Photo-oxidation of 7-Methylbenz[*c*]acridine in Methanol. Identification of Two Primary Photoproducts

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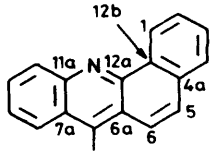
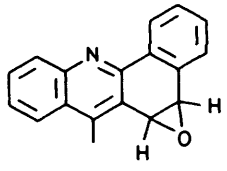
Irradiation at 365 nm of an oxygenated solution of 7-methylbenz[*c*]acridine in methanol yields a mixture of photoproducts of which two were shown by ^{1}H and ^{13}C n.m.r. to be *trans*-6-hydroxy-5-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine and *trans*-5-hydroxy-6-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine.

The carcinogenic activity of the environmental pollutant, benzo[*a*]pyrene is believed to be mediated by metabolic activation through a dihydro diol epoxide derivative which can link covalently to 3 of the 4 bases in both DNA and RNA.[1] Chemical bonding between benzo[*a*]pyrene and DNA *in vitro* can also be achieved by exposure to near u.v. light in oxygenated conditions.[2]

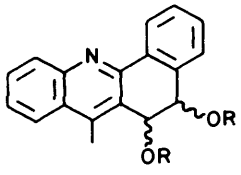
Metabolism studies in our laboratories have been conducted on the polycyclic aza-aromatic hydrocarbon, 7-methylbenz[*c*]-acridine (**1**), which is carcinogenic[3] and is representative of a group of urban air pollutants, the alkylbenz[*c*]acridines.[4] Metabolic oxidation occurs at the 1,2-, 5,6-, 8,9-, and 10,11-positions and at the methyl substituent.[5,6] In parallel, we are investigating photochemical oxidation as an alternative mechanism of activation of 7-methylbenz[*c*]acridine.



(1)



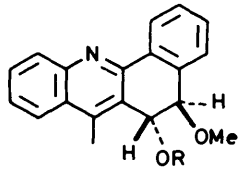
(5)



(4) R/R = H/Me

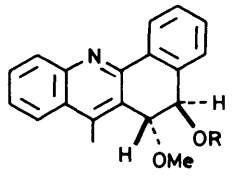
Irradiation with u.v. light (365 nm) of an oxygenated solution of compound (**1**) in methanol yielded a complex mixture of photoproducts which were separated by h.p.l.c. as shown in the Figure. Two of the products with retention times of 37.0 and 40.7 min respectively (Figure) were detectable from the very early stages of irradiation. In this paper, we show that the faster eluting photoproduct is *trans*-6-hydroxy-5-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine (**2a**) while the slower eluting one is *trans*-5-hydroxy-6-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine (**3a**).

Photoproducts (**2a**) and (**3a**) have the same molecular formula $C_{19}H_{17}NO_2$. For each photoproduct the presence of hydroxy and methoxy groups is shown by the methane chemical ionization (c.i.) mass spectrum. Thus there were losses from the MH^+ ion of MeOH [to yield *m/z* 260 (60—80%)], and of H_2O + CH_2O [to yield *m/z* 244 (5—10%)]. Each product forms a mono-trimethylsilylated derivative which under methane c.i. conditions showed losses from the MH^+ ion (*m/z* 364, base

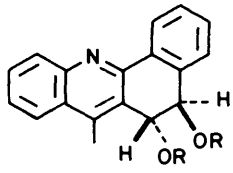


(2)

a; R = H
b; R = Ac



(3)



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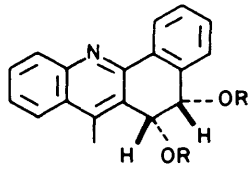


(7)

peak) of Me_3SiOH [to yield *m/z* 274 (*ca.* 85%)], of MeOH [to yield *m/z* 332 (*ca.* 40%)], and of Me_3SiOH + CH_2O [to yield *m/z* 244 (10%)].

The ^{1}H n.m.r. spectrum of the photoproduct (**2a**) (Tables 1,2) shows the presence of methoxy (δ 3.22) and arylmethyl groups

Table 1. ^{1}H N.m.r. data[a] of upfield signals of 5,6-*trans*-compounds

		(2a)[b]	(2b)	(3a)	(3a)[c]	(3b)	(6a)[d]
5-H	δ	4.52d	4.46d	5.02	5.06d	6,30d	4.90[e]
	J	3.2	3.0		*ca.* 3	3.5	
	$W_{h/2}$	1.2	1.4[f]	1.2	2.6[g]	1.4[h]	
6-H	δ	5.42d[i]	6.69d	5.02	5.10d[i]	5.02d	5.34dd
	J	3.2	3.0		3.3	3.5	3.2, 5.1
	$W_{h/2}$	*ca.* 3[g]	0.8	1.2	0.6	0.8	
7-Me	δ	2.83	2.77	2.52	2.86	2.81	2.78
OMe	δ	3.22	3.28	3.30	3.37	3.49	—
OAc	δ	—	1.92	—	—	1.88	—

[a] Chemical shifts in δ relative to $SiMe_4$ and coupling constants *J* and half-height-width $W_{h/2}$ in Hz as measured in $CDCl_3$ at 90 MHz unless otherwise stated. Upfield shifts on increase of concentration due to ring stacking are generally observed. [b] Measured in $CDCl_3$ at 400 MHz. [c] Measured in $(CD_3)_2CO$ at 400 MHz. [d] Measured in $(CD_3)_2SO$–$CDCl_3$ (1:4 v/v) at 100 MHz. For corresponding chemical shifts and n.O.e. in CD_3OD, see ref. 7. In either solvent W-coupling between 1-H and 5-H of *ca.* 0.5 Hz was observed. [e] Masked by OH signals. [f] Signal narrowed by 0.6 Hz upon saturation of 1-H. [g] Apparently signal broadened by coupling to OH. [h] Signal narrowed by 0.3 Hz upon saturation of 1-H. [i] N.O.e. observed (see Table 4) when 7-Me was irradiated.

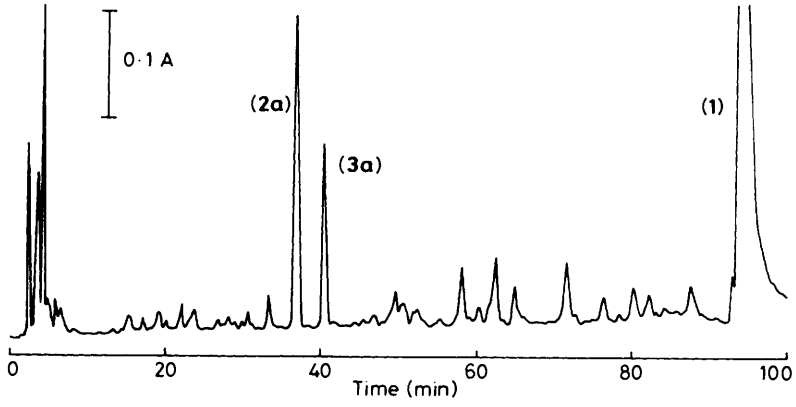


Figure. Chromatogram obtained by analytical scale h.p.l.c. (detector wavelength 254 nm) with a water–methanol gradient, of a solution of 7-methylbenz[*c*]acridine (0.33 mmol) in methanol after 1 h irradiation. Chromatographic conditions are described in the Experimental section.

Table 2. ^{1}H N.m.r. data[a] of aromatic protons of 7-methyl-5,6-dihydrobenz[*c*]acridine compounds

Compd.	(2a)[b]	(3a)[b]	(5)	(6a)		(6b)	(7a)	(7b)	
Solvent	$CDCl_3$	CD_3COCD_3	$CDCl_3$	$(CD_3)_2SO$–$CDCl_3$ (1:4 v/v)	CD_3OD	CD_2Cl_2	$(CD_3)_2SO$–$CDCl_3$ (1:4 v/v)	CD_2Cl_2	$CDCl_3$
1-H	8.65	8.62	8.94	8.52	8.52	8.69	8.48	8.63	8.66
2-H	7.58[c]	7.45—7.50	7.4—7.8	7.4—7.5	7.4—7.6	7.4—7.65	7.4—7.7	7.4—7.6	7.4—7.6
3-H	7.46[d]								
4-H	7.44[e]								
8-H	8.03[f]	8.17[f]	7.94	7.99[g]	8.07	8.09[g]	8.08	8.06[g]	8.05
9-H	7.54	7.60	7.4—7.8	7.66	7.71[h,i]	7.58	7.7—7.8	7.57	7.56[i]
10-H	7.70[h]	7.74		7.58	7.63[h]	7.76		7.75	7.74[i]
11-H	8.13	8.08	8.08	8.07	8.15	8.14	8.08	8.14	8.13

[a] Unless otherwise stated chemical shifts are in p.p.m. from $SiMe_4$ as measured at 100 MHz for 0.1—0.3M solutions. $J_{1,2}$ is 7.5 Hz, $J_{8,9}$ and $J_{10,11}$ are 8.5 Hz, $J_{9,10}$ is 6.5 Hz, and $J_{8,10}$ and $J_{9,11}$ are 1.4 Hz. $J_{9,10}$ was not measured for compounds (**5**) and (**7a**). $J_{8,11}$ is 0.6 Hz for compound (**3a**). Assignments were by selective decoupling experiments. [b] 400 MHz. [c] On irradiation of 1-H, collapse of *ca.* 8 Hz splitting observed. [d] On irradiation of 1-H, collapse of *ca.* 1 Hz splitting observed. [e] N.O.e. observed upon irradiation of OMe (see Table 4). [f] N.O.e. observed upon irradiation of 7-Me (see Table 4). [g] N.O.e (5—25%) observed upon irradiation of 7-Me under degassed conditions. [h] On irradiation of 8-H or 11-H removal of J_{ortho} observed. [i] On irradiation of 8-H or 11-H removal of J_{meta} observed.

Table 3. U.v. absorption and fluorescence characteristics[a]

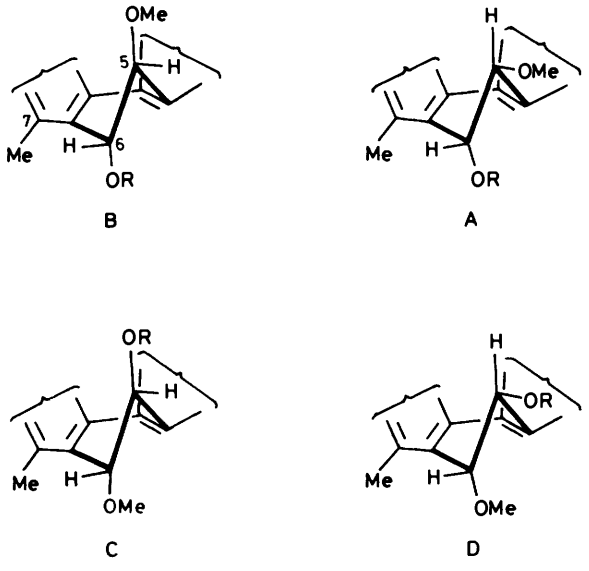
	$\lambda_{abs.}$	(ε)	$\lambda_{em.}$	φ_F[b]
(**2a**)	257.9	(1 900)	348	0.004
	267.7	(2 040)	363	
	293.3	(605)		
	312.4	(515)		
	326.4	(490)		
	341.5	(460)		
(**3a**)	259.9	(2 080)	348	0.004
	267.2	(2 280)	370sh	
	294.0	(660)	385sh	
	311.5	(535)		
	326.0	(510)		
	341.2	(485)		
(**6a**)[c]	259		345	
	267		365	
	294		388	
	312			
	326			
	342			

[a] Absorption and emission maxima (λ_{abs} and λ_{em}) in nm and ε (m^2 mol^{-1}) were measured for methanol solutions. [b] Fluorescence quantum yield measured relative to quinine sulphate in 0.05M-H_2SO_4 (φ_F = 0.55). [c] Data of ref. 5.

(δ 2.83). The presence of methine signals at δ 4.52 and 5.42 (doublets, *J* 3.2 Hz) establishes that the methoxy and hydroxy groups are attached to adjacent carbons. The spectrum of photoproduct (**3a**) (Tables 1,2) shows the same functional groups. For this product the signals for the two vicinal 'carbinol' hydrogen atoms are not resolved at 90 MHz in $CDCl_3$, CD_2Cl_2 or CD_3COCD_3, but are observed at 400 MHz as doublets at δ 5.06 and 5.10 (*J* 3.3 Hz) (in CD_3COCD_3). The above data suggest an intact 7-methylbenz[*c*]acridine skeleton with a monomethylated dihydrodiol system at the 5,6-position [see general structure (**4**)]. In support, the u.v. absorption and fluorescence characteristics (Table 3) and the ^{1}H n.m.r. data of the aromatic signals (Table 2) parallel those of reference 7-methyl-5,6-dihydrobenz[*c*]acridine derivatives (**5**), (**6a,b**), and (**7a,b**). Indeed, treatment of the 5,6-epoxide (**5**)[7] with 10M-HCl in methanol at room temperature yielded a mixture from which products (**2a**) and (**3a**), identical with samples from the photoreaction, were isolated by preparative h.p.l.c.

Complete elucidation of the structures of the photoproducts requires the location of the methoxy *vis-a-vis* the hydroxy group, and the assignment of configuration and conformation at positions 5 and 6. *X*-Ray analysis of *cis*-5,6-dihydroxy-7,12-dimethyl-5,6-dihydrobenz[*a*]anthracene suggests that the 1,2-dihydrobenzene ring in K-region dihydro-compounds generally exists as a pseudo-half-chair.[8] Furthermore, a substituent on the

substituent which is *peri* to the 7-methyl group in the 7-methyl-5,6-dihydrobenz[*c*]acridine series), generally adopts the pseudo-axial conformation to minimize non-bonded interactions.[8,9] The above considerations lead to four possible structures for the two photoproducts, with conformation and relative configuration represented by partial structures (A), (B) (with the methoxy group at position 5), and (C) and (D) (with the methoxy group at 6). Distinction between these structures



cannot be made from the vicinal coupling constant $^3J_{5,6}$, observed to be 3 Hz for both photoproducts (see Table 1). For either structure (B) and (C) (with di-pseudoaxial substituents) or (A) and (D) (with pseudoaxial and pseudoequatorial substituents) the relevant dihedral angle is *ca.* 60 °, leading to *J* 1.5—5 Hz.[10] However, four types of n.m.r. data presented below show that both photoproducts are *trans* di-pseudoaxial at the 5,6 position and establish their structures as (**2a**) (faster eluting species in h.p.l.c.) and (**3a**) (slower eluting), corresponding to partial structures (B) and (C) respectively.

Firstly, compatible with the expected pseudoaxial orientation of the 6-substituent [7] is the observation for both photoproducts of positive nuclear Overhauser effects (n.O.e.) of the n.m.r. signal of 6-H (as well as 8-H) when the 7-methyl signal is saturated (Table 4).

Secondly, we show that the 5-substituent is pseudoaxial in both photoproducts. Photoproduct (**2a**) readily formed a mono-acetate (**2b**) $C_{21}H_{19}NO_3$ on acetylation. Likewise, photo-product (**3a**) formed an isomeric acetate (**3b**). For each acetate, the 'carbinol' proton signal in the n.m.r. spectrum is 1.3 p.p.m. downfield of its counterpart in the parent alcohol (see Table 1). Upon saturation of the characteristically low field 1-H signal near δ 8.6, the C*H*OMe doublet signal (δ 4.46) of the acetate (**2b**) and the C*H*OAc doublet (δ 6.30) of the acetate (**3b**) were sharpened by 0.6 and 0.3 Hz respectively. These experiments show that 5-H in both photoproducts is pseudoequatorial, thus giving rise to *W*-type long-range coupling [11] to 1-H. In addition, the experiments establish the position (C-5) and conformation (pseudoaxial) of the methoxy group in photoproduct (**2a**), and of the hydroxy group in photoproduct (**3a**).

Thirdly, the chemical shifts of the acetoxy protons in the two acetates are used as criteria of conformation. It had been shown [10] that benzylic acetoxy groups of dihydro diol derivatives of polynuclear aromatic hydrocarbons are shielded by the surrounding aromatic rings if pseudoaxial, and deshielded if pseudoequatorial, giving rise to chemical shifts

Table 4. Nuclear Overhauser effects (%)[a] observed for photoproducts (**2a**) and (**3a**)

Signal observed	Irradiation of 7-Me (**2a**)	Irradiation of 7-Me (**3a**)	Irradiation of OMe (**2a**)
4-H			+3.3
5-H			+7.2
6-H	+12.2	> +6.5[b]	
8-H	+10.6	> +6.5[b]	

[a] Enhancements given were estimated by spectral subtraction (irradiated signal, −100% per proton). Measurements were made *without* degassing and at 400 MHz for solutions in $CDCl_3$ [compound (**2a**)] or in $(CD_3)_2CO$ [compound (**3a**)]. [b] N.O.e.s recorded are lower limits as the irradiated Me signal overlaps with an H_2O signal.

(δ_{Ac}) of *ca.* 1.9 and 2.3 respectively in $CDCl_3$. The acetates (**2b**) and (**3b**) have δ_{Ac} of 1.90 ± 0.02 (Table 1), thus confirming that the acetoxy groups are pseudoaxial.

Finally, ^{13}C shieldings are employed to support the above conclusions. In Table 5, the ^{13}C chemical shifts of the methyl ethers (**2a**) and (**3a**) are compared with those of the corresponding *trans*-diol (**6a**), the *cis*-diol (**7a**), and the 5,6-epoxide (**5**).[7] By comparison of the *cis*- and *trans*-diols (**6a**) and (**7a**), it would be expected that for the former there would be an increased γ-gauche effect of the pseudoequatorial 5-hydroxy group on C-4. Indeed upfield shifts of C-4 and C-5 (*ca.* 3 and 2 p.p.m., respectively) are observed. The chemical shift of C-4 in each methyl ether (**2a**) and (**3a**) is, as expected, similar to that in the *trans*-diol (**6a**). Furthermore, in agreement with the structural assignment, the 6-methoxy carbon of the ether (**3a**) gives rise to a β-effect on C-6 of 8.5 p.p.m. [76.3 p.p.m. in the ether (**3a**) *vs.* 67.8 p.p.m. in the *trans*-diol (**6a**)], while the 5-methoxy carbon of the ether (**2a**) causes a similar effect on C-5.

The distinction between the methine carbons C-5 and C-6 in the *trans*-diol (**6a**) was made from correlation with 5-H and 6-H through selective off-resonance decoupling and Birdsall-type plots.[12] Such correlations lead to the assignment of all protonated carbons in the *trans*-diol (**6a**) except carbons 2, 3, and 10. The C-9 signal is recognized by comparison with 4-methylquinoline. The assignment of the latter in turn is aided by comparison with quinoline, there being a deshielding effect of the 4-methyl group on C-5 *peri* to it (see Table 5). Assignment of signals of compounds (**5**), (**7a**), (**2a**), and (**3a**) follows from that of the *trans*-diol (**6a**).

It is of interest to note that in the *trans*-diol (**6a**), C-6 is more shielded than C-5 by 3.5 p.p.m. due to steric compression of the 7-methyl group *peri* to it. The complementary deshielding of 6-H (0.44 p.p.m.) (Table 1) is also observed.

With the structure of the photoproducts (**2a**) and (**3a**) unambiguously assigned, it was of interest to determine whether or not the formation of these products proceeds through the 5,6-epoxide (**5**) as an intermediate. We conclude that the epoxide (**5**) is not an intermediate for products (**2a**) and (**3a**) based on the following experiments.

Firstly, thermal decomposition of epoxide (**5**), either thermally or through methanolysis, was not significant under the conditions involved in the work-up of the irradiation mixture and analysis by h.p.l.c. The stability of the epoxide (**5**) observed here is in contrast to the report that a K-region oxide metabolite of 7,12-dimethylbenz[*a*]anthracene was found to undergo on-column methanolysis during h.p.l.c. analysis with a methanol–water gradient.[13] When a sample of the epoxide (**5**) was added to the photoproduct mixture, it eluted at R_t 72.0 min, and was only partially resolved from another photoproduct with R_t 71.2 min (see the Figure). The partially resolved

Table 5. ^{13}C N.m.r. Chemical Shifts

	Quinoline[a,b]	4-Methyl-quinoline[a,c,d]	(5)[c]	(7a)[e]	(6a)[e]	(2a)[c]	(3a)[c]
Methyl carbons							
7-OMe	—	18.0	13.1	13.6	13.5	13.3	13.9
OMe	—	—	—	—	—	56.0	56.6
Methine carbons							
5			55.3	69.9	71.4	80.0	69.1
6			52.3	67.3	67.8	66.7	76.3
1			126.7	125.6*	126.1[f]	126.0	125.9
4			129.6*	126.4*	128.9[g]	130.8*	129.6*
8	128.5 (C-5)	123.2	123.5	124.8	124.0[f]	123.8	124.0
9	127.0 (C-6)	125.7	126.2	125.6*	125.9[h]	126.6	126.8
11	130.3 (C-8)	129.5[f]	130.1*	129.9**	129.8[f]	129.6*	129.6*
10,2,3	129.9 (C-7)	128.5	129.4*	127.1	128.7	129.0	129.3
			129.4	129.6**	129.7	129.2	129.4*
			130.1	130.0**	130.2	129.8*	130.2*
Quaternary carbons							
7,11a,12a	— (C-4)	143.6	144.9	142.9	143.9	144.2	*i*
	149.1 (C-8a)	147.4	146.9	147.4	147.1	147.0	145.4
			148.9	151.1	151.1	150.2	151.0
7a	128.9 (C-4a)	127.7	*i*	127.8	127.7	127.6	127.3
6a			122.0	*i*	127.9	*i*	*i*
4a,12a			132.7	133.3	133.9	133.1	132.6
			i	140.3	138.3	133.4	136.8

[a] In the Table, chemical shifts of relevant carbons of these model compounds are listed against the corresponding carbons in the 7-methylbenz[*c*]acridine derivatives (**5**)—(**7a**), (**2a**), and (**3a**). The correct systematic numberings are also given (in brackets). [b] Data taken from J. B. Stothers, 'Carbon-13 NMR Spectroscopy, Academic Press, New York, 1972, p. 262. [c] In $CDCl_3$ with δ_C ($CDCl_3$) 76.9 p.p.m. [d] Other signals (systematic numbering): C-2, 149.5[f], C-3, 121.3[f] p.p.m. [e] In 2:3 (v/v) $(CD_3)_2SO$–$CDCl_3$ with δ_C [$(CD_3)_2SO$] 39.9 p.p.m. [f] Assignment confirmed by Birdsall-type plot.[12] [g] In the off-resonance spectrum, with irradiation upfield of $SiMe_4$, residual coupling (J_{CCCH}) to 1-H was observed. [h] In the off-resonance spectrum, with irradiation downfield of δ 10, residual coupling (J_{CCCH}) to 11-H was observed. [i] Not observed, being either masked or too weak or having identical chemical shift to that of another quaternary carbon signal.
*,** Signals within a vertical column may be reversed.

chromatographic peaks were shown to be spectroscopically distinct compounds, by means of the diode array spectrophotometric detector. Thus the epoxide (**5**) was not present in the photoproduct mixture, nor had it decomposed during work-up.

Secondly, u.v. irradiation of a solution of the epoxide (**5**) (0.4 mmol) in methanol resulted in rapid decomposition to products with R_t 48.0, 78.5, and 80.0 min, but there was no evidence of products (**2a**) or (**3a**). Therefore, if the epoxide (**5**) was formed photochemically, it would be photolysed rapidly to products other than (**2a**) and (**3a**).

Experimental

N.m.r. data were collected using Bruker WM400 (^1H and n.O.e.), JEOL FX90Q (^1H and ^{13}C) and Varian CFT20 (^{13}C) spectrometers. For c.i. mass spectrometry and silylation procedures see ref. 16. Molecular weight determinations by electron impact mass spectrometry (e.i.m.s.) were performed on an AEI MS902 spectrometer. U.v. spectra were recorded using a Perkin-Elmer Lambda 5 spectrophotometer, and fluorescence characteristics were determined on a Perkin-Elmer MPF44B spectrofluorimeter with corrected spectra accessory DCSU-2. Light petroleum refers to the fraction boiling at 40—60 °C.

Photolysis of 7-Methylbenz[c]*acridine* (**1**) *and Isolation of Photoproducts* (**2a**) *and* (**3a**).—7-Methylbenz[*c*]acridine (**1**)[14] (0.33 mmol) in oxygenated methanol was irradiated at 30 °C for 4 h in a Hanovia 1 litre photochemical reactor with a 125 w medium pressure mercury lamp encased in a Pyrex glass sheath.[15] The irradiated solution was evaporated to dryness, redissolved in light petroleum–dichloromethane (3:1 v/v) and the photoproducts separated from unchanged material by elution from a silica column (45 × 45 mm; H60, Merck) with light petroleum–dichloromethane mixtures: (i) 3:1 v/v (400 ml), (ii) 2:1 v/v (150 ml), and (iii) 1:1 v/v (100 ml). The desired compounds (**2a**) and (**3a**) eluted in eluants (i) and (ii), respectively. Further purification was achieved by preparative h.p.l.c. using an Altex 334 system[16] with a 500 × 9 mm column packed with 10 μm Spherisorb ODS. A methanol–water gradient was used as follows: (i) 15% methanol at 4.5 ml min^{-1} for 2 min, (ii) 15—30% methanol at 4.5 ml min^{-1} over 18 min, (iii) 30% methanol at 8 ml min^{-1} for 2 min, (iv) 30—70% methanol at 8 ml min^{-1} over 80 min, and (v) 70—100% methanol at 8 ml min^{-1} over 10 min. The purity of collected fractions was monitored by analytical h.p.l.c. using an Aquapore RP300 column (250 × 4 mm, Brownlee Labs.) and the gradient described previously.[16] In some cases a Hewlett-Packard 1040A linear diode array spectrophotometric detector

was used to obtain spectra of the eluted peaks. Peak fractions of retention time 55 min (preparative system) were collected and evaporated to yield *trans*-6-hydroxy-5-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine (**2a**) [Found: M^+ (by e.i.m.s.), 291.128. $C_{19}H_{17}NO_2$ requires *M*, 291.126]. Likewise, fractions of retention time 60 min (preparative system) yielded *trans*-5-hydroxy-6-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine (**3a**) [Found: M^+ (by e.i.m.s.), 291.126. $C_{19}H_{17}NO_2$ requires *M*, 291.126].

Acetylation of the Photoproducts (**2a**) *and* (**3a**).—A solution of the photoproduct (**2a**) in anhydrous pyridine was treated with acetic anhydride (1 mol equiv.) at room temperature overnight. After the addition of water, the product mixture was extracted with chloroform. The washed (water) and dried (Na_2SO_4) extract was evaporated, and the residue purified by chromatography over silica [eluant: dichloromethane–light petroleum (2:1 v/v)] to give in quantitative yield *trans*-6-acetoxy-5-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine (**2b**) [Found: M^+ (by e.i.m.s.), 333.137. $C_{21}H_{19}NO_3$ requires *M*, 331.137]. In a similar manner, the photoproduct (**3a**) was acetylated to give *trans*-5-acetoxy-6-methoxy-7-methyl-5,6-dihydrobenz[*c*]acridine (**3b**) [Found: M^+ by (e.i.m.s.), 333.136. $C_{21}H_{19}NO_3$ requires *M*, 331.137].

Acid Treatment of the Epoxide (**5**).—The epoxide (**5**) was treated with 10M-hydrochloric acid–methanol mixture (1:50 v/v) at room temperature for 2 h. After neutralization with dilute ammonium hydroxide, the solution was evaporated to dryness and worked-up as for the photolysis reaction to yield compounds (**2a**) and (**3a**), identical (by h.p.l.c. and ^1H n.m.r.) to the photoproducts.

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