February, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 59, 657—658 (1986)* 657

A Practical Synthesis of 1,3-Diene Using Allyltriphenylsilane and Titanium Tetraisopropoxide

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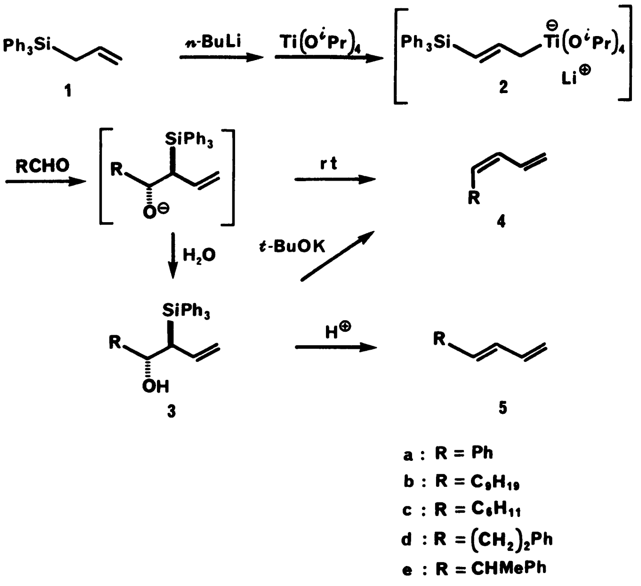
(Received September 12, 1985)

Synopsis. A practical method for the stereoselective preparation of 1,3-dienes by the use of allyltriphenylsilane as a key reagent is described.

A Peterson reaction involves the addition of a stoichiometric quantity of an α-silyl carbanion to a carbonyl group.[1] Recently, the scope of this process has been extended significantly.[2] One problem which had not been resolved was the control of regio- and stereoselectivity in the reaction of α-silylallyl carbanions with aldehydes and ketones.[3] This problem has now been solved by converting carbanions into the corresponding organotitanium compounds. Thus, Reetz and Sato recently reported independently the regio- and stereochemistry in reactions of trimethylsilylallyl anions with aldehydes as being highly controlled via the corresponding titanium reagent.[4] We also described a similar synthesis of 1,3-dienes using phenyl 1-(trimethylsilyl)-2-propenyl sulfide and titanium tetraisopropoxide.[5] During the course of our work, we found that the triphenylsilyl group has excellent potential as a control element in Peterson olefination since the three phenyl groups provide strong steric screening, not only for the silicon to which they are attached but to the next atom and even beyond. Furthermore, and much more importantly, it was found to be that, because of the inductive effect of three phenyl groups, the proton-metal exchange reaction of triphenylsilyl derivatives using butyllithium is much easier compared to the more common trimethylsilyl derivatives.[6] In this note we illustrate the utility of allyltriphenylsilane[7] for the synthesis of 1,3-dienes.

Alylltriphenylsilane (**1**), mp 92—94 °C, was readily prepared in 86% yield from allylmagnesium bromide and 1 equiv of chlorotriphenylsilane in ether at 0 °C.[7] It undergoes clean metallation with butyllithium in tetrahydrofuran (THF) (0 °C for 30 min) to form lithio derivative of **1**. In contrast to the metallation of allyltrimethylsilane, the reaction proceeded smoothly in the absence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) or hexamethylphosphoric triamide (HMPA).[6] The addition of titanium tetraisopropoxide to this solution at −78 °C generated a solution of the titanium reagent **2** which is a highly useful reagent for the synthesis of either (*Z*)- or (*E*)-1,3-dienes. Thus, a reaction of **2** with an equivalent of aldehyde was completed in 1 h at −78 °C. After the usual work-up, β-triphenylsilyl alcohols (**4**) were obtained. A treatment of **3** with potassium *t*-butoxide at room temperature for 10 min yielded (*Z*)-1,3-diene **4**, *E/Z*=<1:50. With sulfuric acid in THF for 16 h, followed by a similar work-up, **3** yielded (*E*)-1,3-diene **5**, *E/Z*=>50:1. The geometry was verified by a spectral comparison and/or gc analyses with alternatively prepared samples of 1,3-dienes using the conventional Wittig reactions.



Experimental

The IR spectra were determined on a Hitachi 260-10 spectrometer in a CCl_4 solution unless otherwise stated. The NMR spectra were recorded on a JNM-PMX 60 spectrometer, using TMS (tetramethylsilane) as an internal standard. The analyses were performed at the Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University. Tetrahydrofuran was distilled from benzophenone ketyl. All the experiments were carried out under an argon atmosphere. Purification of the product was carried out by column chromatography on silica gel Fuji BW-820.

1-Phenyl-2-triphenylsilyl-3-buten-1-ol (3a): To a solution of allyltriphenylsilane (901 mg, 3.0 mmol) in dry THF (6 ml) was added butyllithium (1.6 mol cm^{-3} hexane solution, 1.57 ml, 2.5 mmol) at 0 °C. The resulting pale-yellow solution was stirred at 0 °C for 1 h, turning redish brown, and cooled to −78 °C. Titanium tetraisopropoxide (0.80 ml, 2.7 mmol) was added at −78 °C and the mixture was stirred for 30 min at this temperature, during which period the color changed to bright yellow. Finally, a solution of benzaldehyde (211 mg, 2.0 mmol) in dry THF (2 ml) was added at −78 °C, and the reaction mixture was then stirred for 1 h. The reaction was quenched by an addition of ice-cold aqueous hydrochloric acid. The product was extracted twice with hexane, dried over $MgSO_4$, concentrated in vacuo, and purified by column chromatography on silica gel to give the alcohol **3a** as colorless crystals (732 mg, 90% yield): Mp 135—137 °C; IR (neat) 3550, 3030, 1425, 1100, 1040, 910, 735, and 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.87 (br, 1H, OH), 2.84 (dd, *J*=3 and 10 Hz, 1H), 4.68 (dd, *J*=2 and 17 Hz, 1H), 4.90 (dd, *J*=2 and 11 Hz, 1H), 5.13 (br, 1H), 6.05 (ddd, *J*=11, 17, and 10 Hz, 1H), 6.74—8.08 (m, 5H). Anal. ($C_{28}H_{26}OSi$) C, H.

3-Triphenylsilyl-1-tridecen-4-ol (3b) was obtained in 83%

yield as a colorless liquid: IR (CCl_4) 2880, 1410, and 990 cm^{-1}; ^1H NMR (CCl_4) δ=0.53—2.17 (br, 20H), 2.59 (dd, J=11 and 3 Hz, 1H), 3.85 (br, 1H), 4.70—5.20 (m, 2H), 5.95 (ddd, J=16, 11, and 11 Hz, 1H). Anal. ($C_{31}H_{40}OSi$) C, H.

(*Z*)-1-Phenyl-1,3-butadiene (4a): To a solution of the alcohol **3a** (296 mg, 0.73 mmol) in dry THF (3 ml) was added potassium *t*-butoxide (92 mg, 0.80 mmol) at room temperature. The mixture was stirred at room temperature for 10 min. TLC analyses showed the complete consumption of the starting alcohol. After the usual work-up, the crude product was purified by column chromatography on silica gel using pentane as an eluant to afford the diene **4a** as a clear liquid (95 mg, 100%): IR (neat) 3100, 3040, 2980, 2950, 1820, 1640, 1610, 1500, 1455, 1440, 1085, 1040, 1010, 955, 915, 870, 820, 790, 760, 700 cm^{-1}; ^1H NMR (CCl_4) δ=4.96—5.49 (br m, 2H), 5.93—7.49 (m, 8H). Anal. ($C_{10}H_{10}$) C, H.

A gc analysis of the product revealed an *E/Z* ratio of 1:50. An authentic mixture of the diene was prepared independently via allyl Wittig reagent and benzaldehyde.

Direct preparation of the (*Z*)-diene **4a**: After the addition of decanal, the reaction mixture was stirred at −78 °C for 1 h and at 30 °C for 3 h. After the usual work-up, (*Z*)-1,3-tridecadiene was obtained in 70% yield.

(*Z*)-1,3-Tridecadiene (4b) was similarly prepared in a quantitative yield as a colorless oil: IR (neat) 3100—2750, 1805, 1640, 1590, 1460, 1380, 970, 900, 780, 720 cm^{-1}; ^1H NMR (CCl_4) δ=0.67—2.50 (br, 19H), 4.86—5.60 (m, 3H), 5.88 (dd, J=11 and 11 Hz, 1H), 6.53 (ddd, J=11, 11, and 16 Hz); Anal. ($C_{13}H_{24}$) C, H.

(*Z*)-1-Cyclohexyl-1,3-butadiene (4c) was prepared in 69% yield as a colorless oil: IR (CCl_4) 3074, 2990, 1645, 1600, 1002, 967, 910 cm^{-1}; ^1H NMR (CCl_4) δ=0.66—2.35 (br. m, 10H), 2.41 (br. m, 1H), 4.85—5.44 (m, 3H), 5.79 (dd, J=11 and 11 Hz, 1H), 6.57 (ddd, J=11, 11 and 17 Hz, 1H); Anal. ($C_{10}H_{16}$) C, H.

(*Z*)-6-Phenyl-1,3-hexadiene (4d) was prepared in quantitative yield as a colorless oil:[8] IR (CCl_4) 3020, 2920, 1595, 1490, 1450, 1430, 990, 900 cm^{-1}; ^1H NMR (CCl_4) δ=2.20—2.90 (br. m, 4H), 4.83—5.62 (m, 3H), 5.91 (dd, J=11 and 11 Hz, 1H), 6.51 (ddd, J=11, 11 and 16 Hz, 1H), 7.07 (5H). Anal. ($C_{12}H_{14}$) C, H.

(*Z*)-5-Phenyl-1,3-hexadiene (4e) was prepared in 82% yield as a colorless oil: IR (CCl_4) 2970, 2930, 1600, 1490, 1450, 995, 905 cm^{-1}; ^1H NMR (CCl_4) δ=1.31 (d, J=7 Hz, 3H), 3.90 (dq, J=7 and 9 Hz, 1H), 4.94—5.58 (m, 3H), 5.87 (dd, J=10 and 10 Hz, 1H), 6.61 (ddd, J=10, 10, and 16 Hz, 1H), 7.06 (5H). Anal. ($C_{12}H_{14}$) C, H.

(*E*)-1-Phenyl-1,3-butadiene (5a): A mixture of the alcohol **3a** (217 mg, 0.53 mmol) and a catalytic amount of sulfuric acid (2 drops) in dry THF (10 ml) was stirred at room temperature for 16 h. The mixture was poured into water and the product was extracted with hexane, dried, and purified by column chromatography on silica gel to give the diene **5a** as an oil (57 mg, 82%): IR (CCl_4) 3070, 3005, 1795, 1625, 1593, 1480, 1440, 1155, 1065, 950, 890, 850 cm^{-1}; ^1H NMR (CCl_4) δ=4.92—5.49 (m, 2H), 6.07—6.89 (m, 3H), 6.89—7.59 (m, 5H). Anal. ($C_{10}H_{10}$) C, H.

(*E*)-1,3-Tridecadiene (5b): A mixture of the alcohol **3b** (220 mg, 0.48 mmol) and a catalytic amount of sulfuric acid (2 drops) in dry THF (6 ml) was stirred at reflux for 4 h. The mixture was poured into water and the product was extracted with hexane, dried, and purified by column chromatography on silica gel to give the diene **5b** as an oil (65 mg, 75%). IR (CCl_4) 3150—2800, 1870, 1660, 1610, 1560, 1480, 1390, 1265, 1130, 1050, 960, 905, 870 cm^{-1}; ^1H NMR (CCl_4) δ=0.63—2.47 (br, 19H), 4.70—6.53 (m, 5H). Anal. ($C_{10}H_{10}$) C, H.

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6) The deprotonation of allyltrimethylsilane with butyllithium is very slow in the absence of HMPA and/or TMEDA. In the presence of HMPA and/or TMEDA, the titanium reaction turned out to be unsatisfactory.

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8) Although the attempted separation of stereoisomers by gc was unsatisfactory, the NMR spectrum revealed the absence of the other isomer.