Pergamon

Tetrahedron Letters 39 (1998) 7705–7708

TETRAHEDRON LETTERS

Cycloadditions of Allylsilanes, Part 13.[1]

Lewis Acid-Promoted Stereospecific [2+2] Cycloaddition of Crotylsilanes and Methyl Propynoate

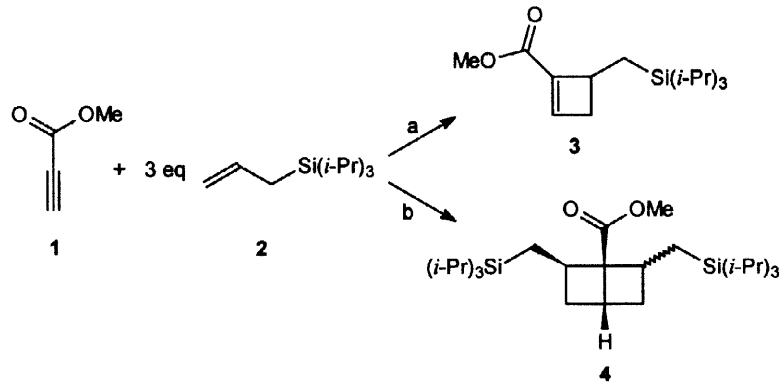
Hans-Joachim Knölker,*[a] *Elke Baum*,[b] and *Oliver Schmitt*[a]

[a] Institut für Organische Chemie, Universität Karlsruhe, Richard-Willstätter-Allee, 76131 Karlsruhe, Germany
[b] Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstraße, 76128 Karlsruhe, Germany

Received 21 July 1998; accepted 7 August 1998

Abstract: The titanium tetrachloride-promoted reaction of the (*Z*)- and (*E*)-crotylsilanes **6** and **9** with methyl propynoate (**1**) provides by stereospecific [2+2] cycloaddition the *cis*- and *trans*-3,4-disubstituted cyclobutenes **7** and **10**.

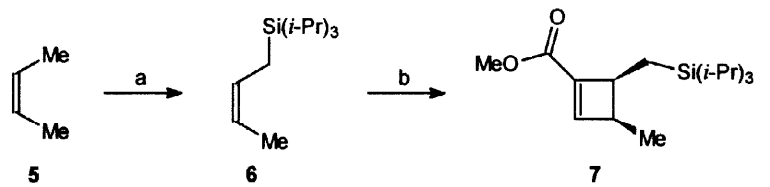
Allylsilanes have found a broad range of applications in synthetic organic chemistry.[2] Over the past years the Lewis acid-promoted cycloaddition of sterically hindered allylsilanes has developed to a useful synthetic method for the stereoselective construction of carbo- and heterocyclic ring systems.[3] The [3+2] cycloaddition of allylsilanes and electron-deficient alkenes proceeds *via* a cationic 1,2-silyl shift and provides a stereoselective access to silylcyclopentanes.[4] The kinetic intermediates of this reaction are silylmethylcyclobutanes which are obtained as major products depending on the substrates and reaction conditions.[5,6] The Lewis acid-promoted [2+2] cycloaddition of allylsilanes opens up a versatile synthesis of four-membered ring systems including heterocyclic derivatives, *e. g.* cycloaddition to carbonyl groups and imines provides oxetanes[7] and azetidines.[8] The [3+2] and [2+2] cycloaddition of allylsilanes and electron-deficient alkenes were shown to be stereospecific with respect to the configuration of the olefinic double bond.[5,4k] The cycloaddition products of allylsilanes are of synthetic value because silyl groups can be converted into hydroxy groups by the Fleming-Tamao oxidation.[9] Modified procedures of this transformation can be applied to oxidize the carbon–silicon bond of the sterically hindered triphenylsilyl,[10] diisopropylsilyl,[11] and *tert*-butyldiphenylsilyl groups[11] of the cycloaddition products. Thus cyclopentanols and cyclobutylmethanols are readily available by [3+2] and [2+2] cycloaddition of the corresponding allylsilanes and electron-deficient alkenes followed by the modified Fleming-Tamao oxidation.[10-12]



Scheme 1. a) $TiCl_4$, CH_2Cl_2, –78°C to –20°C, 19 h (98%); b) $TiCl_4$, CH_2Cl_2, 25°C to 40°C, 19 h (64% of **4**, *anti*/*syn* = 3:1, 34% of **3**).

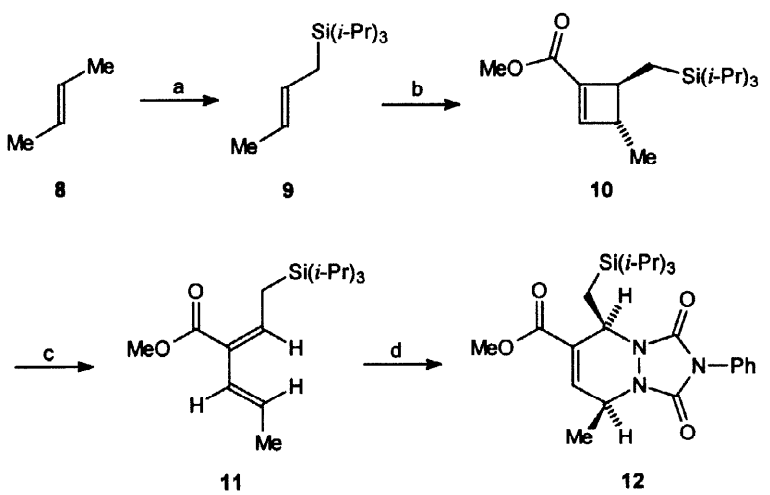
0040-4039/98/$ - see front matter
PII: S0040-4039(98)01678-5

We have shown that the titanium tetrachloride-promoted [2+2] cycloaddition of allylsilanes and methyl acrylates afforded the diastereoisomeric *anti*- and *syn*-silylmethylcyclobutanes in high yields.[5,11] Reaction of methyl propynoate (**1**) with an excess of allyltriisopropylsilane (**2**) at low temperatures afforded by a single [2+2] cycloaddition quantitatively the silylmethylcyclobutene **3**, while in dichloromethane at reflux a domino [2+2] cycloaddition to the bicyclo[2.2.0]hexane **4** occurred (Scheme 1).[5] We now describe the stereospecificity of the [2+2] cycloaddition with **1** to silylmethylcyclobutenes by having *E* and *Z* configurated double bonds in the allylsilane moiety.



Scheme 2. a) KO*t*-Bu, *n*-BuLi, THF, –90°C, then *i*-Pr_3SiCl, –90°C, 2 h (90%); b) methyl propynoate (**1**), $TiCl_4$, CH_2Cl_2, –78°C to –20°C, 19 h (65%).

Deprotonation of (*Z*)-2-butene (**5**) with *n*-butyllithium in the presence of potassium *tert*-butoxide (*Schlosser's base*) at –90°C and subsequent addition of chlorotriisopropylsilane provided (*Z*)-crotyltriisopropylsilane (**6**) isomerically pure in 90% yield (Scheme 2).[4h,13] The Lewis acid-promoted [2+2] cycloadditions of crotylsilanes and methyl propynoate (**1**) were investigated by using our standard set of reaction conditions[4,5] leading to the formation of cyclobutenes as described above for the synthesis of **3**. Titanium tetrachloride promoted reaction of the (*Z*)-crotylsilane **6** with methyl propynoate (**1**) afforded stereospecifically the *cis*-3,4-disubstituted cyclobutene **7** in 65% yield.[14]



Scheme 3. a) KO*t*-Bu, *n*-BuLi, THF, –90°C, then *i*-Pr_3SiCl, –90°C, 10 min (92%, *E*/*Z* = 7:1); b) methyl propynoate (**1**), $TiCl_4$, CH_2Cl_2, –78°C to –20°C, 19 h (70%, *anti*/*syn* = 7:1); c) benzene, 80°C, 2 h (100%); d) PTAD, CH_2Cl_2, –10°C to room temp., 2 h (84%).

On the other hand deprotonation of (*E*)-2-butene (**8**) by *Schlosser's base* at –90°C followed by addition of chlorotriisopropylsilane provided (*E*)-crotyltriisopropylsilane (**9**) in 92% yield as a 7:1 mixture with the *Z*-isomer **6** (Scheme 3).[4h,13] The high degree of stereospecificity of the Lewis acid-promoted [2+2] cycloaddition was emphasized by reaction of the (*E*)-crotylsilane **9** with methyl propynoate (**1**) in the presence of titanium

tetrachloride using our standard reaction conditions. Reaction of the 7:1 mixture of the (*E*)- and (*Z*)-crotylsilanes **9** and **6** with methyl propynoate (**1**) afforded in 70% yield a 7:1 mixture of the *trans*-3,4-disubstituted cyclobutene **10** and the *cis*-isomer **7**. The pure *trans*-isomer **10** was isolated by flash chromatography on silica gel at 10°C.[15] When the *trans*-isomer **10** was allowed to stay in solution at room temperature slow electrocyclic ring opening to a butadiene occurred. This observation was exploited for an unambiguous structure determination of **10**. Heating a solution of the *trans*-isomer **10** in benzene for 2 h at reflux provided quantitatively the butadiene **11**.[16] Diels-Alder cycloaddition of the butadiene **11** with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD)[17] afforded compound **12**. Stereochemical assignment for **12** is based on an X-ray crystal structure determination which unequivocally confirmed the *cis* relationship of the triisopropylsilylmethyl substituent and the methyl group (Figure 1).[18]

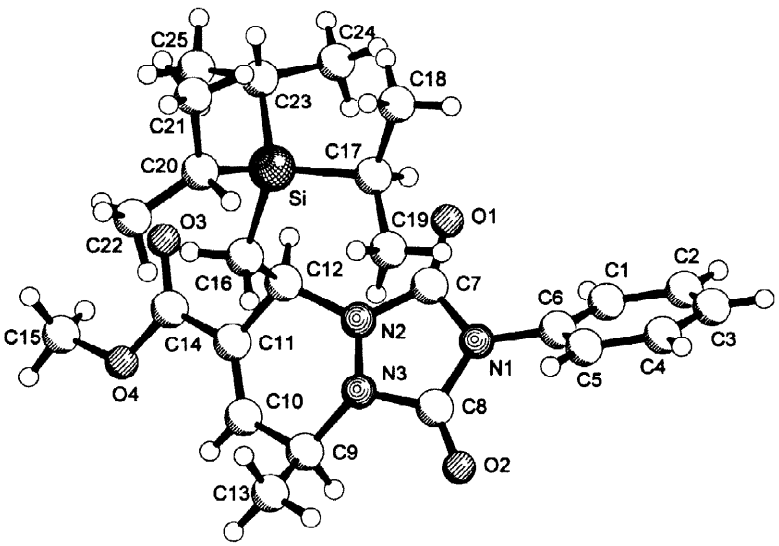


Figure 1. Molecular structure of compound **12** in the crystal.

The stereochemistry of **12** is rationalized by a thermally induced conrotatory electrocyclic reaction[19] of the *trans*-3,4-disubstituted cyclobutene **10** to the butadiene **11** and subsequent stereospecific Diels-Alder reaction. The electrocyclic ring opening reactions of the *cis*-isomer **7** and the cyclobutene **3** have significantly higher activation barriers and require 2 h in toluene at reflux in order to come to completion. The easy ring opening of the *trans*-isomer **10** to the butadiene **11** not only confirms the structural assignments but also provides an access to stereochemically defined hexa-2,4-dienylsilanes.

Acknowledgements: This work was supported by the Deutsche Forschungsgemeinschaft (Kn 240/5-3) and the Fonds der Chemischen Industrie.

References and Notes

1. Part 12: H.-J. Knölker, N. Foitzik, C. Gabler, R. Graf, *Synthesis* **1998**, in print.
2. Reviews: H. Sakurai, *Pure Appl. Chem.* **1982**, *54*, 1; A. Hosomi, *Acc. Chem. Res.* **1988**, *21*, 200; I. Fleming, J. Dunoguès, R. Smithers, *Org. React.* **1989**, *37*, 57; G. Majetich, in *Organic Synthesis, Theory and Applications* (Ed.: T Hudlicky), JAI Press, Greenwich (CT), **1989**, Vol. 1, p. 173; C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293; E. Langkopf, D. Schinzer, *Chem. Rev.* **1995**, *95*, 1375; I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.
3. For a review, see H.-J. Knölker, *J. Prakt. Chem.* **1997**, *339*, 304.

4. (a) H.-J. Knölker, P. G. Jones, J.-B. Pannek, *Synlett* **1990**, 429; (b) H.-J. Knölker, P. G. Jones, J.-B. Pannek, A. Weinkauf, *Synlett* **1991**, 147; (c) H.-J. Knölker, N. Foitzik, H. Goesmann, R. Graf, *Angew. Chem.* **1993**, *105*, 1104; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1081; (d) H.-J. Knölker, R. Graf, *Tetrahedron Lett.* **1993**, *34*, 4765; (e) H.-J. Knölker, N. Foitzik, R. Graf, J.-B. Pannek, P. G. Jones, *Tetrahedron* **1993**, *49*, 9955; (f) R. L. Danheiser, B. R. Dixon, R. W. Gleason, *J. Org. Chem.* **1992**, *57*, 6094; (g) J. S. Panek, N. F. Jain, *J. Org. Chem.* **1993**, *58*, 2345; (h) R. L. Danheiser, T. Takahashi, B. Bertók, B. R. Dixon, *Tetrahedron Lett.* **1993**, *34*, 3845; (i) H.-J. Knölker, R. Graf, *Synlett* **1994**, 131; (j) M.-J. Wu, J.-Y. Yeh, *Tetrahedron* **1994**, *50*, 1073; (k) H.-J. Knölker, P. G. Jones, R. Graf, *Synlett* **1996**, 1155; (l) H.-J. Knölker, N. Foitzik, H. Goesmann, R. Graf, P. G. Jones, G. Wanzl, *Chem. Eur. J.* **1997**, *3*, 538; (m) G. M. Choi, S. H. Yeon, J. Jin, B. R. Yoo, I. N. Jung, *Organometallics* **1997**, *16*, 5158.
5. H.-J. Knölker, G. Baum, R. Graf, *Angew. Chem.* **1994**, *106*, 1705; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1612.
6. M. Hojo, K. Tomita, Y. Hirohara, A. Hosomi, *Tetrahedron Lett.* **1993**, *34*, 8123; H. Monti, G. Audran, J.-P. Monti, G. Léandri, *Synlett* **1994**, 403; G. P. Brengel, C. Rithner, A. I. Meyers, *J. Org. Chem.* **1994**, *59*, 5144; W. S. Murphy, D. Neville, *Tetrahedron Lett.* **1997**, *38*, 7933.
7. T. Akiyama, M. Kirino, *Chem. Lett.* **1995**, 723; T. Akiyama, M. Yamanaka, *Synlett* **1996**, 1095.
8. T. Uyehara, M. Yuuki, H. Masaki, M. Matsumoto, M. Ueno, T. Sato, *Chem. Lett.* **1995**, 789.
9. For recent reviews, see: I. Fleming, *Chemtracts–Organic Chemistry* **1996**, *9*, 1; G. R. Jones, Y. Landais, *Tetrahedron* **1996**, *52*, 7599; K. Tamao, in *Advances in Silicon Chemistry*, JAI Press, Greenwich (CT), **1996**, Vol. 3, p. 1.
10. H.-J. Knölker, G. Wanzl, *Synlett* **1995**, 378.
11. H.-J. Knölker, P. G. Jones, G. Wanzl, *Synlett* **1998**, 613.
12. G. P. Brengel, A. I. Meyers, *J. Org. Chem.* **1996**, *61*, 3230.
13. M. Schlosser, J. Hartmann, V. David, *Helv. Chim. Acta* **1974**, *57*, 1567; M. Schlosser, J. Hartmann, *J. Am. Chem. Soc.* **1976**, *98*, 4674; reviews: M. Schlosser, *Pure Appl. Chem.* **1988**, *60*, 1627; M. Schlosser, O. Desponds, R. Lehmann, E. Moret, G. Rauchschwalbe, *Tetrahedron* **1993**, *49*, 10175; M. Schlosser, in *Organometallics in Synthesis–A Manual* (Ed.: M. Schlosser), Wiley, Chichester, **1994**, p. 1.
14. **7**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.68 (dd, J = 15.6, 10.0, 1 H), 1.01-1.09 (m, 22 H), 1.10 (d, J = 7.2, 3 H), 2.90 (dq, J = 4.4, 7.2, 1 H), 3.25 (br dt, J = 10.0, 3.7, 1 H), 3.70 (s, 3 H), 6.75 (s, 1 H).
15. **10**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.64 (dd, J = 15.2, 12.2, 1 H), 1.01-1.09 (m, 21 H), 1.17 (d, J = 7.8, 3 H), 1.35 (dd, J = 15.2, 2.2, 1 H), 2.34 (br q, J = 7.0, 1 H), 2.59 (ddd, J = 12.2, 1.9, 1.6, 1 H), 3.72 (s, 3 H), 6.75 (s, 1 H).
16. **11**: ^{1}H-NMR (500 MHz, C_6D_6): δ = 0.99-1.12 (m, 21 H), 1.62 (dd, J = 6.7, 1.6, 3 H), 2.19 (d, J = 9.4, 2 H), 3.46 (s, 3 H), 5.78 (dq, J = 15.5, 6.7, 1 H), 6.14 (t, J = 9.4, 1 H), 6.21 (dd, J = 15.5, 1.0, 1 H).
17. J. Sauer, B. Schröder, *Chem. Ber.* **1967**, *100*, 678; R. C. Cookson, S. S. H. Gilani, I. D. R. Stevens, *J. Chem. Soc. C* **1967**, 1905; C. J. Moody, *Adv. Heterocycl. Chem.* **1982**, *30*, 1.
18. *Crystal data* for **12**: $C_{25}H_{37}N_3O_4Si$, M = 471.67, crystal size: 0.84 × 0.48 × 0.2 mm, monoclinic, $P2_1/c$, a = 12.756(5), b = 24.338(3), c = 8.5711(9) Å, β = 99.54(2)°, V = 2624.2(11) Å^3, Z = 4, D_c = 1.194 g cm^{-3}, μ = 0.123 mm^{-1}, F(000) 1016, 1.62° < θ < 28.99°, Mo-Kα radiation, λ = 0.71069 Å, T = 293(2) K; 6982 independent reflections collected, goodness of fit on F^2 = 1.028, R_1 = 0.0588 [$I > 2\sigma(I)$], wR_2 = 0.1662, largest diff. peak and hole 0.427 and –0.313 e Å^{-3}; the structure was solved by direct methods (SHELXS-86) and refined anisotropically by full-matrix least-squares based on all unique F^2 (SHELXL-93); the program SCHAKAL-97 was used for the graphical representation of the crystal structure. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
19. R. B. Woodward, R. Hoffmann, *J. Am. Chem. Soc.* **1965**, *87*, 395.