spectroscopy (CSCM)[5] as shown in formula **1a**. Thus, the presence of two CH_2CH_2 groups in a bicyclic system along with a carbonyl, a trisubstituted double bond, a quaternary methyl, and an isopropyl moiety strictly represents the 5/7 ring system for aphanamol I as in formula **1**. The stereochemistry was determined by proton NOE experiments. Upon irradiation of the angular methyl protons (H-11) at δ 1.27, significant enhancement was observed of the H-4 (δ 2.27) and H-8β (δ 2.81) signals. Another strong NOE was detected between H-3 (δ 1.66) and the sole vinyl proton (H-5, δ 5.51). Structure **1b** is the conformation consistent with the spectral observations.

Aphanamol II (**2**) was obtained as colorless oil in 0.005% yield [LC_{50} 27 ppm (48 h); $[\alpha]^{18}_D$ +6.9° (*c* 0.94, $CHCl_3$); IR (neat) 3450, 2720, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (3 H, d, J = 7 Hz), 0.93 (3H, d, J = 7 Hz), 1.04 (3H, s), 3.40 (1 H, dd, J = 11, 6 Hz), 6.62 (1H, d, J = 5 Hz), 9.37 (1H, s); ^{13}C NMR shown in formula **2**]. From this evidence, combined with the spectral correlation with aphanamol I (**1**), an α,β-unsaturated aldehyde structure **2** is derived.

When aphanamol II (**2**) was treated with $LiAlH_4$ in ether, diol **3** was obtained quantitatively. The identical diol was formed from aphanamol I (**1**) by $LiAlH[OC(CH_3)_3]_3$ reduction as a minor product along with the epimeric diol **4** (1:4 ratio). Considering the conformation of the parent ketone **1b**, preferential hydride attack on the carbonyl group should take place from the less hindered β-face, affording α-alcohol **4** as the major product. Therefore, the *sec*-hydroxyl group of **2** is assigned the β-orientation. These assignments are also in agreement with the coupling pattern of the carbinyl protons of the epimers (δ 3.43, dd, J = 11, 6 Hz for **3**, and δ 3.51, dd, J = 5, 3 Hz for **4**) and the observed NOE (3.13%) between H-11 (δ 1.06) and H-9 (δ 3.51) in the major alcohol **4**.

The structure of the aphanamols represents a very rare type of carbon skeleton for naturally occurring sesquiterpenoids. Recently, the structure of a component of peppermint oil, mintsulphide, was established as **5** by X-ray analysis.[6] A sexual stimulant of the American cockroach, periplanone A (**6**), is also postulated to have the same carbon framework.[7] In connection with the possible biogenesis of the aphanamols, it may be noted that the skeletally related compounds **7** and **8** are produced by acidic rearrangement of humulene[8] or epoxygermacrene D,[9] respectively.

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Registry No. **1**, 91410-61-6; **2**, 91410-62-7; **3**, 91410-63-8; **4**, 91464-56-1.

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Supplementary Material Available: Full spectral data of compounds 1–4 (4 pages). Ordering information is given on any current masthead page.

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Heteroannulation via Intramolecular (π-Allyl)palladium Displacement

Summary: Conjugated and nonconjugated dienes, as well as vinylcyclopropanes, react with $LiPdCl_3$ and organomercurials bearing carboxylic acid, phenol, alcohol, and amide functionality to generate (π-allyl)palladium compounds which readily undergo intramolecular displacement of palladium upon addition of an appropriate base to give a wide variety of oxygen and nitrogen heterocycles.

Sir: (π-Allyl)palladium compounds have recently become very valuable intermediates in organic synthesis.[1,2] The majority of synthetic applications have involved displacement of the palladium moiety by either stabilized carbon nucleophiles[3-8] or amines.[9-15] Relatively little work has been reported on analogous alkoxide,[16-18] aryl oxide,[16] or carboxylate[19,20] processes. We report a convenient, new,

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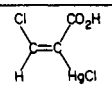
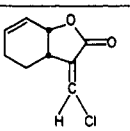
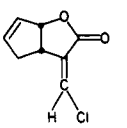
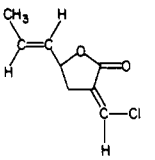
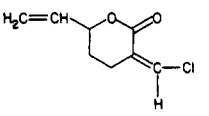
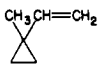
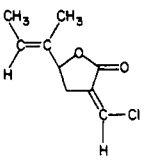
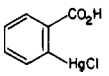
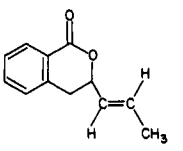
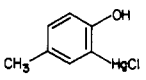
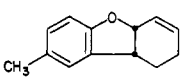
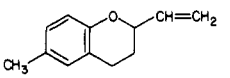
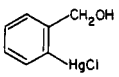
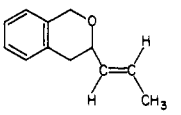
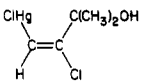
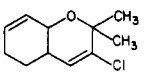
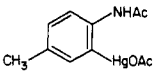
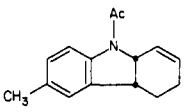
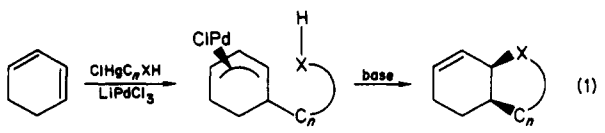
Table I. Heteroannulation via Intramolecular (π-Allyl)palladium Displacement

entry	organomercurial	olefin (equiv)	base	product(s)[a]	% isolated yield
1		 (5)	K_2CO_3		71
2		 (5)			59
3		*cis*-H_2C=CHCH=$CHCH_3$ (2)			74
4		H_2C=$CHCH_2CH$=CH_2 (>2)			64
5		 (2)			60[b]
6		*cis*-H_2C=CHCH=$CHCH_3$ (2)			76
7		 (5)	NaH		86[c]
8		H_2C=$CHCH_2CH$=CH_2 (>2)			62[c]
9		*cis*-H_2C=CHCH=$CHCH_3$ (5)			40[c]
10		 (5)			51[c,d]
11					74

[a] All products gave mass, NMR, and IR spectral data consistent with the indicated structures. [b] The product is isomerically pure and assumed to be that shown based on mechanistic arguments. [c] The reaction was started at −20 °C. [d] One equivalent of MgO was added to the reaction and $(CH_3CN)_2PdCl_2$ was used instead of $LiPdCl_3$. The stereochemistry of the product is unknown, but probably cis.

one-pot approach to a wide variety of heterocycles which starts with dienes or vinylcyclopropanes and functionally substituted organomercurials and involves initial (π-allyl)palladium formation and subsequent intramolecular (π-allyl)palladium displacement by a variety of oxygen and nitrogen nucleophiles (eq 1). Our results to date are summarized in Table I.



(1)

Our process employs readily available organomercurials bearing carboxylic acid, phenol, alcohol, and amide functionality.[21-23] Transmetalation by $LiPdCl_3$ in acetonitrile (1 mmol in 20 mL) and addition of the resulting organopalladium intermediate to conjugated dienes[24] proceeds at 0 °C to room temp. (−20 °C to room temperature for mercurated phenols and alcohols) overnight to generate the anticipated (π-allyl)palladium compound. Analogous additions to nonconjugated dienes[25] and unsaturated cy-

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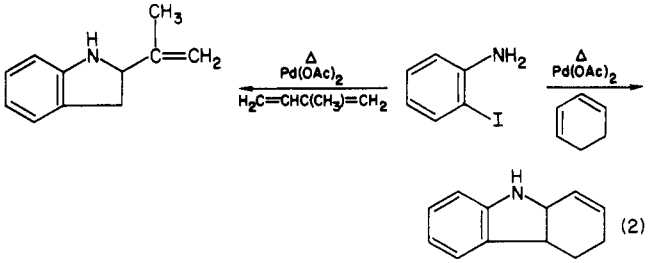
clopropanes and cyclobutanes[26] have recently been reported by us to result in (π-allyl)palladium formation, thus greatly expanding this heteroannulation approach (see entries 4, 5, and 8). Addition of an appropriate base (2 equiv, 5 h reflux) liberates the nucleophile which undergoes facile intramolecular displacement of the palladium moiety. These displacement reactions proceed much more readily than previously suggested by the literature. Addition of ether, aqueous ammonium chloride workup, and column chromatography affords the products indicated in Table I.

While the stereochemistry of organopalladium additions to cyclic conjugated dienes does not appear to have been established,[24] it seems likely that such additions proceed in a syn manner, based on other organopalladium additions where stable intermediates have been isolated.[27-32] Assuming that, it is noteworthy that all of our displacements, where the stereochemistry could be readily determined, apparently proceed with frontside displacement of the palladium moiety (entries 1, 2, 7, and 11). Previous work with amine,[5,9,15] carboxylate,[19,20] and alkoxide[17] nucleophiles suggests that there is a fine balance between frontside and backside displacement processes.

While related to an earlier heteroannulation process employing aryl olefins[33-35] and a reaction reported by Dieck et al.[36] during the course of our own work (eq 2), our approach is much more general. Our intramolecular displacement processes are not limited to amines and stabilized carbon nucleophiles. Anions derived from carboxylic acids, phenols, alcohols, and amides can also be utilized effectively. Our heteroannulation approach is not restricted to aryl olefins or conjugated dienes either. One can take advantage of the remarkable ability of palladium to migrate by employing nonconjugated dienes and unsaturated cyclopropanes and cyclobutanes. A wide variety of functional groups should also be readily accommodated by this process.



(2)

We emphasize that this simple heteroannulation procedure involves simultaneous formation of both a new carbon–carbon bond and a new carbon–heteroatom bond. It allows easy entry into a multitude of heterocyclic systems of varying ring sizes, including the α-methylene-γ-butyrolactone unit common to a large number of biologically important sesquiterpenes[37,38] (the chlorine is readily removed by reduction with a Zn–Ag couple[39]). We are presently preparing new heteroannulation reagents and exploring the scope and limitations of this procedure.

Acknowledgment. The generous financial support of the National Institutes of Health and loans of palladium chloride from Johnson Matthey, Inc. and Engelhard Industries are much appreciated.

Registry No. *cis*-H_2C=CHCH=$CHCH_3$, 1574-41-0; H_2C=$CHCH_2CH$=CH_2, 591-93-5; *cis*-3-((*Z*)-chloromethylene)-3a,4,5,7a-tetrahydro-2(3*H*)-benzofuranone, 91713-30-3; *cis*-3-((*Z*)-chloromethylene)-3,3a,4,6a-tetrahydro-2-(2*H*)-cyclopenta[*b*]furanone, 91713-31-4; 3-((*Z*)-chloromethylene)tetrahydro-5-((*E*)-1-propen-1-yl)-2-furanone, 91713-32-5; 3-((*Z*)-chloromethylene)-6-ethenyltetrahydro-2-pyranone, 91713-33-6; 5-((*E*)-2-buten-2-yl)-3-((*Z*)-chloromethylene)tetrahydro-2-furanone, 91713-34-7; 3-((*E*)-1-propen-1-yl)-3,4-dihydro-1*H*-2-benzopyran-1-one, 90992-07-7; *cis*-1,2,4a,9b-tetrahydro-8-methyldibenzofuran, 91713-35-8; 2-ethenyl-3,4-dihydro-6-methyl-2*H*-1-benzopyran, 91713-36-9; 3,4-dihydro-3-((*E*)-1-propen-1-yl)-1*H*-2-benzopyran, 91713-37-0; 3-chloro-4a,5,6,8a-tetrahydro-2,2-dimethyl-2*H*-1-benzopyran, 91713-38-1; *cis*-9-acetyl-3,4,4a,9a-tetrahydro-6-methyl-9*H*-carbazole, 91713-39-2; (*E*)-(1-carboxy-2-chloroethenyl)chloromercury, 91713-40-5; (2-carboxyphenyl)chloromercury, 23000-65-9; chloro(2-hydroxy-5-methylphenyl)mercury, 23068-68-0; chloro(2-hydroxymethylphenyl)mercury, 91713-41-6; (*E*)-chloro(2-chloro-3-hydroxy-3-methyl-1-butenyl)mercury, 63025-10-5; 12-(acetylamino)-5-methylphenyl)acetyloxymercury, 91741-80-9; 1,3-cyclohexadiene, 592-57-4; cyclopentadiene, 542-92-7; 1-ethenyl-1-methylcyclopropane, 16906-27-7.

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α-Haloalkanesulfonyl Bromides in Organic Synthesis. 3. α-Alkylidene Ketones and 1,3-Oxathiole 3,3-Dioxides from Trimethylsilyl Enol Ethers[1]

Summary: α-Alkylidene ketones and 1,3-oxathiole 3,3-dioxides can be conveniently prepared by treatment of trimethylsilyl enol ethers with α-haloalkanesulfonyl bromides followed by an amine base such as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).

Sir: Recently we reported the use of the new reagent bromomethanesulfonyl bromide (**1a**, $BrCH_2SO_2Br$) to convert olefins into 1,3-dienes.[1] We now describe the role of **1a** and related reagents in a process which transforms trimethylsilyl enol ethers into α-alkylidene ketones and/or 1,3-oxathiole 3,3-dioxides in ratios which vary with reagent, substrate, and reaction conditions.

Thus, a solution of 1-(trimethylsiloxy)-1-cycloheptene (**2**, 0.01 mol) and **1a** (0.014 mol) in 4 mL of ethylene oxide

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