if they possessed two aromatic groups or one aromatic and one aliphatic ring group. Except for methyl phenyl sulfoxide, compounds with only one aromatic group per molecule could not be resolved.

In comparison to the known column materials, all of which have been naturally occurring and synthetic organic polymers,[5] the clay–chelate adducts have the following advantages: (i) The material is prepared simply by mixing silica gel coated with a clay and an optically active chelate. (ii) The material is not subject to chemical deterioration caused by oxidation and hydrolysis. (iii) The method is extremely versatile, as it can be varied indefinitely by changing the primarily adsorbed chelate.

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New Strategy for [3 + 2] Annulation: Applications to the Synthesis of Functionalized Di- and Triquinanes[1]

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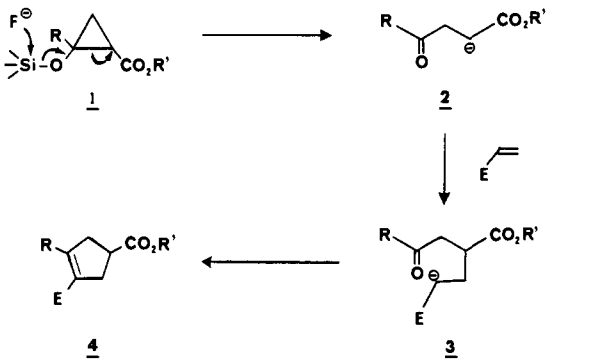
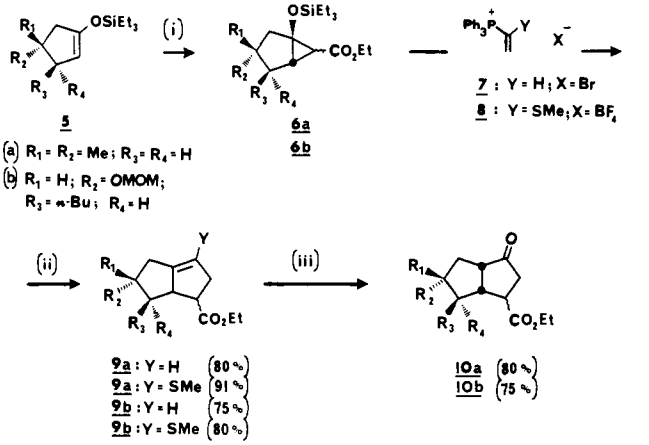
Oxycyclopropanes, in particular those having an additional electron-withdrawing substituent, have become valuable intermediates in synthetic organic chemistry. Their best known reaction is the facile ring opening under acidic, basic, or thermal conditions, which has been extensively used to prepare γ-keto esters and lactones, β,γ-unsaturated ketones, cyclopentanones, and furans.[2] Less attention, however, has been placed upon the use of such a reaction for the formation of a carbon–carbon bond.[3] Recently, Reissig has described that 2-(silyloxy)cyclopropane carboxylate esters of general structure **1** react under equimolar amounts of a symmetrical ketone and titanium tetrachloride to afford γ-lactols in high yield.[4] This was the first report of the direct use of a "donor–acceptor-substituted cyclopropane" in the formation of a five-membered ring.

As part of our research program directed toward efficient pentannulations,[5] we envisioned that a (silyloxy)cyclopropane ester such as **1** could serve as a three-carbon synthon for cyclopentene syntheses. In particular, the fluoride-induced desilylation and concomitant ring opening should give rise to the elusive γ-oxo ester enolate system **2**. The successful trapping of **2** in a Michael reaction with an activated alkene should provide access to intermediates such as **3** and, finally, to highly functionalized cyclopentenes **4** (Scheme I). This new strategy for [3 + 2] annulatiion would allow the introduction of the three-carbon synthon as a nucleophile, therefore complementing previous approaches to cyclopentenes involving electrophilic cyclopropanes.[5,6]

Scheme I



Scheme II



We wish to report the successful application of the above methodology to the synthesis of functionalized di- and triquinane systems. Our initial results focus on the use of (2-(silyloxy)-cyclopropane esters **6**, derived from triethylsilyl enol ethers of cyclopentanones and ethyl diazoacetate. The specific activated alkenes are vinylphosphonium salts. These Michael acceptors were chosen because of their ability to generate in situ a Wittig reagent that could intramolecularly react with the incipient ketone.[7] Employment of 1-thio-substituted vinylphosphonium salt allowed for subsequent hydrolysis of the resulting vinyl sulfides to the corresponding bicyclooctanones. The overall sequence of reactions from the silyl enol ethers is shown in Scheme II.

In general, the reaction of silyl enol ether **5a**[8] and **5b**[9] with carbethoxycarbene (generated by the cupric sulfate catalyzed decomposition of ethyl diazoacetate) gave high yields of (silyloxy)cyclopropane esters **6**. In the case of **6b**, only one stereoisomer was formed at the ring fusion, while a 4:1 mixture of *exo*- and *endo*-carbethoxy isomers, respectively, was produced.[10] When the cyclopropanes **6** were treated with either vinylphosphonium salt **7**[11] or **8**,[12] in the presence of potassium fluoride and a catalytic

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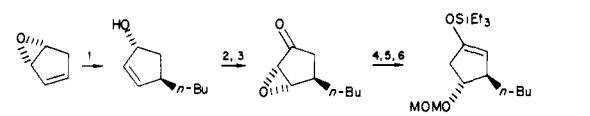
(9) Prepared by the sequence of reactions given below:



Reagents: (1) Li[CuCN-*n*-Bu], Et_2O, −40 °C; (2) *t*-BuOOH, $VO(acac)_2$, PhH, 40 °C; (3) CrO_3·pyr, CH_2Cl_2; (4) LDA, THF, −78 °C; then, Et_3SiCl; (5) $LiAlH_4$, Et_2O, room temperature; (6) MOMCl, *i*-Pr_2EtN, CH_2Cl_2

(10) The stereochemical assignments are based on the following ^1H NMR (360 MHz) data: For the exo isomer of **6b**, $J_{3,4} = 0$ and $J_{2,3} = 4.0$ Hz; for the endo isomer of **6b**, $J_{3,4} = 1.6$ and $J_{2,3} = 9.8$ Hz.

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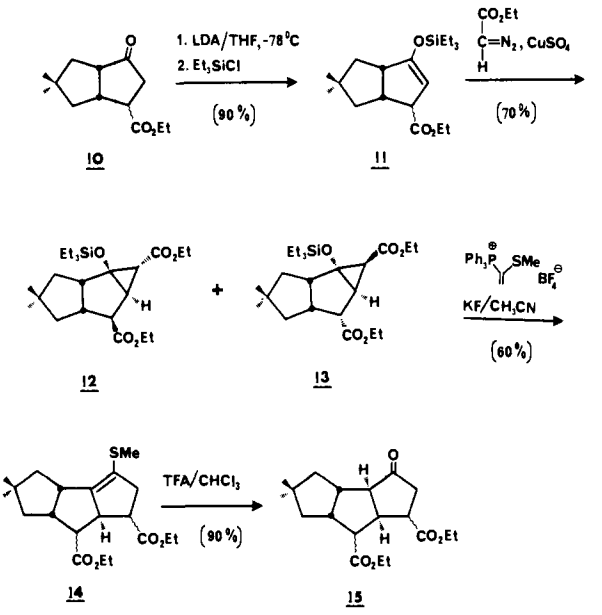
Scheme III



amount of 18-crown-6 in refluxing acetonitrile, high yields of bicyclo[3.3.0]octenes **9** were obtained. The bicyclooctenyl sulfides produced from the reaction with **8** could be easily hydrolyzed to the corresponding bicyclooctanones **10** with trifluoroacetic acid in chloroform.[13]

The stereochemistry at the ring juncture in **9b** was fixed by the cyclopropanation reaction, and in **10b**, the more stable cis fusion is required. While the stereochemistry of the carbethoxy group in **9** and **10** is mixed (β/α = 2/1),[14] the less thermodynamically stable α-isomer could be epimerized to the β-isomer. Alternatively, the carbon atom bearing the ester group could be further transformed into a carbonyl group.[15]

The conditions for the disilylation–trapping step are quite well-defined experimentally. The 18-crown-6 ether is needed to help solubilize the potassium fluoride. The use of more acidic desilylation agents, such as n-Bu_4F, was deleterious to the reaction of **6b**, since the intermediate γ-oxo ester enolate was either protonated or equilibration of ester–ketone enolates occurred.

The potential of this strategy for the construction of functionalized tricyclo[6.3.0.$0^{2,6}$]undecanes ("linear triquinanes"[16]) prompted us to carry out a reiterative [3 + 2] annulation as outlined in Scheme III.

Thus, the addition of carboethoxycarbene to the kinetic silyl enol ethers **11** of bicyclooctanones **10a** (2:1 mixture of β- and α-carbethoxy isomers, respectively) afforded the expected tricyclic diesters **12** and **13** (ca. 2:1 ratio, respectively) in 70% yield from **10a**. It should be mentioned that the observed stereoselectivity for this reaction is the one expected on steric grounds and agrees with the reported antiselectivity of carbethoxycarbene.[17] Treatment of the (silyloxy)cyclopropane esters **12** and **13** with the thio-substituted vinylphosphonium salt **8** under the conditions described for the [3 + 2] annulation provided the tricyclic vinyl sulfides **14** (mixture of all four possible isomers). Subsequent hydrolysis gave the corresponding tricyclo[6.3.0.$0^{2,6}$]undecanones **15** in good overall yield. It should be noted that the cis,anti ring fusion of the final products **15** is secured from that of the starting tricyclic (silyloxy)cyclopropane esters **12** and **13**.

In summary, the present strategy provides a mild and expeditious route for the construction of functionalized bicyclo[3.3.0]octanes and tricyclo[6.3.0.$0^{2,6}$]undecanes in high yield. Work is under way to elaborate the resulting intermediates into suitable precursors for the synthesis of naturally occurring compounds and to extend the present methodology to other ring systems.

Acknowledgment. We acknowledge NSF for partial support of a Brüker WM-360 FT NMR spectrometer. E.L. thanks the American Chemical Society for a grant to assist his participation at the 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 26–31, 1984.

Supplementary Material Available: Characterization data on all new compounds (10 pages). Ordering information is given on any current masthead page.

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(Diethylamino)sulfur Trifluoride in Organic Synthesis. 2. The Transformation of Sulfoxides to α-Fluoro Thioethers[1]

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New methods for the introduction of fluorine into organic molecules are of increasing importance, especially for the design of novel enzyme-activated irreversible inhibitors.[2] Several β-fluorophenethylamines,[1] β-fluoroamino acids,[3] 3-fluoroallylamines,[4] and amino acids[5] (vinyl fluorides) have proven to be specific irreversible inhibitors of selected enzymes. A convenient synthetic route to vinyl fluorides[6] would make molecules containing this functionality more attractive as synthetic targets.

This activity has prompted us to explore new routes to fluoro compounds utilizing (diethylamino)sulfur trifluoride (DAST).[1] We wish to report a novel synthetic transformation that provides the previously unreported α-fluoro thioethers **2**, which are convenient precursors to vinyl fluorides via the thermolysis of the corresponding fluoro sulfoxides (**3**).[6d] This transformation offers a superior alternative to the Wittig reaction[6a] for the synthesis of terminal vinyl fluorides.

We reasoned that DAST should react with sulfoxides as does acetic anhydride in the Pummerer rearrangement[7] and found that the proposed transformation was readily accomplished. For example, when methyl phenyl sulfoxide was treated with DAST in chloroform at room temperature for 24 h and then at 50 °C for several hours (until complete by ^{1}H NMR), an 85% yield of fluoromethyl phenyl sulfide (**2a**) resulted.[8] Sulfide **2a** was readily

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