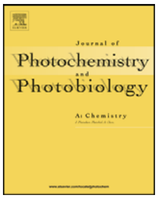
Journal of Photochemistry and Photobiology A: Chemistry 201 (2009) 39–44

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photochemical reaction of 9-nitro-substituted anthracene-like molecules 9-methyl-10-nitroanthracene and 12-methyl-7-nitrobenz[*a*]anthracene☆

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ARTICLE INFO

Article history:
Received 21 May 2008
Received in revised form 5 September 2008
Accepted 19 September 2008
Available online 17 October 2008

Keywords:
Photoreaction
9-Methyl-10-nitroanthracene
7-Nitrobenz[a]anthracene,
12-Methyl-7-nitrobenz[a]anthracene
Nitro-rearrangement

ABSTRACT

Photolysis of 9-methyl-10-nitroanthracene in chloroform or methanol produces mainly two products 9-methyl-9-nitrosoanthracen-10-one and 9,10-anthraquinone in about 4:1 ratio under ambient air. The formation of 9-methyl-9-nitrosoanthracen-10-one confirms the proposed excited state rearrangement reaction of the nitro group peri to two hydrogens and perpendicular to the aromatic rings. The nitro group rearranges to a nitrite, followed by breaking of the N–O bond producing NO radical. The NO radical further forms a bond with the carbon on the opposite site of the benzene ring through radical recombination. Photolysis of 12-methyl-7-nitrobenz[a]anthracene produced several nitroso ketone-like compounds which further convert to an aldehyde. Photolysis of the desmethyl nitro compounds, 9-nitroanthracene and 7-nitrobenz[a]anthracene, produced the respective quinones.

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1. Introduction

Nitro-polycyclic aromatic hydrocarbons (nitro-PAHs) are believed to account for a significant part of the mutagenicity of air-borne particulate matter [1–5]. In diesel particulates, approximately 40% of the direct-acting mutagenicity is believed to be due to nitro-PAHs [1,6]. Nitro-PAHs are formed as a result of incomplete combustion of organic materials both from natural events and human activities [7–9]. They are also formed in the atmosphere as PAHs react with NO_2 or NO_3 radicals [10–15]. Nitro-PAHs undergo photochemical reactions when exposed to sunlight. It has been proposed that the photochemical reaction mechanism for nitro-PAHs is dependent on the orientation of the nitro group, whether co-planar or perpendicular to the aromatic rings [2,11,16–19]. A Nitro-PAH with its nitro group situated with two *peri*-hydrogens is forced into a perpendicular orientation to the aromatic moiety due to steric hindrance. Nitro groups with only one or no *peri*-hydrogen will maintain a parallel orientation to the aromatic moiety [4]. Nitro-PAHs with a perpendicular nitro group react faster under light irradiation due to a nitro to nitrite rearrangement as it was proposed [20–24]. Nitro-PAHs with a perpendicular nitro group are less mutagenic than those with a parallel nitro groups due to their inability to be metabolized into reactive intermediates that form covalent DNA adducts [5,25]. Nitro-PAHs with parallel nitro groups to the aromatic rings undergo photo-oxidation of the aromatic rings [26–28].

In 9-nitroanthracene-like molecules, the nitro group is next to two *peri*-hydrogens and preferentially adopts a perpendicular position to the aromatic rings. Upon absorbing light energy, the nitro group rearranges to a nitrite, which decomposes to a NO radical and phenoxy radical. The phenoxy radical then rearranges to become a carbon centered radical in the anthracene ring [20,29,30]. The NO radical will react with the most stable carbon radical on the opposite site of the nitro group in a concerted fashion and form a nitroso ketone, which is usually unstable and continues on to become anthraquinone. In the reaction with 10-chloro, cyano, benzoyl, and nitro substituted 9-nitroanthracenes, such a nitroso ketone intermediate was observed [21,24,31].

In this report, 9-methyl-10-nitroanthracene and 12-methyl-7-nitrobenz[*a*]anthracene (Fig. 1) were prepared to study the light-induced rearrangement reaction of the nitro group. The presence of

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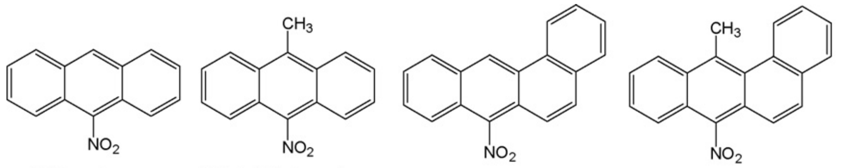
1010-6030/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jphotochem.2008.09.016



9-Nitroanthracene 9-Methyl-10-nitroanthracene 7-Nitrobenz[a]anthracene 12-Methyl-7-nitrobenz[a]anthracene

Fig. 1. Structures of nitroanthracene derivatives used for this study.

the methyl group supposes to stabilize the nitroso ketone and thus to be isolated and characterized.

2. Materials and methods

9-Methylanthracene, sodium nitrate, acetic anhydride and trifluoroacetic acid were purchased from Aldrich (Milwaukee, WI, USA) and used without further purification. HPLC analysis was carried out using a Shimadzu HPLC system with a RP-18 column (25 cm × 4.0 mm, 5 μm). The eluent used was 90% methanol in water. The flow rate was 1.0 mL/min, and detected at wavelength of 273 nm. Proton NMR was recorded with a Bruker 300 MHz NMR spectrometer as well as a JOEL 400 MHz spectrometer in $CDCl_3$ or acetone-d6. GC–MS instrument used was Hewlett Packard 6890 gas chromatograph coupled to a Hewlett Packard 5973 mass selective detector. The instrument was equipped with a HP-5 MS (30 m × 250 μm × 0.25 μm) column: the injector temperature was 250 °C; carrier gas He at a constant flow rate of 1 mL/min; the oven temperature was held at 100 °C for 2 min, and then heated to 280 °C at 10 °C/min. MS system: ionization of the CI reagent gas was performed with 150 eV beam of electrons produced from a heated rhenium filament. Methane served as the reagent gas. The ion source temperature was held at 280 °C. UV absorption: UV spectra for the 9-methyl-10-nitroanthracene were recorded on a CARY 300E UV–vis absorption spectrophotometer from Varian Inc. (Houston, TX).

2.1. Light source

The light source was a 100-W UVA lamp (Type B, UVP, Upland, CA, USA) that produced a main emission band of 365 nm. A stream of cold air was blown across the bottom of the support during irradiation in an effort to displace any heat generated by the lamp.

2.2. Synthesis of 9-nitroanthracene-like nitro-PAHs

12-Methyl-7-nitrobenz[*a*]anthracene, 7-nitrobenz[*a*]anthracene, and 9-methyl-10-nitroanthracene were prepared by nitration of 12-methylbenz[*a*]anthracene, benz[*a*]anthracene, and 9-methylanthracene, respectively, with sodium nitrate (1:1 molar ratio) in trifluoroacetic acid/acetic anhydride (1/1, v/v) under argon at ambient temperature with stirring. The reaction products were partitioned between ethyl acetate and water containing a small amount of sulfuric acid (>1%). The organic layer was collected, washed with water, dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The yellowish residue was column chromatographed over silica gel. Elution with hexane gave the recovered substrate. Elution with hexane/ethyl acetate (2/1 v/v) gave the desired compounds with yields 70–80%. Spectral data of 7-nitrobenz[*a*]anthracene [32,33] and 9-methyl-10-nitroanthracene [34] matched the known compounds. 12-Methyl-7-nitrobenz[*a*]anthracene has not been synthesized before. The spectral data are as follows: MS – m/z: 287 (M^+), 257 $(M–NO)^+$ and 241 $(M–NO_2)^+$. ^1H NMR (acetone-d_6): 3.43 (s, 3, CH_3), 7.70 (d, 1, $J_{5,6} = 10$ Hz, H_6), 7.65–7.88 (m, 4, $H_{2,3,9,10}$), 8.02 (d, 1, H_5), 8.13 (dd, 1, $J_{3,4} = 9.5$ Hz, H_4), 8.23–8.37 (m, 2, $H_{8,11}$), and 8.53 ppm (dd, 1, H_1).

2.3. Photolysis of nitro-PAHs and isolation of nitroso ketone

Photolysis of 9-methyl-10-nitroanthracene (0.1 mM) and other nitro-PAHs were carried out in methanol or chloroform for HPLC/TLC analysis. To isolate the photoproduct, 9-methyl-10-nitroanthracene (33 mg) was dissolved in freshly distilled $CHCl_3$ (33 mL) in a Pyrex glass round bottom flask. The solution was irradiated with two UVA lamps for 180 min under stirring. The disappearance of 9-methyl-10-nitroanthracene was monitored by TLC. After the reaction was complete, the solvent was evaporated and the residue dissolved in 1 mL of ethyl acetate and was absorbed onto 41 mg of silica. The ethyl acetate in the silica was evaporated and remaining silica was loaded on the top of a silica gel column prepared with 350 mg of silica. The product was chromatographed using a solvent gradient of 0–5% ethyl acetate in hexane. Fractions containing the desired product were collected and the solvent evaporated at room temperature using a rotary evaporator to obtain a total of 9.7 mg of purified 9-methyl-9-nitrosoanthracene-10-one (yield 30%). ^1H NMR ($CDCl_3$): 8.27 (dd, 2H); 7.97 (dd, 2H); 7.72 (td, 2H); 7.56 (td, 2H); and 1.70 ppm (s, 3H). MS: M^+ 237. Fragments: 209 (M–CO), 207 (M–NO), 178 (M–HCONO), and 152 (M–HCONO & C_2H_2), but no M–NO_2 fragment. IR (KBr): cm^{-1}: 2964, 1650, 1600, 1322, 1261, 1095, 1022, 802, 694.

2.4. Photolysis kinetics

A 0.5 mg of 9-methyl-10-nitroanthracene or 12-methyl-7-nitrobenz[*a*]anthracene dissolved in 0.5 mL $CDCl_3$ was placed in an NMR tube and kept in the dark until it was to be irradiated. The NMR tube was placed 43 mm above the UVA lamp and irradiated. A stream of cool air was blown across the top of the lamp during irradiation to eliminate heat. After each irradiation interval, an NMR spectrum was recorded. For the same experiments under argon or nitrogen atmosphere, argon or nitrogen gas was used to purge the solution in ice bath for 15 min before the NMR tube was sealed with a cap and rapped tightly with parafilm.

3. Results and discussion

3.1. Photochemical reaction of 9-nitroanthracene-like chemicals and photoproduct purification and characterization

Fig. 2 is the HPLC chromatogram of light irradiated 9-methyl-10-nitroanthracene (1 mM) solution in $CHCl_3$ with a UVA lamp. Three photoproducts were detected, and they are numbered P_0, P_1, and P_2. The same three products were also detected if CH_3OH was used as solvent. P_0 was unstable and difficult to be isolated, and P_2 was identified as 9,10-anthraquinone by comparing its UV, NMR and MS spectra with the authentic sample. In order to identify the structure of P_1, a preparative photolysis starting with 9-methyl-10-nitroanthracene in $CHCl_3$ was carried out. Upon disappearance of the reactant as shown with TLC, P_1 was isolated via silica gel chro-

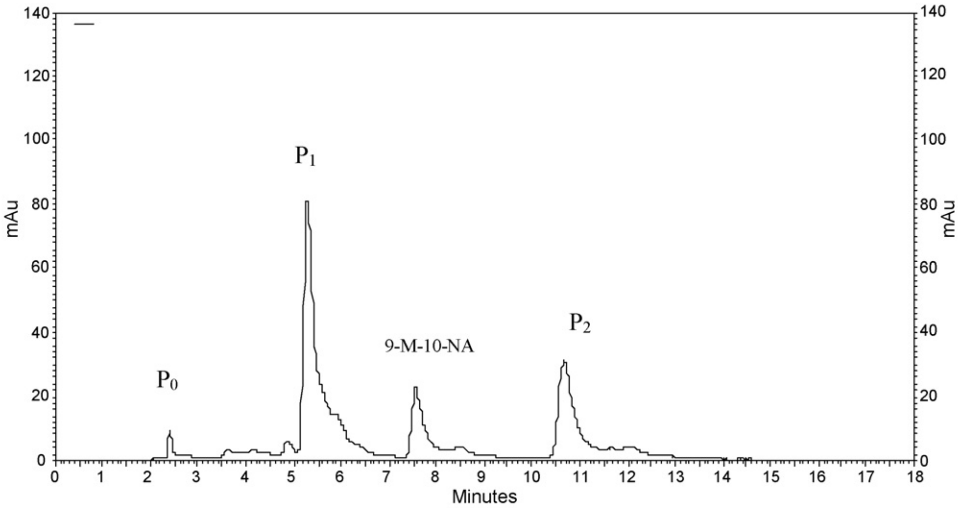


Fig. 2. HPLC profiles of 9-methyl-10-nitroanthracene in $CHCl_3$ (1 mM) irradiated for 30 min with a UVA lamp.

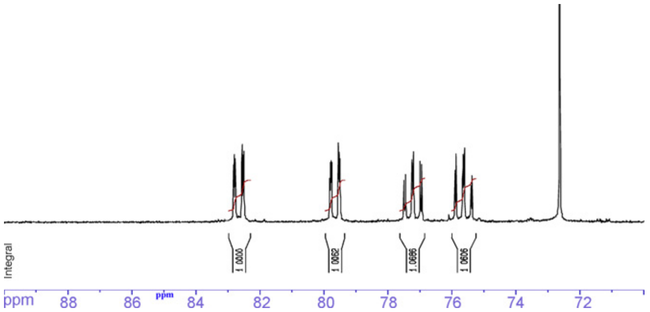


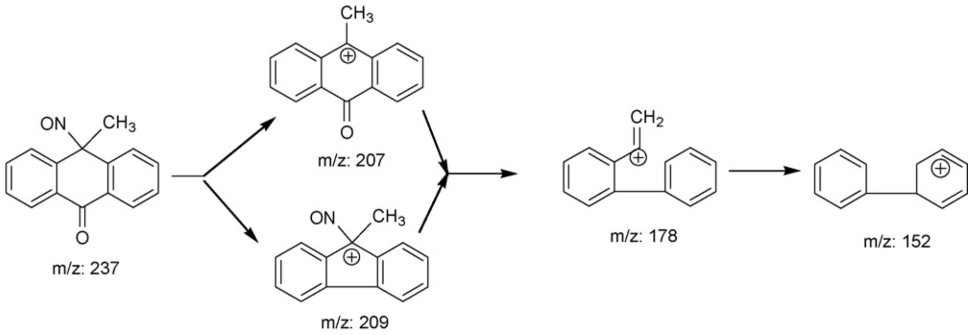
Fig. 3. ^{1}H-NMR of the aromatic region of 9-methyl-9-nitrosoanthracen-10-one.

matography and the resulting product was subjected to NMR, IR, and MS analysis.

The MS spectrum of P_1 has the molecular ion (m/z) of 237, the same molecular mass as the starting material 9-methyl-10-nitroanthracene, but with different ion patterns when compared with the starting material. The electron impact fragmentation of P_1 has the following ions: 209 (M–CO), 207 (M–NO), 178 (M–HCONO), and 152 (M–HCONO and C_2H_2), but no M–NO_2 fragment. This indicates that P_1 is an isomer of 9-methyl-10-nitroanthracene without the nitro group. The ^{1}H NMR spectra (Fig. 3) of the purified P_1 has four signals in the aromatic region 8.25, 7.95, 7.73, and 7.53 ppm for the four hydrogen atoms in the benzene ring and a signal resonates at 1.7 ppm for the methyl group. This indicates that there are no substitutions on the two benzene rings of anthracene. Combining the information, we assign P_1 to be 9-methyl-9-nitrosoanthracen-10-one. The fragmentation of 209 (M–CO) is also supportive for 9-methyl-9-nitrosoanthracen-10-one. Scheme 1 depicts the pathway by which the respective ions in the mass spectrum are formed.

Photolysis of 7-nitrobenz[*a*]anthracene produced 7,12-benz[*a*]anthraquinone, identified through comparison with authentic sample. Irradiation of 12-methyl-7-nitrobenz[*a*]anthracene in $CDCl_3$ in an NMR tube produced several products. After 30 min of irradiation, >80% of the starting compound disappeared as shown by the disappearance of the methyl signal at 3.4 ppm and other signals in the aromatic region. Several sets of aromatic signals and at least 3 singlet signals at 2–3 ppm (methyl) appeared, indicating that at least three rearrangement products formed. At the same time, a small signal at 9.8 ppm appeared. After 90 min of irradiation, the three methyl signals at 2–3 ppm nearly disappeared and the signal at 9.8 ppm increased. This doublet signal is a typical aldehyde proton with one neighboring proton. This indicates that irradiation of 12-methyl-7-nitrobenz[*a*]anthracene first converts it to at least three rearrangement products, which further converts into a 12-carboxaldehyde.

No aldehyde signal was observed when 9-methyl-10-nitroanthracene was irradiated. However, prolonged stay (6 months) of the isolated photoproduct, 9-methyl-9-nitrosoanthracen-10-one, in $CDCl_3$ in an NMR tube wrapped with aluminum foil in a refrigerator did produce an aldehyde singal at 12 ppm. In comparison to the aldehyde formed from the 12-methyl-7-nitrobenz[*a*]anthracene which has a doublet signal at 9.8 ppm, this aldehyde signal is a singlet and is much further down field at 12 ppm. This indicates



Scheme 1. Possible pathways for the generation of electron impact fragmentations of P_1.

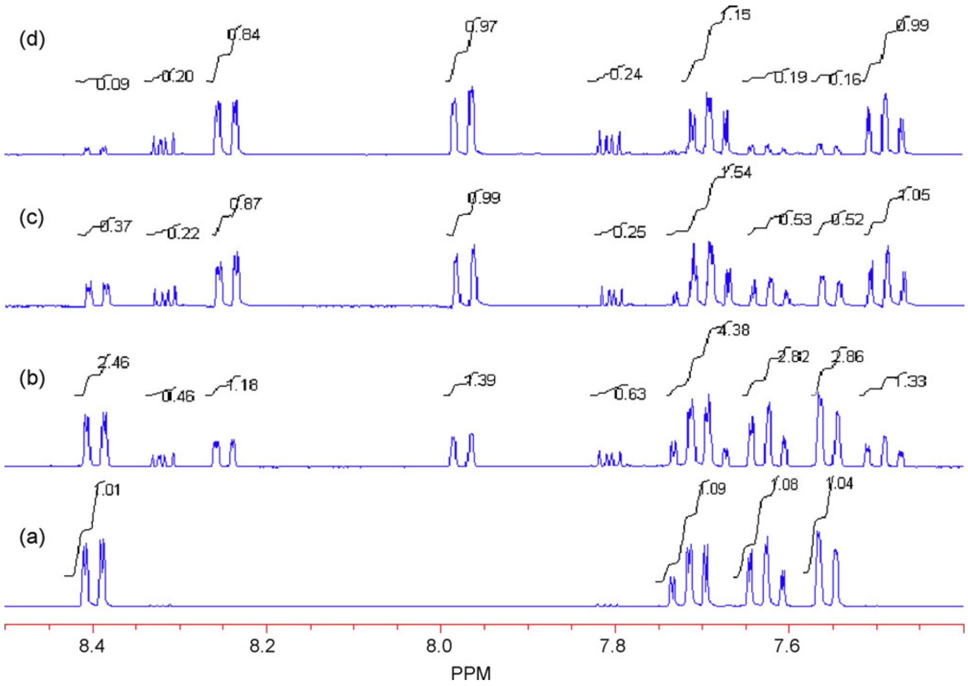


Fig. 4. ^{1}H NMR spectra of 9-methyl-10-nitroanthracene in $CDCl_3$ in ambient air irradiated for (from bottom to top): (a) 0 min; (b) 15 min; (c) 30 min; (d) 45 min.

that the 12-carboxaldehyde in benz[*a*]anthracene-7-one adopts a ketone form and the 9-carboxaldehyde in anthracene-10-one adopts a hydroxyl form (Scheme 2). The large down field shift (>2 ppm) is due to the deshielding effect of the anthracene ring.

3.2. Kinetic analysis of the photoreaction

Since the photoreaction of 9-methyl-10-nitroanthracene dissolved in $CHCl_3$ produces two main products, the photoreaction was followed by NMR by placing the 9-methyl-10-nitroanthracene solution in $CDCl_3$ in an NMR tube and irradiated. The proton NMR spectrum was recorded at each irradiation time interval. Fig. 4 shows the aromatic proton signals at irradiation times of 0, 15, 30, and 45 min, respectively, in ambient air. The majority of the starting material disappeared at 45 min, and was completely gone at 60 min. Meanwhile, 9-methyl-9-nitrosoanthracen-10-one and the 9,10-anthraquinone appeared. The same experiment was carried out for nitrogen and argon gas purged samples.

The progress of the photoreaction of 9-methyl-10-nitroanthracene in $CDCl_3$ under ambient air or purged with N_2 is plotted in Fig. 5. As can be seen, the disappearance of the starting compound was faster in air than purged with N_2. Treating the photolysis of 9-methyl-10-nitroanthracene in $CDCl_3$ as a first order reaction ($\ln([A]_0/[A]_t) = kt$), the plot $\ln([A]_0/[A]_t)$ vs irradiation time (t) yielded a straight line (data not shown). Thus the degradation half-life ($t_{1/2} = 0.693/k$) was determined. The degradation half-life for 9-methyl-10-nitroanthracene in $CDCl_3$ under ambient air was 14 min, while it was 20 min when purged with N_2. At the end of the photolysis (60 min), the ratio of 9-methyl-9-nitrosoanthracene-10-one/9,10-anthraquinone is 80/20 in ambient air and 60/40 when purged with nitrogen. The higher amount of 9,10-anthraquinone formed under nitrogen was surprising since it was thought that the quinone was transformed from the nitroso ketone via further oxidation. It clearly shows here that the 9,10-anthraquinone could be formed even under oxygen free system.

3.3. Mechanism of photoreaction

According to the HPLC, GC–MS and NMR analysis results, the proposed mechanism of photoreaction of 9-methyl-10-nitroanthracene is formulated in Scheme 2. Upon absorption of light energy, the molecule is promoted to excited singlet state, which intersystem crosses to the excited triplet state. The nitro group rearranges to a nitrite in the excited triplet state [24,31,35]. Breaking of the N–O bond of nitrite forms a nitroso radical and an oxygen-centered radical in the anthracene moiety. The nitroso radical either recombines to go back to nitrite or forms a C–N bond

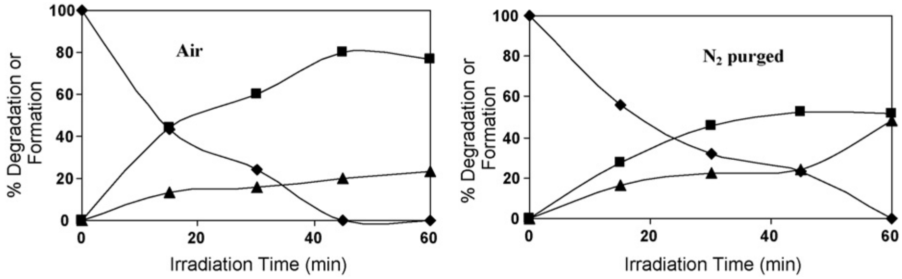
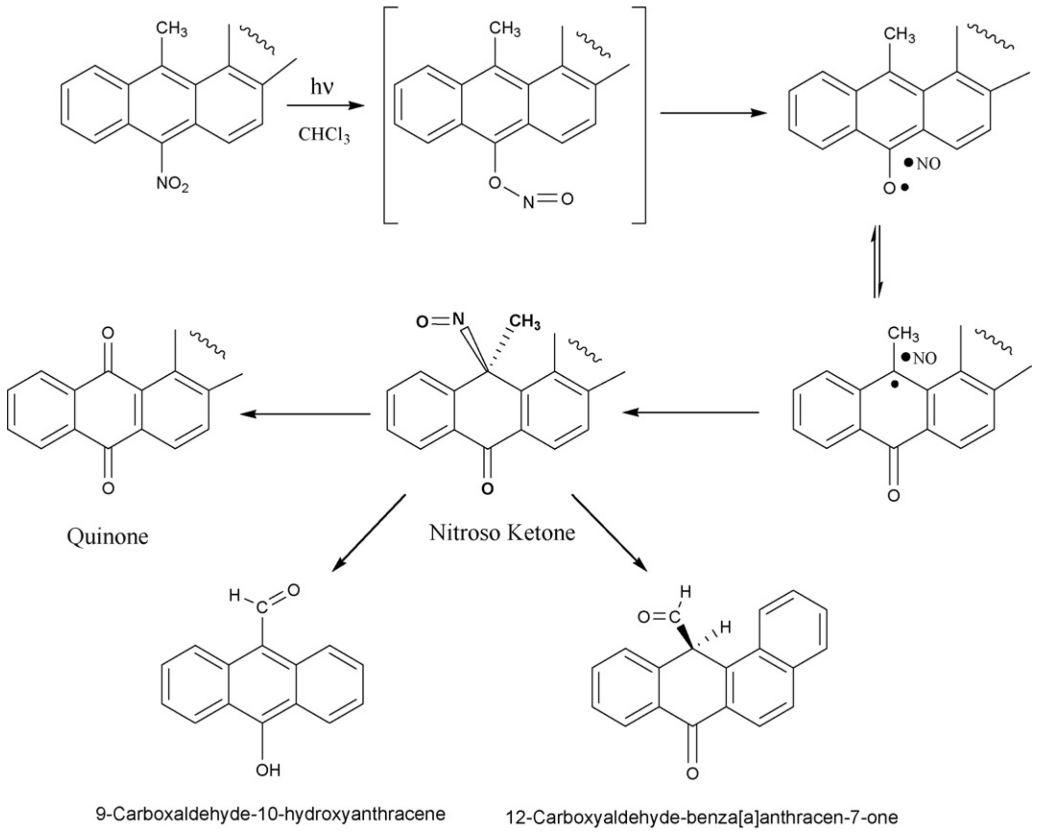


Fig. 5. Photolysis of 9-methyl-10-nitroanthracene (◆) transforms it into 9-methyl-9-nitroso-anthracene-10-one P_1 (■) and 9,10-anthraquinone P_2 (▲) in ambient air (left) or purged with N_2 (right).



Scheme 2. Mechanism of the photoreaction of 9-methyl-10-nitroanthracene and 7-nitro-12-methylbenz[*a*]anthracene in methanol or chloroform.

with the carbon on the opposite side of the benzene ring, the most reactive site in anthracene, thus, forming a nitroso ketone (9-methyl-9-nitrosoanthracen-10-one). In the case of 12-methyl-7-nitrobenz[*a*]anthracene, other carbons are also possible since more than one nitro ketones are seen in the NMR spectra. In the case of non-methyl substituted nitroanthracenes, photolysis of 9-nitroanthracene, and 7-nitrobenz[*a*]anthracene under the same conditions produced only the respective anthraquinones (data not shown). This is why 9,10-anthraquinone is usually the major photoproduct for the photolysis of 9-nitroanthracene and the nitroso ketone was not isolated. The 9-methyl-9-nitrosoanthracen-10-one is relatively stable and converts to an aldehyde after prolonged stay in the refrigerator without light irradiation. The 10-carboxyanthracene-9-one adopts an enol form since the aldehyde hydrogen is a singlet in proton NMR. In contrast, the 12-methyl-7-nitrobenz[*a*]anthracene rearrangement product nitroso ketones are not stable and readily converts to the aldehyde (12-carboxaldehyde-benz[*a*]anthracene-7-one). The doublet of the aldehyde hydrogen indicates that this aldehyde adopts a ketone form due to steric constraint of the extra benzene ring. In the presence of a substituent in the opposite position of the nitro group in anthracene, benzoyl, chloro, cyano, or nitro [21,24], the formation of the nitroso ketone was observed. The chloronitroso and nitronitroso ketones were isolated with low yields (12%). The majority of the photoproduct was anthraquinone. In our study with the methyl substituent, more than 80% of the photoproducts were the nitroso methyl ketone when irradiated under air. When bubbled with nitrogen or argon, the amount of the nitroso ketone decreased to about 60%. The 9-methyl-9-nitrosoanthracen-10-one is stable in the solid state. The chloroform solution of 9-methyl-9-nitrosoanthracen-10-one in an NMR tube was relatively stable. However, some of the nitroso ketone converted to anthracene aldehyde after the solution was left in refrigerator for 6 months.

However, prolonged irradiation of the 9-methyl-9-nitrosoanthracen-10-one converted it into the anthraquinone. Therefore, we believe the photochemical reaction of 9-nitroanthracene follows the mechanism above. The conversion of the 9-methyl-9-nitrosoanthracen-10-one to anthraquinone appears to be independent of oxygen. The conversion of the *gem*-chloronitrosoanthracene or *gem*-nitronitrosoanthracene to the quinone was also not dependent on oxygen [21]. It was proposed that *gem*-chloronitroso or *gem*-nitronitroso in aliphatic systems readily converts into ketone [36], not depending on oxygen.

In conclusion, light irradiation of 9-nitro-substituted anthracene-like molecules causes the nitro group to rearrange to become a nitrite followed by a concerted rearrangement reaction that places the nitroso group on the electron-rich carbon on the opposite end of the six-membered aromatic ring, and at the same time, the phenolic oxygen to become a ketone.

Acknowledgement

This research has been supported by the National Institutes of Health through a generous grant: NIH-RCMI G12 RR13459. This research has also been supported by the “211” program of Central University for nationalities of China. G.S. wishes to thank the US Department of Education for stipend support through the Title III grant: P031B040101-07. The authors wish to thank Mr. Kui Zeng for assistance in the mass spectroscopic analysis.

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