which was analyzed by HPLC and found to consist of a mixture of *N*-methylaniline (identical chromatographically with an authentic sample) and unreacted starting material. The yield of *N*-methylaniline was 40%, based on added C_6H_5IO (1100% yield, based on added BLM).

The demethylation of *N,N*-dimethylaniline was also effected by using Fe^{III}·BLM in the presence of ascorbate and O_2. A solution containing 3.0 mg (2.1 μmol) of BLM A_2 in 100 μL of H_2O was combined with a 3.0-mL methanolic solution containing 15 mg (0.12 mmol) of freshly distilled *N,N*-dimethylaniline in 2 mL of methanol. Ferrous ammonium sulfate (0.85 mg, 2.16 μmol) in 0.2 mL of 50% aqueous CH_3OH was added, followed by solid sodium ascorbate (20 mg, 0.10 mmol). The reaction mixture was stirred in the presence of air for 1 h, then treated with 20 mL of $CHCl_3$ and extracted with water (2 × 20 mL). The dried organic layer was analyzed by HPLC and found to contain a mixture of *N*-methylaniline (yield 140%, based on bleomycin) and unreacted *N,N*-dimethylaniline.

Oxidation of Olefins with Fe^{III}·BLM Analogues and Iodosobenzene. In a typical experiment, an anaerobic solution containing 50 μg (0.096 μmol) of $Fe(ClO_4)_3 \cdot 9H_2O$ and 100 μg (0.09 μmol) of deglycobleomycin A_2 in 45 μL of 65% aqueous methanol was treated with 2 mg (11.1 μmol) of *cis*-stilbene in 100 μL of methanol. Iodosobenzene (0.5 mg, 2.3 μmol) was then added dropwise via a microsyringe from a 20-μL methanol solution over a period of 10–15 min. After 1 h at room temperature, the reaction mixture was concentrated and the products were analyzed by HPLC vs. authentic samples and by ^1H NMR spectroscopy at 360 MHz.

Acknowledgment. We thank Dr. William Bradner, Bristol Laboratories, for samples of tallysomycin A and blenoxane and Dr. Li-Ho Chang for preparation of the bleomycin analogues. We thank Dennis Shaw (University of Virginia) and Walter Johnson, Gerald Roberts, and Dr. Susan Rottschaefer (Smith Kline & French Laboratories) for assistance in determining the isotope ratios reported. Some of the GC–mass spectra were obtained with the assistance of Harvey Laboratories, Charlottesville, VA. This work was supported by Research Grant CA-29235, awarded by the National Cancer Institute, Department of Health and Human Services.

Communications to the Editor

Control of Ring Junction Stereochemistry via Radical Cyclization

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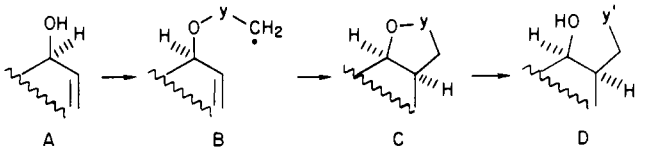
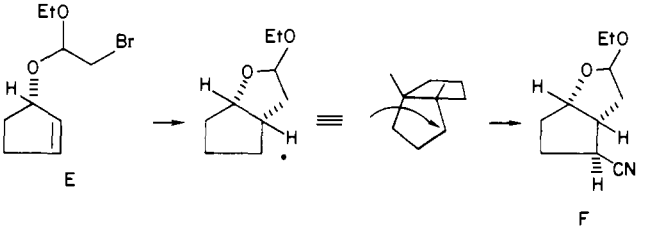
Continuation of our work on the use of free radical reactions in the control of the stereochemistry of carbon–carbon bonds[1-3] has now led us to a new method which appears promising for the control of ring junction stereochemistry.

We have reported[1-3] that it is possible to use an allylic hydroxyl to introduce a functional alkyl chain such that the new carbon–carbon bond not only has defined (hydroxyl vicinal) *regio*chemistry but also, when starting with cyclic allylic alcohols, totally determined stereochemistry (cis to the original hydroxyl). The formal scheme is illustrated.



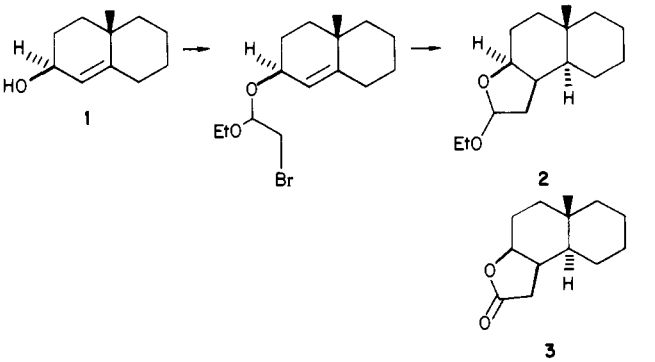
The success of this scheme depended (1) on finding means of achieving an easily removed connection of a two-atom chain terminating in a carbon-centered radical and (2) on the fact that the transition-state geometry for addition of the radical center (B → C) can only lead to the cis fusion of the new five-membered ring. A special virtue of this general process is that, after the necessary allylic hydroxyl has served its stereochemical control function, it can, in principle, be either inverted or removed.

Stereo- and regiochemical control at the near end of the allylic double bond is not the only control that can be derived from the original allylic hydroxyl. The newly formed cis-fused five-membered ring imposes a cup shape on the resulting bicyclic system, so that, in the absence of overriding competing steric hindrance, access to the radical resulting from the initial closure should be largely restricted to the convex side. This is well illustrated, using a mixed-acetal function to achieve a temporary link to the allylic hydroxyl, by the highly stereoselective transfer of a cyano group (E to F).[4]



It is the ability of this type of radical cyclization process to control stereochemistry at the far end of the double bond of a cyclic allylic alcohol that makes possible the control of ring junction stereochemistry.

Consider the allylic alcohol **1** (from sodium borohydride reduction of the corresponding octalone). Reaction of its mixed bromoacetal with tributylstannane leads to a cyclic acetal **2** in which the newly formed decalin fusion is trans: The lactone **3**



derived from Jones oxidation has a singlet methyl at δ 1.06, a position that strongly suggests the trans ring junction which would result from the approach of tributylstannane from the convex side. Confirmation of this stereochemical conclusion was easily obtained from the 1,3-glycol derived from the use of a silyl ether[5] rather

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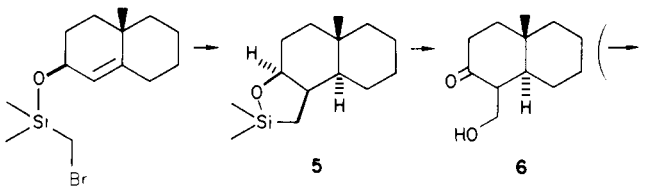
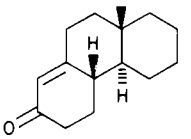
than a mixed acetal as the temporary connection. Reaction of the allylic alcohol **1** with commercially available (bromomethyl)chlorodimethylsilane (1 equiv, 10% NEt_3 in CH_2Cl_2, catalytic DMAP) followed by refluxing the resulting silyl ether **4** in benzene with 1.5 equiv of tributylstannane (1/20 equiv of AIBN, 30 min) produced, in about 65% yield, the cyclic siloxane **5**. This was essentially one isomer. The angular methyl at δ 1.02 in the decalin system again indicated a trans junction. This was rigorously established by removal of the silicon (KF-DMF, 30% H_2O_2),[6] oxidation of the resulting diol (NaOCl, acetic acid)[7] to the ketol **6**, acetylation, and annulation, using ethyl acetoacetate,[8,9] to give the known tricyclic enone **7**, mp 120-122 °C, identical (mp of mixture, spectra) with an authentic sample.[8]



4 **5** **6**



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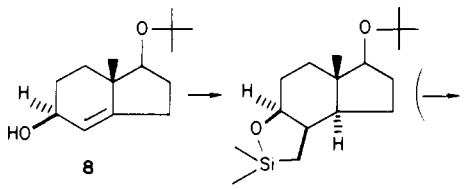
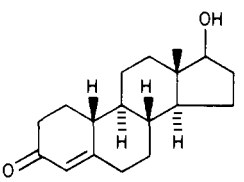
The allylic alcohol **8** provides an even more impressive example of this method of stereocontrol. The same sequence of steps just described transformed **8** into **9** (NMR δ 0.89).[10] The stereochemistry was easily established as that of a *trans*-hydrindane by conversion, as above, using the proper analogue of ethyl acetoacetate,[9] into 19-nortestosterone, identical with an authentic sample.



8 **9**



The overall process just described thus achieves the operational equivalent of the net trans addition of a functionalized alkane to the double bond of cyclic allyl alcohols so that when a ring junction stereochemistry is generated (cf. **1** and **8**) the junction hydrogen is introduced trans to the original hydroxyl function of the allylic system. Further work is planned to test the generality of the method.

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Registry No. 1, 31654-83-8; **2**, 93756-51-5; **3**, 93756-52-6; **5**, 93756-53-7; **7**, 719-18-6; **8**, 93756-54-8; **9**, 93756-55-9; Bu_3SnH, 688-73-3; $BrCH_2SiClMe_2$, 16532-02-8; 2-[(2-bromo-1-ethoxyethyl)oxy]-4a-methyl-2,3,4,4a,5,6,7,8-octahydronaphthalene, 93756-50-4.

(5) Removable connection to an allyl alcohol via a silyl ether is conceptually very similar to our previously used mixed acetal connection but differs in that it introduces a one-rather than a two-carbon functional chain at the α-carbon of the allylic alcohol double bond, via the carbon-silicon cleavage method of ref 6. Experiments on the silyl ether connection, using (bromomethyl)dimethylchlorosilane with allylic alcohols, were carried out in 1983 by Dr. Pawel Fludzinski in our laboratory. For a recent illustration of the silyl variation of the acetal cyclization, see: Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984**, *49*, 2298.

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(10) The yield (unoptimized) of pure **9** was only 36%, but we could find no evidence of the presence of any *cis*-hydrindane in the crude cyclization product.

An Organothorium-Nickel Phosphido Complex with a Short Th-Ni Distance. The Structure of $Th(\eta^5\text{-}C_5(CH_3)_5)_2(\mu\text{-}PPh_2)_2Ni(CO)_2$

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Two different transition metals brought into close proximity in a bimetallic complex may display chemistry unique from that found in the individual separated fragments.[2-4] Heterobimetallic centers have been formed and stabilized in such altered environments by construction of metal-metal bonds, ligand bridges, or a combination of both structural features. In this regard, phosphido ligands have been found in some instances to provide particularly stable bridge anchors which retard fragmentation of the bimetallic unit.[5] On the other hand, bridging phosphido ligands can also participate in interesting complex reactions.[6]

In our efforts to expand the chemistry of phosphido ligands to the actinides, we have recently prepared and structurally characterized a phosphido complex of thorium, $ThCp^*_2(PPh_2)_2$ (**1**).[7,8] Further, we have investigated the reactivity of this species with a variety of transition-metal complexes and now report the synthesis and structure of a nickel-carbonyl derivative. Most im-

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(7) Abbreviations used in the text include Cp* = η^5-$C_5(CH_3)_5$, THF = tetrahydrofuran, COD = 1,5-cyclooctadiene, Ph = phenyl.

(8) Wrobleski, D. A.; Ryan, R. R.; Wasserman, H. J.; Moody, D. C.; Paine, R. T.; Salazar, K. V., manuscript in preparation. $ThCp^*_2(PPh_2)_2$ was prepared from $ThCp^*_2Cl_2$ and $LiPPh_2$. Average Th-P distance = 2.866 (7) Å, P-P distance = 4.12 (2) Å, ∠P-Th-P = 92.0 (2)°.

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