Pd(0) Catalyzed Stereoselective Synthesis of Dialkyl 1-(Trimethylsilyl) alkenylphosphonates

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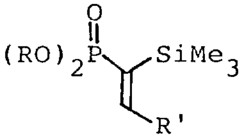
Alkenylphosphonates[1] with the trimethylsilyl group at α-position, depicted as below, are considered as synthetically valuable intermediates in organophosphorus chemistry since the recent development[2] of the transformation of the vinyl silane moieties into other functionalities, especially olefin activation toward nucleophilic addition by virtue of the polarizing silyl group has attracted much attention.



Dialkyl 1-(trimethylsilyl)-alkenylphosphonate

Only a few synthetic methods, however, have been reported for the synthesis of dialkyl 1-(trimethylsilyl) alkenylphosphonates. For example, direct deportonation[3] of vinylphosphonates by use of the strong bases, such as LDA, takes place indeed but in low yield and α-lithiated species are unstable under the reaction conditions to give decomposed products on a prolonged period. Coupling[4] of 1-(trimethylsilyl) alkenyl halides with dialkyl phosphites in the presence of nickel halide requires severe reaction condition and the stereochemistry of the products has not been fully clarified.

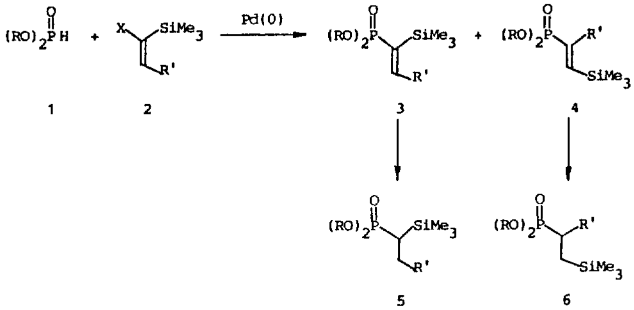
Here we report the scopes and limitations for the stereoselective synthesis of dialkyl 1-(trimethylsilyl)alkenyl phosphonates **3**. The title compounds were synthesized by the direct coupling of dialkyl phosphites **1** and (*E*)-1-(trimethylsilyl) alkenyl halides **2**[5] in the presence of a catalytic amount of tetrakis(triphenylphophine)palladium and triethylamine by a modification of the method of Hirao[6](Scheme 1).

Triphenylphophine as an additive ligand (Ph$_3$P/Pd(0) = 3-4) brought about the enhancement of the reaction rate and improved yields by the effective recycling of Pd(0) catalyst. The results were summarized in Table 1.[7]

Table 1. Coupling of Dialkyl Phosphites **1** and (*E*)-1-(trimethylsilyl) Alkenylhalides **2**

entry	R.	R	X	react. time(h)	3 + 4^a (yield, %)	3/4^b
1	Et	H	Br	1	**3a** + **4a** (99)	90/10
2	i-Pr	H	Br	1.5	**3b** + **4b** (94)	92/8
3	n-Bu	H	Br	1.5	**3c** + **4c** (97)	87/13
4	Et	n-Bu	Br	3	**3d** + **4d** (95)	90/10
5	i-Pr	n-Bu	Br	8	**3e** + **4e** (40)	92/8
6	n-Bu	n-Bu	Br	4	**3r** + **4f** (92)	90/10
7	Et	Ph	I	2.5	**3g** + **4g** (97)	70/30
8	i-Pr	Ph	I	12	**3h** + **4h** (67)	75/25
9	n-Bu	Ph	I	3	**3i** + **4i** (92)	73/27

^{a} GC yield based on dialkyl phosphites **1**. ^{b} Determined by GC and ^{1}H nmr.



Scheme 1

Only (*E*)-**3** were stereoselectively formed from (*E*)-1-(trimethylsilyl)alkenyl halides **2** with retention of the double bond stereochemistry while (*Z*)-**2** retarded coupling presumably due to the steric bulkiness of the environment of the halide in (*Z*)-**2**. Interestingly, a small portion of the rearranged regioisomers **4** were accompanied and could be readily separated by SiO$_2$ chromatography. The structures of **3** and **4** were characterized[8] by spectral properties (nmr, ir and ms) and confirmed[9] by comparison with the hydrogenated products **5** and **6** (H$_2$/Pd-C). The formation of the regioisomers **4** might be temporarily rationalized by that the intermediates Pd(II) complexes resulting from the primary reaction of Pd(0) and (*E*)-**2** rearranged[10] into isomeric species which underwent oxidative addition of dialkyl phosphites, followed by reductive elimination with retention to give **4**.

Thus we synthesized dialkyl 1-(trimethylsilyl)alkenylphosphonates stereoselectively by using Pd(0) catalyst and are currently examining the synthetic utilities of the title compounds.

References

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7. General procedure; To a stirred mixture of dialkyl phosphite (1 mmol), triethylamine (1 mmol), tetrakis (triphenylphosphine) palladium (3 mol %) and triphenylphosphine (12 mol%) in toluene (1 m*l*), was added (*E*)-1-(trimethylsilyl)alkenyl halide (1 mmol). The resultant mixture was stirred at 90-100 °C until the reaction completed (GC, TLC). After cooling to rt, ether (30 m*l*) was added and ammonium salt was removed by filtration. Filtrate was evaporated to give the products. Pure sample were obtained by SiO_2 column chromatography (EtOAc/*n*-Hex).
8. Representative spectral data of **3** and **4**. **3a**: ^{1}H-NMR ($CDCl_3$); δ 0.27 (s, 9H), 1.37 (t, J = 7Hz, 6H), 4.10 (p, J = 7Hz 4H), 6.34 (dd, J = 58Hz, J = 3.5Hz, 1H), 6.76(dd, J = 34Hz, J = 3.5Hz, 1H). **4a**: ^{1}H-NMR ($CDCl_3$); δ 0.17 (s, 9H), 1.37 (t, J = 7Hz, 6H). 4.10 (p, J = 7Hz 4H), 6.20 (dd, J = 28Hz J = 20Hz, 1H), 7.15 (dd, J = 35Hz, J = 20Hz, 1H).
9. Representative spectral data of **5** and **6**. **5a**: ^{1}H-NMR ($CDCl_3$): δ 0.18 (s, 9H), 1.18 (t, 3H), 1.40 (t, J = 7Hz, 6H), 2.60 (m, 1H), 4.10 (q, J = 7Hz, 4H). **6a**: ^{1}H-NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.28 (t, 2H), 1.40 (t, J = 5Hz, 6H), 2.30 (m, 2H), 4.10 (q, J = 7Hz, 4H).
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Synthesis and Structural Characterization of a Zwitterionic Triphenylphosphine Derivative of the Dicarbollide Anion: [*nido*-9-$P(C_6H_5)_3$-7,8-$C_2B_9H_{11}$]

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Received February 16, 1989

Recently, the icosahedral carborane has been employed in the area that ranges from basic inorganic chemistry[1-3] to biomedical applications.[4-6] The final ligand form used in the former area has the polyhedral framework of C_2B_9 cage of the nido dicarbollide anion.[7] As observed in our recent reports of the synthesis and structure of the unprecedented clustered cluster with a pinwheel ligand array,[3b,c] reduction of the formal charge of [*nido*-$C_2B_9H_{11}$]$^{2-}$ (**1**)[7] by the substitution of a terminal hydride on boron with a neutral Lewis base has been adopted as a way of tuning the reaction conditions. Among the possible Lewis bases, phosphine might be useful in the synthesis of a charge-compensated carborane ligand in which the substituent is not innocent sterically as well as electronically. Here we wish to report the synthesis and structural characterization of [*nido*-9-$P(C_6H_5)_3$-7,8-$C_2B_9H_{11}$] (**2**), a zwitterionic triphenylphosphine derivative of the dicarbollide anion.

A slurry of AgBr (2 mmol) and triphenylphosphine (1 mmol) in 40 m*l* of dichloromethane was allowed to react anaerobically with the dithallium salt[8] (1 mmol) of **1** at ambient temperature for 12 hrs, producing colorless solution and black precipitate. Recrystallization (CH_2Cl_2/*n*-heptane) of the white crystalline solids obtained by treating the concentrated filtrate with *n*-heptane afforded white crystalline **2** in a yield of 74%.[9] The nature of **2** was established by single-crystal X-ray analysis[10] as well as other means.[11]

Spectroscopic data[11] for **2** revealed the presence of the dicarbollide cage and triphenylphosphine group. The $^{11}B\{^1H\}$ NMR spectrum of **2** consists of ten resonances among which two signals at -14.41 and -15.37 ppm remain unchanged in the proton coupled ^{11}B NMR spectrum and thus can be ascribed to the B-P coupling with J = 155 Hz. The feature of the B-P coupling was further confirmed by 96.295 MHz ^{11}B NMR spectra. Although spectroscopic data for **2** could not lead to the positional assignment of the phosphorus-substituted boron atom, the number and the ratio of the resonances suggested that the formation of the B-P bond had occurred asymmetrically to make nine boron nuclei nonidentical.

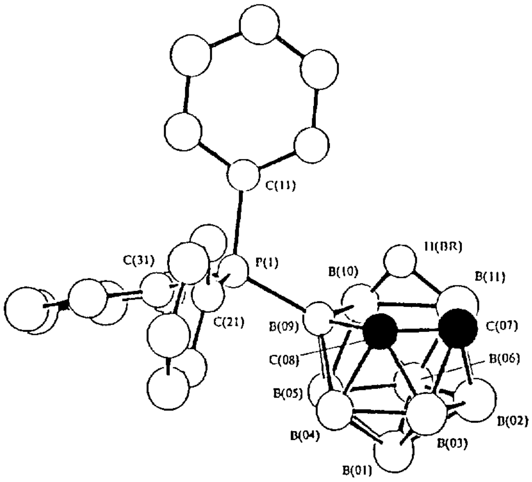

Figure 1. Structure of *nido*-9-$P(C_6H_5)_3$-7,8-$C_2B_9B_{11}$ showing the atom labeling scheme. All hydrogens except the *B-H-B* bridge have been omitted for clarity. Selected values of interatomic distances (Å). P(1)-B(09), 1.912(2); C(07)-C(08), 1.551(3); C(07)-B(11), 1.621(4); C(08)-B(09), 1.589(3); B(09)-B(10), 1.792(4); B(10)-B(11), 1.863(4).

The C_1 molecular symmetric nature of **2** is illustrated in