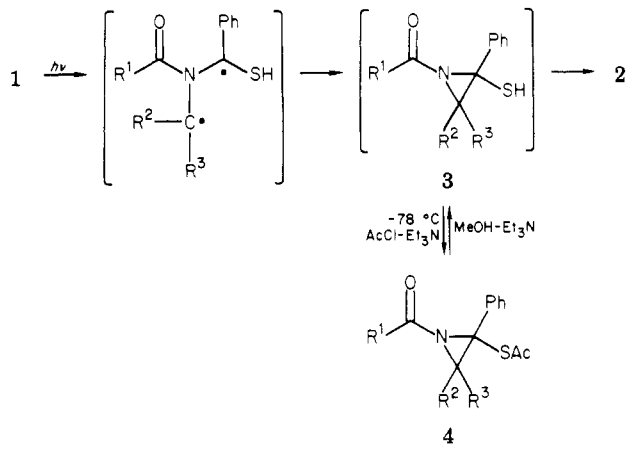
Scheme I



ketones **2b–e** in good yields as shown in Table I. Although photolysis of **1f** also gave the thioketone **2f** in 43% yield, this compound was unstable and decomposed gradually even at room temperature. The photoreaction of **1g** was much slower than that of other monothioimides (**1a–f**), and prolonged irradiation gave an intractable mixture.

The formation of the thioketones **2** is reasonably explained in terms of ring opening of an aziridine (**3**), which is produced by cyclization of **1** (Scheme I). The intermediacy of **3** was confirmed by the following experiments. Irradiation of **1c** in toluene at −78 °C resulted in the loss of the red thioimide color. On warming to room temperature, the colorless solution turned purple and **2c** was obtained as a main product. This finding indicated the presence of an intermediate that did not possess a thiobenzoyl moiety. When the colorless solution obtained in the low-temperature photolysis was treated with acetyl chloride in the presence of triethylamine at −78 °C, 2,3-diphenyl-2-(acetylthio)-1-benzoyl-3-methylaziridine (**4c**, 85%) was obtained, accompanied by a small amount of **2c** (9%). The structure of **4b** was assigned on the basis of elemental analysis and spectral data. The IR spectrum (KBr) exhibited carbonyl frequencies at 1705 and 1660 $cm^{-1}$. The $^1H$ NMR spectrum ($CDCl_3$) showed signals at $\delta$ 1.14 (s, 3 H, $CH_3$), 2.01 (s, 3 H, C(=O)$CH_3$), 7.3–7.8 (m, 13 H, Ph), and 8.1–8.2 (m, 2 H, Ph), and $^{13}C$ NMR exhibited resonances at 26.3 (q), 31.3 (q), 80.6 (s), 104.7 (s), 126.6 (d), 127.7 (d), 128.0 (d), 128.5 (d), 128.6 (d), 131.9 (s), 139.0 (s), 140.9 (s), 161.6 (s), and 191.8 (s) ppm. The mass spectrum showed molecular ion at $m/z$ 387 ($M^+$) and fragment peaks at $m/e$ 312 [M − SC(=O)Me], and 207 [M − SC(=O)Me − PhC(=O)]. Furthermore, the fact that the base-catalyzed methanolysis (MeOH–$NEt_3$) of **4b** gives **2b** almost quantitatively is also consistent with the mechanism shown in Scheme I.

β-Hydrogen abstraction appears to be very rare occurrance in carbonyl photochemitry, giving precedence to the Norrish type II, intermolecular hydrogen abstraction or simply other photochemical reactions.[6] Although a few instances of β-hydrogen abstraction of thioketones have been reported,[1e,f] they are limited to thiones where only β-hydrogens are abstractable or β-hydrogens are strongly activated by substituents. The present photorearrangement involving unprecedented 1,2-thiobenzoyl shift also provides the first example of β-hydrogen abstraction of thioimides.

(6) (a) Padwa, A.; Gruber, R. *J. Am. Chem. Soc.* **1970**, *92*, 107. (b) Padwa, A.; Eisenhardt, W. *Ibid.* **1971**, *93*, 1400. (c) Cormier, R. A.; Schreiber, W. L.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1972**, 729. (d) Scheffer, J. R.; Bhandari, K. S.; Gaylar, R. E., *J. Am. Chem. Soc.* **1975**, *97*, 2178.

**Registry No.** **1a**, 89873-85-8; **1b**, 89873-86-9; **1c**, 89873-87-0; **1d**, 89873-88-1; **1e**, 89873-89-2; **1f**, 49590-28-5; **1g**, 89873-90-5; **2a**, 89873-91-6; **2b**, 89873-92-7; **2c**, 89873-93-8; **2d**, 89873-94-9; **2e**, 89873-95-0; **2f**, 89873-96-1; **4a**, 89873-98-3; **4b**, 89873-99-4; **4c**, 89873-97-2; **4d**, 89874-00-0; **4e**, 89874-01-1; **4f**, 89874-02-2; hydrogen, 1333-74-0.

**Supplementary Material Available:** Experimental procedures and spectral data of starting materials and photoproducts are described (2 pages). Ordering information is given on any current masthead page.

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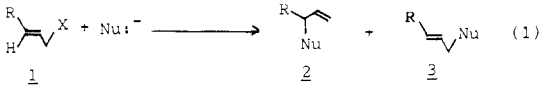
## Regiospecific Alkylation on Allylic Halides with Latent γ-Functionality

*Summary:* Completely regiospecific alkylation on stereospecifically γ-silylated allylic bromides was achieved with a variety of anionic nucleophiles of a wide range of strength.

*Sir:* Advantageous aspects of using electrophilic allylic reactants in organic synthesis can never be underestimated because they are more reactive than the corresponding saturated analogues, and their obvious precursors, the corresponding allylic alcohols, can be prepared stereospecially.[1] But development of allylation reactions possessing high regio- and stereoselectivities has been a long-standing problem in organic chemistry, mainly because of the preponderant $S_N2'$, reactions especially with strong nucleophiles (eq 1), and numerous attempts to control the site of reaction have been made.[1]



Herein is reported a solution for this problem in which by placing a sterically demanding proton equivalent on the γ-position of the allylic halide **1** or the corresponding stereoisomer, the unwanted reaction at γ-position ($S_N2'$) is curtailed. Additionally, if the allylic reactants would be available and the proton equivalent is removed (or replaced by other funtionality), both stereospecifically, this method would render a general synthesis of alkenes. To this end, a trialkylsilyl group would be a perfect choice for the requirements.[2]

Consequently, a number of stereospecifically 3-trimethylsilylated allylic alcohols **4** and **5** were prepared[3,4]

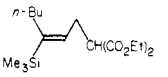
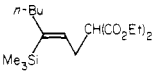
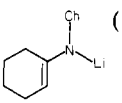
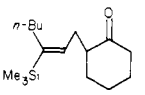
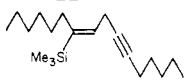
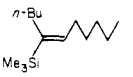
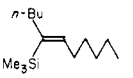
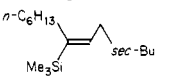
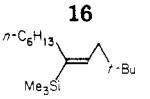
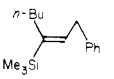
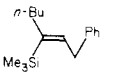
(1) (a) Magid, R. M. *Tetrahedron*, **1980**, *36*, 1901. (b) Calo, V.; Lopez, L.; Pesce, G.; Calianno, A. *J. Org. Chem.* **1982**, *47*, 4482. (c) Goering, H. L.; Kantner, S. S.; Tseng, C. C. *Ibid.* **1983**, *48*, 715.

(2) For reviews of organosilicon chemistry, see: Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15. "Silicon in Organic Synthesis"; Butterworth: London, 1981. Paquette, L. A. *Science (Washington, D.C.)* **1982**, *217*, 1793. Chan, T. H. *Acc. Chem. Res.* **1977**, *10*, 442. Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

(3) 3(*E*)-(Trimethylsilyl)allylic alcohols **4** were prepared by either of the following methods. (a) Titanocene dichloride catalyzed syn-hydromagnesiation of propargylic alcohols (Sato, F.; Ishikawa, H.; Watanabe, H.; Miyake, T.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 718), followed by trimethylsilylation with trimethylsilyl chloride in the presence of HMPT. (b) Hydroalumination ($LiAlH_4$–NaOMe)–iodination of 3-(trimethylsilyl)-2-propyn-1-ol, followed by cuprate reaction on the 3-(*E*)-iodoallylic alcohols (Corey, E. J.; Katzenellenbogen, J. A.; Gilman, N. W.; Roman, S. A.; Erickson, B. W. *J. Am. Chem. Soc.* **1968**, *90*, 5618).

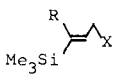
0022-3263/84/1949-1838$01.50/0 

Table I. Reactions of 3-(Trimethylsilyl)allylic Bromides with Nucleophiles[a]

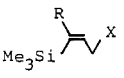
| entry | starting material (R) | reaction condition | product[b] (yield, %) |
|---|---|---|---|
| 1 | **6** (*n*-Bu) | $NaCH(CO_2Et)_2$ (1.2 equiv) 0→23 °C (3 h), THF |  **8** (60) |
| 2 | **7** (*n*-Bu) | |  **9** (79) |
| 3 | **6** (*n*-Bu) |  (**10**) (1.5 equiv) −15→23 °C (3 h), THF |  **11** (86)[c] |
| 4 | **6** ($n$-$C_6H_{13}$) | $Li_2(n\text{-}C_5H_{11}C{\equiv}C)_2CuCN$ (**12**) (1.0 equiv), 0 °C (0.5 h), THF |  **13** (85) |
| 5 | **6** (*n*-Bu) | $LiCu(n\text{-}Bu)_2$ (2.2 equiv), −78→−40 °C (2 h), ether |  **14** (100) |
| 6 | **7** (*n*-Bu) | |  **15** (100) |
| 7 | **6** ($n$-$C_6H_{13}$) | *sec*-BuCu (3.0 equiv), −78→−40 °C (2 h), ether |  **16** (100) |
| 8 | **6** ($n$-$C_6H_{13}$) | *t*-BuCu (2.0 equiv), −78→−40 °C (2 h), ether |  **17** (100) |
| 9 | **6** (*n*-Bu) | $LiCuPh_2$ (2.5 equiv), −78→−0 °C (3 h), ether |  **18** (76) |
| 10 | **7** (*n*-Bu) | |  **19** (85) |

[a] All reactions were carried out (0.1–0.3 M concentration) under rigorous exclusion of moisture and oxygen. Reaction was monitored by TLC, and, when complete, extractive workup was performed in the usual way. [b] The product was isolated pure by chromatography on silica gel and fully substantiated by spectral data. [c] After hydrolysis in 4% aqueous oxalic acid (23 °C, 1 h).

and subsequently converted to the corresponding bromides **6** and **7**.[5]



**4** X=OH
**6** X=Br



**5** X=OH
**7** X=Br

The allylic bromides **6** and **7** were individually subjected to displacement reactions with various nucleophiles. Some representative results, which are summarized in Table I, fulfill our expectation with complete regiospecificity. Moreover, the stereochemistry of the allylic bromides was fully conserved in the alkylation products, which vividly testifies to the subtle influence of the silyl group.[6,7]

It should be noted that there were in fact some interesting observations in the aforementioned reactions. Lithium enolates reacted smoothly to form monoalkylated products,[6] but by far the cleanest alkylation could be conducted with metalloenamine derivatives (entry 3, Table I). Also, the mixed cuprate **12**[8] (entry 4, Table I) provided cleanly the skipped enyne **13** whereas the reaction with the corresponding lithium acetylide in a THF–HMPA mixed solvent[9] gave considerable amounts of the corresponding ene–allene in this example.

Far more interesting results were obtained in the reactions with organocopper reagents. Thus, reactions of the allylic bromides with lithium di-*n*-butylcuprate afforded

(4) 3(*Z*)-(Trimethylsilyl)allylic alcohols **5** were prepared by Wurtz-type silylation (sodium dispersion, $Me_3SiCl$, toluene, reflux) of trimethylsilyl ether of 3(*Z*)-iodoallylic alcohols, which was available from the aforementioned hydroalumination–iodination of propargylic alcohols. For a similar approach, see ref 6. Another method, although more laborious, was found to work equally well, see: Miller, R. B.; Al-Hassan, M. I. *Tetrahedron Lett.* **1983**, *24*, 2055.

(5) The bromides **6** and **7** were prepared in more than 90% yields from the corresponding alcohols by modification of the existing method (1.5 equiv of $CBr_4$, 1.7 equiv of $Ph_3P$, 1 equiv of 2,6-lutidine, $CH_2Cl_2$, 23 °C, 2–3 h). Kocienski, P. J.; Cernigliaro, G.; Feldstein, G. *J. Org. Chem.* **1977**, *42*, 353.

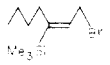
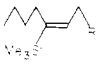
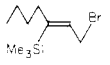
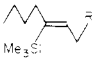
(6) Stork, G.; Jung, M. E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684.

(7) Cf. Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1983**, *48*, 721 and references therein.

(8) For applications of analogous reagents, see: Lipshutz, B. H.; Kozlowski, J. A.; Wilhelm, R. S. *J. Org. Chem.* **1983**, *48*, 546 and references therein.

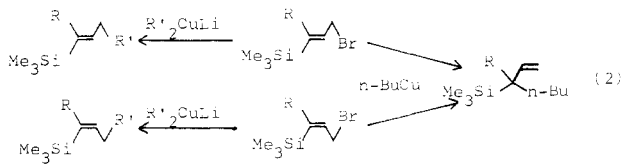
(9) Schill, G.; Keller, U. *Synthesis* **1972**, 621.

Table II. Reactions of 3-(Trimethylsilyl)allylic Bromides with Alkylcopper Reagents[a]

| starting material (R = n-Bu) | alkylcopper RCu (equiv) | products and yield,[b] % | |
|---|---|---|---|
|  | |  20 |  21 |
| | *n*-BuCu (2) | 0 | 100 |
| | *n*-BuCu·$BF_3$ (2) | 0 | 100 |
| | PhCu (2) | 16[c] | 82[c] |
| | *sec*-BuCu (3) | 100 | 0 |
| | *t*-BuCu (2) | 100 | 0 |
|  | |  22 |  21 |
| | *n*-BuCu (2.5) | 0 | 100 |

[a] Reactions were done under the identical conditions (with those in Table I). [b] The products were isolated pure by chromatography unless otherwise noted. [c] Determined by NMR.

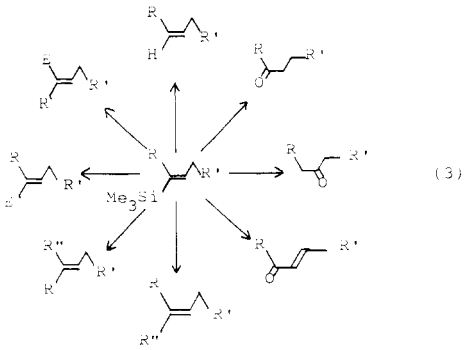
straightforwardly $S_N2$ products (entries 5 and 6, Table I), while, irrespective of stereochemistries of allylic bromides, the corresponding reactions with either *n*-butylcopper or *n*-BuCu·$BF_3$[10] provided exclusively same $S_N2'$ product, **21** (Table II). This is, to our knowledge, the first instance where clear and sharp distinction of reaction paths exists between reactions of dialkylcuprates and alkylcoppers (eq 2).



(2)

Unfortunately, though, the difference faded gradually as the alkyl groups on copper became larger (Table II). Thus, with *sec*- or *tert*-butyl groups, even the corresponding alkylcopper reagents were effective for $S_N2$ reactions, but with *n*-butyl or phenyl groups, use of cuprate reagents was necessary for $S_N2$ product formation (Table I).

In conclusion, γ-(trimethylsilyl)allylic bromides are superb substrates for regiospecific $S_N2$ functionalization and the resulting stereodefined alkenylsilanes are valuable synthetic intermediates convertible to a number of functional groups of variable oxidation states[2,11] (eq 3).



(3)

(10) Maruyama, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1977**, *99*, 8068.
(11) (a) Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263. Hudrlik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993. (b) Hirao, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Chem. Lett.* **1982**, 1977.

**Acknowledgment.** Financial support from the Korean Science and Engineering Foundation and experimental assistance by Ms. Seung Hee Hann are gratefully appreciated.

**Registry No.** **6** (R = *n*-Bu), 89828-12-6; **6** (R = *n*-$C_6H_{13}$), 89828-13-7; **7** (R = *n*-Bu), 89828-14-8; **8**, 89828-15-9; **9**, 89828-16-0; **10**, 89828-17-1; **11**, 89828-18-2; **12**, 89828-11-5; **13**, 89828-19-3; **14**, 89828-20-6; **15**, 89828-21-7; **16**, 89828-22-8; **17**, 89828-23-9; **18**, 89828-24-0; **19**, 89828-25-1; **20** (R = *sec*-Bu), 89828-26-2; **20** (R = *t*-Bu), 89828-27-3; **21** (R = *n*-Bu), 89828-28-4; **21** (R = Ph), 89828-29-5; $NaCH(CO_2Et)_2$, 34727-00-9; $LiCu(n\text{-}Bu)_2$, 24406-16-4; *sec*-BuCu, 89828-30-8; *t*-BuCu, 56583-96-1; $LiCuPh_2$, 23402-69-9; *n*-BuCu, 34948-25-9; *n*-BuCu·$BF_3$, 68079-35-6; PhCu, 3220-49-3.

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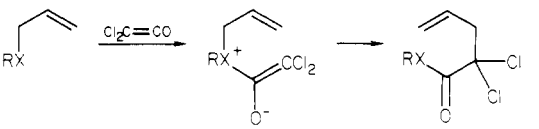
## Macrolide Synthesis via Dichloroketene Ring Expansion

*Summary:* The reaction of allyl sulfides with dichloroketene followed by [3,3] sigmatropic rearrangement has been adapted for the efficient ring expansion of α-alkenyl cyclic sulfides.

*Sir:* Belluš and Malherbe have described a remarkable [3,3] sigmatropic rearrangement of allyl ethers or sulfides upon treatment with dichloroketene:[1]



It occurred to us that this reaction should also be applicable to the synthesis of medium or large ring thiolactones from cyclic α-alkenyl sulfides that are available by sulfur ylide ring expansion techniques.[2] In particular, we were interested in potential applications where the rearranged product would contain an ω-hydroxyalkyl substituent because thiolactones of this type have been shown to rearrange to seven–ten-membered mercapto lactones by S to O acyl transfer.[3] The key steps correspond to Scheme I, **3** to **4** (dichloroketene ring expansion) and **5** to **6** (S to O acyl transfer). After our work was well under way, Belluš et al. published an apparently close analogy to the desired [3,3] sigmatropic ring expansion, the conversion of **1** into **2**, but in a disappointing yield of 8%.[4] Although we have not repeated this specific example, our results suggest that a modified dichloroketene ring expansion procedure (reflux during slow addition of excess $Cl_3CCOCl$) gives consistently good yields. The method has been used to prepare ω-hydroxyalkyl thiolactones **5** and **12**, which provide convenient access to 11- and 14-membered lactones, respectively, by S to O acyl transfer.

The starting material **3** for both lactone series was available from previous work.[5] Treatment of **3** with $Cl_2C{=}C{=}O$, generated in situ by syringe pump addition

(1) Malherbe, R., Belluš, D. *Helv. Chim. Acta* **1978**, *61*, 3096.
(2) (a) Vedejs, E.; Hagen, J. P.; Roach, B. L.; Spear, K. L. *J. Org. Chem.* **1978**, *43*, 1185. (b) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *Ibid.* **1978**, *43*, 4831. (c) Vedejs, E.; Dophin, J. M.; Mastalerz, H. *J. Am. Chem. Soc.* **1983**, *105*, 127.
(3) Vedejs, E.; Powell, D. W. *J. Am. Chem. Soc.* **1982**, *104*, 2046.
(4) Malherbe, R.; Rist, G.; Belluš, D. *J. Org. Chem.* **1983**, *48*, 860.
(5) Vedejs, E.; Arnost, M. J.; Hagen, J. P. *J. Org. Chem.* **1979**, *44*, 3230.

0022-3263/84/1949-1840$01.50/0 