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Regioselective alkylation and olefination of allylic carbanion stabilized by two different heteroatoms: phosphorus and silicon

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Abstract—Treatment of allylphosphonate with LiHMDS, followed by successive addition of chlorotrimethylsilane and carbonyl reagent, afforded dienylsilanes in good yields. 3-Substituted dienylsilanes were obtained by alkylation and olefination of allylic carbanion of 3-trimethylsilylallylphosphonates. © 2001 Elsevier Science Ltd. All rights reserved.

The reactions of allyl anions, stabilized by two different heteroatoms at the α - and γ -positions, have been one of the well-known methods of introducing various functional groups at the allylic position over the years.¹ Allylic systems bearing two different heteroatoms-sulfur with oxygen, silicon, or halogen,^{2a} oxygen with nitrogen or silicon,^{2b} and nitrogen with sulfur or silicon^{2c}—have been studied particularly. The regioselectivity of an allylic carbanion is determined by numerous factors, including steric effects, electron density, ionizing cosolvents and various species of electrophiles.³ Presently, our interest focused on functionalized allylic phosphonates that could be transformed into versatile compounds.⁴ In the course of our study, a lithiated 3-trimethylsilylallylphosphonate, i.e. an allylic system of phosphorus and silicon, was expected to be a useful precursor for various transformations, but its tendency toward olefination and alkylation has been rarely studied. We herein report a facile synthetic route to substituted dienylsilanes, which are valuable precursors for Diels-Alder reactions,⁵ using regioselective alkylation and olefination of lithiated 3trimethylsilylallylphosphonate.

The lithiated 3-trimethylsilylallylphosphonate (I) was generated by treatment of phosphonate (1) with 2 equiv. of LiHMDS in THF at -78°C, followed by addition of chlorotrimethylsilane (Scheme 1). The trimethylsilyl group exclusively took the γ -position of allylphosphonate.⁶ Protonolysis of intermediate (I) at -78°C or room temperature afforded 2a exclusively. The α -carbanion stabilizing power of the diethylphosphonyl group seemed to be superior to that of trimethylsilyl group, because the position of double bond indicates that the α -carbon of diethylphosphonyl group has a higher electron density. Also, all efforts to isolate the intermediate, 3-trimethylsilvl-1-propenylphosphonate, failed. Exposure of I to carbonyl reagents afforded dienylsilanes (3) by Horner-Wadsworth-Emmons olefination⁷ in good yields. The Peterson olefination⁸ product, i.e. the γ -addition product, was not detected by ¹H NMR analysis of the crude product. The α -selectivity of lithiated allylic systems containing diethylphosphonyl and trimethylsilyl groups could be explained by the higher electron density, and both by α -selectivity⁹ of allylic phosphonate and γ selectivity10 of allylic trialkylsilane in reaction with



Scheme 1.

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Table 1. Olefination of lithiated 3-trimethylsilylallylphosphonate



^a Yield of isolated product. ^b Geometries of 3, 4-olefins of trimethylsilyl group were

determined by NOE and ¹H NMR analysis.

carbonyl compounds. Table 1 summarizes some results of olefination with various carbonyl reagents, including easily enolizable (entry 4) and sterically hindered reagents (entry 6). Most olefins at the 1,2-position of the trimethylsilane group were typically in a pronounced *E*-geometry. The geometries of 3,4-olefins were E/Z mixtures, except for entries 1 and 2. Only one stereoisomer was obtained when aldehydes were added as carbonyl reagents. The geometries were identified by NOE experiments and ¹H NMR analysis.

To investigate how regioselectivity of the allylic anion is affected by substituents, alkylation and olefination were carried out by LiHMDS in THF at -78°C, as shown in Scheme 2. 1-Alkylated-3-trimethylsilylallylphospho-

nates containing methyl (2b), ethyl (2c), and benzyl (2d) substituents were obtained. Alkylation occurred exclusively at the α -carbon of diethylphosphonyl groups. Then, exposure of II to carbonyl reagents afforded 3-alkylated dienylsilanes (4) in good yields. It is note-worthy that although benzylation of unsubstituted allylphosphonate gave α , γ -added (1:1) mixtures, only one regioisomer was obtained when both silylation and benzylation were carried out in one pot. It could be assumed that the trimethylsilyl group, introduced firstly, served as a blocking group for γ -benzylation. The substituents of methyl, ethyl, and benzyl at the α -carbon of the diethylphosphonyl group had little effect on orientation of olefination of the diethylphosphonyl-trimethylsilyl allylic anion, because α -selectivity



^a Yield of isolated product. ^b Geometries of 3, 4-olefins of trimethylsilylgroup were determined by NOE and ¹H NMR analysis.

of allylic anion (II) still occurred at the same carbon. The high regioselectivity of alkylation and olefination at the α -carbon of the diethylphosphonyl group was likely to somewhat overwhelm steric hindrance, which was generated by alkylation. Therefore, to synthesize 3-functionalized dienylsilane, 3-trimethylsilylallylphosphonate seems to be a more appropriate precursor than 1,3-bis(trimethylsilyl)propene,¹¹ which has been practically used for synthesis of dienylsilanes, because alkylation and olefination could not occur at the same carbon in a lithiated 1,3-bis(trimethylsilyl)propene anion stabilized by two identical heteroatoms.

In summary, we demonstrated the regioselectivity of an allylic anion of two different heteroatoms containing phosphorus and silicon, and an efficient route to 3-substituted dienylsilanes, using regioselectivity of the lithiated 3-trimethylsilylallylphosphonate.

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References

 For reviews, see: (a) Alan, R. K.; Michael, P.; Hengyuan, L.; Ernst, A. Chem. Rev. 1999, 99, 665; (b) Yamamoto, Y.; Asao, N. Chem. Rev. 1993, 93, 2207; (c) Hoffmann, R. W. Angew. Chem., Int. Ed. Engl. 1987, 99, 489; (d) Stowell, J. C. Chem. Rev. 1984, 84, 409; (e) Yamamoto, Y.; Yatagai, H.; Saito, Y.; Maruyama, K. J. Org. Chem. 1980, 45, 4597; (f) Carter, M. J.; Fleming, I. J. Chem. Soc., Chem. Commun. 1976, 679; (g) Carter, M. J.; Fleming, I.; Percival, A. J. Chem. Soc., Perkins Trans. 1 1981, 2415; (h) Corriu, R. J. P.; Escudie, N.; Guerin, C. J. Organomet. Chem. 1984, 264.

- (a) Tiedemann, R.; Narjes, F.; Schaumann, E. Synlett 1994, 594; Craig, D.; Etheridge, C. j.; Smith, A. M. Tetrahedron Lett. 1992, 33, 7445; Ukai, J.; Ikeda, Y.; Ikeda, N.; Yamamoto, H. Tetrahedron Lett. 1984, 25, 5173; Lansbury, P. T.; Britt, R. W. J. Am. Chem. Soc. 1976, 98, 4577; (b) Katritzky, A. R.; Wu, H.; Xie, L.; Rachwal, S.; Rachwal, B.; Jiang, J.; Zhang, G.; Lang, H. Synthesis 1995, 1315; Trost, B. M.; Self, C. R. J. Am. Chem. Soc. 1983, 105, 5942; Trost, B. M.; Brandi, A. J. Org. Chem. 1984, 49, 4811; (c) Fitt, J. J.; Gschwend, H. W. J. Org. Chem. 1979, 44, 303; Ibanes, P. L.; Najera, C. Tetrahedron Lett. 1993, 34, 2003; Ahlbrecht, H.; Sudheendranath, C. S. Synth. Commun. 1982, 717.
- 3. Still, W. C.; McDonald, T. L. J. Org. Chem. 1976, 41, 3620.
- Lee, B. S.; Lee, S. Y.; Oh, D. Y. J. Org. Chem. 2000, 65, 4175.
- Fleming, I.; Barbero, A.; Walter, D. Chem. Rev. 1997, 97, 2063.
- Yuan, C.; Yao, J.; Li, S. Phosphorus Sulfur Silicon 1990, 53, 21.
- (a) Wadsworth, W. S.; Emmons, W. D. J. Am. Chem. Soc. 1961, 83, 1733; (b) William, A. J.; William, C. K.; Alexander, K. O. S.; David, A. D. Ylides and Imines of Phosphorus; John Wiley & Sons: New York, 1993; pp. 307–358.
- 8. Peterson, D. J. J. Org. Chem. 1968, 33, 780.
- 9. Yuan, C.; Li, C. Heterocyclic Chem. 1992, 3, 637.
- (a) Corriu, R. J. P.; Masse, J.; Samate, D. J. Organomet. Chem. 1975, 93, 71; (b) Ehlinger, E.; Magnus, P. Tetrahedron Lett. 1980, 21, 11; (c) Ehlinger, E.; Magnus, P. J. Am. Chem. Soc. 1980, 102, 5004.
- (a) Chan, T.-K.; Li, J.-S. J. Chem. Soc., Chem. Commun. 1982, 17, 969; (b) Corriu, R.; Escudie, N.; Guerin, C. J. Organomet. Chem. 1984, 264, 207; (c) Jun-ichi, Y.; Toshiki, M.; Sachihiko, I. Tetrahedron Lett. 1987, 28, 211.