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PHOTO-OXIDATION OF N-METHYL-2-(p-NITROPHENYL)-1,2-DIHYDRO-3,1-BENZOXAZIN-4-ONE.

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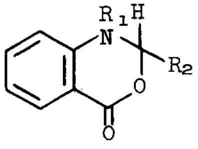
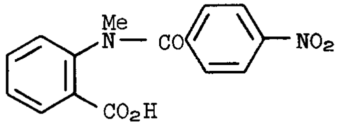
The photoaddition of oxygen to organic molecules is a well documented reaction (1,2a) but the title compounds do not appear to have been studied in this connection.

Irradiation (3) of a benzene solution of the oxazinone (Ia) (4) in aerated solutions gave a product, m.p. 213-6° (ex-acetone) for which structure (II) is assigned on the basis of its elemental analysis, molecular weight (mass spectrometer), infrared and n.m.r. spectra. Conclusive proof of structure (II) was furnished by comparing the photoproduct with an authentic sample obtained by the Schotten-Baumann reaction of N-methylanthranilic acid and p-nitrobenzoyl chloride. Compound (II) reacted with ethereal diazomethane to give a methyl ester, m.p. 121-2°.



(I)

	R_1	R_2
(a)	Me	p-$NO_2C_6H_4$
(b)	Me	Ph
(c)	Ph	p-$NO_2C_6H_4$
(d)	Me	2′-pyridyl
(e)	Me	m-$NO_2C_6H_4$
(f)	Me	o-$NO_2C_6H_4$



(II)

The yield of the photoproduct was increased when oxygen was bubbled through the solution and a solvent of 10% acetone in benzene was employed. No product could be detected when nitrogen gas was substituted for oxygen nor when oxygen was bubbled through a solution of (Ia) in refluxing benzene in the dark.

Other benzoxazinones, namely (Ib-d) were unsuccessfully irradiated in the hope of extending the photochemical reaction. This result is rather surprising

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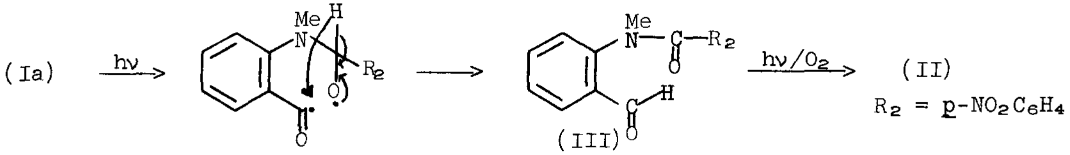
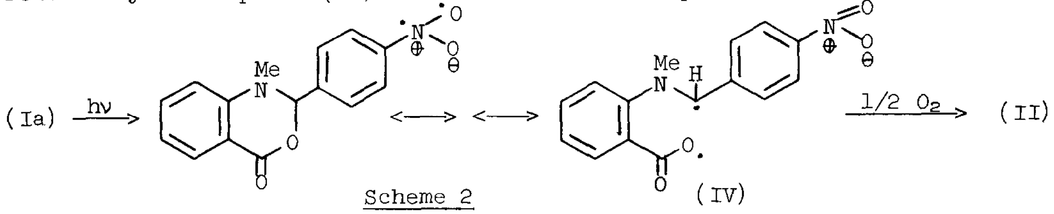
since all the compounds studied have very similar ultraviolet absorption spectra viz. bands at ca. 350 and 250 nm, the former showing solvent shifts characteristic of π→π* transitions (5). Compound (Ic) has additional conjugation due to the N-phenyl group which does not allow strict comparison with (Ia, b and d). In the ground state of benzoxazinone (Ia), C_2 is expected to be more electron deficient than in the case of (Ib) but this does not account for the reactivity of (Ia) since on this basis the unreactive compound (Id) should behave like (Ia).

A possible mechanism for the photoreaction of compound (Ia) is proposed in Scheme 1. Autoxidation of compound (III) is analogous to that of benzaldehyde (6) and should occur with high efficiency. However, all attempts to isolate, detect or, indeed, thermally prepare the aldehyde (III) have so far been unsuccessful.



Scheme I

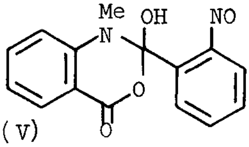
A second mechanism is presented in Scheme 2 which allows for the unique reactivity of compound (Ia) in this series of compounds. The electronic excitation of the nitro group invisaged is formally analogous to the n→π* transition of the carbonyl chromophore (2b,c). If Scheme 2 is operating then the benzoxazinone (If) would be expected to react photochemically in a similar manner to (Ia). Compound (Ie), however, cannot rearrange to a diradical similar to (IV) upon excitation and should not yield a product analogous to (II).



Scheme 2

Irradiation (3) of benzoxazinone (Ie) in benzene or acetone-benzene (10%, v/v) solvent in the presence of oxygen gave a small quantity of a 10-component oil which has as yet proved inseparable. The m-nitro isomer of compound (II) could not be detected in this mixture.

Compound (If) upon irradiation (3) in oxygen- and nitrogen-saturated solutions gave a product in high yield for which structure (V) is proposed on



(V)

the basis of the following evidence. The product is a colorless solid at room temperature whereas its melt or solutions are green indicative of a C-nitroso compound. This was confirmed by diagnostic chemical tests (7). Elemental analysis and molecular weight (mass spectrometer) are consistent with an isomer of (If). The infrared spectrum (nujol mull) of the product has broad OH absorption in the region 3100-3200 cm.$^{-1}$ and a strong carbonyl band at 1725 cm.$^{-1}$ [cf. 1720 cm.$^{-1}$ for (If)]. An n.m.r. spectrum [$(CD_3)_2CO$] contains a 9H multiplet at τ 2.8-3.5, 8 aromatic and an OH proton and three singlets at τ 6.50 (2H), τ 6.65 (0.35H) and τ 6.84 (0.65H) attributable to an N-Me group. The N-Me group proton signals suggest an isomer mixture. Finally, $\lambda_{max.}^{EtOH}$ are at 282.5 nm (6300 l. mole^{-1} cm.$^{-1}$), 310 nm (5020 l. mole^{-1} cm.$^{-1}$) and a shoulder at 348 nm (1420 l. mole^{-1} cm.$^{-1}$) [cf. nitrosobenzene (8) 282 nm (7200 l. mole^{-1} cm.$^{-1}$), ca. 310 nm (4000 l. mole^{-1} cm.$^{-1}$); (If) 347 nm (3150 l. mole^{-1} cm.$^{-1}$)].

There are many examples in the literature of the nitro group reaction of which the photoreaction of compound (If) is typical (see ref. 2c for review). The reaction is presumed to involve $n\rightarrow\pi^*$ excitation of the nitro group to give a triplet state in which an oxygen atom is somewhat like that in the $^3(n,\pi^*)$ state of a carbonyl group. It, therefore, seems probable that the nitro group in compound (Ia) could also be excited to a $^3(n,\pi^*)$ state which lends support to the mechanism outlined in Scheme 2. Hydrogen abstraction is obviously more efficient in benzoxazinone (If), than rearrangement to a diradical intermediate similar to (IV), and is sterically hindered in (Ie).

Other compounds which contain the 2-(p-nitrophenyl)-3,1-oxaza grouping are unstable in light (9) and this reaction is being investigated further.

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References

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2. D. C. Neckers, Mechanistic Organic Photochemistry, Reinhold Publishing Corporation, New York, (1967), (a) p. 148; (b) p. 184; (c) p. 207.
3. A Hanovia 100 w. medium pressure mercury vapour lamp was used in conjunction with a borosilicate glass (Pyrex) filter. Irradiation times of 3-8 hrs. were employed.
4. All the benzoxazinones (Ia-f) were prepared by the condensation of the appropriate N-substituted anthranilic acid and the appropriate aryl aldehyde.
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9. This work was prompted by the observation of Drs. T. A. Crabb and R. O. Williams that one of this class of compounds darkened in colour upon standing on the open bench.