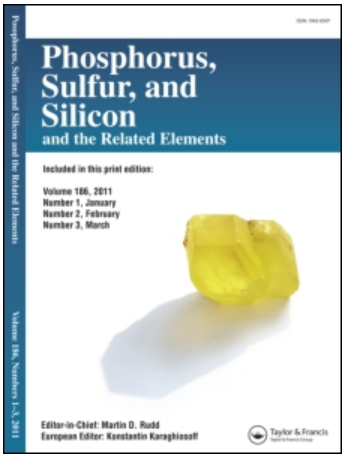

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Trialkylsilyl group-directed regioselective transformations of alkynyl thioacetals to alkynylcyclopropanes and enynes are described.

Keywords Alkynly thioacetals; carbene complexes; cyclopropanes; enyes; titanocene(II)

INTRODUCTION

We have established a straightforward method for the preparation of a variety of titanium carbene complexes **1** by the desulfurization of thioacetals **2** and related organosulfur compounds with the titanocene(II) species **3** (Scheme 1). These organotitanium species **1** react with various organic molecules including the ones having a carbon-heteroatom or carbon-carbon multiple bond.[1]

The titanium alkenylcarbene complexes **4** generated by the desulfurizative titanation of β,γ-unsaturated thioacetals **5** or 1,3-bis(phenylthio)alk-1-enes **6** with **3** react with terminal olefins to produce alkenylcyclopropanes **7**. We assume that this reaction proceeds *via* the formation of titanacyclobutane intermediate **8** and following

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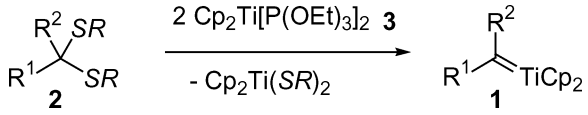
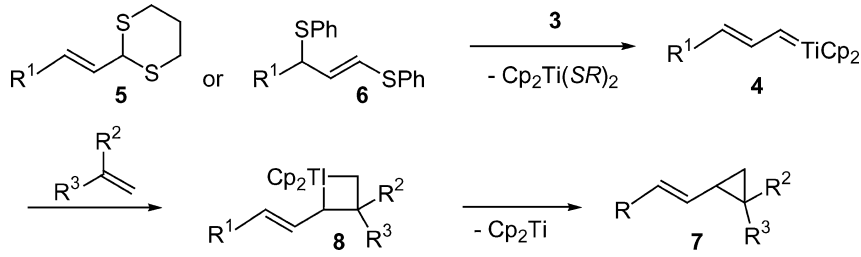


SCHEME 1

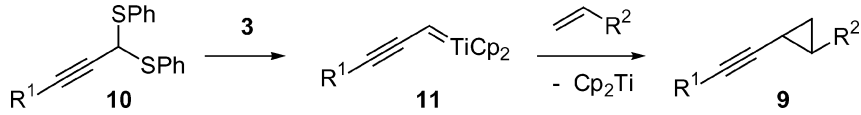
reductive elimination (Scheme 2).[2] In connection with this study, we have investigated the preparation of titanium alkynylcarbene complexes by the desulfurizative titanation of alkynyl thioacetals with the titanocene(II) species **3** and their reactions with olefins and carbonyls.



SCHEME 2

RESULTS AND DISCUSSION

We found that the similar cyclopropanation proceeded to afford the alkynylcyclopropanes **9** in good yields when the thioacetals of α,β-acetylenic aldehydes **10** were treated with the titanocene(II) species **3** in the presence of terminal olefins.[3] The unsubstituted alkynylcyclopropanes (**9**; $R^2 = H$) were readily obtained by the simple treatment of the thioacetals **10** with **3** under ethylene atmosphere. The first step of this reaction would be the reductive titanation of the thioacetals **10** to form the titanium alkynylcarbene complexes **11**.

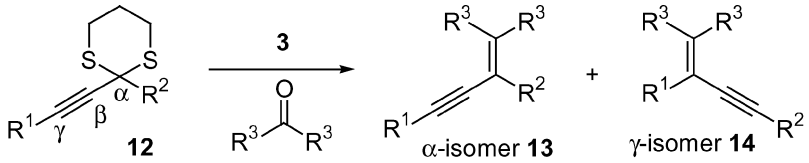


SCHEME 2

The increased interest in the regioselectivity in the formation of highly substituted nonheteroatom-substituted alkynylcarbene complexes,[4] especially the isomerization of these complexes to their regioisomers,[4b,d,i,e] prompted us to investigate the generation of highly

substituted alkynylcarbene complexes from the β,γ-acetylenic thioacetals bearing an α-substituent. The preparation of titanium carbene complexes from thioacetals suffers a serious drawback in that it is largely affected by steric hindrance,[5] hence the highly substituted carbene complexes (**1**; $R^2 \neq H$) cannot be formed effectively from thioacetals prepared from ketones. Only the thioacetals of less-hindered ketones such as cyclobutanone and acetone can be employed for the preparation.[6] Despite these results, we expected that the less bulky alkynyl group would alleviate the steric crowding of the thioacetals and their reaction with the titanocene(II) species **3** would produce the α-substituted alkynylcarbene complexes. Then, we examined the regioselective formation of highly substituted titanium alkynylcarbene complexes from α-substituted β,γ-acetylenic thioacetals and their reactions with olefins and carbonyl compounds.

First we examined the titanocene(II)-promoted carbonyl olefination of ketones with α-alkyl-β,γ-acetylenic thioacetals **12** (Scheme 3 and Table I). The successive treatment of **12** with the titanocene(II) reagent **3** and ketones produced the two isomers of carbonyl olefination products, conjugated enynes **13** (α-isomers) and **14** (γ-isomers). These results indicate that the highly substituted titanium alkynylcarbene complexes can be generated from the alkynyl thioacetals **12**. In all cases examined, the regioisomeric mixtures of enynes were formed in moderate yields, which might suggest the nonregioselective generation of the alkynylcarbene complexes. The ratio of the isomers depends on the structures of the thioacetal **12** and ketone that were employed. The regioselectivity for γ-isomers **14** was increased with increase in the bulkiness of the α-substituent R_2 of **12**.



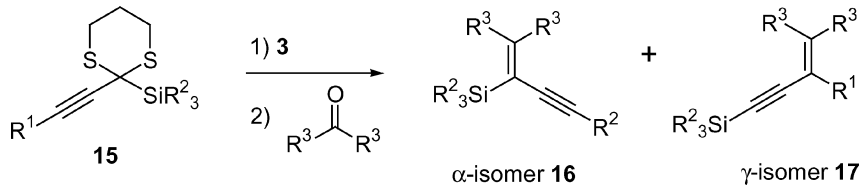
SCHEME 3

We expected that the reactions of the alkynyl thioacetals that have a bulky trialkylsilyl group at α-position were more regioselective than the thioacetals that have an α-alkyl group. The successive treatment of the α-(trialkylsilyl)-β,γ-acetylenic thioacetals **15** with the titanocene(II) reagent **3** and ketones produced the two isomers of carbonyl olefination products, conjugated enynes **16** and **17** (Scheme 4).[7] As was expected, the reaction proceeded regioselectively, and the major isomers were the trimethylsilylacetylenes **17** (γ-isomers), the formation of which

TABLE I

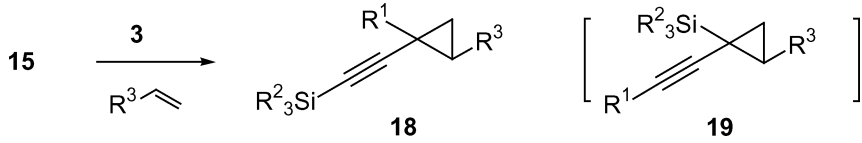
R^1	R^2	R^3	Yield %	α-isomer **13**:γ-isomer **14**
$Ph(CH_2)_3$	CH_3	CH_3	44%	85:15
$Ph(CH_2)_3$	CH_3CH_2	$Ph(CH_2)_2$	62%	52:48
$Ph(CH_2)_3$	CH_3CH_2	$-(CH_2)_5^-$	54%	68:32
$Ph(CH_2)_3$	$CH_3(CH_2)_3$	CH_3	57%	58:42

involved an allylic rearrangement. Essentially complete regioselective formation of **17** was observed either when a less bulky ketone or the alkynyl thioacetal bearing a less bulky substituent at γ position of the propargylic system, was employed.



SCHEME 4

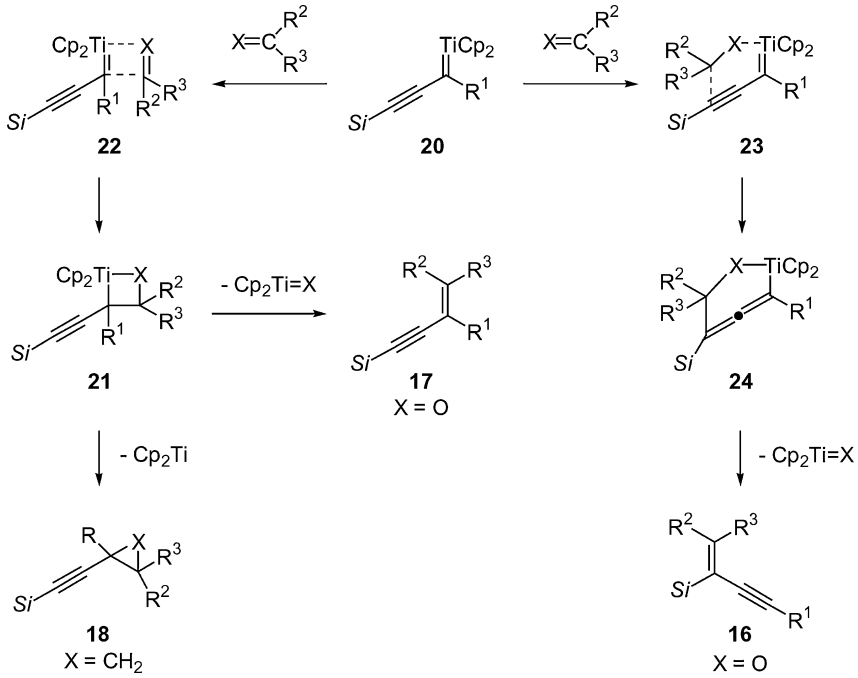
When the alkynyl thioacetals **15** were treated with titanocene(II) species **3** in the presence of terminal olefins, (trimethylsilyl ethynyl)cyclopropanes **18** were obtained as sole products in good yields and no formation of the expected trimethylsilylcyclopropane **19** was observed in all reactions examined (Scheme 5). The silylacetylenes **17** and **18** were protodesilylated to give the corresponding terminal alkynes.



SCHEME 5

We tentatively assume that the intermediate of both the carbonyl olefination and cyclopropanation is the (trialkylsilyl ethynyl)carbene complex **20**. The reaction sequence involving the formation of the propargyltitanium intermediate **21** *via* the four-membered transition state **22** and its metathesis-type degradation or reductive elimination affords the major product of carbonyl olefination **17** and the alkynylcyclopeopane **18**. In the case of the reaction with sterically hindered

ketones, the transition state **22** is destabilized to a certain extent by steric repulsion between the α-substituent of **20** (R^1) and the substrate. As a result, the reaction partially follows the path involving the six-membered transition state **23**, and the metathesis-type degradation of the allenyltitanium intermediate **24** affords the minor product **16** (Scheme 6).



SCHEME 6

REFERENCES

[1] T. Takeda and A. Tsubouchi, *Modern Carbonyl Olefination*, T. Takeda, Ed. (Wiley-VCH: Weinheim, 2004), p. 151; T. Takeda, *Titanium and Zirconium in Organic Synthesis*, I. Marek, Ed. (Wiley-VCH: Weinheim, 2002), p. 475.

[2] Y. Horikawa, T. Nomura, M. Watanabe, T. Fujiwara, and T. Takeda, *J. Org. Chem.*, **62,** 3678 (1997).

[3] T. Takeda, S. Kuroi, K. Yanai, and A. Tsubouchi, *Tetrahedron Lett.*, **43,** 5641 (2002).

[4] For Re-complexes, see a) C. P. Casey, S. Kraft, and D. R. Powell, *J. Am. Chem. Soc.*, **122,** 3771 (2000); b) C. P. Casey, S. Kraft, and M. Kavana, *Organometallics*, **20,** 3795 (2001); c) C. P. Casey, S. Kraft, and D. R. Powell, *Organometallics*, **20,** 2651 (2001); d) C. P. Casey, S. Kraft, and D. R. Powell, *J. Am. Chem. Soc.*, **124,** 2584 (2001). For Mn-complexes, see e) Y. Ortin, Y. Coppel, N. Lugan, R. Mathieu, and M. J. McGlinchey,

Chem. Commun., 1690 (2001); f) Y. Ortin, Y. Coppel, N. Lugan, R. Mathieu, and M. J. McGlinchey, *Chem. Commun.*, 2636 (2001); g) C. P. Casey, T. L. Dzwiniel, S. Kraft, M. A. Kozee, and D. R. Powell, *Inorg. Chim. Acta*, **345,** 320 (2003); h) Y. Ortin, A. Sournia-Saquet, N. Lugan, and R. Mathieu, *Chem. Commun.*, 1060 (2003). For Rh-complexes, see i) A. Padwa, D. J. Austin, Y. Gareau, J. Kassir, and S. L. Xu, *J. Am. Chem. Soc*., **115,** 2637 (1993). For W-complexes, see j) N. Iwasawa, K. Maeyama, and M. Saitou, *J. Am. Soc. Chem*., **119,** 1486 (1997).

[5] T. Takeda, R. Sasaki, and T. Fujiwara, *J. Org. Chem.*, **63,** 7286 (1998).

[6] T. Fujiwara, N. Iwasaki, and T. Takeda, *Chem. Lett.*, 741 (1998).

[7] T. Takeda, S. Kuroi, M. Ozaki, and A. Tsubouchi, *Org. Lett.*, **6,** 3207 (2004).