These and other questions regarding this unusual pathway[18] are currently under investigation.

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Intramolecular $S_{N'}$ Cleavage of Allylic Ethers by Enolate Anions

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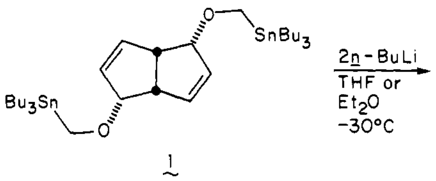
A fundamental property of allylic systems relates to their ability to engage nucleophiles in $S_{N'}$ reaction. Extensive theoretical[2] and experimental investigations[3] over many years attest to the significance attached to the phenomenon. Despite the wide-ranging nature of these studies, however, no attention has been purposefully directed to bimolecular nucleophilic substitution of allyl alkyl ethers, perhaps because of a predetermination that these systems would prove as inert toward displacement as dialkyl ethers. One interesting example known to us is due to Farnum and Monego who showed that dimetalation of **1** proceeds with subsequent proton abstraction from solvent to give **2**, which then experiences intramolecular $S_{N'}$ displacement of methoxide.[4]



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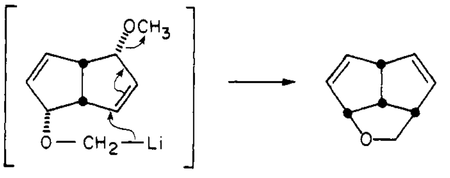

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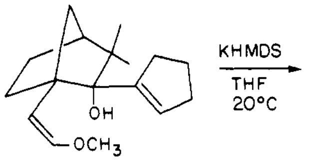
As part of ongoing investigations of anionic oxy-Cope rearrangements,[5,6] our research groups have independently examined the ability of medium-ring enolates to undergo transannular cyclization concomitant with $S_{N'}$ displacement of a methoxyl leaving group. The result is rapid and efficient construction of structurally intricate polycyclic systems.

For example, when alcohol **4**[7] was stirred in anhydrous tetrahydrofuran solution with 1.1 equiv of potassium hexamethyldisilazide at 20 °C for 4 days, smooth conversion to ketone **6** was observed. Chromatographically purified material, isolated in 51% yield, crystallized as colorless, rectangular plates well suited to X-ray analysis.[8] The suggested pathway to the product diquinane involves initial [3,3]sigmatropic electron reorganization via a chair-like transition state to generate **5**. This process establishes three stereocenters and the double bond geometry. The β-configuration of the methoxyl-substituted carbon results in proper alignment of the C–OCH_3 bond with the flanking π orbital, thereby allowing for the onset of the intramolecular $S_{N'}$ ring closure.



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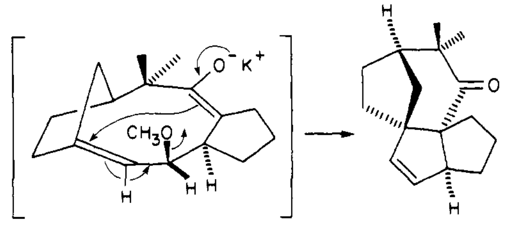
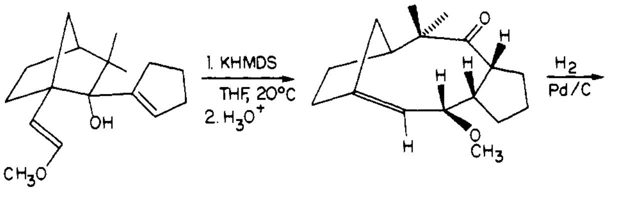


5 6

Support for this mechanistic analysis was gained by subjecting **7** to comparable ring expansion. In this instance, **8** was produced efficiently (88%) after only 5.5 h at room temperature. Since crystals of **8** of suitable quality could not be grown, saturation of its double bond was undertaken. The structure of **9** was subsequently established by crystallographic methods to be as shown.[8] These data indicate the **7** → **8** conversion to be mediated by an



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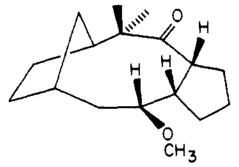

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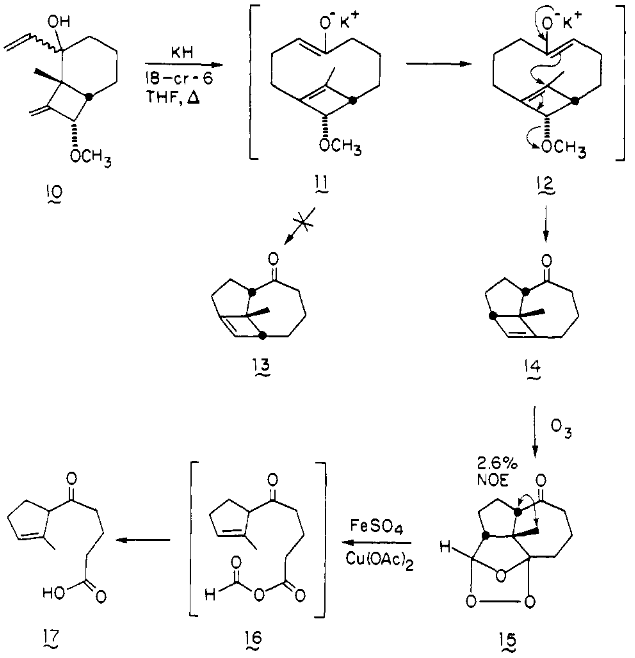
(7) Details relating to the synthesis of this compound will appear elsewhere.

(8) We thank Dr. J. C. Gallucci of the Ohio State University Crystallographic Facility for these analyses.

exo-boat transition state.[9] Since the methoxyl substituent in the initially generated enolate anion is consequently α-oriented, i.e., positioned nearly orthogonal to the π electrons, further transannular C–C bond formation is now stereoelectronically disfavored and does not operate.

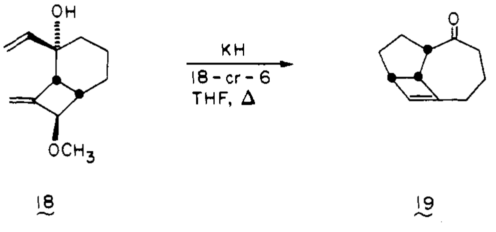
In yet another fascinating reaction, heating of **10** with potassium hydride and 18-crown-6 in dry tetrahydrofuran afforded **14** (40%).



Because detailed spectroscopic analysis of this tricyclic ketone did not allow for definitive determination of the position of its cyclobutene double bond, suitable degradation was undertaken. Thus, ozonolysis of **14** and subsequent treatment of stable ozonide **15** with $FeSO_4/Cu(OAc)_2$[10] in methanol gave the cyclopentene derivative **17**. The formation of **17** unequivocally establishes the site of unsaturation to be as in **14** rather than **13**.

This transformation is believed to originate from enolate anion **11** as the first-formed intermediate. Due to the large amount of strain associated with the bicyclo[3.2.0]hept-1(6)-ene part structure of **13**, intramolecular displacement of methoxide in **11** is energetically disfavored. Instead, enolate isomerization of **11** to **12** operates, with tetrahydrofuran or 18-crown-6 perhaps acting as the proton source, followed by S_N' transannular "scaffolding" to deliver the observed tricyclic product.

In order to scrutinize the kinetic consequences of methoxyl stereochemistry, alcohol **18** was also heated as its potassium salt. Under the same conditions, **19** was isolated in ca. 60% yield.



Charge annihilation within the intermediate enolate anion by $S_{N'}$ ejection of methoxide must consequently also be facile. This is because modest conformational flexing within cyclobutenes conveniently permits attainment of the necessary stereoalignment from either π face.

Among the many interesting facets of these reactions is their mixed stereochemical course. Whereas the **5** → **6** and **18** → **19** processes involve a trans-antiplanar arrangement of the entering and leaving groups, the conversion of **12** to **14** occurs in syn fashion (as does **2** → **3**). Further, the preceding observations show the $S_{N'}$ displacement of methoxide by enolate ions to proceed with reasonable efficiency and to constitute an exceptionally powerful synthetic method.

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[9] The various mechanistic pathways open to these alcohols will be discussed in detail at a later date.

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An Efficient Silylformylation of Alkynes Catalyzed by $Rh_4(CO)_{12}$

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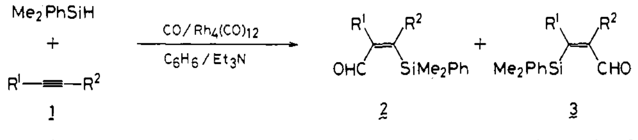
A combination of transition-metal complexes and hydrosilanes is a useful tool for highly selective transformations of alkenes, alkynes, and carbonyl groups.[1] In particular, cobalt-catalyzed incorporation of carbon monoxide is interesting as a unique method for the homologation of alkenes, aldehydes, and cyclic ethers, in which $R_3Si–Co(CO)_4$ plays an important role.[2] On the other hand, while hydroformylation is one of the most useful processes for the practical synthesis of aldehydes,[3] no analogous operation toward acetylenic compounds has been developed because of the concomitant formation of undesired products.[4] An excellent precedent is the selective acylation of 1-alkynes at the terminal carbon with the assistance of $Rh_4(CO)_{12}$,[5] or with a stoichiometric amount of R-$Mn(CO)_5$,[6] to give α,β-unsaturated enones. A formal silylformylation of 1-alkynes to give 3-silyl-2-alkenals **2**[7] can represent a useful synthetic approach to these valuable building blocks, due to the ready accessibility and elaboration of alkynes. We have designed a simple formylation reaction of alkynes in the presence of carbon monoxide, employing dimethylphenylsilane (Me_2PhSiH) instead of H_2, and $Rh_4(CO)_{12}$ as catalyst and have found a novel and selective formylation pattern of alkynes to give **2**. We report here the scope and limitations of this new catalytic silylformylation of alkynes.



When an alkyne **1** was allowed to react with 1 equiv each of Me_2PhSiH and Et_3N, using a catalytic amount (1 mol %) of $Rh_4(CO)_{12}$ in benzene solution under CO (30 kg/cm^2) at 100 °C

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