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Desulfurizative Cyclopropanation of 2-(1-Alkenyl)-1,3-dithianes and Substituted 1,3-Bis(phenylthio)-1-propenes with Titanocene-Olefin Complexes

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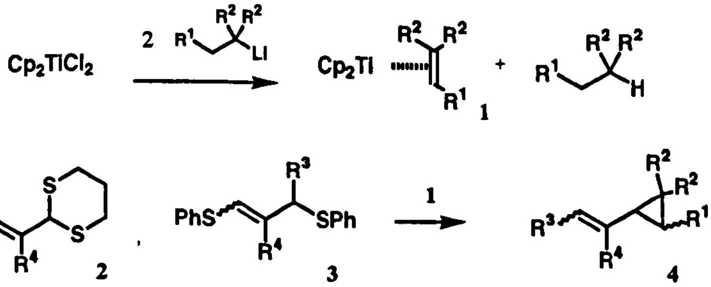
Abstract: The reaction of 2-(1-alkenyl)-1,3-dithianes with the titanocene-olefin complexes, prepared by the reaction of titanocene dichloride with 2 equiv of alkyllithiums, in the presence of triphenylphosphine gave 1-alkenylcyclopropanes in good yields. The similar reaction of substituted 1,3-bis(phenylthio)-1-propenes also proceeded to produce the cyclopropanes.

We have shown recently that the allyltitanium compounds are formed by the treatment of allylic sulfides with low-valent titanium species **1** prepared by the reaction of titanocene dichloride with two equivalents of butyllithium.[1)] This result suggests that **1** holds great promise for being a desulfurizating agent in the synthesis involving organosulfur intermediates. In connection with this study, we examined the reactions of thioacetals of α,β-unsaturated aldehydes **2** and substituted 1,3-bis(phenylthio)-1-propenes **3** with **1**. What is interesting is that alkenylcyclopropanes **4**, a part of which was originated from the olefin formed when **1** was prepared by the treatment of titanocene dichloride with alkyllithium,[2)] were selectively produced by these reactions as illustrated in the following scheme.



When 2-(2-phenylethenyl)-1,3-dithiane (**2a**) was treated with 2 equiv of **1** prepared by the treatment of titanocene dichloride with *t*-butyllithium, 1,1-dimethyl-2-(2-phenylethenyl)cyclopropane (**4a**) was produced in 72% yield (run 1 in Table 1). Although 1-ethyl-2-(2-phenylethenyl)cyclopropane (**4b**) was also obtained by the similar reaction of **2a** with **1** prepared from *n*-butyllithium, the yield was only moderate (run 2). Further, in the case of 2-(1-octenyl)-1,3-dithiane (**2b**), the corresponding cyclopropane **4c** was obtained in a poor yield, even when the titanium species **1** generated with *t*-butyllithium was used (run 4). Since it was suspected that the low yields of **4b** and **c** were attributable to the instability of titanocene-olefin complex **1** under the reaction conditions, the use of certain ligands which can stabilize the titanium species was then examined. After several attempts, we found that the cyclopropanes **4b** and **c** were obtained in good yields when the reactions were carried out in the presence of triphenylphosphine (runs 3 and 5). In a similar manner, alkenylcyclopropanes **4** were also obtained by the reaction of 2- or 3-alkyl-1,3-bis(phenylthio)-1-propenes **3** with **1** in the presence of triphenylphosphine or triethyl phosphite.

The typical experimental procedure is as follows; to a THF (3 ml) suspension of titanocene dichloride (249 mg, 1 mmol) was added a pentane solution of *t*-butyllithium (1.3 ml, 2 mmol) at -78 °C. After 15 min, a THF (2 ml) solution of 4-phenyl-1,3-bis(phenylthio)-1-butene (**3a**) (174 mg, 0.5 mmol) and triethyl phosphite (0.17 ml, 1 mmol) was successively added. The reaction mixture was further stirred for 15 min at the same temperature and then the cooling bath was removed. After being stirred for an additional 3 h, the reaction mixture was diluted with dry hexane and filtered through Celite. The filtrate was condensed under reduced pressure and the residue was purified by silica-gel chromatography (hexane) to give 1,1-dimethyl-2-(3-phenyl-1-propenyl)cyclopropane (**4d**) (75 mg) in 80% yield.

Although the pathway of the reaction has not yet been clear, the equations below illustrate those which should be considered. On the basis of the facts observed in the reaction of titanocene-olefin complex **1** with allylic sulfides,$^{1)}$ it is reasonable to assume that the first step is the reductive cleavage of one of carbon-sulfur bonds of **2** or **3**. Further reduction of the resulting allyltitanium species **5** with **1** proceeds to form the vinylcarbene complex **7** which then reacts with the coordinated olefin to produce the cyclopropane **4** (Path A). Alternatively, the insertion of coordinated olefin to **5** affords the alkyltitanium compound **8** which in turn eliminates the titanium thiolate **6** to give the cyclopropane **4** (Path B).

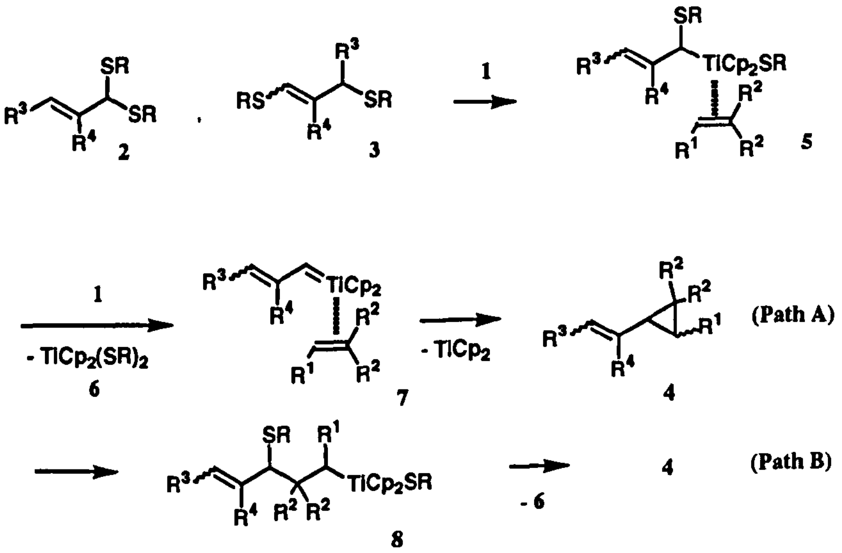
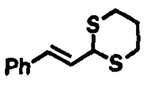
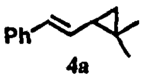
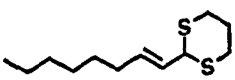
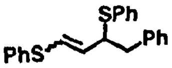
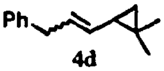
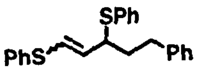
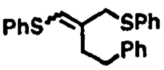
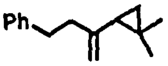
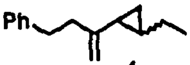


Table 1. The Reactions of 2-(1-Alkenyl)-1,3-dithianes **2** and Substituted 1,3-Bis(phenylthio)-1-propenes **3** with Titanocene-Olefin Complexes **1**.$^{a)}$

Run	**2** or **3**	Alkyllithium	Additive	Time$^{b)}$ h	Product	Yield$^{c)}$ %
1	 **2a**	*t*-BuLi	-	3	 **4a**	72
2		*n*-BuLi	-	3	 **4b**	54
3		*n*-BuLi	Ph3P	24		77
4	 **2b**	*t*-BuLi	-	3	 **4c**	37
5		*t*-BuLi	Ph3P	23		76
6	 **3a**	*t*-BuLi	-	3	 **4d**	40
7		*t*-BuLi	(EtO)3P	3		80
8	 **3b**	*t*-BuLi	-	3	 **4e**	48
9		*t*-BuLi	(EtO)3 P	3		56
10	 **3c**	*t*-BuLi	Ph3P	25	 **4f**	62$^{d)}$
11		*n*-BuLi	(EtO)3 P	2	 **4g**	63$^{d)}$

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a) All reactions were performed with a similar procedure as described in the text, unless otherwise noted. b) The reaction time after the removal of cooling bath. c) The structures of these compounds were supported by IR and NMR spectra. d) The NMR spectrum contained some unidentified signals.

Since alkenylcyclopropanes are regarded as useful homologues of 1,3-dienes, their preparation and reactions have been extensively studied.3) Typically, these compounds are synthesized by the reactions of metal carbene complexes or carbenes with dienes,4) the reactions of metal vinylcarbene complexes with olefins,5) the Wittig type reactions of cyclopropyl ketones and cyclopropanecarbaldehydes.6) Moreover, various methods using a variety of starting materials were reported.7) Since the starting materials **2** and **3** are readily obtained by the reaction of α,β-unsaturated aldehydes with 1,3-propanedithiol and the alkylation of 1,3-bis(phenylthio)-1-propene, the present reaction provides a facile method for the preparation of 1-alkenylcyclopropanes with various substituents.

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