heteroatom (O or N from the ester or amide) is present, which further stabilizes the formal cationic terminus of the dipole. This stabilization sufficiently retards the rate of intramolecular cycloaddition with the tethered olefin to allow bimolecular cycloaddition with an activated alkyne to predominate. In the case of **9**, however, this stabilization is absent and the intramolecular cycloaddition to the internal π-bond is too rapid to allow bimolecular trapping of the intermediate carbonyl ylide.

The high efficiency of the cycloaddition coupled with the simplicity of the procedure promises to provide an efficient route to a variety of oxapolycycles. The tandem cyclization–cycloaddition sequence allows for the creation of three new rings containing two (or more) contiguous quaternary centers with fixed stereochemistry in a single step. We are continuing to explore the scope and mechanistic details of the reaction and will report additional findings at a later date.

Acknowledgment. We gratefully acknowledge the National Cancer Institute for generous support of this work.

Registry No. **4a**, 114491-32-6; **4b**, 114491-34-8; **5a**, 114491-33-7; **5b**, 114491-35-9; **6a**, 114491-36-0; **6b**, 114491-43-9; **7a**, 114491-37-1; **7b**, 114491-44-0; **8a**, 114491-38-2; **8b**, 114491-45-1; **9a**, 114491-39-3; **9b**, 114491-46-2; **10a**, 114491-40-6; **10b**, 114491-47-3; **11**, 114491-41-7; **12**, 114491-42-8; $Rh_2(OAc)_4$, 15956-28-2; $HC{\equiv}CCO_2CH_3$, 922-67-8; PhCHO, 100-52-7.

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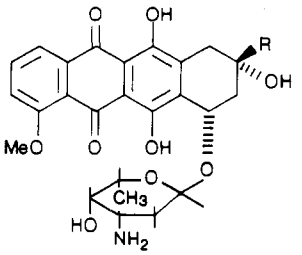
Photodemethylation of Methoxy-Substituted 9,10-Anthraquinones in Methanol

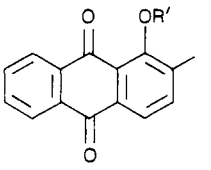
Summary: Irradiation of methoxy-substituted 9,10-anthraquinones with visible or ultraviolet light results in a demethylation reaction involving free radical intermediates.

Sir: 9,10-Anthraquinones comprise an important class of compounds that are used as dyes,[1] function as catalysts in the delignification of wood,[2] and bear a substitution pattern reminiscent of the clinically important antitumor anthracyclines **1**. As a result, considerable effort has been directed toward the synthesis of not only anthraquinones[3] but also anthracyclines[4] and their analogues.[5]

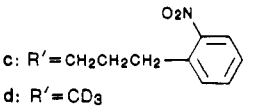
We recently prepared a variety of methoxy-substituted 9,10-anthraquinones as models for the antitumor anthracyclines daunorubicin (**1a**) and adriamycin (**1b**).[6] Solutions of several of these compounds in methanol became intensely yellow upon exposure to room light. In this report we present our preliminary findings on this photochemical process which appears to involve free radical intermediates.



1a: R=$COCH_3$
b: R=$COCH_2OH$



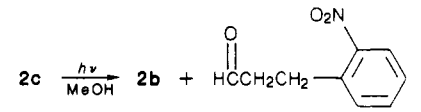
2a: R'=CH_3
b: R'=H



c: R'=$CH_2CH_2CH_2$
d: R'=CD_3

Exposure of solutions of 1-methoxy-2-methyl-9,10-anthraquinone (**2a**) in methanol (0.5–1.0 mM) to a tungsten lamp or xenon chloride eximer laser (308 nm) in the presence or absence of oxygen led to nearly a quantitative yield of 1-hydroxy-2-methyl-9,10-anthraquinone (**2b**) following removal of solvent. This photodemethylation does not occur in $CHCl_3$ or CCl_4 or in the absence of solvent, but does occur in other protic solvents such as ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol, albeit at slightly lower rates.

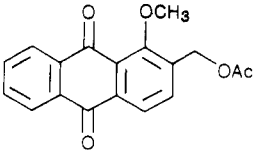
We were unable to determine the fate of the methyl group in this reaction using standard analytical techniques. Consequently, anthraquinone **2c** was prepared to facilitate isolation and identification of the other cleavage product. The 3-(*o*-nitrophenyl)propyl group, which is stable toward tungsten light, was chosen as a substitute for CH_3 in **2a** because it absorbs strongly in the ultraviolet and is relatively nonvolatile. Photolysis of **2c** (0.5 mM in methanol) with a 300-W tungsten lamp for 15 h led to greater than 80% isolated yields of **2b** and 3-(*o*-nitrophenyl)propanal (eq 1). Plots of ln [**2b**] vs time for the photolysis of **2a**



(1)

and **2c** under identical conditions were linear and had comparable slopes. Thus, it is likely that similar mechanisms are operative in the photolysis of these compounds.

How general is this photodemethylation? Anthraquinone **3** cleanly demethylates to 1-hydroxy-2-(acetoxymethyl)-9,10-anthraquinone with a quantum yield of 0.050. Anthraquinone **4**, which possesses two methoxy groups, demethylates stepwise when a 308-nm laser is used, but at a much lower rate than **2a**. Anthraquinone **5**, also undergoes photolysis slowly like **4**, but produces a complex mixture of products that have not been identified. In-



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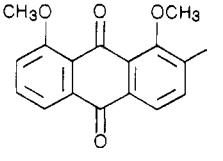

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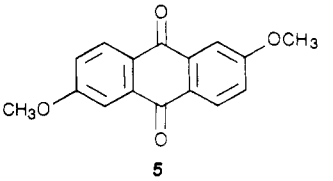

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(1) Lubs, H. A., Ed. *The Chemistry of Synthetic Dyes and Pigments*; Reinhold: New York, 1955; Chapter 7.
(2) Holton, H. H. *Pulp Paper Can.* **1977**, *78*, T218.
(3) (a) Banville, J.; Brassard, P. *J. Chem. Soc., Perk. Trans. 1* **1976**, *613*. (b) Brisson, C.; Brassard, P. *J. Org. Chem.* **1981**, *46*, 1810. (c) Russell, R. A.; Warrener, R. N. *J. Chem. Soc., Chem. Commun.* **1981**, 108. (d) Savard, J.; Brassard, P. *Tetrahedron* **1984**, *40*, 3455. (e) Roberge, G.; Brassard, P. *J. Org. Chem.* **1981**, *46*, 4161. (f) Krohn, K. *Tetrahedron Lett.* **1980**, *21*, 3557. (g) Kelly, T. R.; Parekh, N. D.; Trachtenberg, E. N. *J. Org. Chem.* **1982**, *47*, 5009.
(4) (a) Kraus, G. A.; Fulton, B. S. *J. Org. Chem.* **1985**, *50*, 1782. (b) Wulff, W. D.; Jung, P.-C. *J. Am. Chem. Soc.* **1984**, *106*, 434 and references therein.
(5) (a) Kelly, J. R.; Vaya, J.; Ananthasubramonian, L. *J. Am. Chem. Soc.* **1980**, *102*, 5983. (b) Israel, M.; Potti, P. G.; Seshadri, R. *J. Med. Chem.* **1985**, *28*, 1223 and references therein.
(6) Blankespoor, R. L.; Schutt, D. L.; Tubergen, M. B.; De Jong, R. L. *J. Org. Chem.* **1987**, *52*, 2059.

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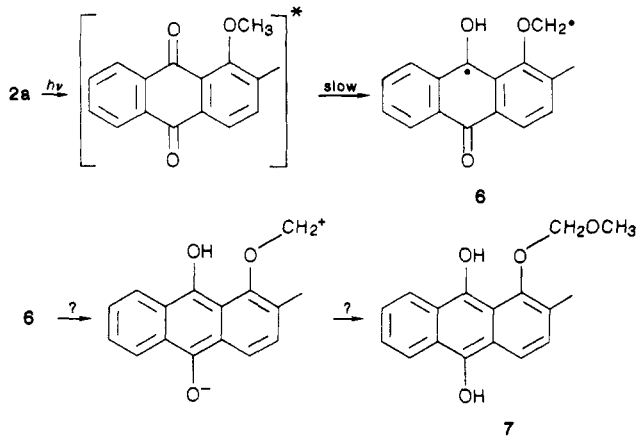
Scheme I



terestingly, there are reports in the literature that anthracyclines are unstable in the presence of visible[7] and ultraviolet light,[8] although products from these photolyses have not been identified. Demethylation does not occur if the anthraquinone is reduced to its corresponding anthrahydroquinone prior to irradiation. 1-Methoxy-2-methyl-9,10-dihydroxyanthracene, prepared by the electrochemical reduction of **2a**, was recovered quantitatively after exposure to the xenon chloride eximer laser for relatively long periods (>20 min).

To probe the mechanism of this photodemethylation, the deuteriated anthraquinone **2d** was prepared. With either a tungsten lamp or the 308 nm laser, a quantum yield of 0.0080 was obtained. This compares to a value of 0.020 for **2a**, giving a k_H/k_D ratio of 2.5, which is within the range of values for a reaction that exhibits a primary hydrogen isotope effect.

These preliminary results suggest the partial mechanism in Scheme I. The isotope study supports a 1,6-H atom transfer from an excited state of **2a** leading to the free radical intermediate **6**. Similar hydrogen atom transfers have been observed in photoexcited naphthoquinones[9] and β-alkoxypropiophenones.[10] One can only speculate how the reaction proceeds beyond this point but primary photoproduct **7** would give the observed products upon workup (e.g., exposure to oxygen and chromatographic separation on silica gel). One possible pathway to **7** could involve an intramolecular electron transfer to form a zwitterion followed by methanol capture. The observation that **4** reacts much more slowly than **2a** supports an electron-transfer step since an anthraquinone containing two methoxy groups would be more difficult to reduce. Also, the failure of **5** to demethylate cleanly is consistent with its inability to undergo intramolecular hydrogen transfer. Efforts thus far, however, to isolate the presumably air- and acid-sensitive anthrahydroquinone **7** have been unsuccessful. Work is in progress aimed at further elucidating the mechanism and determining the scope of this photodemethylation reaction.

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Synthesis of (α-Hydroxyalkyl)trialkylsilanes via a Reverse Brook Rearrangement

Summary: The transmetalation and rearrangement of [α-((trialkylsilyl)oxy)alkyl]trialkylstannanes have been achieved, providing a method for the direct conversion of several aldehydes and cyclohexanone into (α-hydroxyalkyl)trialkylsilanes in reasonable yields.

Sir: The Brook rearrangement,[1] an intramolecular migration of silicon from carbon to oxygen, readily proceeds for (α-hydroxybenzyl)trialkylsilanes with a catalytic amount of base. The stereospecific intramolecular rearrangement is driven forward due to the favorable increase in the thermodynamic bond strength in changing from a C–Si bond to an O–Si bond. The reverse, or anti-Brook rearrangement, the migration of silicon from oxygen to carbon, has been demonstrated for (α-trialkylsilyloxy)-benzylic ethers.[2] The "reverse" process requires an excess of base and presumably proceeds due to the stability of the alkoxide anion vs the carbanion. The reverse rearrangement has apparently been limited to silyl ethers that can be deprotonated at the ether carbon to generate the requisite carbanion. Benzylic systems are well-known[2,3] and allylic silyl ethers also readily rearrange upon deprotonation with strong base.[4] There have been no reports of an analogous reverse Brook rearrangement occuring for an aliphatic silyl ether.[5] We would now like to report that the reverse Brook rearrangement can be readily accomplished through the intermediacy of an [α-((trialkylsilyl)oxy)alkyl]trialkylstannane.

α-Alkoxy organostannanes are now well-known as a source of α-alkoxy lithio species[6] and have also provided α-alkoxy organocuprates.[7] The facile transmetalation of Sn to Li is readily accomplished at low temperatures in ethereal solvents. We initially assessed the feasibility of affecting a reverse Brook rearrangement by trans-

(1) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.
(2) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214.
(3) Eisch, J. J.; Galle, J. W.; Piotrowski, A.; Tsai, M.-R. *J. Org. Chem.* **1982**, *47*, 5051.
(4) (a) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668. (b) Danheiser, R. L.; Fink, D. M.; Okano, K.; Tsai, Y. M.; Szczepanski, S. W. *J. Org. Chem.* **1985**, *50*, 5393.
(5) The Brook rearrangement (forward sense) has been carried out in aliphatic systems, see ref 11b and: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809.
(6) (a) Still, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. (b) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1985**, *50*, 4655. (c) Sawyer, J. S.; MacDonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 3376. (d) Duchene, A.; Quintard, J. P. *J. Chem. Soc., Chem. Commun.* **1987**, 29.
(7) (a) Linderman, R. J.; Godfrey, A. *Tetrahedron Lett.* **1986**, *27*, 4553. (b) Linderman, R. J.; Godfrey, A.; Horne, K. *Tetrahedron Lett.* **1987**, *28*, 3911. (c) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4930.
(7) Tavoloni, N.; Guarino, A. M.; Berk, P. D. *J. Pharm. Pharmacol. Commun.* **1980**, *32*, 860.
(8) Williams, B. A.; Trittan, T. R. *Photochem. Photobiol.* **1981**, *34*, 131.
(9) (a) Edwards, O. E.; Ho, P.-T. *Can. J. Chem.* **1978**, *56*, 733. (b) Baldwin, J. E.; Brown, J. E. *Chem. Commun.* **1969**, 167. (c) Otsuki, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3089.
(10) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134.

0022-3263/88/1953-2878$01.50/0