Oxidation of 1-(Triphenylsilyl)cyclopropenes with Dimethyldioxirane

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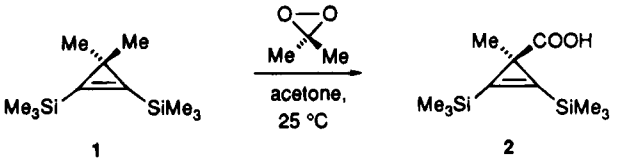
Received June 27, 1994

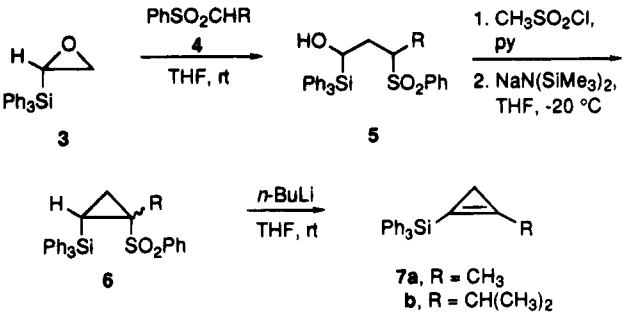
In the 10 years since its appearance on the chemical scene,[1] dimethyldioxirane (DMD) has emerged from the realm of a chemical curiosity to become an important oxidant in its own right[2] and a notably useful probe of chemical reactivity. In the latter context, the recent finding by Maynard and Paquette that cyclopropene **1** reacts with DMD to give carboxylic acid **2** as the major



product[3] was considered to be remarkable for several reasons. Not only does this oxidative process differ from that followed upon reaction of **1** with *m*-chloroperbenzoic acid (epoxidation of the double bond with ensuing rearrangement) or ozone (conventional cleavage of the olefinic linkage) but is likewise dissimilar from the response of 1,2-bis(trimethylsilyl)alkenes which are converted quantitatively into their epoxides under identical conditions.[3] Although the ability of DMD to oxidize nonactivated C–H bonds has been noted,[4,5] the response of **1** was considered to be sufficiently unique to warrant further investigation of other silyl-substituted cyclopropenes.

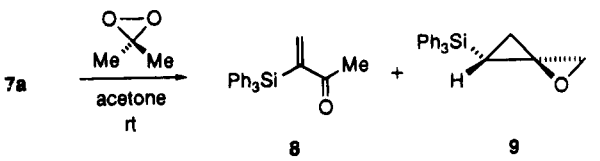
Jankowski and Wicha have demonstrated that α-sulfonyl carbanions such as **4** are capable of promoting the cleavage of silyl epoxide **3** to produce the heavily functionalized carbinols **5**.[6] Activation of the hydroxyl group in **5** by conversion to the mesylate allows for cyclization to the cyclopropanes, from which benzenesulfinic acid can be conveniently eliminated by exposure to *n*-butyllithium in THF at rt. The resulting silylated cyclopropenes **7** are stable crystalline solids amenable to storage under ordinary conditions.[7]

The cyclopropenes **7a** and **7b** were selected for the present study. Both highly strained cyclic olefins offer a reactive double bond less sterically congested than that



present in **1**. In addition, both offer two potentially reactive allylic carbons. Attack by DMD at the ring methylene site might be expected to result in cyclopropenone formation and provide a new alternative synthetic entry to this class of compounds if ring cleavage is skirted. Progression from **7a** to **7b** results in significantly increased steric shielding of the cyclopropenylcarbinyl carbon and could provide insight into the extent to which increased alkyl substitution can alter relative reaction rates involving this oxidant. Normally, tertiary C–H bonds are significantly more reactive toward oxidants (particularly of the radical variety) than are primary C–H bonds.

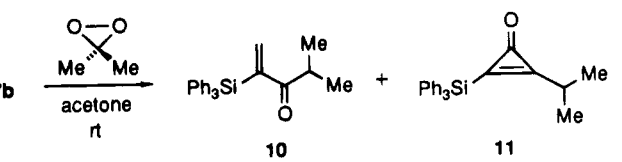
Treatment of **7a** with DMD in acetone at rt resulted in complete consumption of the silyl cyclopropene in 6 h and conversion to two major products. Following their



separation by chromatography on silica gel, the highly crystalline major product was identified as the α,β-unsaturated ketone **8** (44%). Its infrared carbonyl absorption appeared at 1665 cm^{-1}. As expected for this structure, the high-field ^1H NMR spectrum consisted uniquely of an aryl proton multiplet, two mutually coupled olefinic protons, and a methyl singlet.

The less abundant product proved to be the spiro epoxide **9** (9%). Its oxiranyl protons appear as two well-defined absorptions at δ 3.10 (d, J = 4.8 Hz) and 2.94 (dd, J = 4.8, 0.7 Hz) in $CDCl_3$ solution. The minor coupling in the latter signal arises from a W-plan arrangement with a cyclopropyl methylene proton (δ 1.58, ddd, J = 11.6, 5.5, 0.7 Hz). Further structural confirmation derives from the fact that the four ring carbons of **9** appear at higher field (57.0, 49.9, 6.5, and −0.9 ppm).

Comparable oxidation of **7b** was seen to proceed more rapidly and to be complete within 3.5 h. The structurally related enone **10** was obtained in comparable yield (46%).



The more polar coproduct was identified as cyclopropenone **11** (22%) chiefly on the strength of its infrared carbonyl stretching band (1816 cm^{-1}) and the character-

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(1) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

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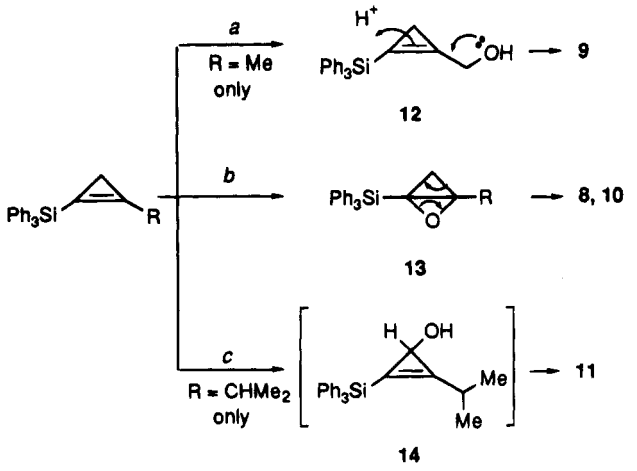
Scheme 1

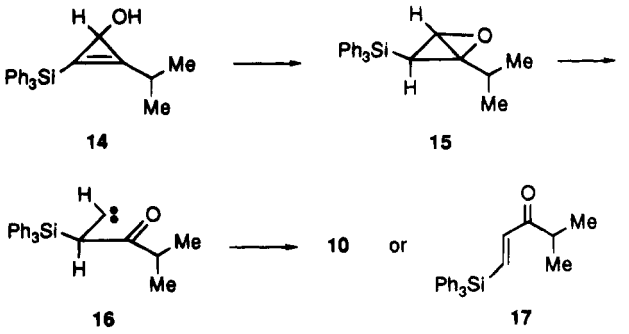


istic ^{13}C signals of the unsaturated three-membered ring (183.2, 167.6, and 166.0 ppm).[8]

Since our samples of **7a** contain none of the isomeric methylenecyclopropane, the formation of **9** is consistent with oxidation of the external methyl group (path a) in competition with attack at the double bond (path b, Scheme 1). Once carbinol **12** is produced, cyclization presumably occurs to alleviate ring strain. Formation of oxabicyclobutane **13**, a process common to both derivatives, is followed by facile electronic reorganization in well-precedented fashion.[9] The obvious preference exhibited by DMD to oxidize the methyl substituent in **7a** as opposed to the ring methylene group may be a consequence of the greater s character resident in those σ bonds attached directly to the cyclopropene and the nonintervention of a cyclopropenium cation intermediate. The $^{13}C-^{13}C$ spin–spin coupling constants earlier determined for **7a** indicate the C–C single bonds of the ring to possess > 90% p character and the pendant C–Me bond to be experiencing a high s orbital contribution from the olefinic carbon to which it is attached.[10] For **7b** to deviate from this reactivity pattern attests to the fact that the steric hindrance inherent in the isopropyl group is adequate to direct the DMD to enter into reaction with an inherently stronger C–H bond. Perhaps the conformation of **7b** is such that the tertiary C–H bond on the isopropyl group is oriented in the plane of the cyclopropene ring rather than allylically aligned with the π orbitals.

The initial oxidation of hydrocarbons to alcohols is recognized to be rather sluggish.[4,11] Consequently, the formation of **14** is expected to be controlled by a rate constant slower than that associated with its subsequent oxidative conversion[12] to **11**. Under normal circumstances, a hydroxy cyclopropene such as **14** would be expected to undergo ring fragmentation readily with production of one or both of the corresponding acrolein derivatives. Perhaps because the DMD reaction medium is neutral, the lifetime of **14** is more than sufficient to allow for continued oxidation to prevail. More advanced oxidation of **12** is precluded by virtue of spiro epoxide formation. If **14** were to experience mechanistically related ring closure to generate oxabicyclobutane **15**, an alternative route would be opened to **10** via **16** (Scheme 2). This possibility cannot be dismissed, although the formation of **17** was not detected, as would have been expected.[13]

Scheme 2



The high regioselectivity observed in the allylic oxidation of **7a** and **7b** at two different sites is noteworthy. It will be interesting to see if these findings foreshadow the ability to control and direct reactions involving DMD in a synthetically advantageous manner.

Experimental Section

Oxidation of 7a. A 79 mg (0.25 mmol) sample of **7a** was added to a magnetically stirred solution of dimethyldioxirane (5 mL of 0.1 M in acetone)[14] at rt. Fresh DMD (2 mL) was added at 2 h intervals. After 6 h, the solvent was evaporated and the residue was chromatographed on silica gel (gradient elution with 5–10% ethyl acetate in hexanes). The first compound to elute was **9** (8 mg, 9%), a colorless solid of mp 71–73 °C: IR (CH_2Cl_2, cm^{-1}) 2930, 1690, 1550, 1110, 830; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56–7.51 (m, 6 H), 7.50–7.33 (m, 9 H), 3.10 (d, J = 4.8 Hz, 1 H), 2.94 (dd, J = 0.7, 4.8 Hz, 1 H), 1.58 (ddd, J = 11.6, 0.7, 5.5 Hz, 1 H), 1.34 (dd, J = 7.9, 11.6 Hz, 1 H), 0.94 (dd, J = 5.5, 7.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 135.6, 133.9, 129.8, 128.0, 57.0, 49.9, 6.5, −0.9; MS m/z (M^+) calcd 328.1283, obsd 328.1283.

Continued elution afforded **8** (36 mg, 44%) as a colorless solid, mp 98–100 °C (from hexanes): IR (KBr, cm^{-1}) 1665, 1425, 1265, 1105, 700; ^1H NMR (300 MHz, $CDCl_3$) δ 7.62–7.52 (m, 6 H), 7.49–7.29 (m, 9 H), 6.82 (d, J = 1.7 Hz, 1 H), 6.21 (d, J = 1.7 Hz, 1 H), 2.33 (s, 3 H); ^{13}C NMR (75MHz, $CDCl_3$) ppm 203.5, 150.0, 142.8, 136.2, 133.5, 129.6, 127.9, 27.1; MS m/z (M^+) calcd 328.1283, obsd 328.1283. Anal. Calcd for $C_{22}H_{20}OSi$: C, 80.44; H, 6.14. Found: C, 80.35; H, 6.18.

Oxidation of 7b. A 75 mg (0.22 mmol) sample of **7b** was added to a magnetically stirred solution of dimethyldioxirane (5 mL of 0.1 M in acetone) at rt. Additional 5 mL aliquots were introduced after every hour. When no starting material was detected by TLC (3.5 h), the solvent was evaporated and the residue was chromatographed on silica gel (gradient elution with 20–50% ethyl acetate in hexanes). The first product to elute was **10**, a colorless oil (36 mg, 46%): IR (CH_2Cl_2, cm^{-1}) 1670, 1110, 1020; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56–7.53 (m, 6 H), 7.44–7.33 (m, 9 H), 6.71 (d, J = 1.8 Hz, 1 H), 6.14 (d, J = 1.8 Hz, 1 H), 3.18 (sept, J = 6.8 Hz, 1 H), 1.01 (d, J = 6.8 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 210.0, 149.7, 139.7, 136.2, 133.5,

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129.6, 127.8, 36.4, 18.7; MS m/z (M^+) calcd 356.1596, obsd 356.1596. Anal. Calcd for $C_{24}H_{24}OSi$: C, 80.85; H, 6.78. Found: C, 80.82; H, 6.87.

Continued elution afforded **11** (17 mg, 22%) as a colorless solid, mp 107–109 °C (from hexanes): IR ($CDCl_3$, cm^{-1}) 1816, 1571, 1430, 1114, 670; ^1H (300 MHz, $CDCl_3$) δ 7.63–7.54 (m, 6 H), 7.51–7.40 (m, 9 H), 3.01 (sept, J = 7.0 Hz, 1 H), 1.08 (d, J = 7.0 Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 183.2, 167.6, 166.0, 135.7, 131.0, 128.4, 29.5, 19.6; MS m/z (M^+) calcd 354.1440, obsd 354.1442. Anal. Calcd for $C_{24}H_{22}OSi$: C, 81.31; H, 6.25. Found: C, 80.74; H, 6.30.

Acknowledgment. This investigation was supported at The Ohio State University by the National Science Foundation.

Additions and Corrections

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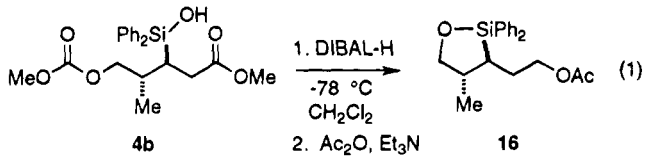
Michael R. Hale and Amir H. Hoveyda*. Diastereoselective Heteroatom-Directed Conjugate Additions of Silylcuprate Reagents to Unsaturated Carbonyls. A Stereoselective Route to β-Carbonyl Siloxanes.

Page 4373, column 1. Equation 1 should be corrected as shown:



Page 4373, column 1. The stereochemistry of the product shown in eq 2 is that of the minor diastereomer.