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Titanocene(II)-promoted carbonyl allenation utilizing 1,1-dichloroalk-1-enes

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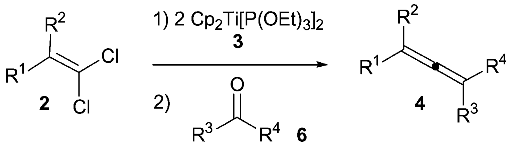
Treatment of 1,1-dichloroalk-1-enes with $Cp_2Ti[P(OEt)_3]_2$ produced organotitanium species, which afford allenes on treatment with aldehydes and ketones.

Allenes are an interesting class of compounds for organic chemists by virtue of their unique structure and reactivity.[1] Therefore synthesis of these compounds has been extensively studied and a number of methods have been developed. One of the most straightforward approaches is the Wittig-type olefination of carbonyl compounds, which includes reactions of phosporus ylides with ketenes[2] and phosphaallene ylides with ketones and aldehydes.[3] The latter reaction seems to be the most facile for the preparation of highly substituted allenes. However, only the ylides bearing two aryl, trifluoromethyl or alkoxy groups at β-carbon have been employed for the reaction. Although titanium vinylidene complexes, generated by the carbotitanation of 1-alkynyldimethylalanes with Cp_2TiCl_2–$AlMe_3$,[4] reaction of titanacyclobutanes with allenes[5] and the reaction of titanocene dichloride with alkenylmagnesium reagents,[6] were employed for the allenation of carbonyl compounds, those procedures suffer the constraint on the availability of starting materials.

On the basis of our previous findings,[7] we investigated the preparation of titanium vinylidene complexes **1** by the reaction of 1,1-dichloroalk-1-enes **2** with $Cp_2Ti[P(OEt)_3]_2$ **3**. Here we report the preparation of allenes **4** and vinylallenes **5** by the titanocene(II) **3**-promoted reaction of dichlorides **2** with carbonyl compounds **6** (Scheme 1).†

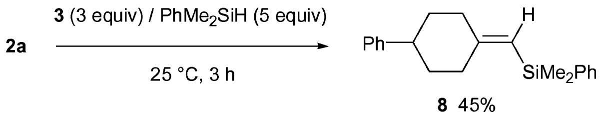


Scheme 1

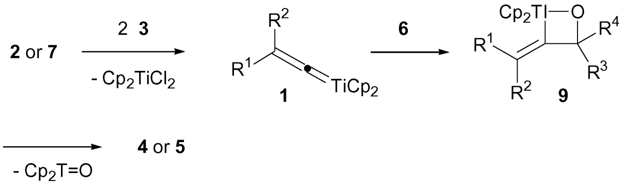
After treatment of 1-(dichloromethylidene)-4-phenylcyclohexane **2a** (2 eq.) with the titanocene(II) reagent **3** (5 eq.) for 3 h, the resulting organotitanium species was reacted with 1,5-diphenylpentan-3-one **6a** to produce the tetrasubstituted allene **4a** in 66% yield (Table 1, entry 1). Similar titanocene(II) **3**-promoted reactions of various dichloroalkenes **2** with carbonyl compounds **6** gave the corresponding highly substituted allenes **4**. For the preparation of trisubstituted allenes **4**, it is desirable to use a combination of β-disubstituted dichlorides and aldehydes instead of β-monosubstituted ones and ketones (see entries 8 and 9).

The synthetic utility of this new method was further demonstrated by preparation of vinylallenes **5**. The two types of reactions were examined; the first approach employed 1,1-dichloroalk-1-enes **2** and α,β-unsaturated ketones. The second starting materials were 1,1-dichloroalk-1,3-dienes **7** and saturated ketones. As shown in Table 2, both reactions gave vinylallenes **5** in good yields.

Based on the fact that the carbenoid insertion type product **8** was produced when **2a** was treated with **3** in the presence of excess dimethylphenylsilane (Scheme 2),[8] we tentatively assume that the first step of this reaction is the formation of titanocene–vinylidene complex **1** by the reductive titanation of dichloride **2** or **7** with titanocene(II) species **3**. Formation of oxatitanacyclobutane **9** and its metathesis type degradation afford allene **4** or **5** (Scheme 3).



Scheme 2



Scheme 3

In conclusion, we have established a new procedure for the preparation of allenes **4** using 1,1-dichloroalk-1-enes **2** and titanocene(II) species **3**. The method first realized the preparation of vinylallenes **5** by carbonyl olefination. The starting materials, 1,1-dichloroalk-1-enes **2** and **7**, were readily prepared by the carbonyl dichloromethylidenation using carbon tetrachloride–triphenylphosphine.[9] The highly substituted dichlorides **2** are also available by the olefination of ketones with a carbon tetrachloride–titanocene(II) **3** system.[10] Therefore the reduction of dichlorides **2** with **3** is a convenient way for the preparation of a variety of titanium vinylidene complexes **1** or their equivalents. Further study on the reactions of these organotitanium species is currently underway.

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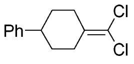
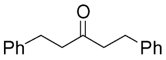
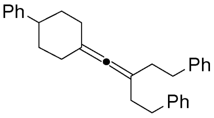
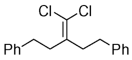
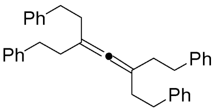
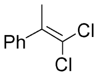
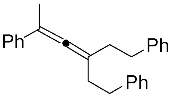
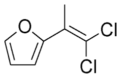
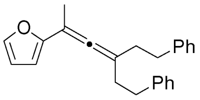
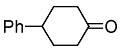
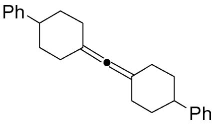
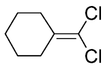
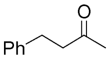
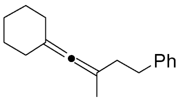
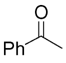
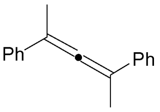
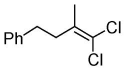
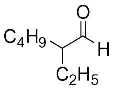
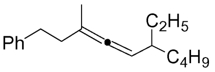
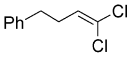
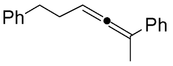
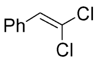
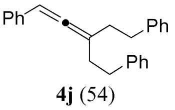
Table 1 Preparation of allenes **4**[a]

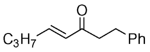
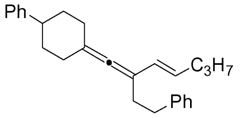
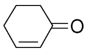
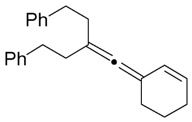
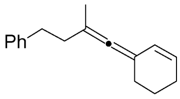
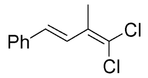
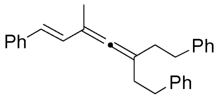
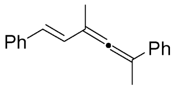
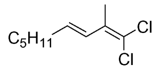
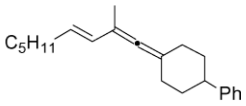
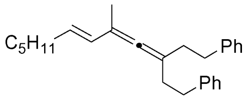
Entry	Dichloride **2**	Carbonyl compound **6**	Allene **4**, yield (%) in parenthesis
1	 **2a**	 **6a**	 **4a** (66)
2	 **2b**	**6a**	 **4b** (64)
3	 **2c**	**6a**	 **4c** (64)
4	 **2d**	**6a**	 **4d** (67)
5	**2a**	 **6b**	 **4e** (60)
6	 **2e**	 **6c**	 **4f** (60)
7	**2c**	 **6d**	 **4g** (85)
8	 **2f**	 **6e**	 **4h** (54)
9	 **2g**	**6d**	 **4i** (30)
10	 **2h**	**6a**	 **4j** (54)

[a] All the reactions were performed with a similar procedure, as described in the text.

Notes and references

† A typical experimental procedure: finely powdered molecular sieves 4 A (150 mg), magnesium turnings (37 mg, 1.5 mmol) and Cp$_2$TiCl$_2$ (374 mg, 1.5 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure (2–3 mm Hg). After cooling, THF (3 mL) and P(OEt)$_3$ (0.51 mL, 3.0 mmol) were added successively with stirring at 25 °C under argon, and the reaction mixture was stirred for 3 h. A THF (1 mL) solution of **2a** (145 mg, 0.6 mmol) was added to the mixture. After 3 h, a THF (1 mL) solution of **6a** (72 mg, 0.3 mmol) was added to the mixture. After being stirred for 2 h, the reaction was quenched by addition of 1 M NaOH. The insoluble materials were filtered off through Celite and washed with ether. The layers were separated, and the aqueous layer was extracted with ether. The combined organic extracts were dried over Na$_2$SO$_4$. The solvent was removed and the residue was purified by silica gel PTLC (hexane–ethyl acetate = 98 : 2, *v*/*v*) to afford the allene **4a** (78 mg, 66%).

Table 2 Preparation of vinylallenes **5**[a]

Entry	Dichloride **2** or **7**	Ketone **6**	Vinylallene **5**, yield (%) in parenthesis
1	**2a**	 **6f**	 **5a** (54)
2	**2b**	 **6g**	 **5b** (70)[b]
3	**2f**	**6g**	 **5c** (73)[c]
4	 **7a**	**6a**	 **5d** (76)
5	**7a**	**6d**	 **5e** (70)
6	 **7b**	**6b**	 **5f** (60)
7	**7b**	**6a**	 **5g** (59)

[a] All the reactions were performed with a similar procedure, as described in the text. [b] Contaminated with 1-chloro-2-phenethyl-4-phenylbut-1-ene and 2-phenethyl-4-phenylbut-1-ene. The yield was determined by NMR analysis. [c] Contaminated with 1-chloro-2-methyl-4-phenylbut-1-ene. The yield was determined by NMR analysis.

1 For examples, see: (*a*) D. R. Taylor, *Chem. Rev.*, 1967, **67**, 317; (*b*) W. T. Brady, in *The Chemistry of Ketenes, Allenes, and Related Compounds, Part 1*, ed. S. Patai, John Wiley & Sons, Chichester, 1980, p. 279; (*c*) C. Bruneau and P. H. Dixneuf, in *Comprehensive Organic Functional Group Transformations, vol. 1*, ed. A. R. Katritzky, O. Meth-Cohn and C. W. Rees, Pergamon, Cambridge, 1995, p. 953; (*d*) A. S. K. Hashimi, *Angew. Chem., Int. Ed.*, 2000, **39**, 3590; (*e*) R. W. Bates and V. Satcharoen, *Chem. Soc. Rev.*, 2002, **31**, 12; (*f*) L. K. Sydnes, *Chem. Rev.*, 2003, **103**, 1133.

2 (*a*) J. Meyer, *Chem. Ber.*, 1956, **89**, 842; (*b*) Z. Hamlet and W. D. Barker, *Synthesis*, 1970, 543.

3 (*a*) H. Gilman and R. A. Tomasi, *J. Org. Chem.*, 1962, **27**, 647;

(*b*) K. W. Ratts and R. D. Partos, *J. Am. Chem. Soc.*, 1969, **91**, 6112; (*c*) H. J. Bestmann, R. W. Saalfrank and J. P. Snyder, *Chem. Ber.*, 1973, **106**, 2601; (*d*) H. J. Bestmann, *Angew. Chem., Int. Ed.*, 1977, **16**, 349.

4 T. Yoshida and E. Negishi, *J. Am. Chem. Soc.*, 1981, **103**, 1276.

5 S. L. Buchwart and R. H. Grubbs, *J. Am. Chem. Soc.*, 1983, **105**, 5490.

6 N. A. Petasis and Y.-H. Hu, *J. Org. Chem.*, 1997, **62**, 782.

7 T. Takeda, R. Sasaki and T. Fujiwara, *J. Org. Chem.*, 1998, **63**, 7286.

8 T. Takeda, N. Nozaki and T. Fujiwara, *Tetrahedron Lett.*, 1998, **39**, 3533.

9 (*a*) A. J. Speziale, G. J. Marco and K. W. Ratts, *J. Am. Chem. Soc.*, 1960, **82**, 1260; (*b*) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, 1962, **84**, 854; (*c*) W. G. Salmond, *Tetrahedron Lett.*, 1977, **18**, 1239; (*d*) G. Burton, J. S. Elder, S. C. M. Fell and A. V. Stachulski, *Tetrahedron Lett.*, 1988, **29**, 3003; (*e*) P. Vinczer, S. Struhar, L. Novak and C. Szantay, *Tetrahedron Lett.*, 1992, **33**, 683.

10 T. Takeda, Y. Endo, A. C. S. Reddy, R. Sasaki and T. Fujiwara, *Tetrahedron*, 1999, **55**, 247.