

A Novel Synthesis of Symmetric Trienes

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This paper describes a novel synthesis of trienes by treatment of *trans*-2-alkenyl triphenylphosphonium bromides with BuLi in THF solution. Compounds, 5,7,9-tetradecatriene, 1,6-diphenyl-1,3,5-hexatriene, and 2,6,11,16-tetramethyl-2,6,8,10,14-hexadecapentaene were prepared in the yields of 40%, 9%, and 46%, respectively. Cross-coupling of *trans*-2-heptenyltriphenylphosphonium bromide and *trans*-3-phenyl-2-propenyltriphenylphosphonium bromide gave a mixture of 5,7,9-tetradecatriene (10.6%), 1,6-diphenyl-1,3,5-hexatriene (0.5%), and 1-phenyl-1,3,5-decatriene (9.4%).

INTRODUCTION

The formation of carbon-carbon double-bond from alkyl halides and phosphine was found by Wittig.^{1,2} Phosphorus ylids formed by alkyl halide and triphenylphosphine react with an aldehyde or ketone to give alkenes.³ Poulain and Noiret⁴ reported a synthesis of symmetrical *Z*-olefins from alkyl phosphonium salts via an auto-

oxidation process. However, to our knowledge the synthesis of trienes by the coupling reactions of phosphonium salts in the presence of base has never been reported. In this paper we report the formation of carbon-carbon double bonds by the reactions of alkenyl phosphoranes and their precursors, phosphonium salts.

RESULT

trans-2-Heptenol (1a) and Geraniol (1b) were brominated. The *trans*-2-heptenyl bromide (2a), Geranyl bromide (2b), and *trans*-3-phenyl-2-propenyltriphenyl bromide (2c) were treated with triphenyl phosphine to

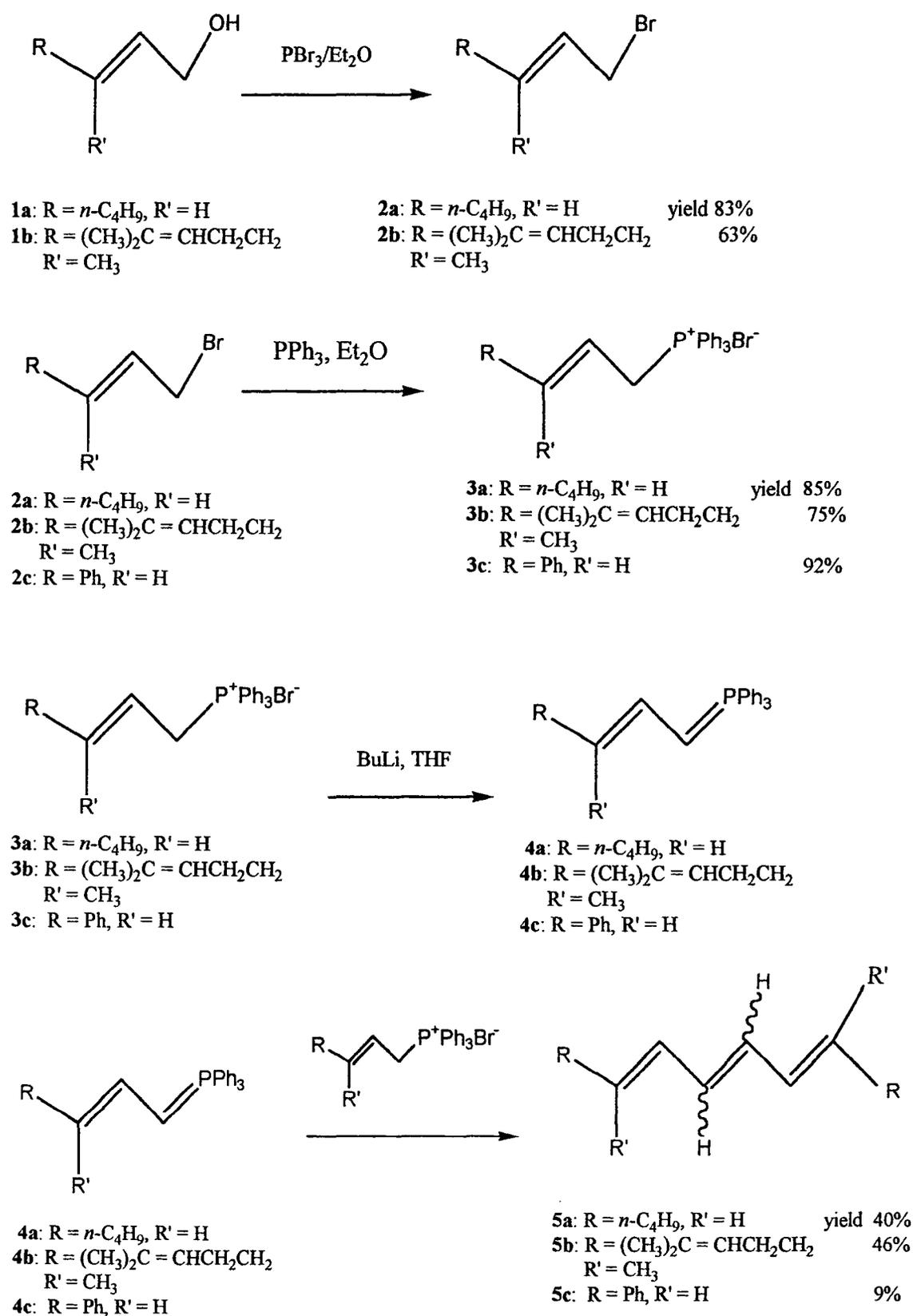
give phosphonium compounds 3a, 3b, and 3c. The treatment of phosphonium salts with BuLi gave symmetric trienes 5a, 5b, and 5c in the yields of 9-46%, as shown in Scheme 1.

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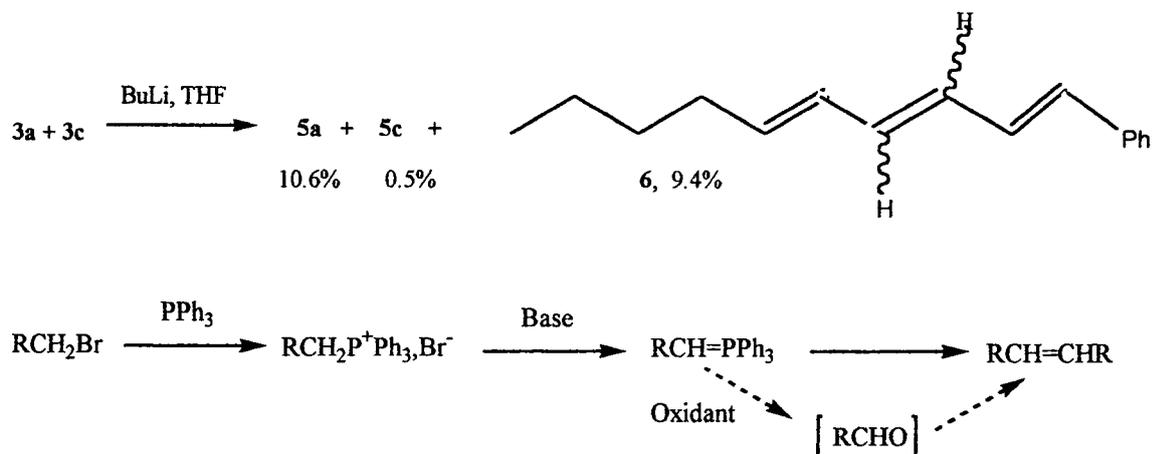
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Scheme 1.



A cross-coupling reaction of phosphonium Scheme 2. Poulain and Noiret⁴ reported a bromides 3a and 3c in the presence of BuLi synthesis of symmetrical *Z*-olefins from alkyl gave triene compounds 5a, 5c, and 6 in 10.6%, phosphonium salts via an auto-oxidation 0.5%, and 9.4% yields, respectively, as shown in process.

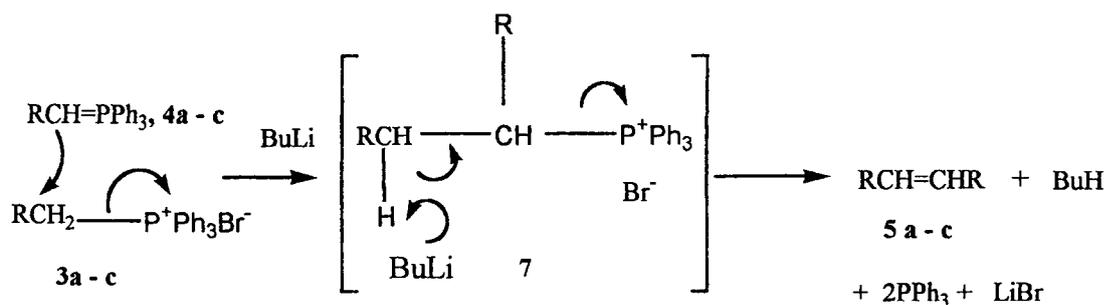
Scheme 2



All experiments of preparation of symmetrical trienes were carried out under an atmosphere of nitrogen. Triphenylphosphine was found in the mixture of products. The process happened during present experiments is not an auto-oxidation. The mechanism of the

reaction is suggested that nucleophilic alkenyl phosphorane 4a-c attacked alkenyl phosphonium bromides 3a-c to form the intermediate 7, which eliminated proton and triphenylphosphonium bromide to give trienes 5a-c, as shown in Scheme 3.

Scheme 3.



EXPERIMENTAL SECTION

The melting points and boiling points are uncorrected. Mass spectra were measured on a Shimadzu model GC-MS QP 5000 at 70 eV. ^1H and ^{13}C NMR spectra were performed on a Varian Gemini 200 NMR spectroscopy. IR spectra were determined on a JASCO model FT-IR 5000 apparatus. *trans*-2-Heptenol, Cinnamyl alcohol, Geraniol and Cinnamyl bromide are commercially available from TCI (Tokyo Chemical Industry Co.).

trans-2-Heptenyl Bromide (2a).⁵ To a 25 ml two-necked round flask under an atmosphere of nitrogen, was added 0.918g (3.39 mmol) of phosphorus tribromide. The flask was cooled to 0°C on ice-water bath. An ether solution of *trans*-2-heptenol 1.03g (9.23 mmol) in 12.4 ml ether was dropped and the mixture was stirred at same temperature for 6 hr. The mixture was quenched with ice water and extracted with ethyl acetate. The organic layer was washed with saturated NaCl solution, dried over anhydrous MgSO_4 . After evaporation of the solvent, the crude product was purified on a silica gel column chromatography, giving 1.35g (82% yield) of 2a.

Geranyl Bromide (2b). To a 25 ml two-necked round flask under an atmosphere of nitrogen, were added 10 ml of dry ether and 1.00g (6.48 mmol) of Geraniol, then cooled to 0°C with ice-water bath. Then, 0.67g (2.4 mmol) of phosphorus tribromide was added dropwise and the mixture was stirred for 1 hr at 0°C. The temperature rose to room temperature. The mixture was stirred for 32 hr and then quenched

with ice water. The mixture was extracted with ether (20ml x 3). The organic layer was washed with saturated NaCl solution, and dried over anhydrous MgSO_4 . After evaporation of the solvent the crude product was purified on a silica gel column chromatography, giving 0.889g (63% yield) of 2b: bp 112-115 °C / 3mmHg.

trans-2-Heptenyltriphenylphosphonium Bromide (3a).⁶ To a 25 ml 2-necked round flask under an atmosphere of nitrogen, were added 15 ml of Benzene, 0.774g (4.4 mmol) of *trans*-2-heptenyl bromide and 1.15g (4.4 mmol) of triphenylphosphine. The mixture was stirred for 24 hr at room temperature under darkness. White crystals were filtrated, and washed with ether. Recrystallization from ethanol gave 1.45g (85% yield) of 3a: mp 168 – 170 °C; ^1H NMR (200 MHz, CDCl_3) δ 0.781 (t, 3H, $J = 6.7$ Hz), 1.048 – 1.218 (m, 4H), 1.860 – 1.980 (m, 2H), 4.680 – 4.790 (dd, 2H), 5.170 – 5.360 (m, 1H), 5.380 (m, 1H), 7.620 – 7.890 (m, 15H).

trans-2,7-Dimethyl-2-octadienyltriphenylphosphonium bromide (3b) was prepared as shown in the preparation of compound 3a: 75% yield; IR (KBr, cm^{-1}) 2916, 2886, 1437, 1114, 1073, 752, 716, 685, 547; ^1H NMR (200 MHz, CDCl_3) δ 1.32 – 1.86 (m, 9H), 1.82 – 1.97(m, 4H), 4.56 – 4.67 (dd, 2H), 4.88 (br, 1H), 5.09 – 5.13 (q, 1H), 7.68 – 7.19 (m, 15).

trans-3-Phenyl-2-propenyltriphenylphosphonium bromide (3c) was prepared as shown in the preparation of compound 3a: 92% yield. Anal. Calc for $\text{C}_{27}\text{H}_{24}\text{BrP}$: C, 70.6%; H, 5.26%. Found: C, 70.06%; H, 5.27%.

5,7,9-Tetradecatriene (5a).

To a 5 ml two-necked round flask under an atmosphere of nitrogen were added 0.275g (0.58 mmol) of **3a**, 2.5 ml of THF, and 0.36 ml (0.57 mmol) of BuLi (1.6 M/L). The mixture was stirred at 0 °C ~ room temperature for 24 hr and 5 ml of 5% HCl was added. The mixture was extracted with hexane (10 ml x 3). The organic layer was washed with saturated NaCl solution, dried over anhydrous MgSO₄. After evaporation of the solvent, the crude product was purified on a silica gel column chromatography (hexane as an eluent), giving 22 mg (40%) yield of **5a**: GC-MS (70 eV) m/z 192 (M⁺), 163, 149, 135, 121, 107, 93. ¹H NMR (200 MHz, CDCl₃) δ 0.887 (t, 6H), 1.345 (m, 8H), 2.083 (q, 4H), 5.103 – 5.720 (m, 2H), 5.960 – 6.130 (m, 4H).

2,6,11,15-Tetramethyl-2,6,8,10,14-hexadecapentaene (5b).⁷

To a 20 ml two-necked round flask under an atmosphere of nitrogen were added 0.661g (1.3 mmol) of Geranyltriphenylphosphonium bromide, 10 ml of THF, and 1.22 ml (1.33 mmol) of BuLi (1.6 M/L) at room temperature. The mixture was heated to reflux temperature for 0.5 hr and then 3 ml of 5% HCl was added. The mixture was extracted with hexane (10 ml x 3). The organic layer was washed with saturated NaCl, dried over anhydrous MgSO₄. After evaporation of the solvent, the crude product was purified on a silica gel column chromatography (hexane as an eluent), giving 81.3 mg (46% yield) of **5b**: GC-MS (70 eV) m/z 272 (M⁺), 218, 160, 135, 133.

1,6-Diphenyl-1,3,5-hexatriene (5c).

To a 5 ml two-necked round flask under an atmosphere of nitrogen were added 0.375g (0.77 mmol) of Cinnamyltriphenylphosphonium bromide and 2.5 ml of THF, 0.48 ml (0.77 mmol) of BuLi (1.6 M/L) at 0 °C. The mixture was stirred at 0 °C for 3 hr, and then at room temperature for 24 hr. Then 3 ml of 5% HCl was added. The mixture was extracted with hexane (10 ml x 3). The organic layer was washed with saturated NaCl, and dried over anhydrous MgSO₄. After evaporation of the solvent, the crude product was purified on a silica gel column chromatography (hexane as an eluent), giving 16 mg (9% yield) of **5c**: GC-MS (70 eV) m/z 232 (M⁺), 215, 202, 178, 135, 141, 128, 115.

Reaction of 3a and 3c in the presence of BuLi. 1-Phenyl-1,3,5-decatriene (6).

To a 5 ml two-necked round flask under an atmosphere of nitrogen were added 0.43g (0.98 mmol) of **3c**, 0.55g (1.2 mmol) of **3a**, 15 ml of THF and 1.36 ml (2.18 mmol) of BuLi (1.6 M/L) at 0 °C. The mixture was stirred at 0 °C for 2 hr, and then at room temperature for 18 hr. Then 5 ml of 5% HCl was added. The mixture was extracted with hexane (10 ml x 3). The organic layer was washed with saturated NaCl, dried over anhydrous MgSO₄. After evaporation of the solvent, the crude product was purified on a silica gel column chromatography (hexane as an eluent), giving 20 mg (9.4% yield) of **6**, 12.2 mg (10.6% yield) of **5a**, and 6 mg (0.5% yield) of **5c**.

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