Jones reagent is allowed to react with the benzyl ether of 2-octanol at 0 °C, using a 1-min addition and 4 min of stirring, 74% starting material is recovered in addition to 16% 2-octanone and 3% of the benzoate ester. Jones oxidation of 2-octanol is complete after a 1-min addition and 4 min of stirring under identical reaction conditions. Consequently, considerable benzyl ether oxidation will occur during alcohol oxidation with excess Jones reagent as these oxidations are often run.

Other chromium oxidizing agents were examined. For example, Collins reagent oxidizes alcohols to ketones in 15 min without affecting benzyl ethers;[7] however, after 15 h, 2-octyl benzyl ether gives 24% 2-octanone, 20% 2-octyl benzoate, and 45% starting material (the benzoic acid was not isolated). Pyridinium dichromate (PDC)[8] does not affect the benzyl ether of 2-octanol over a 16-h period.

There are several literature reports of oxidation of benzyl ethers.[9] For example, benzyl ether itself reacts with oxygen at elevated temperatures to give benzaldehyde, benzoic acid, benzyl benzoate, and toluene.[10] Benzaldehyde is produced from benzyl ethers and either uranium hexafluoride[11] or nitronium tetrafluoroborate[12] while electrolysis of benzyl ethers gives benzaldehyde and benzoate esters.[5] Benzyltriethylammonium permanganate converts benzyl ethers into benzoates[13] and chromium trioxide in glacial acetic acid yields esters from ethers.[14] In addition, there is one isolated report of the oxidation of a cyclic ether into a lactone with chromic acid in acetone.[15] Ruthenium tetroxide also effects the latter conversion[16] although benzyl ethers probably will be destroyed.[13]

In conclusion, oxidation of compounds containing benzyl ethers cannot be accomplished cleanly with Jones reagent if the desired oxidation is slow.[17] Collins reagent is an acceptable alternative for easily oxidized alcohols while PDC is satisfactory even for alcohols requiring prolonged reaction times.[18] Rapid oxidation by Jones reagent presents no difficulty.

Experimental Section

NMR spectra were recorded on a Varian T-60 spectrometer and IR spectra were obtained on a Perkin-Elmer 297 spectrometer. Melting points were run with a Thomas-Hoover melting-point apparatus. GC analyses were conducted with a Varian 90P instrument, using an SE-30 column.

Typical Oxidation Procedure. The benzyl ether (5.0 mmol) was dissolved in 100 mL of dry acetone and cooled in an ice bath. The Jones reagent[3] (4 equiv) was added dropwise over the appropriate period of time and the reaction was allowed to stir mechanically. The reaction mixture was quenched with ether and water and then extracted with four 50-mL portions of ether. The combined ether layers were washed with three 30-mL portions of saturated aqueous $NaHCO_3$, dried, and concentrated to give the benzoate ester, ketone, and benzyl ether if the reaction had not gone to completion. This mixture was analyzed by GC and NMR comparison with authentic samples. The combined $NaHCO_3$ extracts were acidified and cooled to 0 °C, and the benzoic acid was obtained by filtration. Melting point and NMR confirmed the identity of this product.

Registry No. Benzyl 1-methylheptyl ether, 67810-87-1; benzyl *p*-menth-3-yl ether, 76480-46-1; benzyl α-methylbenzyl ether, 2040-37-1; benzyl 2-bornyl ether, 76480-47-2; benzyl cyclohexyl ether, 16224-09-2; benzyl *p*-menth-8-en-3-yl ether, 76480-48-3; 2-octanone, 111-13-7; *p*-menthan-3-one, 89-80-5; acetophenone, 98-86-2; camphor, 76-22-2; cyclohexanone, 108-94-1; *p*-menth-8-en-3-one, 29606-79-9; 1-methylheptyl benzoate, 6938-51-8; menthol benzoate, 612-33-9; α-methylbenzyl benzoate, 13358-49-1; 2-bornanol benzoate, 20279-54-3; cyclohexyl benzoate, 2412-73-9; *p*-menth-8-en-3-ol benzoate, 76480-49-4; benzoic acid, 65-85-0.

(7) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.
(8) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.
(9) For an excellent review of benzylic oxidations using chromium reagents, see: Wiberg, K. B. In "Oxidation in Organic Chemistry"; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Vol. 5A, pp 83-105.
(10) Eichel, F. G.; Othmer, D. F. *Ind. Eng. Chem.* **1949**, *41*, 2623.
(11) Olah, G. A.; Welch, J.; Ho, T.-L. *J. Am. Chem. Soc.* **1976**, *98*, 6717.
(12) Ho, T.-L.; Olah, G. A. *J. Org. Chem.* **1977**, *42*, 3097.
(13) Schmidt, H.-J; Schafer, H. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 69.
(14) (a) Olson, D. H. *Diss. Abstr.* **1962**, *23*, 839. (b) Harrison, I. T.; Harrison, S. *J. Chem. Soc., Chem. Commun.* **1966**, 752. (c) Angyal, S. J.; James, K. *Carbohydr. Res.* **1970**, *12*, 147.
(15) Henbest, H. B.; Nicholls, B. *J. Chem. Soc.* **1959**, 221, 227.
(16) Smith, A. B., III; Scarborough, R. M., Jr. *Synth. Commun.* **1980**, *10*, 205.
(17) At the very least, this is true when an α,β-unsaturated acid like compound **2** is desired.
(18) Allylic alcohols give only α,β-unsaturated aldehydes with PDC but saturated primary alcohols yield aldehydes or acids depending on the solvent.[8] Collins reagent gives only aldehydes from primary alcohols.[7]

Chemical Reduction of Actinomycin D and Phenoxazone Analogues to Free Radicals[1]

Hiroyuki Nakazawa,* Feng-te E. Chou, Paul A. Andrews, and Nicholas R. Bachur

Laboratory of Clinical Biochemistry, Baltimore Cancer Research Program, DCT, NCI, Baltimore, Maryland 21201

Received September 3, 1980

The naturally occurring antibiotic actinomycin D (1, AMD) inhibits DNA-directed RNA synthesis[2,3] and is used clinically to treat Wilm's tumor, gestational choriocarcinoma, mixed metastatic embryonal carcinoma of the testes, and other tumors. In addition to the antibiotic's action of binding to DNA and inhibiting biochemical reactions involving DNA, the antibiotic causes chromosomal damage.[4,5] The clathrogenic nature of the antibiotic is not easily explained by simple DNA binding and appears to require active cell processes to occur. In our earlier investigations of AMD[6] we have shown that the phenoxazone ring system is capable of enzymatic single-electron reduction to a free radical intermediate with subsequent transfer of the electron to oxygen to yield superoxide. The similarity of quinone-containing antibiotics (for example, anthracyclines, mitomycin C, streptonigrin, etc.) and the quinonimine structure of AMD suggested the possibility of bioreductive capability of AMD that may fit the criteria of AMD being a "site-specific free radical".[7] We have proposed that some antibiotics are structurally prone to single-electron reduction to a free radical state and also have structural affinity for cellular components. As such "site-specific free radicals", these forms may be the critical activated form of the antibiotic to cause intracellular macromolecular damage and subsequent cell death.

In this work we have attempted to establish the chemical reductive nature of the quinonimine structure of AMD. We have utilized several chemical reducing agents and have followed the reaction by spectrophotometric and

(1) This paper was presented in part at the FASEB Meetings in Anaheim, CA, Apr 13-18, 1980.
(2) Homma, M.; Graham, A. F. *Biochim. Biophys. Acta* **1962** *61*, 642.
(3) Reich, E.; Franklin, R. M.; Shatkin, A. J.; Tatum, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 1238.
(4) Ostertag, W.; Kerten, W. *Exp. Cell Res.* **1965**, *39*, 296.
(5) Bridge, M. F.; Melamed, M. R. *Cancer Res.* **1972**, *32*, 2212.
(6) Bachur, N. R.; Gordon, S. L.; Gee, M. V. *Cancer Res.* **1978**, *38*, 1745.
(7) Bachur, N. R.; Gee, M. V.; Gordon, S. L. *Proc. Am. Assoc. Cancer Res.* **1978**, *19*, 75.

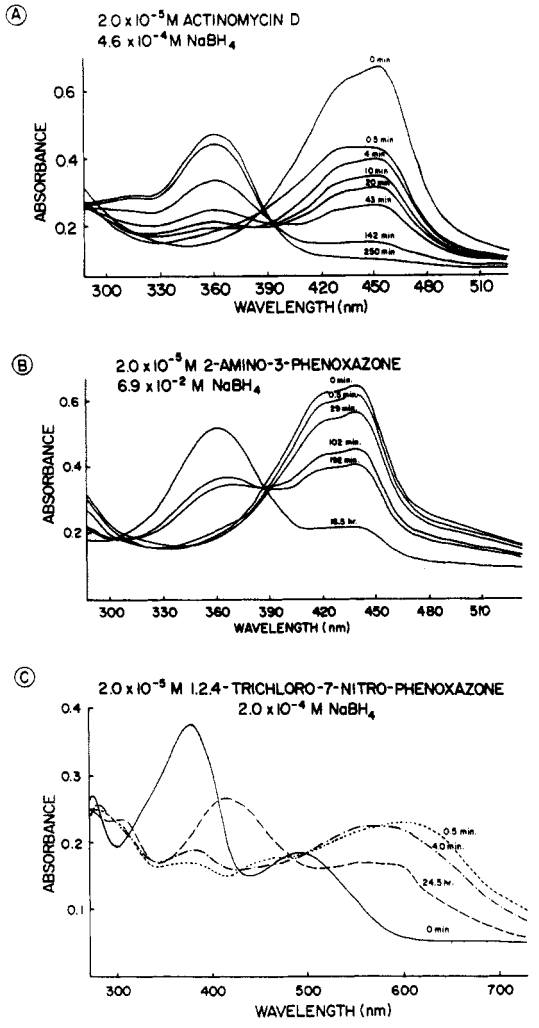


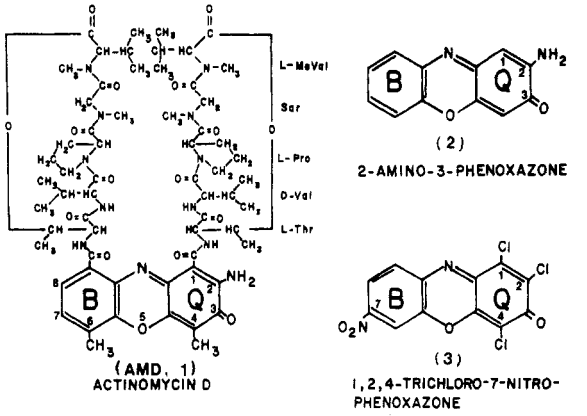
Figure 1. (A) Absorption spectra of AMD during $NaBH_4$ reduction. The reaction mixture contained 2.0×10^{-5} M actinomycin D and 4.6×10^{-4} M $NaBH_4$ in Me_2SO. Spectral scans were made at 0, 0.5, 4, 10, 20, 43, 142, and 250 min after addition of $NaBH_4$ to AMD. (B) Absorption spectra of 2-amino-3-phenoxazone during $NaBH_4$ reduction. The reaction mixture contained 2.0×10^{-5} M 2-amino-3-phenoxazone and 6.9×10^{-2} M $NaBH_4$ in Me_2SO. Spectral scans were made at 0, 0.5, 29, 102, and 192 min and 18.5 h after addition of $NaBH_4$ to 2. (C) Absorption spectra of 1,2,4-trichloro-7-nitrophenoxazone during $NaBH_4$ reduction. The reaction mixture contained 2.0×10^{-5} M 1,2,4-trichloro-7-nitrophenoxazone and 2.0×10^{-4} M $NaBH_4$ in Me_2SO. Spectral scans were made at 0, 0.5, and 4.0 min and at 24.5 h after addition of $NaBH_4$ into 3.

electron paramagnetic resonance spectrometry and thereby have proposed reductive pathways for the phenoxazone moiety.

Results

(A) Reduction with $NaBH_4$. The reduction of AMD by $NaBH_4$ was scrutinized by the change of absorption maximum in the range of 300–550 nm. The gradual decrease of absorbance intensity at 452 nm and increased absorbance at 362 nm was monitored after mixing a 2×10^{-5} M solution of AMD with 4.6×10^{-4} M $NaBH_4$ in dimethyl sulfoxide (Me_2SO; Figure 1A). The absorption peak at 452 nm disappeared after reaction at room temperature for 4.2 h. The new absorption maximum at 362 nm stabilized at 4.2 h and remained unchanged after 22.4 h of standing. Disappearance of the reddish orange color also indicated that the reaction was complete. The rate of reduction was measured from the relative changes of absorbance of these two distinctive peaks with time. A

Chart I.[a] **Structures of Actinomycin D, 2-Amino-3-phenoxazone, and 1,2,4-Trichloro-7-nitrophenoxazone**



[a] B and Q denote the benzenoid and quinoid portions, respectively, of the phenoxazone ring.

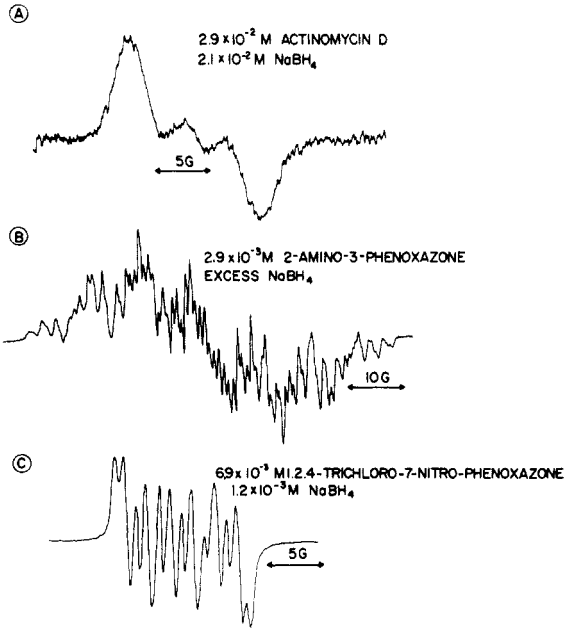


Figure 2. (A) ESR spectrum of AMD (2.9×10^{-2} M) free radical from $NaBH_4$ (2.1×10^{-2} M) reduction in Me_2SO. Spectrometer settings are as follows: microwave power, 5 mW; microwave frequency, 9.265 GHz; modulation amplitude, 8 G; time constant, 1.0 s; scan rate, 3.1 G/min; receiver gain, 1.0×10^5. Here and in the other figures, the arrow indicates the resonance of a strong pitch standard ($g = 2.0028$). (B) ESR spectrum of a free radical from 2-amino-3-phenoxazone (2.9×10^{-3} M) reacted with excess solid $NaBH_4$ in Me_2SO. Spectrometer settings are as follows: microwave power, 20 mW; microwave frequency, 9.265 GHz; modulation amplitude, 0.80 G; time constant, 0.250 s; scan rate, 12.5 G/min; receiver gain, 1.0×10^4. (C) ESR spectrum of a free radical from 1,2,4-trichloro-7-nitrophenoxazone (6.9×10^{-3} M) with $NaBH_4$ (1.2×10^{-3} M) in Me_2SO. Spectrometer settings were as follows: microwave power, 15 mW; microwave frequency, 9.268 GHz; modulation amplitude, 0.063 G; time constant, 0.250 s; scan rate, 12.5 G/min; receiver gain, 8.0×10^3.

similar spectral pattern for the reduction of 2-amino-3-phenoxazone (2, Chart I) in Me_2SO with $NaBH_4$ was observed by noting the shift of λ_{max} from 441 to 360 nm (Figure 1B). However, the reduction of 1,2,4-trichloro-7-nitro-3-phenoxazone (3) with $NaBH_4$ gave more than one peak early in the reaction. After 24.5 h, two absorption peaks at 417 and 598 nm replaced the original adsorption maximum of 385 and 495 nm (Figure 1C).

The reduction of AMD with $NaBH_4$ in Me_2SO generated an EPR signal with broad resonance peaks (Figure 2A).

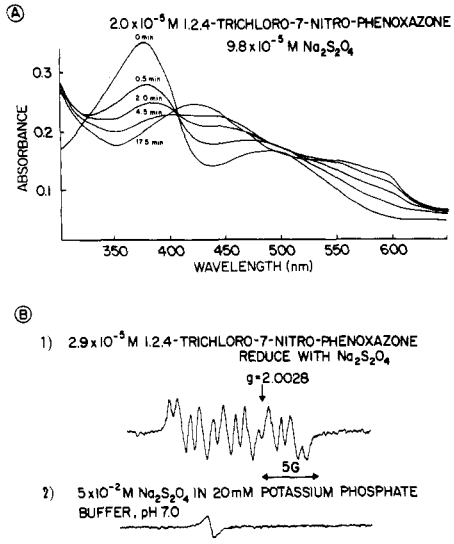


Figure 3. (A) Absorption spectra of 1,2,4-trichloro-7-nitrophenoxazone with $Na_2S_2O_4$ reduction. Final concentrations of 1,2,4-trichloro-7-nitrophenoxazone and $Na_2S_2O_4$ in Me_2SO were 2.0×10^{-5} and 9.8×10^{-5} M, respectively. Spectral scans were made at 0, 0.5, 2.0, 4.5, and 17.5 min. (B) (1) ESR spectrum of a free radical from 1,2,4-trichloro-7-nitrophenoxazone with $Na_2S_2O_4$. The spectrum was obtained from 2.9×10^{-3} M 1,2,4-trichloro-7-nitrophenoxazone in Me_2SO (200λ) with a 2λ of 1.0×10^{-1} M $Na_2S_2O_4$ in 20 mM potassium phosphate buffer (pH 7.0). (2) ESR spectrum of a free radical from 5.0×10^{-2} M $Na_2S_2O_4$ in 20 mM potassium phosphate buffer (pH 7.0).

In contrast, hyperfine EPR spectra were obtained from the reduction of **2** and **3** with $NaBH_4$. AMD, **2** or **3** alone in Me_2SO yielded no detectable free-radical signals. The rates of free-radical formation are quite different between **2** and **3**. Compound **3** gave rapid appearance of the radical signal (approximately 4 min) whereas **2** formed the free radical slowly (about 2 h). The fast formation, strong EPR signal intensity, and long lifetime for the free radical obtained from **3** reflect the increased stability of this free-radical form. Calculated *g* values for free radicals of AMD, **2**, and **3** are 2.0037, 2.0046, and 2.0054, respectively.

The infrared spectrum of the reduced product of **2** with $NaBH_4$ in THF indicates the disappearance of the carbonyl band (1600 cm^{-1}) as a result of reduction.

(B) Reduction with $Na_2S_2O_4$. The changes of absorption spectra (Figure 3A) and EPR spectral developments (Figure 3B-1) from the reduction of **3** with $Na_2S_2O_4$ resembled those obtained in $NaBH_4$ reductions (Figures 1C and 2C). However, dithionite alone in 5.0×10^{-2} M phosphate buffer produced a free-radical signal which has a *g* value close to the previously reported value[8] (Figure 3B-2). Because the dithionite free radical has a *g* value and pattern similar to AMD and **2**, free-radical experiments with $Na_2S_2O_4$ were difficult to interpret and were abandoned.

(C) Reduction with Other Reducing Agents. Other reducing agents such as $NaBH_3(CN)$ (sodium cyanoborohydride), NADPH, ascorbic acid, cysteine, and glutathione were assessed by being reacted with Me_2SO solutions of **3**. Only $NaBH_3(CN)$ and NADPH produced a reaction which yielded detectable free radicals of the phenoxazone compound.

(D) Dilute Alkaline Cleavage of AMD. AMD (2×10^{-5} M) was cleaved with 9.8×10^{-3} N NaOH in a 50% aqueous–ethanol solution. The rate of decrease of the 452-nm peak is equal to the rate of increase of the 344-nm peak (Figure 4). An isosbestic point at 380 nm indicates that there is no intermediate involved in these reactions.[9] Dilute alkaline hydrolysis of AMD gave no detectable free-radical signal.

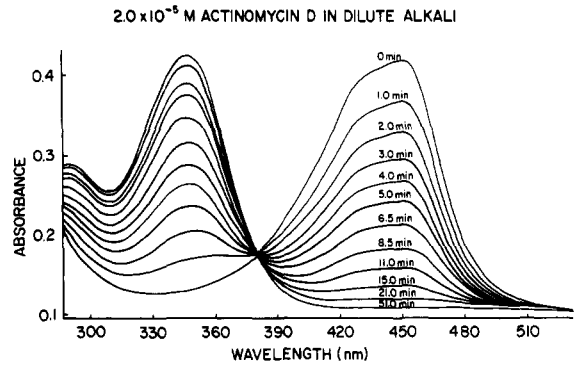
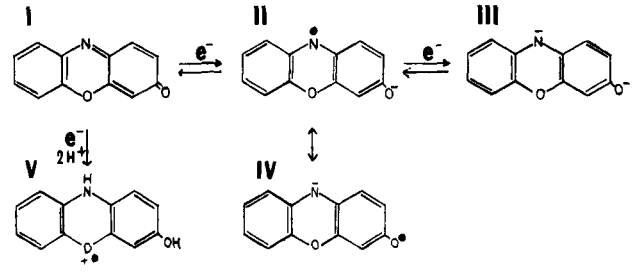


Figure 4. Absorption spectra during reaction between AMD and dilute alkali. Reaction mixture contained 2.0×10^{-5} M AMD and 9.8×10^{-3} N NaOH in 50% aqueous ethanol solution. spectral scans were made at 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.5, 8.5, 11.0, 15.0, 21.0, and 51.0 min after addition of sodium hydroxide solution in AMD in 50% aqueous ethanol solution.

Scheme I. Proposed Mechanism for the Reduction Pathway of Phenoxazone



Discussion

The chemical reduction of AMD with $NaBH_4$ is similar to that of anthraquinones.[10-12] In aprotic solvents, two reduction steps occur, each corresponding to the addition of one electron. If the reduction of anthraquinones is carried out in a protic solvent, the radical anion may obtain a proton from the solvent to form a radical, which can then be reduced further to give product. It is well understood that polarographic reduction of anthraquinones yields two waves corresponding to the stepwise single electron transfer in aprotic solvents such as acetonitrile, DMF,[13] pyridine,[14] Me_2SO,[15] etc. Addition of proton donor causes the second step to shift to more positive potentials and eventually to merge with the first potential step to produce the reversible two-electron process observed in aqueous systems.[16]

In our experiments on the chemical reduction of AMD, the reactions were performed in Me_2SO, so that AMD and **2** are expected to form their anion radicals (Scheme I). One-electron reduction of the quinone imine can be expected to yield two possible anion radicals; the radical site can be either on the nitrogen atom (N10, II) or the ring

(8) Milicevic, B.; Eigenmann, G. *Helv. Chim. Acta* **1963**, *46*, 192.
(9) Angyal, S. J.; Bullock, E.; Hanger, W. G.; Howell, W. C.; Johnson, A. W. *J. Chem. Soc.* **1957**, 1592.
(10) Sinha, B. K. *Chem.-Biol. Interact.* **1980**, *30*, 67.
(11) Lown, J. W.; Chen, H. H.; Plambeck, J. A.; Acton, E. M. *Biochem. Pharmacol.* **1979**, *28*, 2563.
(12) Lown, J. W.; Sim, S. K.; Chen, H. H. *Can. J. Biochem.* **1978**, *56*, 1042.
(13) Wawzonek, S; Berkey, R.; Blaha, E. W.; Runner, M. E. *J. Electrochem. Soc.* **1956**, *103*, 456.
(14) Turner, W. R.; Elving, P. J. *J. Electrochem. Soc.* **1965**, *112*, 1215.
(15) Kolthoff, I. M.; Reddy, T. B. *J. Electrochem. Soc.* **1961**, *108*, 980.
(16) Jones, R.; Spotswood, T. M. *Aust. J. Chem.* **1962**, *15*, 492.

oxygen atom (O3, IV). Bil'kis et al.[17] characterized the cation and anion radicals of some substituted phenoxazones as the nitrogen atom (N10) being the radical site for the anion radical (II) and an oxygen (O5, V) being the radical site for the cation radical. Because of Bil'kis' conclusion, we assigned the radical site of AMD to the nitrogen atom (N10, II). Compound **3**, however, has an additional reducible substituent besides the quinonimine nucleus, namely, the nitro group. By brief analysis of the hyperfine splitting pattern of the radical, the radical site also seems to be located on N10. The examination of substituent effects on redox potential is being examined at present.

$NaBH_4$ is the strongest among the reducing agents we used for this study. Anion radical formation can be effected by careful addition of $NaBH_4$; however, excess reagent tends to enhance further reduction to the dianion.[18] With respect to the hypsochromic modification of AMD, it has been reported that dilute alkaline solutions cause a cleavage of the phenoxazone ring system and associated disappearance of color.[9] In this instance, the water content of the Me_2SO may lead to formation of a strongly basic reaction product as observed by Schlesinger et al.[19] ($NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$) which could then cause ring cleavage. $NaBH_4$ reduction, however, yields a product with a λ_{max} of 362 nm and no definitive isosbestic point. These differences indicate that the integrity of the fused ring system is preserved during $NaBH_4$ reduction.

Among common biochemical reducing agents such as NADPH, cysteine, ascorbic acid, and glutathione, only NADPH is effective as a cofactor in the enzymatic reduction of anthraquinones.[20] In our experiments, however, NADPH is not as effective for AMD generation of free radicals under similar conditions.[7] This tends to suggest that phenoxazone is a weaker oxidant than anthracyclines.

Rat liver NADPH cytochrome P-450 reductase catalyzed the single-electron reduction of quinone antibiotics to a semiquinone free-radical state with NADPH as the electron donor.[20] After chemical reductive activation, adriamycin and daunorubicin cause DNA breakage and damage.[21] We find that rat liver microsomes and NADPH cytochrome P-450 reductase catalyzed NADPH-dependent oxygen consumption with AMD and produced an AMD free radical,[7] which is similar to anthracycline drugs. Since AMD is known to cause DNA damage in cells, the free radical form of AMD produced chemically or enzymatically may be the means by which this damage is produced. This action may be the source of pharmacologic activity and toxicity of these drugs. In order to understand more quantitatively the reaction mechanism for reduction and free radical formation, we are presently engaged in electrochemical studies of AMD and its analogues.

Experimental Section

AMD was obtained from the Drug Development Branch, DCT, NCI, Bethesda, MD. 2-Amino-3-phenoxazone (**2**) and 1,2,4-trichloro-7-nitro-3-phenoxazone (**3**) were synthesized according to published methods[22,23] and were purified by preparative TLC (Chart I).

Preparative silica gel G plates (Merck, Darmstadt) were activated by being heated at 130 °C for 30 min. One to two milliliters of a concentrated tetrahydrofuran (THF) solution of **2** or **3** was applied in a streak and dried in air. Compound **2** was developed in ethyl acetate/chloroform (1:1) and **3** in chloroform/methanol/acetic acid (200:4:5). The band of interest was removed and eluted with THF to yield pure product. UV-visible absorption spectra were obtained on an Aminco DW-2 UV-visible spectrometer with a scan speed of 20 nm/s. Infrared spectra were obtained from a Perkin-Elmer 197 infrared spectrophotometer in a 0.2-mm sodium chloride cell with THF as solvent. EPR spectra were acquired at room temperature on a Varion E-9 spectrometer with 100-KHz field modulation and a flat sample cell. The g values were calculated against a strong pitch as standard. Oxygen was purged off with bubbling nitrogen gas for 5 min in order to get the EPR spectra and absorption spectra.

Acknowledgment. The authors are indebted to Dr. H. Kon, Laboratory of Chemical Physics, National Institute of Arthritis, NIH, for technical advice on the electron spin resonance measurements. We also thank Ms. H. Chlewicki and B. Dressel for preparation of this manuscript.

Registry No. 1, 50-76-0; 2, 1916-59-2; 3, 13437-03-1.

(17) Bil'kis, I. I.; Boguslavskii, E. G; Viktorova, T. S.; Afanaseva, G. B.; Postovskii I. Y.; Shein, S. M. *Tezisy Dokl. Vses. Soveshch. Kompleksam Perenosom Zaryada Ion-Radikal'nym Solyam, 3rd.* **1976**, 92.

(18) A reviewer commented that $NaBH_4$ may be a two-electron reducing agent, i.e., a hydride donor. With a deficiency of $NaBH_4$, the two-electron reduction product may disproportionate with starting material to form radicals.

(19) Schlesinger, H. I.; Brown, H. C.; Finholt, A. E.; Gilbreath, J. R.; Hoekstra, H. R.; Hyde, E. K. *J. Am. Chem. Soc.* **1953**, *75*, 215.

(20) Bachur, N. R.; Gordon, S. L.; Gee, M. V.; Kon, H. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 954.

(21) Lown, J. W.; Sim, S. K.; Majundar, K. C.; Chang, R. Y. *Biochem. Biophys. Res. Commun.* **1977**, *76*, 705.

(22) Abu El-Haj, M. J.; Dominy, B. W.; Johnston, J. D.; Haddadin, M. J.; Issidorides, C. H. *J. Org. Chem.* **1972**, *37*, 589.

(23) Mital, R. L.; Jain, S. K. *J. Chem. Soc. C* **1971**, 1875.

One-Electron Photooxidation of Carbazole in the Presence of Carbon Tetrachloride

Bogumil Zelent† and Gilles Durocher*

Département de Chimie, Université de Montréal, C.P. 6210, Succ. A. Montréal, Québec, Canada H3C 3V1

Received August 13, 1980

It has been shown that aromatic amine molecules like indole interact in their triplet excited states with halocarbon molecules through normal external spin-orbital coupling or by complexation when chlorine atoms were part of the halocarbon molecule.[1] Similar results have recently been obtained with carbazole except that the interaction with halocarbons is much less than that with indole.[2] Ground-state charge-transfer complexes between carbazole derivatives and strong electron-acceptor molecules like chloranil and tetracyanoethylene have been observed.[3] On the other hand, an exciplex mechanism for the quenching of singlet excited states of aliphatic ketones[4] and aromatic hydrocarbons[5-7] by carbon tetrachloride has been proposed. Even though we were unable to show any evidences of ground-state complexation between carbazole and carbon tetrachloride, a good correlation was obtained between the fluorescence quenching rate constants and the quenchers half-wave reduction potentials ($E_{1/2}$), suggesting that the quenching mechanism involved an electron trasfer from the excited singlet carbazole to the halocarbon molecules.[8] Whether an excited triplet state of carbazole might play a role or not in the primary photochemical electron-transfer event is not ruled out at the moment.[9,10] We report here on the photochemical aspect of the problem which confirms the mechanism discussed above.

†On leave from the Department of Chemistry, Univeristy of Gdansk, 80-952 Gdansk, Poland.

0022-3263/81/1946-1496$01.25/0