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PHOTOCHEMISTRY OF
9,10-DIPHENYLANTHRACENE ENDOPEROXIDE [1]

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It is well known that 9,10-diphenylanthracene endoperoxide 1a releases molecular oxygen almost quantitatively upon heating, whereas the unsubstituted 1b or *meso*-alkylated analogues, such as 1c, suffer essentially an O-O bond homolysis, leading to degradation products or to rearranged isomers of types 8 and 10 [2]. Trapping experiments have shown that these isomers originate from the subsequent transformations of primary intermediates : the *meso*-diepoxides 6, unstable in these conditions [3]. Because of the similarities with 1-4 endoperoxides of naphthalenes and anthracenes, where irradiation leads to isolable 1,2-3,4 diepoxides,[4] we were interested in studying the photochemical behaviour of 1a.

Endoperoxide 1a was submitted to UV irradiation under various conditions. Five main products, which are produced concurrently in variable proportions, were always detected by v.p.c., or isolated by t.l.c. on silica gel. These are :

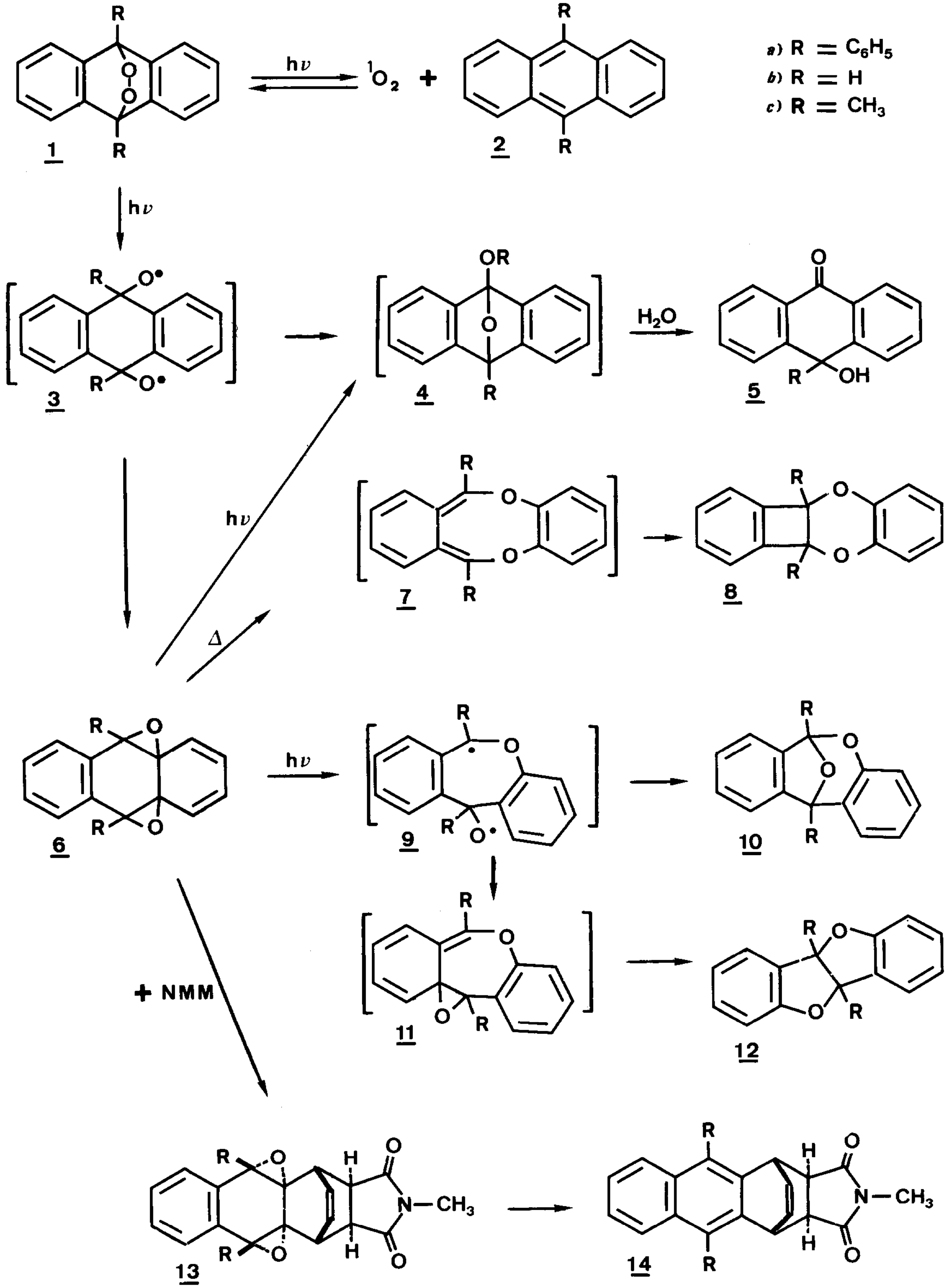
- 9,10-diphenylanthracene 2a, arising from photo-dissociation
- 10-hydroxy-10-phenylanthrone 5a, resulting from a degradation process,

and the following three isomers :

- 4*b*,10*a*-diphenyl-4*b*,10*a*-dihydro-benzo[3,4]cyclobuta[1,2-*b*]benzo[1,4]dioxan 8a, m.p. 166-167°C (CH_3OH) - N.M.R. (^1H), $\delta^{TMS}_{CDCl_3}$: 6.76(m,4H : $H_6H_7H_8H_9$), 7.34 (s,4H : $H_1H_2H_3H_4$), 6.80-7.18 (m,10H,phenyls) - UV (ether) λ_{max}nm(logε) : 272(3.60) ; 266(3.54) ; 261 (3.40) M/e (70ev.) : 362 (M^+).
- 6,11-diphenyl-6,11-dihydro-6,11-epoxydibenzo[*b*,*e*]oxepin 10a, m.p. 169-170°C (CH_3OH) - UV (ether) λ_{max}nm(logε) : 286(3.48) ; 279(3.49). previously obtained from the acid-catalyzed isomerization of 1a [5,6].
- 4*b*,9*b*-diphenyl-4*b*,9*b*-dihydro-benzofuro[3,2-*b*]benzofuran 12a , m.p. 199-200°C (C_2H_5OH) - N.M.R. (^{13}C) $\delta^{TMS}_{CDCl_3}$: 103.0ppm (only one kind of sp^3C) - UV (ether) λ_{max}nm(logε) : 282(3.85) - M/e (70 ev.) : 362 (M^+).

12a, resulting from the migration of both side-nucleus to oxygen, is the first example of this kind, not found up to now in the thermolysis or photolysis of anthracenic endoperoxides [7].

A wavelength effect on the distribution of these products was observed. It can be understood if one takes into account the following considerations :


a) R = C₆H₅
b) R = H
c) R = CH₃
1
2
3
4
5
6
7
8
9
10
11
12
13
14
hν
¹O₂ +
hν
hν
H₂O
Δ
hν
+ NMM
OR
OH
N—CH₃

- The three photoisomers, which exhibit a strong absorption in the same spectral region as photo-oxide 1a ($\lambda<310$ nm), can be further decomposed at different rates during the course of the irradiations (in particular at 253 nm). However 12a is the most photostable ; in contrast with the others, it is recovered nearly unchanged when submitted alone to irradiation with a high-pressure Hg lamp in a Pyrex vessel.

- The UV spectrum of photo-oxide 1a shows a weak tail absorption above 350 nm whose extinction coefficient is difficult to evaluate precisely owing to unavoidable traces of 2a. Extended irradiation in this region does induce photolysis of 1a under conditions where the resulting products are photostable.

It is clear from the accompanying Table (Runs 1, 2 and 3) that photodissociation is important only at short wavelengths, promoting, besides, isomer 12a, and to a lesser extent 10a. At long wavelengths isomerization to 8a predominates. Accordingly, conditions could be adjusted to prepare 12a (Run 4) and 8a (Run 5) in reasonable yields.

Table : Yields of detected or isolated photoproducts

	Conditions				Products (%)								
Run	Excitation (λnm)	Solvent	Temp. (°C)	Time (Hrs)	1a	2a	5a	8a	10a	12a	13a	Residu	
1	253,7 [a]	ether	20	2	5	40	i	i	5	15	-	30	f
2	> 280 [b]	ether	-70	18	14	2	3	i	15	48	-	18	
3	> 400 [c]	ether	20	30	23	2	2	60	i	5	-	8	
4	> 280 [d]	cyclohexane	20	4	10	3	32	11	10	25	-	8	h
5	> 350 [e]	benzene	20	33	14	2	15	50	i	i	-	18	
6	> 400 [d]	benzene	20	120	4	1	14	72	4	2	-	3	
7	> 400 [c]	benzene	20	27	6	1	4	1	1	6	59	22	

[a] Rayonet R-U-L.235,7 nm lamp ; [b] Osram X-O-B Xenon lamp - Pyrex filter ; [c] Osram X-O-B Xenon lamp - solid glass filter : Sovirel type VjV3 ; [d] water-cooled Philips SP 500 lamp - pyrex filter ; [e] Mazda halogen lamp 500 W ; [f] based on v.p.c. analysis ; [h] based on preparative t.l.c. ; [i] traces.

It was probable that 8a derived from the intermediate diepoxide 6a ; in fact, irradiation of 1a under conditions giving 8a (Run 6) in the presence of a large excess of *N*-methyl-maleimide (30 moles) (Run 7) led to an adduct (60%), $C_{31}H_{23}O_4N$, F_{inst} 317-318°C

(EtOH), for which the steric structure 13a, analogous to the known 13b [3], could be deduced from the following spectral data ; NMR $\delta^{TMS}_{CDCl_3}$: 2.89 (s,3H,N-CH$_3$), 2.78 (m,2H,H$_1$,H$_4$), 6.13 (q,2H,H$_2$,H$_3$), 3.61 (t,2H,H$_{11}$,H$_{12}$) ; UV (ether) λ_{max}nm(logε) : 279(3.04), 272(3.04), 265(3.03), 259(3.00), 253(2.93).

Reduced in aqueous acetic acid by Zn and KI + NaOAc, 13a gives 14a, $C_{31}H_{23}O_2N$, F$_{inst}$ 285-286°C (AcOEt)- NMR $\delta^{TMS}_{CDCl_3}$: 2.88 (s,3H,N-CH$_3$), 4.50 (m,2H,H$_1$,H$_4$), 6.50 (q,2H,H$_2$,H$_3$), 3.03 (t,2H,H$_{11}$,H$_{12}$) ; UV (ether) λ_{max}nm(logε) ; 295(3.99),286(4.03) , which is identical with one of the two stereoisomeric adducts obtained by direct 1-4 addition of NMM on 2a, at 220°C in a sealed tube [8].

A closer insight into the mechanism could be obtained by irradiating a solution of photooxide 1a in the conditions of Run 3, but at -70°C, in order to stop at 6a. Simply warming up a fraction to room temperature afforded only 8a. When the warming up was preceded by a second irradiation at short wavelengths, a mixture was obtained containing only 10a and 12a. One can then infer that diepoxide 6a is formed first at long wavelengths, and that it rearranges thermally, through 7a, to 8a. At short wavelengths, it undergoes photoisomerizations leading to 10a and 12a possibly through intermediates 9a and 11a.

Moreover it is noteworthy that the wavelength effect, leading primarily to dissociation or homolysis, is in accord with the theoretical predictions made on the behaviour of excited states of endoperoxides [9].

REFERENCES and NOTES

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3) J. RIGAUDY, J. BARANNE-LAFONT, A. DEFOIN and NGUYEN KIM CUONG, C.R.Acad.Sci. Paris, 1975, 280, Série C, p. 527.
4) For various examples, see : J. RIGAUDY, Pure and Applied Chem., 1968, 16, p. 169.
5) J. RIGAUDY and C. BRELIERE, Bull. Soc. Chim. Fr., 1972, p. 1390.
6) An analogous bicyclic acetal has been found also during the photooxygenation of 7,12 - dimethyl-benz(a)anthracene. M.K. LOGANI, W.A. AUSTIN and R.E. DAVIES, Tetr. Letters, 1977 p. 2467.
7) Chemical evidence in complete agreement with the proposed structures have been obtained. They will be reported in a forthcoming paper.
8) For other examples of 1-4 additions of dienophiles on 9,10-diphenylanthracene, see : J. RIGAUDY and NGUYEN KIM CUONG, C.R.Acad.Sci. Paris, 1961, 253, p. 1705.
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