Photochemical Reactions of an αβ-Unsaturated Nitro Compound

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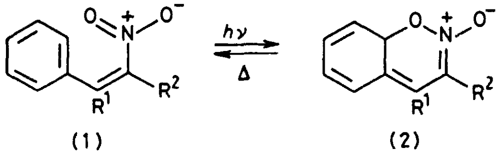
(*E*)-2-Nitro-1-(9-phenanthryl)prop-1-ene on irradiation in solution undergoes geometric isomerisation to the *Z*-isomer ($\phi_{E\rightarrow Z}$ 0.50), and also yields small amounts of phenanthrene-9-carbaldehyde. No other products are detected at low conversions to the *Z*-isomer. The *Z*-isomer behaves differently and yields 2-methylphenanthro-[9,10-*b*]furan and phenanthrene-9-carbaldehyde, the former being formed from an excited singlet state of the *Z*-isomer and the latter from an excited triplet state. Flash photolysis and low temperature n.m.r. studies demonstrate the presence of a photochromic transient formed from the *Z*-isomer and the probable structure of this transient is suggested.

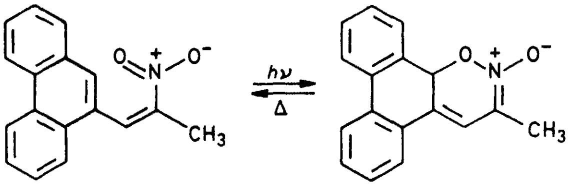
INTEREST in the photochemical reactions of αβ-unsaturated nitro compounds has resulted in the examination of their photochemical rearrangement reactions,[1-4] cycloaddition reactions,[5,6] and photogeometric isomerizations.[7] In addition, since some unsaturated nitro compounds exhibit photochromic properties, studies of the metastable intermediates formed on photolysis have also been initiated.[8]

Work carried out in these laboratories[9] has concentrated on two aspects of the photochemistry of αβ-unsaturated nitro compounds: (1) identification of postulated intermediates and, in particular, the electrocyclic ring closure products [*e.g.* (1) $\rightleftharpoons$ (2)] previously proposed[8] in the photochemistry of β-nitrostyrenes; and (2) the investigation of rates and quantum yields of the photochemical processes so as to identify trends in structure–reactivity relationships.



(1) (2)

R ,R = alkyl or aryl



(*Z*) - (3) (4)

The compound chosen for this present study was 2-nitro-1-(9-phenanthryl)prop-1-ene (3) since it was anticipated that the lower resonance stabilization energy of the 9,10-double bond would stabilize the phenanthrene analogue (4) of (2), relative to (2). Thus, the lifetime of (4) should be increased if (2) and (4) are indeed the structures of the photochromic intermediates and provided no new fast decay processes of (4) are present.

EXPERIMENTAL

Dioxan (B.D.H.) was purified by distilling twice. Cyclohexane (Koch–Light spectroscopic grade) was purified by passing twice through a silica column. Ethanol (Koch–Light spectroscopic grade) was distilled once before use. Chloroform (B.D.H. spectroscopic grade) was distilled once before use. Deuteriochloroform from Rivan Ltd. was used as received. 1-Bromohexane (Koch–Light) was distilled once before use. Camphorquinone (Aldrich), m.p. 198 °C, was recrystallized once from spectroscopic hexane. N.m.r. spectra were obtained using a Varian HA 100 instrument (except for the low temperature experiments, see later) and mass spectra were obtained using an A.E.I. MS12 instrument.

Syntheses.—(E)-2-*Nitro*-1-(9-*phenanthryl*)*prop*-1-*ene* (E)-(3). Phenanthrene-9-carbaldehyde (5), m.p. 99—101 °C, was prepared from 9-bromophenanthrene (Aldrich) by the method of Dornfield and Coleman[10] and recrystallized from ethanol. The aldehyde (5.0 g), nitroethane (1.75 g), and n-butylamine (0.1 ml) were stirred in dioxan (5 ml) at 40 °C for 20 h. The product (36%) was precipitated by the addition of a few drops of water and recrystallized from ethanol, m.p. 119—121 °C (lit.,[11] 120—121 °C); $\nu_{\text{max.}}$ (Nujol) 1 520 cm^{-1} ($C-NO_2$); *m/e* 263 (M^+) and 217 ($M - NO_2$, 100%); $\lambda_{\text{max.}}$(ethanol) ($\varepsilon \times 10^{-4}$) 214 (2.3), 253 (5.0), and 345 nm (0.79); δ(100 MHz; $CDCl_3$) 2.38 (d, *J* 0.9 Hz, CH_3) and 7.5 and 8.5 (m, aromatic and olefinic H). Decoupling experiments revealed protons at δ 8.46 (olefinic) and 7.49 (10-H). Pascual's formula, using Descates values[12] for the shielding effects of *cis*- and *trans*-nitro groups, gave calculated values for the position of the olefinic proton of δ 8.1 and 6.8 for the *Z*- and *E*-isomers, respectively.

2-*Methylphenanthro*[9,10-b]*furan* (8).—The literature method[13] for this synthesis was scant in detail and was modified somewhat. Phenanthraquinone (1.5 g), acetone

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[6] D. B. Miller, P. W. Flanagan, and H. Shechter, *J. Amer. Chem. Soc.*, 1972, **94**, 3912.

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[12] G. Descates, Y. Bahurel, M. Bourillot, and G. Pingeon, *Bull. Soc. chim. France*, 1970, 282.

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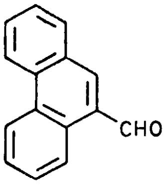
(1.8 g), and ammonia (*d* 0.88; 1.2 ml) were stirred together in a stoppered flask for 20 min. An off-white solid was deposited (1.9 g, 98%). Japp believed this compound to be an imide. However, it is almost certainly the imine (6), m.p. 143—145° (decomp.) (lit.,[13] 144 °C); $\nu_{max.}$ (Nujol) 3 450 (O–H), 1 700 (C=N), and 1 650 cm^{-1} (C=O stretch); δ(CDCl$_3$) 1.90 (s, CH$_3$), 2.15 (m), 2.55br (=NH), and 2.80 (OH); *m/e* 265 (M^+) and 42 (100%). The imine (1.9 g), suspended in water (10 ml), was added slowly to oxalic acid (2.7 g) in water (25 ml) with stirring. After standing for 24 h a semi-crystalline solid was deposited and recrystallization from diethyl ether gave (7) (1.0 g, 52%), m.p. 86—88 °C (lit.,[13] 89 °C); *m/e* 266 (M^+) and 43 (100%). The final reductive cyclization step using Zn–AcOH caused some difficulties and the following method, although giving only poor yields, was the best that could be achieved. The hydroxydione (7) (0.8 g) was dissolved in glacial acetic acid (5 ml) and zinc dust (0.5 g) was added over four days. The mixture was then poured into water and extracted with ether. This residue was applied to a neutral alumina t.l.c. plate. Elution with toluene produced first a blue fluorescent band which was subsequently extracted with ether. Recrystallization of the solid obtained in this way from ethanol gave the furan (0.15 g), m.p. 120—121 °C (lit.,[13] 121 °C); $\lambda_{max.}$(ethanol) (ε × 10^{-4}) 241 (3.6), 251 (5.1), 258 (6.4), 282 (1.56), 297 (1.1), and 310 nm (1.2); δ (100 MHz; CDCl$_3$) 2.50 (d, *J* 1.5 Hz, CH$_3$), 6.77 (m, collapses to s when decoupled from CH$_3$ 3-H), 7.5, 8.0, 8.25, and 8.60 (m, aromatic H).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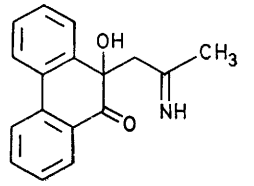
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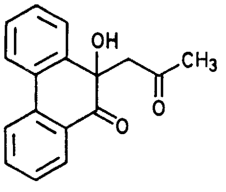
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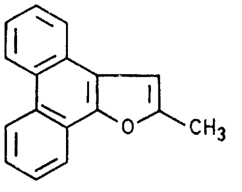
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(Z)-2-*Nitro*-1-(9-*phenanthryl*)*prop*-1-*ene* (Z)-(3). The *E*-isomer (*E*)-(3) (25 mg) dissolved in chloroform (5 ml) was irradiated with a medium pressure mercury lamp and a Corning filter (No. 7380, transmits above 355 nm) so that only the long wavelength tail could absorb. The progress of the photolysis was monitored by u.v. absorption spectroscopy and by t.l.c. (neutral alumina) and when a reasonable conversion into the *Z*-isomer was achieved (but before the build up of other products, see later) the reaction was stopped. After removal of most of the solvent the residue was applied to a preparative alumina t.l.c. plate. Apart from the *E*-isomer (5 mg) and small amounts of other products described later the *Z*-isomer (10 mg) was obtained and recrystallized from ethanol, m.p. 119—121 °C; *m/e* 263 (M^+) and general fragmentation pattern similar to that of the *E*-isomer; $\lambda_{max.}$ (ε × 10^3) 296 (8.95) and 340sh nm (2.6); δ 1.53 (s, CH$_3$) and 7.6 and 8.7 (m, aromatic and olefinic H).

Photolyses.—Preparative photolysis. An immersion system utilising a 450 W medium pressure mercury lamp and a Pyrex immersion well was employed. Oxygen was removed from the solution by purging with nitrogen.

Quantitative photolysis and quantum yield determination. Method A. A cylindrical photolysis cell with optically flat windows (volume 3 ml; path length 1 cm) and facilities for freeze–pump–thaw degassing was mounted in a machined cell housing. The excitation source was a 200 W high pressure mercury arc lamp–high intensity Bausch and Lomb monochromator combination. The light output from the excitation source was continuously monitored by means of an R.C.A. 935 photodiode, as was the intensity of light transmitted by the photolysis cell. The photodiodes were calibrated in quanta min^{-1} μA^{-1} by reference to a potassium ferrioxalate actinometer.[14] Using photodiodes in this way avoids the need for frequent actinometry. Product formation was monitored by either u.v.–visible spectroscopy or by g.l.c. The latter technique was carried out using a 5 ft 5% OV 1 on Chromasorb G column run at 260 °C.

Method B. This method consisted of irradiating five Pyrex tubes, one containing potassium ferrioxalate solution (the ferrioxalate solution was used to monitor intensity changes and not to obtain quantum yields). The tubes were irradiated in a home-made roundabout apparatus which was enclosed in a steel drum. A window cut in the side of the drum could be fitted with a range of glass band pass or cut-off filters. A 450 W medium pressure mercury lamp was placed just outside the filter window. Product analysis was as before. The filters used in the above apparatus are shown below: (1) relative rates of product formation on irradiating (*E*)-(3), Corning cut-off filter (No. 7740); (2) relative yields of product formation in dioxan and 1-bromohexane, Corning filter 5860; (3) camphorquinone sensitization experiments, Corning cut-off filter 3387 (transmits above 460 nm).

Flash photolysis equipment. The instrument employed was home-made and will be described in detail in a later publication. The time resolution obtained to date is 20 μs. The cells used were either a 50 mm path length jacketed cell with thermal control from 5 to 65 °C (by means of circulating water) or a 100 mm path length cell for work at room temperature. Flash energies used were typically 50—112 J per flash and in order to obtain approximate quantum yield measurements under flash photolysis conditions, the outputs from the flash lamps were determined in quanta per flash using potassium ferrioxalate as the actinometer. The approximate absorption spectrum of the photochromic transient was obtained by point-by-point measurements.

Low Temperature N.m.r. of Transients.—Light from a 200 W high pressure short arc mercury lamp was focused onto a 45° quartz prism placed on a cradle of non-ferrous metal and Perspex which fitted directly into the cavity of the n.m.r. instrument (XL-100). A length of 4 mm diameter quartz rod was fitted into a standard n.m.r. tube (after the solution had been introduced) and held snugly in place by means of an O ring such that it was held below the surface of the solution and protruded from the top of the n.m.r. tube (by *ca.* 1 cm). Irradiating a solution of (*E*)-(3) in CDCl$_3$ resulted first in conversion into (*Z*)-(3) and subsequently the development of a new absorption at

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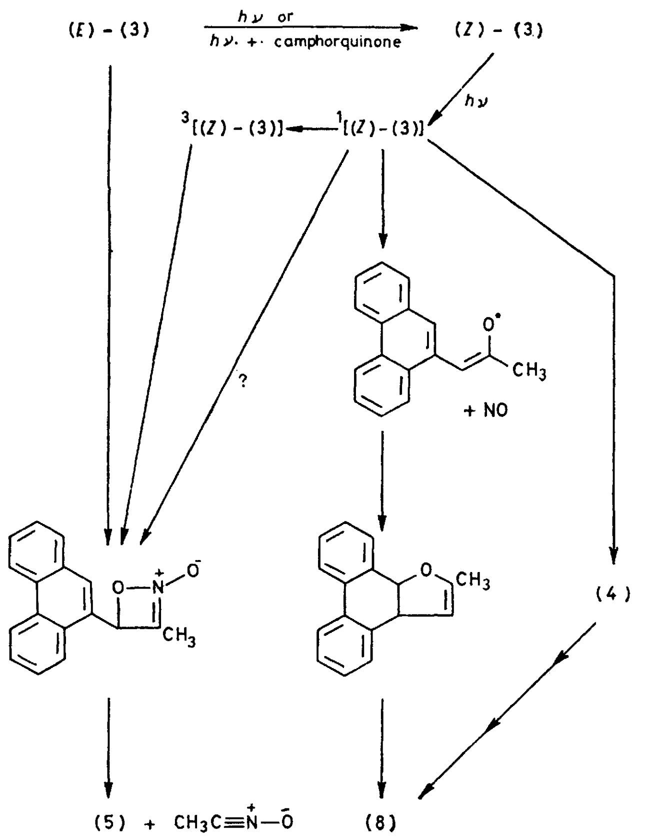
[14] C. A. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

δ 2.2 was observed. On formation of this new signal other changes in the spectrum were noted but since these occurred in the aromatic and olefinic proton regions it was difficult to make any analysis of them. On removal of the light the δ 2.2 signal slowly disappeared and simultaneously the methyl signal of (*Z*)-(3) (at δ 1.53) was observed. The rate of growth of the δ 1.53 signal was measured and taken to be the rate of thermal decay of the transient to (*Z*)-(3).



SCHEME

RESULTS AND DISCUSSION

The Scheme shows the structures of the photoproducts obtained on direct irradiation of either (*E*)- or (*Z*)-(3). The structure of the furan derivative (8) was indicated by its n.m.r. and mass spectrum and confirmed by independent synthesis.

The Figure gives an indication of the time dependence of product formation on irradiation of (*E*)-(3) in dioxan. Both (5) and (8) appear to be primary photoproducts of (3) as expected. However, since conversion of (*E*)- into (*Z*)-(3) would be considerable within 1 h, we cannot differentiate between the production of (5) and (8) from (*E*)- and (*Z*)-(3). (*Z*)-(3) was obtained by irradiation of the *E*-isomer which rapidly produced a mixture of the geometric isomers containing >96% of the *Z*-isomer. The mixture was further irradiated to give the product quantum yields from (*Z*)-(3). Table 1 also contains the product chemical yields on prolonged irradiation based on g.l.c. analysis of three experiments. Isolated yields for one experiment are given in the Experimental section.

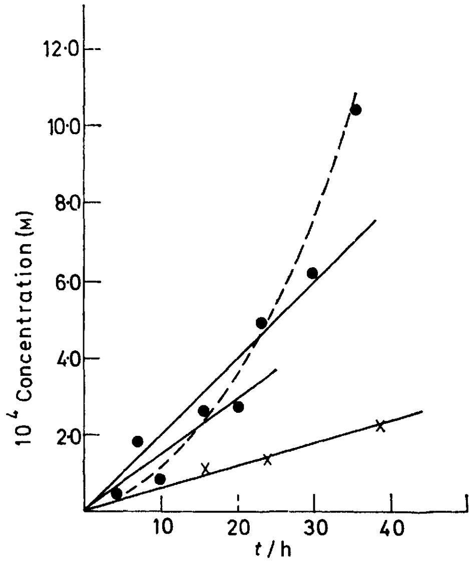
Both heavy atom solvent and triplet sensitization experiments were carried out in order to obtain information about the multiplicities of the states from which the reactions occurred. Irradiation of 1-bromohexane solutions of (*E*)-(1) in the roundabout apparatus (Method B) at the same time as dioxan solutions gave the results shown below. For the same irradiation periods [20% loss of (*E*)- and (*Z*)-(3)] the 1-bromohexane solution gave the aldehyde (5) (ϕ *ca.* 5×10^{-4}) but no furan (8). The dioxan solutions gave aldehyde and furan in the same ratio obtained in the quantum yield determination experiments. These observations indicate that the aldehyde is formed from a triplet state of (*E*)- and (*Z*)-(3) and the furan is a singlet state derived product. The low quantum yield of the aldehyde in the heavy atom solvent is not entirely unexpected, since although the heavy atom effect will induce S_1–T_n intersystem-crossing it will also induce T_1–S_0 intersystem-crossing.

TABLE 1

Quantum yields of product on irradiation of (*E*)- and (*Z*)-(3) in dioxan (obtained by Method A, see text)

	Products			
	E-(3)	(*Z*)-(3)	(5)	(8)
Z-(3)	$<10^{-3}$		7.0×10^{-3} (25%)	2.0×10^{-3} (4%)
(*E*)-(3)		0.50	4.0×10^{-3}	$<10^{-3}$

Selecting a triplet sensitizer for use with (*E*)- or (*Z*)-(3) proved difficult because of their extensive absorption over a wide wavelength range. Finally camphorquinone (E_T 210 kJ mol^{-1}) was selected but because of the presence of photochemical reactions resulting in the slow degradation of camphorquinone and the formation of a number of new products (which interfered with g.l.c. analysis) only very low conversions, with resulting inaccuracies, were possible. Under these conditions and running a number of experiments, while the aldehyde was produced with a chemical yield of



Time dependence of product formation on irradiation of 10^{-2}M-(*E*)-(3) in dioxan: aldehyde (5) ●; furan (8) ×

5.0% no furan was detected. The sensitization experiment therefore confirms the conclusions reached from the heavy atom solvent experiments. It should be noted that we have no evidence which allows us to exclude the possibility that the aldehyde (5) is formed both from the singlet and triplet states on direct irradiation.

Both direct irradiation and camphorquinone sensitization of (*E*)-(3) lead to the efficient formation of the *Z*-isomer (ϕ 0.50), so that in studying the photochemistry of (*E*)-(1) it is very difficult to be sure that any photoproduct is derived from (*E*)- and not from (*Z*)-(3). In contrast, (*Z*)-(3) does not photoisomerize to (*E*)-(3). This indicates that in addition to producing the furan (8) and the aldehyde (5), the excited state(s) of (*Z*)-(3) must undergo some very efficient non-radiative process.

The nature of this non-radiative process was indicated by the detection of a strongly absorbing transient on flash photolysis of (*Z*)-(3) ($\lambda_{max.}$ 405 nm). This transient was not seen on initial flash photolysis of (*E*)-(3) [on repeated flashing, conversion of (*E*)- to (*Z*)-(3) gave rise to the transient absorption]. By analogy with an earlier suggestion [8] for the structure of transients of β-nitrostyrenes [*i.e.* (1) $\rightleftharpoons$ (2)], the transient was tentatively assigned structure (4). The very long lifetimes observed for (4) are in line with our expectations (Table 2). Measurements of the lifetime at a series of temperatures from 0 to 50 °C allowed the activation energies of the first-order thermal decay to be obtained (Table 2).

TABLE 2

Lifetimes of the photochromic transient from (*Z*)-(3) as a function of solvent and first-order activation energies for the thermal decay (obtained over the temperature range 0—60 °C)

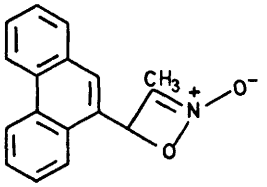
Solvent	τ/s (30 °C)	E_a/kJ mol^{-1}
Cyclohexane	12.9	73
Chloroform	7.1	67
Ethanol	6.1	37

Cf. τ for 1-nitro-2-phenylprop-1-ene (cyclohexane; 15 °C) = 2×10^{-5} s.[8]

The very long lifetime of the transient indicated the possibility of determining its n.m.r. spectrum at low temperatures. Irradiation of a $CDCl_3$ solution of (*E*)-(3) in the cavity of a 100 MHz n.m.r. spectrometer held at −20 °C did indeed provide some information. At first the methyl protons of (*E*)-(3) were observed to decrease with simultaneous increase in the methyl protons due to the *Z*-isomer. On further irradiation a new peak appeared at δ 2.2. This we attribute to the transient having the absorption obtained by flash photolysis, on the grounds that the rate of reformation of (*Z*)-(3) in the n.m.r. experiment on removal of the light source (1 120 s) is within experimental error of the lifetime of the transient (at −20 °C) obtained from flash photolysis data (1 050 s), using an activation energy of 67 kJ mol^{-1}.

An unambiguous assignment of the structure of the transient is more difficult. The n.m.r. spectrum of the irradiated mixture shows only one absorption for the transient which is distinct from the (*Z*)- and (*E*)-(3) absorptions. This is the peak at δ 2.2 and is what might be expected if the structure of the transient is (4). However in making an assignment of the δ 2.2 signal two difficulties arise. No realistic model compounds are available in the literature for a comparison of the n.m.r. signals and since shifts in the signals occur with temperature changes, even if model compound data were available, comparisons would be difficult. The only other structure which may be considered is that of the 1,2-oxazetidine 2-oxide (9). Such intermediates have been suggested as the precursors to aromatic aldehyde formation in the photolysis of β-nitrostyrene derivatives.[2]

The u.v.–visible absorption data allow us to eliminate this possibility, since the longest wavelength band for compound (10) [15] is at 222 nm (ε 7.4×10^{-3}), a much lower wavelength than the $\lambda_{max.}$ observed for the transient (no conjugative effect due to the phenanthrene ring is expected). Furthermore, there seems to be no reason why (9) should be formed more easily from (*Z*)- than from (*E*)-(3).



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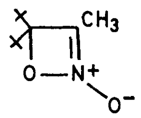

(10)

The aldehyde may well be formed *via* the intermediate (9) as previously shown for similar systems. However attempts to trap out $CH_3C{\equiv}N^+{-}O^-$ [produced as the other fragment on decomposition of (9)], using cyclopentene, failed.

The furan (8) may be formed in two ways (see Scheme). However, the nitro–nitrite route seems unlikely on the grounds that the nitro–nitrite rearrangement in β-nitrostyrenes has been seen to occur from both *Z*- and *E*-isomers. We therefore favour a route which involves the photochromic transient as an intermediate. Experiments designed to investigate the nature of the formation of (8) from (4) are in progress.

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