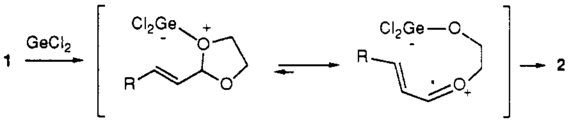
Reaction of germanium(II) chloride with α,β-unsaturated dimethoxy and diethoxy acetals yields acyclic dichloroalkoxygermanes. The stereoselectivity in these reactions is not as high, however, as that obtained with the corresponding dioxolanes. The dimethoxy acetal of cinnamaldehyde, for example, yielded a mixture of cis and trans enol ethers in a 4:1 ratio after 30 min; after a reaction time of 4 h the ratio was 1:1. Reaction of the dimethoxy acetal of *trans*-2-hexenal with germanium(II) chloride gave a mixture of cis–trans enol ethers in a ratio of 1:9. Once again, the ratio of enol ethers was 1:1 when the reaction time was increased to 4 h.

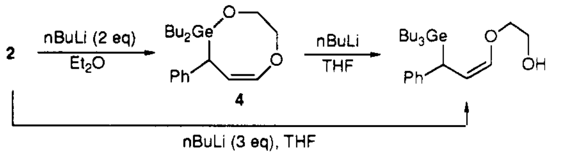
The mechanism of the rearrangement is thought to begin with coordination of the Lewis acidic germanium to an acetal oxygen forming an ylide (eq 3).[15,16] Stereochemical and equilibrium results suggest that the next step involves opening of the acetal to an oxocarbenium ion intermediate. Finally, conjugate addition of germanium to the α,β-unsaturated oxocarbenium ion yields the enol ether. Trans enol ethers predominate in reactions where the intermediate is stabilized by an n-aliphatic group. In contrast, cis enol ethers are formed in reactions when the intermediate is stabilized by an aryl group.



(3)

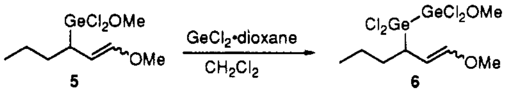
If an aldehyde is added to germacycle **2**, an acetal exchange reaction occurs. For example, addition of benzaldehyde to compound **2** yielded 2-phenyldioxolane along with a cinnamaldehyde–$GeCl_2$ polymer.[17] In addition, we observed partial conversion of **2** to the starting dioxolane, 2-(2(*E*)-phenethylenyl)-1,3-dioxolane, when the germacycle was dissolved in THF. Thus, these germacycles are relatively unstable and appear to exist in equilibrium with their α,β-unsaturated acetals.

Both the cyclic and acyclic dichloroalkoxygermanes produced in this reaction are labile. To provide additional support for our structure assignments, these compounds were converted to either a dibutyl or tributyl derivative.[18] For example, reaction of germacycle **2** with 2 equiv of *n*-BuLi in *diethyl ether* at −78 °C for 1 h gave **4** in good yield (eq 4). Preparation of the tributyl derivative could be done in one of two ways: (1) by adding 1 equiv of *n*-BuLi to **4** in *tetrahydrofuran* (procedure A) or (2) by adding 3 equiv of *n*-BuLi to **2** in *tetrahydrofuran* (procedure B).[19]



(4)

We have also observed that the enol ethers produced in this addition reaction will undergo further insertion chemistry with germanium(II) chloride. More specifically, a second equivalent of germanium(II) chloride can be inserted into the Ge–alkoxy bond of the first product (eq 5).



(5)

Furthermore, the insertion product can be obtained in a single step by reaction of the α,β-unsaturated acetal with 2 equivalents of germanium(II) chloride. Cyclic enol ethers, such as **2**, also give insertion products upon addition of a second equivalent of germanium(II) chloride.

Acknowledgment. We wish to thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (GM42732) for support of this research.

Supplementary Material Available: Representative procedures and compound characterization data (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(15) Ando, W.; Itoh, H.; Tsumuraya, T. *Organometallics* **1989**, *8*, 2759. Nefedov, O. M.; Kolesnikov, S. P.; Rogozhin, I. S. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1980**, 170. Inoguchi, Y.; Okui, S.; Mochida, K.; Itai, A. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 974. Kolesnikov, S. P.; Rogozhin, I. S.; Shteinschneider, A. Y.; Nefedov, O. M. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1988**, 2654.

(16) For recent studies on Lewis acids and acetals, see: Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1991**, *113*, 8089; *J. Org. Chem.* **1991**, *56*, 6458, 6485. Mori, I.; Ishihara, K.; Flippin, L. A.; Nozaki, K.; Yamamoto, H.; Bartlett, P. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 6107. Ishihara, K.; Hanaki, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 7074. Hopkins, M. H.; Overman, L. G.; Rishton, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 5354.

(17) Control experiments show that germanium dichloride forms an oligomer with 2-phenyldioxolane. We conclude, therefore, that there is no germanium dichloride remaining in solution.

(18) Particularly in the acyclic acetal cases, it proved more helpful to prepare the tributyl derivatives. Mironov, V. F.; Berliner, E. M.; Gar, T. K. *Zh. Obshch. Khim.* **1969**, 2701; **1970**, 109. Lappert, M. F.; Sanger, A. R.; Power, P. P.; Srivastava, R. C. *Metal and Metalloid amides*, Wiley: Chichester, 1980.

(19) The alkoxide substituent on germanium can be displaced efficiently when the reaction is run in THF. However, THF allows **2** to equilibrate with starting material during the addition of butyllithium, thus decreasing the cis–trans ratio of the enol ethers. Rearrangement products that have an aliphatic substituent at the β-position, **3**, are less prone to isomerization in THF and can be derivatized with butyllithium without change in enol ether ratio.

Reactivity of *o*-Styryl Oxazolines with Nucleophiles

Julio A. Seijas,* M. Pilar Vázquez-Tato, Luis Castedo, Ramón J. Estévez, and María Ruiz
Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Santiago, Campus de Lugo, Aptdo. 280, 27080-Lugo, Spain

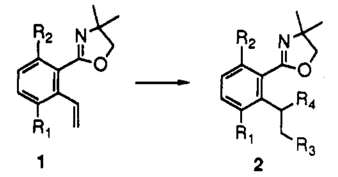
Received June 2, 1992 (Revised Manuscript Received July 22, 1992)

Summary: The reaction of *o*-styryl oxazolines with organolithium reagents leads to conjugated addition to the exocyclic double bond in very good yields.

The oxazoline has proved to be an efficient auxiliary to achieve substitution in aromatic rings by displacement of an *o*-methoxy group with nucleophiles.[1] Oxazolines are also used to direct ortho metalation of aromatic rings in order to introduce electrophiles in this position.[1] Recently, Meyers and co-workers have been carrying out studies on the conjugated addition to naphthalene rings with an ox-

---

(1) Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837.



2	R_1	R_2	R_3	R_4
a	OMe	H	n-Bu	Me
b	OMe	H	n-Bu	H
c	OMe	H	t-Bu	Me
d	OMe	H	t-Bu	H
e	OMe	H	Me	Me
f	OMe	H	H	Me
g	OMe	H	Ph	Me
h	OMe	H	Ph	H
i	OMe	H	Et	H
j	H	H	n-Bu	Me
k	H	H	t-Bu	Me
l	H	H	Me	Me

a R_1 = OMe, R_2 = Me
b R_1 = OMe, R_2 = H
c R_1 = H, R_2 = H
d R_1 = H, R_2 = OMe

Figure 1.

Table I. Nucleophilic Addition to Styryl Oxazolines

oxazoline	nucleo.	electro.	*T* (°C)	*t* (h)	product (yield, %)
1b	*n*-BuLi	MeI	−55	2	**2a** (91)
	n-BuLi	MeOH	−55	2	**2b** (84)
	t-BuLi	MeI	−55	2	**2c** (70)
	t-BuLi	MeOH	−35	2	**2d** (71)
	MeLi	MeI	−35	22	**2e** (70)
	MeLi	MeOH	−35	22	**2f** (91)
	PhLi	MeI	−45	2	**2g** (84)
	PhLi	MeOH	−45	2	**2h** (80)
	$CH_2{=}CHMgBr$	MeOH	rt		
	EtMgBr	MeOH	rt	48	**2i** (25)
	PhMgBr	MeOH	rt		
	Me_2CuLi	MeOH	rt		
1c	*n*-BuLi	MeI	−55	5	**2j** (95)
	t-BuLi	MeI	−55	2	**2k** (80)
	MeLi (TMEDA)	MeI	−55	0.08	**2l** (60)
	PhLi	MeI	−45		
	$CH_2{=}CHMgBr$	MeI	rt		
	EtMgBr	MeI	rt		

azoline group, resulting in 1,2-dihydronaphthalenes,[2] and to α,β-conjugated oxazolines.[3]

In the course of our research we needed to prepare oxazoline **1a** (Figure 1). Following a standard procedure for alkylation of aryloxazolines, we treated styryl oxazoline **1b**[4] first with BuLi, to metalate the ortho position and then with methyl iodide to alkylate the resulting anion. To our surprise,[5] instead of compound **1a** we obtained oxazoline **2a** due to conjugated addition of the butyllithium to the exocyclic double bond followed by trapping of the anion with the electrophile. This result prompted us to investigate the conjugated addition of nucleophiles to ortho styryl oxazolines, as a potential route to alkylbenzenes.

We studied the behavior of several nucleophiles in order to see their influence on the course of the reaction. Alkyllithiums afforded very good yields when quenched with MeOH or MeI (Table I).[6] When phenyllithium was used, the dihydrostilbenes **2g** and **2h** were obtained in 84% and 80% yield, respectively, showing that our method is a viable alternative to other routes to dihydrostilbenes. No reaction was observed with softer lithium anions (2-dithianyl and *tert*-butylacetyl). When magnesium and copper nucleophiles were tried, addition products were obtained only in low yields with alkyl Grignard reagents (Table I).

Figure 2.

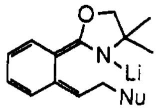


Figure 3.

To study how the substitution pattern of the aromatic ring influences the reactivity, we prepared oxazoline **1c**,[4] which has no methoxy group on the phenyl ring. Addition of *n*-BuLi and *t*-BuLi took place in good yield, and MeLi required the presence of TMEDA to achieve a 65% yield of oxazoline **2l** (no addition product was obtained in the presence of HMPA). The poorer reactivity of **1c** may be attributed to the lack of stabilization of the benzylic anion by an *o*-methoxy group (as for **1b**, Figure 2). This feature seems to be a useful complement to the stabilization due to the oxazoline ring (Figure 3). When stabilization by the oxazoline ring is hindered by the presence of a methoxy group at position 6 (compound **1d**, Figure 1), no reaction with nucleophiles was observed with any of the alkyl- or aryllithium reagents used.

Acknowledgment. We thank the DCICYT for financial support and the "Xunta de Galicia" for a predoctoral grant awarded to M.R.

Supplementary Material Available: Additional experimental details and spectral data for compounds **2a–2l** (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

[2] Gant, T. G.; Meyers, A. I. *J. Am. Chem. Soc.* **1992**, *114*, 1010 and references cited therein.

[3] Meyers, A. I.; Shipman, M. J. *J. Org. Chem.* **1991**, *56*, 7098.

[4] Meyers, A. I.; Gabel, R.; Mihelich, E. D. *J. Org. Chem.* **1978**, *43*, 1372.

[5] It is known that *m*-styryl oxazolines undergo nucleophilic substitution without addition: Patten, A. D.; Nguyen, N. H.; Danishefsky, S. J. *J. Org. Chem.* **1988**, *53*, 1003.

(6) A typical experimental procedure for compounds in Table I is described. A solution of **1b–d** (0.43 mmol) in 5 mL of dry ether was cooled, under an argon atmosphere, to the temperature indicated in Table I. To this solution was added 1.1–2 mmol of organometallic reagent in the appropriate solvent dropwise. The resulting red solution was stirred at the indicated temperature until TLC (ethyl acetate–hexane) indicated the absence of starting material (2–22 h). The electrophile (MeI or MeOH) was then added dropwise, and the reaction mixture was allowed to warm to room temperature, treated with saturated ammonium chloride solution, and extracted with ether (3 × 30 mL). The extract was washed with brine, dried (sodium sulfate), and concentrated. The products were purified by flash column chromatography on silica gel (ethyl acetate–hexane).