

1965

Photochemical studies on 9-nitroanthracene

John William Reasoner
Iowa State University

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PHOTOCHEMICAL STUDIES ON 9-NITROANTHRACENE

by

John William Reasoner

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

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TABLE OF CONTENTS

	Page
VITA	vi
INTRODUCTION	1
HISTORICAL	5
RESULTS	25
DISCUSSION	51
EXPERIMENTAL	65
SUMMARY	104
LITERATURE CITED	106
ACKNOWLEDGEMENT	111

LIST OF FIGURES

	Page
Figure 1. Energy levels of the carbonyl and the nitro groups	3
Figure 2. Spectral considerations for the irradiation of 9-nitroanthracene (I)	32
A. Ultraviolet spectrum of 9-nitroanthracene (I)	
B. Absorption curve for Pyrex glass	
C. Output of a typical Hanovia Type A lamp	
Figure 3. Infrared spectra	40
Top - Anthraquinone (II)	
Middle - Anthraquinone monooxime (LXXXVIII)	
Bottom - Reaction mixture from anthraquinone monooxime (LXXXVIII) plus nitric oxide	
Figure 4. Infrared spectra	42
Top - Anthrone (LXXXIX)	
Middle - 10,10'-Bianthrone (IV)	
Bottom - $\Delta^{10,10'}$ -Dehydrobianthrone (XC)	
Figure 5. Infrared spectra	44
Top - Nitric oxide from the irradiation of 9-nitroanthracene (II)	
Middle - Nitric oxide (authentic sample)	
Bottom - 9,10-Dinitroanthracene (XCI)	
Figure 6. Infrared spectra	46
Top - 9-Nitroanthracene (I)	

	Page
Middle - 9-Nitroanthracene (I) after 1 minute irradiation in KBr	
Bottom - 9-Nitroanthracene (I) after 2 minutes irradiation in KBr	
Figure 7. Infrared spectra	48
Top - 9-Nitroanthracene (I) after 5 minutes irradiation in KBr	
Middle - 9-Nitroanthracene (I) after 10 minutes irradiation in KBr	
Bottom - 9-Nitroanthracene (I) after 15 minutes irradiation in KBr	
Figure 8. Infrared spectra	50
Top - 9-Nitroanthracene (I) after 30 minutes irradiation in KBr	
Bottom - 9-Nitroanthracene (I) after 60 minutes irradiation in KBr	
Figure 9. Mechanistic path	53
Figure 10. Possible mechanistic path for the forma- tion of anthraquinone (II) from 9-nitro- anthracene (I) in the absence of oxygen	61
Figure 11. Diagram showing method of purification of nitrogen	70

LIST OF TABLES

	Page
Table 1. Irradiation of 9-nitroanthracene (I)	33
Table 2. Photooxidation of 10,10'-bianthrone (IV)	36
Table 3. Photochemistry of anthraquinone mono-oxime (LXXXVIII)	37
Table 4. Summary of control (dark) experiments	38

VITA

The author was born on a farm near Winona, Missouri, on February 28, 1940, to Mr. and Mrs. G. A. Reasoner. He attended Morehouse High School, Morehouse, Missouri, where he graduated in May, 1958. In June, 1958, he enrolled at Southeast Missouri State College, Cape Girardeau, Missouri. He was granted the Bachelor of Science degree from Southeast Missouri State College in May, 1961, with majors in chemistry and physics.

The author, on June 10, 1961, was married to the former Sandra Marie Schott. On April 27, 1962, the union was blessed with the arrival of David William Reasoner.

In July, 1961, the author enrolled at Iowa State University as a graduate student with a teaching assistantship. He carried out research in the area of organic chemistry under Dr. O. L. Chapman. In June, 1965, he was awarded a Procter and Gamble Summer Fellowship. He was granted the Doctor of Philosophy degree from Iowa State University in November, 1965.

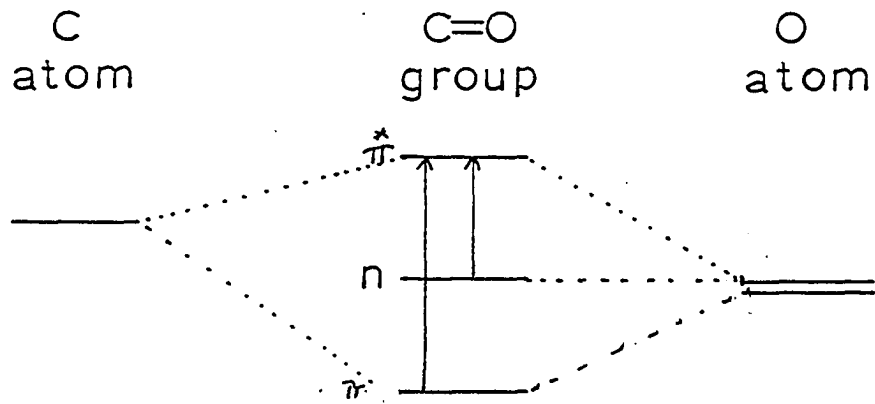
INTRODUCTION

The photochemistry of nitrocompounds has received little attention in recent years compared to that given to the photochemical reactions of ketones. The nitro group is known to undergo $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation analogous to that of ketones (1). The similarity in the excitation (see Figure 1, page 3) would lead one to expect similarities in the photochemical reactions. The three atom system of the nitro group, however, should lead to significant differences between the photochemical reactions of ketones and nitrocompounds.

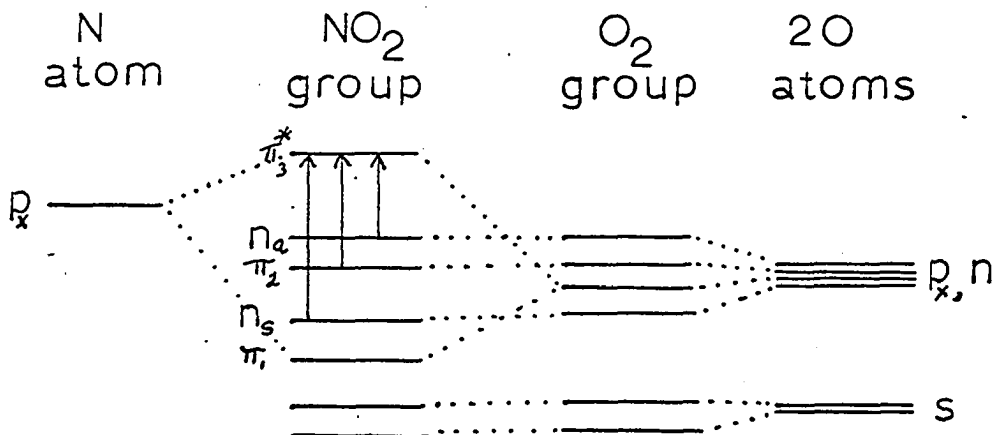
A search of the literature revealed that the irradiation of 9-nitroanthracene (I) in the presence of oxygen in carbon disulfide gave anthraquinone (II) and 9-nitroanthrone (III) (2,3) while irradiation in the absence of oxygen gave 10,10'-bianthrone (IV) and nitric oxide (4). Various 9-nitroanthracenemonosulfonic acids have also been irradiated (5). Products from the sulfonic acid irradiations were not characterized.

The author's work on the aromatic nitrocompounds began in earnest with the observation that the "photooxidation" of 2,3-dimethyl-1-nitronaphthalene (V) and 9-nitroanthracene (I) to 2,3-dimethyl-1,4-naphthoquinone (VI) and anthraquinone (II) did not require oxygen but proceeded in degassed solu-

Figure 1. Energy levels of the carbonyl and the nitro groups



Diagrammatic representation of the energy levels of the carbonyl group.



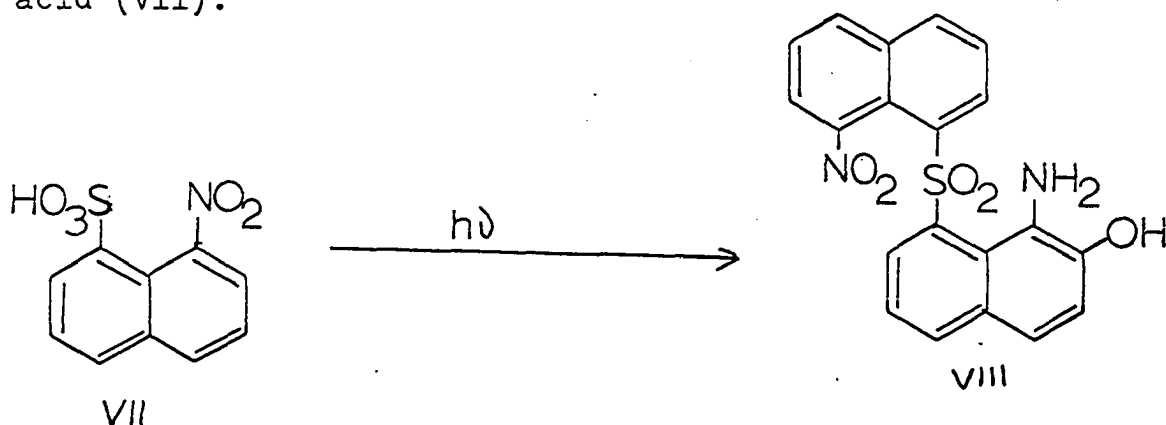
Diagrammatic representation of the energy levels of the nitro group.

tions. The work described here is a study of the photochemical reactions of 9-nitroanthracene (I) in degassed and non-degassed solutions. The photochemical reactions of 9-nitroanthracene (I) with oxygen and nitric oxide were also studied. An attempt was made to define the mechanistic path of the photochemical conversion of 9-nitroanthracene (I) to anthraquinone (II) in the absence of oxygen.

HISTORICAL

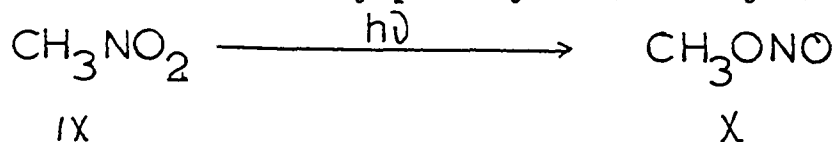
The Photochemical Reactions of Nitrocompounds

The fact that certain nitrocompounds are sensitive to light was discovered through the action of sunlight on nitrated coloring matters (6). The colors were found to turn brown when exposed to sunlight. In most cases the photochemically produced material was not isolated and characterized. Vorozhtsov and Gribov (7,8) studied the effect of ultraviolet light on various α -nitronaphthalene sulfonic acids. The 1,8-isomer (VII) was found to be the most sensitive to light. It was found that meso-nitroanthracenemonosulfonic acids were also sensitive to light (5). Vorozhtsov and Kozlov (9) postulated (on the basis of inadequate evidence) 1-amino-8-(8-nitro-1-naphthylsulfonyl)-2-naphthol (VIII) as the product from the action of light on 1-nitronaphthalene-8-sulfonic acid (VII).

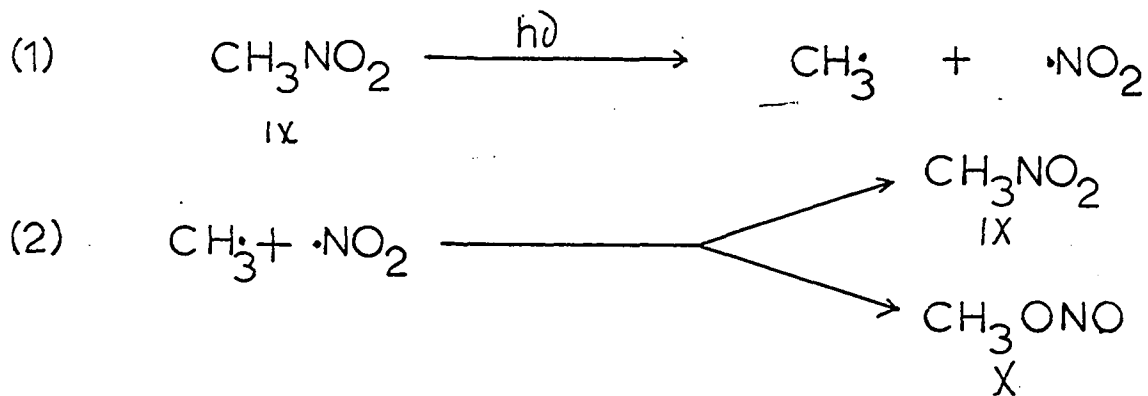


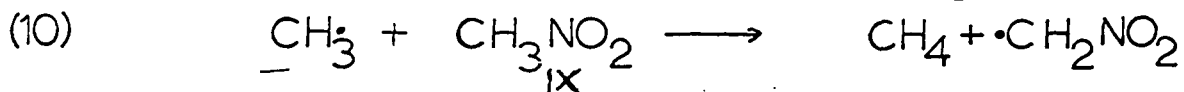
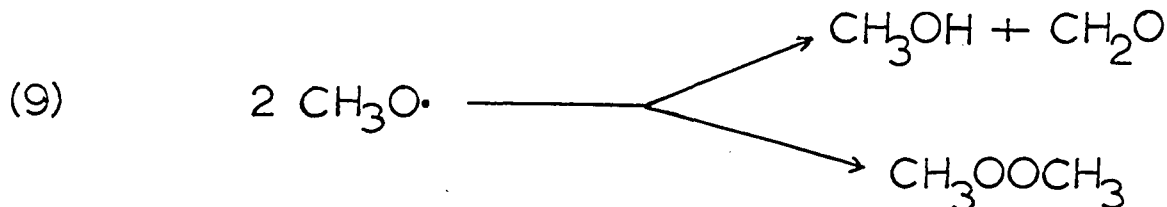
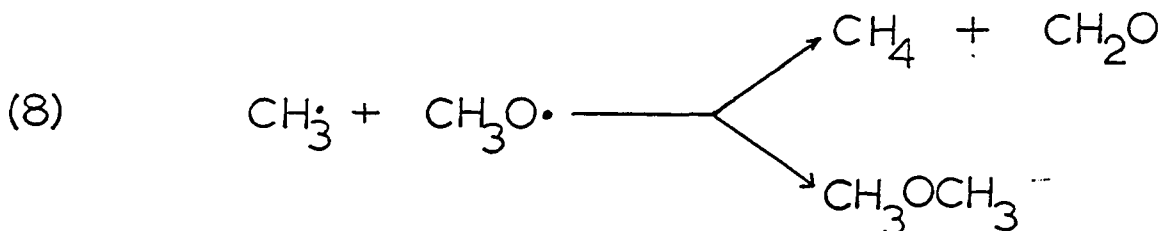
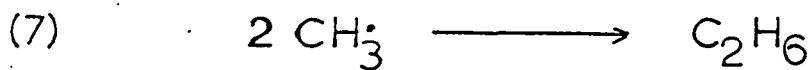
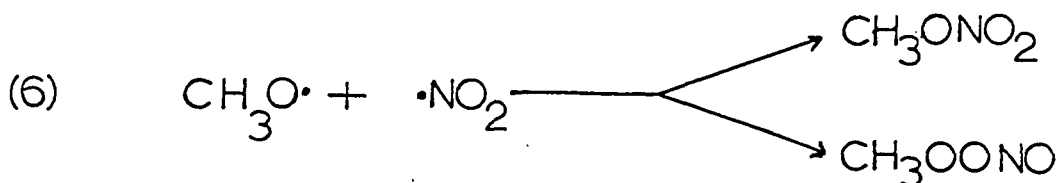
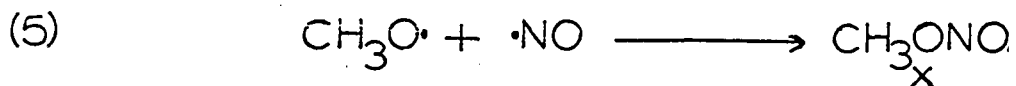
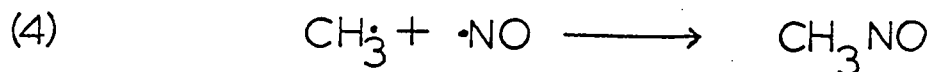
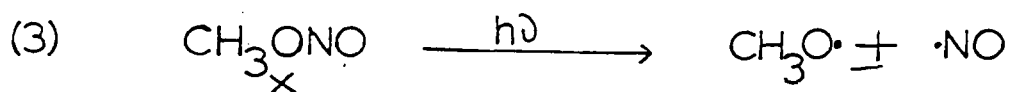
Devore et al. (10) have studied the effect of light of various wave lengths on the decomposition of nitrocellulose films. The decomposition of nitroglycerine under the influence of ultraviolet has also been studied (11).

Brown and Pimentel (12) have studied the photolysis of nitromethane (IX) in an argon matrix at 20°K. It was reported that the primary process was the isomerization of nitromethane (IX) to methyl nitrite (X). All other products were explained on the basis of a secondary photolysis of methyl nitrite (X).



Rebbert and Slagg (13) studied the photolysis of nitromethane (IX) and nitroethane in the gaseous and liquid phases. The main products from nitromethane (IX) were methyl nitrite (X) and nitric oxide. Other products formed were methane, ethane, methanol, methyl nitrate, formaldehyde, carbon monoxide, and hydrogen. The primary process was postulated as a photochemical cleavage to the methyl radical and nitrogen dioxide. A reaction mechanism was postulated.

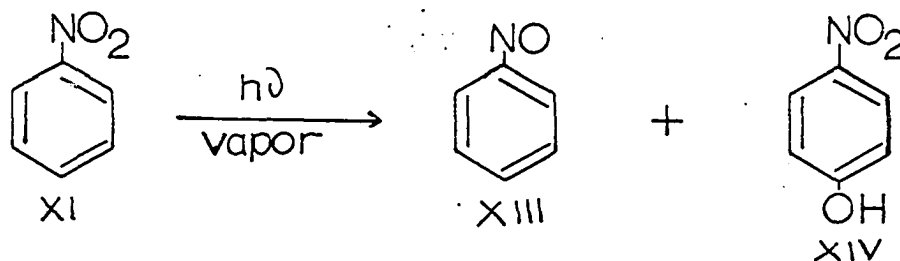




Nitroethane gave ethyl nitrite, ethylene, acetaldehyde, and nitric oxide as the main products.

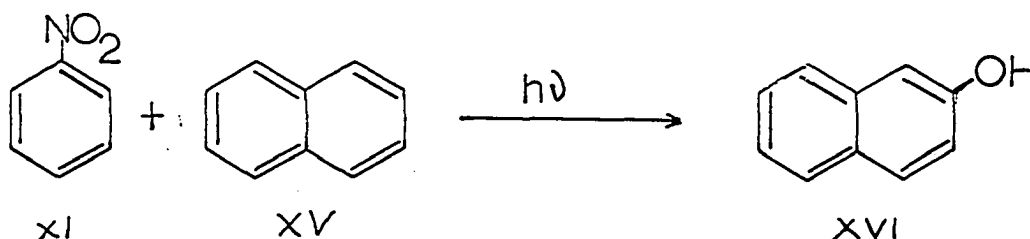
It has been reported that the photochemical decomposition of nitrobenzene (XI) vapor gave phenol (XII), nitrogen dioxide, dinitrobenzene, and trinitrobenzene (14). Hastings and Matsen (15) have reported that the photolysis of nitro-

benzene (XI) in the vapor phase gave only nitrosobenzene (XIII) and *p*-nitrophenol (XIV).

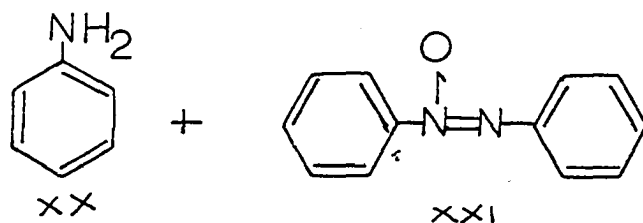
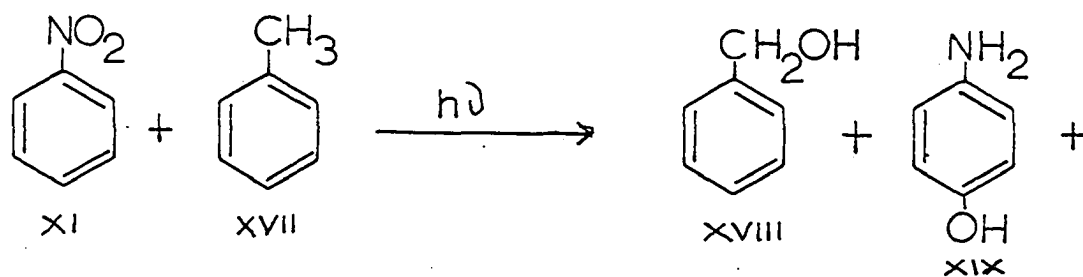


Neither polynitrated benzenes nor nitrogen dioxide could be found by Hastings and Matsen (15).

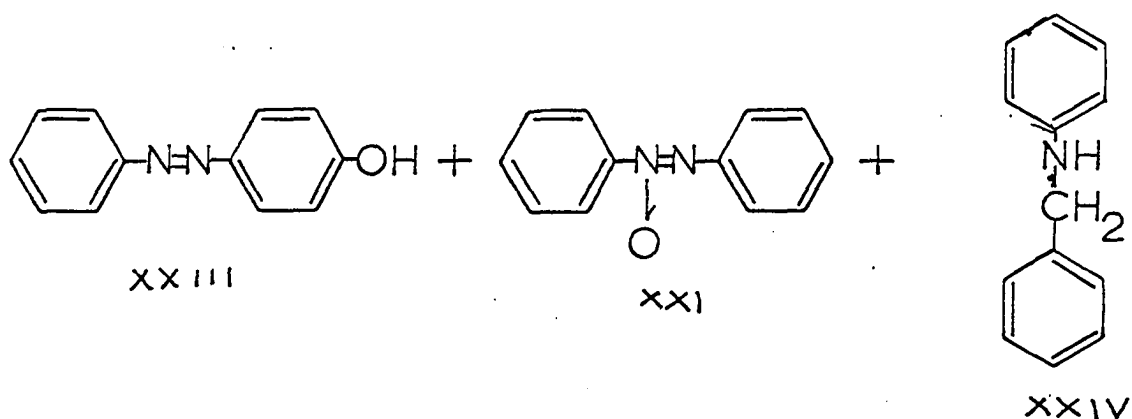
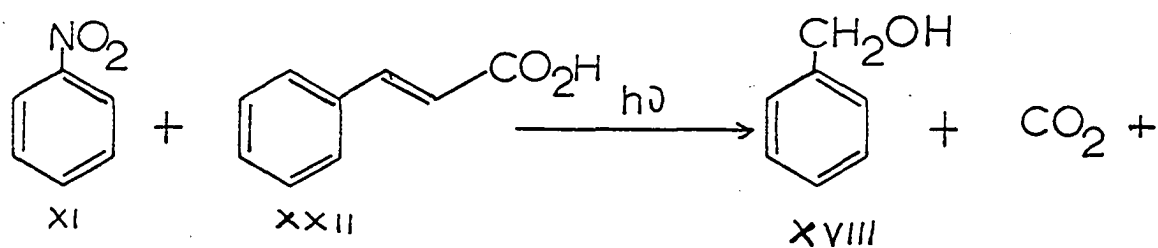
Vecchiotti and Zanetti (16,17) have studied the effect of nitrobenzene (XI) on various organic compounds under the influence of light. The compounds were usually irradiated for six months in the sunlight under a nitrogen atmosphere. Irradiation of nitrobenzene (XI) with naphthalene (XV) gave β -naphthol (XVI) as the only product identifiable.



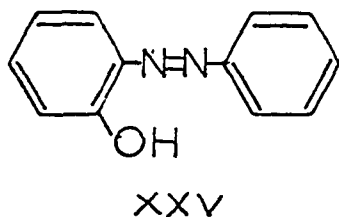
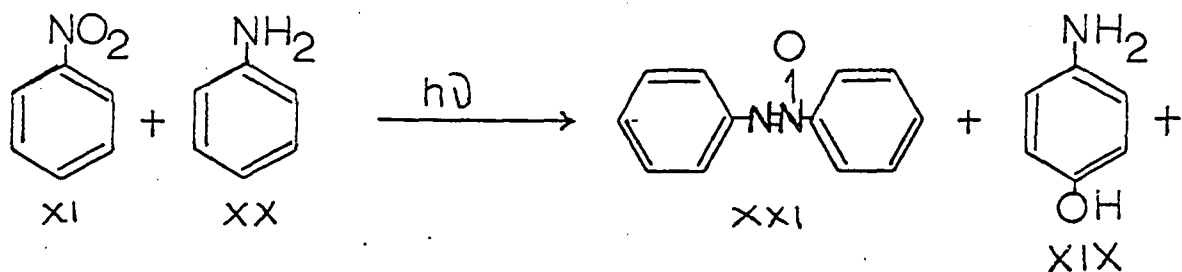
Irradiation of nitrobenzene (XI) and toluene (XVII) gave benzyl alcohol (XVIII), *p*-aminophenol (XIX), aniline (XX), and azoxybenzene (XXI).



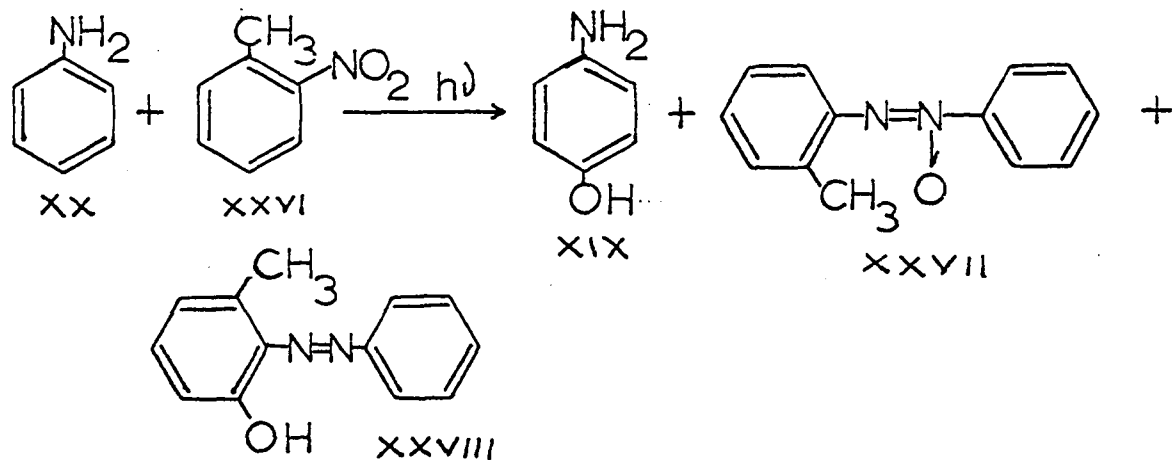
Irradiation of nitrobenzene (XI) with cinnamic acid (XXII) gave benzyl alcohol (XVIII), carbon dioxide, p-hydroxyazobenzene (XXIII), azoxybenzene (XXI), and XXIV.



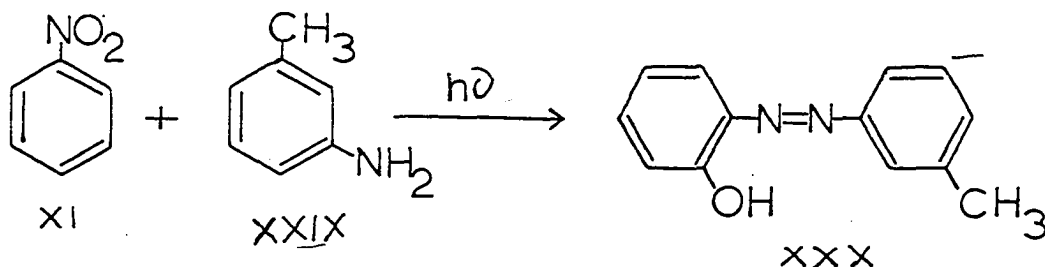
Nitrobenzene (XI) was irradiated in the presence of aniline (XX) by Vecchiotti and Piccinini (18). This gave azoxybenzene (XXI), *p*-aminophenol (XIX), and *o*-hydroxyazobenzene (XXV). Azoxybenzenes are known to photoisomerize to *o*-hydroxybenzene derivatives (19).



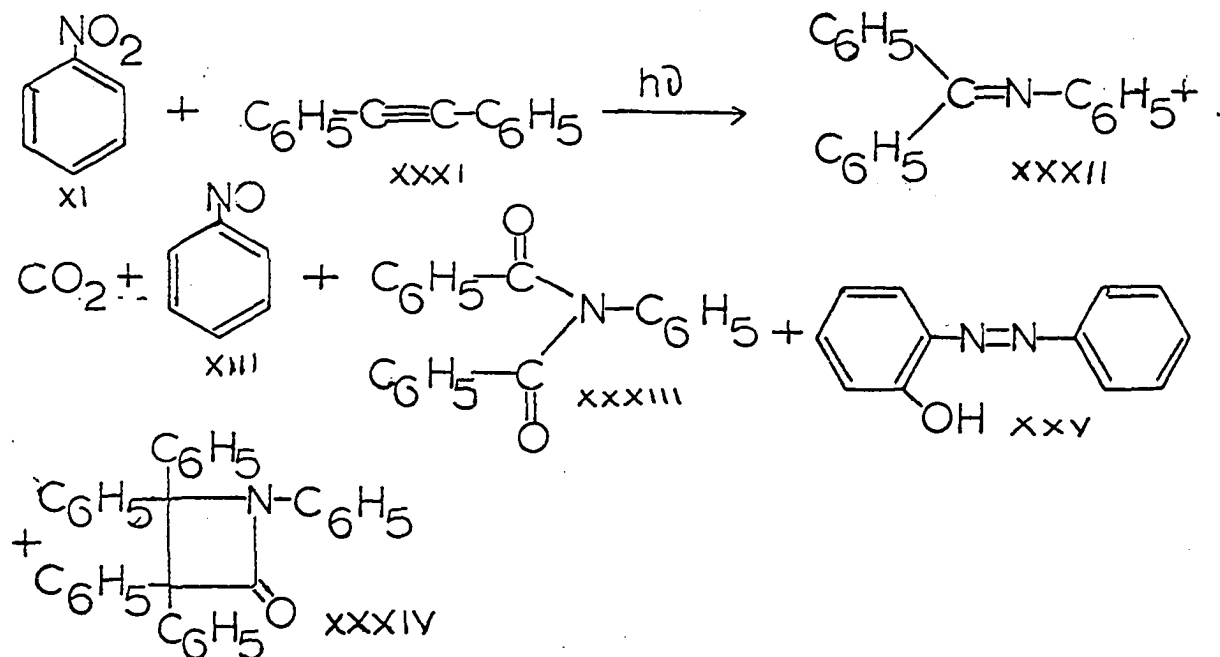
A solution of aniline (XX) and *o*-nitrotoluene (XXVI) was exposed to sunlight for six months (20). This gave *p*-aminophenol (XIX), XXVII, and XXVIII.



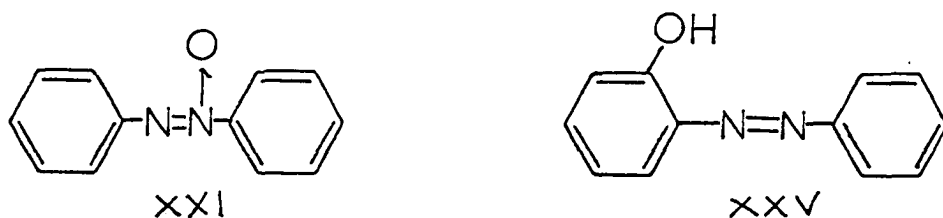
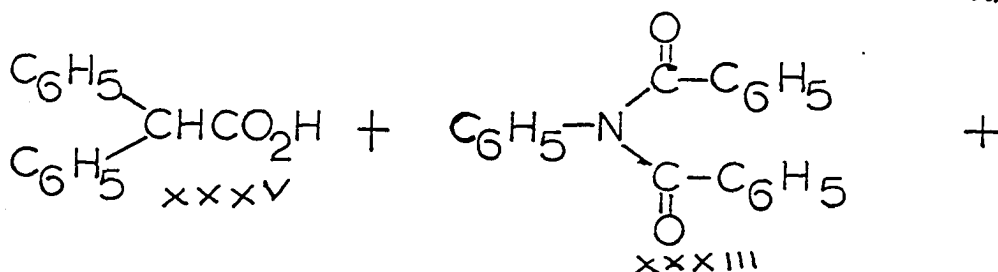
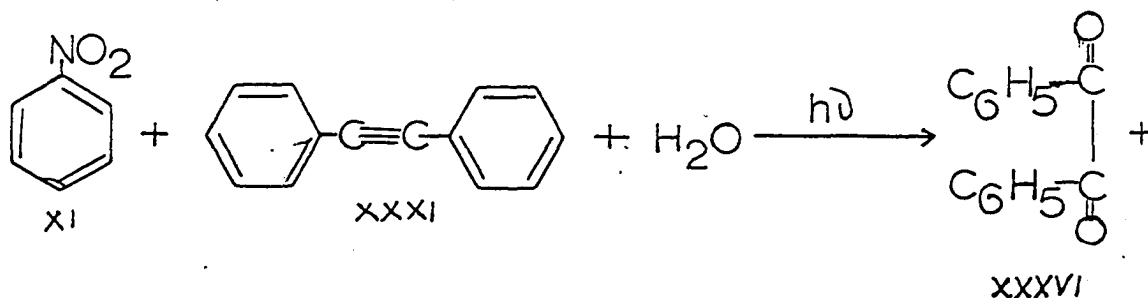
A solution of nitrobenzene (XI) and *m*-aminotoluene (XXIX) was irradiated by Vecchiotti and Piccinini (21). This gave XXX as the only product isolated.



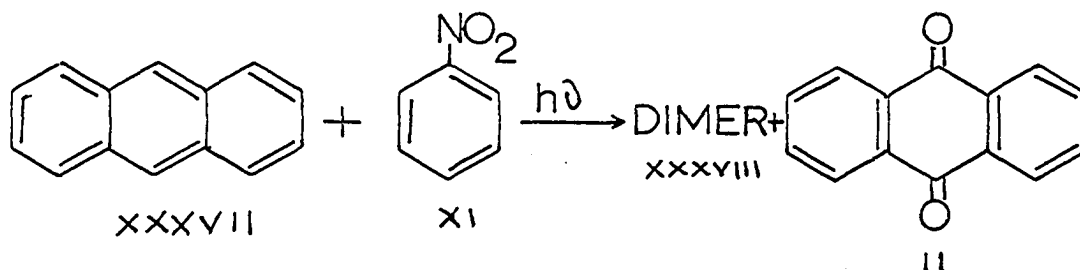
Scheinbaum (22) irradiated a solution of nitrobenzene (XI) and tolane (XXXI) in petroleum ether for three days with a Hanovia Type A medium-pressure mercury arc lamp. This gave benzophenone-anil (XXXII), carbon dioxide, nitrosobenzene (XIII), dibenzanilide (XXXIII), 2-hydroxyazobenzene (XXV), and the β -lactam of *N*-phenyl- β -aminotetraphenylpropionic acid (XXXIV).



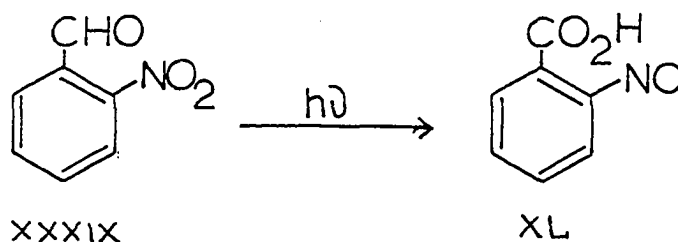
Irradiation of nitrobenzene (XI) and tolane (XXXI) in aqueous dioxane gave diphenylacetic acid (XXXV), dibenzanilide (XXXIII), benzil (XXXVI), azoxybenzene (XXI), and 2-hydroxyazobenzene (XXV).



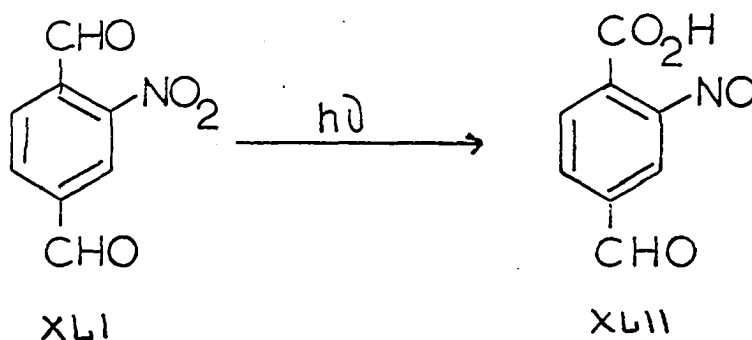
It has been reported that irradiation of anthracene (XXXVII) in the presence of nitrobenzene (XI) gave an anthracene dimer (XXXVIII) and anthraquinone (II) (23).



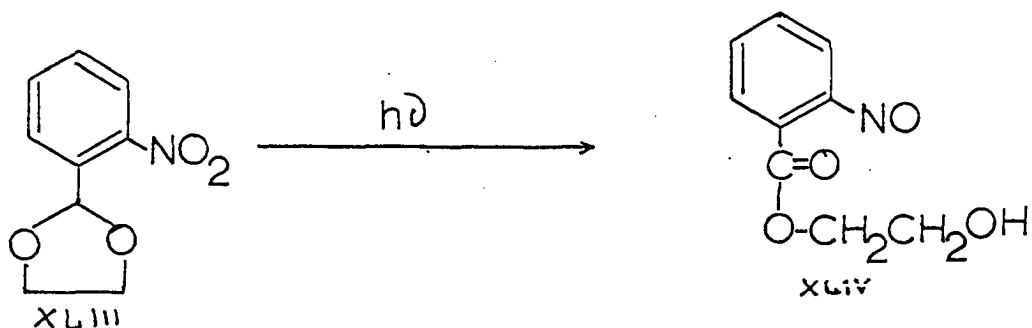
Several workers have studied the photochemical o-nitrobenzaldehyde rearrangement (24-26). This type of reaction is probably the largest and most extensively studied of all the photochemical reactions involving the nitro group. This reaction was first discovered by Ciamician and Silber (24) when they irradiated o-nitrobenzaldehyde (XXXIX) and isolated o-nitrosobenzoic acid (XL).



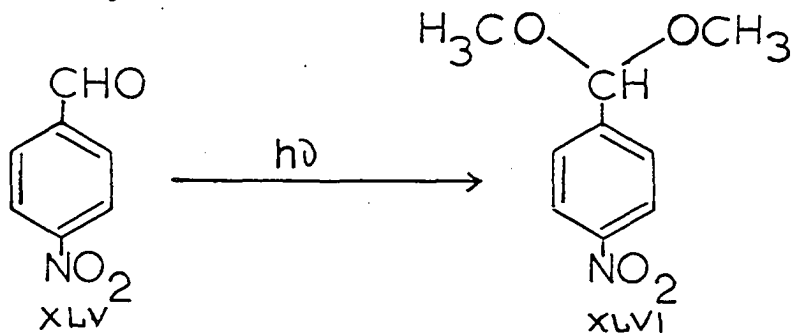
Kailan (27) found that the reaction proceeds more rapidly in quartz than in glass. Janssen (28) has irradiated an acetone solution of nitroterephthaldehyde (XLI) and isolated the nitrosoacid (XLII).



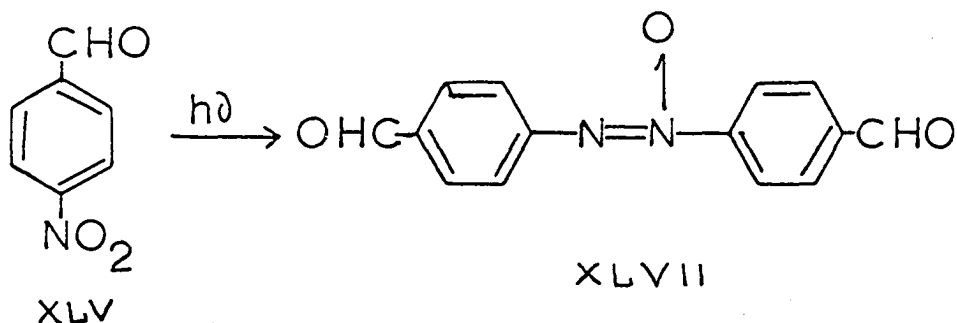
Bamberger and Elger (29) have studied several nitrobenzaldehydes. Irradiation of o-nitrobenzylideneglycol (XLIII) gave the open ring compound XLIV.



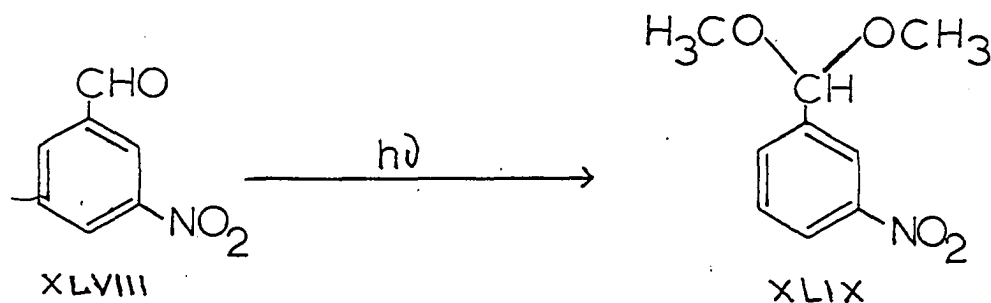
Irradiation of p-nitrobenzaldehyde (XLV) in methanol gave the dimethyl acetal XLVI.



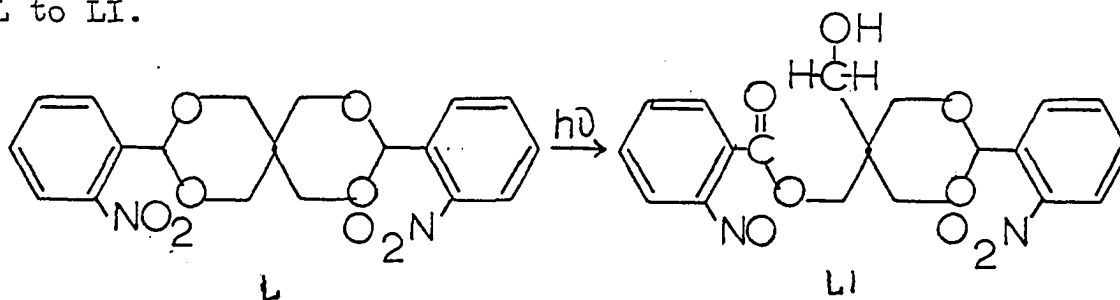
Irradiation of p-nitrobenzaldehyde (XLV) in diethyl ether gave XLVII.



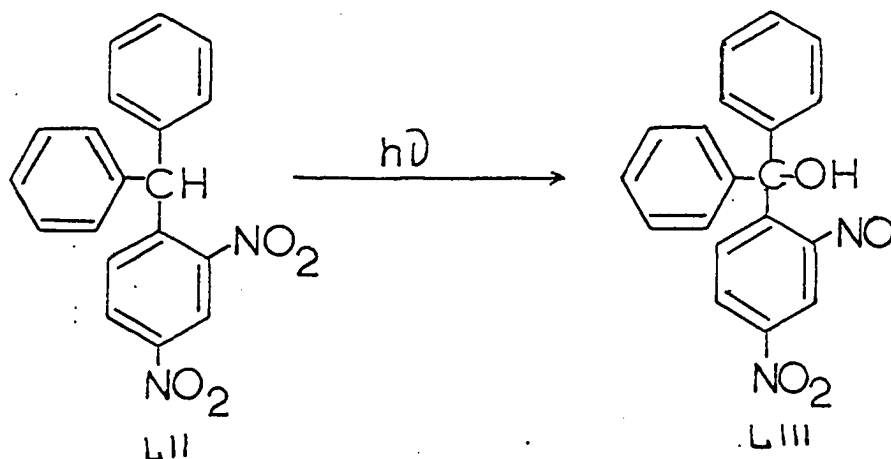
Irradiation of *m*-nitrobenzaldehyde (XLVIII) in methanol gave the dimethyl acetal XLIX.



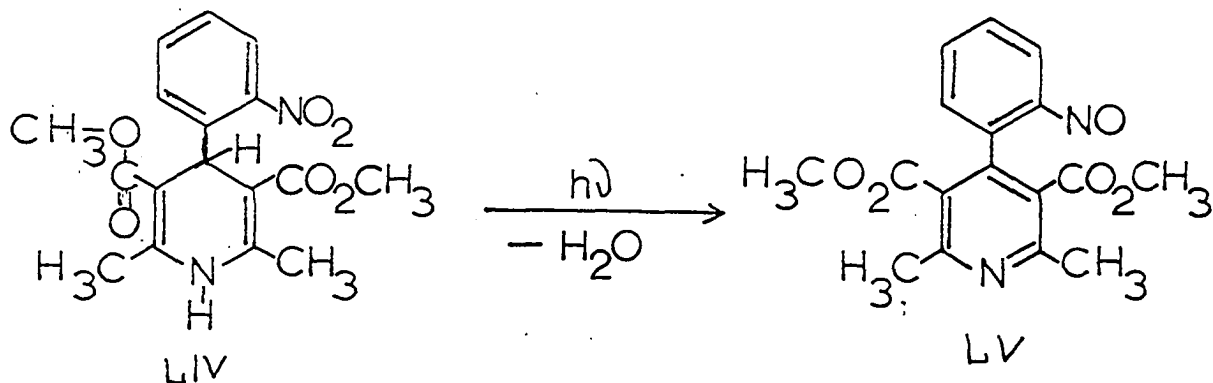
An extensive series of *o*-nitrobenzylidene acetals were studied by Tanasescu *et al.* (30-41). It was found that they were all subject to a general type of photochemical reaction. An example of this type of reaction is the transformation of L to LI.



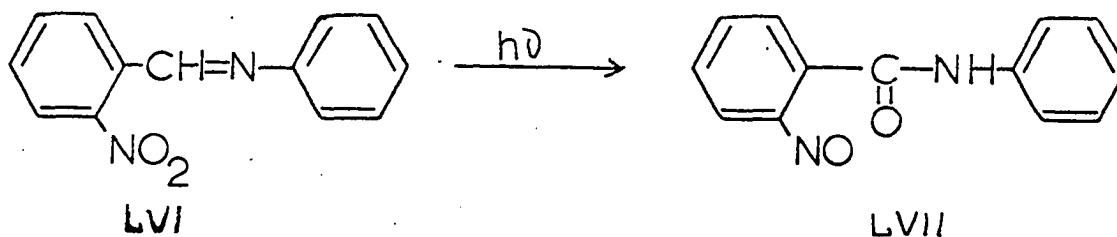
Irradiation of LII in pyridine gave a nitrosocarbiniol LIII (42).



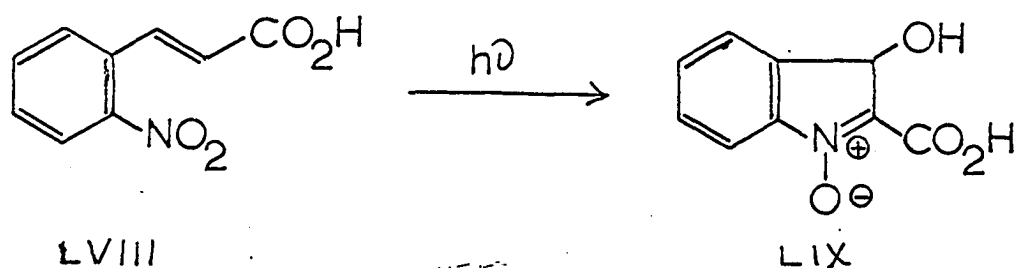
The photochemical transformation of LIV to LV has been reported by Berson and Brown (43).



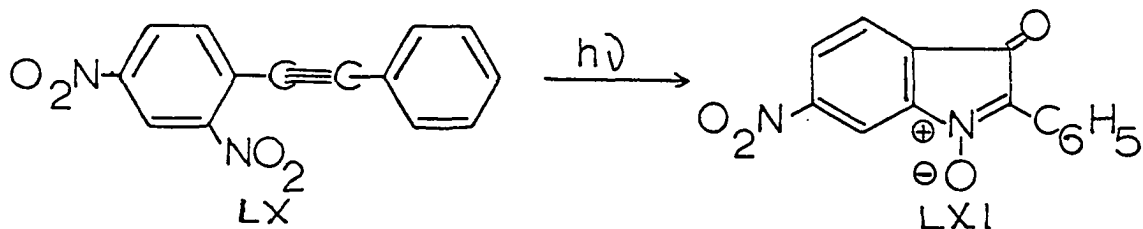
Another example of the o-nitrobenzaldehyde type rearrangement is the photochemical transformation of LVI to LVII reported by Sachs and Kempf (44).



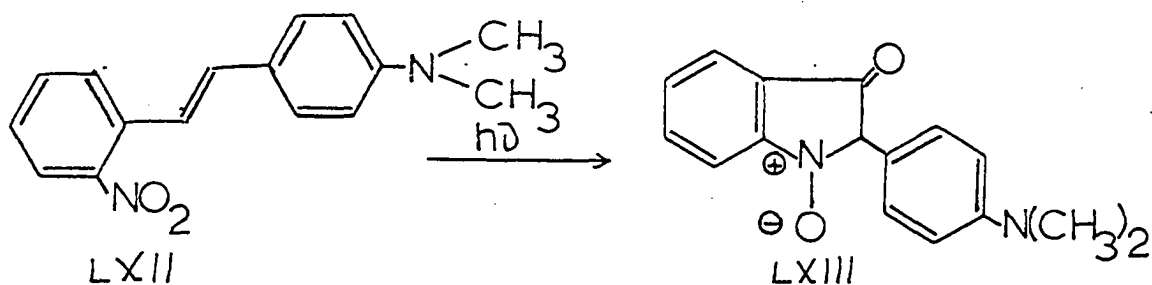
Irradiation of o-nitrocinnamic acid (LVIII) gave LIX (45).



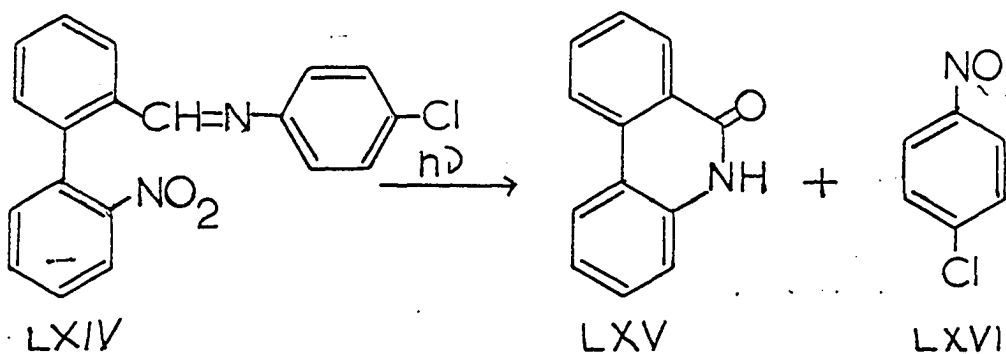
Irradiation of 2,4-dinitrotolane (LX) gave the isatogen LXI (46).



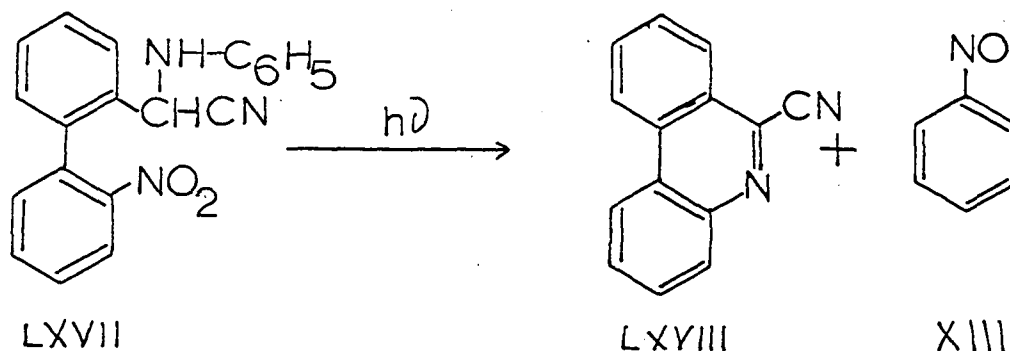
Irradiation of o-nitrostilbenes were also reported to give this class of compound (47). An example is the transformation of LXII to LXIII.



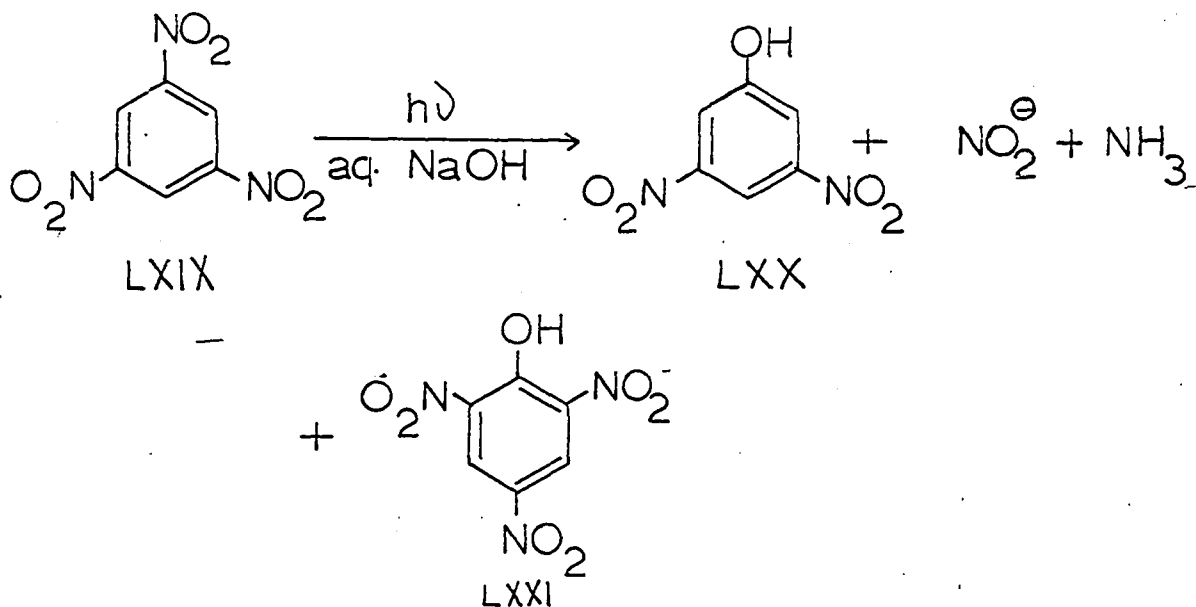
Irradiation of the p-chlorophenyl anil of o-nitro-o'-formylbiphenyl (LXIV) in ethanol resulted in the formation of 5(6H)-phenanthridone (LXV) and p-chloronitrosobenzene (LXVI) (48).



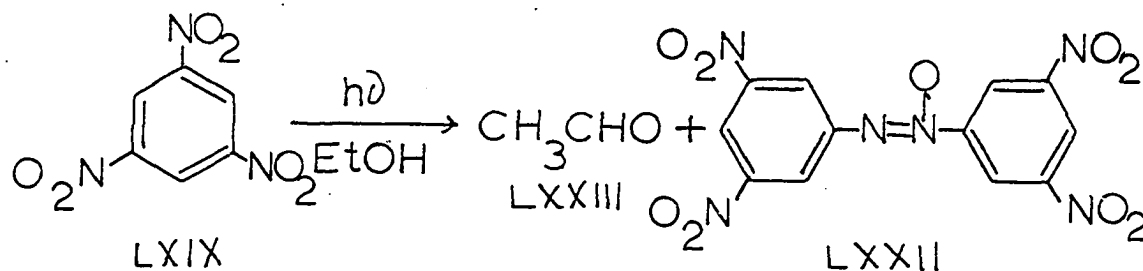
Irradiation of *o*-(cyanoanilinomethyl)-*o'*-nitrobiphenyl (LXVII) gave 6-cyanophenanthridine (LXVIII) and nitrosobenzene (XIII) (48).



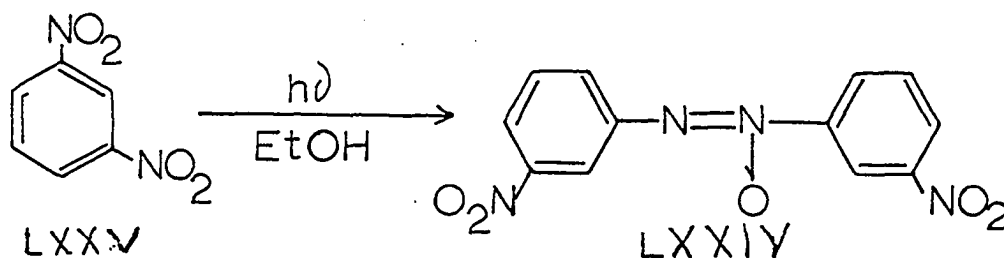
Reaction of 1,3,5-trinitrobenzene (LXIX) with aqueous sodium hydroxide gave 3,5-dinitrophenol (LXX). The photochemical reaction also gave 3,5-dinitrophenol (LXX) as the major product (49). The rate of formation in the light reaction was 50 times larger than in the dark reaction. A trace of picric acid (LXXI) was also isolated.



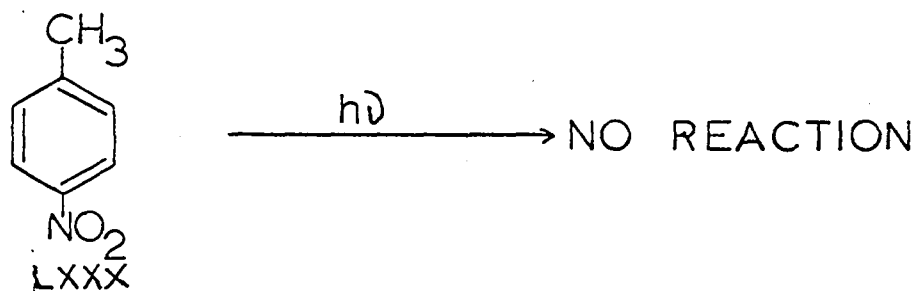
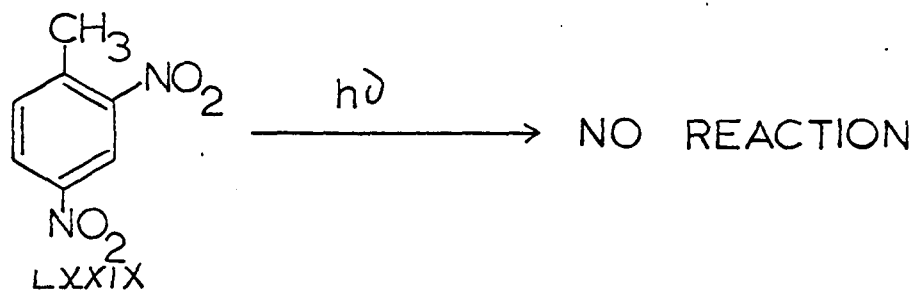
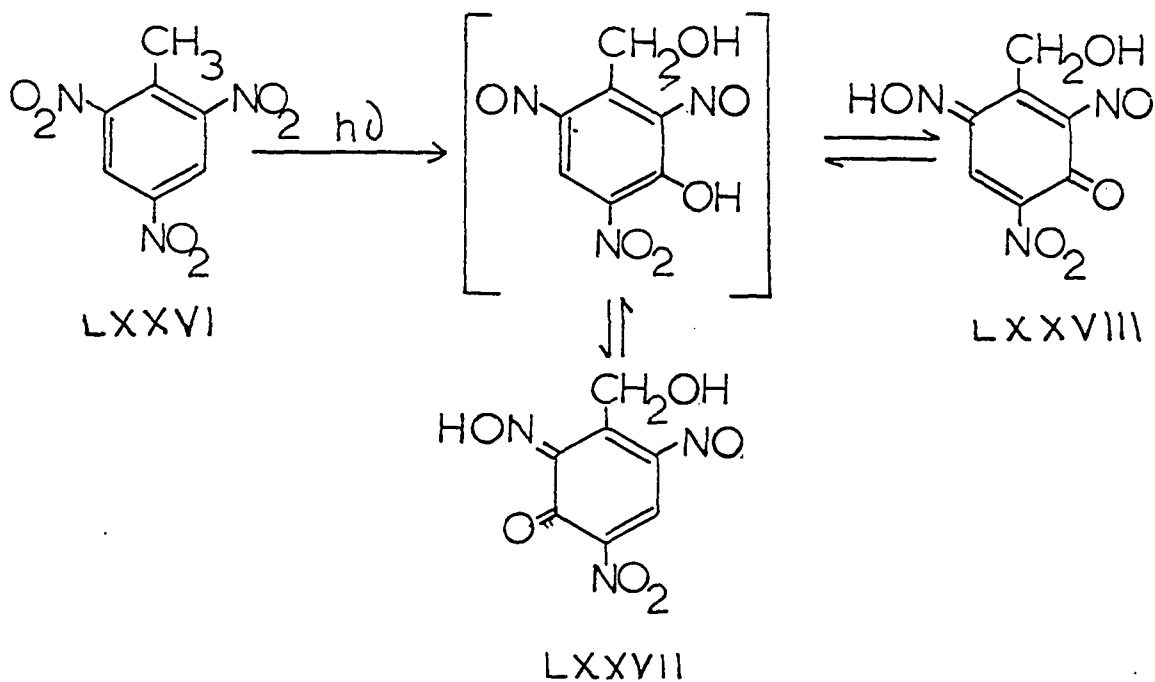
Stenberg and Holter (50) have also studied the photochemistry of 1,3,5-trinitrobenzene (LXIX). They have reported that irradiation of 1,3,5-trinitrobenzene (LXIX) in 95% ethanol gave 3,5,3',5'-tetranitroazoxybenzene (LXXII) and acetaldehyde (LXXIII).



Stenberg and Holter (50) have also reported that 3,3'-di-nitroazoxybenzene (LXXIV) was isolated from the irradiation of 1,3-dinitrobenzene (LXXV) in ethanol.

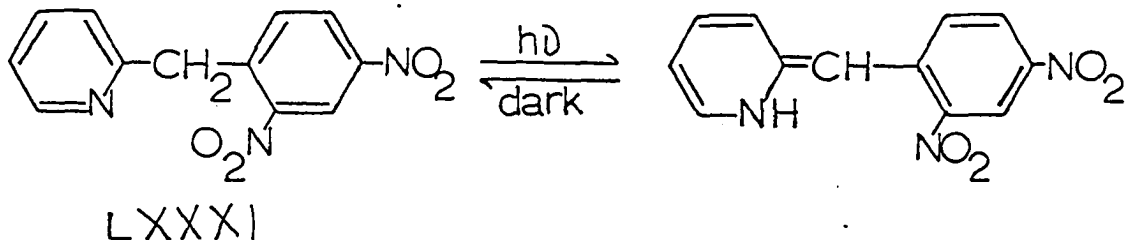


Schultz and Gancaly (51) have studied a series of polynitrated toluenes. Irradiation of 2,4,6-trinitrotoluene (LXXVI) gave two tautomeric *o*- (LXXVII) and *p*-quinone oxime (LXXVIII) derivatives. They also found that 2,4-dinitrotoluene (LXXIX) and *p*-nitrotoluene (LXXX) were photochemically unreactive under the same conditions that 2,4,6-trinitrotoluene undergoes rearrangement.

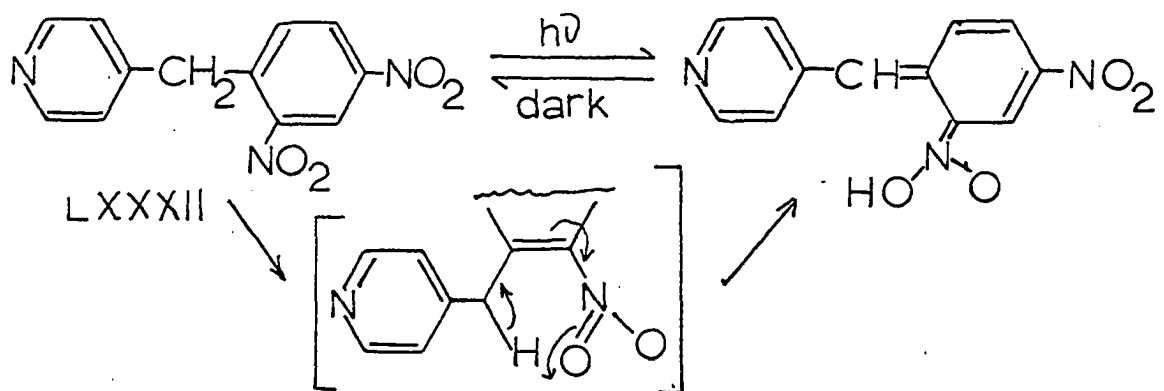


Tchitchibabine et al. (52) irradiated 2-(2',4'-dinitrobenzyl)-pyridine (LXXXI) in the crystalline state. The compound turned violet in the presence of light. The violet

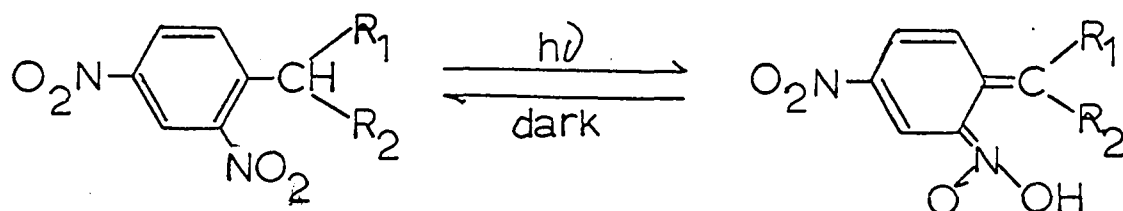
color was found to fade when the light was removed. A tautomeric equilibrium was postulated.



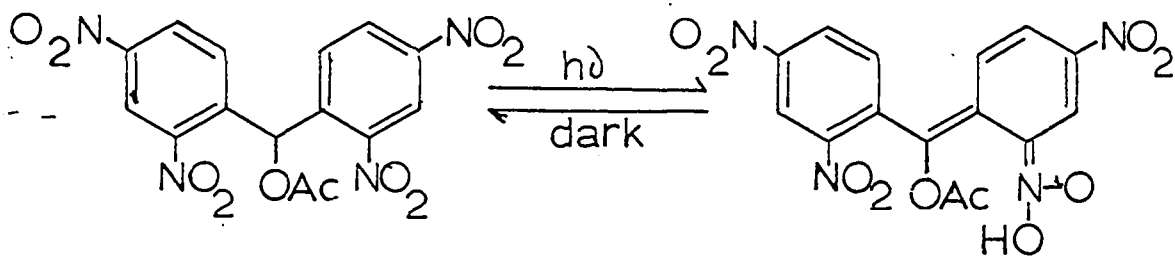
Mosher et al. (53) postulated a different type of tautomeric equilibrium for the irradiation of 4-(2',4'-dinitrobenzyl)-pyridine (LXXXII).



Margerum et al. (54) found that there were two requisites for the type of photochemical isomerization postulated by Mosher et al. (53). A hydrogen on a benzyl carbon must be sufficiently activated by ortho or para substituents, and a nitro group must be ortho to the benzyl carbon. Hirshberg and Fischer (55) have reported a general type of photochemical isomerization.

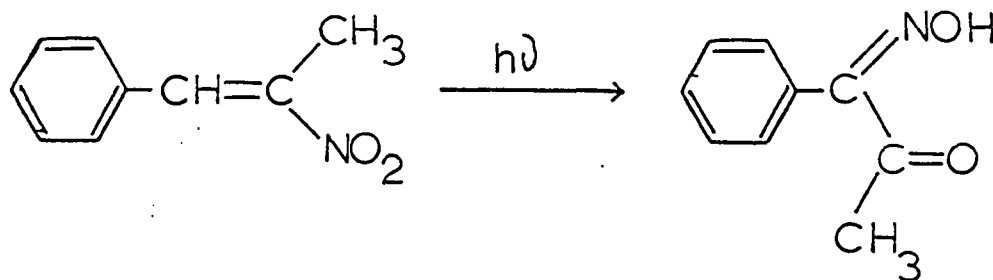


Bluhm et al. (56) have studied the photochemical equilibrium of methyl bis-(2,4-dinitrophenyl) acetate (LXXXIII).



LXXXIII

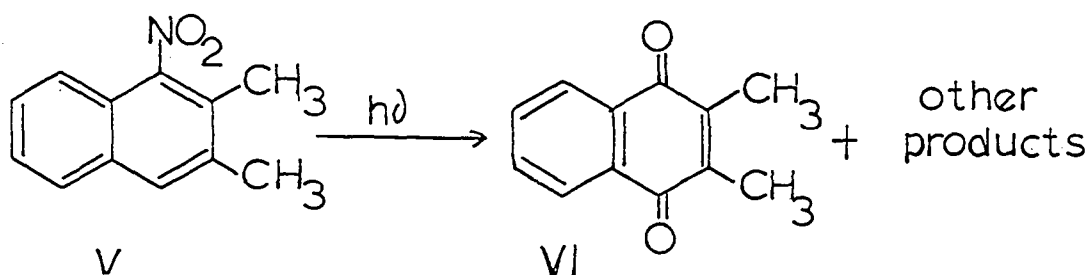
The photochemical transformation of β -methyl- β -nitro-styrene (LXXXIV) to LXXXV has been reported by Chapman et al. (57).



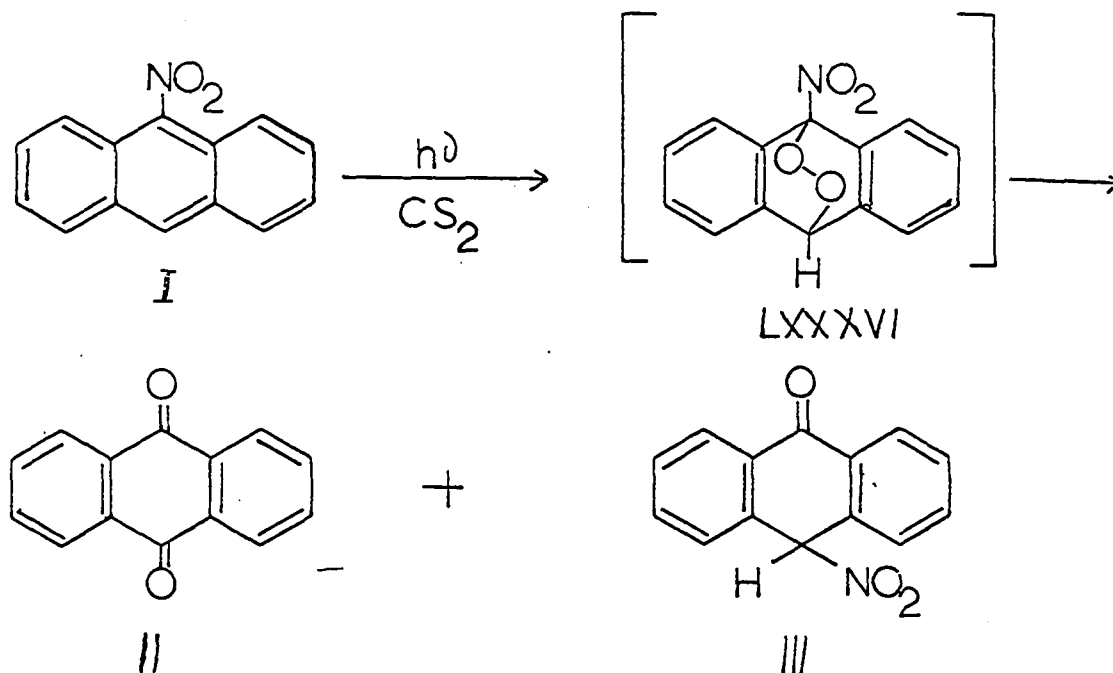
LXXXIV

LXXXV

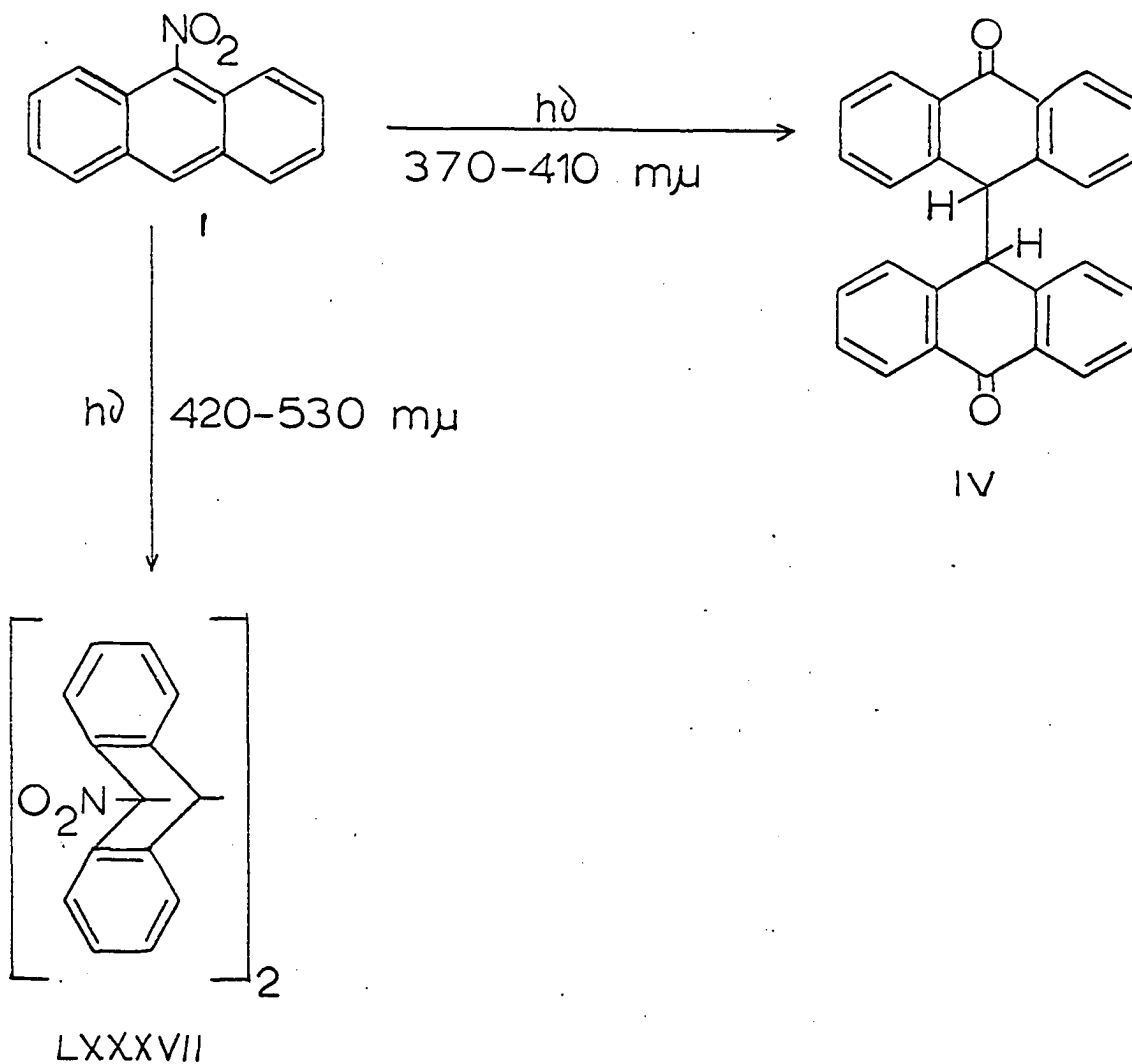
Irradiation of 2,3-dimethyl-1-nitronaphthalene (V) has been shown to give 2,3-dimethyl-1,4-naphthoquinone (VI) among a variety of other products (57).



It has been reported that irradiation of 9-nitroanthracene (I) in the presence of oxygen gave anthraquinone (II) and 9-nitroanthrone (III) (2,3). It was suggested that a peroxide (LXXXVI) is an intermediate in the photochemical oxidation (3).



Greene (4) has reported that 9-nitroanthracene (I) on irradiation with light of wave length 420-530 millimicrons gives a photodimer (LXXXVII) while light of 370-310 millimicrons gives 10,10'-bianthrone (IV) and nitric oxide (4).



RESULTS

Previous reports in the literature indicated that anthraquinone (II) is formed by the photochemical reaction of 9-nitroanthracene (I) with oxygen (2,3). The author, however, isolated anthraquinone (II) from 9-nitroanthracene (I) irradiations in which oxygen had been rigorously excluded. The photochemical reactions of 9-nitroanthracene (I) were investigated in an attempt to define a mechanistic path for the formation of anthraquinone (II) in degassed solutions.

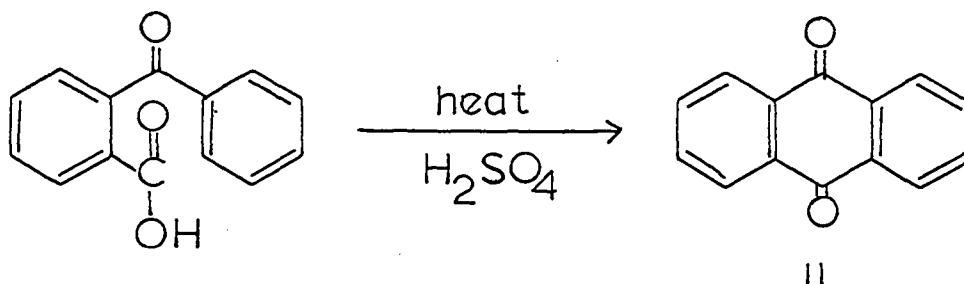
Solutions of 9-nitroanthracene (I) were irradiated under a variety of conditions in order to evaluate the effect of oxygen on the yield of anthraquinone (II) and 10,10'-bianthrone (IV). Greene (4) has reported that 10,10'-bianthrone (IV) is the product formed by irradiation of 9-nitroanthracene (I) in the absence of oxygen.

A standard chromatographic procedure was developed. The photochemical reaction mixture was chromatographed on silica gel and, if necessary, the products were recrystallized to give pure products with satisfactory melting points. Each experiment (unless otherwise indicated) was analysed chromatographically on silica gel, and the percent pure (recrystallized) product was reported.

Each product (except 9,10-dinitroanthracene) was compared to an authentic sample prepared by a non-photochemical syn-

thetic procedure. The samples of 9-nitroanthracene (I) were obtained commercially (Aldrich Chemical Company) or prepared using a procedure similar to that of Dimroth (58). The infrared spectrum (Figure 5) of 9-nitroanthracene (I) is shown on page 46.

An authentic sample of anthraquinone (II) was prepared according to the method outlined by Fieser (59). The infrared spectrum (Figure 3) of anthraquinone (II) is shown on page 40.

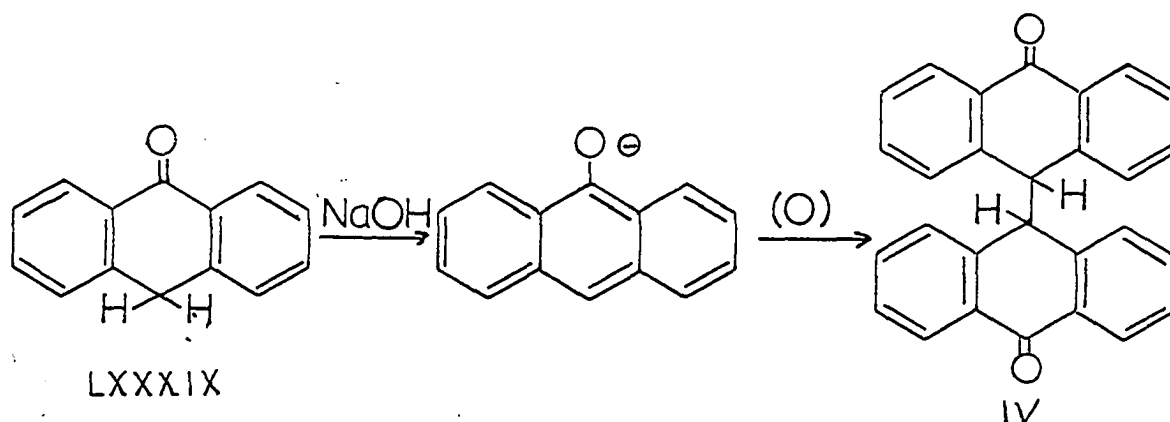


An authentic sample of anthraquinone monooxime (LXXXVIII) was prepared according to the procedure of Meisenheimer (60). An elemental analysis gave the correct composition for $C_{14}H_9NO_2$. The compound was hydrolyzed to anthraquinone (II) with dilute mineral acid in dioxane. Treatment of anthraquinone monooxime (LXXXVIII) with nitric oxide gave a material of unknown composition. The infrared spectrum (Figure 3, page 40) did not contain bands identifiable as belonging to either anthraquinone (II) or anthraquinone monooxime (LXXXVIII). Chromatography on silica gel, however, gave a 75% yield of anthraquinone (II). The infrared spectrum of

the crude reaction mixture from the irradiation of anthraquinone monooxime (LXXXVIII) in the presence of nitric oxide showed the anthraquinone carbonyl band at 5.97 microns.

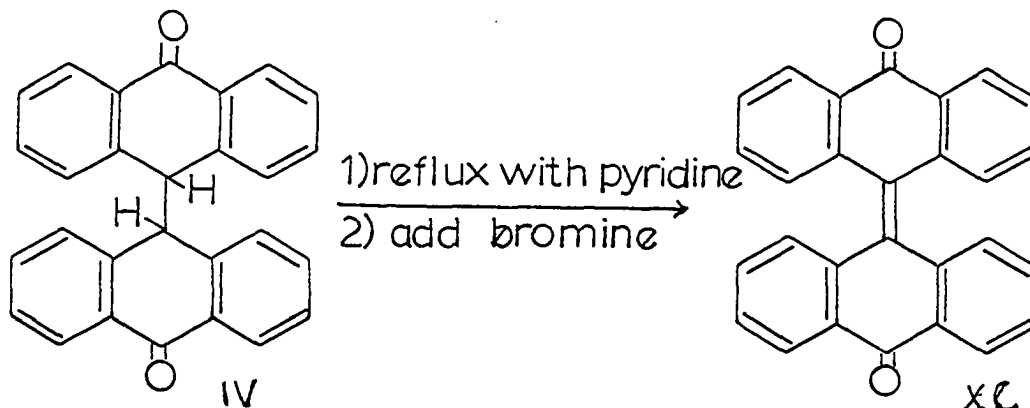
Several melting points appear in the literature for anthraquinone monooxime (LXXXVIII). Julian *et al.* (61) report 224-225° as the melting point. Schors *et al.* (62) report 226° as the melting point for anthraquinone monooxime (LXXXVIII). The author's best sample of anthraquinone monooxime (LXXXVIII) melted at 231-231.5° using a Kofler hot stage. The infrared spectrum of anthraquinone monooxime (LXXXVIII) is shown in Figure 3 on page 40.

Authentic samples of 10,10'-bianthrone (IV) were prepared according to two different procedures. A sample was prepared from anthracene (XXXVII) according to the procedure of Barnett and Matthews (63). The anthracene (XXXVII) used must be pure or the 10,10'-bianthrone (IV) will be contaminated with anthraquinone (II). A better method of preparation involves the oxidative coupling of two molecules of 9-hydroxyanthracene.



Anthrone (LXXXIX) (see Figure 4, page 42, for the infrared spectrum) was treated with 10% sodium hydroxide. An aqueous solution of potassium ferricyanide was then added dropwise. This gave a 50% yield of 10,10'-bianthrone (IV). There are several melting points reported for 10,10'-bianthrone (IV). Meyer (64) has reported that 10,10'-bianthrone darkens at about 245° and melts at 250° . Dimroth (58) reports a melting point between 246° and 255° . Campbell and Ofstead (65) reported $259-261^{\circ}$ as the melting point of 10,10'-bianthrone (IV). Arndt and Schlatter (66) have reported that the compound melts at 275° with decomposition. The author obtained a melting point of $259-261^{\circ}$ for an authentic sample using the Kofler hot stage. The highest melting point obtained by the author was $262-263.5^{\circ}$. The melting point of 10,10'-bianthrone (IV) appears to be very sensitive to the purity of the sample. The infrared spectrum of 10,10'-bianthrone (IV) (Figure 4) is shown on page 42.

A sample of $\Delta^{10,10'}$ -dehydrobianthrone (XC) was prepared according to the procedure of Barnett and Matthews (63). The



sample was prepared so that the infrared spectrum and melting point could be compared to the infrared spectrum and melting point of 10,10'-bianthrone (IV).

Nitric oxide from the irradiation of 9-nitroanthracene (I) was identified by means of infrared comparison with an authentic sample and by means of the brown ring test with ferrous sulfate. The infrared spectrum of nitric oxide from the irradiation of 9-nitroanthracene (I) is shown with the infrared spectrum of an authentic sample of nitric oxide in Figure 5 on page 44.

Samples of 9,10-dinitroanthracene (XCI) were obtained from the dark reaction of nitric oxide with 9-nitroanthracene (I), the irradiation of 9-nitroanthracene (I) with an excess of nitric oxide, and from the sealed tube irradiation of 9-nitroanthracene (I) in carbon tetrachloride saturated with oxygen. Elemental analysis gave the correct composition for $C_{14}H_8N_2O_4$. Meisenheimer and Connerade (67) reported that 9,10-dinitroanthracene (XCI) melted at 294° . Barnett (68) reported a melting point of 310° for 9,10-dinitroanthracene (XCI). The author obtained a melting point of $309-310^\circ$ using the Kofler hot stage.

Several samples of 9-nitroanthracene (I) were irradiated for various lengths of time in potassium bromide pellets. The course of the irradiation was followed by infrared comparison (see Figures 6 - 8, pages 46-50). After two minutes

irradiation time the infrared spectrum showed a carbonyl band at 5.97 microns (characteristic of the anthraquinone carbonyl group) and a carbonyl band at 6.02 microns (characteristic of the 10,10'-bianthrone carbonyl group). The relation of the irradiation in the solid state (KBr) to the irradiation in solution is not known.

The ultraviolet absorption spectrum of 9-nitroanthracene (I) is shown in Figure 2 on page 32 (69). The use of a Pyrex immersion well cuts out most of the light below 290 millimicrons. The output of a typical Hanovia Type A medium-pressure mercury arc lamp is shown in Figure 2 on page 32. Only the light of a wave length longer than 290 millimicrons is passed through the Pyrex flask into the solution being irradiated. With a Hanovia Type A mercury arc lamp the main output above 290 millimicrons occurs at 313 and 366 millimicrons.

The results of the irradiation of 9-nitroanthracene (I) are shown in Table 1, page 33. The results from the photo-oxidation of 10,10'-bianthrone (IV) and the photochemistry of anthraquinone monooxime (LXXXVIII) are shown in Table 2, page 36, and Table 3, page 37. Table 4, page 38, shows the results from the control experiments.

Figure 2. Spectral considerations for the irradiation of 9-nitroanthracene (I)

- A. Ultraviolet spectrum of 9-nitroanthracene (I)
- B. Absorption curve for Pyrex glass
- C. Output of a typical Hanovia Type A lamp

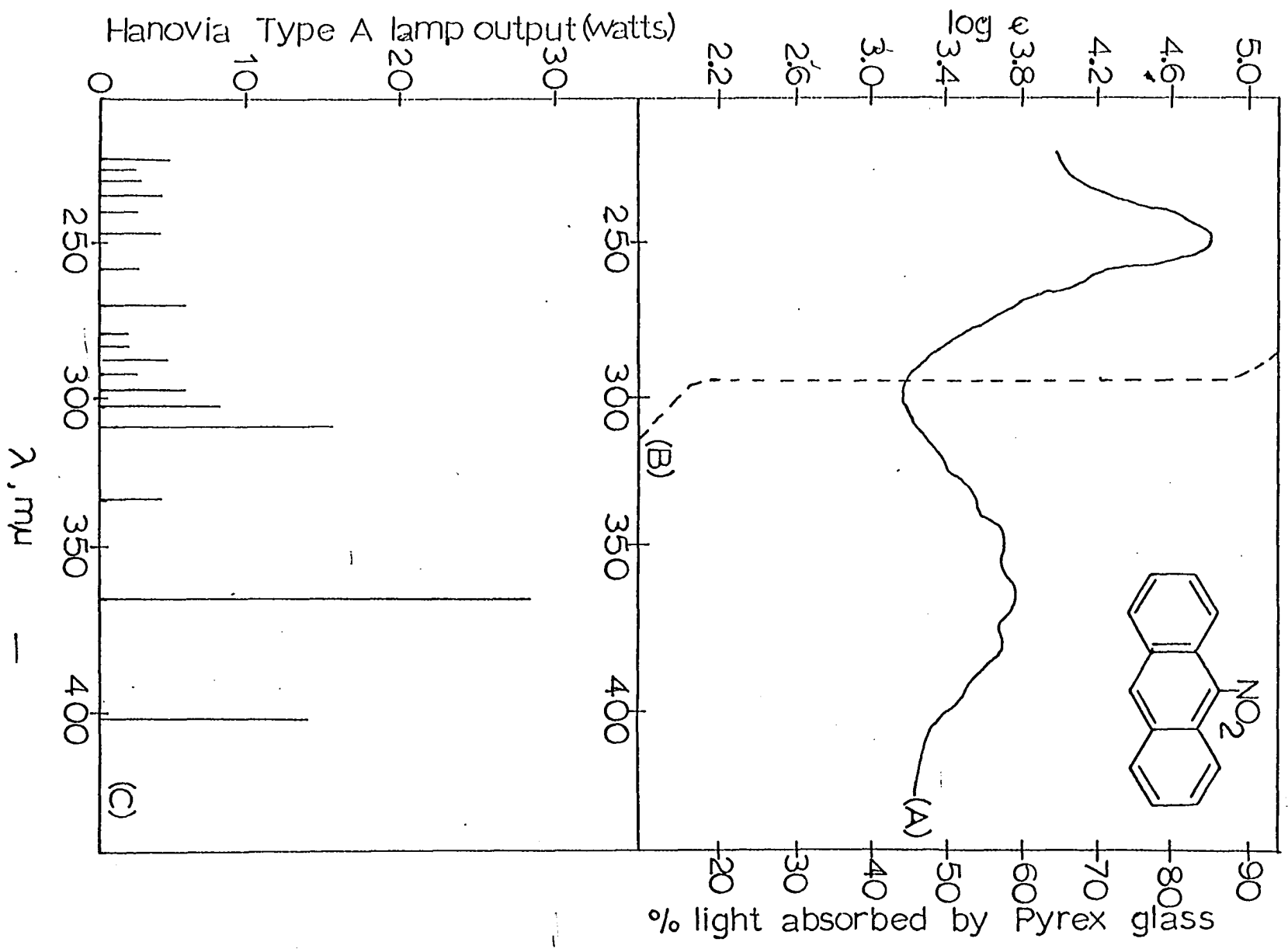


Table 1. Irradiation of 9-nitroanthracene (I)

Conditions	% Pure compound isolated				Page
	Starting material	Anthraquinone	Anthraquinone monooxime	10,10'-bi-anthrone	
1½ hrs. irradiation in degassed acetone in a Pyrex flask. Type A lamp (internal).	21	30	11	34	68
6½ hrs. irradiation in degassed acetone in a Pyrex tube (sealed). Type A lamp (external).	--	6	12	61	75
5 hrs. irradiation in degassed carbon tetrachloride in a Pyrex tube (sealed). Type A lamp (external).	--	6	--	86	77
2 hrs. irradiation in degassed acetone in a Pyrex flask with a slow nitrogen flush (Teflon tube). Type A lamp (internal). ^a	--	8	26	49	79

^aNitric oxide was also isolated and identified from this irradiation.

Table 1. (continued)

Conditions	% Pure compound isolated				Page
	Starting material	Anthraquinone	Anthraquinone monooxime	10,10'-bi-anthrone	
3 hrs. irradiation in degassed acetone in a Pyrex flask with a rapid nitrogen flush (gas dispersion tube). Type A lamp (internal).	1	6	--	74	82
2 hrs. irradiation in acetone-HOAc (95-5) in a Pyrex flask. Type A lamp (internal).	8	21	--	55	83
24 days irradiation in chloroform in a quartz tube open to the atmosphere. Type UA-3 lamp (external).	--	62	--	--	85
3 hrs. irradiation in chloroform saturated with oxygen in a Pyrex flask. Type A lamp (internal).	2	35	--	33	86
3 hrs. irradiation in acetone in a Pyrex flask with an oxygen flush. Type A lamp (internal).	--	88	--	--	88

Table 1. (continued)

Conditions	% Pure compound isolated				Page
	Starting material	Anthraquinone	Anthraquinone monooxime	10,10'-bi-anthrone	
5½ hrs. irradiation in carbon tetrachloride saturated with oxygen in a Pyrex tube (sealed). Type A lamp (external). ^b	--	48	--	36	89
3 hrs. irradiation in acetone in a Pyrex flask with a nitric oxide flush. Type A lamp (internal). ^c	--	55	--	6	92

^bAn 8% yield of 9,10-dinitroanthracene was also isolated.

^cA 2% yield of 9,10-dinitroanthracene was also isolated.

Table 2. Photooxidation of 10,10'-bianthrone (IV)

Conditions	% Pure compound isolated		Page
	Anthraquinone	10,10'-bianthrone	
162 hours irradiation in chloroform in a quartz tube open to the atmosphere. Type UA-3 lamp (external).	42	--	95
3 hrs. irradiation in chloroform saturated with oxygen in a Pyrex flask. Type A lamp (internal).	13	59	97
1 hr. irradiation in acetone in a Pyrex flask with an oxygen flush. Type A lamp (internal).	72	--	97

Table 3. Photochemistry of anthraquinone monooxime (LXXXVIII)

Conditions	% Pure compound isolated		Page
	Anthraquinone	Anthraquinone Monooxime	
3½ hrs. irradiation in degassed acetone in a Pyrex flask with a nitrogen flush. Type A lamp (internal).	10	23	99
3½ hrs. irradiation in degassed acetone-water (95-5) in a Pyrex flask. Type A lamp (internal).	13	81	100
3 hrs. irradiation in acetone saturated with nitric oxide in a Pyrex flask. Type A lamp (internal).	22	68	100
3½ hrs. irradiation in acetone in a Pyrex flask with a nitric oxide flush. Type A lamp (internal).	83	--	101

Table 4. Summary of control (dark) experiments

Substance	Experiment	Results	Page
Anthraquinone monooxime	Reflux with dilute mineral acid in aqueous dioxane.	96% yield of anthraquinone.	72
10,10'-bianthrone	Treatment of nitrogen (IV) oxide in acetone.	6% anthraquinone and a 79% recovery of starting material.	91
9-nitroanthracene	Treatment with nitric oxide in acetone.	5% anthraquinone and a 76% yield of 9,10-dinitroanthracene.	94
10,10'-bianthrone	Treatment with oxygen in refluxing acetone.	97% recovery of starting material. No anthraquinone was isolated.	98
Anthraquinone monooxime	Treatment with nitric oxide in acetone.	Gave a product of unknown composition which on chromatography on silica gel gave a 75% yield of anthraquinone.	103

38

Figure 3. Infrared spectra

Top - Anthraquinone (II)

Middle - Anthraquinone monooxime (LXXXVIII)

Bottom - Reaction mixture from anthraquinone
monooxime (LXXXVIII) plus nitric oxide

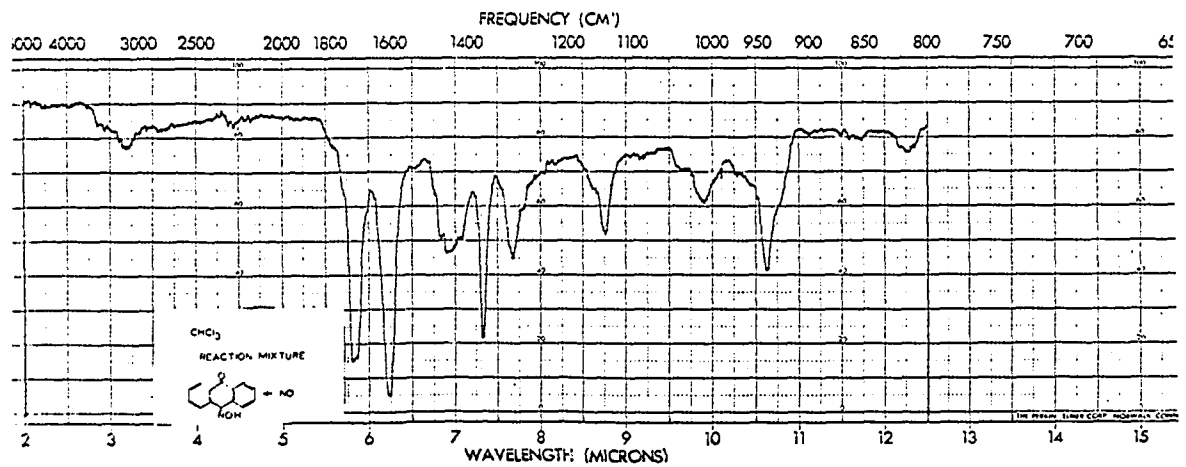
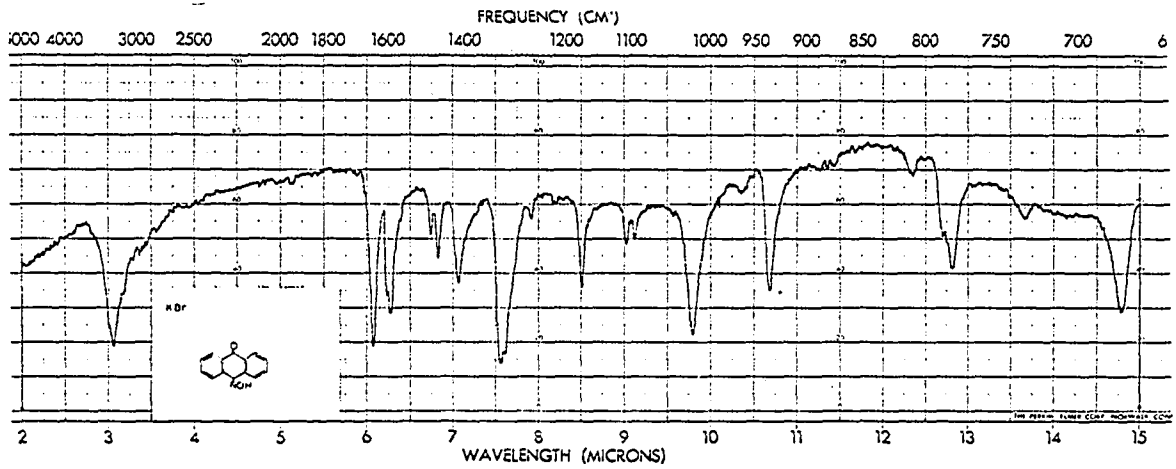
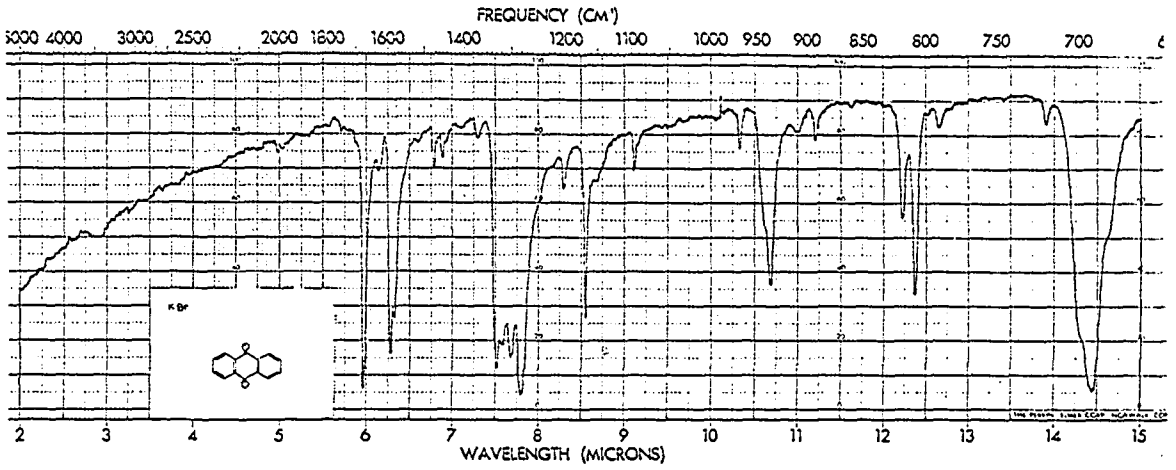


Figure 4. Infrared spectra

Top - Anthrone (LXXXIX)

Middle - 10,10'-Bianthrone (IV)

Bottom - $\Delta^{10,10'}$ -Dehydrobianthrone (XC)

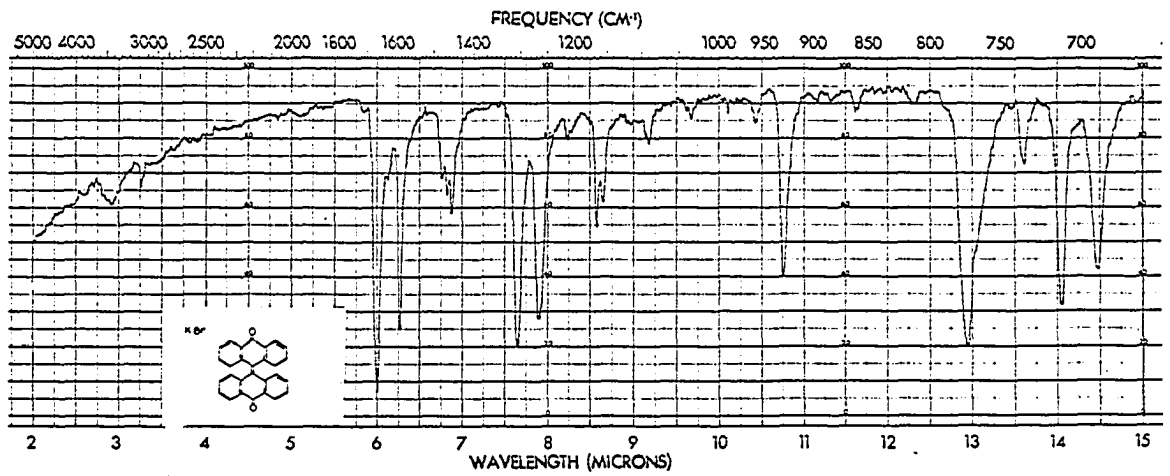
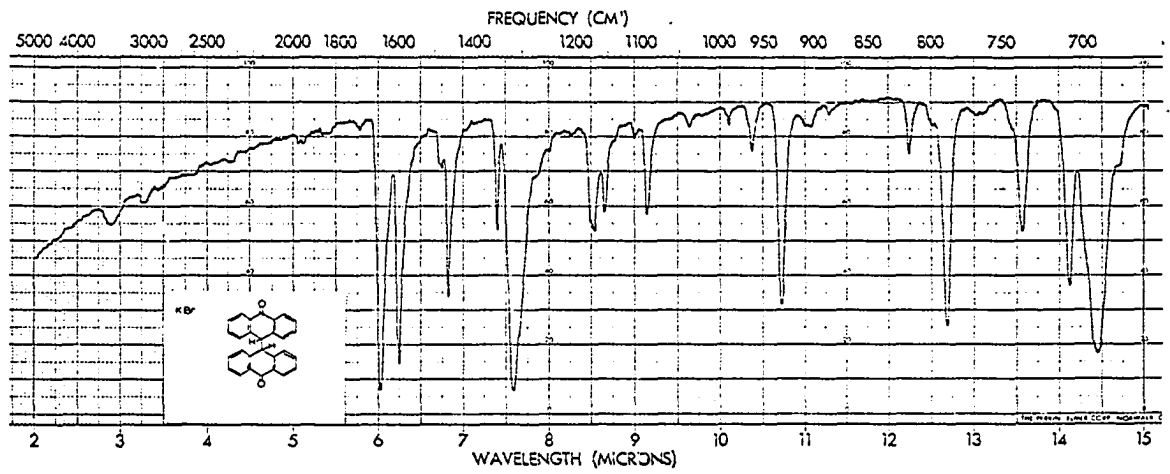
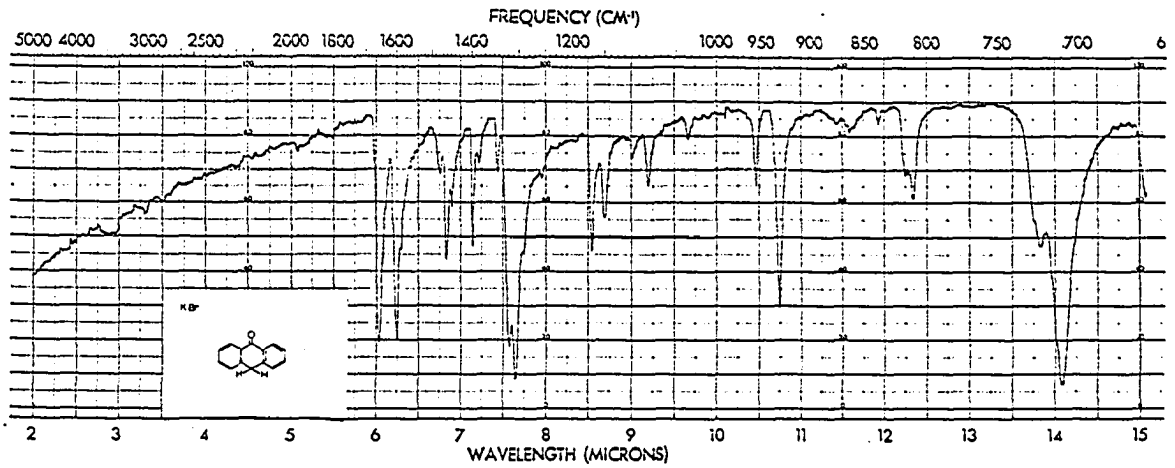


Figure 5. Infrared spectra

Top - Nitric oxide from the irradiation of
9-nitroanthracene (I)

Middle - Nitric oxide (authentic sample)

Bottom - 9,10-Dinitroanthracene (XCI)

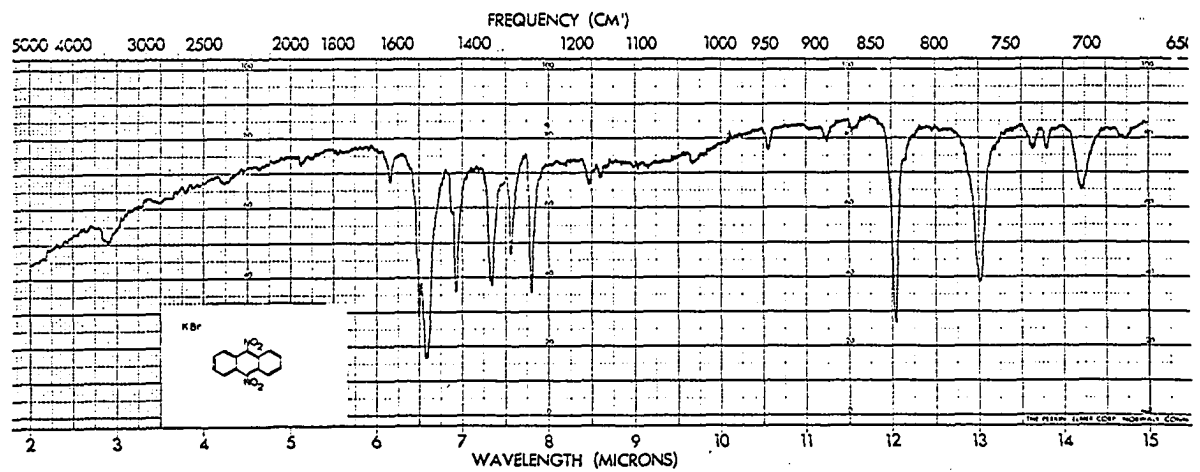
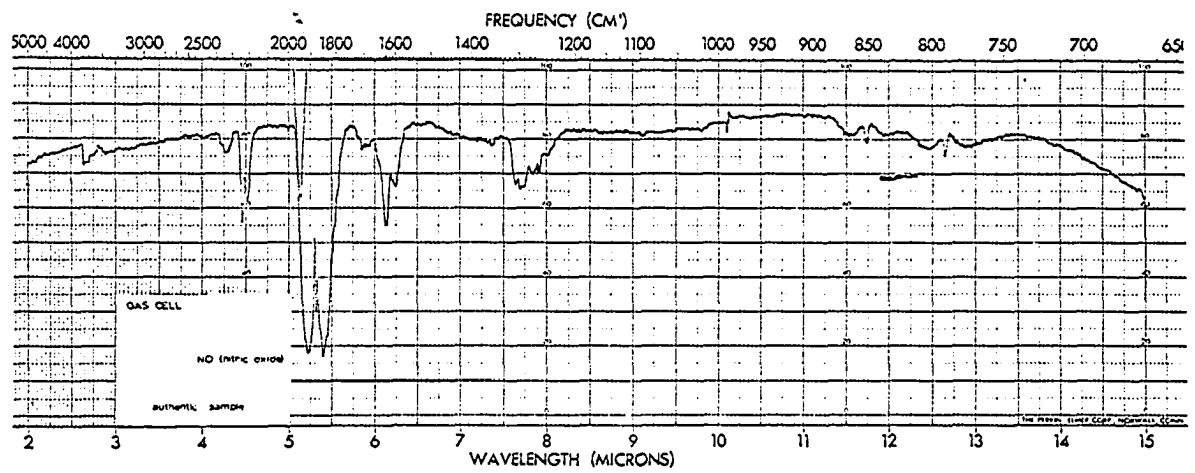
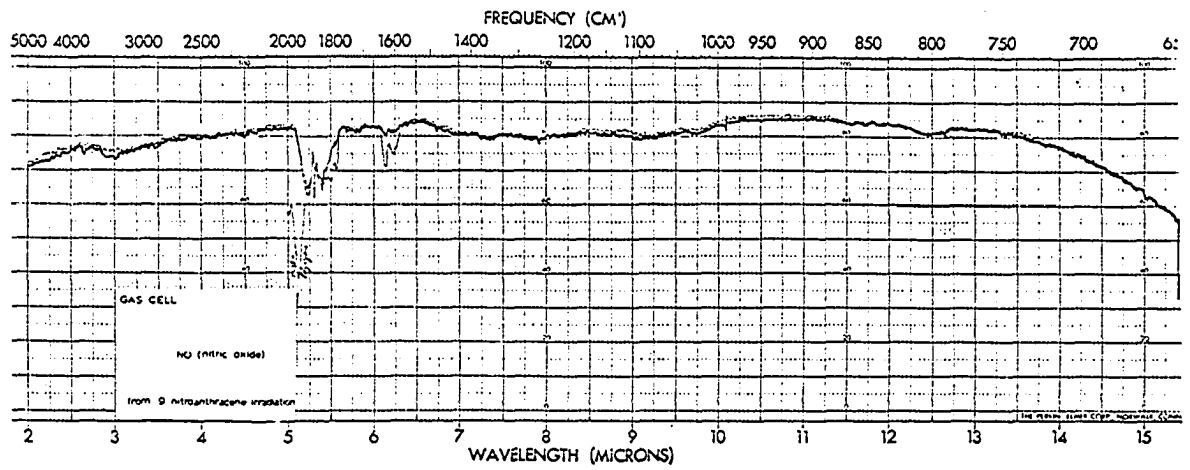


Figure 6. Infrared spectra

Top - 9-Nitroanthracene (I)

Middle - 9-Nitroanthracene (I) after 1 minute
irradiation in KBr.

Bottom - 9-Nitroanthracene (I) after 2 minutes
irradiation in KBr.

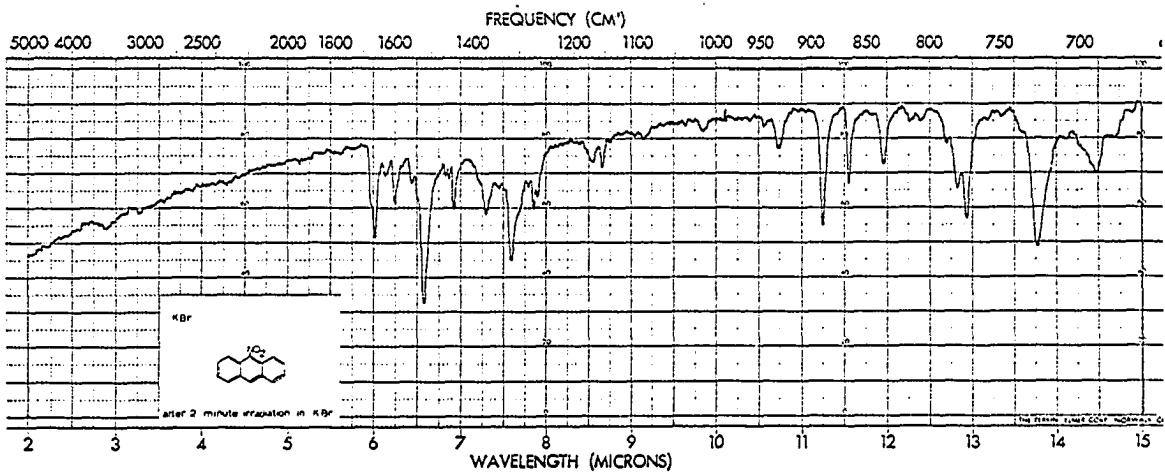
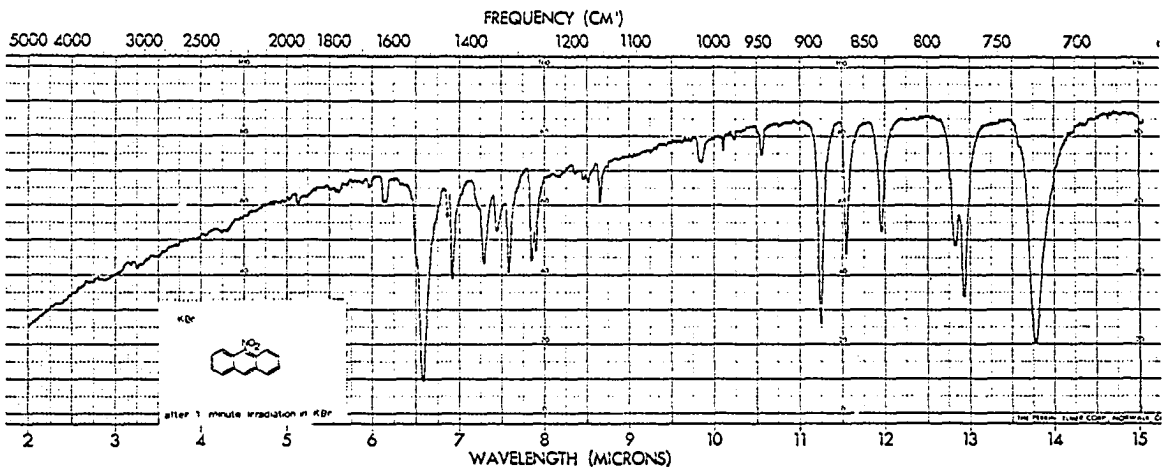
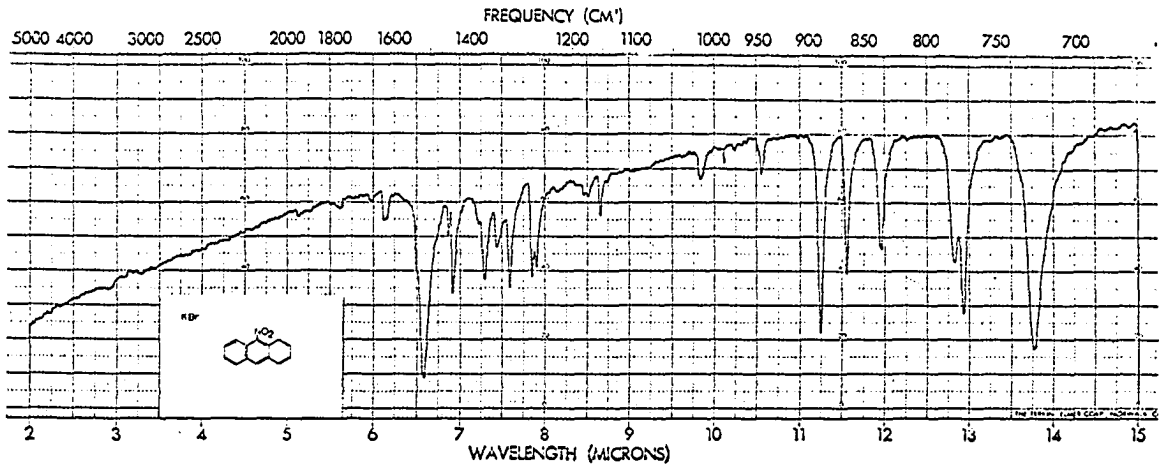


Figure 7. Infrared spectra

- Top - 9-Nitroanthracene (I) after 5 minutes irradiation in KBr.
- Middle - 9-Nitroanthracene (I) after 10 minutes irradiation in KBr.
- Bottom - 9-Nitroanthracene (I) after 15 minutes irradiation in KBr.

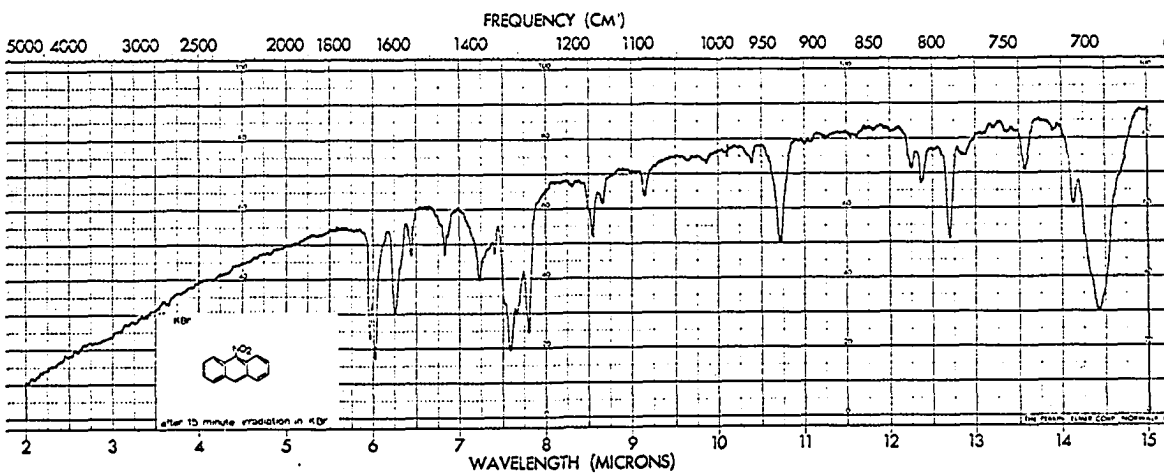
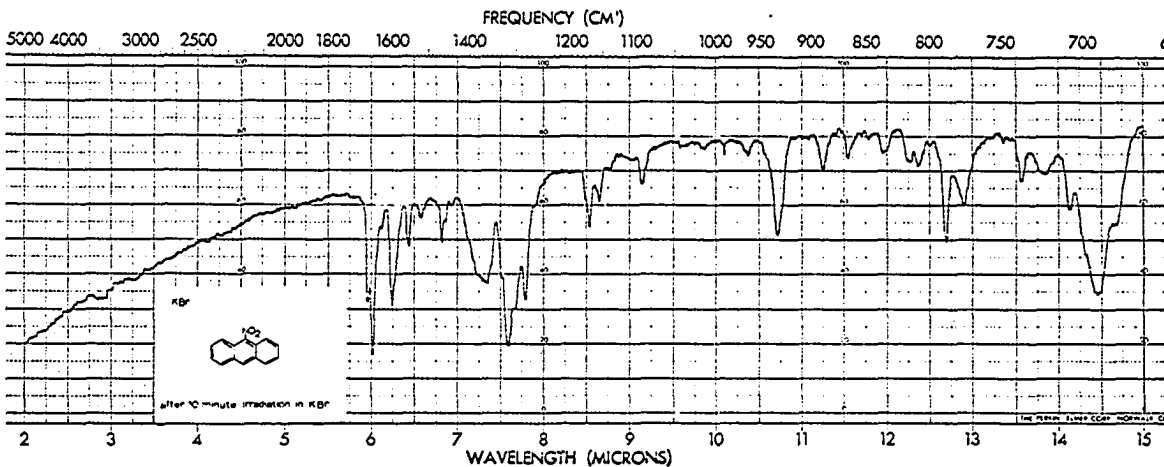
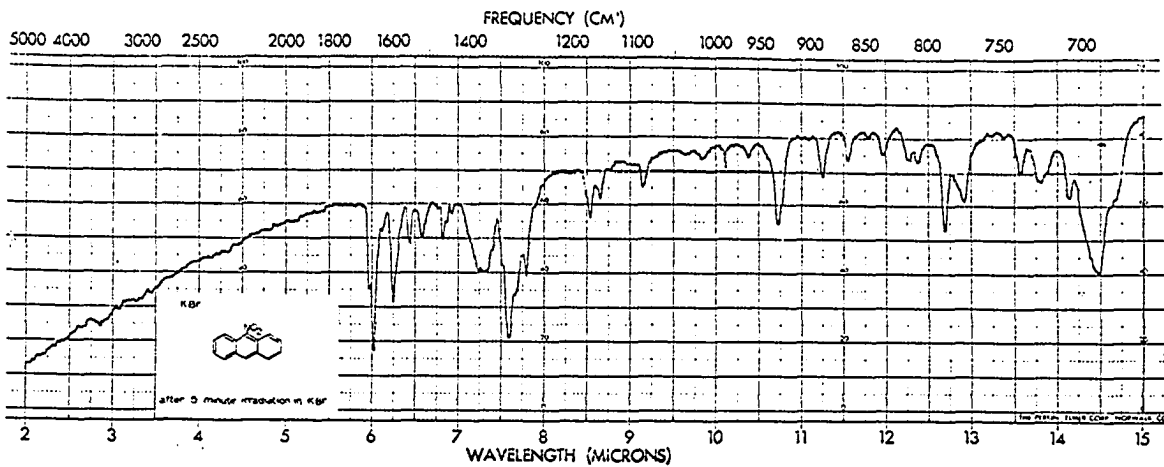
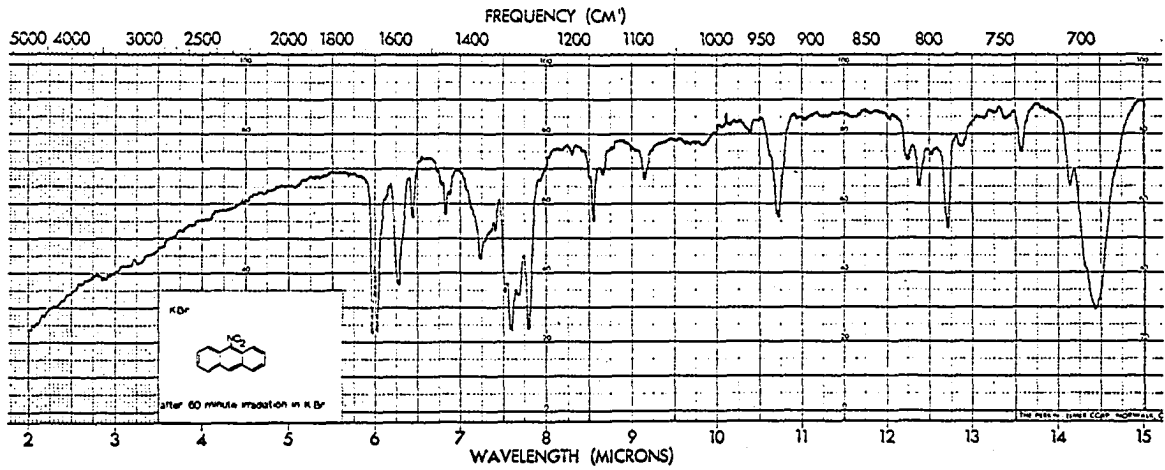
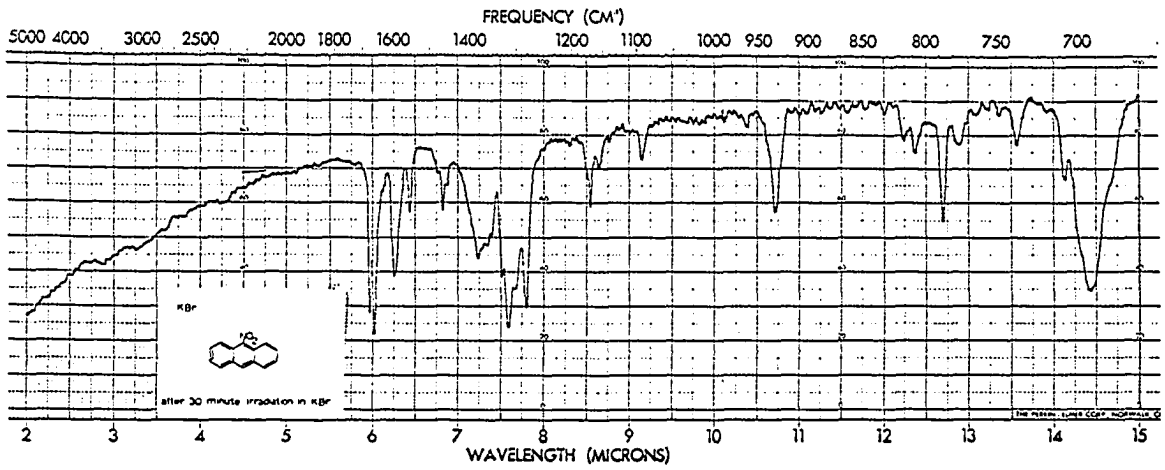


Figure 8. Infrared spectra

Top - 9-Nitroanthracene (I) after 30 minutes
irradiation in KBr.

Bottom - 9-Nitroanthracene (I) after 60 minutes
irradiation in KBr.



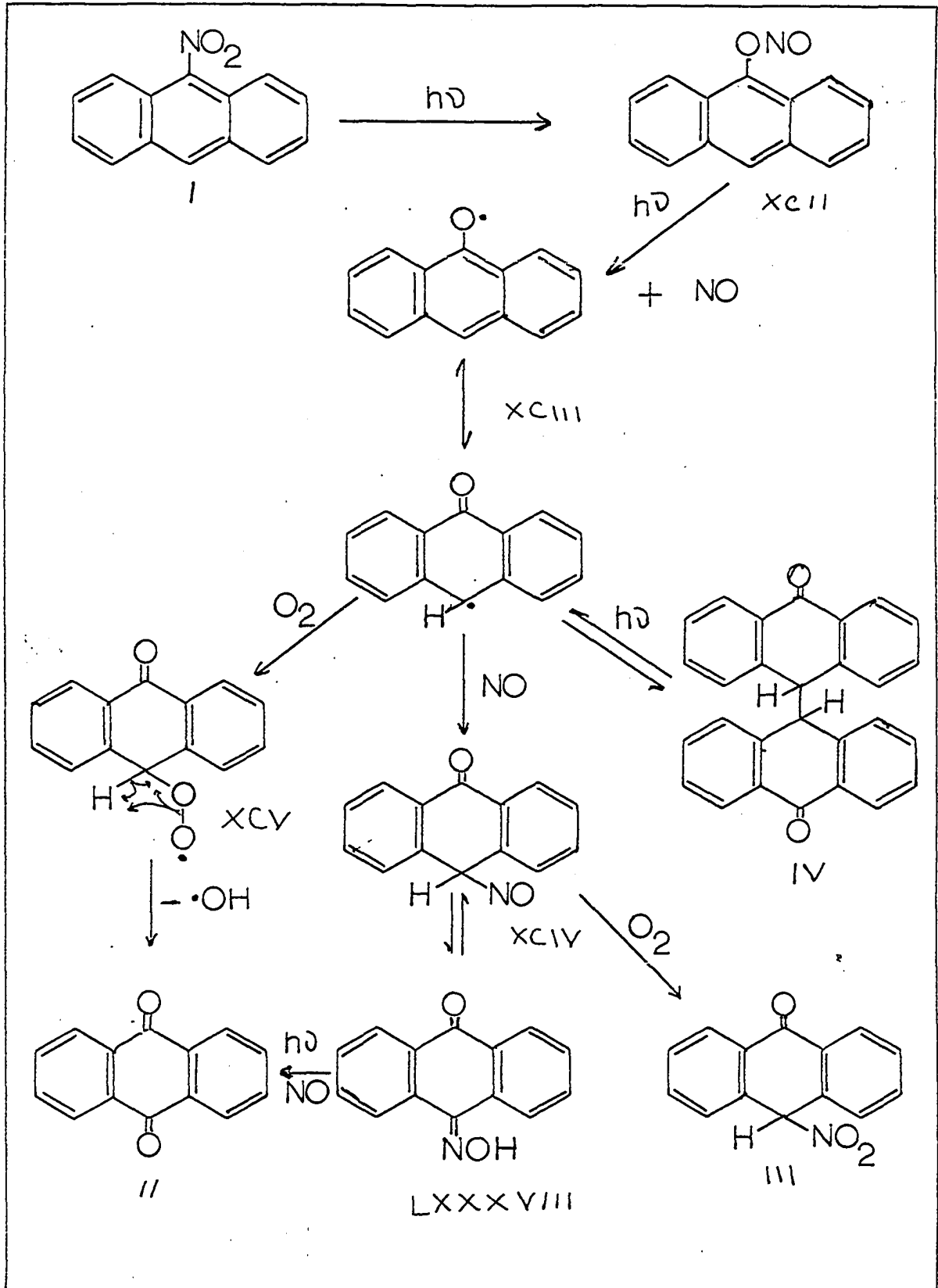
DISCUSSION

Photochemistry of 9-Nitroanthracene

The results described in the previous section can be considered in terms of the mechanistic path shown in Figure 9, page 53. Photoisomerization of the nitro compound (I) gives the nitrite ester (XCII) which can cleave thermally or photochemically to the 9-anthroxy radical (XCIII) and nitric oxide. Dimerization of two 9-anthroxy radicals (XCIII) would give 10,10'-bianthrone (IV), while addition of nitric oxide would give the nitrosoketone (XCIV). Addition of oxygen would give the ketoperoxy radical (XCV). Decomposition of the ketoperoxy radical (XCV) could give anthraquinone (II) and the hydroxyl radical. Oxidation of the nitrosoketone (XCIV) could give the nitroanthrone (III) reported by Dufraisse and Priou (3). Isomerization of the nitrosoketone (XCIV) would give anthraquinone monooxime (LXXXVIII). Irradiation of anthraquinone monooxime (LXXXVIII) in the presence or absence of nitric oxide gives anthraquinone (II). Each step in the mechanistic path will now be considered in the light of previous chemical knowledge and present results.

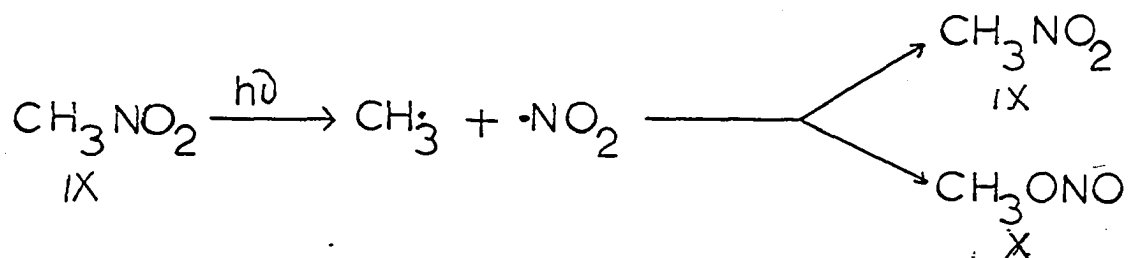
The wave length of the light involved in the irradiation of 9-nitroanthracene (I) must be longer than 290 millimicrons. An $n \rightarrow \pi^*$ excitation could occur from absorption of light of

Figure 9. Mechanistic path

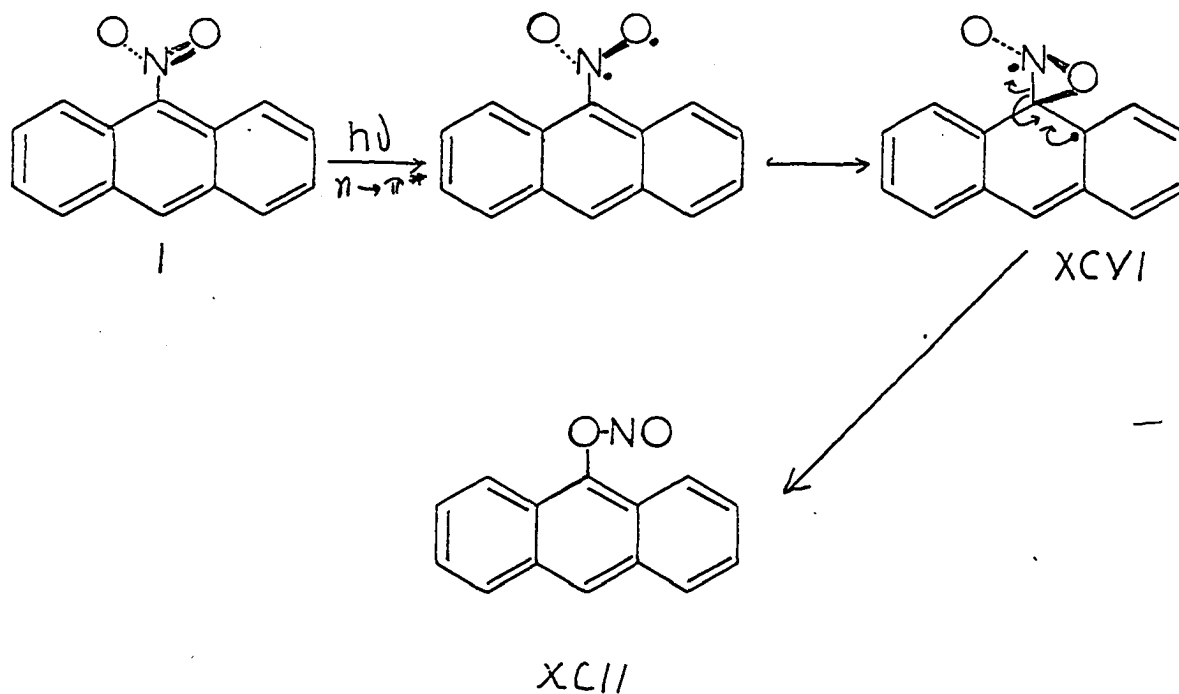


a wave length longer than 290 millimicrons. This would be consistent with the observation that an $n \rightarrow \pi^*$ excitation occurs in nitromethane at 270 millimicrons (1). Cherkasov (70,71) has observed that 9-nitroanthracene (I) does not fluoresce as do many of the 9-substituted anthracenes. This would suggest the possibility of efficient intersystem crossing to a triplet state. Greene (4) has reported that irradiation of 9-nitroanthracene (I) with light of wave length 370-410 millimicrons gives 10,10'-bianthrone (IV) (product from photochemical isomerization) and nitric oxide while light of wave length 420-530 millimicrons gives a photodimer (LXXXVII). Yang (72) has suggested that photoisomerization arises from an upper ($n \rightarrow \pi^*$) triplet state while photochemical dimerization arises from the low lying ($\pi \rightarrow \pi^*$) triplet state.

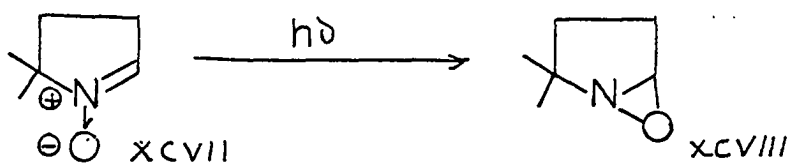
The photochemical isomerization of nitroalkanes to alkyl nitrites has been reported (12,13). At low temperature (20° K. in an argon matrix) the quantum yield for the conversion of nitromethane (IX) to methyl nitrite (X) is unity (12). Nitromethane (IX) gives methyl nitrite (X) and nitric oxide as the main products of the irradiation in the gas phase. Rebbert and Slagg (13) consider the primary process to be a photochemical cleavage of nitromethane (IX) to the methyl radical and nitrogen (IV) oxide. This type of mechanism may also be considered for the photochemical isomerization of 9-nitroanthracene (I). A second type of mechanism is also possible for



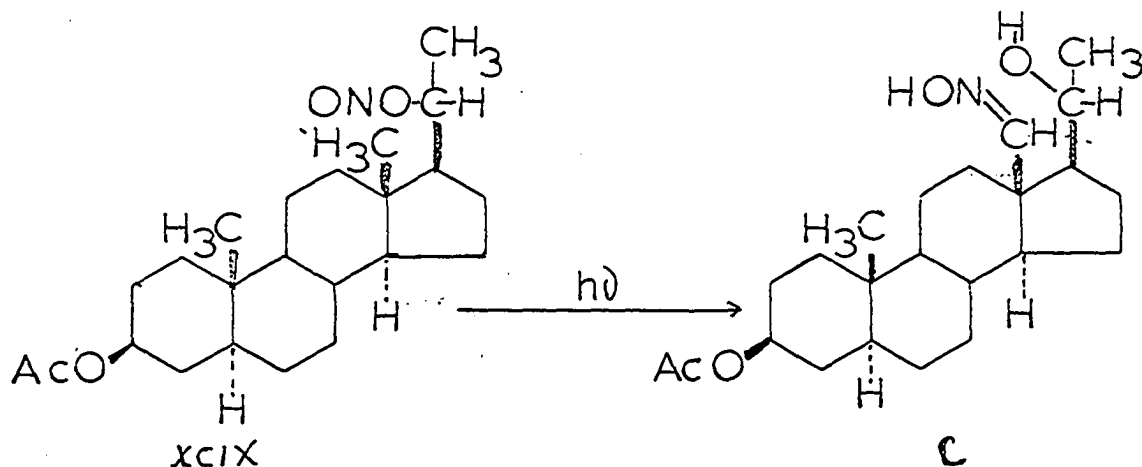
aryl nitrocompounds. Trotter (73) has reported that in the crystalline state the plane of the nitro group of 9-nitroanthracene (I) is tilted 85° out of the aromatic plane about the C-N bond.



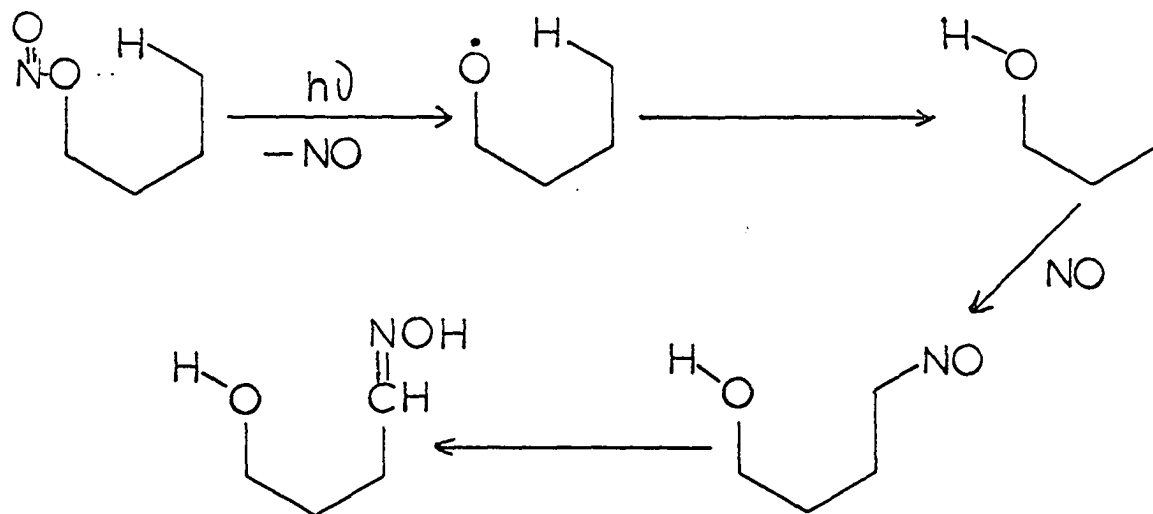
An analogy for the photoisomerization to the oxaziridine ring (XCVI) is the photochemical isomerization of XCVII to XCVIII (74).



The photolysis of organic nitrites has been recently reviewed (75). The photochemical cleavage of a nitrite to an alkoxy radical and nitric oxide is well known. Barton et al. (76) have studied, for example, the photochemical isomerization of XCIX to C. Barton et al. (76) have demonstrated that



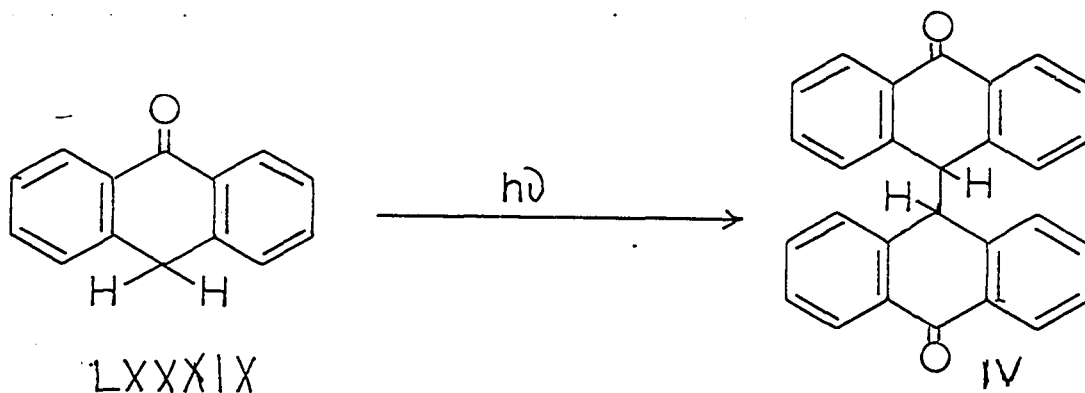
this type of reaction is general as shown in the scheme below.



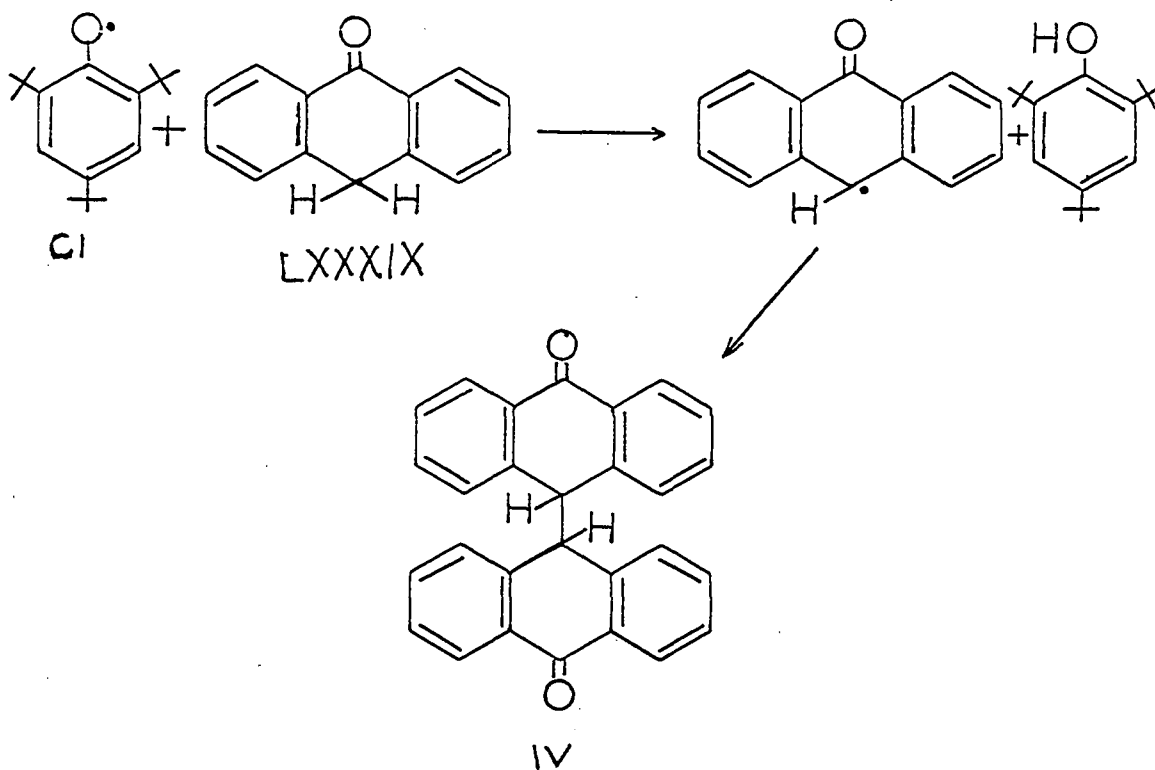
Photochemical or thermal cleavage of the nitrite ester (XCII) to the 9-anthroxy radical (XCIII) and nitric oxide is

consistent with the known reactions of organic nitrites.

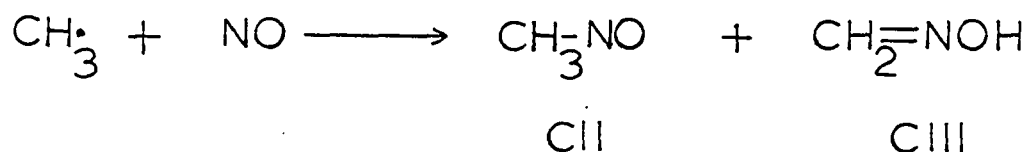
The dimerization of two 9-anthroxyl radicals (XCIII) to give 10,10'-bianthrone (IV) has several analogies. Irradiation of anthrone (LXXXIX) in benzene gives 10,10'-bianthrone (IV) (77). Treatment of anthrone (LXXXIX) with ferric chlo-



ride in hot acetic acid (58) or 2,4,6-tri-t-butylphenoxy radical (CI) also gives 10,10'-bianthrone (IV) (78).



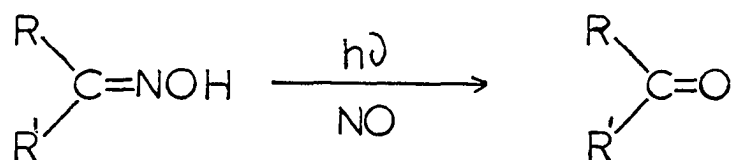
The reaction of the 9-anthroxy radical (XCIII) with nitric oxide is not unusual. Nitric oxide is considered to be a good radical scavenger. Coe and Doumani (79) have shown that the methyl radical reacts with nitric oxide to give nitrosomethane (CII) and formaldoxime (CIII).



The author knows of no analogy for the oxidation of the nitrosoketone (XCIV) to nitroanthrone (III) in neutral solution. The nitroanthrone (III) was isolated by Dufraisse and Priou (3). It was obtained from the irradiation of 9-nitroanthracene (I) in carbon disulfide in the presence of oxygen. The author has not isolated nitroanthrone (III) from the irradiation of 9-nitroanthracene (I) in chloroform, acetone, or carbon tetrachloride in the presence of oxygen.

The irradiation of anthraquinone monooxime (LXXXVIII) to give anthraquinone (II) has been reported by Meisenheimer (60). The author has verified this report. The conversion of anthraquinone monooxime (LXXXVIII) to anthraquinone (II) by irradiation in solution is too slow to account for the formation of anthraquinone (II) in the irradiation of 9-nitroanthracene (I). It has been shown in the present study, how-

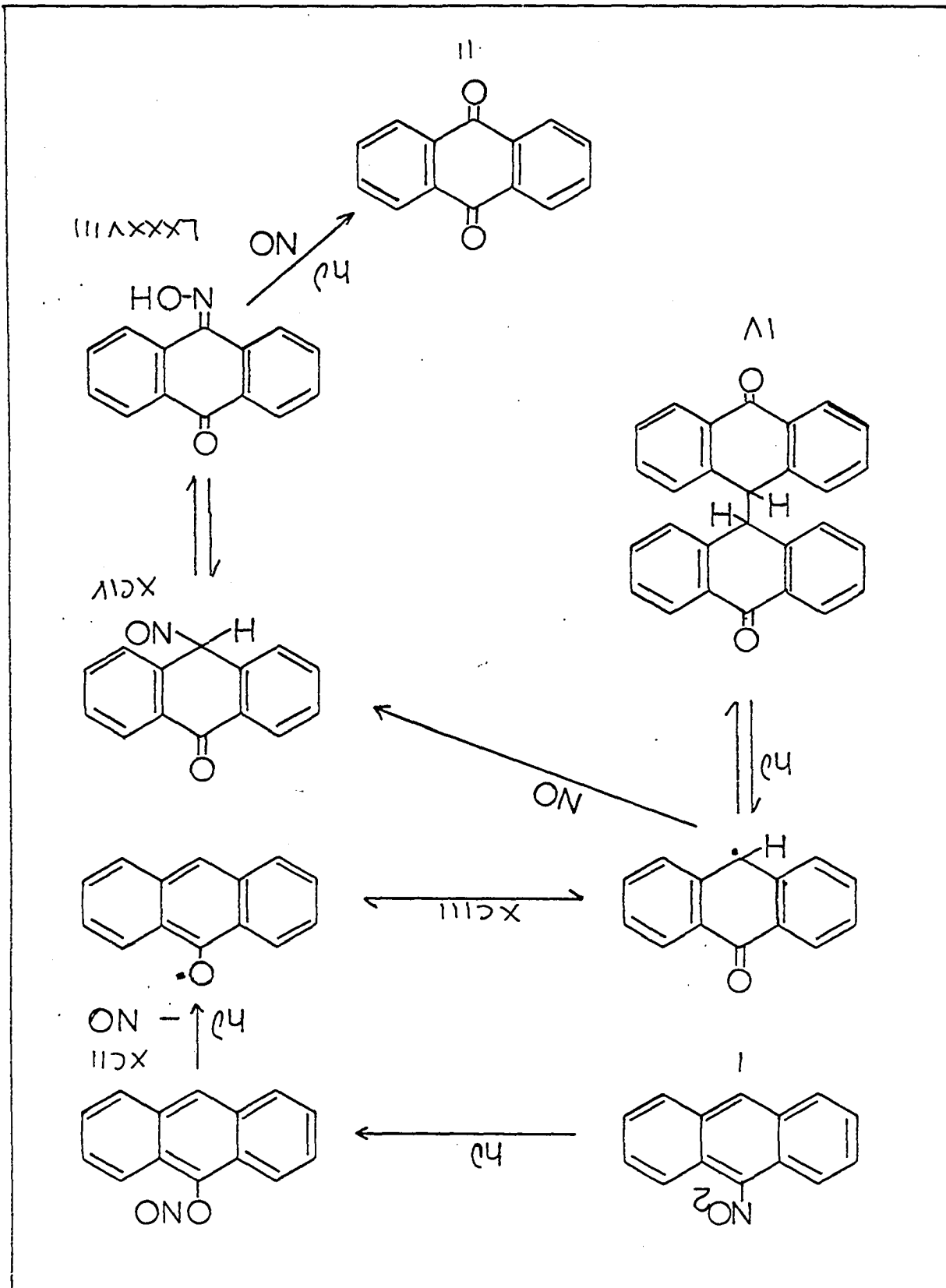
ever, that this photochemical transformation proceeds rapidly in the presence of nitric oxide. Nitric oxide apparently reacts with anthraquinone monooxime (LXXXVIII) in the dark to give a product of unknown composition. No anthraquinone carbonyl absorption is observed in the crude reaction mixture (see Figure 3, page 40). Chromatography of the reaction mixture on silica gel, however, gives a 75% yield of anthraquinone (II). The anthraquinone carbonyl band at 5.97 microns does appear in the infrared spectrum of the reaction mixture from the irradiation of anthraquinone monooxime (LXXXVIII) in the presence of nitric oxide. Chapman and Heckert (80) have shown that photochemical conversion of oximes to ketones in the presence of nitric oxide is a general reaction.



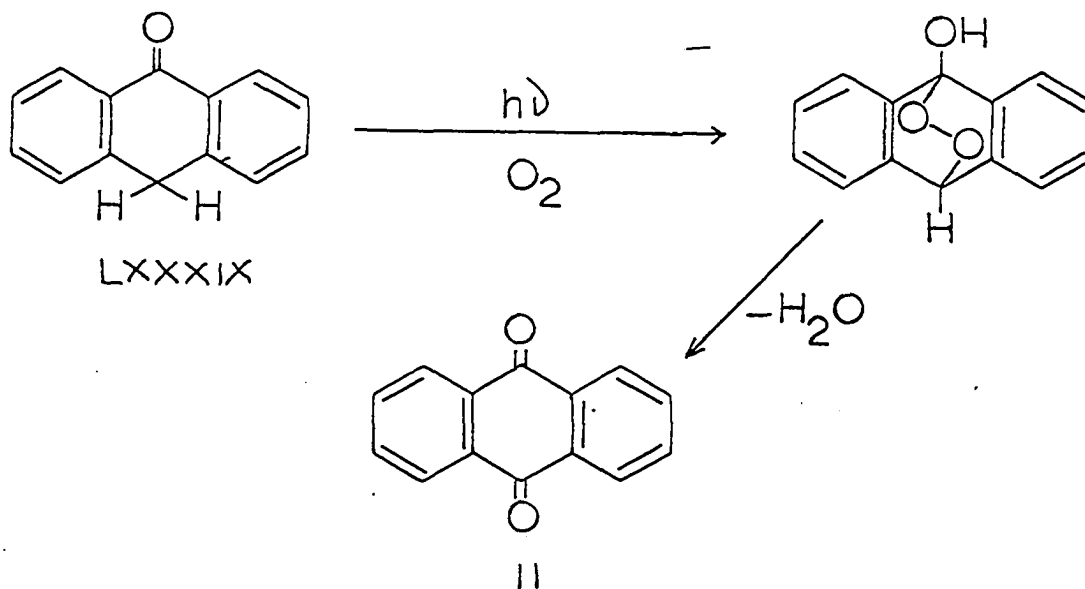
Apparently the low yields of anthraquinone (II) observed in the irradiation of rigorously degassed solutions of 9-nitroanthracene (I) arise from this type of reaction (see Figure 10, page 61). The primary reaction occurring in this case is the dimerization of two 9-anthroxy radicals (XCIII) to give 10,10'-bianthrone (IV).

The observation that the irradiation of anthrone (LXXXIX)

Figure 10. Possible mechanistic path for the formation of anthraquinone (II) from 9-nitroanthracene (I) in the absence of oxygen

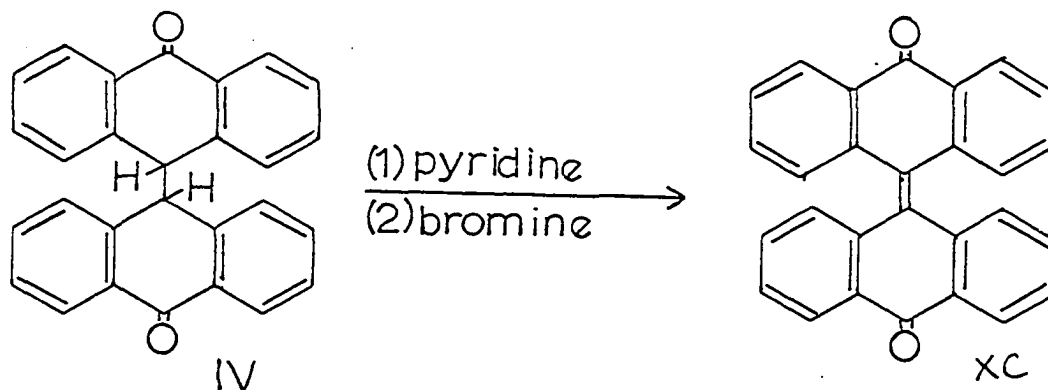


in the presence of oxygen gives a 90% yield of anthraquinone (II) is consistent with the postulated mechanistic path. The formation of an epidioxide, however, must also be considered in the case of the photochemical oxidation of anthrone (LXXXIX).

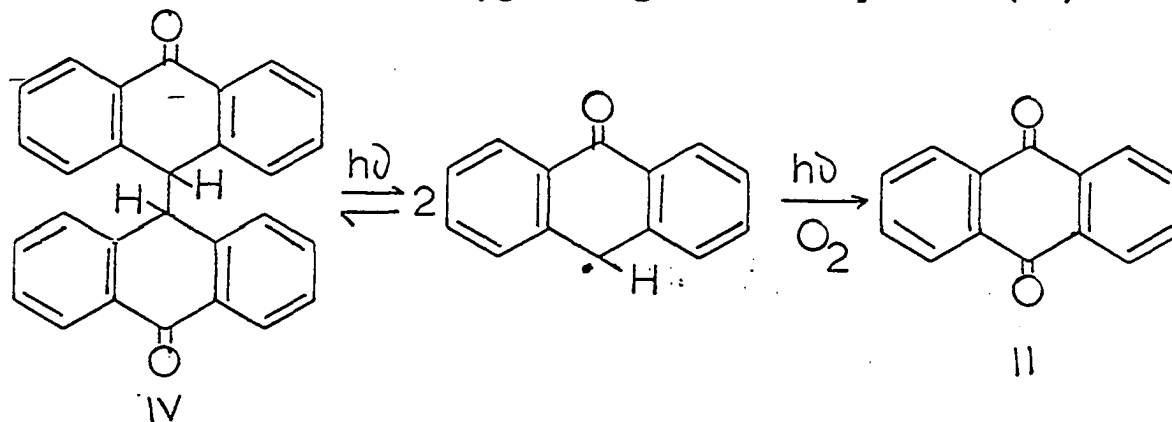


Photooxidation of 10,10'-Bianthrone
and Anthrone

A search of the literature reveals that 10,10'-bianthrone (IV) is relatively inert to further oxidation. A sample of 10,10'-bianthrone (IV) may be recrystallized from fuming nitric acid without change according to Meyer (81). A sample of 10,10'-bianthrone may be oxidized to $\Delta^{10,10'}$ -dehydrobianthrone (XC) by refluxing with pyridine followed by dropwise addition of bromine (63).



The author has found that 10,10'-bianthrone (IV) is inert to oxygen in the absence of light at the temperature of refluxing acetone. In the presence of light 10,10'-bianthrone (IV) is converted into anthraquinone (II) in 72% yield. This would suggest the possibility that irradiation of 10,10'-bianthrone (IV) could cause cleavage to two 9-anthroxy radicals (XCII) which could react with oxygen to give anthraquinone (II).



Anthrone (LXXXIX) reacts with mild oxidizing agents to give bianthrone (IV). Vigorous oxidation is required to convert anthrone (LXXXIX) to anthraquinone (II). The author has observed that irradiation of anthrone (LXXXIX) in a large excess of oxygen gives a 90% yield of anthraquinone (II).

Photochemistry of Anthraquinone Monooxime

Meisenheimer (60) has reported that anthraquinone monooxime (LXXXVIII) on exposure to light gives anthraquinone (II). Studies in this laboratory have shown that this conversion takes place slowly in acetone solution. It was found that the conversion occurs much more readily in the presence of nitric oxide. Chapman and Heckert (80) have irradiated several oximes in the presence of nitric oxide. They have found that the conversion of an oxime to a ketone-by irradiation in the presence of nitric oxide is a general reaction. The mechanism of this transformation is under active investigation by Chapman and Heckert (80).

EXPERIMENTAL

Instruments and Methods

All melting points are uncorrected and were measured on a Kofler microscope hot stage equipped with a polarizer.

The infrared spectra of all the compounds were obtained in potassium bromide unless otherwise indicated. The spectra were recorded on a Perkin-Elmer Model 21 spectrometer.

The analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York, unless otherwise noted.

A standard chromatographic procedure was used for the analysis of the products from the photochemical reaction.

The glass column was filled with benzene and a piece of Glass Wool was placed in the bottom of the column. A 2 to 3 centimeter layer of sand was added, and the column was tapped to level and pack the sand. The silica gel was weighed out (approximately 50 grams of silica gel per 1 gram of the material to be chromatographed). Enough benzene was added to make a slurry. The slurry was added dropwise to the column from a separatory funnel. The column was tapped during the dropwise addition of the silica gel to facilitate level packing. A 2 to 3 centimeter layer of sand was added to the top of the column to prevent the level of silica gel from being disturbed during addition of solvents.

The solvent from the photochemical reaction mixture was removed under reduced pressure. The residue was taken up in just enough hot benzene to effect solution. The benzene solution was poured onto the top of the column. Benzene (100%) was used as the first eluent. Fractions (150 milliliters unless otherwise specified) were collected and immediately evaporated under reduced pressure using a Rotovac. The forerun was discarded, and the bright yellow band of 9-nitroanthracene (I) was collected. As each of the 150 milliliter fractions was collected and evaporated, the residue was washed into a common pot with acetone or with chloroform. This was continued until no significant residue remained on the evaporation of a 150 milliliter fraction. As the chromatography was continued (still using 100% benzene as the eluent) any traces of residue were washed into a second common pot. This was continued until evaporation of a fraction (150 milliliter) gave a significant residue (anthraquinone). The anthraquinone (II) band was collected in the same manner as the 9-nitroanthracene (I) band.

An eluent of 100% benzene was also used to collect the anthraquinone monooxime (LXXXVIII) band if present. After no significant residue of anthraquinone monooxime (LXXXVIII) remained on evaporation of a fraction (150 milliliter), the eluent was changed to 100% chloroform or if after the anthraquinone (II) band had been collected and an additional 800 to

1000 milliliters of benzene had been passed through the column without isolation of anthraquinone monooxime (LXXXVIII), the eluent was changed to 100% chloroform.

The 10,10'-bianthrone (IV) was collected using 100% chloroform as the eluent. The 10,10'-bianthrone (IV) band was collected in the same manner as the 9-nitroanthracene (I) band. After no significant residue of 10,10'-bianthrone (IV) was obtained on evaporation of a fraction (150 milliliters) of chloroform, the eluent was changed to 100% methanol. The 100% methanol removed any remaining material from the silica gel column. The chromatography was continued until evaporation of a fraction of methanol gave no significant residue (tar).

Experimental for the Photochemistry
of 9-Nitroanthracene

Synthesis of 9-nitroanthracene (I) from anthracene (XXXVII)

Concentrated nitric acid (10 ml., 0.16 mole) was added to a solution of XXXVII (20.0 g., 0.11 mole) in glacial acetic acid (250 ml.). The reaction mixture was allowed to react for $\frac{1}{2}$ hour with the temperature being kept below 35°. The unreacted anthracene (XXXVII) was filtered off, and the filtrate was diluted with 4 volumes of distilled water. This solution was extracted twice with chloroform. The chloroform layers were combined and washed with 10% aqueous sodium carbonate and

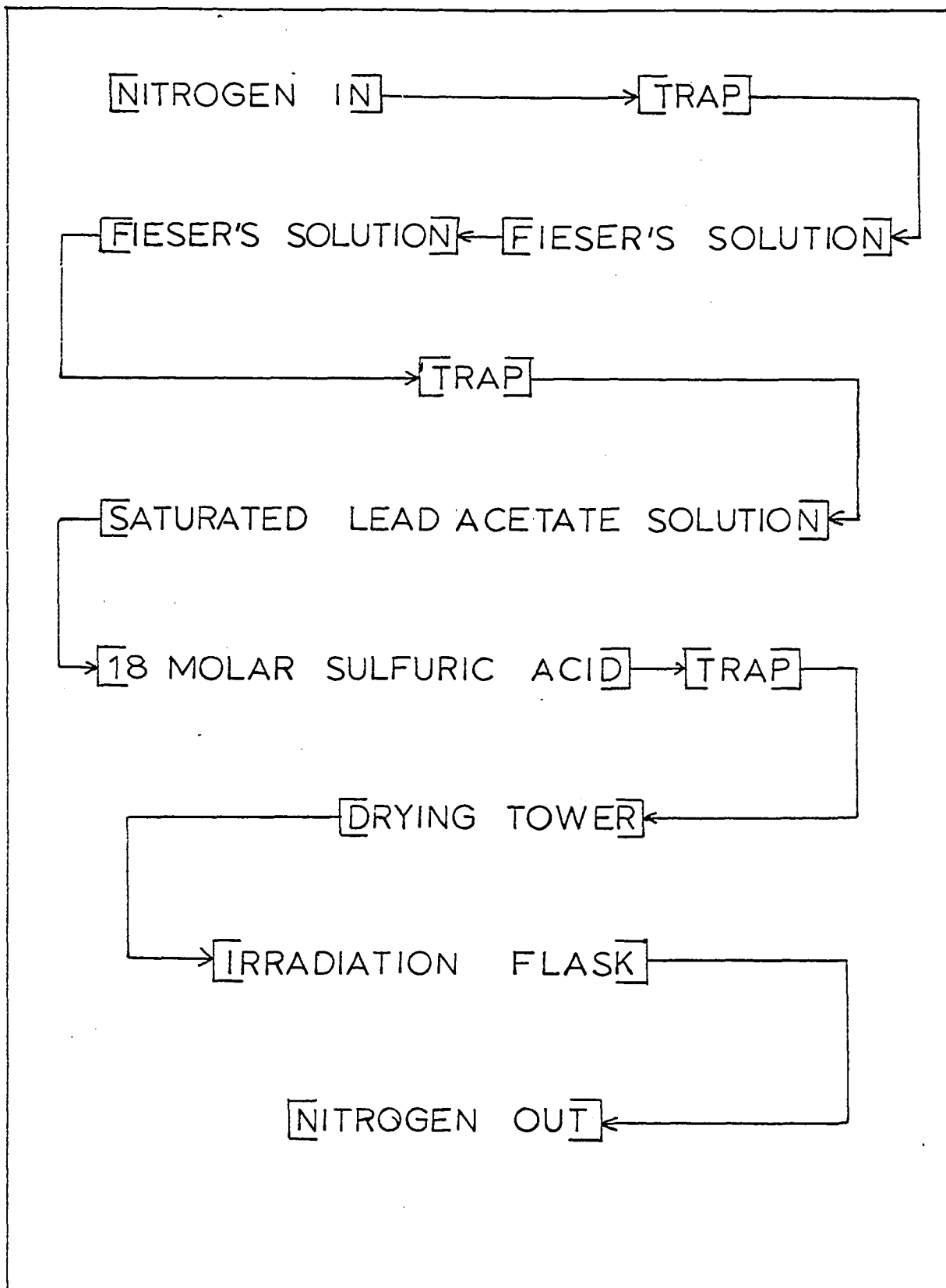
dried over anhydrous magnesium sulfate. The chloroform was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 400 g. of grade 1 neutral alumina. An eluent of 100% benzene gave 9-nitroanthracene (I) (13.41 g., 55% yield). The melting point was 144-146° (reported (82), 146°). The infrared spectrum (Figure 6, page 46) showed the nitro bands at 6.49 and 6.57 microns.

Irradiation of 9-nitroanthracene (I) in degassed acetone

A solution of I (4.0 g., 0.018 mole) in 250 ml. of acetone was degassed by passing purified nitrogen (see Figure 11, page 70) into the acetone solution with continuous stirring for $\frac{1}{2}$ hour. The solution was sealed in a Pyrex immersion well using rubber septum caps. The solution was irradiated for $1\frac{1}{2}$ hours with a Hanovia Type A medium-pressure mercury arc lamp. The acetone was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 300 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.83 g.	solid (m.p. 142-144°)
100% benzene	B	1.12 g.	solid (m.p. 285-286°)
100% benzene	C	0.15 g.	solid (m.p. 225-227°)
100% benzene	D	0.43 g.	solid (m.p. 193-220°)
100% chloroform	E	1.18 g.	solid (m.p. 246-253°)

Figure 11. Diagram showing method of purification of nitrogen



Fraction A (0.83 g., 21% of the sample weight) was shown by melting point (reported (82), 146°) and by infrared comparison with an authentic sample to be 9-nitroanthracene (I).

Fraction B (1.12 g., 30% yield) was shown by melting point (reported (83), $285-286^{\circ}$) and by infrared comparison with an authentic sample to be anthraquinone (II).

Fraction C (0.15 g., 4% yield) was shown by melting point (authentic sample melted at $228-230^{\circ}$), by hydrolysis to anthraquinone (II) in mineral acid, and by infrared comparison with an authentic sample to be anthraquinone monooxime (LXXXVIII).

Fraction D (0.43 g., 11% of the sample weight) was recrystallized from benzene-Skelly B to give 0.28 g. of a white solid. The melting point was $231-231.5^{\circ}$ (authentic sample melted at $228-230^{\circ}$). The infrared spectrum was identical with that of an authentic sample of anthraquinone monooxime (LXXXVIII). The yield of anthraquinone monooxime (LXXXVIII) isolated was 7%. The total yield from Fractions C and D was 11%.

Fraction E (1.18 g., 34% yield) was shown by infrared comparison with an authentic sample to be 10,10'-bianthrone (IV). An authentic sample of 10,10'-bianthrone (IV) melted at $259-261^{\circ}$.

Synthesis of anthraquinone (II) from
o-benzoylbenzoic acid (CIV)

Anthraquinone (II) was prepared according to the method outlined by Fieser (59). CIV (5.0 g., 0.022 mole; m.p. 126-127.5°) was placed in a 200 ml. round bottom flask and 25 ml. of 18 molar sulfuric acid added. The mixture was warmed on a steam bath until all the solid had dissolved. The solution was heated to 150-155° with a bunsen burner and held at that temperature for 5 minutes. The solution was allowed to cool to 100°, and 10 ml. of water was added dropwise. The reaction mixture was cooled to room temperature, and an additional 100 ml. of distilled water was added. The reaction mixture was filtered and washed twice with 1:5 dilute aqueous ammonia and once with water. The filter cake was washed twice with methanol and dried. This gave II (4.06 g., 88% yield) melting at 282-284° (reported (83), 285-286°). The infrared spectrum (Figure 3, page 40) showed the conjugated carbonyl at 5.97 microns in KBr.

Hydrolysis of anthraquinone monooxime (LXXXVIII)

LXXXVIII (0.22 g., 0.001 mole) was placed in a 50 ml. round bottom flask. Dioxane (10.0 ml.) and 20 ml. of 6 normal hydrochloric acid was added. This mixture was refluxed for 2½ hours. The reaction mixture was cooled and filtered. The filter cake was washed 3 times with distilled water and dried.

This gave 0.20 g. (96% yield) of anthraquinone (II) melting at 285-286° (reported (83), 285-286°).

Synthesis of anthraquinone monooxime (LXXXVIII) from 9-nitroanthracene (I)

Anthraquinone monooxime (LXXXVIII) was prepared by a method similar to that used by Meisenheimer (60). Potassium hydroxide (5.0 g., 0.075 mole) was dissolved in 50 ml. of methanol and 9-nitroanthracene (I) (2.0 g., 0.0089 mole) added. The mixture was refluxed for 8 hours on a steam bath. The reaction mixture was cooled in an ice bath, and cold dilute hydrochloric acid was added to pH 2. The acidified reaction mixture was extracted twice with diethyl ether, and the combined ether layers were dried over anhydrous magnesium sulfate. The ether was removed, and the residue was recrystallized from benzene to give anthraquinone monooxime (LXXXVIII) (1.94 g., 39% yield) melting at 228-230°. The infrared spectrum (Figure 3, page 40) showed the oxime hydroxyl band at 3.06 microns and the conjugated carbonyl at 6.07 microns in KBr.

Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.27; O, 14.35. Found: C, 75.25; H, 4.15; N, 6.45; O, 14.44.

Synthesis of 10,10'-bianthrone (IV) from anthracene (XXXVII)

The method of Barnett and Matthews (63) was used for the preparation of 10,10'-bianthrone (IV) from anthracene

(XXXVII). Recrystallized anthracene (XXXVII) (50.0 g., 0.28 mole) was added to 200 ml. of glacial acetic acid and 18 ml. (0.28 mole) of concentrated nitric acid was added. The mixture was allowed to react $\frac{1}{2}$ hour with occasional cooling to keep the temperature below 50° . The reaction mixture was filtered to remove unreacted anthracene (XXXVII), and the yellow solution was placed in a 500 ml. round bottom flask with a condenser and heated on a steam bath for 45 minutes. The reaction mixture was cooled in an ice bath and filtered. This gave a light yellow solid. The solid was recrystallized from benzene to give 12.60 g. (24% yield) of 10,10'-bianthrone (IV) melting at $259-261^{\circ}$ with decomposition. The infrared spectrum (Figure 4, page 42) showed the conjugated carbonyl at 6.02 microns in KBr.

Synthesis of 10,10'-bianthrone (IV) from anthrone (LXXXIX)

A 10% solution of sodium hydroxide in distilled water was heated on a steam bath and degassed by passing nitrogen into the hot solution for 15 minutes. LXXXIX (10.0 g., 0.052 mole) was added, and a solution of potassium ferricyanide (16.5 g., 0.05 mole) in 100 ml. of distilled water was added dropwise. The stream of nitrogen was maintained during the addition of potassium ferricyanide. The reaction mixture was filtered, and the filter cake was washed twice with water and once with acetone. The filter cake was dried and recrystallized from

benzene-Skelly B to give 4.90 g. (50% yield) of 10,10'-bi-anthrone (IV) melting at 259-261° with decomposition. The infrared spectrum (Figure 4, page 42) showed the conjugated carbonyl at 6.02 microns in KBr.

Synthesis of $\Delta^{10,10'}$ -dehydrobianthrone (XC) from 10,10'-bianthrone (IV)

The preparation of $\Delta^{10,10'}$ -dehydrobianthrone (XC) followed the method of Barnett and Matthews (63). Pyridine (40 ml.) was added to IV (5.0 g., 0.013 mole; m.p. 258-260°), and the mixture was refluxed for 10 hours. The reaction mixture was cooled in an ice bath. Bromine (2.1 g., 0.013 mole) in 15 ml. of pyridine was added dropwise. The mixture was allowed to react for 1 hour at room temperature. The solid was filtered off and washed once with pyridine and twice with diethyl ether. The solid was added to 100 ml. of 10% hydrochloric acid and boiled for one hour. The solid was filtered off and dried. This gave $\Delta^{10,10'}$ -dehydrobianthrone (XC) (2.1 g., 41% yield) with a melting point above 325° (reported (84), above 300°). The infrared spectrum (Figure 4, page 42) showed a conjugated carbonyl at 6.01 microns in KBr.

Sealed tube irradiation of 9-nitroanthracene (I) in degassed acetone

A solution of I (1.5 g., 0.0067 mole) in 120 ml. of acetone in a Pyrex tube fitted with a vacuum stopcock was degas-

sed with purified nitrogen (see Figure 11, page 70). This was accomplished by passing purified nitrogen into the solution for 1 hour. The tube was sealed and irradiated with a Hanovia Type A medium-pressure mercury arc lamp for $6\frac{1}{2}$ hours. The lamp was encased in the condenser from a Pyrex immersion well for cooling. The distance from the lamp to the irradiation tube was 3 cm. There was a vigorous liberation of gas when the stopcock was opened after the irradiation. This solution was purged with nitrogen to remove the nitric oxide. The acetone was removed under reduced pressure. The residue was taken up in hot benzene and chromatographed on 75 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.09 g.	solid (m.p. 285-286°)
100% benzene	B	0.09 g.	solid (m.p. 219-222°)
100% benzene	C	0.10 g.	solid (m.p. 220-223°)
100% chloroform	D	0.80 g.	solid (m.p. 254-258°)

Fraction A (0.09 g., 6% yield) was shown by melting point (reported (83), 285-286°) and by infrared comparison with an authentic sample to be anthraquinone (II).

Fraction B (0.09 g., 6% yield) was shown by the melting point (authentic sample melted at 228-230°) and by infrared comparison with an authentic sample to be anthraquinone monooxime (LXXXVIII).

Fraction C (0.10 g., 6% yield) was shown from the melting

point (authentic sample melted at 228-230°) to be anthraquinone monooxime (LXXXVIII). The infrared spectrum (Figure 3, page 40) of Fraction C was shown to be identical to that of an authentic sample of anthraquinone monooxime (LXXXVIII).

Fraction D (0.80 g., 61% yield) was shown by melting point (authentic sample melted at 259-261°) to be 10,10'-bianthrone (IV). The infrared spectrum (Figure 4, page 42) was shown to be identical with that of an authentic sample of 10,10'-bianthrone (IV).

Sealed tube irradiation of 9-nitroanthracene (I)
in degassed carbon tetrachloride

A solution of I (2.05 g., 0.009 mole) in 120 ml. of carbon tetrachloride was poured into a Pyrex tube fitted with a vacuum stopcock. The solution was degassed by passing purified nitrogen (see Figure 11, page 70) into the solution for 2 hours. The carbon tetrachloride solution was frozen in a Dry Ice-acetone bath and pumped on with an oil diffusion pump at 0.9 mm. of mercury for $\frac{1}{2}$ hour. The tube was sealed and the carbon tetrachloride solution allowed to liquify. The tube was placed in a Dry Ice-acetone bath and the solution was refrozen. The tube was pumped on with an oil diffusion pump at 0.8 mm. of mercury for $\frac{1}{2}$ hour. The tube was sealed and the carbon tetrachloride solution allowed to reliquify. The tube was placed in a Dry Ice-acetone bath and the solution frozen again. The tube was pumped on with an oil diffusion

pump at 0.9 mm. of mercury for $\frac{1}{2}$ hour. The tube was sealed with the vacuum stopcock, and the carbon tetrachloride solution was allowed to warm to room temperature. The tube was irradiated for 5 hours with a Hanovia Type A medium-pressure mercury arc lamp. The lamp was encased in the condenser from a Pyrex immersion well for cooling purposes. The irradiation tube was clamped 3 cm. from the lamp. The vacuum stopcock was opened, and evolution of gas was observed. The carbon tetrachloride was taken off under reduced pressure. The residue was taken up in hot benzene and chromatographed on 75 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.12 g.	solid (m.p. 250-270°)
100% benzene	B	0.07 g.	solid (m.p. 262-274°)
100% chloroform	C	1.34 g.	solid (m.p. 252-256°)
100% chloroform	D	0.15 g.	solid (m.p. 262-263.5°)

Fraction A (0.12 g., 6% of the sample weight) was shown by infrared comparison to be impure anthraquinone (II).

Fraction A was treated with hot methanol. Filtration of the cooled solution gave 0.05 g. (3% yield) of anthraquinone (II) melting at 278-281° (reported (83), 285-286°).

Fraction B (0.07 g., 3% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.05 g. (3% yield) of anthraquinone (II) melting at 282-284° (reported (83), 285-286°). The infrared spectrum (Figure 3,

page 40) of the recrystallized sample was identical with that of an authentic sample of anthraquinone (II).

Fraction C (1.34 g., 77% yield) was shown by the melting point (authentic sample melted at 259-261°) and by infrared comparison with an authentic sample to be 10,10'-bianthrone (IV).

Fraction D (0.15 g., 9% yield) was shown by melting point (authentic sample melted at 259-261°) and by infrared comparison with an authentic sample to be 10,10'-bianthrone (IV).

Irradiation of 9-nitroanthracene (I) in acetone with nitrogen flush

A solution of I (2.25 g., 0.010 mole) in 250 ml. of acetone in a Pyrex immersion well was degassed by passing purified nitrogen (see Figure 11, page 70) into the solution for $\frac{1}{2}$ hour. The solution was irradiated for 2 hours with a Hanovia Type A medium-pressure mercury arc lamp. A stream of nitrogen was maintained during the irradiation. The exit gases from the irradiation flask were passed through 2 Dry Ice-acetone traps. The gasses from the Dry Ice-acetone traps were bubbled through 2 bottles of cold concentrated ferrous sulfate solution. At the end of the irradiation the ferrous sulfate solutions were a deep brown color. The ferrous sulfate solutions were combined and connected to a vacuum line and allowed to warm under reduced pressure. The gasses liberated during the warming were collected in the vacuum line and passed

through a Dry Ice-acetone trap into a liquid nitrogen trap. The material which had collected in the liquid nitrogen trap was collected in an infrared gas cell, and the infrared spectrum (Figure 5, page 44) was taken. The infrared was shown to be identical with the infrared spectrum (Figure 5, page 44) of an authentic sample of nitric oxide. The gas which had collected in the liquid nitrogen trap also gave a brown ring test with a ferrous sulfate solution.

The acetone solution from the irradiation was filtered to give 0.62 g. of white crystals melting at 260-262° with decomposition (authentic sample melted at 259-261°). Infrared comparison with an authentic sample indicated the compound to be 10,10'-bianthrone (IV). The filtrate was warmed under reduced pressure to remove the acetone. The residue was taken up in hot benzene and chromatographed on 150 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.01 g.	solid (m.p. 138-250°)
100% benzene	B	0.17 g.	solid (m.p. 282-284°)
100% benzene	C	0.09 g.	solid (m.p. 195-210°)
100% benzene	D	0.07 g.	solid (m.p. 215-218°)
100% chloroform	E	0.71 g.	solid (m.p. 198-237°)
100% chloroform	F	0.10 g.	solid (m.p. 250-255° dec.)

Fraction A (0.01 g., 0.4% of the sample weight) was shown by infrared comparison to be a mixture of starting material

and anthraquinone (II). No further characterization was attempted.

Fraction B (0.17 g., 8% yield) was shown by melting point (reported (83), 285-286°) and by comparison of the infrared spectrum (Figure 3, page 40) with the infrared spectrum of an authentic sample of anthraquinone (II).

Fraction C (0.09 g., 4% of the sample weight) was recrystallized from benzene to give 0.02 g. of white crystals melting at 216-218° (authentic sample melted at 228-238°). The infrared spectrum (Figure 3, page 40) was found to be identical with the infrared spectrum of an authentic sample of anthraquinone monooxime (LXXXVIII). The recrystallized yield was 1%.

Fraction D (0.07 g., 3% yield) was shown by melting point (authentic sample melted at 228-230°) and infrared comparison with an authentic sample to be anthraquinone monooxime (LXXXVIII).

Fraction E (0.71 g., 32% of the sample weight) was shown by infrared comparison to be a mixture of 10,10'-bianthrone (IV) and anthraquinone monooxime (LXXXVIII). Fraction E was recrystallized from benzene to give 0.49 g. of anthraquinone monooxime (LXXXVIII). Infrared analysis of the residue from the mother liquor (0.19 g.) indicated it to be nearly pure 10,10'-bianthrone (IV). The yields were 22% anthraquinone monooxime (LXXXVIII) and 12% 10,10'-bianthrone (IV).

Fraction F (0.10 g., 5% yield) was shown by melting point (authentic sample melted at 259-261°) and by comparison of the spectrum with that of an authentic sample to be 10,10'-bianthrone (IV).

Irradiation of 9-nitroanthracene (I) in acetone with nitrogen flush

A solution of I (4.2 g., 0.019 mole) in 400 ml. of acetone was degassed with purified nitrogen (see Figure 11, page 70) for $\frac{1}{2}$ hour. The degassing was accomplished by passing purified nitrogen into the continuously stirred solution. The solution was irradiated for 3 hours with a Hanovia Type A medium-pressure mercury arc lamp. A rapid stream of nitrogen from a gas dispersion tube was passed into the solution during the irradiation. The acetone was removed under reduced pressure. The residue was taken up in hot benzene and chromatographed on 300 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.06 g.	solid (m.p. 134-142°)
100% benzene	B	0.25 g.	solid (m.p. 274-282°)
100% benzene	C	0.05 g.	solid (m.p. 204-248°)
100% chloroform	D	3.08 g.	solid (m.p. 235-240°)

Fraction A (0.06 g., 1% of the sample weight) was recrystallized from cyclohexane to give 0.04 g. (1% yield) of starting material melting at 141-143° (reported (82), 146°). The

infrared spectrum (Figure 6, page 46) was identical with that of the starting material.

Fraction B (0.25 g., 6% of the sample weight) was treated with hot methanol. The cooled solution was filtered to give 0.22 g. (6% yield) melting at 280.5-282° (reported (83), 285-286°). The infrared spectrum (Figure 3, page 40) was shown to be identical with that of an authentic sample of anthraquinone (II).

Fraction C (0.05 g., 1% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.03 g. (1% yield) of white crystals melting at 246-250° (authentic sample melted at 259-261°). The infrared spectrum (Figure 4, page 42) was shown to be identical with that of an authentic sample of 10,10'-bianthrone (IV).

Fraction D (3.08 g.) was treated with hot methanol. Filtration of the cooled solution gave 2.93 g. (80% yield) of white crystals melting at 245-249° with decomposition (authentic sample melted at 259-261°). The infrared spectrum (Figure 4, page 42) was shown to be identical with that of an authentic sample of 10,10'-bianthrone (IV).

Irradiation of 9-nitroanthracene (I) in non-degassed acetone-acetic acid (95-5)

A solution of I (4.8 g., 0.022 mole) in 250 ml. of acetone-acetic acid was irradiated for 2 hours with a Hanovia Type A medium-pressure mercury arc lamp in a Pyrex immersion

well. Filtration of the solution after irradiation gave 1.90 g. (45% yield) of white crystals melting at 256-261° with decomposition (authentic sample melted at 259-261°). Infrared comparison with an authentic sample indicated that the compound was 10,10'-bianthrone (IV). The irradiation solvent was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 250 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.43 g.	solid (m.p. 131-139°)
100% benzene	B	0.93 g.	solid (m.p. 285-286°)
100% chloroform	C	0.46 g.	solid (m.p. 252-255°)
100% methanol	D	0.18 g.	tar

Fraction A (0.43 g., 9% of the sample weight) was shown by infrared comparison to be impure starting material. Fraction A was recrystallized from cyclonexane to give I (0.38 g., 8% yield) melting at 142-144° (reported (82), 146°).

Fraction B (0.93 g., 21% yield) was shown by melting point (reported (83), 285-286°) and by infrared comparison with an authentic sample to be anthraquinone (II).

Fraction C (0.46 g., 11% yield) was shown by melting point (authentic sample melted at 259-261°) and by infrared comparison with an authentic sample to be 10,10'-bianthrone (IV).

Fraction D (0.18 g., 4% of the sample weight) was found

to have a rather ill-defined infrared spectrum. Attempted recrystallization from methanol was unsuccessful. No further characterization was attempted.

Irradiation of 9-nitroanthracene (I) in chloroform open to the atmosphere

A solution of I (1.47 g., 0.0066 mole) in 200 ml. of chloroform in a quartz tube with an internal cooling coil was irradiated for 24 days with a General Electric UA-3 medium-pressure mercury arc lamp. The lamp was located 30 cm. from the irradiation tube. The chloroform was removed under reduced pressure. The residue was taken up in hot benzene and chromatographed on 150 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.19 g.	gum
100% benzene	B	0.90 g.	solid (m.p. 281-284°)
100% benzene	C	0.04 g.	solid (m.p. 240-276°)
100% chloroform	D	0.02 g.	tar
100% methanol	E	0.26 g.	tar

Fraction A (0.19 g., 13% of the sample weight) had an ill-defined infrared spectrum. Fraction A could not be recrystallized from methanol or acetone. No further characterization was attempted.

Fraction B (0.90 g., 61% yield) was shown by melting point (reported (83), 285-286°) and by infrared comparison

with an authentic sample to be anthraquinone (II).

Fraction C (0.04 g., 3% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.02 g. (1% yield) of anthraquinone (II) melting at 282-284° (reported (83), 285-286°).

Fraction D (0.02 g., 1% of the sample weight) could not be recrystallized from methanol or from acetone. No further characterization was attempted.

Fraction E (0.26 g., 18% of the sample weight) gave an ill-defined infrared spectrum. Fraction E could not be obtained in crystalline form. No further characterization was attempted.

Irradiation of 9-nitroanthracene (I) in chloroform saturated with oxygen

A solution of I (4.2 g., 0.019 mole) in 250 ml. of chloroform in a Pyrex immersion well was saturated with oxygen by passing oxygen into the continuously stirred solution for $\frac{1}{2}$ hour. The solution was irradiated open to the atmosphere for 3 hours using a Hanovia Type A medium-pressure mercury arc lamp. At the end of this time the chloroform solution was very dark in color. The chloroform was taken off under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 250 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.10 g.	solid (m.p. 98-102°)
100% benzene	B	1.37 g.	solid (m.p. 278.5-280°)
100% benzene	C	0.05 g.	solid (m.p. 272-280°)
100% chloroform	D	1.21 g.	solid (m.p. 259-261° dec.)
100% methanol	E	0.94 g.	tar

Fraction A (0.10 g., 2.4% of sample weight) was shown by infrared comparison to be impure starting material. Fraction A was recrystallized from cyclohexane to give I (0.07 g., 2% yield) melting at 141-143° (reported (82), 146).

Fraction B (1.37 g., 35% yield) was shown by melting point (reported (83), 285-286°) and by infrared comparison with an authentic sample to be anthraquinone (II).

Fraction C (0.05 g., 1% of sample weight) was shown by infrared comparison to be impure anthraquinone (II). No further characterization was attempted.

Fraction D (1.21 g., 33% yield) was shown by melting point (authentic sample melted at 259-261°) and by infrared comparison with an authentic sample to be 10,10'-bianthrone (IV).

Fraction E (0.94 g., 22% of sample weight) had a rather ill-defined infrared spectrum. Recrystallization attempts from methanol and acetone were unsuccessful. No further characterization was attempted.

Irradiation of 9-nitroanthracene (I) with oxygen flush

A solution of I (4.2 g., 0.019 mole) in 400 ml. acetone was irradiated for 3 hours with a Hanovia Type A medium-pressure mercury arc lamp. A continuous stream of oxygen was bubbled through the solution during the irradiation. The acetone solution was filtered and the filter cake was washed twice with Skelly B. This gave 2.55 g. (65% yield) of yellow needles melting at 283-285° (reported (83), 285-286°). The infrared spectrum (Figure 3, page 40) was identical to that of an authentic sample of anthraquinone (II). The filtrate and washings were combined and the solvent removed under reduced pressure. The residue was taken up in hot benzene and chromatographed on 100 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.05 g.	solid (m.p. 185-198°)
100% benzene	B	0.98 g.	solid (m.p. 260-281°)
100% chloroform	C	0.62 g.	gum
100% methanol	D	0.56 g.	tar

Fraction A (0.05 g., 1% of the sample weight) had an ill-defined infrared spectrum. No further characterization was attempted.

Fraction B (0.98 g., 23% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.91 g. (23% yield) of anthraquinone (II) melting at 279-281°

(reported (83), 285-286°). The infrared spectrum was shown to be identical to that of an authentic sample of anthraquinone (II).

Fraction C (0.62 g., 15% of the sample weight) was taken up in hot methanol and recrystallization attempted. No crystalline products could be obtained. No further characterization was attempted.

Fraction D (0.56 g., 14% of the sample weight) was taken up in hot methanol and recrystallization attempted. Only tars could be recovered. No further characterization was attempted.

Sealed tube irradiation of 9-nitroanthracene (I) in carbon tetrachloride saturated with oxygen

A solution of I (2.0 g., 0.009 mole) in 120 ml. of carbon tetrachloride in a Pyrex tube fitted with a vacuum stopcock was saturated with oxygen. This was accomplished by passing oxygen into the solution for 1 hour. The stopcock was closed and the solution irradiated for 5½ hours with a Hanovia Type A medium-pressure mercury arc lamp encased in the condenser from a Pyrex immersion well. The distance from the lamp to the irradiation tube was 3 cm. The presence of a brown gas was noted after the irradiation. The stopcock was opened. The carbon tetrachloride was removed under reduced pressure, and the residue was taken up in hot benzene and chromatograph-

ed on 75 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.27 g.	solid (m.p. 240-292°)
100% benzene	B	0.66 g.	solid (m.p. 258-277°)
100% benzene	C	0.33 g.	solid (m.p. 252-273°)
100% chloroform	D	0.62 g.	solid (m.p. 261-263° dec.)

Fraction A (0.27 g., 13% of the sample weight) was recrystallized from benzene-methanol to give 0.20 g. (8% yield) yellow needles melting at 308-309° (reported (68), 310°). The infrared spectrum (Figure 5, page 44) was shown to be identical with that of the compound obtained from the dark reaction of nitric oxide with 9-nitroanthracene (I).

Fraction B (0.66 g.) and Fraction C (0.33 g.) were combined and recrystallized from benzene-methanol to give 0.90 g. (48% yield) yellow needles melting at 280-283° (reported (83), 285-286°). The infrared spectrum (Figure 3, page 40) was shown to be identical to that of an authentic sample of anthraquinone (II).

Fraction D (0.62 g., 36% yield) was shown by melting point (authentic sample melted at 259-261°) and by infrared comparison with an authentic sample to be 10,10'-bianthrone (IV).

Reaction of nitrogen (IV) oxide with 10,10'-bianthrone (IV) in the absence of light

In the absence of light IV (2.0 g., 0.0052 mole) in 100 ml. of carbon tetrachloride was treated with nitrogen (IV) oxide (nitrogen (IV) oxide was generated in situ by adding nitrogen (II) oxide in the presence of an excess of oxygen) at room temperature for 5 hours. The reaction mixture was filtered to give 1.05 g. (51% of the sample weight) of a white crystalline solid melting at 254-256° with decomposition (authentic sample melted at 259-261°). The infrared spectrum (Figure 4, page 42) was identical to that of an authentic sample of 10,10'-bianthrone (IV). The filtrate was evaporated under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 75 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.02 g.	solid (m.p. 192-243°)
100% benzene	B	0.15 g.	solid (m.p. 264-273°)
100% chloroform	C	0.56 g.	solid (m.p. 221-239°)

Fraction A (0.02 g., 1% of the sample weight) was shown by infrared comparison to be impure anthraquinone (II). No further characterization was attempted.

Fraction B (0.15 g., 7% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.12 g. (6% yield) of yellow solid melting at 279-281° (re-

ported (83), 285-286°). The infrared spectrum (Figure 3, page 40) was identical with that of an authentic sample of anthraquinone (II).

Fraction C (0.56 g., 28% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.45 g. (22% yield) of white crystals melting at 252-255° with decomposition (authentic sample melted at 259-261°). The infrared spectrum (Figure 4, page 42) was identical with that of an authentic sample of 10,10'-bianthrone (IV).

Irradiation of 9-nitroanthracene (I) with a nitric oxide flush

A solution of I (5.02 g., 0.022 mole) in 400 ml. of acetone was degassed for 1 hour with purified nitrogen (see Figure 11, page 70). This was accomplished by passing purified nitrogen into the continuously stirred solution. Nitric oxide was passed into the solution for $\frac{1}{4}$ hour and the irradiation started. The solution was irradiated for 3 hours with a Hanovia Type A medium-pressure mercury arc lamp. The nitric oxide stream was maintained during the irradiation. After the irradiation the solution was purged with nitrogen to remove the excess nitric oxide. The acetone was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 300 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.21 g.	solid (m.p. 229-293°)
100% benzene	B	2.53 g.	solid (m.p. 284-286°)
100% chloroform	C	0.95 g.	tar
100% methanol	D	1.33 g.	tar

Fraction A (0.21 g., 4% of the sample weight) was recrystallized from methanol-benzene to give 0.12 g. (2% yield) of yellow needles melting at 309-310° (reported (68), 310°). The infrared spectrum (Figure 5, page 44) was identical to that of the compound isolated from the dark reaction of nitric oxide with 9-nitroanthracene (I). The compound analysed for $C_{14}H_8N_2O_4$ (see later experimental section).

Fraction B (2.53 g., 55% yield) was shown by melting point (reported (83), 285-286) and by infrared comparison with an authentic sample to be anthraquinone (II).

Fraction C (0.95 g., 19% of the sample weight) was recrystallized from methanol to give 0.25 g. (6% yield) of white crystals melting at 248-252° with decomposition (authentic sample melted at 259-261°). The infrared spectrum (Figure 4, page 42) of the white crystals was identical to that of an authentic sample of 10,10'-bianthrone (IV). Concentration of the mother liquor gave only tar.

Fraction D (1.33 g., 26% of the sample weight) was found to have an ill-defined infrared spectrum. The tar was taken

up in methanol and recrystallization was attempted. Only tar was obtained. No further characterization was attempted.

Reaction of 9-nitroanthracene (I) with nitric oxide in the absence of light

Nitric oxide was passed into a solution of I (1.0 g., 0.0045 mole) in 50 ml. of acetone for 3 hours. This gave a green solution. The acetone was removed under reduced pressure. The residue was taken up in hot benzene and chromatographed on 50 g. of silica gel. This gave 0.92 g. (76% yield) of a yellow solid melting at 299-305° (reported (68), 310°). Anthraquinone (II) (0.05 g., 5% yield) melting at 278-281° (reported (83), 285-286°) was also isolated from the chromatography. Benzene (100%) was used as the eluent for both compounds.

Anal. Calcd. for $C_{14}H_8N_2O_4$: C, 62.68; H, 3.01; N, 10.44; O, 23.87. Found: C, 62.95; H, 3.00; N, 10.10; O, 23.77.

Irradiation of 9-nitroanthracene (I) in potassium bromide

Several potassium bromide pellets containing approximately equal amounts of 9-nitroanthracene (I) were prepared. The pellets were placed in a desiccator under helium. The desiccator and irradiation vessels (Pyrex weighing bottles with flat tops) were placed in a glove box. The irradiation vessels were filled 3/4 full of a desiccant. A layer of Glass

Wool was packed over the top of the desiccant. The glove box was purged with helium for 12 hours. The KBr pellets were transferred from the desiccator to the weighing bottles. The weighing bottles were sealed under helium in the glove box and placed in a desiccator. The desiccator was sealed and removed from the glove box. The samples were immediately irradiated using a Hanovia Type A medium-pressure mercury arc lamp. The lamp was encased in the condenser from a Pyrex immersion well. The weighing bottles were located 3 cm. from the lamp during irradiation. The course of the irradiation was followed by infrared comparison (see Figures 6-8 , pages 46-50). After 2 minutes irradiation the infrared spectrum showed carbonyl bands at 5.97 (anthraquinone carbonyl) and 6.02 (10,10'-bianthrone carbonyl) microns. After 60 minutes irradiation the bands at 5.97 and 6.02 microns were of approximately equal intensity. The bands from the nitro group at 6.49 and 6.57 microns were no longer apparent in the infrared spectrum.

Experimental for the Photooxidation
of 10,10'-Bianthrone and Anthrone

Irradiation of 10,10'-bianthrone (IV) in chloroform
open to the atmosphere

A solution of IV (0.95 g., 0.0024 mole) in 150 ml. chlo-

roform in a quartz tube was irradiated open to the atmosphere for 6 days and 18 hours with a General Electric UA-3 medium-pressure mercury arc lamp. The lamp was located at a distance of 30 cm. from the irradiation tube. The chloroform was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 75 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	0.45 g.	solid (m.p. 278-282°)
100% benzene	B	0.01 g.	gum.
100% chloroform	C	0.24 g.	gum
chloroform-methanol (85-15)	D	0.04 g.	tar

Fraction A (0.45 g., 47% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 0.42 g. (42% yield) of anthraquinone (II) melting at 282-284° (reported (83), 285-286°). The infrared spectrum (Figure 3, page 40) was shown to be identical with that of an authentic sample of anthraquinone (II).

Fraction B and Fraction C (0.25 g., 26% of the sample weight) were combined and taken up in hot methanol and recrystallization attempted. Only tars could be isolated from the fractions. The infrared spectrum was ill-defined. No further characterization was attempted.

Fraction D (0.04 g., 4% of the sample weight) could not

be obtained in crystalline form. Recrystallization attempts resulted in the recovery of tar. No further characterization was attempted.

Irradiation of 10,10'-bianthrone (IV) in chloroform saturated with oxygen

A solution of IV (3.0 g., 0.0077 mole) in 250 ml. of chloroform in a Pyrex immersion well was saturated with oxygen by passing a stream of the gas into the continuously stirred solution for $\frac{1}{2}$ hour. The solution was irradiated for 3 hours with a Hanovia Type A medium-pressure mercury arc lamp. The chloroform was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 250 g. of silica gel. Anthraquinone (II) (0.41 g., 13% yield) was isolated using 100% benzene as the eluent. Using 100% chloroform as the eluent 10,10'-bianthrone (IV) (1.77 g., 59% of the sample weight) was recovered. Both products were identified by means of infrared comparison with authentic samples.

Irradiation of 10,10'-bianthrone (IV) with an oxygen flush

A solution of IV (1.50 g., 0.0039 mole) in 400 ml. of warm acetone in a Pyrex immersion well was irradiated for 1 hour with a Hanovia Type A medium-pressure mercury arc lamp. A stream of oxygen was passed into the solution during the

irradiation. The acetone was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 100 g. of silica gel. Anthraquinone (II) (1.17 g., 72% yield) was isolated using 100% benzene as the eluent. Only tar was obtained using 100% chloroform as the eluent.

Irradiation of anthrone (LXXXIX) with an oxygen flush

A solution of LXXXIX (2.0 g., 0.01 mole) in 400 ml. of acetone was irradiated for $\frac{1}{2}$ hour with a Hanovia Type A medium-pressure mercury arc lamp. A stream of oxygen was passed into the solution during the irradiation. The solution was filtered and the filter cake washed twice with Skelly B. S. This gave 1.35 g. of anthraquinone (II) melting at $284-28-286^{\circ}$ (reported (83), $285-286^{\circ}$). The filtrate and washings were combined and the solvent removed under reduced pressure. The residue was treated with hot methanol. Filtration of the cooled solution gave 0.52 g. of anthraquinone (II) melting at $280-282^{\circ}$. The total yield of anthraquinone (II) was 1.87 g. (90% yield).

Attempted dark oxidation of 10,10'-bianthrone (IV) with oxygen

A stream of oxygen was passed into a refluxing solution of IV (1.0 g., 0.0026 mole) in 150 ml. acetone for $3\frac{1}{2}$ hours. The acetone was removed under reduced pressure. Hot benzene was added to the residue. The benzene solution was filtered

while still hot to give 0.74 g. (74% of the sample weight) of 10,10'-bianthrone (IV) melting at 259-263° with decomposition (authentic sample melted at 259-261°). The infrared spectrum (Figure 4, page 42) was identical with the spectrum of an authentic sample of 10,10'-bianthrone (IV). Chromatography of the mother liquor on 50 g. of silica gel gave 0.23 g. (23% of the sample weight) of 10,10'-bianthrone (IV) melting at 261-263° with decomposition. The infrared spectrum (Figure 4, page 42) was identical to that of an authentic sample of 10,10'-bianthrone (IV). The total recovery of starting material was 97%. No anthraquinone (II) was isolated.

Photochemistry of Anthraquinone Monooxime

Irradiation of anthraquinone monooxime (LXXXVIII) in acetone with nitrogen flush

A solution of LXXXVIII (1.85 g., 0.008 mole) in 250 ml. of acetone in a Pyrex immersion well was degassed by passing a stream of nitrogen into the continuously stirred solution for $\frac{1}{2}$ hour. The solution was then irradiated for $3\frac{1}{2}$ hours with a Hanovia Type A medium-pressure mercury arc lamp. The nitrogen stream was maintained during the irradiation. The acetone was then removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 150 g. of silica gel. Anthraquinone (II) (0.17 g., 10% yield)

was isolated using 100% benzene as the eluent. Anthraquinone monooxime (LXXXVIII) (0.43 g., 23% of the sample weight) was recovered using 100% chloroform as the eluent. Both products were identified by means of comparison of their infrared with those of authentic samples.

Irradiation of anthraquinone monooxime (LXXXVIII)
in degassed acetone-water (95-5)

A solution of LXXXVIII (0.82 g., 0.0037 mole; m.p. 229-231°) in 250 ml. of an acetone-water (95-5) solvent system in a Pyrex immersion well was degassed by passing a stream of nitrogen into the continuously stirred solution for $\frac{1}{2}$ hour. The irradiation flask was sealed with rubber septum caps, and the solution was irradiated for $3\frac{1}{2}$ hours with a Hanovia Type A medium-pressure mercury arc lamp. The solvent was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 150 g. of silica gel. Anthraquinone (II) (0.10 g., 13% yield) was isolated using 100% benzene as the eluent. Anthraquinone monooxime (LXXXVIII) (0.66 g., 81% of the sample weight) was recovered using 100% chloroform as the eluent. Both products were identified by means of infrared comparison with authentic samples.

Irradiation of anthraquinone monooxime (LXXXVIII) in
acetone saturated with nitric oxide

A solution of LXXXVIII (1.16 g., 0.0052 mole) in 250 ml.

of acetone in a Pyrex immersion well was degassed by passing a stream of nitrogen into the acetone solution for $\frac{1}{2}$ hour with continuous stirring. Nitric oxide was passed into the solution for an additional $\frac{1}{2}$ hour. The irradiation flask was sealed with rubber septum caps and irradiated for 3 hours using a Hanovia Type A medium-pressure mercury arc lamp. The acetone was removed under reduced pressure, and the residue was taken up in hot benzene and chromatographed on 150 g. of silica gel. Anthraquinone (II) (0.24 g., 22% yield) was isolated using 100% benzene as the eluent. Anthraquinone monooxime (LXXXVIII) (0.79 g., 68% of the sample weight) was recovered using 100% chloroform as the eluent. Both products were identified by means of infrared comparison with authentic samples.

Irradiation of anthraquinone monooxime (LXXXVIII) in acetone with a nitric oxide flush

A solution of LXXXVIII (1.60 g., 0.0072 mole) in 250 ml. of acetone in a Pyrex immersion well was degassed by passing a stream of nitrogen into the continuously stirred solution for $\frac{1}{2}$ hour. Nitric oxide was passed into the solution for $\frac{1}{4}$ hour, and the solution was then irradiated for $3\frac{1}{2}$ hours using a Hanovia Type A medium-pressure mercury arc lamp. The stream of nitric oxide was maintained during the irradiation. The acetone was removed under reduced pressure. The infrared

spectrum showed the anthraquinone carbonyl at 5.97 microns. The residue was taken up in hot benzene and chromatographed on 150 g. of silica gel. The following fractions were collected:

Eluent	Fraction	Weight	Form
100% benzene	A	1.30 g.	solid (m.p. 276-280°)
100% benzene	B	0.04 g.	solid (m.p. 275-281°)
100% chloroform	C	0.03 g.	solid (m.p. 190-273°)
methanol-chloroform (25-75)	D	0.21 g.	gum

Fraction A (1.30 g., 87% of the sample weight) was treated with hot methanol. Filtration of the cooled solution gave 1.22 g. (80% yield) of anthraquinone (II) melting at 282-284° (reported (83), 285-286°). The infrared spectrum (Figure 3, page 40) was identical with that of an authentic sample of anthraquinone (II).

Fraction B (0.04 g., 3% yield) was shown by infrared comparison with an authentic sample to be anthraquinone (II).

Fraction C (0.03 g., 2% of the sample weight) was shown by infrared analysis to be a mixture of anthraquinone (II) and starting material. No further characterization was attempted.

Fraction D (0.21 g., 13% of the sample weight) was a gum with a rather ill-defined infrared spectrum. Attempted recrystallization from methanol was unsuccessful. No further characterization was attempted.

The total yield of anthraquinone (II) from the irradiation was 83%.

Reaction of nitric oxide with anthraquinone monooxime (LXXXVIII) in the absence of light

Nitric oxide was passed into a solution of LXXXVIII (0.15 g., 0.0007 mole) in 25 ml. of acetone for $2\frac{1}{2}$ hours in the absence of light. This gave a green solution. The acetone was removed under reduced pressure. The infrared spectrum (Figure 3, page 40) did not show the anthraquinone carbonyl at 5.97 microns. The residue was taken up in hot benzene and chromatographed on 75 g. of silica gel. This gave anthraquinone (II) (0.11 g., 75% yield) with 100% benzene as the eluent. Another solid (0.03 g., 20% of the sample weight) was obtained using 100% chloroform as the eluent. The substance was found to have a very poorly-defined infrared spectrum. No further characterization was attempted.

SUMMARY

The formation of anthraquinone (II) from 9-nitroanthracene (I) does not require oxygen. Anthraquinone (II) has been isolated from the irradiation of rigorously degassed solutions of 9-nitroanthracene (I). Nitric oxide was isolated and identified as a product from the irradiation of 9-nitroanthracene (I).

Flushing the 9-nitroanthracene (I) solution with purified nitrogen (to remove the nitric oxide formed during the irradiation) raises the yield of 10,10'-bianthrone (IV) to as high as 74% and lowers the anthraquinone (II) yield to 6%.

Anthraquinone monooxime (LXXXVIII) was isolated from the irradiation of 9-nitroanthracene (I). This compound had not been isolated by earlier workers. Anthraquinone monooxime (LXXXVIII) is converted rapidly into anthraquinone (II) by the action of light and nitric oxide.

The formation of anthraquinone (II) from 10,10'-bianthrone (IV) becomes important in the presence of light and oxygen. In the absence of light 10,10'-bianthrone (IV) is stable to oxygen in refluxing acetone.

A consistent mechanistic path which correlates these results is presented. Photoisomerization of the nitro compound (I) gives the nitrite ester (XCII) which can cleave thermally or photochemically to the 9-anthroxy radical

(XCIII) and nitric oxide. Dimerization of two anthroxyl (XCIII) radicals would give 10,10'-bianthrone (IV), while addition of nitric oxide would give the nitrosoketone (XCIV). Addition of oxygen would give the ketoperoxy radical (XCV). Decomposition of the ketoperoxy radical (XCV) could give anthraquinone (II) and the hydroxyl radical. Oxidation of the nitrosoketone (XCIV) could give nitroanthrone (III). Isomerization of the nitrosoketone (XCIV) would give anthraquinone monooxime (LXXXVIII). Irradiation of anthraquinone monooxime (LXXXVIII) in the presence of nitric oxide gives anthraquinone (II).

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