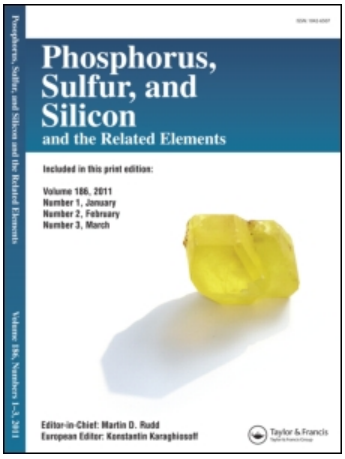

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Desulfurizative Titanation of Organosulfur Compounds

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DESULFURIZATIVE TITANATION OF ORGANOSULFUR COMPOUNDS

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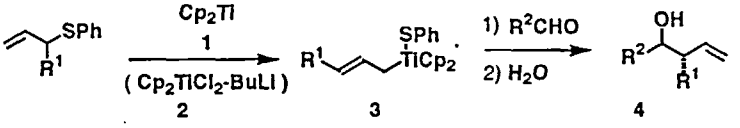
Desulfurizative titanation of allylic sulfides and thioacetals, and the subsequent reactions of resulting organotitanium species were studied.

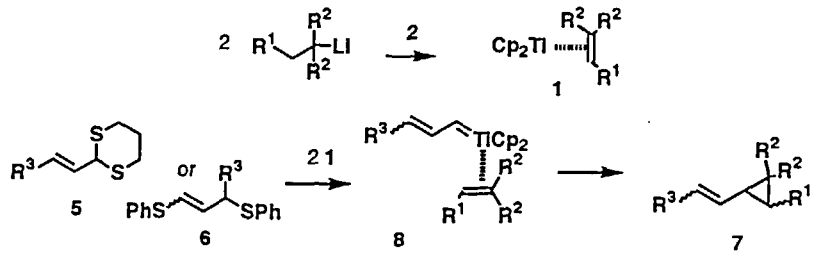
DESULFURIZATION OF ALLYLIC SULFIDES

Although the desulfurizative metallation which affords reactive organometallics is synthetically useful for further transformations, only a few methods for such reduction have been investigated. We found that the low-valent titanium species **1**, formed by the reduction of Cp_2TiCl_2 **2** with butyllithium, reacted with allyl sulfides to give allyltitaniums **3** which gave *anti*-homoallyl alcohols **4** with high regio and diastereoselectivity on treatment with aldehydes.[1]

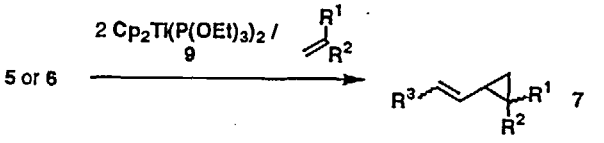


DESULFURIZATION OF THIOACETALS

The similar desulfurization of thioacetals of α,β-unsaturated aldehydes **5** or their analogues, 1,3-bis(phenylthio)-1-alkenes **6**, gave vinylcyclopropanes **7**. Although the pathway of this reaction is not clear at present, we tentatively assume that the intermediate of this reaction would be a vinylcarbene complex of titanium **8**.[2]

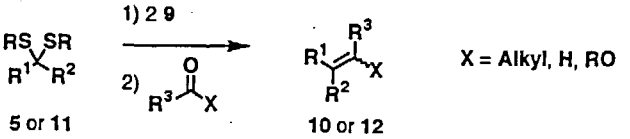


Since synthetic application of the above reaction is largely restricted by the fact that a part of cyclopropane is inevitably originated from the olefin formed by the treatment of **2** with alkyllithiums, we studied an alternative method for the preparation of **7** using appropriate low-valent titanium. It was found that the desulfurization of **5** or **6** with $Cp_2Ti[P(OEt)_3]_2$ **9** in the presence of various olefins gave **7** in good to high yields. The low-valent titanium species **9** was easily prepared by the reduction of **2** with magnesium in the presence of triethyl phosphite and molecular sieves 4A.



CARBONYL OLEFINATION

Titanium methylidene is a well-known chemical species and its reaction with carbonyl compounds is a useful synthetic tool for the Wittig-like methylenation of carbonyl compounds. Therefore we expected that 1,3-dienes were obtained by the reaction of unsaturated thioacetals with carbonyl compound via **8**. In fact, the successive treatments of **5** or **6** with **9** and ketones or aldehydes gave 1,3-dienes **10** in good yields. What is striking that this reaction is not limited to unsaturated thioacetals. The reactions using saturated thioacetals **11** with carbonyl compounds gave olefins **12** in good yields. Furthermore the present olefination could be successfully applied to the transformation of carboxylic esters to enol ethers.



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2. Y. Horikawa, T. Nomura, M. Watanabe, I. Miura, T. Fujiwara, and T. Takeda, *Tetrahedron Lett.* **36**, 8835 (1995).