Supplementary Material Available: Listing of final atomic parameters, anisotropic thermal parameters, and bond lengths and angles for **1**, **5**, and **6** (8 pages); listing of observed and calculated structure factor amplitudes for **1**, **5**, and **6** (15 pages). Ordering information is given on any current masthead page.

Novel Photochemical Route to the Mitomycin and FR-900482 Series

Kim F. McClure, John W. Benbow, and Samuel J. Danishefsky*

Department of Chemistry, Yale University, New Haven, Connecticut 06511

Gayle K. Schulte

Yale University Center for Chemical Instrumentation New Haven, Connecticut 06511

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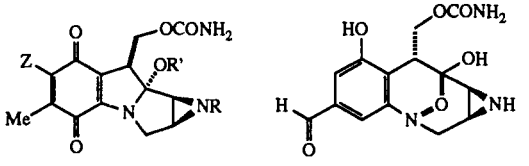
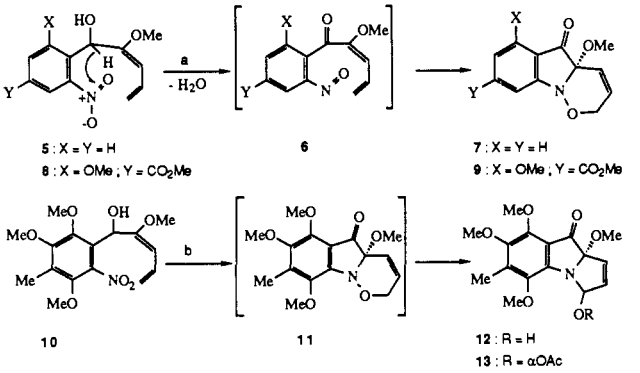
Organic chemists have long been fascinated by the mitomycins.[1,2] The novel structure of these compounds is clearly a contributing factor. Emerging descriptions of mechanisms for their bioactivation[3,4] and increasingly detailed insights into their interactions with nucleic acid receptors[5] continue to fuel interest in the field. The recent isolation of mitomycin variants from natural sources with synthetically challenging structural features[6,7] has served to promote new research in this series. Finally, the fact that mitomycin C is a clinically useful antineoplastic drug[8] provides incentives at the pharmaceutical level for fresh departures. Herein we disclose a new synthetic strategy which has potential for reaching either the mitomycins, the recently discovered FR-900482 (**1**),[9] or congeners of these drugs.



Mitomycins 1 = FR-900482

Scheme I[a]

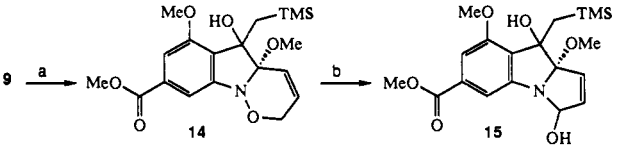


5 : X = Y = H; 8 : X = OMe; Y = CO_2Me — 6 — 7 : X = Y = H; 9 : X = OMe; Y = CO_2Me

10 — 11 — 12 : R = H; 13 : R = αOAc

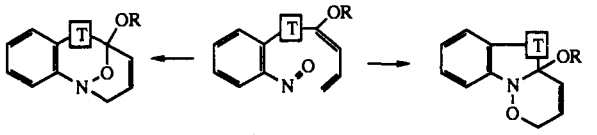
[a] (a) 0.01 M in MeOH, *hν* (366 nm); (b) 0.01 M in MeOH, *hν* (350 nm).

Scheme II



(a) $TMSCH_2MgCl$, Et_2O/PhH.
(b) 0.01M in THF, *hν* (254nm).

We started with consideration of an intramolecular cycloaddition of a dienyl nitroso system (see generalized system **2**).[10] In principle, such a process could lead to a bridged oxazine derivative (cf. **3**) or to a fused version (cf. **4**). The nature of the outcome would, presumably, be strongly influenced by the nature of the diene and by the character and length of the T "tether".[11]



3 bridged mode **2** T = tether **4** fused mode

In order to address such questions, it would be necessary to develop a route to reach **2**. Our solution contemplated unveiling the nitroso function with the diene already present via a photochemically driven redox reaction of an *o*-nitrobenzyl alcohol prototype.[12] In our opening investigation of this possibility, we examined a system with a minimum C_1 tether on the grounds that candidate substrates of this type could be assembled rapidly. Below we demonstrate the feasibility of the photochemical redox route to produce nitroso dienes, and the rather interesting chemistry which ensues therefrom.

Reaction of *o*-nitrobenzaldehyde with 1-methoxy-1-lithiobutadiene[13] generates carbinol **5** (Scheme I). Photolysis of **5**

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afforded a 75% yield of **7**. As was envisioned in advance, the photolytic redox reaction of **5** had apparently given rise to **6**, which in a 2 + 4 cycloaddition (presumably a "dark" step)[14] yielded the fused oxazine **7**. The effects of incorporating aromatic substituents of relevance to the synthesis of **1** were explored. Reaction of methyl 4-formyl-3-methoxybenzoate[15] with the butadienyl anion afforded a 56% yield of **8**. Photolysis of **8**, as above, afforded a 60% yield of **9**, the structure of which was proven by crystallographic means.

We next studied the possibility of incorporating "pre-mitomycin" functionality on the aromatic ring. Accordingly, the addition of the butadienyl anion to 4-methyl-6-nitro-2,3,5-trimethoxybenzaldehyde[15] was carried out. The product, **10**, obtained in 80% yield, was photolyzed as above. In this case there was directly obtained a 45% yield of the pyrroloindoxyl derivative **12**. That the expected **11** is at least a permissible intermediate in this amazing transformation was shown by its isolation in low yield from the same reaction and its conversion to **12** by subsequent photolysis under the same conditions. The structure of **12** was fully corroborated by a crystallographic determination of its derived acetate **13**.[16]

We were intrigued by the difference in photochemical behavior in the two series. Thus, **7** and **9**, each produced from photolysis reactions, are apparently photostable under the conditions of their formation. In contrast, **11** suffers photochemically induced conversion to **12**. It seemed possible that the confluence of highly electron donating substituents in the aromatic nucleus of **11** favors its photoconversion to **12**. While maintaining the aromatic substitution pattern of the pre-FR-900482 series, we examined the consequences of removing the electron-withdrawing "keto" group[17] of **9**. The hope was that the resultant product would be more electronically similar to **11**. In the event, compound **9** was smoothly (80%) converted to **14** through the agency of $TMSCH_2MgCl$.[18] Interestingly, photolysis of **14** produced an 80% yield of **15** (Scheme II).

Our experiments have not thus far been directed to providing new insights as to the precise nature of the transformation of **11** and **14** to **12** and **15**, respectively. Certainly, the sequence of photocleavage of an NO bond, C → N hydrogen migration, and cyclization is not without precedent.[19] In summary, a highly concise entry to intermediates closely related to the mitomycins[20] and FR-900482 has been developed.

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Supplementary Material Available: Complete experimental details, NMR, IR, and mass spectral data for all reactions reported, UV spectral data for compounds **5**, **8**, **9**, **11**, and **14**, and experimental details, ORTEP drawings, and tables containing fractional coordinates, temperature factors, bond distances, torsional angles, and anisotropic temperature factors for the X-ray crystallographic analyses of compounds **9** and **13** (26 pages). Ordering information is given on any current masthead page.

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(15) The preparation of the aromatic aldehydes is described in the supplementary material.

(16) While the stereochemistry of the acetate **13** is known, we have not rigorously shown that the alcohol and acetate have the same configurations.

(17) Since the conversion of oxazine **11** to the hemiaminal **12** is reasoned to begin with homolysis of the N–O bond (ref 19), the transformation is in part a function of the N–O bond strength. In the absence of competing electron donation, the presence of a carbonyl group in conjugation with the nitrogen seems to impart stability to the N–O bond, possibly by stabilizing the aminyl radical.

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Synthesis of Bis(buckminsterfullerene)nickel Cation, $Ni(C_{60})_2^+$, in the Gas Phase

Yongqing Huang and Ben S. Freiser*

H. C. Brown Laboratory of Chemistry, Purdue University
West Lafayette, Indiana 47907

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The advent of a simple synthesis for generating macroscopic amounts of the fullerenes,[1] C_{60} and C_{70}, has spawned an intensive effort to study the physical and chemical properties of this new state of carbon.[2] One of the most intriguing aspects of the fullerenes is their topography, which, as exemplified by the "soccer ball" structure of buckminsterfullerene (C_{60}), has an internal volume and an external surface.[3] Incorporation of elements,[4a] particularly transition metals,[4b,c] and perhaps even small compounds, inside the carbon cage may lead to useful new materials with unique properties. Alternatively, the fullerenes may prove to be highly versatile ligands for the generation of unusual organometallic complexes. The aromatic nature of the fullerenes, together with their five- and six-membered-ring makeup and low reduction potentials, suggests that they may function like cyclopentadienyl or benzene ligands. Exemplifying the feasibility of this approach is the recent report of a cyclopentadienyl–ruthenium–C_{60} compound.[5]

Expanding the potential utility of the fullerenes as ligands, we felt that a bis-C_{60} metal ion complex should be formed in the gas phase in analogy to the bis-benzene or metallocene complexes. This idea was realized with the formation of the bis complex $Ni(C_{60})_2^+$, which was observed in a Fourier transform mass spectrometer to arise at longer trapping times in the presence of a background of C_{60} as a result of direct attachment of C_{60} to NiC_{60}^+.[6] Figure 1 shows selected mass spectra from the multistep (in situ) synthesis[7] of the bis complex, which entailed (1) laser desorption of Ni^+,[8] (2) isolation of the $^{58}Ni^+$ isotope by double

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