Photochemical Studies on 9-Nitroanthracene[1]

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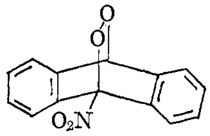
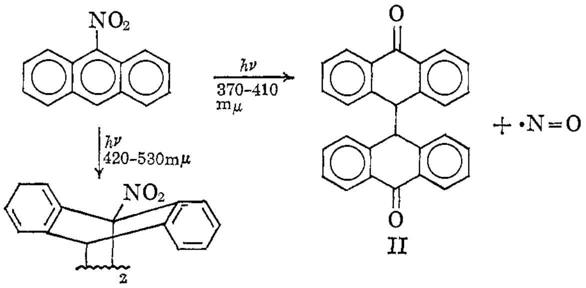
Abstract: Irradiation of 9-nitroanthracene in acetone solution gives, in addition to previously described products, anthraquinone and anthraquinone monoxime. A mechanistic scheme is presented which relates the formation of these products to certain other photoisomerizations of nitro olefins. Anthraquinone is formed from anthraquinone monoxime on irradiation in the presence of nitrogen(II) oxide. This novel transformation probably proceeds by way of the iminoxyl radical. Ceric ammonium nitrate oxidation of anthraquinone monoxime gives the iminoxyl radical which has been characterized by esr spectroscopy. The relationship of the photochemical isomerization of aryl and vinyl nitro compounds to aryl and vinyl nitrites to a related rearrangement which occurs on electron impact induced ionization is discussed.

Early studies of the photochemistry of 9-nitroanthracene were concerned with photooxidation. The products isolated from the photooxidation were anthraquinone[2,3] and 10-nitroanthrone.[2] Dufraisse suggested that the 9,10-epidioxide (I) might be an intermediate in the formation of anthraquinone.[2] Greene reported in 1960 that photoproducts from 9-nitroanthracene in the absence of oxygen depended on the wavelength of light used.[4] Light of wavelength 370–410 $m\mu$ gave 10,10′-bianthrone (II) and nitrogen(II) oxide.[4] Longer wavelength (420–539 $m\mu$) light gave in addition a dimer (III) of 9-nitroanthracene.[4]



I

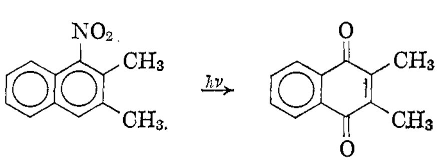


II

III

Studies of quantum yield of disappearance for a series of 9-substituted anthracenes showed that 9-nitroanthracene disappeared with surprisingly high efficiency for a negatively substituted anthracene.[5] No secure conclusions can be drawn from these studies since product studies were not made. It was assumed that all 9-substituted anthracenes react by dimerization and oxidation (to the 9,10-epidioxide).

In the course of an investigation of the photochemistry of 1-nitro-2,3-dimethylnaphthalene (IV) it was observed that one of the many products was 2,3-dimethyl-1,4-naphthoquinone (V).[6] Furthermore, this product was formed in the absence of oxygen; *i.e.*, some novel mechanism must be available for conversion of IV to V. The complexity of the product mixture from IV suggested that more detailed studies should be carried out on another system. It seemed probable that a large number of by-products from IV were derived from attack on the methyl group adjacent to the nitro group. This probability and the results of earlier studies suggested that 9-nitroanthracene was a reasonable selection for detailed study.



IV V

Results

Irradiations of 9-nitroanthracene were carried out in acetone solution, unless otherwise specified, with a mercury arc lamp. The lamp emission passed through Pyrex (~6 mm) but was otherwise unfiltered. All reaction mixtures were chromatographed on silica gel columns under standard conditions. All yields are based on recrystallized products with satisfactory melting point and spectroscopic properties.

Careful scrutiny of the products of irradiation of 9-nitroanthracene in the absence of oxygen under a variety of conditions showed that anthraquinone was in fact formed together with 10,10′-bianthrone. Mechanistic speculations (see Discussion) suggested that anthraquinone monoxime should be an intermediate in the formation of anthraquinone from 9-nitroanthracene. Under controlled conditions it was possible to obtain anthraquinone monoxime in yields up to 26% together with anthraquinone and 10,10′-bianthrone from irradiations in acetone solution. It seemed probable that anthraquinone monoxime was formed *via* 9-nitrosoanthrone by combination of nitrogen(II) oxide and 9-anthryloxy radicals. This would imply that addition

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[1] Photochemical Transformations, part XVII. Portions of this research were described at the Symposium on Organic Photochemistry, Strasbourg, France, July 20–24, 1964. The authors are indebted to Professor R. Campbell for informing us of his results in this area prior to publication.

[2] C. Dufraisse and R. Priou, *Compt. Rend.*, 212, 906 (1941).

[3] M. Battegay, P. Brandt, and J. Moritz, *Bull. Soc. Chim. France*, 31, 915 (1922).

[4] F. Greene, *ibid.*, 1356 (1960).

[5] T. Vember, L. A. Kiyanskaya, and A. S. Cherkasov, *J. Gen. Chem. USSR*, 33, 2281 (1963); *Zh. Obshch. Khim.*, 33, 2342 (1963).

[6] O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *J. Pure Appl. Chem.*, 9, 585 (1964).

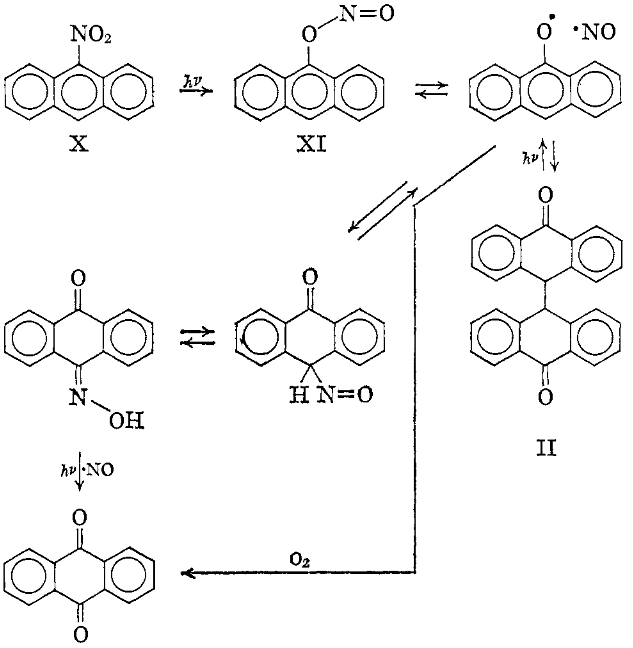
of nitrogen(II) oxide to the irradiation solution should increase the yield of anthraquinone monoxime and thus of anthraquinone. When solutions of 9-nitroanthracene were irradiated while nitrogen(II) oxide was bubbled through the solution, anthraquinone (55–77% yield) was the major product. Small amounts of 10,10'-bianthrone were isolated, but no anthraquinone monoxime was isolated. It should also be possible to sweep out nitrogen(II) oxide with an inert gas and thus increase the yield of 10,10'-bianthrone which formally is a dimer of the 9-anthryloxy radical. High sweep rates did increase the yield of 10,10'-bianthrone to 81%. The yield of 10,10'-bianthrone was affected also by solvent. In carbon tetrachloride, in which 10,10'-bianthrone is less soluble than it is in acetone, the irradiation of 9-nitroanthracene gives high yields (86%) of 10,10'-bianthrone and small amounts (6%) of anthraquinone. Experiments in which oxygen was passed through acetone solutions of 9-nitroanthracene during irradiation confirmed earlier reports[2,3] that anthraquinone (88%) was the major product in the presence of oxygen. Irradiation of 10,10'-bianthrone under identical conditions also gives high yields of anthraquinone (72%). Isolation of anthraquinone monoxime suggested that it probably was a precursor of anthraquinone. Indeed it has been reported that irradiation of anthraquinone monoxime gives anthraquinone.[7] Irradiation of anthraquinone monoxime in acetone using the same lamp employed for the 9-nitroanthracene gave anthraquinone, but the rate of conversion was much too slow to account for this transformation in the irradiation of 9-nitroanthracene. In an attempt to reproduce as nearly as possible the conditions prevailing in the irradiation of 9-nitroanthracene, nitrogen(II) oxide was added to a solution of anthraquinone monoxime in acetone during irradiation. Under these conditions anthraquinone monoxime was converted rapidly in high yield (83%) to anthraquinone. Subsequently, it was shown that the conversion of ketoximes to ketones by irradiation in acetone solution containing nitrogen(II) oxide is a general process.[8]

Discussion

It is not a simple matter to discuss excitation of 9-nitroanthracene. The absorption spectrum is complex and irradiation in the 300–400-mμ region probably populates both n,π* and π,π* states.[9] It has been suggested by Yang[10] that the dependence of photoproducts from 9-nitroanthracene noted by Greene[4] may be due to reaction *via* upper and lower excited states of 9-nitroanthracene. The upper state would give rise to the processes described in this report, and the lower state would lead to the 9-nitroanthracene dimer.[10] This explanation would be exactly analogous to that suggested by Yang[10] for competing oxetane formation and dimerization of anthracene-9-carboxaldehyde. It is not known whether the 9-nitroanthracene dimer is stable to the shorter wavelength light. The absence of the dimer in the irradiations using shorter wavelength light could be due to rapid decomposition of dimer to other products at these wavelengths. No dimer was observed in our studies. It seems quite reasonable that the nitro to nitrite rearrangement (see below) arises from an n,π* excited state. Spectroscopic studies[11] which show a generally high intersystem crossing efficiency for nitroaromatics and the fact that 9-nitroanthracene does not fluoresce[5] make it likely that crossover from the excited singlet manifold to the excited triplet manifold occurs with reasonably high efficiency. The experimental information does not provide a basis for a decision concerning the multiplicity of the reactive state of 9-nitroanthracene. Studies in this area are in progress.

Most of the irradiations in this study were carried out in acetone. This selection was made because the reactions in acetone gave less tar-like by-products. Acetone, of course, could function as a photosensitizer. It may actually function in this capacity, but this is not a requirement since the reactions do go in other solvents.

The known facts concerning the photochemistry of 9-nitroanthracene are correlated by the following mechanistic scheme. This scheme provides the basis for the discussion which follows.



Three rearrangements which resemble that of 9-nitroanthracene are known. The conversion of 1-nitro-2,3-dimethylnaphthalene has been mentioned. The other analogs involve isomerization of nitro olefins. Irradiation of β-methyl-β-nitrostyrene (VI) in acetone rapidly equilibrates the *cis* and *trans* isomers and leads ultimately to 1-phenyl-1-oximino-2-propanone (VII).[12] Similar irradiation of 6-nitro-$\Delta^{3,5}$-cholestadiene (VIII) in acetone gives 3-oximino-6-oxo-Δ^4-cholestene (IX).[12] In each case it is reasonable to invoke a C=C—NO₂ to C=C—O—N=O rearrangement (X → XI). The rearrangement, however, is

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(7) J. Meisenheimer, *Ann.*, 323, 205 (1902).

(8) O. L. Chapman and D. C. Heckert, unpublished observations.

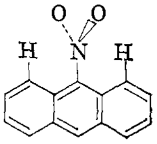
(9) For a discussion of the excitation of nitrocompounds see H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 182 ff.

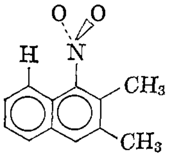
(10) N. C. Yang, *J. Pure Appl. Chem.*, 9, 591 (1964); N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964).

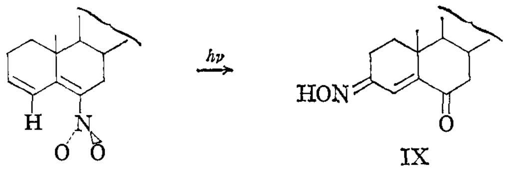
(11) M. Kasha, *Radiation Res. Suppl.*, 2, 243 (1960).

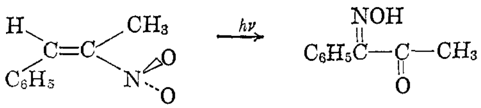
(12) O. L. Chapman, P. G. Cleveland, and E. D. Hoganson, *Chem. Commun.*, 101 (1966).

not general. Nitrobenzene, for example, is stable to the conditions used to convert 9-nitroanthracene to anthraquinone and 10,10′-bianthrone. The feature which each of the four compounds which undergo the rearrangement have in common is an arrangement of atoms which keeps the plane of the nitro group out of the plane of the adjacent aromatic ring or double bond.

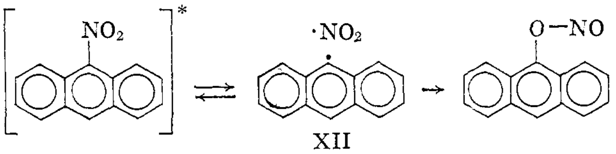



IV

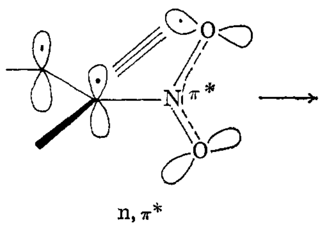

VIII IX

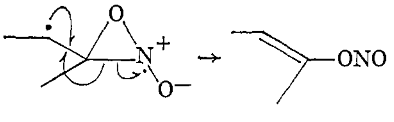

VI VII

In 9-nitroanthracene this is achieved by two *peri*-hydrogens, in 1-nitro-2,3-dimethylnaphthalene (IV) by a *peri*-hydrogen and an *o*-methyl group, in 6-nitro-$\Delta^{3,5}$-cholestadiene (VIII) by the C-4 hydrogen and in β-methyl-β-nitrostyrene we assume rearrangement proceeds *via* the isomer in which nitro and phenyl groups are *cis* (VI). Two types of mechanism may be considered for the nitro to nitrite rearrangement, a dissociation–recombination mechanism and an intramolecular rearrangement mechanism. In the dissociation–recombination mechanism the C–N bond would cleave in the excited 9-nitroanthracene giving a 9-anthryl radical XII and nitrogen(IV) dioxide. Recombination on the oxygen atom of the nitrogen(IV) dioxide would give the nitrite.


XII

Such a mechanism has been invoked in the photochemistry of nitromethane[13,14] and nitroethane.[14] Some fraction of the 9-anthryl radicals and nitrogen(IV) dioxide molecules which would be formed by dissociation should diffuse apart, and products derived from these species should be isolated. Specifically, anthracene and nitrogen(IV) dioxide should be found among the products. These products were not found in the irradiation mixtures. The intramolecular mechanism for the nitro to nitrite rearrangement is most conveniently described in terms of an n,π* excited state of the 9-nitroanthracene. Since the plane of the nitro group is almost at right angles (85° in the crystal[15]) to the plane of the anthracene ring, the nitro group may be regarded as essentially nonconjugated. A very crude valence-bond description of the n,π* excited 9-nitroanthracene is shown (XIII). The key feature of the excited state is the overlap of the half-vacant nonbonding orbital of the nitro group (which is essentially a p atomic orbital of oxygen)[16] with the adjacent orbital of the aromatic ring. This overlap, which is a result of the out-of-plane nitro group, leads to formation of an oxaziridine ring XIV which collapses to the nitrite.[17]


n, π*
XIII


XIV

The mass spectrum (70 ev) of 9-nitroanthracene shows an intense peak at *m/e* 193 (M − 30). This behavior is characteristic of aromatic compounds[18] but not aliphatic nitro compounds (which tend to lose HNO_2).[19] The M − 30 peak in the mass spectra of aromatic nitro compounds is due to loss of NO and is considered to be a result of the rearrangement of the nitroaryl cation radical to the aryl nitrite cation radical followed by elimination of nitrogen(II) oxide.[18]

$$ArNO_2 \xrightarrow[\text{impact}]{\text{electron}} [ArNO_2]\cdot^+ \longrightarrow [ArON{=}O]\cdot^+ \longrightarrow [ArO]^+ + \cdot NO$$

As the ionizing voltage is lowered, the M − 30 ion in the mass spectrum of 9-nitroanthracene increases in intensity until it becomes the most intense fragment ion.[20] Below 19 ev the M − 30 ion is virtually the only fragment ion observed. Observation of the rearrangement at very low ionizing voltages suggests that it can be initiated by the lowest energy ionization of 9-nitroanthracene. The lowest energy ionization presumably involves removal of an electron from the antisymmetric nonbonding orbital of the nitro group. The species thus produced is like an n,π* excited state in that it has a half-vacant nonbonding orbital but differs in that there is no electron in the antibonding (π*) orbital. The rearrangement which occurs in the mass spectrometer can be expressed in the same fashion as the intramolecular mechanism for the photochemical isomerization. At the low pressures used in mass spectrometry, dissociation–

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[13] H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, 29, 883 (1958).

[14] R. E. Rebbert and W. Slagg, *Bull. Soc. Chim. Belges*, 71, 709 (1962).

[15] J. Trotter, *Acta Cryst.*, 12, 237 (1959).

[16] Actually, the two nonbonding p atomic orbitals combine to give symmetric (n_s) and antisymmetric (n_a) nonbonding molecular orbitals.[9] The p orbital representation is used for convenience.

[17] Oxaziridines have been isolated from irradiations of nitrones; see, for example, J. S. Splitter and M. Calvin, *J. Org. Chem.*, 30, 3427 (1965), and references cited therein.

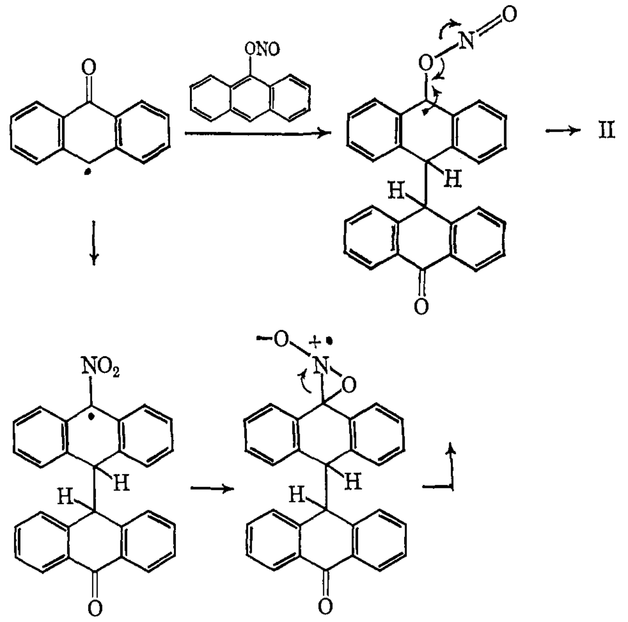
[18] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Ind. Chim. Belge*, 311 (1964).

[19] R. T. Aplin, M. Fisher, D. Becker, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, 87, 4888 (1965).

[20] T. H. Kinstle and J. Stam, unpublished observations.

recombination mechanisms are not reasonable. The absence of products such as nitrogen(IV) dioxide and anthracene in the irradiation of 9-nitroanthracene together with the analogous nitro to nitrite rearrangement observed in the mass spectrometer suggest that the intramolecular mechanism is the most reasonable view of the rearrangement of 9-nitroanthracene to 9-anthryl nitrite.

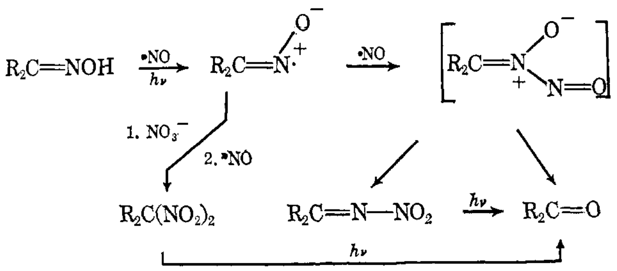
Cleavage of the 9-anthryl nitrite (XI) to the 9-anthryloxy radical and nitrogen(II) oxide is quite reasonable. Production of 10,10′-bianthrone from 9-anthryloxy radicals is demonstrated by formation of 10,10′-bianthrone in good yield in the potassium ferricyanide oxidation of 9-hydroxyanthracene anion. Formation of 10,10′-bianthrone may involve attack on 9-anthryl nitrite or 9-nitroanthracene by the 9-anthryloxy radical as well as dimerization of these radicals.



All attempts to prepare 9-anthryl nitrite from 9-hydroxyanthracene and nitrosyl chloride gave 10,10′-bianthrone as the only isolable product even at low temperatures. Combination of 9-anthryloxy radical with nitrogen(II) oxide to give the nitroso ketone is reasonable, and equilibration of the nitroso ketone and anthraquinone monoxime is expected. The formation of the nitroso ketone may occur through both caged radical pairs and solvent-separated radicals and nitrogen(II) oxide molecules. In the irradiation of the nitro olefins (VI and VIII) nitrogen(II) oxide is not detected in the solution, and the transfer of nitrogen(II) oxide must be largely intramolecular or *via* radical pairs which combine faster than they diffuse apart. The absence of nitrogen(II) oxide in the solution is responsible for the stability of the oxime VII which is isolated. If nitrogen(II) oxide is added to the solution during irradiation, the oxime VII is converted to the diketone.[8]

We consider it most likely that photooxidation of 9-nitroanthracene to anthraquinone involves reaction of oxygen with 9-anthryloxy radicals rather than formation and decomposition of the 9,10-epidioxide. Electronegative substituents in general retard epidioxide formation and dimerization.[5] The rate of disappearance of 9-nitroanthracene is not grossly different in the presence or absence of oxygen. It has been demonstrated that 10,10′-bianthrone is photooxidized rapidly to anthraquinone. This reaction presumably involves photodissociation of 10,10′-bianthrone to two anthryloxy radicals which then react with oxygen.[21] The amount of photodissociation of 10,10′-bianthrone depends on the solubility of 10,10′-bianthrone in the solvent since material which precipitates collects in the bottom of the vessel where it is protected from direct irradiation.

The conversion of ketoximes to ketones by irradiation in solution in the presence of nitrogen(II) oxide is a general process which will be described elsewhere.[8] Anthraquinone monoxime did not prove to be well adapted to mechanistic studies, but major processes responsible for the production of ketones from ketoximes have been delineated by study of other ketoximes.[8] These processes are summarized below.



It is quite possible that there are additional processes by which the iminoxyl radical may be converted to ketone. The iminoxyl radical from anthraquinone monoxime was not observed in the presence of nitrogen(II) oxide, although iminoxyl radicals derived from other oximes have been observed under these conditions.[8] Oxidation of anthraquinone monoxime with ceric ammonium nitrate did give the nitroxyl radical which could be detected by esr using flow techniques.[22,23] Anthraquinone was isolated from the ceric ion oxidation.

The scheme presented for the chemical transformations initiated by irradiation of 9-nitroanthracene constitutes a minimum description of this complex system. Alternate paths may be available for several of these processes. Studies in this area are continuing.

Experimental Section

All product mixtures were separated by a standard chromatographic procedure. Yields are reported as per cent pure product with satisfactory melting point and spectroscopic properties. Products (except 9,10-dinitroanthracene) were identified by direct comparison with authentic samples synthesized by unambiguous methods.

Standard Chromatographic Procedure. Silica gel (50 g per 1 g of material to be chromatographed) was slurried with benzene and introduced to a column containing benzene. The material to be chromatographed was taken up in the minimum amount of hot benzene and placed on the column. Elution with benzene gave first unreacted 9-nitroanthracene, then anthraquinone, then anthraquinone monoxime. Elution with chloroform gave 10,10′-bianthrone. Finally, the column was stripped with methanol.

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(21) The details of this process are not obvious, and this transformation is now under investigation.

(22) The esr spectrum of this radical has been observed independently by B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Phys. Org. Sect.*, 86 (1966).

(23) Ceric ammonium nitrate oxidation of oximes as a means of producing nitroxyl radicals has been reported previously: J. R. Thomas, *J. Am. Chem. Soc.*, **86**, 1446 (1964).

Irradiation of 9-Nitroanthracene in Acetone. A solution of 9-nitroanthracene (1.5 g) in acetone (120 ml) was degassed and sealed in a Pyrex tube. The solution was irradiated for 6.5 hr with an external mercury arc lamp (Hanovia Type A) encased in a Pyrex water-cooled jacket at a distance of 3 cm. The tube was opened, and the solution was purged with nitrogen to remove nitrogen(II) oxide. The acetone was removed under reduced pressure, and the residue was chromatographed on silica gel as described above.

The following fractions were collected: A, anthraquinone (0.09 g, 6%, mp 285–286°); B, anthraquinone monoxime (0.09 g, mp 219–222°); C, anthraquinone monoxime (0.10 g, mp 220–223°, total yield 12%); and D, 10,10′-bianthrone (0.80 g, 61%, mp 254–258°). Products were identified by comparison of infrared absorption with authentic samples.

A solution of 9-nitroanthracene (2.25 g) in acetone (250 ml) was flushed continuously with a slow stream of oxygen-free nitrogen prior to and during irradiation. The irradiation source was a mercury arc lamp (Hanovia Type A) encased in a water-cooled Pyrex immersion well. The exit gas from the nitrogen flush was bubbled through cold concentrated ferrous sulfate solution. After 2-hr irradiation, the ferrous sulfate solution was placed in a vacuum line and allowed to warm up under reduced pressure. The gases from the ferrous sulfate solution were collected then passed through a Dry Ice–acetone trap into a liquid nitrogen trap. No nitrogen(IV) dioxide could be detected in the Dry Ice–acetone trap. The nitrogen(II) oxide which had collected in the liquid nitrogen trap was identified by infrared comparison. Filtration of the acetone solution from the irradiation gave 10,10′-bianthrone (0.62 g, mp 260–262°). The filtrate was evaporated to dryness under reduced pressure. Chromatography of the residue gave anthraquinone (0.17 g, 8%), anthraquinone monoxime (0.58 g, 26%), and 10,10′-bianthrone (0.29 g, total yield 49%). Repetition of this experiment gave yields of oxime in the range 5–20%. The yield reported is the highest obtained.

Irradiation of 9-nitroanthracene (4.2 g) in acetone (400 ml) with the immersion lamp for 3 hr as described above, but with a very high flow rate of oxygen-free nitrogen (to sweep out nitrogen(II) oxide), gave after chromatography anthraquinone (0.25 g, 6%) and 10,10′-bianthrone (2.98 g, 81%).

Irradiation of 9-Nitroanthracene in Carbon Tetrachloride. A solution of 9-nitroanthracene (2.05 g) in carbon tetrachloride in a Pyrex tube was degassed by freeze–thaw pumping cycles. The tube was then sealed, and the solution was irradiated with an external mercury arc lamp (Hanovia Type A) encased in a water-cooled Pyrex jacket for 5 hr at a distance of 3 cm. The tube was opened and the acetone was removed under reduced pressure. Chromatography of the residue gave anthraquinone (0.10 g, 6%) and 10,10′-bianthrone (1.49 g, 86%).

Irradiation of 9-Nitroanthracene in the Presence of Excess Nitrogen(II) Oxide. A solution of 9-nitroanthracene in acetone was purged with oxygen-free nitrogen for 1 hr. Nitrogen(II) oxide was then bubbled in, and the solution was irradiated for 3 hr with a Hanovia Type A mercury arc lamp in a water-cooled Pyrex immersion jacket. The nitrogen(II) oxide stream was maintained during the irradiation. After the irradiation, the solution was purged with nitrogen to remove excess nitrogen(II) oxide. The acetone was then removed under reduced pressure. Chromatography of the residue gave 9,10-dinitroanthracene (0.12 g, 2%), anthraquinone (2.53 g, 55%), 10,10′-bianthrone (0.25 g, 6%), and tar (1.33 g).

Irradiation of 9-Nitroanthracene in the Presence of Oxygen. A solution of 9-nitroanthracene (4.2 g) in acetone (400 ml) was irradiated for 3 hr with a mercury arc lamp (Hanovia Type A) encased in a water-cooled Pyrex immersion well. A continuous stream of oxygen was bubbled through the solution during the irradiation. Filtration of the acetone solution gave anthraquinone (2.55 g, 65%). Chromatography of the residue after evaporation of the filtrate gave anthraquinone (0.91 g, total yield 88%) and 10,10′-bianthrone (0.56 g, 14%).

Irradiation of 10,10′-Bianthrone in the Presence of Oxygen. A solution of 10,10′-bianthrone (1.50 g) in warm acetone (400 ml) was irradiated for 1 hr with a Hanovia Type A mercury arc lamp encased in a water-cooled Pyrex immersion well. A stream of oxygen was continuously bubbled through the solution during the irradiation. Removal of the acetone and chromatography of the residue gave anthraquinone (1.17 g, 72%). No 10,10′-bianthrone was recovered. The remainder of the material was an intractable tar.

Irradiation of Anthraquinone Monoxime. A solution of anthraquinone monoxime (1.85 g) in acetone was irradiated for 3.5 hr with a water-cooled Hanovia Type A mercury lamp in a Pyrex immersion well. The solution was purged with a stream of oxygen-free nitrogen prior to and during the irradiation. Evaporation of the acetone and chromatography gave anthraquinone (0.17 g, 10%) and recovered anthraquinone monoxime.

Irradiation of Anthraquinone Monoxime in the Presence of Nitrogen(II) Oxide. A solution of anthraquinone monoxime (1.6 g) in acetone (250 ml) was irradiated as described above for 3.5 hr. During the irradiation a stream of nitrogen(II) oxide was bubbled through the solution. Removal of the acetone and chromatography gave anthraquinone (1.26 g, 83%).

Oxidation of 9-Hydroxyanthracene to 10,10′-Bianthrone. A 10% sodium hydroxide solution was heated on a steam bath and purged with a stream of nitrogen for 15 min to remove oxygen. Anthrone (10.0 g) and a solution of potassium ferricyanide (16.5 g) in distilled water (100 ml) were added. The nitrogen stream was maintained during the addition of the potassium ferricyanide solution. The solution was filtered, and the product was washed twice with water and once with acetone. Recrystallization from benzene–Skelly B gave pure 10,10′-bianthrone (4.90 g, 50%).

Oxidation of Anthraquinone Monoxime with Ceric Ammonium Nitrate. A solution of anthraquinone monoxime (1.0 g, 0.0044 mole) in methanol (140 ml) and benzene (20 ml) was prepared and rapidly stirred by means of a magnetic stirrer. A solution of ceric ammonium nitrate (2.45 g, 0.0044 mole) in methanol (5 ml) was added in one portion (5 sec). The resulting solution was stirred rapidly for an additional 30 min, after which time the solvent was removed on a rotary evaporator at 60°. The resulting red solid residue was extracted with two 50-ml portions of benzene, followed by two 50-ml portions of chloroform. The combined extracts were dried over anhydrous magnesium sulfate, concentrated to one-half the original volume, and chromatographed on silica gel (200 g).

Fractions eluted with 1:1 Skelly-B–benzene through chloroform contained 0.76 g (81% yield) of a yellow solid, mp 277–279° (with sublimation), which was shown to be anthraquinone by comparison of the infrared spectrum to that of an authentic sample. The later fractions of the chromatography contained some anthraquinone and a red material which was not characterized. No starting material was recovered.

Electron Spin Resonance Studies. A Varian V4500-10A electron spin resonance spectrometer was used. Solutions of anthraquinone monoxime (2.5×10^{-2} *M*) and ceric ammonium nitrate (1.25×10^{-2} *M*) in methanol were prepared and used in the studies. Hyperfine splitting constants were measured with a Varian "Fieldial" attachment.

Solutions of the reactants were deoxygenated by bubbling nitrogen through them before mixing. Electron spin resonance spectra were recorded at room temperature under nitrogen immediately after mixing the solutions and transfer of the cell to the cavity of the spectrometer.

The expected six-line spectrum of the iminoxyl radical derived from the oxime was observed, with $a_N = 30.3$ gauss and $a_H = 3.4$ gauss, in reasonable agreement with literature values.[24] When higher concentrations of ceric ammonium nitrate were used (*i.e.*, a solution 2.5×10^{-2} *M*), the decay of the signal due to the iminoxyl radical was much more rapid, making observation difficult. Even at lower concentrations of ceric ammonium nitrate, the buildup and decay of signal were rapid, with no signal observable after *ca.* 10 min.

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[24] Values given by Gilbert and Norman[22] for the iminoxyl radical generated by $Pb(OAc)_4$ oxidation of the monoxime in methylene dichloride are $a_N = 29.8$ gauss and $a_H = 2.5$ gauss.