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## Titanocene(II)-Promoted Desulfurizative Tertiary Alkylation of 1,3-Bis(phenylthio)alk-1-enes and β,γ-Unsaturated Thioacetals

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Abstract: The desulfurization of 1,3-bis(phenylthio)alk-1-enes with the low valent titanium species  $Cp_2Ti[P(OEt)_3]_2$  and subsequent reaction with *tert*-alkyl chlorides gave the terminal olefins regioselectively. The similar reactions also took place when  $\beta,\gamma$ -unsaturated thioacetals were treated successively with the titanocene(II) species and *tert*-alkyl chlorides. It was suggested that the present reactions proceeded via the formation of (E)-vinyltitanium intermediate. © 1999 Elsevier Science Ltd. All rights reserved.

Recently we reported titanocene(II)-promoted reactions of thioacetals with various organic compounds such as carbonyls,<sup>1</sup> alkenes,<sup>2</sup> alkynes,<sup>3</sup> and group 14 organometallics.<sup>4</sup> We tentatively assume that all these reactions proceed via the formation of carbene complexes of titanium. Since we expected that such metal carbenes are regarded as Schrock type complexes and would behave as nucleophiles, we have examined their alkylation. Contrary to our expectation, the reactions of carbene complex formed from saturated thioacetal with alkyl halides did not proceed under the various reaction conditions. After several attempts, however, we found that the vinylcarbene complex 1, formed by the desulfurization of 1,3-bis(phenylthio)propene derivative 2 or  $\beta$ ,  $\gamma$ -unsaturated thioacetal 3 with the low-valent titanium species Cp<sub>2</sub>Ti[P(OEt)<sub>3</sub>]<sub>2</sub> 4, did react with *tert*-alkyl chloride 5 (Scheme 1).



The treatment of 4-phenyl-1,3-bis(phenylthio)but-1-ene (2b) with titanocene(II) 4 (3.5 equiv) at 0 °C for 10 min and then with 1.2 equiv of 2-chloro-2-methyl-4-phenylbutane (5a) for 1 h produced the alkylation product 6d in 57% yield. The reaction proceeded with high regioselectivity in which the alkyl halide attacks only at the substituted side of the allylic system. By the use of 2 equiv of 5a, 6d was obtained in 73% yield along with the dehydrochlorination products, 2-methyl-4-phenylbut-1-ene (7a) and 2-methyl-4-phenylbut-2-ene (7b) (17% based on 5a used (7a : 7b = 63 : 37)). When the alkylation was carried out at room temperature, the yields of 7 increased (47% based on 5a used (7a : 7b = 85 : 15)) though 6d was obtained in the same yield (Table 1, entry 4). It was found that an increase of the steric demand of the alkyl chloride by using 3-chloro-3-ethylpentane (5b) led to a drastic decrease of the yield of product 6e (33%) when the desulfurization of 2b and the following alkylation were carried out at 0 °C. However, 6e was obtained in good yield by the treatment of the organotitanium species with 5b at room temperature (entry 5).

In a similar manner, the reactions of several 1,3-bis(phenylthio)propene derivatives 2 with *tert*-alkyl chlorides 5 were performed. As the results listed in Table 1 indicate, the present alkylation regioselectively affords the terminal olefins 6 in good yields even when highly sterically hindered tertiary halides are employed. The typical experimental procedure is as follows; magnesium turnings (51 mg, 2.1 mmol; purchased from Nakarai Tesque Inc. Kyoto, Japan), finely powdered molecular sieves 4 A (175 mg), and Cp<sub>2</sub>TiCl<sub>2</sub> (436 mg, 1.75 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure (2-3 mmHg). Care was taken not to sublimate Cp<sub>2</sub>TiCl<sub>2</sub>. After cooling, THF (3.5 ml) and P(OEt)<sub>3</sub> (0.60 ml, 3.5 mmol) were added successively with stirring at room temperature under argon. After 3 h, **2b** (174 mg, 0.5 mmol) in THF (1.5 ml) was added to the mixture at 0 °C, and stirring was continued for 10 min. Then 2-chloro-2-methylpropane (**5d**) (93 mg, 1 mmol) in THF (1.5 ml) was added and the reaction mixture was stirred for 3.0 min at the same temperature. The cooling bath was removed, and the mixture was further stirred off through Celite. The organic materials were extracted with ether, and the extract was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of solvent, the residue was purified by using PTLC (hexane) to give 3-benzyl-4,4-dimethylpent-1-ene (**6f**) (78 mg, 83%).

Since the vinylcarbene complexes 1 are produced also from  $\beta$ ,  $\gamma$ -unsaturated thioacetals 3, we next examined the desulfurizative alkylation of 3 under the similar reaction conditions. Due to the low reactivity of 3 toward the low-valent titanium species 4, the alkylation products 6 were produced in poor yields when the desulfurization and alkylation of 3 were performed at 0 °C (see entry 1, Table 2). On the other hand, the terminal olefins 6 were obtained in good yields when all the reaction steps took place at room temperature.

In order to prove the reaction pathway, 2b was successively treated with 4 and 1.2 equiv of 5d at 0  $^{\circ}$ C, and the reaction was quenched with excess D<sub>2</sub>O (Scheme 2). The formation of the *trans*-deuterio olefin 8 indicates that the present reaction proceeds via the *trans*-vinyltitanium compound 9 as shown in Scheme 3. On the other hand, no deuterio olefin was produced when the alkylation was performed at room temperature using 2 equiv of 5d and was quenched with D<sub>2</sub>O. This result suggests that the formation of olefin 7 during the alkylation at room temperature is due, to a large extent, to the dehydrochlorination of the halide 5 with 9.



5354

Entry	1,3-Bis(phenylthio)alk-1-e	ne <b>2</b>	Alkyl Halide 5		Product 6		Yield (%)
1	SPh Ph SPh	2a	Ph	5a	Ph	6a	78
2	(E:Z = 94:6) 2a			5b	Ph	6b	72
3	2a		∠ <sup>c</sup> i	5c	Ph	6c	73
4	SPh PhSPh	2b	5a		Ph Comp	6đ	73
5	( <i>E</i> only) <b>2b</b>		5b		Ph	6e	70
6	2b		$X_{ci}$	5d	Ph	6f	83
7	SPh Ph SPh	2c	5b		Ph	6g	74
8	(E only) 2c		5c		Ph	6h	76
9	2c		5d		Ph	6i	78
10	SPh SPh SPh	2d	5a		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	6j	82
11	(E:Z = 80:20) 2d		5b			6k	81
12	2d		5c	~	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	6]	85

a) All reactions were performed following the procedure described in the text.

Entry	$\beta, \gamma$ -Unsaturated Thioace	tal 3	Alkyl Halide 5	Product 6	Yield (%)
1	C S	3a	5a	ба	58 (35) <sup>b</sup>
2	(E only)		67	G	57
2	38		50	60	57
3	3a		5c	6с	59
4	s S	3b	5a	→ ↓ → Ph	<b>6m</b> 65
	(E:Z=89:11)				

Table 2. Desulfurizative Alkylation of  $\beta$ ,  $\gamma$ -Unsaturated Thioacetals  $3^a$ 

a) All reactions were performed at room temperature with the similar procedure as described in the text, unless otherwise noted. b) The reaction was performed at 0  $^{\circ}$ C.

It is well known that organotitanium species such as methyltitanium reagents or titanium enolates react with tertiary halides to afford the substitution products.<sup>5</sup> The titanium tetrachloride-promoted reaction of allylsilanes with tertiary halides was also reported.<sup>6</sup> It should be noted that the present tertiary alkylation of the vinylcarbene complexes 1 provides an alternative way for the construction of quaternary carbon center. Further study on the reaction of vinylcarbene complexes with electrophiles and the subsequent reaction of the resulting vinyltitanium species is now in progress.

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