 proton intensity at 428 c/s, spacing 8·3 c/s (H-3); doublet of doublets, 1 proton intensity at 428 c/s, spacings 8·9 and 2·5 c/s (H-6); broad doublet, 1 proton intensity at 444 c/s, spacing 2·5 c/s; doublet, 1 proton intensity at 459 c/s, spacing 8·9 c/s (H-5); broad doublet 1 proton intensity at 478 c/s, spacing 8·3 c/s (H-4). In particular, it can be seen that no signal with two large splittings, corresponding to H-7 in XV, was observed. Unfortunately, insufficient material was available to enable us to obtain pure samples for analyses.



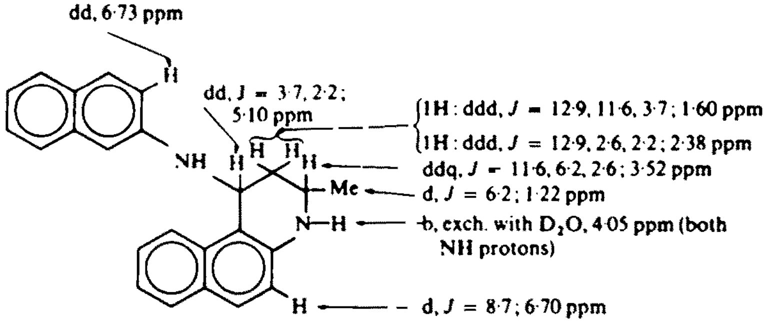
XIII



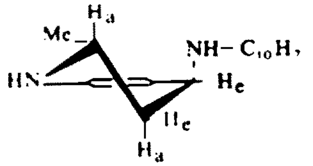
XV

The structures of "Schiff's bases" derived from β-naphthylamine and aliphatic aldehydes were felt to be pertinent to the present investigation in view of the nature of some products of the photolytic reactions (see below). Minkin and Nivorozkin[24] proposed the dimeric structure XVI [1-(2-naphthylamino)3-methyl-1,2,3,4-tetrahydrobenzo[f]quinoline] for a product of reaction from β-naphthylamine and acetaldehyde. NMR data (cf. structure XVI) are in complete agreement with this and strongly suggest the configuration and conformation XVII from consideration of the magnitudes of vicinal coupling constants. The NMR spectrum of the product from n-butyraldehyde and β-naphthylamine shows it to have the analogous structure XVIII. [1-(2-naphthylamino)2-ethyl-3-propyl-1,2,3,4-tetrahydrobenzo[f]quinoline]. The spectrum of XVIII was poorly resolved and no simple assignment of stereochemistry is possible. However, the apparently small magnitude of vicinal coupling constants between H-1, H-2 and H-3 excludes a number of possibilities. A further study of the structure and sterochemistry of dimeric adducts of aliphatic aldehydes and some arylamines is in progress and we have observed the formation of configurational isomers of XVII and its analogues when the reaction was carried out in different solvents.

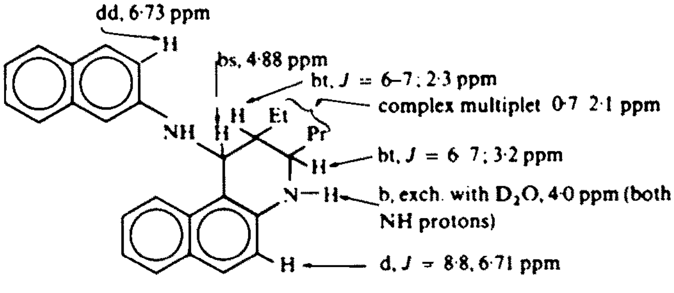
Mass spectral data. Most of the substances investigated gave very intense molecular ions, as expected from polynuclear aromatic structures. The *m/e* values for the molecular ions are listed in Table 2; cracking patterns other than those due to obvious fissions in the aliphatic sidechains are discussed in this section.



XVI



XVII



XVIII

The mass spectrum of IV (R′ = H) shows, besides a strong molecular ion at $m/e = 193$, a strong peak at $m/e = 165$ and a metastable peak due to the process $193^{+\cdot} \rightarrow 165^{+}$. An analogous pattern was also observed in the spectrum of IV (R′ = $CHMe_2$) and may be due to the formation of a fluorenyl (or similar) ion after the elimination of $HN{=}CH$ moiety.

The mass spectrum of VII shows, besides a strong molecular ion at $m/e = 424$, two peaks at $m/e = 297$ and 282 which we consider to be due to the loss of $C_{10}H_7\cdot$ and $C_{10}H_7NH\cdot$ radicals respectively.

The mass spectrum of α,α-bis(2-naphthylamino)dibenzyl (X; R = Ph) shows, besides a strong molecular ion at $m/e = 464$, significant peaks at $m/e = 321$ and 232 which we attribute to the processes shown in Scheme 2.

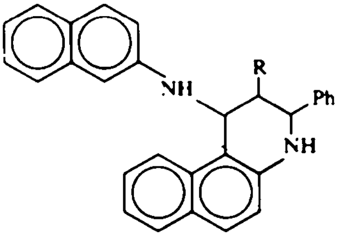
Photochemistry of Schiff's bases in alcohols

(a) *Formation of benzo[f]quinolines.* Comparison of runs 1 and 4 (Table 1) shows that the reactions leading to benzo[f]quinolines III and IV are in fact catalysed by UV light. Comparison of runs 3 and 4 shows further that light of wavelengths longer than about 280 mμ is relatively inefficient.

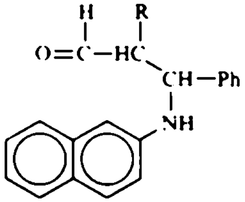
The results obtained from run 2 indicate that in the presence of the aldehyde, derived from the alcohol used as solvent, III and IV can be formed even in the absence of UV light. The very low yields recorded in run 2 may be significant since precautions were taken to prevent the low boiling acetaldehyde being flushed out by the stream of air by adding acetaldehyde continuously.

The considerable reduction of the total yield of benzo[f]quinolines in run 6 as compared with run 4 indicates that a step involving aerial oxidation is rate controlling. This could be a photocatalysed oxidation of the alcohol to the aldehyde (although it has been shown that such reactions may proceed in the absence of oxygen[30]), or a dehydrogenation step which must be postulated on stoichiometric grounds, whatever the mechanism of formation of benzo[f]quinolines. The generally observable formation of *two* benzo[f]quinolines (i.e. III and IV) can be simply explained as due to an aldehyde interchange between the original Schiff's base and the aldehyde derived from the primary alcohol used as solvent.

In view of the dimeric structure (e.g. structures XVI and XVIII) of Schiff's bases derived from β-naphthylamine and aliphatic aldehydes, it must be considered possible that Schiff's bases derived from benzaldehyde derivatives and β-naphthylamine can form "mixed dimers" (e.g. XIX) which could give III by loss of a molecule of amine and (possibly photocatalysed) dehydrogenation. Alternatively, the formation of compounds of type XX, which had been proposed by Kozlov *et al.*[11,12] as intermediates in *acid catalysed* formation of benzo[f]quinolines from Schiff's bases of β-naphthylamine and aldehydes, could be postulated. We have, however, been unable to isolate any intermediates of either type.



XIX



XX

Run 15 shows that reactions analogous to those leading to the formation of benzo[f]quinolines can take place with (at least some) mononuclear compounds although the yields are much lower. No analogous cyclization of the Schiff's base derived from α-naphthylamine (run 16) was, however, observed.

(b) *Formation of other products.* The isolation of appreciable quantities of β-naphthylamine (VIII) from a number of runs is probably due to a slow hydrolysis. This suggested that a number of minor products are in fact derived from β-naphthylamine and this was confirmed in runs 13 and 14.

Compound X was found only in run 6 (exclusion of air). It is most likely the result of a photoreduction of the Schiff's base to the corresponding benzylamine, analogous to the reported photoreduction of benzophenone-N-methylimine,[31] followed by photodimerization at the α-C atom which is apparently general with primary amines.[32]

Compound VII could arise via an oxidation to the 2-amino-1,4-naphthoquinone, followed by the exchange of the amino group for the naphthylamino group (presumably through an addition-elimination sequence) and finally the formation of the anil by one of the quinone carbonyls. It may be significant that the highest yield was recorded in run 3 and that this product was also present in runs 1 and 2, thus suggesting little, if any, participation by UV light. In fact VII has been reported[19,20] as a product of oxidation of β-naphthylamine with several oxidizing agents capable of abstracting single electrons. A closely related compound is a product of irradiation of β-naphthylamine in methanol in the presence of oxygen.[33]

The formation of compound V can also apparently take place in the absence of light,[16] although in this series the yields isolated in the dark runs were significantly lower. Compound VI, on the other hand, is apparently a product of a photochemical process.

5-(2-Naphthylamino)dibenzo[*ah*]phenazine IX (cf. run 3, Table 1) has been previously identified[21] as a product of enzymatic oxidation of β-naphthylamine.

EXPERIMENTAL

General

Mass spectra were recorded with an Atlas model CH4 spectrometer, using ionizing voltage of 70 eV NMR spectra were determined with a Varian Associates Model A-60 spectrometer for 5 10% solns in $CDCl_3$. Chemical shifts were expressed in c/s or ppm downfield from TMS used as internal reference. The relative intensities of all signals were as expected. The signals are described as: s = singlet; d = doublet; dd = doublet of doublets; ddd = doublet of doublets of doublets (8 lines); t = triplet; q = quartet; *m = multiplet*; b = *broad*, W_H = *width at half-height*. M.ps *were taken on a microscope heating stage* model 350 (Leitz Wetzlar). IR spectra were recorded with a Perkin Elmer model 337 spectrophotometer. UV spectra were measured with a Perkin Elmer Spectracord, model 4000A. Microanalyses were performed by the CSIRO Microanalytical Service. The purity of all solvents for irradiation was checked by GLC. *Petrol refers to fraction b.p. 61–64°.*

Irradiation procedure and separation of products

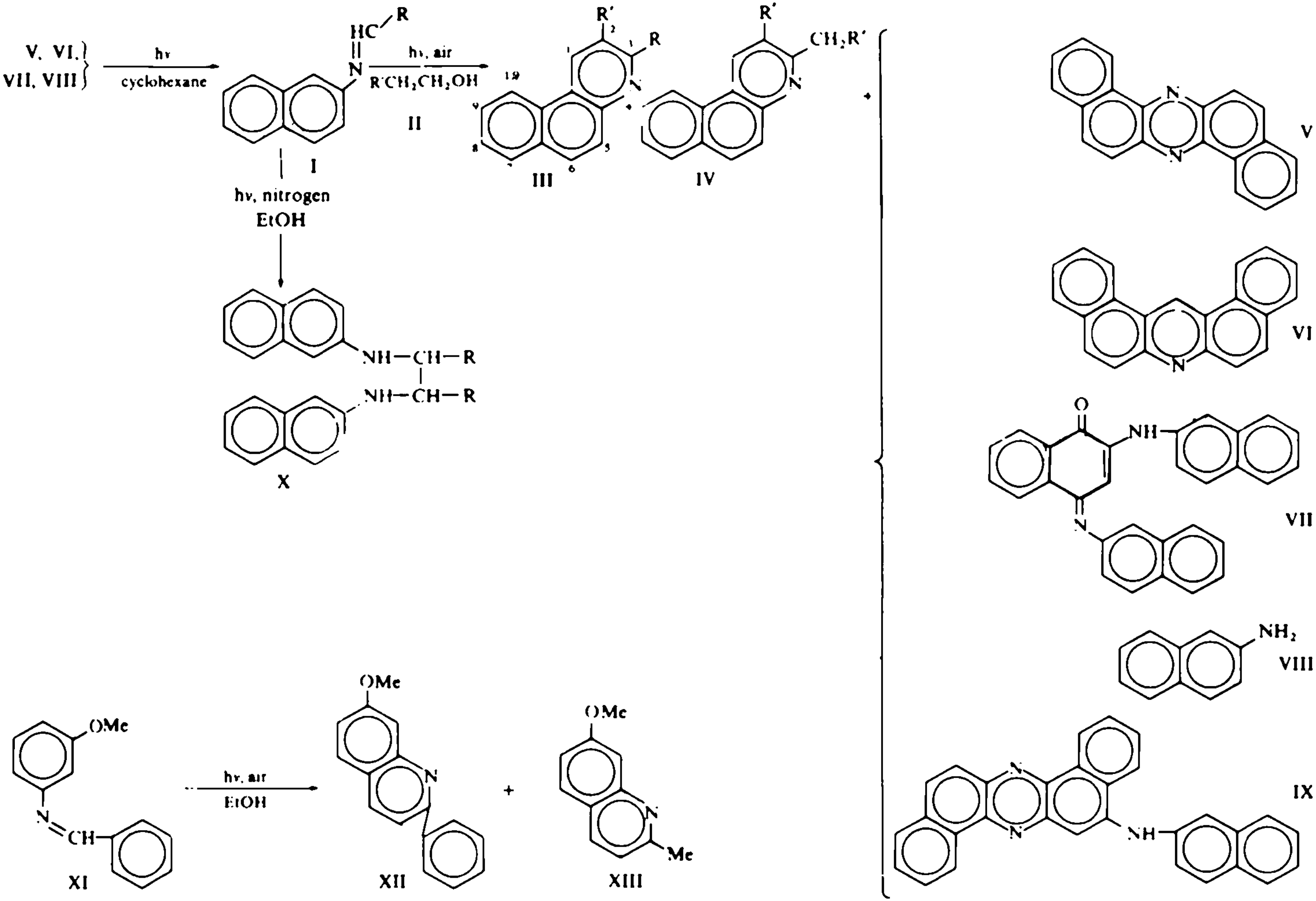
The *light source* was a Philips HPK 125 watt Hg lamp. The irradiation apparatus was of the immersion type and consisted of an outer 450–600 cc Pyrex cylindrical bulb-type flask into which the probe (quartz or Pyrex) was inserted. The flask contained two side arms, one fitted with a condenser capped by a drying tube and thermometer, and the other with a gas inlet tube.

The entire assembly was immersed in a large beaker having a drain inserted near the top; the reaction soln was maintained at the required temp (Table 1) by running a stream of tap water into the bath.

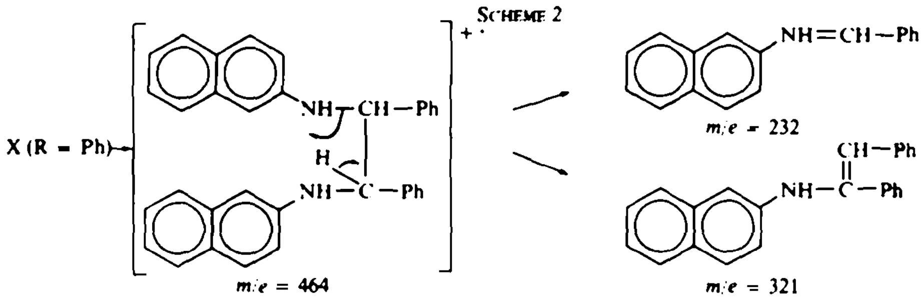
All reaction mixtures were flushed thoroughly with a stream of air N_2 (Table 1) and the gas flow was continued during irradiation, also securing stirring of the mixtures. The progress of the reaction was followed by recording UV spectra at intervals and observing the development and sharpening of absorption peaks near 260, 280 and 301 mμ.

In a typical experiment (Run 4, Table 1) 0·065M soln of I (R = Ph) in 95% EtOH was irradiated for 45 hr; the mixture, which during irradiation turned dark reddish brown and developed a smell of benzaldehyde, was evaporated on a rotary evaporator, dissolved in dry benzene and dried, affording a dark brown gum. This gum was redissolved in benzene–petrol and chromatographed on a column of activated alumina (ratio 1:20). The activation of alumina (BDH) was achieved by heating it for 3–4 hr at 180–190° at *c*. 50 mm Hg (water pump). Elution with solvents of increasing polarity (petrol, petrol–benzene, benzene, benzene–$CHCl_3$, $CHCl_3$ and alcohol), afforded a series of fractions which, as indicated by TLC, consisted of 2 major (III, IV) and several minor components (Table 1). The TLC characteristics (alumina plates, developed with benzene–petrol in 1:1 ratios) of several materials are given in Table 4.

SCHEME 1


V, VI, VII, VIII
hv
cyclohexane
HC
R
N
I
hv, air
R'CH₂CH₂OH
II
hv, nitrogen
EtOH
R'
R
N
1
2
3
4
5
6
7
8
9
10
III
R'
CH₂R'
N
IV
+
V
VI
O
NH
N
VII
NH₂
VIII
NH
N
IX
NH—CH—R
NH—CH—R
X
OMe
N
CH
XI
hv, air
EtOH
OMe
N
XII
+
OMe
N
Me
XIII

SCHEME 2



The major products of irradiation (III, IV) were obtained in pure state after repeated alumina chromatography and crystallization. Combinations of solvents used for elution of each compound are given below:

III, R = Ph, R' = H: eluted with petrol–benzene (1:4) separated from alcohol as colourless plates, m.p. 188°.

III, R = Ph, R' = Me: eluted with benzene petrol and benzene, recrystallized from benzene–petrol colourless needles, m.p. 169–170°.

III, R = Ph, R' = Me_2CH—: eluted with benzene petrol (2:3) crystallized from alcohol m.p. 139°.

III, R = Ph, R' = Bu: eluted with benzene petrol (3:7) recrystallized from benzene–alcohol m.p. 103°.

III, R = p-C_6H_4OMe, R' = H: eluted with petrol benzene (1:9) recrystallized from alcohol m.p. 192–193°.

III, R = Pr, R' = Et: eluted with petrol–benzene, and benzene recrystallized from benzene petrol m.p. 56–57°.

IV, R' = H: eluted with benzene, recrystallized from water–EtOH (1:1) needles m.p. 82°.

IV, R' = Me_2CH: eluted with petrol–benzene (1:9) recrystallized from alcohol m.p. 59°.

IV, R' = Bu: eluted with petrol-benzene (1:9) recrystallized from alcohol m.p. 61°.

The following minor products (in yields depending on the conditions of irradiation, as shown in Table 1) were obtained in pure states by a combination of wet and dry column chromatography and crystallization.

Dibenz[a,h]phenazine V. Eluted with petrol- benzene. The crude product from several irradiations was combined before purification by crystallization from $CHCl_3$ followed by sublimation.

Dibenz[a,j]acridine VI. Eluted with benzene–$CHCl_3$ and characterized by dual yellow-blue fluorescence (alumina plate R_f 0·1). The crude material from several irradiations was combined and after careful dry column chromatography (ratio 1:50) and crystallization from alcohol gave pale-yellow leaflets m.p. 220–221°.

2,2'-naphthylamino-1,4-naphthoquinone 4,2'-naphthylimid (VII). Eluted with benzene immediately after III as dark red-purplish solution; crystallized from benzene and EtOAc as red needles, m.p. 246–247°.

2-naphthylamine (VIII). Eluted with benzene $CHCl_3$ (5–15%) and purified by sublimation.

Compound IX was eluted with benzene from a dry alumina column as a dark-red fluorescent soln. On evaporation, the soln deposited a red solid, m.p. 244 (dec). Crystallization of this material from benzene EtOH or toluene did not change the m.p.

Compound X. This compound was found only in irradiations in an atmosphere of N_2. For this experiment, the apparatus described above was modified by incorporation of a Hg seal to prevent the introduction of O_2 by diffusion against the stream of N_2. The solvent was refluxed prior to the commencement of the irradiation for 2–3 hr to expel dissolved O_2 and was then cooled under N_2.

After the usual work-up, X (R = Ph) was eluted with benzene petrol (1:1) to give a soln which showed a strong bluish-purple fluorescence and was contaminated by III (R = Ph, R' = H) and V. Pure samples of X (R = Ph) were obtained by extraction of this material, in succession, with petrol and cyclohexane and crystallization from benzene petrol.

Preparation of Schiff's base dimers. Compound XVI was prepared by the method of Minkin.[24] The Schiff's base dimer from β-naphthylamine and n-butyraldehyde was prepared by reacting equimolar quantities of the reactants without solvent, dissolving the mixture in butanol and heating at 100° for 5 min. Crystallization from butanol gave pure XVIII, m.p. 152–153°. For properties see Table 2.

TABLE 1. REACTION CONDITIONS AND PRODUCTS

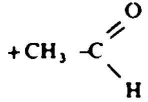
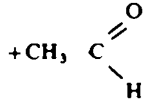
Run No.	Starting materials		Reaction conditions					Products (% yield calculated on I)							
	I	II	Irr. vessel	Conc of I (molar)	Duration (hrs)	Temp (°C)	Atmosphere	III	IV	V	VI	VII	I	VIII	Other Products
1	R = C$_6$H$_5$	R' = H	No irr.	0·065	190	60–65	Air	—	—	trace		trace	~38	~32	
2	R = C$_6$H$_5$	R' = H  $+CH_3-C(=O)H$ (200%)	No irr.	0·065	113	60–65	Air	4·7	3·5	trace	—	trace	<50	20	
3	R = C$_6$H$_5$	R' = H	Pyrex	0·065	45	25–30	Air	7·9	3–4	16	trace	8-10	~20	~30	IX (trace)
4	R = C$_6$H$_5$	R' = H	Quartz	0·065	45	25–30	Air	52–55	13–15	+	trace	+	–	+	
5	R = C$_6$H$_5$	R' = H  $+CH_3-C(=O)H$ (200%)	Quartz	0·065	45	25–30	Air	50–55	~15	+	+	+		+	
6	R = C$_6$H$_5$	R' = H	Quartz	0·065	101	25–30	Nitrogen	15	–	+	+	–	5·8	49	X (10%)

Table 1 *continued*

7	$R = C_6H_5$	Cyclohexane	Quartz	0·065	45	25 30	Air	–	–	17	+	+	~50	~16	
8	$R = C_6H_5$	$R' = CH_3$	Quartz	0·087	44	25 30	Air	56		+	+	+	–		
9	$R = C_6H_5$	$R' - CHMe_2$	Quartz	0·065	45	25 30	Air	25	20	+	+	+	–	+	
10	$R = C_6H_5$	$R' - C_4H_9$	Quartz	0·065	50	25 30	Air	25	37	+	+	+	–	+	
11	p-C_6H_4 OMe	$R' = H$	Quartz	0·080	73	25 30	Air	22	+	+	+	+			
12	XVIII	$R' - C_2H_5$	Quartz	0·10	25	25-30	Air	66	–						
13	VIII	$R' = H$	Quartz	0·10	45	25 30	Air	–	+	+	+	+	–	50	
14	VIII	$R' - C_4H_9$	Quartz	0·10	45	25 30	Air	–	+	+	+	+	–	30	
15	XI	$R' = H$	Quartz	0·065	45	25–30	Air								XII (3%) XIII (3%)
16	*	$R' = H$	Quartz	0·065	45	25 30	Air	–	–	+					* (75%)

* Schiff's base from α-naphthylamine and benzaldehyde.

TABLE 2. PROPERTIES OF PRODUCTS

Compound	Formula	Composition[a] C	Composition[a] H	Composition[a] N	Mol.[b] wt.	m.p. (°C)	Lit. m.p. (°C)	References
III, R = Ph R′ = H	$C_{19}H_{15}N$	89·3 (89·4)	5·1 (5·1)	5·4 (5·5)	255	188	188	10, 11
III, R = Ph R′ = Me	$C_{20}H_{15}N$	88·8 (89·2)	6·0 (5·6)	5·2 (5·2)	269	169 170		
III, R = Ph R′ = CHMe$_2$	$C_{22}H_{19}N$	88·7 (88·9)	6·4 (6·4)	4·6 (4·7)	297	139		
III, R = Ph R′ = C$_4$H$_9$	$C_{23}H_{21}N$	88·7 (88·7)	6·8 (6·7)	4·6 (4·5)	311	103		
III, R = *p*-C$_6$H$_4$OMe R′ = H	$C_{20}H_{15}NO$	84·2 (84·2)	5·3 (5·3)	5·0 (4·9)	285	192–193	191–192	12
III, R = Pr R′ = Et	$C_{18}H_{19}N$	86·7 (86·8)	7·6 (7·6)	5·6 (5·6)	249	56–57		
IV, R′ = H	$C_{14}H_{11}N$			7·2 (7·2)	193	82	82 83	13, 14
IV, R′ = CHMe$_2$	$C_{20}H_{23}N$	86·8 (86·6)	8·6 (8·3)	5·1 (5·0)	277	59		
IV, R′ = Bu	$C_{22}H_{27}N$	86·2 (86·6)	8·7 (8·9)	4·5 (4·6)	305	61		
V	$C_{20}H_{12}N_2$	85·6 (85·7)	4·4 (4·3)	10·0 (10·0)	280	282	282	15, 16

Table 2- continued

Compound	Formula	Composition[a] C	Composition[a] H	Composition[a] N	Mol.[b] wt.	m.p. (°C)	Lit. m.p. (°C)	References
VI	$C_{21}H_{13}N$				279	220–221[c]	220 222	17
VII[d]	$C_{30}H_{20}N_2O$			6·5 (6·6)	424	246	246–247	18, 19, 20
IX[e]	$C_{30}H_{19}N_3$				421	244 dec.	244 dec.	21
X,[f] R = Ph	$C_{34}H_{28}N_2$				464	228	220	22
XII	$C_{16}H_{13}NO$				235			
XIII	$C_{11}H_{11}NO$				173			23
XVI	$C_{24}H_{22}N$					139–140	139 140	24
XVIII[g]	$C_{28}H_{30}N_2$	85·1 (85·0)	7·6 (7·7)	7·1 (7·1)		152·5 153		

[a] Calculated values in brackets.

[b] *m/e* of parent peak in the mass spectrum.

[c] Undepressed by admixture of authentic material prepared by the method of Blout and Corley.[17] The ultraviolet spectra of the two specimens were superimposable.

[d] IR (KCl disc) ν_{max} 3300 cm^{-1} (N-- H), 1660 cm^{-1} (quinone), 1500 cm^{-1} (C═C) and 850 and 720 cm^{-1} (β-substituted naphthalene).

[e] IR (KCl disc) ν_{max} 3300 cm^{-1} (N—H).

[f] NMR data : complex multiplet between 6·7 and 7·8 ppm of relative intensity 24 protons (aromatic H) of which approximately 4 protons resonate between 6·7 and 6·9 ppm (protons *ortho* to NH groups); broad peak of relative intensity of 2 protons at 4·8 ppm exchangeable with D_2O (NH protons) and a broad peak of relative intensity of 2 protons at 5·2 ppm which sharpened appreciably on the exchange of the NH protons with D_2O (N—CH).

[g] IR (KCl disc) ν_{max} 3300 cm^{-1} (N- H).

TABLE 3. NMR DATA FOR THE AROMATIC PROTONS IN BENZO(f)QUINOLINES

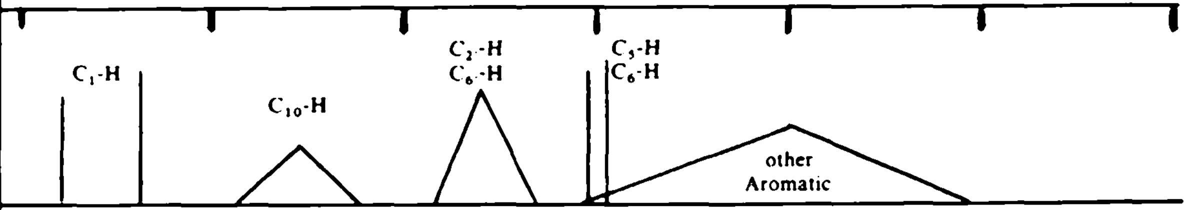
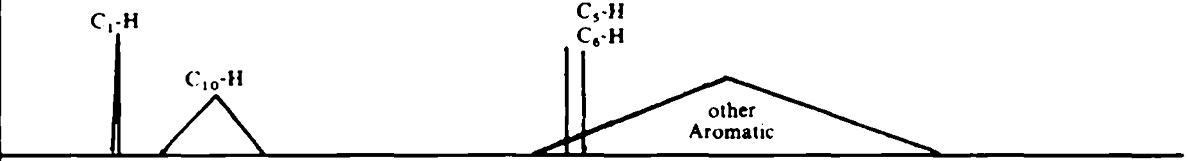
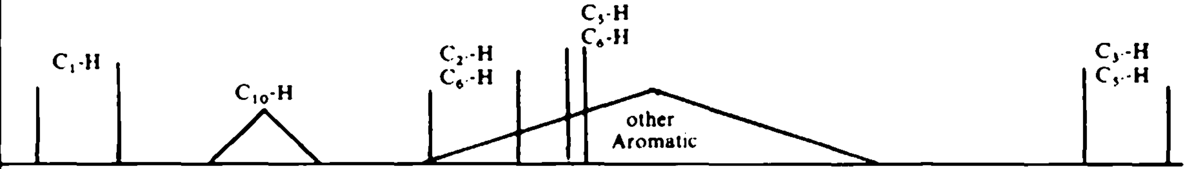
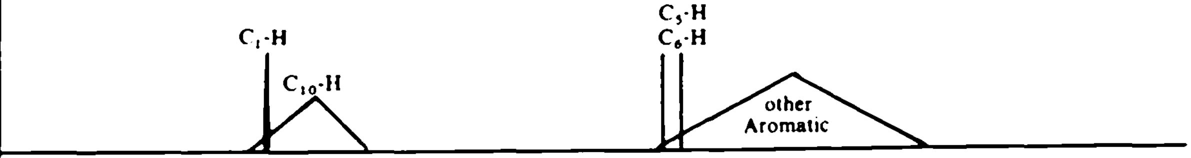
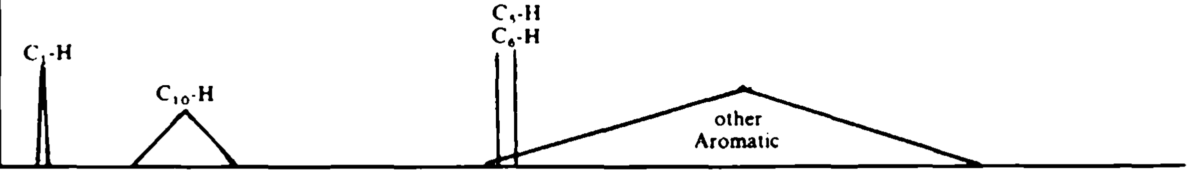
Compound	Aromatic protons
III (R = Ph, R′ = H)	
III (R = Ph, R′ = Me)	
III (R = *p*-OMe—C_6H_4, R′ = H)	
III (R = Pr, R′ = Et)	
III (R = Ph, R′ = $CHMe_2$)	

TABLE 3 *continued*

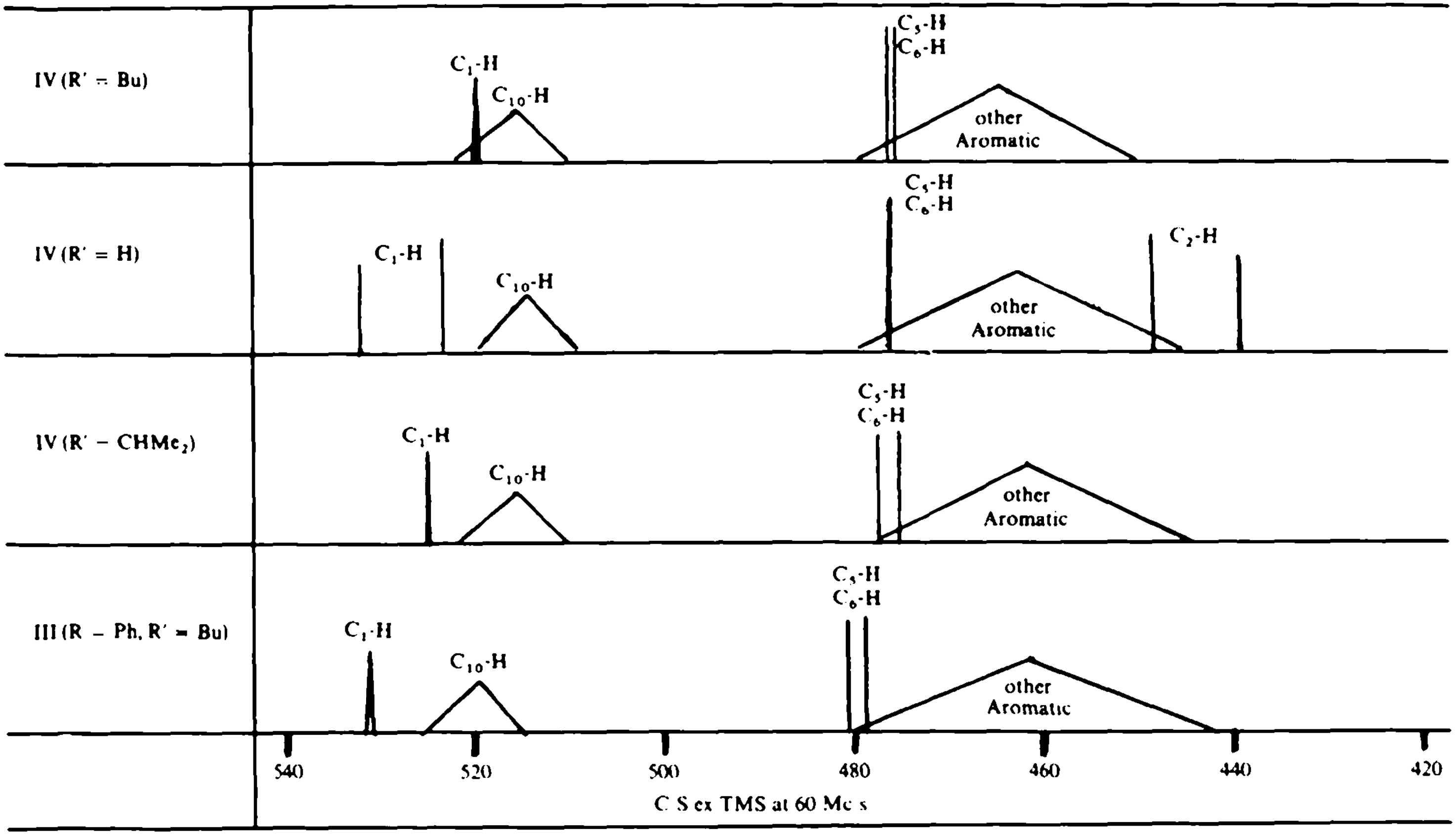


TABLE 4. THIN LAYER CHROMATOGRAPHIC DATA

Compound	R_f	Appearance of spots	
		Daylight	UV light
V	0·95	l. yellow	bright blue fluorescence
III (R = C_6H_5)	0·7	invisible	blue fluorescence
IX	0·55	orange	dark purple, not fluorescing
VII	0·50	purple-red	dark purple
VIII	0·40	dark brown, developed with iodine	purple
IV	0·30	invisible	strong greenish blue fluorescence
VI	0·10	invisible	yellow blue fluorescence

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