

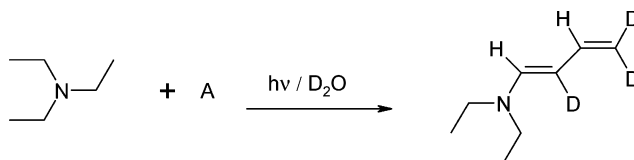
Unexpected Formation of 1-Diethylaminobutadiene in Photosensitized Oxidation of Triethylamine Induced by 2,3-Dihydro-oxoisoaporphine Dyes. A ^1H NMR and Isotopic Exchange Study

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A = 5,6-dimethoxy-, 5-methoxy-, or 2,3-dihydro-1-aza-benzo[de]anthracen-7-ones

Photoreduction of oxoisoaporphine dyes occurs via a stepwise mechanism of electron–proton–electron transfer that leads to the N-hydrogen oxoisoaporphine anion. When triethylamine, TEA, was used as the electron donor in anaerobic conditions, 1-diethylaminobutadiene, DEAB, was one of the oxidation products of TEA, among diethylamine and acetaldehyde. DEAB was identified by ^1H NMR and GC–MS experiments by comparison with the authentic 1-diethylaminobutadiene. This is the first report of a butadienyl derivative formed in the dye-sensitized photooxidation of TEA. In addition, isotopic exchange experiments with TEA- d_{15} and D_2O show that the hydrogens at carbon-2 and carbon-4 of the butadienyl moiety are exchangeable. The observed isotopic exchange pattern could be explained by the head-to-tail coupling of an *N,N*-diethylvinylamine intermediate that exchanges hydrogens at the C- β via the enammonium ion.

Introduction

In the photoreduction of many chromophores by electron donors, excited-state quenching by electron transfer leads to transient ion radical pairs which, due to back electron transfer, give no permanent chemical changes.¹ For some compounds, electron transfer quenching generates basic radical anions that are easily protonated, and semireduced free radicals accumulate.^{1,2} In some examples, a second electron transfer takes place, with generation of stable or metastable products of two-electron reduction or dihydro compounds, among oxidation products of the electron donor. This type of photo-

reaction has been reported for quinone derivatives,^{3,4} thioindigo dyes,⁵ quinoxalin-2-ones,^{6,7} electron-deficient azaarenes,⁸ and more recently, for 2,3-dihydro-oxoisoaporphines.⁹ When amines are the electron donor, the photooxidation products are usually vinylamine, enamine, iminium cation, aldehydes, and dealkylation products.^{10,11}

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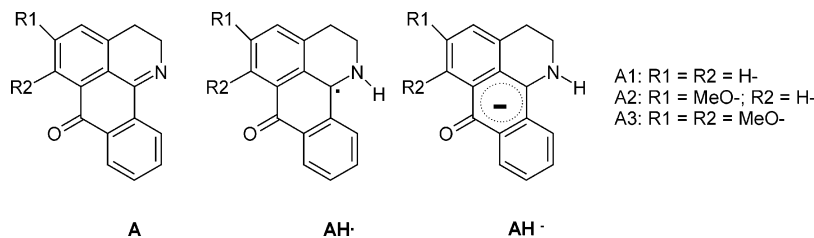
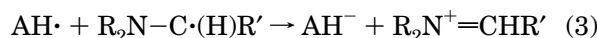
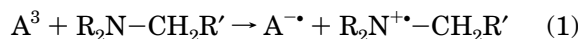


FIGURE 1. Structures of oxoisoaporphines, A, the respective neutral radical, AH•, and the N-hydrogen anion, AH⁻.

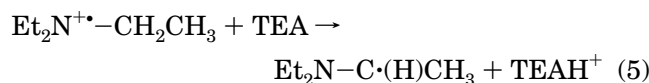
Result and Discussion

In our recent studies on the photoreduction of oxoisoaporphines, A, 2,3-dihydro-1-aza-benzo[de]anthracen-7-ones (**1–3**) by amines,⁹ we have proposed a stepwise mechanism of electron–proton–electron transfer that leads to the N-hydrogen oxoisoaporphine anion, AH⁻, with quantum yields of nearly 0.1. In that study, when TEA was the electron donor, the oxidation product was identified by NMR and GC–MS as 1-diethylaminobutadiene, DEAB.

The proposed mechanism for photoreduction of triplet oxoisoaporphines by amines⁹ involves the formation of the radical ion pair by single-electron transfer from the amine to the excited triplet of the oxoisoaporphine, eq 1. The amine cation radical readily donates a proton to the radical anion of the oxoisoaporphine to generate the dehydrogenated neutral radical of the amine, eq 2, undergoes a second electron transfer, leading to the iminium cation and the N-hydrogen anion of the oxoisoaporphine, AH⁻, eq 3, where the oxoisoaporphine, A, the neutral radical, AH•, and AH, have the structures shown in Figure 1.



The usually found photoproduct of TEA oxidation is the vinylamine that could be generated through the deprotonation of the iminium cation, eq 4, or alternatively by reaction of the TEA radical cation, deprotonated by excess TEA, followed by hydrogen atom transfer between two Et₂N–C(H)CH₃ radicals, eqs 5 and 6.^{10,11}



When other tertiary amines, such as *N,N*-diethylmethylaniline, *N,N*-dimethylethylamine, tri-*n*-propylamine, or tri-*n*-butylamine, were the electron donors, the sole NMR identifiable products, among AH⁻, were the respective aldehyde and the secondary amine dealkylation product,

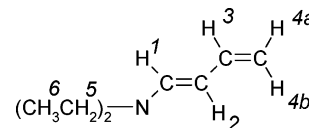
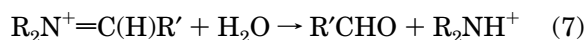


FIGURE 2. Structure of DEAB.

TABLE 1. Chemical Shifts and Coupling Constants for DEAB

hydrogen	δ /ppm	coupling constant/Hz
H-1	6.18	$J_{12} = 13.7$; $J_{13} = -0.5$; $J_{14a} = 0.6$; $J_{14b} = 0.5$
H-2	4.90	$J_{21} = 13.7$; $J_{23} = 10.4$; $J_{24a} = -0.5$; $J_{24b} = -0.5$
H-3	6.13	$J_{31} = -0.5$; $J_{32} = 10.4$; $J_{34a} = 10.4$; $J_{34b} = 16.8$
H-4a	4.26	$J_{4a1} = -0.5$; $J_{4a2} = -0.5$; $J_{4a3} = 10.4$
H-4b	4.51	$J_{4b1} = -0.5$; $J_{4b2} = -0.5$; $J_{4b3} = 16.8$
H-5	3.08	$J_{56} = 7.3$
H-6	1.08	$J_{65} = 7.3$

formed by hydrolysis of iminium cation by adventitious water, eq 7. These products, acetaldehyde and diethylamine, were also observed in the photolysis of TEA.



Notably, only when TEA was the electron donor in the photoreductions of any of the used oxoisoaporphine dyes, A1–A3, was 1-diethylaminobutadiene, DEAB, generated with a quantum yield ca. 0.03, estimated from their ¹H NMR absorptions.

The ¹H NMR spectrum of the photooxidation product of TEA shows signals between 6.0 and 6.3 ppm and between 4.2 and 5.0 ppm (see Figure S1 in the Supporting Information) as well as the ¹H NMR signals of the N–H of the oxoisoaporphine anion, AH⁻, at 5.4 ppm.⁹

These results strongly suggest that the photoproduct of TEA is 1-diethylaminobutadiene, Figure 2. The addition of authentic DEAB, prepared by the method of Hüning and Kahane,¹² to the reaction mixture, confirms the identity of the photoproduct. Table 1 summarizes experimental chemical shifts and coupling constants for DEAB.

The identity of the photoproduct was also confirmed by EI⁺ mass spectroscopy from the molecular ion $m/z^+ = 125$ and the fragment $m/z^+ = 110$, corresponding to loss of CH₃, and comparison with the authentic sample mass spectrum. To further confirm the identity of the photoproduct, we carried out photolysis with perdeuterated TEA, TEA-*d*₁₅, and analyzed the products by GC–mass spectroscopy. As expected, the photoreaction mixture shows a chromatographic peak with the molecular ion of $m/z^+ = 140$, corresponding to perdeuterated DEAB, but surprisingly, the mayor chromatographic peak has a

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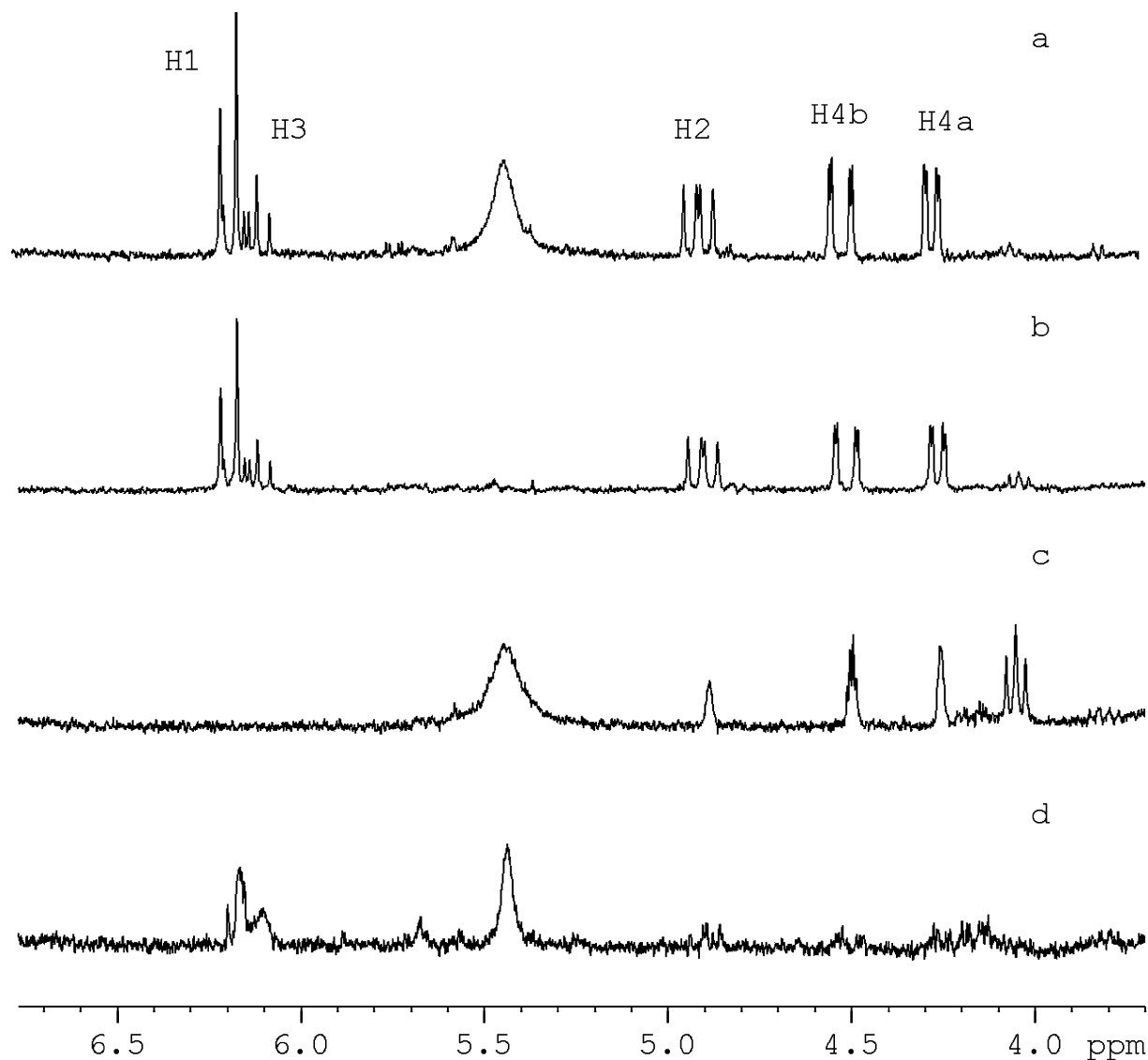


FIGURE 3. ^1H NMR spectra of the photoproduct mixture: (a) photolysis products with TEA- H_{15} , (b) with D_2O added after photolysis, (c) photolysis with TEA- d_{15} , and (d) photolysis with TEA- H_{15} in the presence of D_2O . For comments and assignments see the text.

molecular ion of $m/z^+ = 137$, consistent with exchange of three deuterium atoms of DEAB by hydrogen. The relative peak areas for $m/z^+ 137$ ($R_t = 10.04$ min) and $m/z^+ 140$ ($R_t = 10.21$ min) was 3.3:1, showing that almost 80% of the formed DEAB has exchanged deuterium by hydrogen, claiming for the ^1H NMR experiment using TEA- d_{15} and D_2O . Nevertheless, in the ^1H NMR experiment with TEA- d_{15} , signals corresponding to the perdeuterated DEAB will not be observed, but the isotopic exchange with adventitious H_2O results in signals from the exchanged hydrogen, allowing their assignment (spectrum shown in Figure 3c). The signals in the ^1H NMR spectrum correspond to the hydrogens at C2 and C4 of the butadienyl moiety of DEAB, confirming the formation of $(\text{C}_2\text{D}_5)_2\text{NCD}=\text{CH}-\text{CD}=\text{CH}_2$ ($m/z^+ = 137$) detected as the main photoproduct by GC-MS.

In NMR measurements in which TEA- H_{15} and D_2O were added prior to photolysis, only the hydrogens of C1 and C3 of the butadienyl moiety of DEAB are observed, with those corresponding to C2 and C4 being completely

exchanged with deuterium. To gain more insight into the isotopic exchange reaction, we performed various photolysis experiments with TEA- H_{15} and TEA- d_{15} , whose ^1H NMR results are summarized in Figure 3 and Table 2 together with the GC-MS results.

When D_2O is added to the photolyzed mixture with TEA- H_{15} , only the isotopic exchange of the oxoisoaporphine N-H proton is observed, as shown in Figure 3b. As discussed in preceding paragraph, the photolyzed mixture of TEA- d_{15} shows the ^1H NMR signals corresponding to hydrogens at C2 and C4 of DEAB, due to isotopic exchange, with hydrogen from adventitious water, Figure 3c. If D_2O is added prior to photolysis with TEA- H_{15} , Figure 3d, the ^1H NMR experiments show only protons at C1 and C3 of DEAB. These results prove that the isotopic exchange reaction by hydrogen or deuterium only occurs at C2 and C4 of the butadienyl moiety of DEAB at some stage in the photolysis.

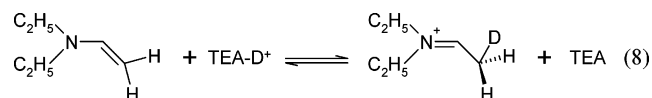
To explain the isotopic exchange pattern we consider the complete isotopic exchange at C- β of the N,N -

TABLE 2. Isotopic Exchange Experiments

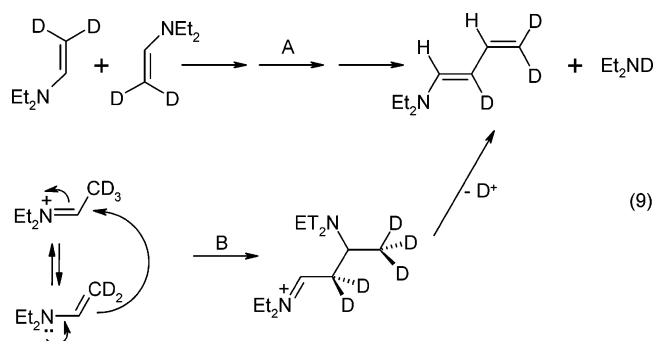
conditions solvent: CD ₃ CN	molecular ions <i>m/z</i> ⁺	isotopic exchange on 1,3-butadienyl moiety				products
		C1	C2	C3	C4	
TEA- <i>H</i> ₁₅ /H ₂ O	125 (110) ^a					(CH ₃ CH ₂) ₂ NCH=CH-CH=C H ₂
TEA- <i>d</i> ₁₅ /H ₂ O	140 (122) ^b 137 (119) ^b		X ^c		X ^c	(CD ₃ CD ₂) ₂ NCD=CD-CD=C D ₂ (CD ₃ CD ₂) ₂ NCD=CH-CD=C H ₂
TEA- <i>H</i> ₁₅ /D ₂ O added prior photolysis			X ^d		X ^d	(CH ₃ CH ₂) ₂ NCH=CD-CH=CD ₂

^a Loss of CH₃. ^b Loss of CD₃. ^c Exchange for H. ^d Exchange for D.

diethylvinylamine intermediate via the enammonium ion^{13–15} in the presence of excess D⁺ or H⁺ (from D₂O or H₂O, respectively), as indicated in eq 8 for deuterium exchange.



Two reaction paths would be possible: (A) The head-to-tail coupling of the resulting β-deuterated vinylamine with elimination of diethylamine should lead to DEAB deuterated at C2 and C4 of the butadienyl moiety, eq 9A. The coupling reaction probably involves a diethylvinylamine cation radical,¹⁶ likely generated by photoinduced electron transfer with the dye¹⁷ or by the formation of a [2 + 2] cycloadduct^{18–20} followed by diethylamine elimination and formation of (C₂H₅)₂NCH=CD-CH=CD₂. (B) Alternatively, the nucleophilic attack²¹ of the vinylamine taking place at the C-α of the iminium cation, followed by the elimination of diethylamine and H⁺, eq 9B, should lead to DEAB with the same isotopic pattern of substitution over C2 and C4 of the butadienyl moiety. In both reactions, butadienyl C2 and C4 were the former C-β of the diethylvinylamine intermediate.



For the photooxidation of tri-*n*-propylamine or tri-*n*-butylamine, the DEAB analogues 2,4-dialkyl-1,3-buta-

dienylamines would be expected, but the only identified products were the respective dialkylamines and aldehydes, whose characteristic ¹H NMR triplets appear near 9.5 ppm. The lack of formation of DEAB analogues when photolysis is carried out with these amines may be explained on the basis of greater steric hindrance that probably prevents addition of the dialkylvinylamine intermediate. The ¹H NMR experiment with a mixture of tripropylamine and TEA,²² 1:1 v/v, does not show the signals assigned to DEAB but shows new ¹H NMR signals between 5.8 and 6.3 ppm, at 5.0 ppm, and also 3.0 ppm (see Figure S9 in the Supporting Information) that could be attributed to other unidentified alkylbutadienes or alkylaminobutadienes likely formed from diethylvinylamine and the vinyl derivative of tripropylamine.

The expected DEAB analogues *N,N*-dialkyl-1,3-butadienylamine for the photooxidation of *N,N*-diethylmethylamine or *N,N*-dimethylethylamine was not formed, probably due to the well-known deprotonation of radical cations of amines to yield the least substituted α-aminoalkyl radical;^{10,11,23–25} thus, with the methyl-substituted trialkylamines the reaction should lead to the methaneiminium cation, RR'N⁺=CH₂, that by hydrolysis leads to formaldehyde and the respective dialkylamine.

Conclusions

To our knowledge, this is the first report of a butadienyl derivative formed in the dye-sensitized photooxidation of TEA. Isotopic exchange experiments with TEA-*d*₁₅ and D₂O show that the hydrogens at C2 and C4 of the butadienyl moiety are exchangeable. The observed isotopic exchange pattern could be explained by the head-to-tail coupling of the diethylvinylamine intermediate that exchanges hydrogen at the C-β via the enammonium ion. The isotopic exchange reaction reported here may provide a method for obtaining 1-diethylaminobutadiene isotopically labeled at C2 and C4 or at C1 and C3 of the butadienyl moiety.

Experimental Section

Amines were stored over potassium hydroxide pellets and vacuum distilled, trap-to-trap, sealed into glass tubes at 10^{−4} mm of Hg, and stored at −18 °C. Before each experiment, a

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new tube was opened to ensure freshness of the amine. Triethyl-*d*₁₅-amine, 99% D from Sigma Aldrich, was used as received.

1-Diethylaminobutadiene, DEAB, was prepared by a literature-reported method¹² in 42% yield: bp 54 °C/8 mm of Hg (lit.¹² 64–66 °C/10 mm of Hg). ¹H NMR data are shown in Table 1. The compound decomposes in air.

NMR Spectral Measurements. Reactions were carried out by direct photolysis (in the NMR tube sealed with a septum) of N₂-purged solutions containing ca. 1.5 mg/mL of the 2,3-dihydrooxoaporphine in CD₃CN. Immediately after purging, an aliquot, 3–10 μL, of pure amine was added through the septum. The solutions were photolyzed with light of 366 nm. During photolysis, several ¹H NMR spectra were recorded in order to test for maximum concentrations of the photoproduct. COSY spectra were taken when no more changes were detected in the NMR spectra. It was not possible to obtain a ¹³C NMR spectrum of the irradiated samples due to the low concentration of the photoproducts.

DEAB quantum yield estimation was made by comparing the integration for the ¹H NMR signals of the methylene

hydrogen of DEAB against the integration of the methylene hydrogen of the N-hydrogen oxoaporphine anion.

GC–MS analyses were performed in a capillary column, starting at 80 °C for 1 min with a 10 deg/min ramp up to 180 °C. EI⁺ detection mode was used, scanning *m/z*⁺ from 47 to 200 with a scan time of 0.15 s and leaving an interscan time of 0.16 s.

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Supporting Information Available: Authentic 1-diethylaminobutadiene ¹H NMR and mass spectra and mass spectra for deuterated DEAB are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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