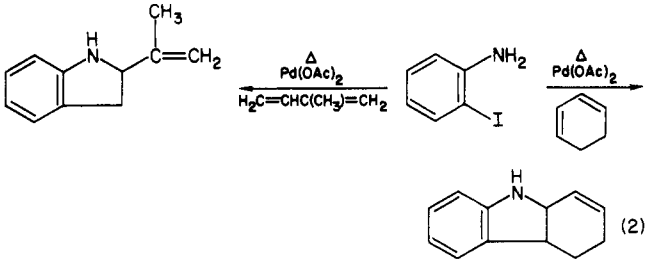
clopropanes and cyclobutanes[26] have recently been reported by us to result in (π-allyl)palladium formation, thus greatly expanding this heteroannulation approach (see entries 4, 5, and 8). Addition of an appropriate base (2 equiv, 5 h reflux) liberates the nucleophile which undergoes facile intramolecular 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

(1) Part 2: Block, E.; Aslam, M.; Eswarakrishnan, V.; Wall, A. *J. Am. Chem. Soc.* **1983**, *105*, 6165–6167. Part 1: Block, E.; Aslam, M. *Ibid.* **1983**, *105*, 6164–6165.

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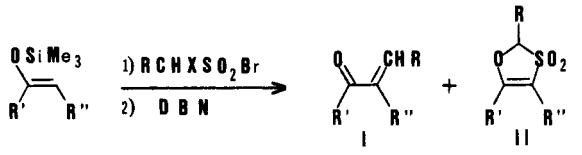
Table I. Synthesis of α-Alkylidene Ketones and 1,3-Oxathiole 3,3-Dioxides from Trimethylsilyl Enol Ethers



entry	R′	R″	R	X	condn[a,b]	products (overall isolated yield)
1		$(CH_2)_5$	H	Br	A	I (61), II (17)
2		$(CH_2)_5$	H	Br	B	I (45), II (16)
3		$(CH_2)_5$	H	Br	C	I (9), II (70)
4		$(CH_2)_5$	H	Cl	B	I (17), II (42)
5		$(CH_2)_5$	H	Cl	C	I (–), II (54)
6		$(CH_2)_5$	H	I	B	I (68), II (1)
7		$(CH_2)_5$	CH_3	Br	C	I (13),[c] II (2)
8		$(CH_2)_4$	H	Br	B	I (19), II (56)
9		$(CH_2)_4$	H	Br	C	I (–), II (46)
10		$(CH_2)_4$	H	I	B	I (32), II (32)
11		$(CH_2)_4$	CH_3	Br	C	I (12),[d] II (6)
12		$(CH_2)_3$	H	Br	B	I (30), II (–)
13	Ph	H	H	Br	B	I (–), II (43)
14	Ph	H	H	Cl	C	I (–), II (50)
15	C_2H_5	CH_3	H	Br	B	I (41), II (5)
16	C_2H_5	CH_3	H	Cl	C	I (–), II (44)

[a] Solvent is ethylene oxide (step 1); Hanovia 450-W lamp is used with sample at −15 °C. [b] DBN is base (step 2), A = CH_2Cl_2, −78 °C, B = CH_2Cl_2, −23 °C, C = C_2H_5OH, 23 °C. [c] 12:1 ratio of *E* to *Z* isomer ^1H NMR δ 6.40 and 5.63 (q), respectively. [d] 20:1 *E* to *Z* ratio.

(an acid scavenger) was irradiated[1] for 1.5 h at −15 °C and then concentrated in vacuo, giving 2-[(bromomethyl)-sulfonyl]cycloheptanone[2] (**3a**) in 77% yield. A free-radical chain reaction (e.g., eq 1a–d) is likely to be involved in the

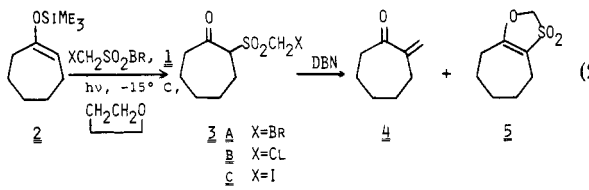
$$XCH_2SO_2Br \xrightarrow{h\nu} XCH_2SO_2\cdot + Br\cdot \quad (1a)$$

$$XCH_2SO_2\cdot + Me_3SiOCR{=}CHR' \rightarrow MeSiO\dot{C}RCHR'SO_2CH_2X \quad (1b)$$

$$Me_3SiO\dot{C}RCHR'SO_2CH_2X \rightarrow Me_3Si\cdot + RC(O)CHR'SO_2CH_2X \quad (1c)$$

$$Me_3Si\cdot + XCH_2SO_2Br \rightarrow Me_3SiBr + XCH_2SO_2\cdot \quad (1d)$$

formation of **3a**.[3] Treatment of a CH_2Cl_2 solution of **3a** with DBN (2.5 equiv) at −78 °C (2 h) and 23 °C (0.5 h), washing with dilute acid, and distillation gave α-methylenecycloheptanone[4] (**4**) in 77% yield (eq 2). A second



(2)

compound, 8,10-oxathiabicyclo[5.3.0]dec-1(7)-ene 10,10-dioxide (**5**), a novel fused ring 1,3-oxathiole 3,3-dioxide,

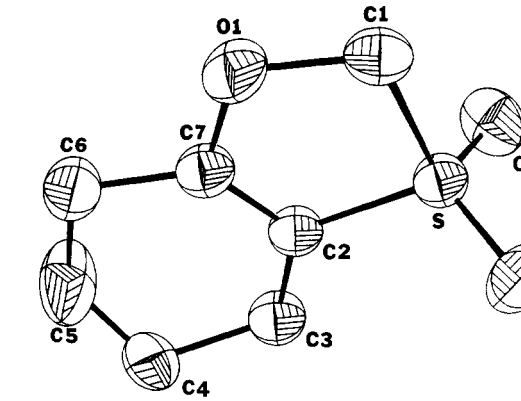


Figure 1. Perspective view of 7,9-oxathiabicyclo[4.3.0]non-1-(6)-ene 9,9-dioxide showing the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Relevant bond distances and angles: S–C1, 1.809 (5) Å; S–C2, 1.727 (5) Å; S–O2, 1.430 (3) Å; C1–O1, 1.414 (6) Å; O1–C7, 1.373 (6) Å; C2–C7, 1.330 (6) Å; C2-C3, 1.501 (6) Å; C3–C4, 1.590 (8) Å; C4–C5, 1.365 (9) Å; C5-C6, 1.535 (8) Å; C6–C7, 1.475 (7) Å; C1–S–C2, 92.1 (2)°; S–C1–O1, 107.4 (3)°; C1–O1–C7, 112.0 (3)°; O1–C7–C2, 118.8 (4)°; C7–C2–S, 109.7 (3)°; C7–C2–C3, 125.0 (3)°; C2–C3–C4, 107.6 (4)°; C3–C4–C5, 116.1 (5)°; C4–C5–C6, 122.1 (5)°; C5–C6–C7, 109.6 (4)°.

was isolated from the distillation residue in 21% yield as colorless needles, mp 55–56 °C.[5] A higher yield of heterocycle **5** (88%) together with 12% of **4** was produced on reaction of an ethanol solution of **3a** with DBN at room temperature. We have also utilized chloromethanesulfonyl bromide[1] (**1b**, $ClCH_2SO_2Br$), iodomethanesulfonyl bromide, (**1c**, ICH_2SO_2Br (prepared in 34% yield as shown in eq 3), and α-bromoethanesulfonyl bromide[6] (**6**,

$$CH_2I_2 \xrightarrow{Na_2SO_3,\ H_2O,\ heat} ICH_2SO_3Na \xrightarrow{PBr_5} \underset{\mathbf{1c}}{ICH_2SO_2Br} + POBr_3 \quad (3)$$

$CH_3CHBrSO_2Br$) in the preparation of α-alkylidene ketones and 1,3-oxathiole 3,3-dioxides. Thus, reaction of **2** with **1b**, **1c**, and **6** gave 2-[(chloromethyl)sulfonyl]cycloheptanone[2] (**3b**, 67% yield), 2-[(iodomethyl)sulfonyl]-cycloheptanone[2] (**3c**, 100% yield), and 2-[(α-bromoethyl)sulfonyl]cycloheptanone[2] (22% yield), respectively. Treatment of compound **3b** with DBN in ethanol at room temperature gave **5**, free from **4**, in 79% yield. On the other hand treatment of **3c** with 2.5 equiv of DBN in CH_2Cl_2 at −23 °C for 2 h gave **4** in 83% yield, with only trace amounts of **5**. Finally, treatment of 2-[(α-bromoethyl)sulfonyl]cycloheptanone with DBN in ethanol at room temperature led to a mixture of 39% (*E*)- and 3% (*Z*)-α-ethylidenecycloheptanone and 6% 9-methyl-8,10-oxathiabicyclo[5.3.0]dec-1(7)-ene 10,10-dioxide (**7**). This latter compound could also be obtained in 74% isolated yield by sequential treatment of **5** with *n*-butyllithium (THF, −78 °C) and methyl iodide. Other examples of the preparation of α-alkylidene ketones and 1,3-oxathiole 3,3-dioxides from trimethylsilyl enol ethers are given in Table I.

The 1,3-oxathiole 3,3-dioxide formed from 1-(trimethylsiloxy)-1-cyclohexene, 7,9-oxathiabicyclo[4.3.0]-non-1(6)-ene 9,9-dioxide, was further characterized by X-ray crystallography. The molecular geometry and the

(2) All new compounds have been fully characterized by spectral means.

(3) (a) The Cu(I)-catalyzed reaction of sulfonyl chlorides with a trimethylsilyl enol ether giving β-keto sulfones is known: Kuroki, Y.; Murai, S.; Sonoda, N.; Tsutsumi, S. *Organomet. Chem. Synth.* **1972**, *1*, 465–466. (b) The Lewis acid mediated reaction of sulfinyl chlorides with trimethylsilyl enol ethers giving β-keto sulfoxides is also known: Meanwell, N. A.; Johnson, C. R. *Synthesis* **1982**, 283–284.

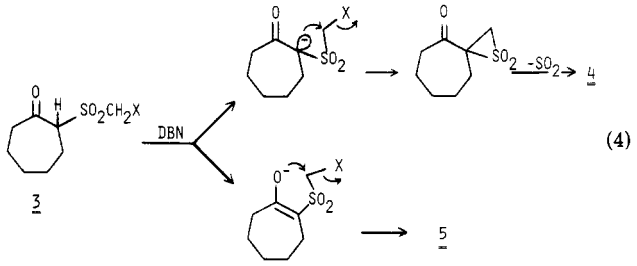
(4) Ksander, G. M.; McMurry, J. E.; Johnson, M. *J. Org. Chem.* **1977**, *42*, 1180–1185. Ryu, I.; Matsumoto, K.; Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1980**, *21*, 4283–4286. Shono, T.; Nishiguchi, I.; Komamura, T.; Sasaki, M. *J. Am. Chem. Soc.* **1979**, *101*, 984–987. Danishefsky, S.; Prisbylla, M.; Lipisko, B. *Tetrahedron Lett.* **1980**, *21*, 805–808.

(5) IR 1660, 1285, 1130 cm^{-1}; ^1H NMR δ 4.65 (s); ^{13}C NMR δ 165, 113, 81, 31, 30, 27, 24, 19.

(6) (a) Prepared in 66% yield by treatment of α-bromoethanesulfonyl chloride[6b] with aqueous sodium sulfite (0 → 25 °C) followed by bromine. (b) Carpino, L. A.; McAdams, L. V., III; Rynbrandt, R. H.; Spiewak, J. W. *J. Amer. Chem. Soc.* **1971**, *93*, 476–484.

atom labeling are shown in Figure 1. The five-membered ring S–C1–O1–C7–C2 is rigorously planar, occupying the crystallographic mirror plane through $y = 1/4$. The S–C2 distance is significantly shorter than S–C1, 1.727 (5) Å and 1.809 (5) Å, respectively, as a consequence of sp^2 hybridization at C2. The sulfone oxygen atoms O2 and O2′ are crystallographically equivalent, related through mirror symmetry. The six-membered ring C2–C3–C4–C5–C6–C7 is nonplanar, with C4 resting off the crystallographic mirror plane and disordered about the molecular plane. Other pertinent structural features are summarized in the figure caption.[7]

As summarized in eq 4, we suggest that reaction of **3a–c** with base generates an enolate ion which may undergo either intramolecular C-alkylation, giving an episulfone which loses sulfur dioxide affording enone **4** (Ramberg-Bäcklund reaction), or O-alkylation giving heterocycle **5**.



(4)

The preference for O-alkylation in **3b** (Cl leaving group) and C-alkylation in **3c** (I leaving group) is in accord with the hard–soft acid–base principle.[8a] The data in the table suggest that O-alkylation is also favored by polar solvents, conjugation, and conformational factors but is disfavored when the Br is on a secondary carbon (steric effects[8b]) and with smaller rings where the resultant heterocycle would be strained.

While other syntheses of α-alkylidene ketones from trimethylsilyl enol ethers have been reported[4] and a few examples of 1,3-oxathiole 3,3-dioxides are known,[9] our method should be particularly useful because of its simplicity.

Acknowledgment. We thank Professor Jon Zubieta for assistance in the determination of the X-ray structure, the National Science Foundation (Grant CHE 8303427), the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Société Nationale Elf Aquitaine, the John Simon Guggenheim Memorial Foundation (E.B.), and the National Institutes of Health (J.H.) for generous support.

Registry No. **1a**, 54730-18-6; **1b**, 59059-72-2; **1c**, 91586-90-2; **2**, 22081-48-7; **3a**, 91586-92-4; **3b**, 91586-93-5; **3c**, 91586-94-6; **4**, 3045-99-6; **5**, 91586-95-7; **6**, 91586-91-3; **7**, 91586-98-0; I (R′,R″ = $(CH_2)_4$, R = H), 3045-98-5; I (R′,R″ = $(CH_2)_3$, R = H), 1489-50-5; I (R′ = C_2H_5, R″ = CH_3, R = H), 25044-01-3; I (R′,R″ = $(CH_2)_5$, R = CH_3), 39896-78-1; I (R′,R″ = $(CH_2)_4$, R = CH_3), 7417-55-2; II (R′,R″ = $(CH_2)_4$, R = H), 91586-96-8; II (R′ = Ph, R″ = R = H), 21120-03-6; II (R′ = C_2H_5, R″ = CH_3, R = H), 91586-97-9; II (R′,R″ = $(CH_2)_4$, R = CH_3), 91586-99-1; 1-(trimethylsiloxy)-1-cyclohexene, 6651-36-1; 1-(trimethylsiloxy)-1-cyclopentene, 19980-43-9; 1-(trimethylsiloxy)-1-phenylethene, 13735-81-4; 3-(trimethylsiloxy)-2-pentene, 17510-47-3.

Supplementary Material Available: Tables of spectroscopic data and elemental analyses, atomic coordinates and temperature factors, bond lengths and angles, anisotropic temperature factors, hydrogen atom positions, and observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(7) Crystal data: $C_7H_{10}O_3S$, M = 174.2; orthorhombic space group $Pcmn$; a = 7.385 (3) Å, b = 7.964 (3) Å, c = 13.419 (4) Å, V = 789.2 (6) Å^3, d_{calcd} = 1.46 g cm^{-3} for Z = 4; 643 independent reflections were collected by the θ–2θ scan technique. The structure was determined by direct methods and refined by full matrix least-squares of the positional and anisotropic thermal parameters of C, O, and S atoms and of the positional and isotropic thermal parameters of the H atoms. The final conventional discrepancy factor was 0.051, and the deviation in an observation of unit weight, 1.86.

(8) (a) Ho, T.-L. "Hard and Soft Acids and Bases Principle in Organic Chemistry"; Academic Press: New York, 1977. (b) Since secondary carbons are considered *harder* than primary carbons it is necessary to invoke steric effects to explain our results.

(9) (a) Dickore, K. *Liebigs Ann. Chem.* **1964**, *671*, 135–146. 4-Phenyl-1,3-oxathiole 3,3-dioxide is formed in 46% yield on treatment of α-[(chloromethyl)sulfonyl]acetophenone with aqueous sodium hydroxide. (b) Nozaki, H.; Takaku, M.; Hayasi, Y.; Kondo, K.; *Tetrahedron* **1968**, *24*, 6563–6572. (c) Elliott, A. J. In "Comprehensive Heterocyclic Chemistry"; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: New York, 1984; Vol. 6, p 749.

(10) Address inquiries on X-ray crystallography studies to Jon Zubieta at SUNY-Albany.

† Fellow of the John Simon Guggenheim Foundation, 1984–1985.

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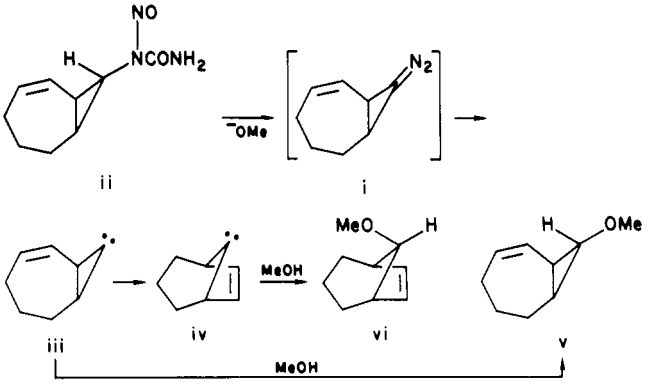
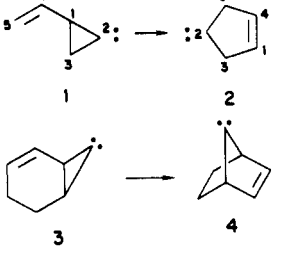
The Skattebol Rearrangement: Evidence for the Carbene to Carbene Mechanism

Summary: This paper addresses the question of whether a free vinylcyclopropylidene can rearrange to a cyclopentenylidene. A study of the decomposition of diazo intermediate i is reported. The concern is whether or not the diazo compound rearranges directly (i to iv) and/or whether iii rearranges to iv. By studying the product ratio (v/vi) as a function of [MeOH], it is concluded that iii does indeed rearrange to iv with a very low barrier of 1–4 kcal/mol.



Sir: The Skattebol rearrangement[1] is an example of a type II[2] carbene reorganization, in which the carbene center retains its identity throughout. As is seen from the two examples shown in eq 1, the reaction amounts to a sig-



(1)

(1) Skattebol, L. *Tetrahedron* **1967**, *23*, 1107.
(2) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.

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