Preparation of Vinylcyclopropanes by the Titanocene-Promoted Reactions of β,γ-Unsaturated Thioacetals and Their Analogues with Alkenes

Yasuo Horikawa, Tadahiro Nomura, Mikako Watanabe, Tooru Fujiwara, and Takeshi Takeda*

Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received December 4, 1996

Preparation of vinylcyclopropanes **6** utilizing 2-(alk-1-enyl)-1,3-dithianes **1** or 1,3-bis(phenylthio)alk-1-enes **2** was studied. The treatment of β,γ-unsaturated thioacetals **1** or their analogues **2** with $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ **5** in the presence of PPh_3 or $P(OEt)_3$ gave vinylcyclopropanes **6** in good yields. A part of the cyclopropane **6** originates from the alkene formed by the thermal degradation of dialkyltitanocene **4**, an intermediate formed during the reduction of Cp_2TiCl_2 with alkyllithium to **5**. By using the titanocene reagent $Cp_2Ti(P(OEt)_3)_2$ **7** as a reducing agent, cyclopropanes **6** were obtained by the reaction of unsaturated organosulfur compounds **1** or **2** with various alk-1-enes. 1,2-Dibromoalkanes could be successfully employed as substitutes for volatile alkenes in this reaction. The intermediate of this reaction is presumed to be a vinylcarbene complex of titanium **8**.

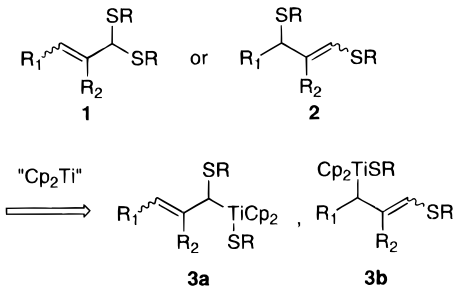
Introduction

Organometallic reagents play an important role in modern synthetic organic chemistry, and a variety of approaches have been developed to prepare these reagents. In particular, we have been interested in the desulfurizative metalation of organosulfur compounds using stannyl- and germylmetal reagents which has shown to be useful in the synthesis of organotin and germanium compounds.[1] Our group has recently shown that the reductive desulfurization of allylic sulfides with the low-valent titanium species "Cp_2Ti", prepared by treatment of Cp_2TiCl_2 with butyllithium, affords allyltitanium species. These species can be converted to the *anti*-homoallyl alcohols with high regio- and diastereoselectivity upon treatment with aldehydes.[2]

In a related study, we were interested in forming the synthetically useful intermediates shown as **3a** and **3b** in Scheme 1[3] via reduction of β,γ-unsaturated thioacetals **1** or 1,3-bis(phenylthio)alk-1-enes **2** with "Cp_2Ti". This proposed reaction pathway was based on the work of Taguchi *et al.*, who reported that the butene complex of zirconocene reacts with acetals of α,β-unsaturated aldehydes to afford either (α- or (γ-alkoxyallyl)zirconium reagents.[4] Contrary to our expectation, however, no allyltitanium species **3** was obtained, and instead vinylcyclopropanes **6** were selectively produced.

Vinylcyclopropanes **6** are valuable synthetic intermediates as homologues of 1,3-dienes and are easily transformed into cyclopentenes or dienes by the thermal, transition metal-catalyzed, or photochemical isomerization.[5−8] In general, vinylcyclopropanes are synthesized

Scheme 1



by reaction of metal−carbene complexes or carbenes with dienes,[9] or reacting Wittig reagent with cyclopropyl ketones or cyclopropanecarbaldehydes.[10] However, all of

⊗ Abstract published in *Advance ACS Abstracts,* May, 1; 1997.

(1) (a) Takeda, T.; Ando, K.; Mamada, A.; Fujiwara, T. *Chem. Lett.* **1985**, 1149. (b) Takeda, T.; Oshima, H.; Inoue, M.; Togo, A.; Fujiwara, T. *Chem. Lett.* **1987**, 1345. (c) Takeda, T.; Ogawa, S.; Ohta, N.; Fujiwara, T. *Chem. Lett.* **1987**, 1967. (d) Yamaguchi, J.; Tamada, Y.; Takeda, T. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 607.

(2) Takeda, T.; Miura, I.; Horikawa, Y.; Fujiwara, T. *Tetrahedron Lett.* **1995**, *36*, 1495.

(3) Furuta, K.; Ikeda, Y.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2781.

(4) Ito, H.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **1992**, *33*, 7873.

(5) Reviews: (a) Goldschmidt, Z.; Crammer, B. *Chem. Soc. Rev.* **1988**, *17*, 229. (b) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1989**, *33*, 247. (c) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, p 899. (d) Khusnutdinov, R. I.; Dzhemilev, U. M. *J. Organomet. Chem.* **1994**, *471*, 1.

(6) For the transformation to cyclopentenes, see: (a) McGaffin, G.; de Meijere, A.; Walsh, R. *Chem. Ber.* **1991**, *124*, 939. (b) Davies, H. M. L.; Hu, B. *Tetrahedron Lett.* **1992**, *33*, 453. (c) Dolbier, W. R., Jr.; McClinton, M. A. *J. Fluorine Chem.* **1995**, *70*, 249. (d) Asuncion, L. A.; Baldwin, J. E. *J. Org. Chem.* **1995**, *60*, 5778. (e) Gajewski, J. J.; Olson, L. P.; Willcott, M. R., III. *J. Am. Chem. Soc.* **1996**, *118*, 299.

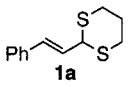
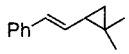
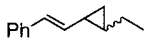
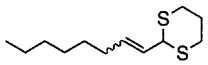
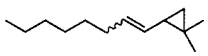
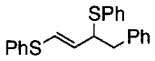
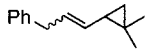
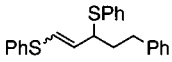
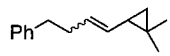
(7) For the transformation to dienes, see: (a) Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4595. (b) Ogle, C. A.; Black, K. C.; Sims, P. F. *J. Org. Chem.* **1992**, *57*, 3499. (c) Hanzawa, Y.; Harada, S.; Nishio, R.; Taguchi, T. *Tetrahedron Lett.* **1994**, *35*, 9421. (d) Dimmock, P. W.; Whitby, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2323.

(8) For the divinylcyclopropane−cycloheptadiene rearrangement, see: (1) Hudlicky, T.; Fan, R.; Reed, J. W.; Gadamasetti, K. G. *Org. React.* **1992**, *41*, 1. (b) Erbes, P.; Boland, W. *Helv. Chim. Acta* **1992**, *75*, 766.

(9) For example: (a) Harvey, D. F.; Lund, K. P. *J. Am. Chem. Soc.* **1991**, *113*, 8916. (b) de Meijere, A.; Schulz, T.-J.; Kostikov, R. R.; Graupner, F.; Murr, T.; Bielfeldt, T. *Synthesis* **1991**, 547. (c) Taber, D. F.; Hoerrner, R. S. *J. Org. Chem.* **1992**, *57*, 441. (d) Shavrin, K. N.; Okonnishnikova, G. P.; Nefedov, O. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, 2552; *Chem. Abstr.* **1992**, *116*, 83002q. (e) Weng, W.-W.; Luh, T.-Y. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2687. (f) Al Dulayymi, J. R.; Baird, M. S.; Rajaram, L.; Clegg, W. *J. Chem. Res. (S)* **1994**, 344. (g) Nishiyama, H.; Itoh, Y.; Sugawara, Y.; Matsumoto, H.; Aoki, K.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1247. For synthesis by the reaction of ruthenium−vinylcarbene complex with styrene, see: Nishiyama, H.; Park, S.-B.; Itoh, K. *Chem. Lett.* **1995**, 599.

S0022-3263(96)02265-7 CCC: $14.00

Table 1. Preparation of Vinylcyclopropanes 6 Using $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ 5[a]

Entry	Thioacetal or 1,3-bis-(phenylthio)alk-1-ene	Alkyllithium	Product	Ratio of Stereoisomers[b]	Yield(%)
1	 **1a**	*t*-BuLi	 **6a**		72
2	**1a**	BuLi	 **6b**	80 : 20[c]	54
3	 **1b** *E* : *Z* = 96 : 4	*t*-BuLi	 **6c**	*E* : *Z* = 89 : 11	37
4	 **2a**	*t*-BuLi	 **6d**	*E* : *Z* = 85 : 15	40
5	 **2b** *E* : *Z* = 87 : 13	*t*-BuLi	 **6e**	*E* : *Z* = 83 : 17	48

[a]All reactions were performed using Procedure A described in Experimental Section. [b]Determined by ^{1}H NMR. [c]The ratio of *cis-trans* isomers.

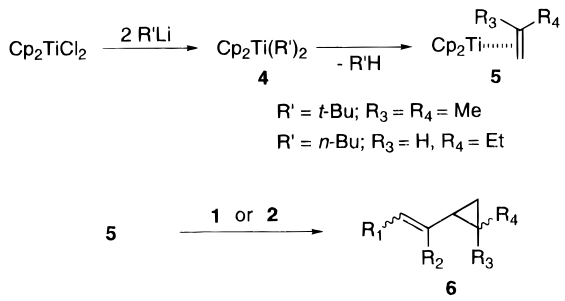
these methods are either limited by the structure of the substituent on the cyclopropane ring or else involve multistep reaction routes. From our standpoint, use of "Cp_2Ti" to form vinylcyclopropanes presented an interesting mechanistic challenge because this reaction should theoretically proceed via a metal−carbene intermediate. Luh *et al.* have shown that $W(CO)_6$ promotes self-coupling of thioacetals,[11] presumably via a metal−carbene, but our reaction presents the first transformation of thioacetals to vinylcyclopropanes that involves cross-coupling reaction of a metal−carbene intermediate with an alkene.

In this paper, we report the preparation of vinylcyclopropanes by treatment of unsaturated thioacetals or their analogues with the titanocene−olefin complexes $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ **5**,[12] including improved procedures which use the alkene-free titanocene $Cp_2Ti(P(OEt)_3)_2$ **7**. This methodology is general for the synthesis of vinylcyclopropanes in good to high yields.

Results and Discussion

Dibutyltitanocenes **4** were prepared by treating THF solution of Cp_2TiCl_2 with 2 equiv of either *n*- or *tert*-butyllithium at −78 °C for 15 min. After addition of 2-(alk-1-enyl)-1,3-dithiane **1**, the reaction mixture was warmed to room temperature, and the vinylcyclopropane

Scheme 2



6 was isolated by thin layer chromatography. It was found that a portion of the products contained substituents which originated from the alkene formed during thermal degradation of **4** (Scheme 2). The formation of alkene by thermolysis of dialkyltitanocene has been well documented by Whitesides *et al.*[13] These results suggest that the reactive intermediate is the alkene complex of titanium(II), $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ **5**. Vinylcyclopropanes **6** were also obtained under similar conditions when treating 1,3-bis(phenylthio)alk-1-ene **2** with **5** (Table 1).

(*E*)-1,1-Dimethyl-2-(2-phenylethenyl)cyclopropane (**6a**) was obtained in an exceptionally good yield by the reaction of 2-(2-phenylethenyl)-1,3-dithiane (**1a**) with $Cp_2Ti(\pi\text{-}CH_2{=}C(CH_3)_2)$ **5**. However, the yields of **6** were generally lower, attributable, in part, to the instability of **5** under the reaction conditions. We then examined various ligands containing phosphorus or nitrogen to stabilize the titanium species **5**. After several attempts, it was found that cyclopropanes **6** were prepared in better yields when the reactions were performed in the presence of PPh_3 or $P(OEt)_3$ (Table 2).

Although the vinylcyclopropanes **6** shown in Table 1 and 2 were obtained in good isolated yields, the synthetic application of this method was largely restricted by the need to prepare a suitable alkyllithium reagent. In

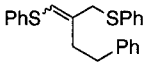
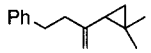
(10) For example: (a) Feldman, K. S.; Simpson, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 4878. (b) Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 4595. (c) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Org. Chem.* **1994**, *59*, 7401. (d) Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1994**, *116*, 2356.

(11) (a) Luh, T.-Y.; Wong, C. S. *J. Org. Chem.* **1985**, *50*, 5413. (b) Yeung, L. L.; Yip, Y. C.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1987**, 981. (c) Wong, C. S.; Leung, W. S.; Yeung, L. L.; Luh, T.-Y. *J. Organomet. Chem.* **1986**, *307*, C49. (d) Ng, D. K. P.; Luh, T.-Y. *Tetrahedron Lett.* **1988**, *29*, 5131. (e) Wang, X.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 263. (f) Yeung, L. L.; Yip, Y. C.; Luh, T.-Y. *J. Org. Chem.* **1990**, *55*, 1874. (g) Tip, Y. C.; Wang, X.-J.; Ng, D. K. P.; Mak, T. C. W.; Chiang, P.; Luh, T.-Y. *J. Org. Chem.* **1990**, *55*, 1881. (h) Kuo, C.-H.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1187.

(12) Preliminary communication: Horikawa, Y.; Nomura, T.; Watanabe, M.; Miura, I.; Fujiwara, T.; Takeda, T. *Tetrahedron Lett.* **1995**, *36*, 8835.

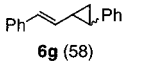
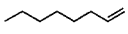
(13) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529.

Table 2. Preparation of Vinylcyclopropanes 6 Using $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ 5/PR_3[a]

Entry	Thioacetal or 1,3-bis-(phenylthio)alk-1-ene	Alkyllithium	PR_3	Time(h)[b]	Product	Ratio of Stereoisomers[c]	Yield(%)
1	**1a**	BuLi	PPh_3	24	**6b**	80 : 20[d]	77
2	**1b**	*t*-BuLi	PPh_3	23	**6c**	*E* : *Z* = 88 : 12	76
3	**2a**	*t*-BuLi	$P(OEt)_3$	3	**6d**	*E* : *Z* = 85 : 15	80
4	**2b**	*t*-BuLi	$P(OEt)_3$	3	**6e**	*E* : *Z* = 87 : 13	56
5	 **2c** 57 : 43[e]	*t*-BuLi	PPh_3	25	 **6f**		62[f]

[a]All reactions were performed using Procedure B described in Experimental Section. [b]The reaction time after the removal of cooling bath. [c]Determined by ^{1}H NMR. [d]The ratio of *cis-trans* isomers. [e]The ratio of *E*- and *Z*-isomers. [f]The NMR spectrum contained some unidentified signals.

Table 3. Preparation of Vinylcyclopropanes 6 by the Reaction of 1a with Alkenes Using $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ 5/$P(OEt)_3$[a]

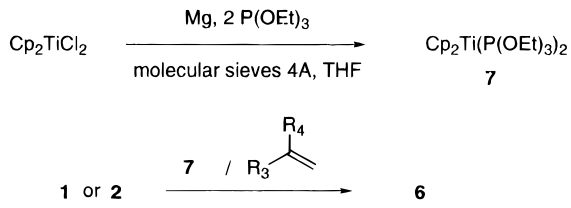
Entry	Alkyllithium	Alkene[b]	Product (Yield / %)	
1	*t*-BuLi		 **6g** (58) *trans* : *cis* = 76 : 24[c]	**6a** (12)
2	BuLi		**6g** (25) *trans* : *cis* = 76 : 24[c]	**6b** (2) 70 : 30[c,d]
3	*t*-BuLi		 **6h** (46) 71 : 29[c,d]	**6a** (11)
4	BuLi		**6a** (4)	**6b** (23) 72 : 28[c,d]

[a]All reactions were performed using Procedure B. [b]Alkene (2 equiv) was added together with $P(OEt)_3$. [c]Determined by ^{1}H NMR. [d]The ratio of *cis-trans* isomers.

addition, complications arose when using an alkene as a starting material in the above preparation because of the formation of another alkene through decomposition of **4**. As a consequence, a mixture of products resulted (Table 3). To counter this problem, an alternative source of titanocene(II), $Cp_2Ti(P(OEt)_3)_2$ **7**, was employed.

The alkene-free titanocene $Cp_2Ti(P(OEt)_3)_2$ **7** was easily prepared by the reduction of Cp_2TiCl_2 with magnesium turnings in the presence of $P(OEt)_3$ and powdered molecular sieves 4A[14] and has proven to be a successful reagent in carbonyl olefination using thioacetals.[15] As was expected, the straightforward treatment of the unsaturated thioacetal **1a** with a mixture of 1 equiv of **7** and styrene (2 equiv) at room temperature produced (*E*)-1-phenyl-2-(2-phenylethenyl)cyclopropane (**6g**) (Scheme 3), in which the *trans* isomer predominated[6d] (entry 3, Table 4). Similarly, 1-hexyl-2-(2-phenylethenyl)cyclopropane (**6h**) was isolated in 42% yield when oct-1-ene was employed as a starting material (entry 4) and 72% yield when 2 equiv of **7** was used (entry 5). In general, the use of 2 equiv of **7** and 4−10 equiv of the alkene produced the highest yields when alk-1-enes other than styrene were employed. Similar reactions of 1,3-bis(phenylthio)alk-1-enes **2** with various alkenes using $Cp_2Ti(P(OEt)_3)_2$ **7** as a reducing agent also gave vinylcyclopropanes **6** in good to high yields.

Scheme 3



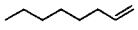
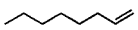
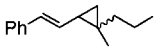
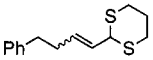
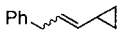
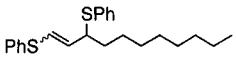
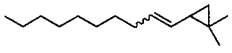
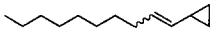
Reactions using volatile alkenes such as ethylene are usually troublesome because they require high pressure equipment and large excesses of alkene in certain cases. From our point of view, the use of 1,2-dibromoalkanes instead of alk-1-enes could alleviate this problem since 1,2-dibromoalkanes are readily reduced with magnesium turnings to form alkenes prior to the reduction of Cp_2TiCl_2 in the same reaction vessel. Results showed that when using 1,2-dibromoalkanes as starting materials the corresponding vinylcyclopropanes **6** were obtained in good yields (entries 2, 10, and 13).

The results summarized in Table 4 indicate that the yield of **6** depends on the steric bulk of groups near the double bond of the alkene. The reaction using the hindered, 2-substituted alk-1-ene, 2-methylpent-1-ene, gave the corresponding vinylcyclopropane **6i** only in a moderate yield (entry 6). A similar trend was observed when using $Cp_2Ti(\pi\text{-}CH_2{=}CR_3R_4)$ **5** in the presence of various alkenes (see Table 3). The fact that 1,1-dimethyl-2-(4-phenylbut-1-enyl)cyclopropane (**6e**) was obtained in a better yield by the reaction of **2b** (entry 11, Table 4) than by that of **1c** (entry 8, Table 4) suggests that 1,3-bis(phenylthio)alk-1-enes **2** are more reactive toward $Cp_2Ti(P(OEt)_3)_2$ **7** than 2-(alk-1-enyl)-1,3-dithianes **1**.

(14) The NMR spectra of **7** in THF-d_8 exhibited a cyclopentadienyl resonance at δ 4.61 (^{1}H NMR) and at δ 91.9 (^{13}C NMR). Although the characterization of **7** is incomplete, these chemical shifts are in good agreement with the reported values of $Cp_2Ti(P(OMe)_3)_2$[a] and $Cp_2Ti(PMe_3)_2$[b]: (a) Chang, M.; Timms, P. L.; King, R. B. *J. Organomet. Chem.* **1980**, *199*, C3. (b) Kool, L. B.; Raush, M. D.; Alt, H. G.; Herberhold, M.; Thewalt, U.; Wolf, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 394.

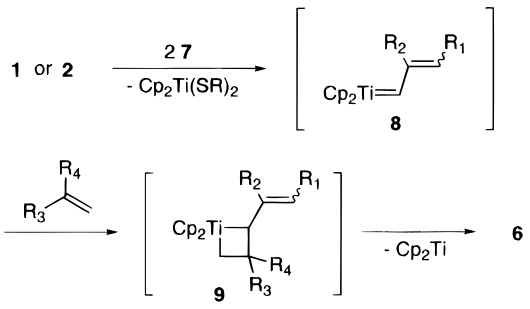
(15) Horikawa, Y.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Am. Chem. Soc.* **1997**, *119*, 1127.

Table 4. Preparation of Vinylcyclopropanes 6 Using $Cp_2Ti(P(OEt)_3)_2$ 7

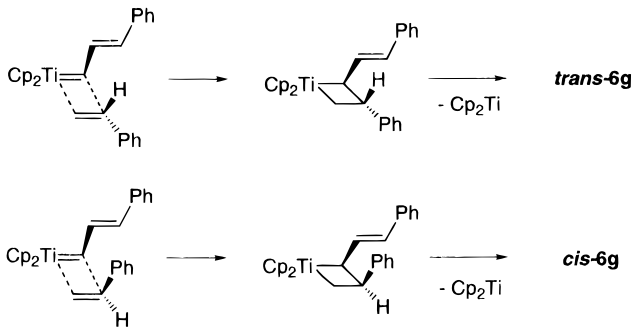
Entry	Thioacetal or 1,3-bis-(phenylthio)alk-1-ene	Alkene or 1,2-Dibromoalkane (equiv)	Procedure[a]	Product	Ratio of Stereoisomers[b]	Yield(%)
1	**1a**	 (10)	C	**6a**		64
2	**1a**	 (4)	D	**6b**	60 : 40[c]	72
3[d]	**1a**	 (2)	C	**6g**	*trans* : *cis* = 78 : 22	68
4[d]	**1a**	 (4)	C	**6h**	62 : 38[c]	42
5	**1a**	 (4)	C	**6h**	60 : 40[c]	72
6	**1a**	 (4)	C	 **6i**	62 : 38[c]	57
7	**1b**	 (10)	C	**6c**	*E* : *Z* = 82 : 18	86
8	 **1c** *E* : *Z* = 89 : 11	 (10)	C	**6e**	*E* : *Z* = 72 : 28	68
9	**2a**	 (10)	C	**6d**	*E* : *Z* = 92 : 8	83
10	**2a**	 (4)	D	 **6j**	*E* : *Z* = 89 : 11	81
11	**2b**	 (10)	C	**6e**	*E* : *Z* = 85 : 15	93
12	 **2d** *E* : *Z* = 79 : 21	 (10)	C	 **6k**	*E* : *Z* = 91 : 9	86
13	**2d**	 (4)	D	 **6l**	*E* : *Z* = 98 : 2	76

[a]Described in Experimental Section. [b]Determined by ^{1}H NMR. [c]The ratio of *cis*-*trans* isomers. [d] Cp_2TiCl_2 (1 equiv) and Mg (4 equiv) were used.

Scheme 4



Scheme 5



This is possibly due to the phenylthio group being a better leaving group than the alkylthio group.

A possible reaction path for our work is illustrated in Schemes 4 and 5. We recently observed that the reaction of the unsaturated thioacetal, 2-(2,2-diphenylethenyl)-1,3-dithiane with excess **7** followed by treatment with D_2O gave the dideuterated alkenes, 1,1-diphenylprop-1-ene-3,3-d_2 and 3,3-diphenylprop-1-ene-1,3-d_2.[15] It follows that the most likely intermediate formed by the desulfurization of an unsaturated thioacetal **1** or its analogue **2** should be the vinylcarbene complex of titanium **8**,[16] which then reacts with an alkene to give **6** *via* a titanacyclobutane intermediate **9** (Scheme 4). The favored *trans*

stereochemistry of the cyclopropane moiety observed in the reaction using styrene (entry 3, Table 4) seems to arise from the favorable transition state geometry depicted in Scheme 5, in which **8** and styrene approach each other so as to minimize steric repulsion.

In conclusion, we have shown that the cyclopropanation of alkenes using thioacetals of α,β-unsaturated aldehydes **1** and 1,3-bis(phenylthio)alk-1-enes **2** is a versatile method for the preparation of vinylcyclopropanes **6**. The intermediate of this reaction is presumed to be a vinylcarbene complex of titanium **8**. Related studies on the reaction of thioacetals with carbon−carbon multiple bonds are currently underway.

Experimental Section

General. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded with $CDCl_3$ as a solvent. All reactions were performed under an argon atmosphere in dried glassware. For thin layer chromatography, Wakogel B-5F was used as an adsorbent. THF was distilled from sodium and benzophenone. 2-(Alk-1-enyl)-1,3-dithianes **1**[17] and 1,3-bis(phenylthio)alk-1-enes **2**[18] were prepared by the methods described in the literature.

Synthesis of (*E*)-1,1-Dimethyl-2-(2-phenylethenyl)cyclopropane (6a). Typical Procedure A. To a THF (3 mL) suspension of Cp_2TiCl_2 (249 mg, 1 mmol) was added butyllithium (2 mmol) at −78 °C. After 15 min, 2-(2-phenylethenyl)-1,3-dithiane (**1a**) (111 mg, 0.5 mmol) in THF (2 mL) was added to the reaction mixture which 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 at room temperature, the mixture was diluted with hexane (30 mL), and the insoluble materials were filtered off through Celite. The filtrate was concentrated under reduced pressure. The crude product was purified by PTLC (hexane) to give **6a** (62 mg, 72%): ^{1}H NMR δ 0.46−0.52 (m, 1 H), 0.74−0.80 (m, 1 H), 1.12 (s, 3 H), 1.13 (s, 3 H), 1.37−1.46 (m, 1 H), 5.98 (ddd, J = 15.6, 9.2, 2.0 Hz, 1 H), 6.46 (d, J = 15.6 Hz, 1 H), 7.12−7.19 (m, 1 H), 7.22−7.35 (m, 4 H); ^{13}C NMR δ 19.66, 20.78, 22.30, 27.07, 28.52, 125.59, 126.46, 128.45, 129.17, 131.66, 137.98; IR (neat) 3060, 2992, 2944, 2867, 1644, 1494, 1448, 1120, 1079, 1027, 1004, 960, 939, 748, 694 cm^{-1}. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.89; H, 9.36.

Synthesis of (*E*)-1-Ethyl-2-(2-phenylethenyl)cyclopropane (6b). Typical Procedure B. To a THF (3 mL) suspension of Cp_2TiCl_2 (249 mg, 1 mmol) was added butyllithium (2 mmol) at −78 °C. After 15 min, a THF (2 mL) solution of **1a** (111 mg, 0.5 mmol) and PPh_3 (262 mg, 1 mmol) was successively added to the reaction mixture which was further stirred for 15 min at the same temperature, and then the cooling bath was removed. After being stirred for 24 h at room temperature, the workup used in procedure A afforded **6b** (66 mg, 77%): ^{1}H NMR δ 0.29−0.35 (m, 0.4 H), 0.56−0.68 (m, 1.2 H), 0.79−0.89 (m, 0.6 H), 0.91−1.05 (m, 3.8 H), 1.22−1.50 (m, 2.6 H), 1.57−1.67 (m, 0.4 H), 5.77 (dd, J = 15.6, 8.8 Hz, 0.6 H), 5.97 (dd, J = 15.6, 8.8 Hz, 0.4 H), 6.40 (d, J = 15.6 Hz, 0.6 H), 6.48 (d, J = 15.6 Hz, 0.4 H), 7.10−7.18 (m, 1 H), 7.20−7.35 (m, 4 H); ^{13}C NMR δ 13.42, 14.06, 14.28, 19.59, 21.40, 22.06, 22.71, 23.36, 26.91, 125.48, 125.57, 126.37, 126.45, 126.73, 128.41, 129.39, 130.93, 134.68, 137.85, 138.00; IR (neat) 3062, 2960, 2873, 1649, 1492, 1461, 1448, 956, 752, 742, 692 cm^{-1}; HRMS calcd for $C_{13}H_{16}$ 172.1251, found 172.1250. Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.63; H, 9.45.

Synthesis of (*E*)-1-Hexyl-2-(2-phenylethenyl)cyclopropane (6h). Typical Procedure C. To a flask charged with finely powdered molecular sieves 4A (50 mg), magnesium turnings (97 mg, 4 mmol), and Cp_2TiCl_2 (249 mg, 1 mmol) were added THF (5 mL), $P(OEt)_3$ (0.34 mL, 2 mmol), and oct-1-ene (224 mg, 2 mmol) successively with stirring at room temperature. After 2 h, **1a** (111 mg, 0.5 mmol) in THF (2 mL) was added to the reaction mixture which was further stirred for 4 h. The usual workup gave **6h** (82 mg, 72%): ^{1}H NMR δ 0.33 (q, J = 4.8 Hz, 0.4 H), 0.59 (dt, J = 12.8, 4.8 Hz, 0.6 H), 0.66 (dt, J = 12.8, 4.8 Hz, 0.6 H), 0.80−1.09 (m, 3.4 H), 1.18−1.49 (m, 10.6 H), 1.61 (dq, J = 8.5, 5.4 Hz, 0.4 H), 5.76 (dd, J = 15.6, 8.8 Hz, 0.6 H), 5.96 (dd, J = 15.6, 8.8 Hz, 0.4 H), 6.40 (d, J = 15.6 Hz, 0.6 H), 6.48 (d, J = 15.6 Hz, 0.4 H), 7.10−7.19 (m, 1 H), 7.19−7.38 (m, 4 H); ^{13}C NMR δ 13.62, 14.07, 14.10, 14.49, 19.58, 19.62, 21.66, 22.36, 22.67, 29.12, 29.17, 29.33, 29.42, 29.73, 31.84, 31.89, 33.88, 125.49, 125.59, 126.39, 126.45, 126.74, 128.43, 129.31, 131.15, 134.73, 137.89, 138.03; IR (neat) 2927, 2856, 1653, 1465, 1448, 1072, 1028, 957, 746, 692 cm^{-1}. Anal. Calcd for $C_{17}H_{24}$: C, 89.41; H, 10.59. Found: C, 89.76; H, 10.63.

Synthesis of (3-Phenylprop-1-enyl)cyclopropane (6j). Typical Procedure D. To a flask charged with finely powdered molecular sieves 4A (50 mg) and magnesium turnings (146 mg, 6 mmol) were added THF (5 mL) and 1,2-dibromoethane (376 mg, 2 mmol) successively with stirring at 0 °C. After 4 h, Cp_2TiCl_2 (249 mg, 1 mmol) and $P(OEt)_3$ (0.34 mL, 2 mmol) were added to the reaction mixture, and stirring was continued for 2 h at room temperature. A THF (2 mL) solution of 4-phenyl-1,3-bis(phenylthio)but-1-ene **2a** (174 mg, 0.5 mmol) was added to the reaction mixture, and it was further stirred for 4 h. The usual workup gave **6j** (64 mg, 81%): ^{1}H NMR δ 0.32−0.47 (m, 2 H), 0.64−0.76 (m, 1.78 H), 0.78−0.85 (m, 0.22 H), 1.36−1.50 (m, 1.78 H), 1.68−1.79 (m, 0.22 H), 3.43 (d, J = 7.2 Hz, 0.89 H), 3.59 (d, J = 7.2 Hz, 0.11 H), 4.93 (t, J = 10.8 Hz, 0.11 H), 5.09 (dd, J = 14.8, 10.8 Hz, 0.89 H), 5.53 (dt, J = 10.8, 7.6 Hz, 0.11 H), 5.69 (dt, J = 14.8, 6.8 Hz, 0.89 H), 7.14−7.46 (m, 5 H); ^{13}C NMR δ 6.44, 6.95, 9.63, 13.50, 33.88, 38.86, 125.82, 125.85, 126.35, 126.57, 128.32, 128.38, 128.45, 134.92, 135.32, 141.01, 141.30; IR (neat) 3083, 3064, 3027, 3006, 2958, 2904, 2838, 1604, 1494, 1454, 1047, 1030, 1022, 960, 740, 698 cm^{-1}; HRMS calcd for $C_{12}H_{14}$ 158.1095, found 158.1089. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.97; H, 9.04.

Acknowledgment. The authors are indebted to Ms. M. Fukuta (Technical Center, Bridgestone Corporation) for mass spectral analysis.

Supporting Information Available: Characterization data for compounds **6c**, **6d**, **6e**, **6f**, **6g**, **6i**, **6k**, and **6l** (3 pages). This material is contained in 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.

JO962265V

(16) A limited number of vinylcarbene complexes of titanium,[a] zirconium,[a] ruthenium,[b] and tungsten[c] have been prepared using 3,3-disubstituted cyclopropenes as starting materials: (a) Binger, P.; Müller, P.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 610. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (c) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130.

(17) Ni, Z.-J.; Luh, T.-Y. *Org. Synth.* **1991**, *70*, 240.

(18) Corey, E. J.; Erickson, B. W.; Noyori, R. *J. Am. Chem. Soc.* **1971**, *93*, 1724.