protons implies that the puckered Os_3C_2 ring must be quite flexible since these two hydrogens are clearly nonequivalent in the solid-state structure.

Interestingly, the ketene moiety of the trimetallacyclopentanone ring retains ketene-like reactivity with nucleophiles. For example, **4** reacts rapidly with both H_2O and CH_3OH to yield CH_3CO_2H and $CH_3CO_2CH_3$, respectively, along with $Os_3(CO)_{12}$.[13] These reactions are most easily conducted by forming $Os_3(CO)_{12}(\eta^2\text{-}(C,C),\mu\text{-}CH_2CO)$ in situ. Thus, $Os_3(CO)_{11}(\mu\text{-}CH_2)$ does not react with H_2O (nor CH_3OH), but when placed in THF solution with ~10 equiv of H_2O *under a CO atmosphere*, it is completely consumed within ~12 h to give $Os_3(CO)_{12}$ and acetic acid in quantitative yield, the latter determined by subsequent titration with standardized NaOH. Such reaction with traces of water, and probably with other nucleophiles as well, likely accounts for the slow solution decomposition of **4** noted above.

A labeling experiment shows that the ketene carbonyl derives from one of the initial $Os_3(CO)_{11}(\mu\text{-}CH_2)$ carbonyl ligands and not from the added CO. When a sample of $Os_3(CO)_{11}(\mu\text{-}CH_2)$ that was 25% ^{13}C enriched in all carbons (prepared from 25% ^{13}CO-enriched $Os_3(CO)_{12}$[7a]) was allowed to react with 90% ^{13}C-enriched CO *in methanol solution*, the ^{13}C NMR spectrum of the methyl acetate produced showed the acetate methyl and carbonyl resonances to be of equal intensity. Thus both of these carbons must come from the initial $Os_3(CO)_{11}(\mu\text{-}CH_2)$, which in turn implies a preequilibrium between $Os_3(CO)_{11}(\mu\text{-}CH_2)$ and a coordinatively unsaturated ketene complex that subsequently adds two CO's to give **4**.

Formation of the ketene complex **4** from the methylene complex **3** is reversible, although the instability of **4** precludes quantitative recovery of **3**. Thus, when a $CDCl_3$ solution of **4** is heated to 60–64 °C for 30 min under reduced pressure, the methylene proton resonances of **3** appear and grow in to ~10% of their expected intensity on the basis of the amount of **4** consumed. This observation is in accord with Arce and Deeming's[7c] recent preparation of **3** from the reaction of $Os_3(CO)_{10}(NCCH_3)_2$ with ketene, a synthesis that perhaps proceeds through the intermediacy of **4**, although this species was not detected in their reaction.

The ease with which the bridging methylene complex **3** reacts with CO to form the new carbon–carbon bond in the ketene complex **4** suggests that such a reaction may be important in the formation of carbon–carbon bonds on metal surfaces during heterogeneous catalysis of CO reduction. Further explorations of the chemistry of **4** and other insertion reactions of **3** are in progress.

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Supplementary Material Available: Tables of positional and thermal parameters, bond lengths, bond angles, and structure factors for **4** (21 pages). Ordering information is given on any current masthead page.

Studies Concerning the Mechanism of Electrophilic Substitution Reactions of Mitomycin C

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Mitomycin C (**1**) has found widespread use for the treatment of various neoplasms.[2] Suggestions have been made that **1** functions as a bioreductive alkylating agent.[3] Recently Moore outlined a detailed mechanism for the cross-linking of DNA by **1**[3d] (Scheme I). Intermediate **3** has been advanced as the biologically active form of **1** that leads to difunctional binding of the genetic material. Evidence in favor of this scenario has been presented by Tomasz and Lipman.[4] These investigators demonstrated that treatment of **1** under reductive conditions (catalytic and enzymatic) near neutral pH in the absence of strong nucleophiles led to the formation of 2,7-diaminomitosene (**6a**) along with other mitomycin-based products. Compound **6a** has been proposed to arise from **3** through an internal reduction–oxidation process[4] (Scheme II).

In this communication, we report direct evidence for the origin of **6a**. The stereochemical features of this substitution reaction are also addressed. A similar issue corresponding to nucleophilic substitution at carbon 1 has been the subject of intensive investigation.[5-12]

Two likely mechanisms exist for the formation of **6a**, and these are outlined as follows (Scheme II): (1) pathway *a* is that proposed by Tomasz and Lipman[4] and involves tautomerization of the quinone methide **3**; (2) pathway *b* would proceed by direct reduction of the aziridine moiety in **2** followed by reoxidation of this species during workup. Such a pathway is precedented since aziridines readily undergo hydrogenolysis under mild conditions to give acyclic amines.[13] Moreover, in 2-phenylaziridines cleavage occurs selectively between the nitrogen and the phenyl-substituted carbon atom.[14]

To test the viability of the second pathway, compound **1** was treated with PtO_2 and D_2 gas under conditions (Na_2HPO_4, H_2O, pH 5.1) identical with those previously described.[4] Isolation of **6a** by liquid chromatography gave a product whose spectral properties showed no deuterium incorporation at carbon 1. This result excludes the direct reduction pathway *b* for the formation of **6a**.

Information in support of the first mechanism and the stereochemical mode of proton addition at carbon 1 was attained by conducting the experiment with PtO_2 and H_2 gas in Na_2DPO_4–D_2O (pD 5.1[15]). Under these conditions, the extent of

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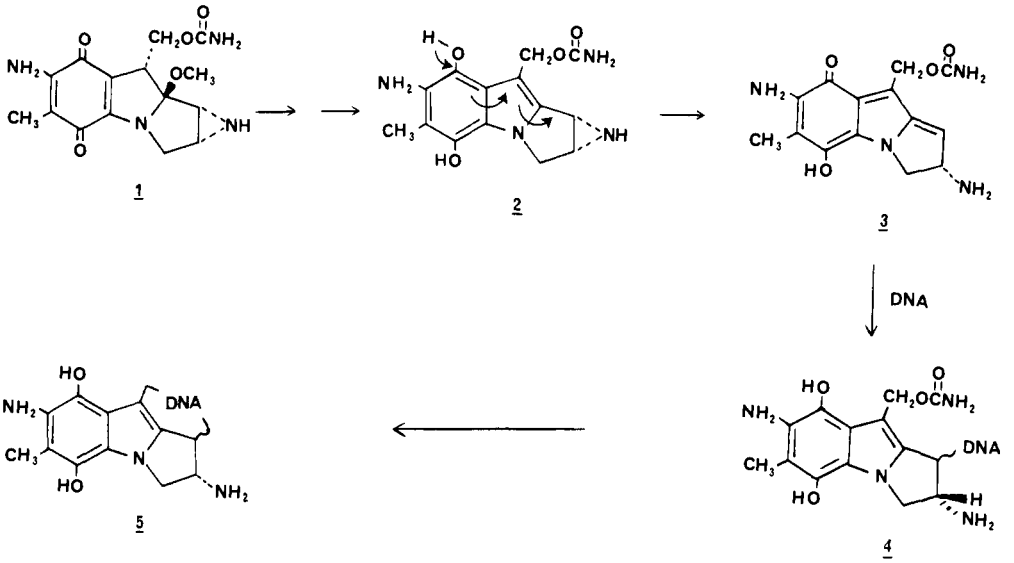
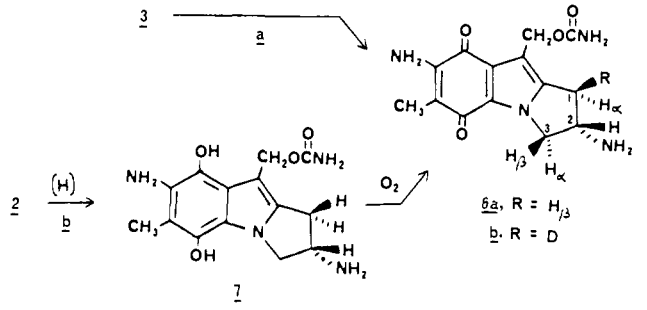
Scheme I



Scheme II



monodeuteration at carbon 1 in **6b** was greater than 80% by ^1H NMR analysis. Moreover, comparison of the ^1H NMR spectrum obtained from the product of this reaction to that obtained in the previous experiment showed the disappearance of the signal at δ 3.10 and the collapse of the doublet of doublets at δ 2.45 to a doublet. Thus, electrophilic substitution at carbon 1 in **1** proceeds with remarkably high stereoselectivity.

The signals at δ 2.45 and 3.10 in **6a** have been tentatively attributed to the C_1H_α and C_1H_β protons, respectively.[16] This assignment is based on analogy to the corresponding chemical shift differences observed for the C_3H_α and C_3H_β protons in a series of mitosenes.[9,17,18] In each case the chemical shift of the β-hydrogen appears downfield ($\Delta\delta \sim 0.5$ ppm) from the corresponding α-hydrogen. Furthermore, a similar analysis of the chemical shift values for the carbon 1 methine hydrogens in isomeric cis- and trans-1,2-disubstituted mitosenes indicated that the carbon 1 proton in the cis adduct (β-H) absorbs downfield ($\Delta\delta \sim 0.15$) from the trans derivative (α-H).[4,6,7,18] This analysis would require a reversal of the assignments previously made for the hydrogens at carbons 1 and 3 in **6a**.[4]

The results of this study provide evidence in favor of the previously proposed route for the formation of **6a**.[4] The high deuterium incorporation observed in the product for the reaction performed in Na_2DPO_4–D_2O suggests that this is the principal pathway leading to **6a**. Moreover, this series of experiments reinforces the overall bioreductive alkylation mechanisms for mitomycin C (**1**).[3d] Our finding that deuterium incorporation occurs selectively in mitomycin C (**1**) from the side opposite the carbon 2 amino group is contrary to the general results observed in nucleophilic substitution reactions that proceed at carbon 1.[5-12] In these latter reactions, substitution yields predominantly the cis adduct. Additional studies concerning this process are in progress.

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Registry No. 1, 50-07-7; **6a**, 85827-92-5; PtO_2, 1314-15-4.

Supplementary Material Available: Select spectral properties for compounds **6a** and **6b** (1 page). Ordering information is given on any current masthead page.

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New Stereoselective Method for the Preparation of Vicinal Diamines from Olefins and Cyanamide

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The vicinal diamino group (**1**) is an ubiquitous structural entity in many naturally occurring compounds and medicinal agents. Surprisingly, few general methods exist for the preparation of this group. Most previous synthetic approaches are extensions of procedures developed to introduce a single amino moiety. These generally entail displacement reactions (i.e., with azides,[2] amino groups,[3] N-aromatic substituted amides[4]), rearrangements (i.e., Curtius[5]), and intramolecular cyclizations.[6] Recently, a series

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