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Silylcyclopropanes by Selective [1,4]-Wittig Rearrangement of 4-Silyl-5,6-dihydropyrans

Luis M. Mori-Quiroz, Emmanuel W. Maloba, and Robert E. Maleczka, Jr.*

Cite This: *Org. Lett.* 2021, 23, 5724–5728 Read Online

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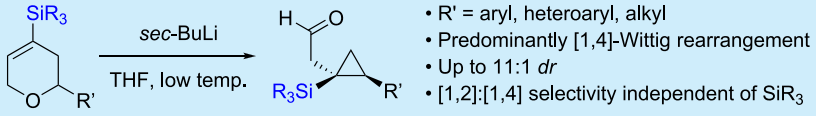


ABSTRACT: 4-Silyl-5,6-dihydropyrans undergo remarkably selective [1,4]-Wittig rearrangements to give silylcyclopropanes in good yields. The selectivity is independent of the silyl group, but it is influenced by the electronic character of the migrating center. Electron-rich and electron-neutral (hetero)aryl groups and aliphatic substituents at the migrating center lead to exclusive [1,4]-migration, whereas electron-deficient aryl groups predominantly afford [1,2]-Wittig products.

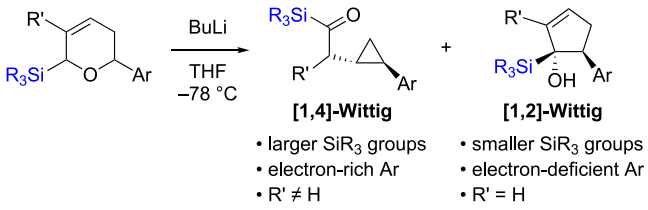
[1,4]-Wittig rearrangements of allyl ethers generate enolates, whereas the more common [2,3]- and [1,2]-pathways produce alkoxides.[1] In addition, the [1,4]-Wittig pathway is inherently interwoven with the [1,2]-manifold, which typically predominates. Despite its synthetic potential, the [1,4]-migration path is largely underdeveloped with selective and efficient [1,4]-Wittig pathways being relatively rare and of limited scope.[2]

In 2006, our research group found that (1-trimethylsilyl)-allylbenzyl ether rearranged selectively through the [1,4]-pathway, forming the acylsilane product.[3] The apparent ability of the silyl group to allow (1) selective allylic deprotonation and (2) selective [1,4]-migration of the benzyl group led us to explore more complex acyclic analogues. These studies were hampered by lower reactivity of such higher analogues, which we speculated was due to sterics hindering access to conformations necessary for deprotonation.[4] In contrast, we found that related cyclic ethers rearrange efficiently to give α-cyclopropyl acylsilanes or α-silylcyclopentenols by [1,4]- and [1,2]-Wittig migrations, respectively.[5] We also learned that cis/trans diastereomers of these cyclic ethers exhibited very different rates of deprotonation, again presumably reflecting their different ability to achieve the optimal conformation for deprotonation. Once deprotonated, [1,4]-migration and the competing [1,2]-pathway proceed in a stereoconvergent fashion, with [1,4]-/[1,2]- selectivity being highly sensitive to steric and electronic factors (Scheme 1).[5]

A question that arose from these studies was whether relocation of the silyl group to the 4-position of the dihydropyran scaffold would favor the [1,4]- or [1,2]-pathway. Herein, we report that 4-silyl-5,6-dihydropyrans undergo highly selective [1,4]-Wittig rearrangement to afford silylcyclopropyl acetaldehydes.

Silylcyclopropanes are versatile building blocks in organic synthesis.[6] For instance, they engage in reactions with both nucleophilic and electrophilic partners. Traditional synthetic approaches (Scheme 2) involve the cyclopropanation of vinylsilanes[7,8] and the addition of silyl carbenoids to olefins.[9] Other metal-catalyzed processes have been developed, such as the addition of silyl reagents to cyclopropenes,[10] intramolecular C−H silylation of cyclopropanes,[11] and annulation reactions.[12] To the best of our knowledge, the synthesis of silylcyclopropanes by means of ring contraction has not been reported.

Scheme 1. Wittig Rearrangements of 2-Silyl-6-aryl-5,6-dihydropyrans

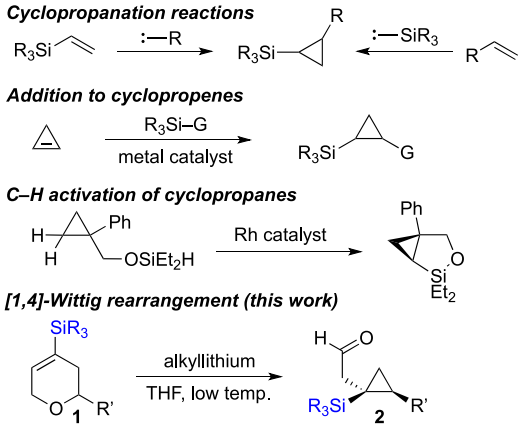


For our purpose, the 4-silyl-5,6-dihydropyrans were prepared from readily available homopropargylic alcohols in three steps involving regioselective alkyne hydrosilylation using Trost catalyst[13] or Tomooka's Pt-catalyzed method,[14] followed by O-allylation, and ring-closing metathesis of the diene precursor using Grubbs' second-generation catalyst (Scheme

Received: June 2, 2021
Published: July 8, 2021

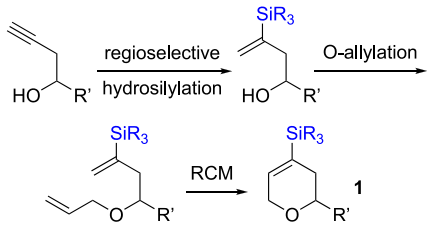
https://doi.org/10.1021/acs.orglett.1c01838
Org. Lett. 2021, 23, 5724–5728

Scheme 2. General Approaches to Silylcyclopropanes



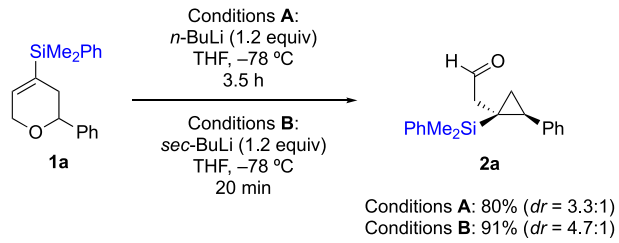
3).[15] A variety of substrates bearing different silyl groups were thus accessed.

Scheme 3. Synthetic Route to Dihydropyrans 1



We started this study by evaluating dihydropyran **1a** under Wittig conditions used in our previous reports (Scheme 4).

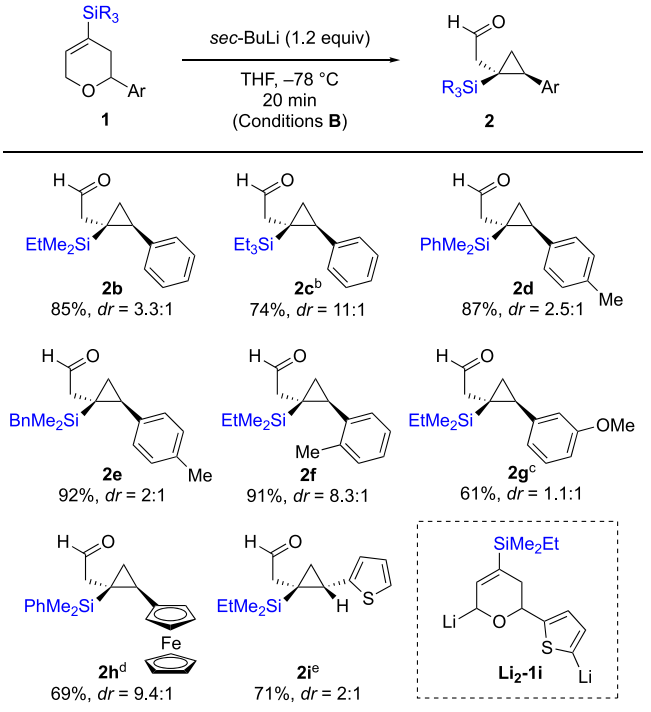
Scheme 4. [1,4]-Wittig Rearrangement of Model Substrate 1a



Treatment of **1a** with *n*-butyllithium in THF at −78 °C for 3.5 h (conditions A) afforded exclusively [1,4]-Wittig product **2a** in 80% yield with modest diastereoselectivity (3.3:1), together with a small amount of unreacted **1a** (7%). The use of the stronger *sec*-butyllithium (conditions B) resulted in complete deprotonation followed by rearrangement to afford **2a** in 91% yield after only 20 min. Slightly higher diastereoselectivity (4.7:1) was also realized. Under both reaction conditions, we were unable to detect any [1,2]-Wittig product by ^{1}H NMR analysis of the crude reaction mixtures.

We next evaluated a variety of substrates bearing different silyl groups at the 4-position and aryl substituents at the migrating carbon (Scheme 5). The smaller $EtMe_2Si$ group afforded silylcyclopropylacetaldehyde **2b** in 85% yield and 3.3:1 diastereoselectivity, whereas the more sterically demanding Et_3Si group led to silylcyclopropane **2c** in a slightly lower yield (70%) but higher diastereoselectivity (11:1). Consistent

Scheme 5. Substrate Scope of Aryl-Substituted Dihydropyrans Bearing Different Silyl Groups[a]



[a]Diastereoselectivity determined by ^{1}H NMR of the crude reaction mixture. [b]Reaction run on a 2 mmol scale. [c]A small amount (<5%) of the presumed [1,2]-Wittig product within a complex mixture was observed but not fully characterized. [d]15% of unreacted dihydropyran **1h** was recovered. [e]2.2 equiv of *sec*-BuLi was used.

with prior observations, electron-donating groups such as a 4-methyl on the phenyl group afforded exclusively silylcyclopropanes **2d** and **2e** bearing $PhMe_2Si$ and $BnMe_2Si$ groups in good yields and low diastereoselectivities. *o*-Methyl substitution at the aryl group was tolerated, leading to silylcyclopropane **2f** in 91% yield and 8.3:1 diastereoselectivity. *m*-Methoxy substitution of the aryl ring, which confers an electron-deficient character to the migrating (benzylic) carbon, afforded predominantly the [1,4]-Wittig product **2g** in 61% yield. This was in contrast with the observation in our previous work on 2-silyl-6-aryl-5,6-dihydropyrans, where a near equal mixture of [1,2], and [1,4] products was observed.[5] Other (hetero)-aromatic substituents at the migrating center such as ferrocenyl and 2-thiophene-yl were tolerated, providing access to silylcyclopropyl acetaldehydes **2h** and **2i** in 69% and 71% yield, respectively. However, in contrast to all previous examples, the major diastereomer in **2i** was trans. This outcome is best explained by the fact that 2.2 equiv of *sec*-BuLi was used to ensure complete allylic deprotonation of **1i**. Such conditions were used because the 2-thiophenyl group undergoes competitive deprotonation at the 5 position, as previously observed.[5] Therefore, the actual species that undergoes rearrangement is likely the dianion $\mathbf{Li_2}$**−1i** (Scheme 5, inset), whose unique electronic characteristics might be responsible for the observed stereochemistry of **2i**.

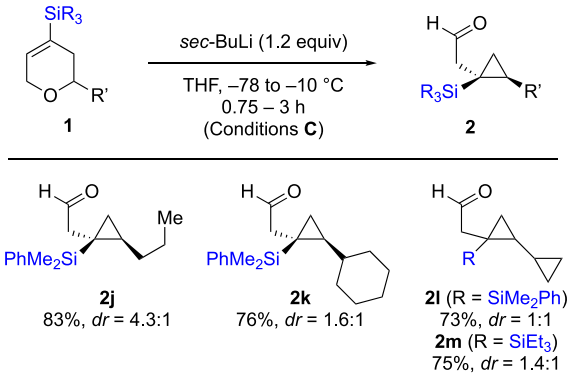
We determined the relative stereochemistry of the major diastereomer in **2a** by NOESY studies and assigned the relative stereochemistry of compounds **2b**−**2i** by comparison. Specifically, protons corresponding to the alkyl groups attached to silicon (Me, Et) appeared upfield in the NMR spectrum

https://doi.org/10.1021/acs.orglett.1c01838
Org. Lett. 2021, 23, 5724−5728

relative to those in the minor diastereomer, presumably due to shielding effects by the *cis*-oriented aromatic group. In addition, protons corresponding to methyl groups in dimethylsilyl products (i.e., **2b**, **2d**−**2h**) became inequivalent due to the expected slow rotation induced by the bulky aryl groups. We further confirmed the structure of compound **2c** by X-ray crystallographic analysis of its 2,4-dinitrophenylhydrazine derivative (see the Supporting Information).

We next evaluated dihydropyrans bearing alkyl substituents at the migrating carbon (Scheme 6). These substrates

Scheme 6. Selective [1,4]-Wittig Rearrangement of Dihydropyrans 1 Bearing Alkyl Groups at the Migrating Center[a]

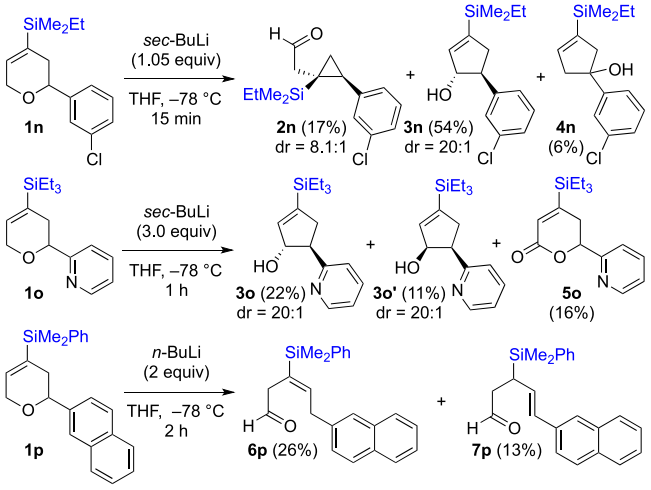


[a]Diastereoselectivity determined by ^{1}HNMR of the crude reaction mixture.

underwent slow deprotonation under conditions A and B (see Scheme 4). However, addition of *sec*-butyllithium at −78 °C and warming to −10 °C (conditions C) allowed deprotonation and rearrangement with excellent [1,4]-selectivity. Dihydropyrans bearing $PhMe_2Si$ groups on the 4-position and *n*-propyl and cyclohexyl substituents at the migrating carbon led to the corresponding silylcyclopropanes **2j** and **2k** in 83% and 76% yields, respectively. The *n*-propyl-substituted dihydropyran (**1j**) rearranged with higher diastereoselectivity compared to the dihydropyrans bearing cycloalkyl groups (Scheme 6). Interestingly, cyclopropyl-substituted dihydropyrans **1l** and **1m** underwent rearrangement without observable formation of the ring-opened products.

Dihydropyrans with electron-deficient aryl groups such as **1n** underwent Wittig rearrangements with flipped [1,4]-/[1,2]-selectivity. Here, the predominant product was the [1,2]-Wittig alcohol **3n** (54%), followed by the [1,4]-silylcyclopropane **2n** (17%) and a small amount of an isomeric [1,2]-Wittig product **4n** (6%). Formation of **4n** indicates that benzylic deprotonation becomes competitive when electron-deficient aryl groups are present. Similarly, 2-pyridyl-substituted dihydropyran (**1o**) predominantly afforded diastereomeric [1,2]-Wittig products **3o** and **3o′** (2:1 ratio), resulting from allylic deprotonation. Unreacted **1o** could not be isolated and instead underwent oxidation during workup and purification to give lactone **5o**.[16] Attempts to access the 4-pyridyl analogue using our established route (Scheme 3) were unsuccessful due to reluctance of the diene precursor to undergo ring-closing metathesis (see the Supporting Information). 2-Naphthyl-substituted dihydropyran (**1p**) failed to undergo Wittig rearrangement, and instead, ring-opened products **6p** and **7p** were observed (Scheme 7).

Scheme 7. Rearrangement of Substrates Bearing Electron-Deficient Aryl Groups and 2-Naphthyl Derivative



On a last note, it is worth comparing the ability of silyldihydropyrans **1** and isomeric **9a**/**b**[5] to undergo clean rearrangements relative to the unsubstituted analogue **8** (Figure 1). While **1** and **9a**/**b** undergo Wittig rearrangements

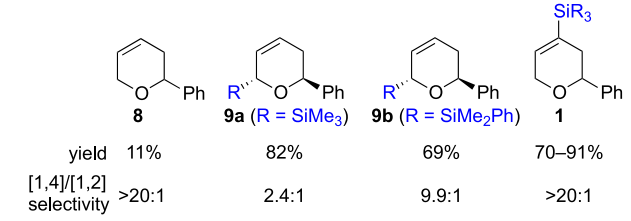
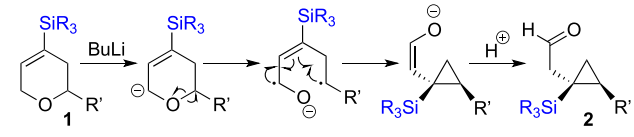


Figure 1. Comparison of yields and [1,4]-/[1,2]-selectivities of **1** vs 2-silyl analogues **9a**/**9b** and desilylated analogue **8**.

in good yields, dihydropyran **8** reacts sluggishly to give a low yield of [1,4]-Wittig product together with a complex mixture of undetermined byproducts. On the other hand, the exclusive [1,4]-selectivity of **1** is independent of the nature of the silyl groups, while those of **9a** or **9b** are very sensitive to the sterics of the silyl group.

In line with our previously proposed mechanistic hypothesis, we maintain that the [1,4]-Wittig rearrangement of silyl dihydropyrans proceeds primarily by a stepwise process involving a homolytic C−O bond cleavage and intramolecular radical/radical anion recombination (Scheme 8),[5] a process

Scheme 8. Proposed Mechanism of the [1,4]-Wittig Rearrangement of 4-Silyl-6-aryl(alkyl)-5,6-dihydroprans



that must be faster than ~7×10^7 s^{-1} given that cyclopropyl-bearing substrates did not lead to ring opened products.[17] As previously reported,[5] the product distributions from **9a** or **9b** suggest that increasing the steric demand of the silyl group prevents [1,2]-recombination due to steric clash with the phenyl group. These observations, together with the exclusive [1,4]-selectivity displayed by **1** suggest that the [1,4]-/[1,2]-

https://doi.org/10.1021/acs.orglett.1c01838
Org. Lett. 2021, 23, 5724−5728

selectivity is determined by the ability of the silyl group to transiently and locally stabilize the allylic radical,[18] guiding recombination toward the Si-bearing carbon.

However, there remains the question as to why varying diastereoselectivities are observed with different silyl or aryl groups (Scheme 5). For instance, the diastereoselectivity increases nearly 3-fold from the relatively small $SiMe_2Et$ group (**2b**, dr = 3.3:1) to the more sterically demanding $SiEt_3$ group (**2c**, dr = 11:1). Similarly, the bulkier aryl group 2-methyl phenyl in **2f** affords a higher diastereoselectivity (8.3:1) relative to the phenyl analogue **2b** (Scheme 5). At this point, we conjecture that a concerted mechanism is operative to a certain extent and leads to the minor diastereomer (*trans*). In this scenario, bulkier silyl or aryl groups preclude such a competitive mechanism, indirectly leading to higher diastereoselectivity by the dominant, stepwise mechanism.

In conclusion, silylcyclopropane acetaldehydes with a variety of silyl groups can be accessed efficiently by selective [1,4]-Wittig rearrangement of 4-silyl-5,6-dihyropyrans. High selectivity is achievable with substrates whose migrating group has an electron-neutral or electron-rich character. In general, the diastereoselectivity of the [1,4]-migration is such that the bulkier groups (silyl and aryl/alkyl) end up in a *cis* relationship.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01838.

Experimental details, characterization of new compounds, copies of ^1H and ^{13}C NMR spectra, and X-ray crystallographic data (PDF)

Accession Codes

CCDC 2031553 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Robert E. Maleczka, Jr. − *Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States;* orcid.org/0000-0002-1119-5160; Email: maleczka@chemistry.msu.edu

Authors

Luis M. Mori-Quiroz − *Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States;* Present Address: Apeel Sciences, Molecular Sciences, 71 S Los Carneros Rd, Goleta, CA 93117; orcid.org/0000-0001-8546-7264

Emmanuel W. Maloba − *Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c01838

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Dr. Richard Staples (Michigan State University) for crystallographic analysis and Michigan State University for funding.

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https://doi.org/10.1021/acs.orglett.1c01838
Org. Lett. 2021, 23, 5724−5728