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PHOTOCHEMICAL REACTIONS OF 2,3-DIPHENYLINDOLES

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Abstract—The UV irradiation of 2,3-diphenylindoles produces two photochemical reactions: a dehydrocyclization with formation of dibenzocarbazoles and a photo-oxygenation which yields benzophenones.

Substituents on the 2,3-diphenylindole have a great influence on the reaction course and in most of the examples here studied only one product was formed.

Some considerations about the excited states involved in these reactions are presented.

In a previous paper we have reported our results on photo-oxidation of 2- and 3-methylindoles where the principal reaction was the conversion of the Me group into an aldehyde group. A series of indole-2- and indole-3-carboxaldehydes were thus prepared.[1]

We have now applied the photochemical method to 2,3-diphenyl-methylindoles to study the possibility of oxidation of a Me group attached to the benzene ring of the indole.

First, we irradiated the 2,3-diphenyl-5-methylindole in acetic acid solution with UV light (Method A). From this reaction a photoproduct was obtained without the characteristic properties of the aldehydes. The NMR spectrum of this compound (Table 4) showed that the original Me group had not been transformed and that the photoproduct had 11 aromatic protons instead of 13 of the starting indole (Table 6). Besides, the mass spectrum showed the base peak at *m/e* 281 M^+ and the elemental analysis agreed with the formula $C_{21}H_{15}N$. On the basis of these data we assigned to this compound the structure of 12-methyl-9H-dibenzo[a.c]carbazole (2) which is formed by a photochemical dehydrocyclization of the 2,3-diphenyl-5-methylindole (Scheme 1).

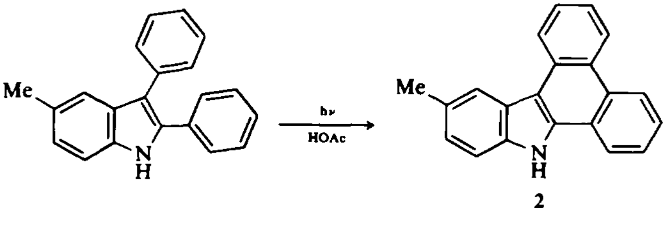
Similar reactions were previously observed employing stilbene and related systems,[2] diphenylfuran,[3] diphenylthiophene[4] and other diphenyl heterocycles.[5]

The photochemical dehydrocyclization of a 2,3-diphenylindole was reported for the first time by Szmuszkovicz[6] who prepared the 3,6-dimethoxy-9H-dibenzo[a.c]carbazole by irradiation of 2,3-*bis*-(*p*-methoxyphenyl)indole.

We have then irradiated 2,3-diphenylindole and its 6 and 7-Me derivatives obtaining in all cases the corresponding dibenzocarbazoles (**1**, **3** and **4**; Table 1).

In the irradiation of 2,3-diphenyl-4,7-dimethylindole two products were formed: the carbazole **5** and the 3,6-dimethyl-2-benzamidobenzophenone (**17**). The structure of the latter was assigned on the basis of physical data (Experimental and Table 5) and because it was also obtained by treatment of the original indole with peracetic acid.

Two N-substituted 2,3-diphenylindoles were submitted to UV irradiation, the N-phenyl and the N-methyl derivatives. In the former case, the photoreaction yielded the carbazole **7**. the 2-(N-phenylbenzamido)benzophenone (**16**) and a third compound of formula $C_{26}H_{17}NO_2$ identified as 1-phenyl-1-aza(3,4:5,6:8,9)tribenzocyclonona-2,7-dione (**20**) on the basis of physical data.. The photochemical origen of **20** was determined because this compound was also obtained from the irradiation of carbazole **7**.



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SCHEME 1.

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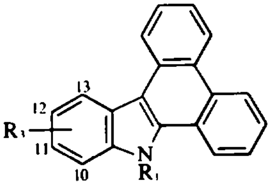
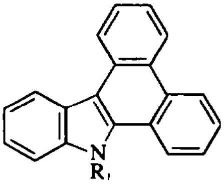
† Research Member of the Consejo Nacional de Investigaciones Científicas y Técnicas.

Table 1. 9H-Dibenzo[a.c]carbazoles obtained by UV irradiation of 2,3-diphenylindoles (solvent, HOAc; irrad. time, 2 h)

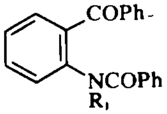


	R_1	R_3	m.p. (°C)	Method A Conv. %	Method A Yield %	Method B Conv. %	Method B Yield %	Formula	Analysis Required/Found C	H	N	λ_{max}. nm (log ϵ) solvent, EtOH
1	H	H	191–93^a	93	58*	84	80	$C_{20}H_{13}N$	89·86 89·58	4·90 4·80	5·24 5·50	370 (3·60); 353 (3·62); 322 (4·24); 314 sh (4·20); 295 (4·22); 277 sh (4·51); 269 (4·76); 263 (4·77)
2	H	12-Me	236–38^b	94	43	87	72	$C_{21}H_{15}N$	89·65 89·32	5·37 5·46	4·98 5·08	372 (3·64); 355 sh (3·69); 328 (4·35); 318 sh (4·29); 298 (4·27); 280 sh (4·59); 271 (4·78); 264 (4·79); 238 sh (4·51)
3	H	11-Me	230–32^b	88	48	80	57	$C_{21}H_{15}N$	89·65 89·40	5·37 5·61	4·98 5·24	372 (3·65); 355 sh (3·67); 327 (4·31); 320 sh (4·29); 296 (4·29); 279 sh (4·55); 270 sh (4·81); 265 (4·86); 238 sh (4·53)
4	H	10-Me	183–85^c	84	39	80	64	$C_{21}H_{15}N$	89·65 89·95	5·37 5·40	4·98 5·18	354 sh (3·68); 323 (4·31); 315 sh (4·27); 296 (4·30); 267 (4·82)
5	H	10,13-Me$_2$	155–57^c	97	12†	98	34†	$C_{22}H_{17}N$	89·46 89·54	5·80 6·09	4·74 4·85	323 (4·33); 296 (4·42); 282 sh (4·72); 266 (4·87)
6	Me	H	142–44^c	95	25†	83	65	$C_{21}H_{15}N$	89·65 89·74	5·37 5·37	4·98 5·15	358 (3·74); 324 (4·29); 316 sh (4·23); 295 (4·23); 273 (4·81); 265 (4·77)
7	Ph	H	196–98^c	95	37†	90	77	$C_{26}H_{17}N$	90·93 91·20	4·99 5·17	4·08 4·03	353 (3·74); 322 (4·34); 314 sh (4·27); 294 (4·22); 272 (4·92); 266 (4·93)

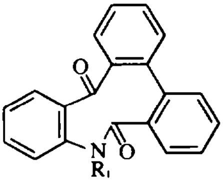
Method A: without I_2; Method B: with I_2; recrystallization solvents: ^{a}EtOH-H_2O; ^{b}benzene; ^{c}benzene–ligroin.
*When this irradiation was performed employing EtOH as solvent 1 was obtained in 55% yield (conv. 76%).
†Other products formed in these cases are described in Experimental.



7: R_1 = Ph
6: R_1 = Me



16: R_1 = Ph
18: R_1 = Me



20: R_1 = Ph
19: R_1 = Me

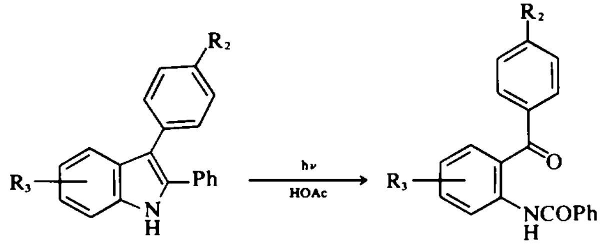
Similar results were obtained employing 1-methyl-2,3-diphenylindole. From this reaction were isolated the carbazole **6**, the 2-(N-methylbenzamido)benzophenone (**18**) and the 1 - methyl - 1 - aza(3,4:5,6:8,9)tribenzocyclonona - 2,7 - dione (**19**). The oxidation of the 1-methyl-2,3-diphenylindole and the carbazole **6** with peracetic acid leads to the formation of **18** and **19** respectively.

All the previously mentioned 2,3-diphenylindoles were irradiated in the presence of iodine (Method B). The results obtained by this method (Table 1) show that the carbazoles are formed in higher yields than by employment of Method A. Besides, no oxygenation products were formed in the cases of the 1-methyl-2,3-diphenylindole and 1,2,3-triphenylindole, whereas from the irradiation of 2,3-diphenyl-4,7-dimethylindole the carbazole **5** and the benzophenone **17** were obtained in better yields.

Other examples studied were several 2,3-diphenyl-nitroindoles and one 2,3-diphenyl-acetylindole. The UV irradiation of these substances yielded the corresponding 2-benzamidobenzophenones (Scheme 2) with the exception of 2,3-diphenyl-6-nitroindole which was recovered unchanged after 20 h irradiation. The benzamidobenzophenones obtained by this way are indicated in Table 2, whereas their NMR spectra are in Table 5.

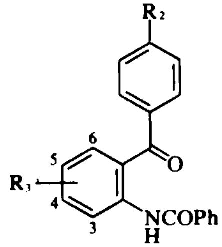
DISCUSSION

The course of the photochemical reaction of a 2,3-diphenylindole depends on the type and position of a substituent present in the molecule. On the basis of the precedent results we can classify the 2,3-diphenylindoles into three groups. In the first group there are 2,3-diphenylindoles which yield dibenzocarbazole as the sole product (2,3-diphenylindole and its 5, 6 and 7-Me derivatives). In the second group there are diphenylindoles which suffer the photocleavage of the C_2–C_3 bond of the indole with formation of 2-benzamidobenzophenones (2,3-diphenyl-nitro- or acetylindoles).



SCHEME 2.

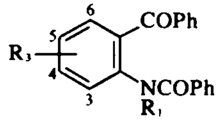
Table 2. 2-Benzamidobenzophenones obtained by UV irradiation of 2,3-diphenyl-nitroindoles and 2,3-diphenyl-5-acetyl-6-methylindole (Method A; solvent HOAc)



	R_2	R_3	m.p. (°C)	Irrad. time (h)	Conv. %	Yield %	Formula	Analysis Required/Found C H N	λ_{max}. nm (log ε) solvent, EtOH
8	NO_2	H	186–89[a]	20	77	31	$C_{20}H_{14}N_2O_4$	Ref 10; m.p. 187–89°	306 (4·26); 248 (4·36)
9	NO_2	5-NO_2	262–64[b]	6	85	55	$C_{20}H_{13}N_3O_6$	Ref 10; m.p. 262–64°	265 sh (4·03)
10*	H	4-Me 5-NO_2	170–71[a]	4	95	44	$C_{21}H_{16}N_2O_4$	69·99 4·48 7·77 69·82 4·75 7·72	325 sh (4·16); 253 (4·43)
11	NO_2	4-Me 5-NO_2	234–35[b]	10	95	32	$C_{21}H_{15}N_3O_6$	62·22 3·73 10·37 62·09 3·92 10·26	266 (3·48)
12	H	4-Me 5-Ac	180–82[a]	15	100	38	$C_{23}H_{19}NO_3$	77·29 5·36 3·92 77·26 5·70 3·89	335 (3·94); 288 sh (4·31); 261 (4·54)

*This compound was obtained in 51% yield employing Method C (irrad. time: 20 h; conv. 78%).
Recrystallization solvents: [a] EtOH; [b] HOAc.

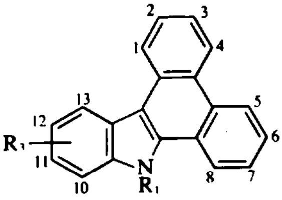
Table 3. 2-Benzamidobenzophenones obtained by irradiation of 2,3-diphenylindoles with a tungsten lamp using methylene blue as sensitizer and EtOH as solvent (Method C)



	R_1	R_3	m.p. (°C)	Irrad. time (h)	Conv. %	Yield %	Formula	Analysis Required/Found C	H	N	λ_{max}. nm (log ϵ) solvent, EtOH
13	H	H	88–91[b]	14	98	50	$C_{20}H_{15}NO_2$	Ref. 11; m.p. 91°			335 (3·36); 248 (4·43)
14	H	5-Me	113–15[b]	15	91	42	$C_{21}H_{17}NO_2$	79·98	5·43	4·44	345 (3·66); 251 (4·38)
								80·17	5·49	4·68	
15	H	4-Me	132–34[b]	16	75	45	$C_{21}H_{17}NO_2$	79·98	5·43	4·44	335 (3·80); 253 (4·47)
								79·98	5·59	4·20	
16	Ph	H	190–92[a]	12	68	47*	$C_{26}H_{19}NO_2$	82·74	5·07	3·71	245 (4·43)
								82·48	4·96	3·92	

*In this case the carbazole 7 (yield 6%) was also obtained.
Recrystallization solvents: [a]EtOH; [b]EtOH-H_2O.

Table 4. NMR spectra of 9H-dibenzo[a.c]carbazoles* (δ values; solvent, DMSO d_6)



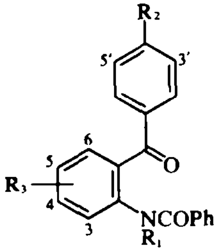
	R_1	R_3	CH_3	Aromatic protons		NH
1	H	H		$H_2, H_3, H_6, H_7, H_{10}, H_{11}, H_{12}$	7·25–8·13	12·40
				$H_1, H_4, H_5, H_8, H_{13}$	8·60–9·18	
2	H	12-Me	2·63	$H_2, H_3, H_6, H_7, H_{10}, H_{11}$	7·25–8·06	12·41
				$H_1, H_4, H_5, H_8, H_{13}$	8·41–9·11	
3	H	11-Me	2·60	H_{12} 7·30 (dd, $J_{10.12}$ 2 c/s; $J_{12.13}$ 9 c/s)		12·45
				$H_2, H_3, H_6, H_7, H_{10}$	7·56–8·10	
				$H_1, H_4, H_5, H_8, H_{13}$	8·45–9·18	
4	H	10-Me	2·80	$H_2, H_3, H_6, H_7, H_{11}, H_{12}$	7·25–8·08	12·00
				$H_1, H_4, H_5, H_8, H_{13}$	8·38–9·13	
5	H	10,13-Me_2	2·70 (10)	H_{11}, H_{12}	6·90–7·22	11·70
			3·05 (13)	H_2, H_3, H_6, H_7	7·30–7·88	
				H_1, H_4, H_5, H_8	8·70–9·10	
6	Me	H	4·43	$H_2, H_3, H_6, H_7, H_{10}, H_{11}, H_{12}$	7·33–8·00	
				$H_1, H_4, H_5, H_8, H_{13}$	8·58–9·13	
7	Ph	H		$C_6H_5, H_2, H_3, H_6, H_7, H_8, H_{10}, H_{11}, H_{12}$	7·00–8·10	
				H_1, H_4, H_5, H_{13}	8·63–9·11	

*All these spectra presented in the aromatic region two complexes groups of signals. The assignments of the protons involved in each group was established taking into account the shielding and deshielding effect of the aromatic rings.

Finally, are the 2,3-diphenylindoles which by UV irradiation form dibenzocarbazoles together with oxygenation products (2,3-diphenyl-4,7-dimethylindole, 1-methyl-2,3-diphenylindole and 1,2,3-triphenylindole).

Probably, the photodehydrocyclization of 2,3-diphenylindoles proceeds *via* an excited singlet state (S_1) as occurs in the case of stilbene analogues.[7] In agreement with this assumption is the fact that nitro or acetyl-2,3-diphenylindoles fail

Table 5. NMR spectra of 2-benzamidobenzophenones (δ values; solvent, DMSO d_6)



	R_1	R_2	R_3	CH_3	Aromatic protons	NH
8	H	NO_2	H		$H_{3'}$ and $H_{5'}$ 8·26 (d, J 9 c/s); 7·25–7·75 (11 H)	11·83
9	H	NO_2	5-NO_2		7·33–8·70	11·25
10	H	H	4-Me 5-NO_2	2·66	H_3 8·05; H_6 8·15; 7·30–7·90 (10 H)	11·10
11	H	NO_2	4-Me 5-NO_2	2·66	7·35–8·40	11·10
12	H	H	4-Me 5-Ac	2·53 2·58	7·36–8·03	10·96
13	H	H	H		7·11–8·10	10·80
14	H	H	5-Me	2·36	7·28–7·90	10·75
15	H	H	4-Me	2·45	7·05–7·98	11·05
16	Ph	H	H		7·05–7·83	
17	H	H	3,6-Me_2	2·06 2·18	7·12–7·85	9·76
18	Me	H	H	3·25	7·00–7·70	

to photocyclize because as it is known[8] these substituents promote the intersystem crossing $S_1 \rightarrow T_1$. To explain the failure of nitrostilbene compounds to photocyclize it was also suggested that the low reactivity at the points of cyclization may be in part responsible.[9] In our opinion the nitro group may have this inhibitory effect when it is attached to the stilbene system but not in the case of the 2,3-diphenyl-5-nitro-6-methylindole.

Timmons[9a] has correlated the effect of electronic impact and the effect of UV irradiation on stilbene compounds and he found that "if photocyclization takes place then cyclodehydrogenation must also occur on electron impact to give a cyclized ion of relative abundance greater than 5%".

The mass spectra of some 2,3-diphenylindoles are included in Table 7.

The 2,3-diphenylindole and its 5, 6 and 7-Me derivatives, compounds which photocyclized in good yields, showed M-1 and M-2 peaks, whereas in the mass spectra of the two nitroindoles tabulated we can observe the lack of these peaks and as it was mentioned these compounds fail to photocyclize. Although the 2,3-diphenyl-nitroindoles do not photocyclize they form 2-benzamidobenzophenones as result of an oxidative cleavage.

On the other hand, we irradiated the indoles in ethanol solution with a tungsten lamp using methylene blue as sensitizer (Method C, Table 3). For the sensitized irradiations we have employed the 2,3-diphenyl-5-nitro-6-methylindole, 1,2,3-triphenylindole (compounds which on UV irradiation yield benzophenones) and three 2,3-diphenylindoles which do not form benzophenones by UV irradiation in acetic acid or ethanol. In all cases benzophenones were obtained from the sensitized irradiations (42–51% yield). Comparative results are compiled in Table 8.

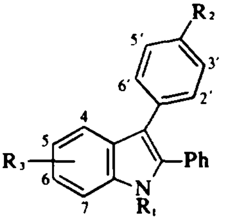
Besides, when 1-methyl-2,3-diphenylindole and 2,3-diphenyl-4,7-dimethylindole were irradiated with UV light in the presence of 2,6-di-t-butylphenol the formation of benzophenones was inhibited. This fact suggests a radical mechanism for the cleavage reaction.

There are several possibilities for the photo-oxygenation of 2,3-diphenylindoles. Between them, the most probable are: the reaction of excited triplet indole molecules with ground state oxygen or the attack of singlet oxygen on ground state indole molecules. Although, according to the precedent results and taking into account the known properties of singlet oxygen[9b] we can assume that the photo-oxygenation of 2,3-diphenylindoles involves excited triplet state (T_1) molecules and ground state oxygen.

In Scheme 3 is represented the course of the photoreactions according to our results.

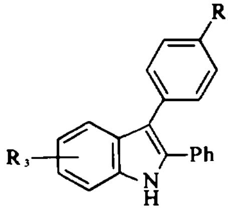
The formation of benzophenones and azacyclononadiones in the UV irradiation of 1-methyl-2,3-diphenylindole and 1,2,3-triphenylindole could be

Table 6. NMR spectra of the 2,3-diphenylindoles used for the photochemical reactions (δ values; solvent DMSO d_6)



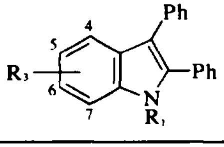
R_1	R_2	R_3	CH_3	Aromatic protons	NH	Ref
H	H	H		6·98–7·61	11·50	12
H	H	5-Me	2·38	H_6 7·05 (dd, $J_{4,6}$ 2 c/s; $J_{6,7}$ 8 c/s); other protons 7·25–7·75	11·50	12
H	H	6-Me	2·45	H_5 6·95 (dd, $J_{5,7}$ 2 c/s; $J_{4,5}$ 8 c/s) other protons 7·23–7·63	11·50	
H	H	7-Me	2·61	7·03–7·75	11·46	12
H	H	4,7-Me_2	1·96 (4) 2·53 (7)	H_5 (or H_6) 6·65 (d, $J_{5,6}$ 8 c/s); H_6 (or H_5) 6·88 (d, $J_{5,6}$ 8 c/s); other protons 7·20–7·50	11·01	12
Me	H	H	3·65	7·00–7·80		12
Ph	H	H		7·16–7·75		13
H	H	6-NO_2		H_4 7·60 (d, $J_{4,5}$ 9 c/s); H_5 7·96 (dd, $J_{5,7}$ 2 c/s; $J_{4,5}$ 9 c/s); H_7 8·35 (d, $J_{5,7}$ 2 c/s); other protons 7·28–7·55	12·36	10
H	NO_2	H		$H_{2'}$ and $H_{6'}$ 7·71 (d, J 9 c/s); $H_{3'}$ and $H_{5'}$ 8·36 (d, J 9 c/s); other protons 7·16–7·90	12·03	10
H	NO_2	5-NO_2		H_4 8·46 (d, $J_{4,6}$ 2 c/s); H_6 8·15 (dd, $J_{4,6}$ 2 c/s; $J_{6,7}$ 9 c/s); H_7 $H_{2'}$ and $H_{6'}$ 7·55–7·80; $H_{3'}$ and $H_{5'}$ 8·31 (d, J 9 c/s); C_6H_5 7·48	12·60	10
H	H	5-NO_2 6-Me	2·71	H_4 8·35; other protons 7·40–7·75	12·31	
H	NO_2	5-NO_2 6-Me	2·70	H_4 8·38; H_7 and C_6H_5 7·42–7·68; $H_{2'}$ and $H_{6'}$ 7·71 (d, J 9 c/s); $H_{3'}$ and $H_{5'}$ 8·36 (d, J 9 c/s)	12·46 11·73	 12
H	H	5-Ac 6-Me	2·50 2·53	H_4 7·96; other protons 7·13–7·63		

Table 7. Mass spectra (partial) of 2,3-diphenylindoles



R_2	R_3	M (%)	M-1 (%)	M-2 (%)
H	H	269 (100)	268 (34)	267 (34)
H	5-Me	283 (100)	282 (7)	281 (3)
H	6-Me	283 (100)	282 (32)	281 (10)
H	7-Me	283 (100)	282 (3)	281 (1)
H	5-NO_2 6-Me	328 (100)		
NO_2	5-NO_2 6-Me	373 (100)		

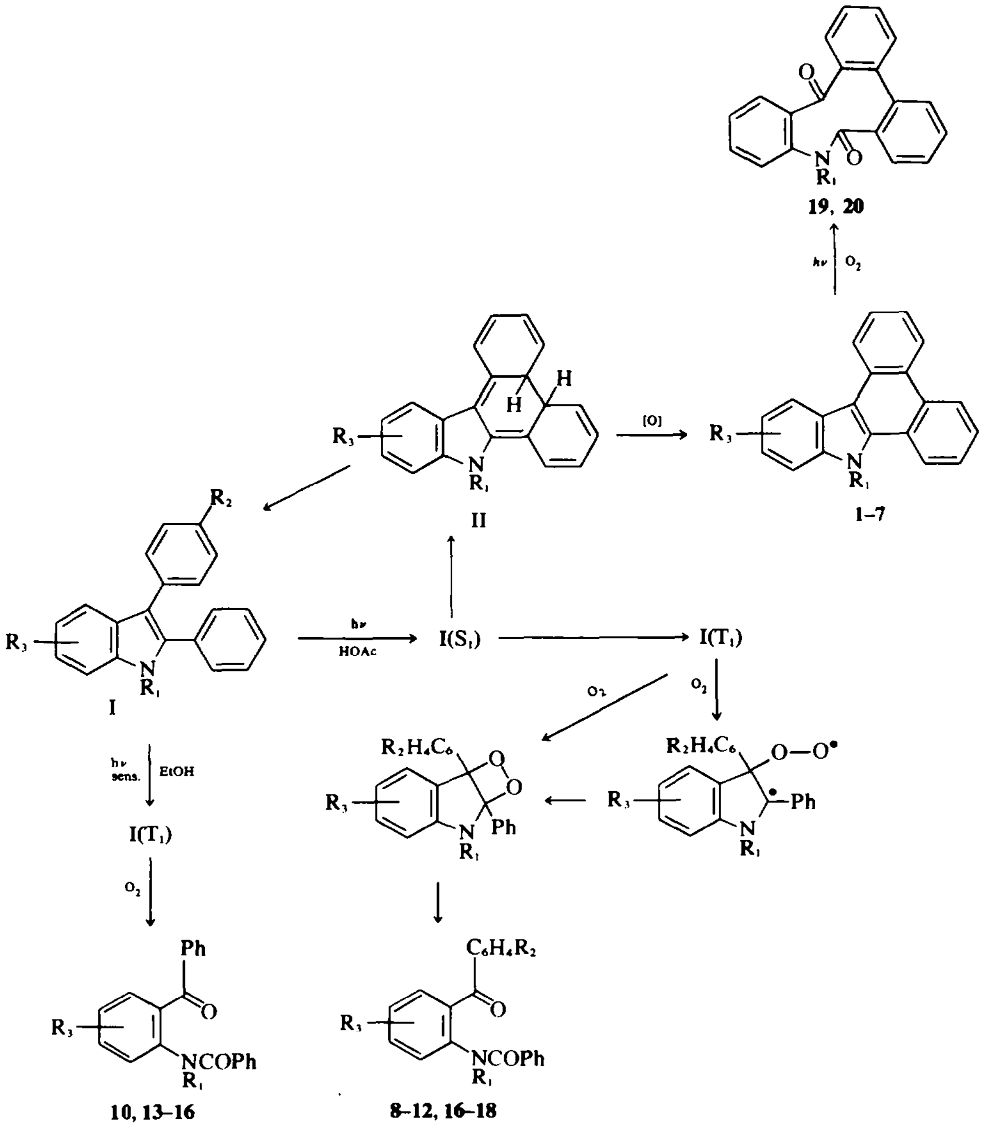
Table 8. Comparative yields of dibenzocarbazoles and benzophenones obtained by Method A (UV light) and Method C (tungsten lamp and methylene blue)*



Substrate		Method A		Method C	
R_1	R_3	Dibenz. %	Benzoph. %	Dibenz. %	Benzoph. %
H	H	58	—	—	50
H	5-Me	43	—	—	42
H	6-Me	48	—	—	45
Ph	H	37†	14	6	47
H	5-NO_2 6-Me	—	44	—	51

*Conversion percentages are given in Tables 1 and 3.

†In this case the azatribenzo-cyclononadione **20** (yield 10%) was also obtained.



SCHEME 3.

explained assuming that the N-substitution facilitates the intersystem crossing $S_1 \rightarrow T_1$. It should be mentioned that the 9H-dibenzocarbazole (**1**) was recovered unchanged after 5 h UV irradiation.

In the case where steric factors hinder the cyclization (2,3-diphenyl-4,7-dimethylindole) the $S_1 \rightarrow T_1$ transition could compete with the formation of the dihydrointermediate II.

EXPERIMENTAL

M.ps are uncorrected. The UV spectra were determined on a Beckman DK-2A spectrophotometer. The NMR spectra were recorded on a Varian A-60 spectrometer using TMS as internal standard.

General methods of irradiation

Method A. The 2,3-diphenylindoles (30 mg) were irradiated in HOAc (15 ml) placed in Pyrex test tubes (16 × 150 mm). The light source was a Hg high-pressure lamp (Philips 400 watts) which was placed 11·5 cm from the tubes.[1] Irradiation times are given in Tables 1 and 2. TLC system: alumina, benzene–ligroin or benzene–EtOH. The reaction mixture was chromatographed on alumina using as eluents, ligroin, the mixture ligroin–benzene or benzene. In all cases, the first eluted fraction contained the non-converted starting indole, whereas the photoproducts eluted in the following order: first the dibenzocarbazoles and then the 2-benzamidobenzophenones. Other products obtained are specially indicated in each case.

The bands on the columns and the spots on the TLC plates were made visible by UV light.

Method B. The 2,3-diphenylindoles (30 mg) dissolved in a soln of iodine (10 mg) in HOAc (15 ml) were irradiated as above. After irradiation iodine was removed washing the extracts with aq soln of sodium thiosulphate. The yields obtained are indicated in Table 1.

Method C. The 2,3-diphenylindoles (30 mg) and methylene blue (6 mg) dissolved in EtOH (15 ml) were irradiated with tungsten lamp (200 watts). The products were isolated as in the other cases (Table 3).

Benzophenones obtained in this work. Samples of benzophenones reported in the literature were prepared by oxidation of the corresponding indoles with chromic or peracetic acid.

Preparation of the indole compounds used for the photochemical reactions

The 2,3-diphenylindoles employed in this work were prepared according to methods described (Table 6) except in the cases indicated below.

2,3-*Diphenyl*-6-*methylindole.* A mixture of benzoin (2·12 g), *m*-toluidine (2·14 g) and $ZnCl_2$ (2·72 g) was boiled for 5 min, then HCl (50%) was added and the mixture was heated under reflux for 15 min. The soln was diluted with water and extracted with benzene. The extracts were washed with 50% HCl aq, water and then with $NaHCO_3$ aq. The residue obtained by evaporation of the solvent was dissolved in ligroin and chromatographed on a silica gel column (eluent: ligroin). The indole compound was obtained from the first eluted fraction (2·06 g). Colourless prisms from ligroin, m.p. 114–16°. (Found: C, 89·20; H, 6·31; N, 5·02. $C_{21}H_{17}N$ requires: C, 89·01; H, 6·05; N, 4·94%); UV (EtOH) λ_{max} 315 nm (log ϵ 4·25); 251 sh (4·38); 224 (4·46).

Ockenden and Schofield[14] described this compound as an oil and Ritchie[12] purified it through the picrate.

Nitration of 2,3-*diphenyl*-6-*methylindole*

The indole (500 mg) was dissolved in conc H_2SO_4 (10 ml). To the mixture, cooled at 0°, a soln of $NaNO_3$ (150 mg) in conc H_2SO_4 (10 ml) was slowly added (2 h). The mixture was then poured into ice and extracted with benzene. The concentrated extracts were chromatographed on alumina (eluent, benzene). From the first fraction the non-converted starting indole (130 mg) was isolated.

2-*Phenyl*-3-(p-*nitrophenyl*)-6-*methylindole.* It was obtained from the second fraction (50 mg; yield 8%). Orange plates from HOAc, m.p. 268–70°. (Found: C, 76·56; H, 5·20; N, 8·37. $C_{21}H_{16}N_2O_2$ requires: C, 76·81; H, 4·91; N, 8·53%); UV (EtOH) λ_{max} 405 nm (log ϵ 3·84); 309 (4·15); 239 (4·36); NMR (DMSO d_6) CH_3 2·43; H_5 6·95 (d, J 9 c/s); H_4, H_7 and C_6H_5 7·23–7·72; $H_{2'}$ and $H_{6'}$ 7·56 (d, J 9 c/s); $H_{3'}$ and $H_{5'}$ 8·21 (d, J 9 c/s); NH 11·68.

The UV spectrum of this compound was almost identical to that of 2-phenyl-3-(*p*-nitrophenyl)indole.[10]

2,3 - *Diphenyl* - 5 - *nitro* - 6 - *methylindole.* It was isolated from the third fraction (109 mg; yield 18%), as yellow prisms from EtOH, m.p. 220–21°. (Found: C, 76·56; H, 5·10; N, 8·55. $C_{21}H_{16}N_2O_2$ requires: C, 76·81; H, 4·91; N, 8·53%); UV (EtOH) λ_{max} 296 nm (log ϵ 4·43); 232 (4·30); the NMR spectrum of this compound is indicated in Table 6.

2 - *Phenyl* - 3 - (p - *nitrophenyl*) - 5 - *nitro* - 6 - *methylindole.* It was obtained from the fourth fraction (245 mg; yield 37%) as yellow prisms from HOAc, m.p. 218–20°. (Found: C, 67·61; H, 4·35; N, 10·98. $C_{21}H_{15}N_3O_4$ requires: C, 67·55; H, 4·05; N, 11·26%); UV (EtOH) λ_{max} 347 sh nm (log ϵ 4·16); 290 (4·58); 230 (4·51); the NMR is indicated in Table 6.

The UV spectrum of this compound was almost identical to that of 2 - phenyl - 3 - (*p* - nitrophenyl) - 5 - nitroindole.[10]

Irradiation of 2,3 - *diphenyl* - 4,7 - *dimethylindole*

Formation of **5** *and* **17**, *Method A.* The mixture was chromatographed on alumina (eluent, ligroin) giving from the first fraction the non-converted indole. By evaporation of the second fraction (ligroin–benzene 9 : 1) **5** was obtained (Table 1).

Compound **17** was obtained from the third fraction using benzene as eluent (yield 21%). Colourless prisms from EtOH–water, m.p. 143–44°. (Found: C, 80·47; H, 6·06; N, 4·50. $C_{22}H_{19}NO_2$ requires: C, 80·22; H, 5·81; N, 4·25%); UV (EtOH) λ_{max} 236 sh nm (log ϵ 4·20); the NMR spectrum is indicated in Table 5.

This compound was identical to that obtained by treatment of the original indole with a 0·04 M soln of H_2O_2 in HOAc.

Method B. The 2,3-diphenyl-4,7-dimethylindole was irradiated in the presence of I_2 according to the general procedure giving the following results: conv. 98%; **5** (yield 34%); **17** (yield 37%).

Irradiation of 1 - *methyl* - 2,3 - *diphenylindole*

Formation of **6**, **18** *and* **19**. The title indole was irradiated according to Method A. The residue obtained by evaporation of the extracts was dissolved in ligroin and chromatographed on alumina giving from the first fraction the non-converted indole, whereas from the second eluted fraction **6** was obtained (Table 1). The third fraction was eluted with a mixture of benzene–ligroin (1 : 1) giving a product (yield 1%) which was identified as **19**, compound which is below described.

Compound **18** (yield 25%) was obtained from the fourth fraction eluted with benzene–EtOH (99·5 : 0·5). Colourless prisms from benzene–ligroin, m.p. 112–13°. (Found: C, 79·80; H, 5·49; N, 4·55. $C_{21}H_{17}NO_2$ requires: C, 79·98; H, 5·43; N, 4·44%); UV (EtOH) λ_{max} 250 nm (log ϵ 4·33); the NMR spectrum is indicated in Table 5.

This compound was also obtained by oxidation of the original indole with a 0·04 M soln of H_2O_2 in HOAc for 24 h at room temp.

Oxidation of 9 - *methyl* - 9H - *dibenzo*[*a.c*]*carbazole* (**6**) *with peracetic acid*

Formation of **19**. The carbazole **6** (100 mg) was dissolved in a 0·04 M soln of H_2O_2 in HOAc (10 ml). The soln was left at room temp for 4 h and then diluted with water and extracted with benzene. The residue obtained was chromatographed on alumina using benzene as eluent. Compound **19** (62 mg; yield 55%) was obtained from the second fraction. Colourless prisms from EtOH–water, m.p. 183–84°. (Found: C, 80·54; H, 5·03; N, 4·47. $C_{21}H_{15}NO_2$ requires: C, 80·49; H, 4·83; N, 4·47%); UV (EtOH) λ_{max} 261 sh nm (log ϵ 3·92); NMR (DMSO d_6) CH_3 2·96; arom. prot. 7·02–8·10 (12 H); IR (Nujol) C=O 1630 and 1655 cm^{-1}; MS *m*/*e* (%) 313 (M^+, 96); 312 ($C_{21}H_{14}NO_2$, 79); 298 ($C_{20}H_{12}NO_2$, 70); 297 ($C_{20}H_{11}NO_2$, 70); 285 ($C_{20}H_{15}NO$, 66); 284 ($C_{20}H_{14}NO$, 73); 269 ($C_{20}H_{13}O$, 92); 268 ($C_{20}H_{12}O$, 100); 228 ($C_{18}H_{12}$, 80).

Irradiation of 1,2,3-*triphenylindole*

Formation of **7**, **16** *and* **20**. The triphenylindole was irradiated according to Method A. The reaction product was chromatographed on alumina; using ligroin as eluent the following compounds were isolated: first, the non-converted indole; second **7** (Table 1).

Compound **20** was obtained from the third fraction eluted with benzene (yield 10%). Colourless prisms from EtOH, m.p. 224–25°. (Found: C, 83·18; H, 4·38; N, 3·96. $C_{26}H_{17}NO_2$ requires: C, 83·18; H, 4·56; N, 3·73%); UV (EtOH) λ_{max} 237 sh nm (log ϵ 4·24); NMR (DMSO d_6) arom. prot. 6·84–8·20; IR (Nujol) C=O 1645 and 1660 cm^{-1}; MS m/e (%) 375 (M^+, 100); 374 ($C_{26}H_{16}NO_2$, 64); 347 ($C_{25}H_{17}NO$, 36); 346 ($C_{25}H_{16}NO$, 56); 228 ($C_{18}H_{12}$, 43); 195 ($C_{13}H_9NO$, 58).

From the fourth fraction **16** was obtained (yield 14%). This compound is described in Table 3 and was also obtained by treatment of the original indole with CrO_3 in HOAc soln at 50°.

When the irradiation time was increased to 5 h the following yields were obtained: **7** 10%; **16** 13% and **20** 32%. On the other hand, when the irradiation was conducted under N_2 **7** was obtained in 77% yield.

Irradiation of 9 - *phenyl* - 9*H* - *dibenzo*[*a.c*]*carbazole* (**7**)

Formation of **20**. Compound **7** (20 mg) dissolved in HOAc (20 ml) was irradiated with UV light for 1·5 h. By chromatography of the reaction mixture **20** was isolated in 38% yield.

Oxidation of 9*H* - *dibenzo*[*a.c*]*carbazole* (**1**) *with peracetic acid*

Formation of 1 - *aza*(3,4:5,6:8,9)*tribenzocyclonona* - 2,7 - *dione* (**21**). Compound **1** (50 mg) was dissolved in a 0·04 M soln of H_2O_2 in HOAc (10 ml). The mixture was left at room temp for 24 h and then diluted with water and extracted with benzene. The concentrated extracts were chromatographed on alumina giving from the second fraction **21** (25 mg; yield 45%). Colourless prisms from benzene–ligroin, m.p. 211–12°. (Found: C, 80·35; H, 4·48; N, 4·84. $C_{20}H_{13}NO_2$ requires: C, 80·25; H, 4·38; N, 4·68%); UV (EtOH) λ_{max} 261 sh nm (log ϵ 4·01); NMR (DMSO d_6) arom. prot. 6·95–8·08; NH 9·78.

The effect of 2,6-*di*-*t*-*butylphenol on the UV irradiation of* 2,3-*diphenylindoles*

1- The 1-methyl-2,3-diphenylindole (30 mg) and the 2,6-di-t-butylphenol (10 mg) were dissolved in HOAc (15 ml) and the soln was irradiated (UV lamp) for 2 h. By chromatography of the mixture **6** (19 mg; yield 63%) was isolated as the sole product. 2- The irradiation of the 2,3-diphenyl-4,7-dimethylindole was performed as in the previous case giving, after chromatography, **5** in 12% yield.

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