

Reductive Photocarboxylation of Phenanthrene: A Mechanistic Investigation

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Irradiation of a solution of phenanthrene (PHN) in DMSO saturated with CO₂ in the presence of *N,N*-dimethylaniline (DMA) produced 9,10-dihydrophenanthrene-9-carboxylic acid (**1**) in 55% yield, *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid (**2**) in 11% yield, a trace of phenanthrene-9-carboxylic acid (**3**), and a trace of 10-[*p*-(*N,N*-dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic acid (**5**). Addition of cumene, a hydrogen donor, or water, a proton donor, decreased the yield of **2**, while addition of certain salts increased its yield. 9-Carboxy-9,10-dihydrophenanthr-10-yl, generated by irradiation of phenanthrene-9-carboxylic acid in the presence of DMA, is proposed to be an intermediate in the formation of the acids. The quantum yield for the formation of **2** increased to a maximum of 0.13 with increasing light intensity. High CO₂ concentrations in DMSO changed the reaction pathway, greatly reducing the yields of **1** and **2**, and phenanthrene-9-carboxylic acid (**3**) and 10-[*p*-(*N,N*-dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic acid (**5**) were formed instead. On the basis of these results reduction of 9-carboxy-9,10-dihydrophenanthr-10-yl with the phenanthrene radical anion is proposed to be a step in the mechanism accounting for *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid formation. Transient spectroscopic evidence in support of this proposal is presented.

Introduction

Recent advances in metal complex catalysis and photoinduced electron-transfer reactions have given rise to a renewed interest in organic reactions involving carbon dioxide.² The carbon atom in CO₂ possesses relatively large partial charge making it susceptible to nucleophilic attack.

Tazuke et al.³ reported that aromatic hydrocarbons, such as anthracene, phenanthrene, and pyrene underwent reductive photocarboxylation when irradiated in DMSO or DMF in the presence of CO₂ and aromatic amines. The highest product yield observed in the case of phenanthrene was that of 9,10-dihydrophenanthrene-9-carboxylic acid which was obtained in 60% yield. The mechanism suggested for its formation involved photoinduced electron transfer reaction between the singlet excited hydrocarbon and the amine, the former being an electron acceptor and the latter being an electron donor. In a polar aprotic solvent the electron transfer step is followed by separation of radical ions with subsequent trapping of the hydrocarbon radical anion with CO₂.

The direction and energetics of the electron transfer reaction to form a radical ion pair can be estimated from the Rehm–Weller equation:⁴

$$\Delta G = E_d^{\text{ox}} - E_a^{\text{red}} - E_{00} + 2.6 \text{ eV}/\epsilon - 0.13 \text{ eV}$$

where E_d^{ox} is an oxidation potential of the donor; E_a^{red} is a reduction potential of the acceptor; E_{00} is excited state energy of the reacting state, and ϵ is dielectric constant of the solvent. Using values for the singlet energy of PHN (3.58 eV),⁵ its reduction potential (–2.44 V in DMF

vs SCE),⁶ and the oxidation potential of DMA (0.71 V vs SCE in CH₃CN),⁶ radical ion formation is calculated to be exergonic by ca. –0.41 eV. Consistent with this value, a diffusion controlled quenching of ¹PHN* by DMA without exciplex emission is observed in polar solvents.⁷ This suggests rapid formation of radical ions which then undergo further reactions with other molecules present in the reaction mixture.

The reduction potential of CO₂ to CO₂^{•–} is reported to be –2.21V vs SCE in DMF.⁸ Thus direct reduction of CO₂ is endergonic for any oxidant in PHN/DMA system.

One can find many analogies between the reductive photocarboxylation of aromatic hydrocarbons and the addition of CO₂ to the adducts of aromatic hydrocarbons formed by electron transfer from the alkali metals⁹ since both are addition reactions of CO₂ to carbon-centered nucleophiles. However, there are also a number of differences. For example, the addition of CO₂ to the phenanthrene–sodium adduct results in formation of *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid as the only product.¹⁰ The mechanism for the formation of 9,10-dihydrophenanthrene-9-carboxylic acid in the photoreaction was recently reported¹¹ while the mechanism of the former reaction remains unclear.

We have conducted a detailed investigation of the reductive photocarboxylation of phenanthrene and isolated several previously unreported products. Our mechanistic studies follow.

Results and Discussion

Product Identification. The Effect of Additives on the Yields of Products. Reductive photocarboxy-

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Scheme 1

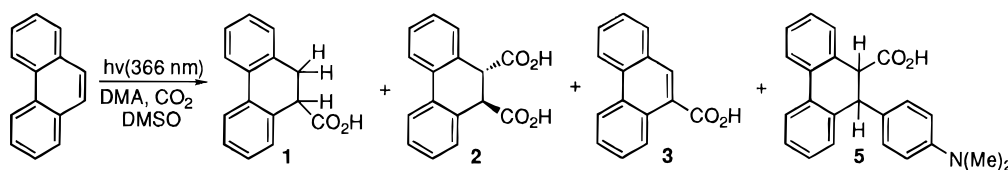


Table 1. Effect of Additives on the Yield of 1 and 2

additive	c, M	time, min	PHN consumption, %	yield of 1, %	yield of 2, %
none	—	90	62	55	11
cumene	1	90	62	59	6
water	1	90	65	68	0.5

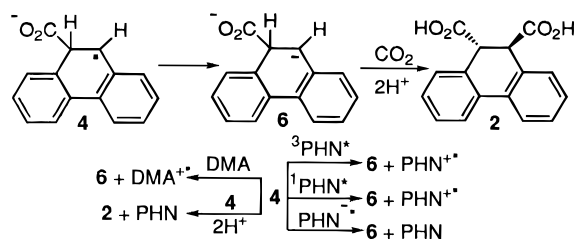
^a Reaction system: [PHN] = 0.05 M, [DMA] = 0.5 M, DMSO saturated with CO₂. ^b Determined by HPLC. ^c Isolated yield is based on consumed PHN. Determined by NMR of the acid mixture.

lation of phenanthrene in DMSO in the presence of *N,N*-dimethylaniline (DMA) produces 9,10-dihydrophenanthrene-9-carboxylic acid (**1**), *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid (**2**), a trace of phenanthrene-9-carboxylic acid (**3**),¹² and a trace of 10-[*p*-(*N,N*-dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic acid (**5**), Scheme 1. The yields of **1** and **2** varied upon inclusion of various additives in the system, Table 1.

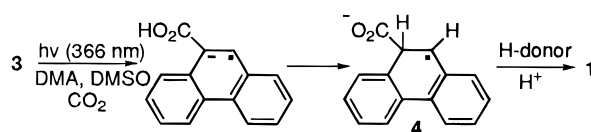
In the absence of additives the yield of **2** was low and, upon the addition of cumene, a hydrogen donor, or water, a proton donor, decreased even further while the yield of **1** increased slightly. Since the observation of an increased yield of **1** with the addition of hydrogen donors was consistent with previously reported data,¹¹ we postulated a common intermediate preceded the formation of both **1** and **2**. Assuming that the addition of CO₂ to the phenanthrene radical anion occurred first, 9-carboxy-9,10-dihydrophenanthr-10-yl anion (**4**) was suggested as an intermediate in the formation of **1**. Cumene, an effective hydrogen donor, trapped **4**, forming **1**. Water is an ineffective hydrogen atom donor hence one can assume that hydrogen abstraction from it is insignificant. When H₂O was replaced with D₂O in the experiment monodeuterated compound **1** was formed as indicated by ¹H NMR and GC-MS data. The ¹H NMR spectrum indicated that the site of deuteration was the 10 position of **1**, and monodeuterated **1** contributed 68% to the total yield of the monocarboxylic acid as calculated from the mass spectrum of the corresponding methyl ester.¹³ We thus concluded that 9-carboxy-9,10-dihydrophenanthr-10-yl was reduced in the course of the reaction with a formation of the corresponding anion **6** which was then trapped with D₂O at the 10 position. We estimated the reduction potential of **4** to be between -1 and -2 V by analogy with the reduction potential of the α -phenylethyl radical being -1.6 V vs SCE in CH₃CN.¹⁴

Protonation of the anions of carboxylic acids can occur as a result of proton transfer from DMA⁺ since proton loss by amino radical cations has been reported previously.¹¹ In addition, the GS-MS analysis of the photo-products which are insoluble in aqueous KOH evidences the presence of compounds with M⁺ = 240 corresponding

Scheme 2



Scheme 3

Table 2. Quantum Yield for the Formation of 2 as a Function of Light Intensity^a

I_0 , ^b Einsteins/s	time, ^c s	quantum yield for the formation of 2
8.01×10^{-8}	5400	0.137
5.69×10^{-8}	6763	0.115
3.61×10^{-8}	12000	0.073
2.15×10^{-8}	20164	0.069

^a Reaction system: [PHN] = 0.01 M, [DMA] = 0.2 M in DMSO saturated with CO₂. ^b Wavelength of irradiation light is centered at 348 nm, 8.5 nm bandpass. ^c The same number of photons is absorbed by each system.

to dimers of DMA radicals formed as a result of such a proton transfer.

It appeared that a strong reductant was required to react with **4**. Possible candidates were DMA, excited phenanthrene, or phenanthrene radical anion. Possible reactions leading to the formation of **2** are presented on Scheme 2. All but one of these pathways were eliminated in the course of our investigation.

We were able to conclude this by employing an alternative method for the generation of 9-carboxy-9,10-dihydrophenanthr-10-yl. Irradiation of **3** in the presence of DMA in DMSO saturated with CO₂ produced **1** in 86% yield. It is not unreasonable to propose that the mechanism of this reaction involves photoinduced electron transfer between **3** and DMA followed by proton transfer and hydrogen abstraction as shown on Scheme 3.

Proton transfer in the above reaction produces radical **4**. Absence of 9,10-dihydrophenanthrene-9,10-dicarboxylic acid allows us to eliminate two proposed pathways presented on the left in Scheme 2.

Quantum Yields of 2 as a Function of Incident Light Intensity. The three pathways presented in a group of three in Scheme 2 each require two photons for the formation of one molecule of 9,10-dihydrophenanthrene-9,10-dicarboxylic acid. Thus the quantum yield of formation of **2** should increase with light intensity (increased number of photons absorbed by PHN) as it does, Table 2.

We filtered UV light through a monochromator (348

(12) Detected by HPLC. Identified by comparison with authentic sample.

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nm with 8.5-nm band pass) to insure all the photons are absorbed by PHN in the quantum yield measurements.

It is possible to rule out singlet excited PHN as the reductant of **4** since values close to the diffusion controlled limit have been observed for its quenching rate constant by DMA in polar solvents.⁷ Under the conditions of our experiment ([DMA] = 0.2 M, [PHN] = 0.01 M) we estimate the lifetime of singlet PHN to be less than 1.5 ns. This value makes unlikely any bimolecular reaction in which ¹PHN* participates.

We were also able to detect triplet excited phenanthrene in this reaction using flash-photolysis, and it has been reported that triplet quenchers did not influence the yield of **1**.¹¹ In our study we found that addition of 2,5-dimethyl-2,4-hexadiene to the reaction did not effect the yield of **2**. In addition, from Rehm–Weller equation reduction of **4** with ³PHN* is an endergonic process ($E^{\text{ox}}(\text{PHN}) = 1.58 \text{ V vs SCE}$, $E_{00}^{\text{t}}(\text{PHN}) = 2.41 \text{ eV}$).^{5,6} Thus we eliminated ³PHN* as a participant in the reduction of **4**.

These results implicate PHN^{•-} as the reductant of **4**. Apparently, PHN^{•-} is a strong reducing agent owing to the fact that its oxidation restores conjugation.

The rate constants of CO₂ addition to carbon centered anions often reach the limits of diffusion control.¹⁵ Since the concentration of CO₂ in DMSO at atmospheric pressure reaches 0.21 M one expects rapid quenching of PHN^{•-}. This process would make the steady-state concentration of PHN^{•-} small, thus reducing the possibility of bimolecular reaction with another radical.

Tazuke et al.¹¹ proposed that equilibria are established in which there are significant concentrations of the ion radical involving the phenanthrene radical anion, CO₂, and the CO₂ adduct. Under such circumstances the concentration of the latter species should be controlled by the concentration (activity) of CO₂ in solution. We thus investigated the influence of [CO₂] on reductive carboxylation of PHN.

Influence of CO₂ Concentration on the Reaction Pathway. CO₂ concentration in DMSO is a major factor in determining the reaction pathway. Though the concentration of CO₂ in a saturated solution of a number of solvents at 25 °C was previously reported,¹¹ our measurement, following the procedure similar to that described by Kraeutler et al.¹⁶ confirmed that the concentration is 0.21 M in DMSO at 23 °C and atmospheric pressure. DMSO is miscible with liquid CO₂ so the value of [CO₂] therein at 50 atm CO₂ partial pressure can reach 10 M. Concentrations lower than 0.21 M were attained through purging DMSO with a mixture of argon and CO₂. The experimental set up assembled to measure the effect of CO₂ concentration in DMSO on the products of the reductive photocarboxylation is shown on Figure 1.

Combination of a 450 W xenon lamp with 340 nm interference filter (10 nm bandpass) produced a narrow wavelength band of UV light of sufficient intensity. 99% of the filtered UV light is absorbed by PHN. The irradiation was conducted for a period of time which corresponded to phenanthrene consumption of less than 10%. All the incident light entering the optical cell was absorbed by the reaction solution. The results are summarized in Table 3.

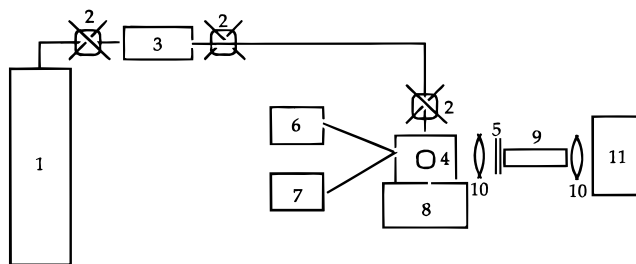


Figure 1. High pressure setup. 1: CO₂ cylinder; 2: pressure valves; 3: water trap; 4: high pressure optical cell; 5: interference filter; 6: temperature control unit; 7: pressure sensor; 8: magnetic stirrer; 9: infrared absorbing filter; 10: lenses; 11: 450 W xenon lamp.

Table 3. Influence of [CO₂] on the Reaction Pathway^a

pressure of CO ₂ , atm	detected products ^b	ratio 1/2 ^c
0.5	1, 2	3.3
1	1, 2	2.5
5	1, 2, 3	3.0
48	3, 5	—

^a Reaction system: [PHN] = 0.01 M, [DMA] = 0.2 M in DMSO. ^b Detected by HPLC. ^c Ratio of HPLC peak areas. UV detection at 280 nm.

We observed changes in the reaction pathway with an increase in the CO₂ partial pressure. At 50 atm CO₂ partial pressure, only trace amounts of **1** and **2** were detected and two other products became dominant. One was identified as **3** from UV-vis spectrum and GC-MS spectrum of methyl ester. The second product was identified as 10-*p*-(*N,N*-dimethylamino)phenyl-9,10-dihydrophenanthrene-9-carboxylic acid (**5**) by comparison of the HPLC traces of the unknown with an authentic sample synthesized by irradiation of phenanthrene-9-carboxylic acid methyl ester in CH₃CN in the presence of DMA followed by hydrolysis. The reactions are summarized in Scheme 4.

If PHN^{•-} is a reductant of **4**, and there is an equilibrium between PHN^{•-} and the CO₂ adduct, then a high CO₂ concentration would increase the concentration of the carboxylated radical while reducing the steady-state concentration of PHN^{•-}, thus making reduction of **4** less likely. This would depress the yield of **2**. Indeed, we observed the absence of **2** among the products of the reductive photocarboxylation at high CO₂ concentration.

These results are consistent with our proposal that PHN^{•-} was a reductant of **4**. They also supported the proposed equilibrium between the phenanthrene radical anion and the CO₂ adduct.

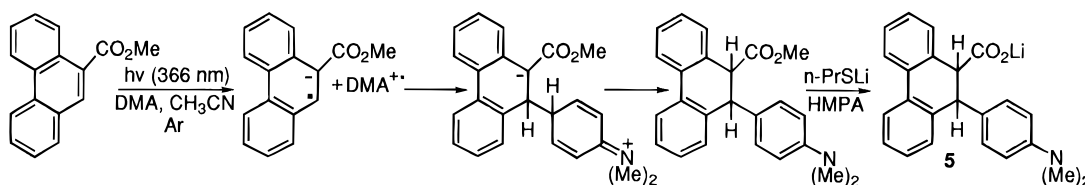
Mechanism of Reductive Photocarboxylation of PHN. The mechanism of reductive photocarboxylation of phenanthrene is outlined in Scheme 5. Electron transfer processes between ¹PHN* and DMA in polar solvents yield mainly free radical ions.⁷ ³PHN* is also formed and this is discussed in the flash photolysis section. Addition of CO₂ to PHN^{•-} is reversible as indicated by the results under high [CO₂].

Significant reduction in the yield of **2** upon addition of H₂O suggested that the addition of CO₂ to **6** is a much slower process than the initial addition of CO₂ to PHN^{•-}. Since, in DMSO, the reactivity of water is lessened by H-bonding, the addition of CO₂ to PHN^{•-} is faster than reaction of H₂O as indicated by the results in the presence of D₂O. Formation of **1** monodeuterated at the 10 position when D₂O was added to the reaction mixture is

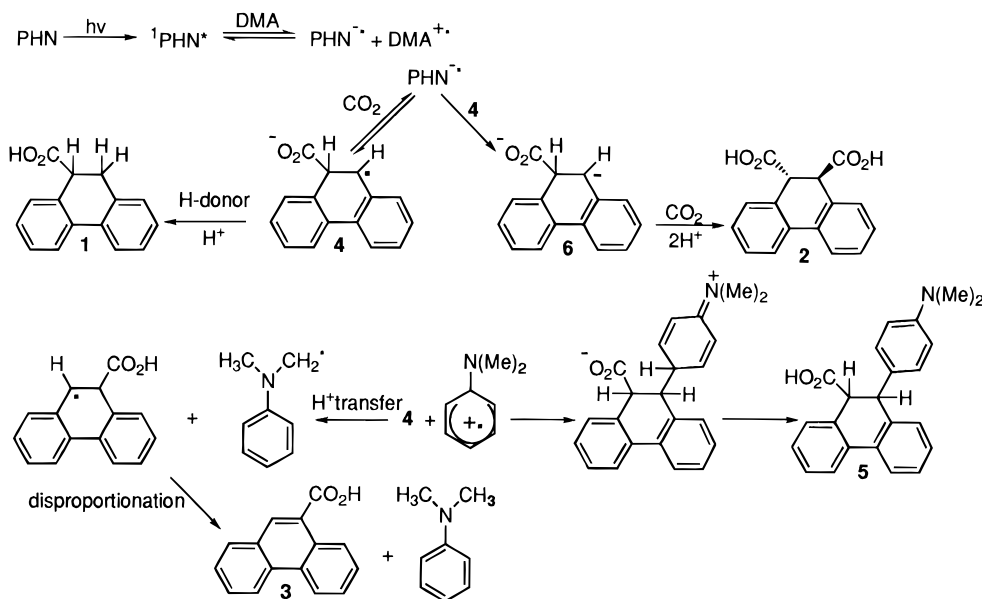
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Scheme 4



Scheme 5



still further evidence in support of the mechanistic scheme described above.

Salt Effect on the Yield of 1 and 2. Recently a number of groups have reported salt effects on photoinduced electron-transfer reactions.¹⁷ Yanagida et al.,¹⁸ for example, reported a 10-fold increase in the yield of benzoic acid in the photoreduction of CO₂ by benzophenone in the presence of tetraethylammonium chloride, while Santamaria observed an increased selectivity in photochemical N-demethylation of tertiary amines in the presence of an added salts such as LiClO₄ or Mg(ClO₄)₂.¹⁹

In our system, a slight increase in the yield of 1 and a 30% increase in the yield of 2 were observed in the presence of 0.1 M Mg(ClO₄)₂. The effects of tetramethylammonium chloride, tetraethylammonium chloride, tetrabutylammonium bromide, and LiClO₄ on the yields of the acids were comparable with experimental error (10%). We propose that the presence of salt effected the reduction of 4 to the corresponding anion. It is possible that the salt suppressed back electron-transfer thus increasing the total yield of 2. The specific nature of the individual salt effects is still to be determined.

Flash-Photolysis Experiments. Flash-photolysis of PHN–DMA system in DMSO was carried out in the presence and absence of CO₂. Transient absorption spectra are presented in Figure 2. We observed absorption from a number of transients in the 400–500 nm region. A difference in the character of the decay at 430

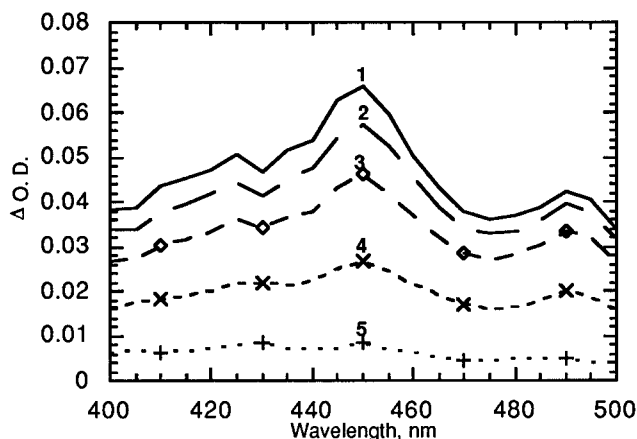


Figure 2. Transient absorption spectra of Ar-purged DMSO solution [PHN] = 0.01 M, [DMA] = 0.2 M: 1: 10 μ s after the pulse; 2: 11.2 μ s; 3: 13.6 μ s; 4: 22 μ s; 5: 54 μ s.

and 490 nm indicated the presence of at least two transient species. We attribute the major portion of the absorption to the phenanthrene radical anion (PHN^{-•}) which has been shown to have a broad absorption with λ_{\max} at 450 nm tailing up to 700 nm.⁹ The absorbance at 490 nm corresponds to the PHN triplet. Addition of the known triplet quenchers, 2,5-dimethyl-2,4-hexadiene or oxygen, to the solution results in the quenching of this transient absorbance consistent with PHN triplet behavior. The wavelength of the absorbance is consistent with that for PHN triplet in polar solvents.²⁰ We did not observe a distinct contribution from *N,N*-dimethylaniline

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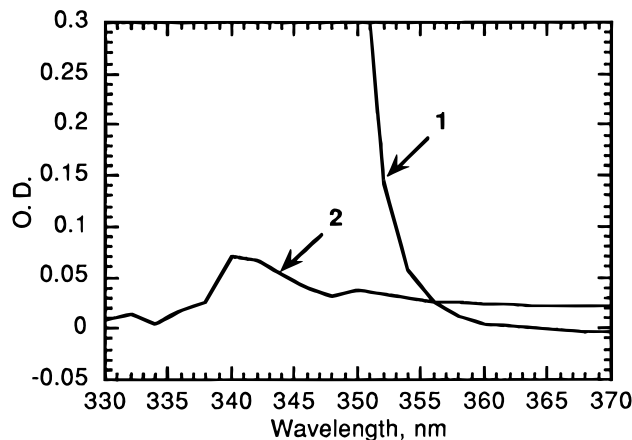


Figure 3. 1: The spectrum of separated solutions of PHN (0.01 M) in DMSO and DMA (0.5 M) in DMSO. 2: Difference absorption spectrum between solution of PHN and DMA in DMSO ([PHN] = 0.01 M, [DMA] = 0.5 M) and the spectrum of separated solutions of PHN in DMSO and DMA in DMSO.

radical cation ($\text{DMA}^{\cdot+}$) likely because the $\text{DMA}^{\cdot+}$ concentration is too low to permit its detection in DMSO.

For the range of concentrations used in our experiments, it was likely that all the singlet PHN was quenched by DMA, thus ruling out formation of triplet PHN via intersystem crossing from singlet PHN.

We have no evidence for complexation of CO_2 with any of these compounds since we found no change in the absorption spectra of PHN, DMA, and PHN-DMA in DMSO upon bubbling with CO_2 .

A number of groups have reported triplet formation in polar solvents resulting from some combination of the deactivation of vibrationally excited exciplexes, the recombination of radical ions, and excited charge-transfer complex deactivation. Ottolenghi et al. proposed this mechanism for a number of aromatic hydrocarbon/amine systems.²¹

We believe that the deactivation of vibrationally excited PHN-DMA exciplex and the recombination of the radical ions is responsible for triplet formation in our system. The difference absorption spectrum of the solutions of PHN and DMA in DMSO indicates the presence of a ground state complex between the hydrocarbon and the amine, Figure 3. For the ratio of concentrations PHN/DMA used in flash-photolysis experiments this complex absorbed 41% of the excitation light at 355 nm. Although it is not confirmed, it is possible that deactivation of excited PHN-DMA charge-transfer complex is also contributing to PHN triplet formation. We have no data on the photochemistry of PHN-DMA charge-transfer complex.

In Ar-purged DMSO solution of PHN and DMA second order decay of $\text{PHN}^{\cdot-}$ was observed, Figure 4. We measured k/ϵ , (k is the rate constant, ϵ is extinction coefficient of $\text{PHN}^{\cdot-}$ at 430 nm), to be $2.26 \pm 0.02 \times 10^6 \text{ cm s}^{-1}$. The observed second order decay of $\text{PHN}^{\cdot-}$ can be explained by assuming the bimolecular reactions of $\text{PHN}^{\cdot-}$ with $\text{DMA}^{\cdot+}$ are taking place. A new fast component was introduced into the decay by purging with CO_2 , Figure 4. We did not determine the rate constants

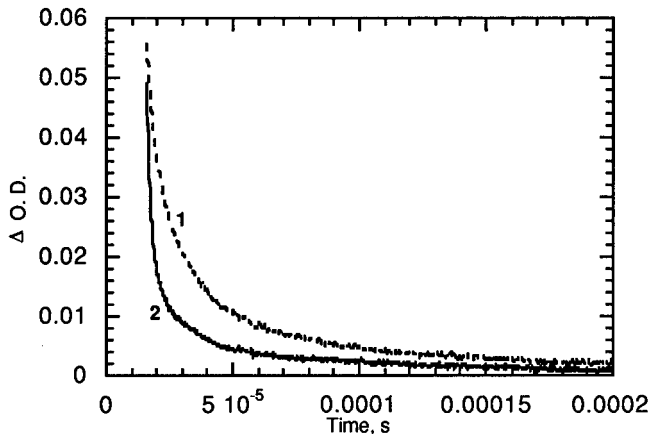


Figure 4. Transient absorption decays of $\text{PHN}^{\cdot-}$ at 430 nm in DMSO. 1: Purged with Ar; 2: purged with CO_2 . [PHN] = 0.01 M, [DMA] = 0.2 M.

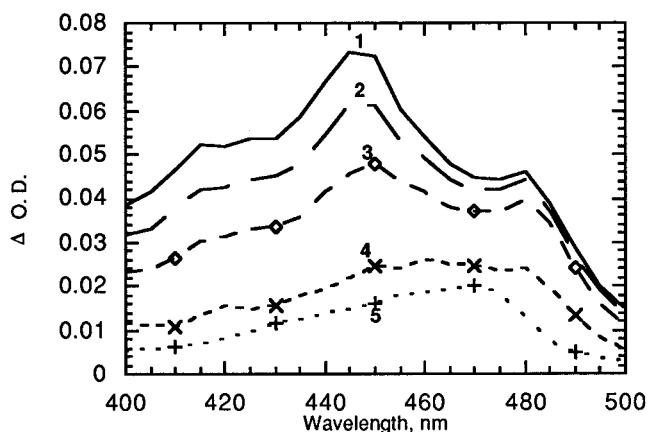


Figure 5. Transient absorption spectra of Ar-purged CH_3CN solution [PHN] = 0.01 M, [DMA] = 0.2 M. 1: 10.15 μs after the pulse; 2: 10.45 μs ; 3: 11.10 μs ; 4: 15 μs ; 5: 50 μs .

of the contributing components due to complexity of the decay in DMSO.

We observed different transient absorption spectra in CH_3CN , Figure 5. An absorbance with $\lambda_{\text{max}} = 465 \text{ nm}$ was observed in the transient spectra at longer time. The rate of decay of this absorbance was slower when compared with that of other transients, and it was possible to observe significant absorbance up to 200 μs after the laser pulse. This absorbance did not appear in the transient spectra when tributylamine replaced DMA as the electron donor. Addition of nitromethane to the acetonitrile solution produced a transient absorption spectrum identical to that observed in the earlier experiment at longer times after the laser pulse. We attribute the absorbance at $\lambda_{\text{max}} = 465 \text{ nm}$ to $\text{DMA}^{\cdot+}$ by comparison of the observed spectrum with that reported by Holcman et al.²²

The kinetics of the decay of $\text{PHN}^{\cdot-}$ in Ar-purged CH_3CN differed from those observed in Ar-purged DMSO, Figure 6. In CH_3CN we observed first-order decay of $\text{PHN}^{\cdot-}$ with a rate constant of $7.5 \pm 0.1 \times 10^5 \text{ s}^{-1}$. Upon purging with CO_2 the decay rate increased and the observed first-order rate constant became $1.28 \pm 0.05 \times 10^6 \text{ s}^{-1}$. Assuming the concentration of CO_2 in CH_3CN as 0.17 M¹¹ we calculated the rate constant of the reaction of $\text{PHN}^{\cdot-}$ with CO_2 to be $3.14 \pm 0.07 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

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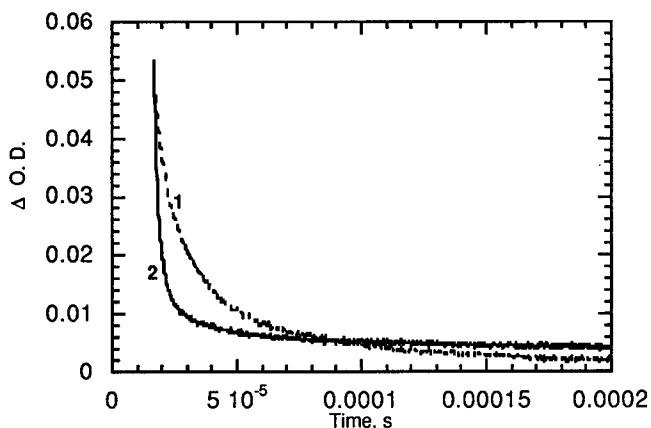


Figure 6. Decays of $\text{PHN}^{\bullet-}$ at 430 nm in (1) Ar-purged DMSO; (2) Ar-purged CH_3CN . $[\text{PHN}] = 0.01 \text{ M}$, $[\text{DMA}] = 0.2 \text{ M}$.

The observed results suggested $\text{PHN}^{\bullet-}$ quenching by CH_3CN which is consistent with the report of Tazuke et al.¹¹ that PHN did not undergo reductive photocarboxylation in that solvent. We found that 9,10-dihydrophenanthrene-9-carboxylic acid was produced in 9% yield and *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid was produced in trace amounts upon irradiation solution of PHN, DMA, and CO_2 in CH_3CN . Under similar experimental conditions, the yield of **1** was lower than that in DMSO. Quenching of $\text{PHN}^{\bullet-}$ by CH_3CN explains the lower yield of the acids formed in reductive photocarboxylation of phenanthrene. Observation of DMA^+ in CH_3CN at longer times after the laser pulse was consistent with proposed quenching of $\text{PHN}^{\bullet-}$ with CH_3CN to produce a less reactive ion radical. In the absence of such quenching one could expect a bimolecular coupling reaction of the ion radicals to consume DMA^+ .

The anion radical of 9,10-dicyanoanthracene is known to react with CH_3CN .²³ We think a similar reaction is occurring with $\text{PHN}^{\bullet-}$. Currently we are investigating this process.

Conclusions

We have shown that reductive photocarboxylation of phenanthrene in the presence of *N,N*-dimethylaniline proceeds via the radical intermediate 9-carboxy-9,10-dihydrophenanthr-10-yl which, upon hydrogen abstraction, forms 9,10-dihydrophenanthrene-9-carboxylic acid. This radical intermediate is also reduced with phenanthrene anion radical producing the corresponding anion and phenanthrene. This pathway results in the formation of *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid. We found that addition of CO_2 to phenanthrene anion radical is a reversible process as indicated by the results at high CO_2 concentration in solution. Considering the similarity between photochemical reductive carboxylation of aromatic hydrocarbons and reductive carboxylation of these using alkali metals, we propose that the same mechanism for the formation of dicarboxylic acids is operating in both cases. This mechanism involves reduction of the radical formed upon primary addition of CO_2 to $\text{PHN}^{\bullet-}$ with a second $\text{PHN}^{\bullet-}$.

Significantly reduced yield of the acids in CH_3CN can be explained by quenching of phenanthrene anion radical

with this solvent as it is shown by flash-photolysis results.

Experimental Section

Materials and Equipment. HPLC grade DMSO, DMF, and acetonitrile were purchased from Aldrich. DMSO and DMF were refluxed over calcium hydride for 1 h and fractionally distilled under vacuum. Acetonitrile was refluxed over phosphorus pentoxide and distilled before use. *N,N*-Dimethylaniline 99.5% (Aldrich) was dried over potassium hydroxide overnight and vacuum distilled. Phenanthrene 98% was purchased from Lancaster and purified according to a procedure previously described.²⁴ CO_2 (99.9%) was purchased from Liquid Carbonic.

NMR spectra were recorded using Varian Gemini-200 and Unity Plus-400 NMR spectrometers. GC-MS was performed on a Hewlett-Packard 5987A instrument. HPLC was performed on a Hewlett-Packard 1050 series instrument equipped with multiple wavelength diode-array and fluorescence detectors. UV spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and IR spectra were collected on a Mattson Instruments 6020 Galaxy Series FT-IR. A Spex Fluorolog 2 spectrofluorimeter was used for quantum yield measurements.

Photoreactions. Large-Scale. A 100 mL Pyrex internal irradiation photochemical reactor (Ace Glass) was used. A 450-W Hanovia high pressure mercury lamp (Ace Glass Inc.) was used as a light source. The standard sample volume was 100 mL. CO_2 , passed through drierite drying tube, was continuously bubbled through sample solution during photo-reaction. The standard concentrations of PHN and DMA were 0.05 M and 0.5 M.

Small-Scale. Small-scale reactions were conducted in a merry-go-round photochemical reactor using a 450 W high pressure mercury lamp placed in a Pyrex cooling immersion well as the irradiation source. Sample solutions were placed in Pyrex test-tubes (13–120 mm) through which CO_2 was bubbled for 15 min before irradiation. The test-tubes were sealed and irradiated for 30 min. The resulting solutions were analyzed by HPLC.

Products Separation and Identification. After photo-reaction, the solvent and amine were removed by vacuum distillation. KOH (40 mL/1 M) was added to the residue. The aqueous mixture was extracted with two 20 mL portions of chloroform and then with 20 mL of ether. The chloroform and ether extracts were combined, dried over anhydrous magnesium sulfate, and evaporated. The resulting residue was analyzed by GC-MS.

The aqueous solution was acidified with 3 M HCl to pH = 4 and extracted with two 20 mL portions of ethyl acetate. The combined ethyl acetate extracts were dried over magnesium sulfate, and the solvent was evaporated. Chloroform (20 mL) was added to the residue and then the mixture was heated. The boiling chloroform mixture was filtered and, when cooled, produced a white solid. The solid was chromatographed on silicic acid, the products being eluted with methylene chloride and ethyl acetate. The first product eluted was identified as 9,10-dihydrophenanthrene-9-carboxylic acid (**1**).³ The second product was *trans*-9,10-dihydrophenanthrene-9,10-dicarboxylic acid (**2**) which was recrystallized from 95% ethanol: mp 234–240 °C dec (lit.¹⁰ 235–242 °C); NMR (DMSO-*d*₆) δ 4.3 (2H, s), 7.3 (6H, m), 7.84 (2H, d), 12.55 (2H, s); MS *m/e* 268 (M^+), 250, 236, 222, 205, 178; HRMS *m/e* measured 268.0741 ($\Delta = -0.6$ mDa); calculated 268.0735; IR (KBr, cm^{-1}) 1702 ($\nu_{\text{C=O}}$). The dimethyl ester of **2** was synthesized using diazomethane and purified by chromatography on silica gel, (yield quantitative, mp 127 °C (lit.¹⁰ 128 °C)).

The chloroform filtrate was concentrated and chromatographed on silicic acid thus also producing a white solid. This compound was identified as 9,10-dihydrophenanthrene-9-carboxylic acid (**1**).

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Analysis by HPLC. The following method was used for carboxylic acid analysis. Tetramethylammonium chloride (2 mL of 0.01 M solution) in H₂O was added to 25 mL of reaction solution. The filtered sample (20 mL) was injected into an HPLC equipped with a Hewlett-Packard 10 μ m LiChrosorb column (200 mm \times 4.6 mm). Water-methanol was used as the mobile phase. The following solvent gradient was used (time, % methanol): (0 min, 10), (10 min, 70), the flow rate being 1 mL/min. The elution was monitored using UV-vis detection at 268 nm. The solid carboxylic acids were analyzed using a similar procedure, except the sample solution was prepared by dissolving the solid acids in methanol. For phenanthrene analysis, 10 mL of reaction solution was injected into HPLC equipped with 5 μ m Hypersil column (200 mm \times 4.6 mm). Hexane was used as the mobile phase, the flow rate being 0.5 mL/min. Detection was performed with UV-vis detector at 346 nm as well as with fluorescence detector (350 nm excitation, 400 nm observation).

Quantum Yield of Formation of 1 and 2 as a Function of Light Intensity. The reaction solution (0.01 M PHN, 0.18 M DMA in DMSO, total 2.5 g) was placed in a quartz cuvette, and CO₂ was bubbled through the sample. The irradiation was performed in a sample compartment of Spex Fluorolog 2 spectrofluorimeter with an excitation monochromator set at 348 nm, 8.5 nm bandpass. Under these conditions all the incident light is absorbed by PHN in the reaction solution. CO₂ was bubbled continuously through the sample during irradiation, and the progress of the reaction was monitored by measuring the UV absorbance of the reaction solution at 348 nm. Neutral density filters (Oriental Instruments) were used to control the light intensity. The time of exposure was varied depending on the intensity of incident light. In all reactions PHN consumption was less than 5%. After irradiation, samples were analyzed for phenanthrene and the carboxylic acids by HPLC as described above. Light intensity at 348 nm was measured using potassium ferrioxalate actinometry.⁵

Influence of CO₂ Concentration on the Pathway of Reductive Photocarboxylation. A high pressure optical cell, equipped with three sapphire windows, was constructed from 303 stainless steel. Cell design has been described elsewhere.²⁵ The cell was equipped with a pressure transducer (Omega Engineering Inc. PX-302-7.5KGV), a temperature control system (Lauda RM 6), and a pressure regulating valve (High Pressure equipment, 30-13HF4). The general scheme of the irradiation set up is presented on Figure 2.

A 500 W Xenon lamp (Oriental Instruments) was used as a light source. A 10 cm quartz tube with water in combination with an interference filter (340 nm, 10 nm bandpass, Oriental Instruments) was used to cut out the desired wavelength range. Experiments were conducted as follows.

The reaction solution (15 mL) was loaded into the optical cell, purged with CO₂ passed through a water trap (molecular sieves, 3A, Aldrich), and pressurized. The cell was equilibrated for 30 min prior to measurement. All the measurements were performed at 25 °C. The solution was continuously stirred during the experiments, and 1 atm partial pressure CO₂ was continuously bubbled through the solution in the optical cell. A 1:1 mixture of Ar and CO₂ was used to obtain 0.5 atm partial pressure of CO₂.

Measurement of CO₂ Concentration in DMSO. DMSO (30 mL) was placed in a 50 mL graduated cylinder connected with a gas mixer and a flask containing 200 mL of 0.1 M NaOH in H₂O saturated with Ba(OH)₂. The experiment was conducted at 22 °C. CO₂ was bubbled through DMSO for 30 min, after which the cylinder was connected to the flask with Ba(OH)₂ and purged with Ar for 30 min, the gas being dispersed in aqueous solution. The white precipitate was filtered under N₂ and weighed. BaCO₃ (1.249 g) corresponded to CO₂ concentration of 0.21 M.

Synthesis of Phenanthrene-9-carboxylic Acid (3). Phenanthrene-9-carboxylic acid (**3**) was synthesized by hydrolysis of 9-cyanophenanthrene (Aldrich, 97%) following the

procedure similar to that described by Anzalone.²⁶ A stirred mixture of 9-cyanophenanthrene (3.75 g, 18 mmol) and NaOH (1.75 g, 43 mmol) in 60 mL diethylene glycol was refluxed for 8 h. The cooled mixture was diluted with 100 mL of H₂O and acidified to pH = 1 with 3 M HCl. The white precipitate of the acid was filtered, dried, and recrystallized from methanol (yield 86%; mp 252 °C (lit.²⁷ 252 °C)). The methyl ester of **3** was synthesized by refluxing the acid in methanol containing a few drops of concentrated sulfuric acid for 4 h. The product was recrystallized from methanol (yield 91%; mp 115 °C (lit.²⁸ 115 °C)).

Synthesis of 9,10-Dihydrophenanthrene-9-carboxylic Acid (1). Phenanthrene-9-carboxylic acid (0.35 g; 1.6 mmol) and DMA (3.81 g; 32 mmol) were dissolved in 50 mL of DMSO and the solution was placed in the photochemical reactor described above, purged with Ar, and irradiated for 180 min. The solvent was evaporated in vacuum, 30 mL of 0.5 M KOH was added to the residue, and the solution was extracted with chloroform and ether. The white amorphous precipitate formed upon acidification of the aqueous solution with 0.5 M HCl was collected and washed with H₂O. Chromatography on silicic acid with CHCl₃ produced 0.29 g (81% yield) of **1**. Mp 111 °C (lit.²⁹ 111 °C dec); NMR (CDCl₃) δ 3.23 (2H, m), 3.84 (1H, t), 7.35 (6H, m), 7.78 (2H, m).

Synthesis of trans-9,10-Dihydrophenanthrene-9,10-dicarboxylic Acid (2). Compound **2** was synthesized via reaction of the phenanthrene sodium adduct with CO₂ following the procedure of Adams et al.¹⁰ Yield 34%. The analytical characteristics are the same as those for compound **2** prepared by the photochemical procedure.

Synthesis of 10-[p-(N,N-Dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic Acid (5). Methyl ester of 10-[p-(N,N-dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic acid was synthesized using the following procedure. Phenanthrene-9-carboxylic acid (0.3 g, 1.27 mmol) methyl ester and N,N-dimethylaniline (3 g, 25 mmol) were dissolved in 100 mL of anhydrous acetonitrile and placed in the photochemical reactor described above; the solution was purged with Ar and then irradiated with 366 nm light. The progress of the reaction was monitored by TLC. Upon completion the solvent was evaporated in vacuum and the products were chromatographed on silica gel with hexane-ethyl acetate (10:1). A 13% yield (61 mg) of 10-[p-(N,N-dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic acid methyl ester was obtained after chromatography: mp 57 °C; ¹H NMR (CDCl₃) δ 2.92 (6H, s), 3.59 (5H, m), 6.67 (2H, d, *J* = 15.9 Hz), 7.04 (2H, d, *J* = 15.8 Hz), 7.25 (6H, m), 7.74 (2H, dd, *J* = 9, 7 Hz). Anal. Calcd for C₂₄H₂₃O₂N: C, 80.67; H, 6.44; N, 3.92%. Found: C, 79.81; H, 6.69; N, 4.06%. MS: 357 (M⁺), 298, 237, 120.

The hydrolysis of 9,10-dihydrophenanthrene-10-(p-N,N-dimethylaminophenyl)-9-carboxylic acid methyl ester was performed following a procedure similar to that described by Bartlett et al.³⁰ 32 mg (0.0089 mmol) of 10-[p-(N,N-dimethylamino)phenyl]-9,10-dihydrophenanthrene-9-carboxylic acid methyl ester was treated with 6 mL of 0.63 M lithium propyl mercaptide in HMPA. The solution was stirred for 2 h, diluted with 50 mL of H₂O, extracted with three 20 mL portions of ether, and acidified with 1 M HCl. The precipitate was washed with H₂O and analyzed by HPLC using the procedure for carboxylic acids described earlier. Retention time and UV spectrum of this amino acid were identical with those obtained for an unknown compound synthesized under high pressure of CO₂.

Flash-Photolysis Experiments. Nanosecond flash-photolysis experiments were performed on a set up described by Ford and Rodgers³¹ using the third harmonic of a Q-switched

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Nd:YAG laser (Continuum, YG660) as an excitation source. Samples were purged with Ar or CO₂ prior to measurements.

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