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PHOTOLYSIS OF 2-AMINO- AND 2-METHYLAMINO-1,4-NAPHTHOQUINONE

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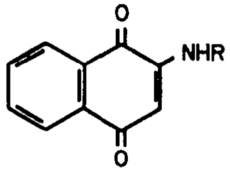
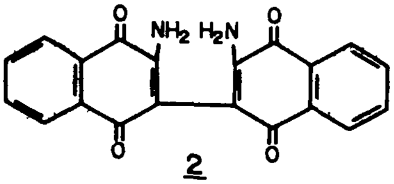
Abstract — Pyrex-filtered sunlight irradiation of solutions of 2-amino-1,4-naphthoquinone unexpectedly failed to produce cyclobutane dimers. Irradiation in acetic anhydride led to the formation of the trimeric 6-[3'-amino-2'-(1,4-naphthoquinonyl)]-dibenzo[b,h]carbazole-5,13:7,12-diquinone as well as 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl and dibenzo[b,h]carbazole-5,13:7,12-diquinone. Similar treatment of 2-methylamino-1,4-naphthoquinone afforded 6-[3'-methylamino-2'-(1,4-naphthoquinonyl)]-dibenzo[b,h]carbazole-5,13:7,12-diquinone and 6-methyl-dibenzo[b,h]carbazole-5,13:7,12-diquinone.

The photodimerisation of 1,4-naphthoquinone[1] and its 2-methyl,[2] 2-phenyl,[3] 2-chloro[4] and 2-ethoxy[5] derivatives has been investigated and it has been shown that the corresponding cyclobutane dimers are readily formed when the substances are irradiated in different solvents. Cyclobutane dimerisation is often accompanied by photo-oxidative cleavage[3] of the cyclobutane ring, leading to the formation of secondary products. These results persuaded us to investigate the photochemical behaviour of the analogous 2-amino-1,4-naphthoquinone (1, R=H) as well as that of 2-methylamino-1,4-naphthoquinone (1, R=CH_3).



1 (R = H, CH_3)



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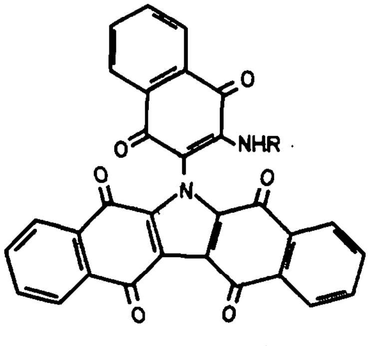


3 (R = H, CH_3, $COCH_3$)

Pyrex-filtered sunlight irradiation of an acetic anhydride solution of 2-amino-1,4-naphthoquinone (1, R=H)[6] produced a highly stable (m.p. 455°C dec.) orange coloured photoproduct (3, R=H) that is insoluble in almost all common organic solvents and only sparingly soluble in nitrobenzene. Due to limited structural information obtained from an infrared study and failure to obtain an electron impact (EI) mass spectrum we conducted a fast atom bombardment (FAB) mass spectrometric investigation.

Since the photoproduct (3, R=H) is insoluble in the conventional FAB matrices we attempted to obtain a FAB mass spectrum by depositing a suspension of the photoproduct (3, R=H) in nitrobenzene on a FAB target coated with a mixture (1:1) of glycerol and concentrated sulphuric acid. The sample was bombarded with a 1 mA beam of 8 kV fast xenon atoms generated in a saddle field neutral beam gun. The structurally related species was observed as $[M+H]^+$ and was registered at a m/z value of 499. In order to verify this result we dissolved the photoproduct (3, R=H) in concentrated sulphuric acid and bombarded the orange coloured solution as described before. A strong molecular ion $[M+H]^+$ was recorded at m/z 499 which suggested a possible trimeric composition. Both mass spectra of 3 (R=H) showed a strong peak at m/z 481 which corresponds to a loss of a molecule of water from the molecular ion and can be attributed to the elimination of water from an amino group and a neighbouring carbonyl group in 3 (R=H).

The infrared spectrum of 3 (R=H) exhibits strong carbonylic absorptions at 1615 and 1684 cm^{-1} which correspond well with the carbonylic absorptions of 2-amino-1,4-naphthoquinone (1, R=H; 1622 cm^{-1}) and dibenzo[b,h]carbazole-5,13 : 7,12-diquinone (9, R=H; 1672 cm^{-1}). The N-H stretching vibrations of 3 (R=H) appear as absorption bands at 3402 and 3311 cm^{-1} which can be attributed to the characteristic asymmetrical and symmetrical N-H stretching modes of a primary amine group.

Confirmatory evidence for the correctness of the structure of 3 was obtained from a ^1H and ^{13}C n.m.r. study. The spectra were recorded as sulphuric acid-d_2 (D_2SO_4) solutions because of low solubility of 3 (R=H) in organic solvents. The n.m.r. data of 3 (R=H) are given in Table 1.

The symmetry in 3 (R=H) is born out by both the ^1H and ^{13}C n.m.r. spectra. The 500 MHz ^1H n.m.r. spectrum only exhibits characteristic AMPX spin patterns for two ortho disubstituted aromatic systems with the one set of peaks twice the intensity of the other. Similarly the broad band proton decoupled 125 MHz ^{13}C n.m.r. spectrum consists of two sets of 10 peaks with the one set more intense than the other. The relaxation time of all the carbon atoms were short, because of the high viscosity of the sulphuric acid solution. Both these two sets of 10 resonances consist of two peaks attributable to two carbonyl atoms, four methine aromatic carbon resonances and four quaternary carbon signals. Six of the carbon signals in every set, the four methine carbon resonances and the two quaternary carbon signals appearing as triplets ($^{>1}J = 7$ Hz), must arise from disubstituted aromatic rings. The chemical shifts of the carbonyl carbon atoms indicate that one type of carbonyl atom (C-7 and C-5) and two further carbonyl atoms (C-1' and C-4') must be near to nitrogen atoms. In the proton coupled ^{13}C n.m.r. spectrum of 3 (R=H) in D_2SO_4 the remaining four quaternary carbon resonances (C-5a, C-12b, C-2' and C-3') appear as relative sharp singlets indicating that they are at least four bonds removed from the nearest proton. When the broad band proton decoupled ^{13}C n.m.r. spectrum of 3 (R=H) was recorded in a 60:40 mixture of D_2SO_4:H_2SO_4 doubling of the peaks at $\delta_C = 157.539$ and $\delta_C = 109.733$ were observed with the corresponding isotope shifts as given in Table 1. This experiment proves that only one carbon atom (C-3') bears a substituent with exchangeable protons (probably NH_3^+ in sulphuric acid).

Through proton-proton decoupling and hetero-nuclear (^{13}C,^{1}H) correlation 2D (HETCOR) experiments the proton and ^{13}C resonances could be sequencially assigned and connected, but not to specific carbons or protons. The assumption was therefore made that the aromatic methine carbon atom C-4 (or C-5') resonate, in comparison with C-1 (or C-8'), at higher frequency. This is in agreement with reported values for substituted naphthoquinones.[4,5] The HETCOR experiment also proves that the resonance of C-4 overlaps that of C-5'.

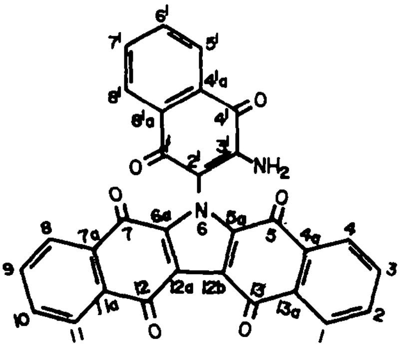


Table 1 ^{1}H and ^{13}C n.m.r. data of 3 (R=H)

	^{1}H		^{13}C			
	δ^{a}	J(Hz)	$\delta^{a,b}$	^{1}J	$>^{1}J$	Isotope shift[c]
1 (11)	7.534 d	7.4	133.494 Dd	167.7	7.2	
2 (10)	7.444 t	7.4	140.012 Dd	167.0	6.0	
3 (9)	7.360 t	7.6	144.081 Dd	168.3	7.2	
4 (8)	7.898 d	7.4	134.764 Dd[d]	163.8	6.8	
4a (7a)			131.250 St		7.0	
5 (7)			178.441 Sm			
5a (6a)			140.817 S			
11a (13a)			136.085 St		6.5	
12 (13)			190.154 Sm			
12a (12b)			128.339 S			
1'			177.720 Sm			
2'			109.733 S			0.04
3'			157.539 S			0.08
4'			177.550 Sm			
4'a			129.621 St		6.8	
5'	7.755 d	7.1	134.764 D[d,e]			
6'	7.360 t	e	140.773 Dd	164.8	6.6	
7'	7.375 t	7.5	141.527 Dd	169.1	6.5	
8'	7.373 d	7.5	132.253 Dd	165.0	7.0	
8'a			131.419 St		7.0	

[a] Solvent: sulphuric acid-d_2. Chemical shifts are relative to TSP.

[b] Symbols in upper case refer to the patterns resulting from directly bonded (C,H) coupling and those in lower case to patterns from (C,H) couplings over more than one bond.

S = singlet, D or d = doublet, T or t = triplet and m = multiplet.

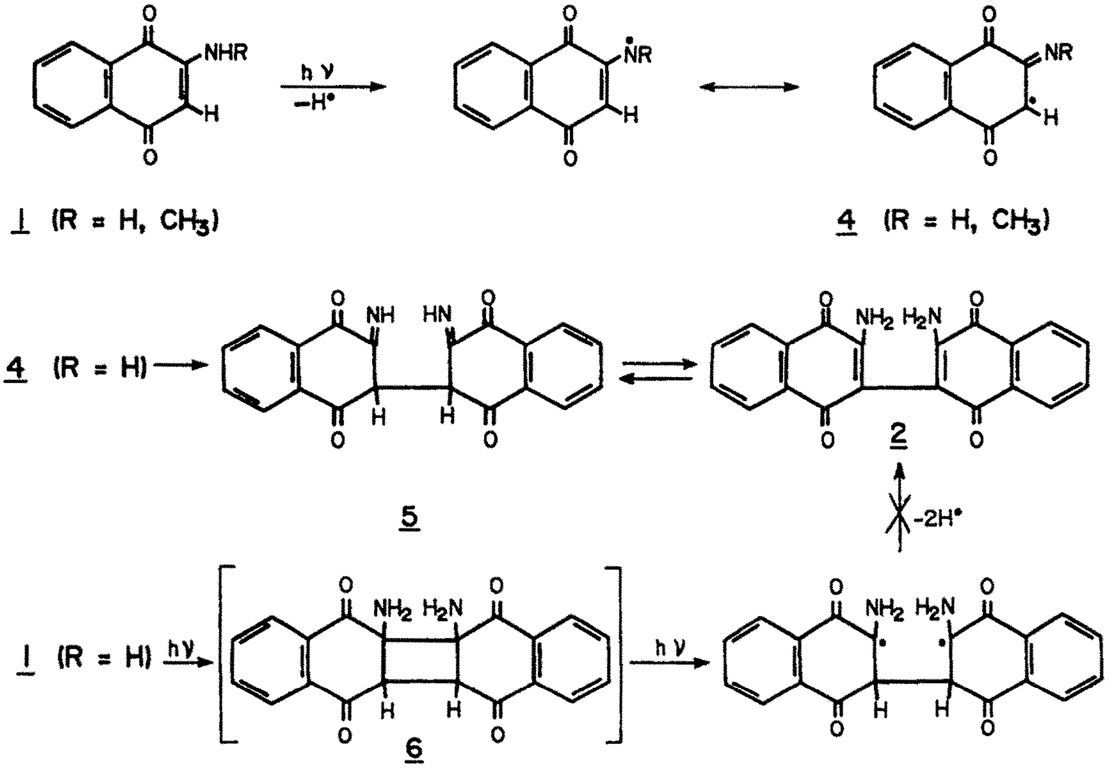
[c] Solvent 40:60 mixture of H_2SO_4:D_2SO_4.

[d] The whole assignment depends on the correctness of this assignment (see text).

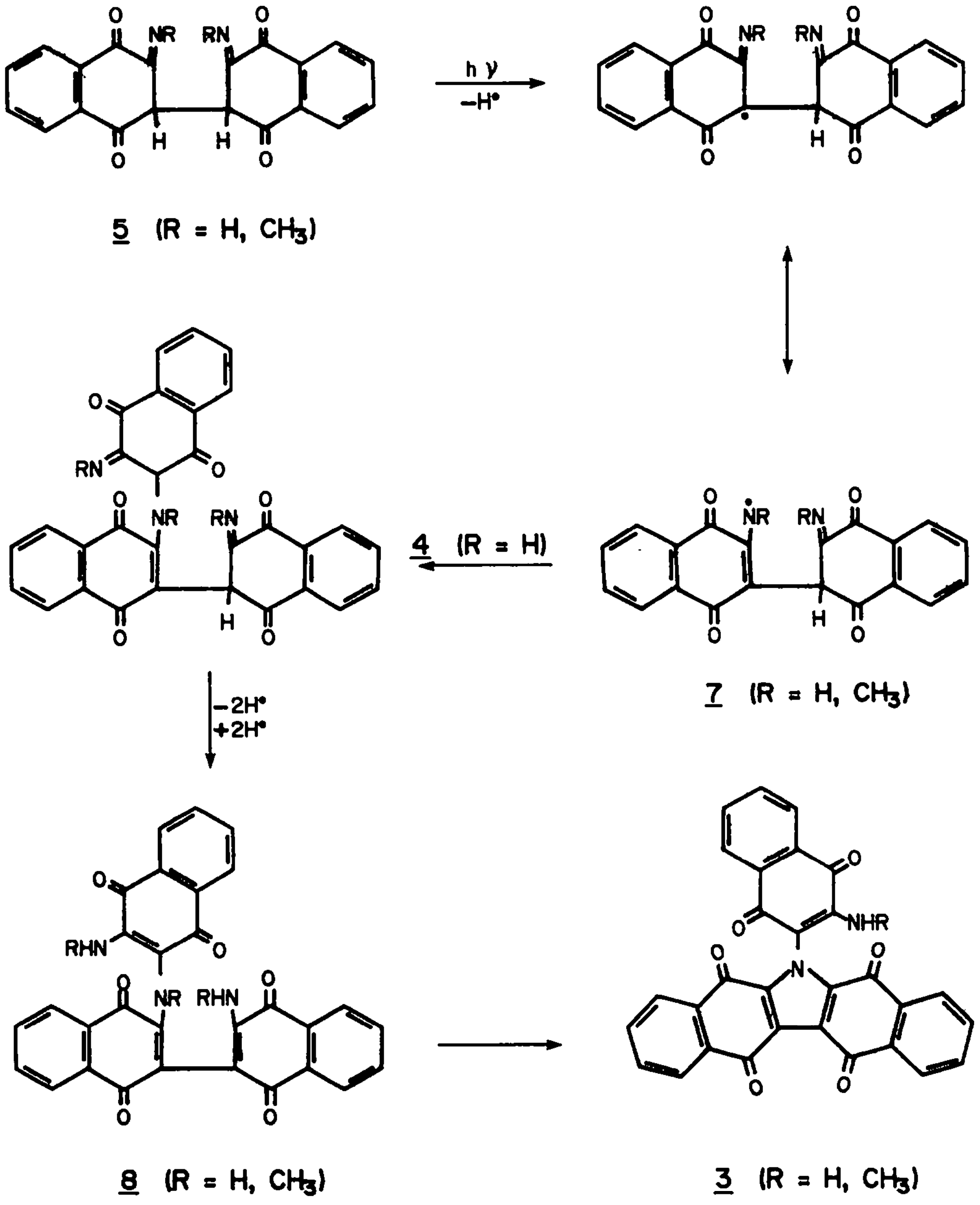
[e] Overlapped by more intense signals.

To gain more information on the structure of 3 (R=H), it was subjected to acetylation by treatment with acetic anhydride containing sodium acetate. A yellow crystalline compound (3, R=$COCH_3$) was obtained which exhibits strong infrared carbonylic absorptions at 1778 and 1720 cm^{-1} corresponding to the presence of an acetyl group as well as free carbonyl groups. A single weak absorption band at 2927 cm^{-1} indicates that N-acetylation indeed occurred. Conformation for the correctness of the allocated structure of 3 (R=$COCH_3$) was found from the FAB mass spectrum (nitrobenzene-glycerol matrix) which exhibits a molecular ion at m/z 541 ($[M+H]^+$).

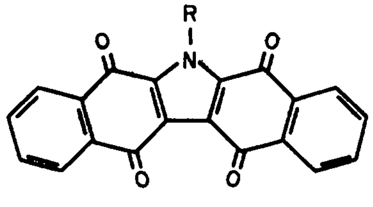
In order to obtain more information on the unexpected photochemical behaviour of 2-amino-1,4-naphthoquinone (1, R=H) we conducted the photolysis of 1 (R=H) in acetone. In addition to 3 (R=H) an orange coloured crystalline compound was obtained which was completely identical to 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl (2).[7] Sunlight irradiation of 2 in acetone produced no photoproducts indicating that 2 is not an intermediate in the formation of 3 (R=H) from 1 (R=H). Clearly the diamino-diquinone (2) can be obtained from direct coupling of an amidyl radical (4, R=H)[7] that can readily be formed from 2-amino-1,4-naphthoquinone (1, R=H). The formation of 2 from 6 is improbable, since the biradical will rather fragment regenerating 1 (R=H). This phenomenon could be one of the reasons why the expected cyclobutane compound 6 could not be isolated from the reaction mixture.



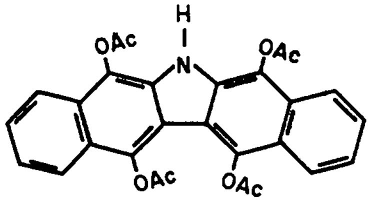
In a similar way the photoproduct 3 (R=H) can be obtained from 5 (R=H) via the elimination of a hydrogen radical whereby the amidyl radical 7 (R=H) is formed. Direct coupling between 7 (R=H) and 4 (R=H) followed by cyclisation of 8 (R=H) produces the carbazole 3 (R=H). Alternatively 8 (R=H) could also be derived from 2 attacking 1 (R=H) in a Michael addition process followed by photochemical dehydrogenation.



The photochemical carbazole cyclisation of the amine group in 8 (R=H) was clearly demonstrated by sunlight irradiation of 2-methylamino-1,4-naphthoquinone (1, R=CH$_3$) in acetic anhydride. A yellow crystalline compound was obtained which was completely identical to 6-methyl-dibenzo[b,h]carbazole-5,13:7,12-diquinone (9, R=CH$_3$) previously synthesised[7] by persulphate oxidation of 1 (R=CH$_3$). The formation of a small quantity of an intensely orange coloured product (3, R=CH$_3$) was also observed.



9 (R = H, CH_3)



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Strong support for the proposed structure of 3 and the formation of 3 from 1 was rendered by the photolysis of 2-methylamino-1,4-naphthoquinone (1, R=CH_3) in absolute methanol. An intensely orange coloured product (3, R=CH_3; m.p. 357°C)

molecular ion at m/z 512. Fragmentation peaks at m/z 483 and m/z 326 can be attributed to the successive losses of CH_2NH and 1,4-naphthoquinonyl fragments respectively and give positive evidence in support of the assigned structure of 3 (R=CH_3). The infrared spectrum of 3 (R=CH_3) closely resembles that of 3 (R=H). The absorption band of the N-H stretching vibrations of 3 (R=CH_3) correlates with that of 1 (R=CH_3).

According to the proposed mechanism for the formation of 3 (R=H) from 1 (R=H) it is expected that the diamino-diquinone (2) must also be formed from the photolysis of 1 (R=H) in acetic anhydride, although we were unable to isolate 2 from diluted reaction mixtures. Pyrex-filtered sunlight irradiation of more concentrated solutions of 1 (R=H) in acetic anhydride produced in addition to 3 (R=H) a yellow crystalline product (9, R=H; m.p. 435°C) which was characterised by its mass spectrum (EI) which showed a molecular ion at m/z 327 and successive losses of four molecules of carbon monoxide. The infrared spectrum of 9 (R=H) exhibits a typical single absorption band at 3197 cm^{-1} corresponding to the N-H stretching vibrations of a secondary amine group. The assigned structure of 9 (R=H) was unambiguously proved by acetylation with acetic anhydride containing zinc powder whereby a tetraacetate (10) was obtained.

For comparison with the photoproduct 9 (R=H) we required an authentic sample of dibenzo[b,h]carbazole-5,13:7,12-diquinone (9, R=H). Thomson and coworkers[7] were unable to cyclise the diamino-diquinone 2 whereby 9 (R=H) could be obtained. On the other hand N-substituted (methyl or ethyl) diamino-diquinones can conveniently be transformed[7] to the corresponding N-alkyl carbazole-diquinones (9, R=CH_3, C_2H_5) by persulphate oxidation or a nucleophilic process by heating an aqueous solution made acidic by prior decomposition of persulphate. This result persuaded us to subject 2 to treatment with boiling acetic acid containing a small quantity of sulphuric acid. A yellow crystalline compound was recovered which was completely identical to the photoproduct (9, R=H) obtained from the photolysis of 2-amino-1,4-naphthoquinone (1, R=H) in acetic anhydride.

EXPERIMENTAL

Infrared spectra (KBr disc) were recorded on a Nicolet 5 DX FT-spectrophotometer. FAB mass spectra were recorded on a VG Analytical 7070-E mass spectrometer equipped with a Ion-Tech FAB gun, operating at 6 kV accelerating potential, resolving power approximately 1000 and scanned at 20 s per decade in the positive ion mode. EI spectra were obtained at 70 eV. Melting points are uncorrected. Elemental analysis were performed on a Hewlett-Packard analyser. The ^1H and ^{13}C n.m.r. spectra were recorded on a Bruker WM 500 spectrometer.

Photolysis of 2-amino-1,4-naphthoquinone (1, R=H)

(a) A solution of 1 (R=H)(0.2 g) in acetic anhydride (100 ml) was sealed in Pyrex test tubes and exposed to direct sunlight for a period of 5 days. The crystalline product was filtered off and refluxed in acetone to give an insoluble orange coloured product 3 (R=H) that was recrystallised from nitrobenzene (0.08 g, m.p. 455°C dec.) ν_{max} 3402, 3311, 1684, 1615, 1592, 1575, 1267, 1056, 1015, 728 and 704 cm^{-1}; FAB m/z 499 ($[M+H]^+$), 481 ($[M+H]^+-H_2O$); Calc. for $C_{30}H_{14}N_2O_6$: C, 72.29; H, 2.81; N, 5.62%. Found: C, 72.25; H, 2.74; N, 5.6%.

(b) A solution of 1 (R=H)(0.3 g) in acetic anhydride (100 ml) was exposed to direct sunlight for a period of 5 days as described before. The crystalline photoproducts were filtered off and refluxed in acetone for 15 minutes, allowed to settle and the suspension of the orange coloured 3 (R=H) (0.06 g) decanted from the yellow coloured product 9 (R=H)(0.11 g), m.p. 435°C) ν_{max} 3190, 1692, 1673, 1277 and 721 cm^{-1}; EI m/z 327 (M^+), 299 (M^+-CO), 271 (M^+-2CO), 243 (M^+-3CO), 215 (M^+-4CO); Calc. for $C_{20}H_9NO_4$: C, 73.39; H, 2.75; N, 4.28%. Found: C, 73.46; H, 2.72; N, 4.32%.

(c) A solution of 1 (R=H)(0.4 g) in acetone (100 ml) was irradiated for 10 days as described before. The crystalline 3 (0.16 g) was filtered off and the excess acetone (60 ml) was removed under reduced pressure whereby 2 (0.1 g) was obtained.

Photolysis of 2-methylamino-1,4-naphthoquinone (1, $R=CH_3$)

(a) A solution of 1 ($R=CH_3$)(0.3 g) in acetic anhydride (100 ml) was exposed to direct sunlight for a period of 5 days as described above. The crystalline photoproducts were boiled in chloroform (25 ml) and the insoluble 3 ($R=CH_3$)(0.02 g) was filtered off. The excess chloroform (15 ml) was removed under reduced pressure whereby 9 ($R=CH_3$)(0.09 g) was recovered. The melting point, infrared and the mass spectra of 9 ($R=CH_3$) were fully identical to that of an authentic sample obtained from the persulphate oxidation of 1 ($R=CH_3$).[7]

(b) A solution of 1 ($R=CH_3$)(0.3 g) in absolute methanol (200 ml) was exposed to Pyrex-filtered sunlight for 5 days. The orange coloured product 3 ($R=CH_3$) (0.12 g) was filtered off. Concentration of the filtrate produced a yellow compound (0.05 g) fully identical to the methylcarbazole 9 ($R=CH_3$).[7] To remove traces of unreacted monomer and 9 ($R=CH_3$) the product 3 ($R=CH_3$) was boiled in acetic anhydride to yield intensely orange coloured needles (m.p. 357°C). ν_{max} 3345, 3288, 1688, 1672, 1614, 1589, 1573, 1302, 1261, 1056, 1015, 744, 728 and 687 cm^{-1}; EI m/z 512 (M^+), 483 (M^+-CH_2NH), 326 ($M^+-CH_2NH-C_{10}H_5O_2$); Calc. for $C_{31}H_{16}N_2O_6$: C, 72.66; H, 3.13; N, 5.47%. Found: C, 72.62; H, 3.11; N, 5.44%.

Acetylation of 3 (R=H)

A suspension of 3 (R=H)(0.3 g) and sodium acetate (0.1 g) in acetic anhydride (20 ml) was boiled under reflux for 3 h. The cooled reaction mixture was stirred with a mixture of ethanol (10 ml) and water (10 ml). The crystalline yellow product was filtered off and recrystallised from acetic acid to give 3 ($R=COCH_3$) (0.18 g, m.p. 160°C). ν_{max} 2927, 1778, 1720, 1395 and 1160 cm^{-1}; FAB m/z 541 ($[M+H]^+$); Calc. for $C_{32}H_{16}N_2O_7$: C, 71.11; H, 2.96; N, 5.19%. Found: C, 71.14; H, 2.93; N, 5.21%.

Acetylation of 9 (R=H)

A mixture of 9 (R=H)(0.3 g), zinc powder (0.5 g) and acetic anhydride (10 ml) was boiled under reflux for 2 h. The unreacted zinc powder was filtered off and the filtrate was stirred with a mixture of ethanol (10 ml) and water (10 ml). The yellow product was filtered off and recrystallised from ethanol to give 10 (0.25 g, m.p. 330°C). ν_{max} 3353, 1770, 1655, 1360, 1204, 1196, 1032 and 761 cm^{-1}; EI m/z 499 (M^+), 457 (M^+-CH_2CO), 415 ($M^+-2\ CH_2CO$), 373 ($M^+-3\ CH_2CO$), 329; Calc. for $C_{28}H_{21}NO_8$; C, 67.33; H, 4.21; N, 2.81%. Found: C, 67.37; H, 4.18; N, 2.83%.

Cyclisation of 2

A suspension of 2 (0.3 g) in acetic acid (50 ml) containing a solution (5 ml) of equal parts by volume of concentrated sulphuric acid and water was rapidly brought to the boiling point. Within fifteen minutes the starting material had completely passed into solution and after another fifteen minutes the carbazole began to separate. After further heating for ten minutes the mixture was cooled and the crystalline product (9, R=H, 0.15 g) collected and recrystallised from nitrobenzene. The m.p., i.r. and m.s. were identical to that of the photoproduct (9, R=H) obtained from the photolysis of 2-amino-1,4-naphthoquinone (1, R=H) in acetic anhydride.

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