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ORIGINAL ARTICLE

Stereoselective dibromination of diphenylphosphorylallenes with *N*-bromosuccinimide under mild conditions

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Abstract A highly stereoselective dibromination of diphenylphosphorylallenes using *N*-bromosuccinimide (NBS) as bromine reagent is developed, wherein a variety of 2-bromo-substituted allyl bromides were obtained in good to excellent yields under mild reaction conditions. Moreover, the dibromination reaction allows a gram-scale synthesis of 2-bromo-substituted allyl bromides, and the products could be successfully transformed to various valuable derivatives.

1. Introduction

Allenes are a class of reactive unsaturated hydrocarbons which can be employed as the prolific building blocks in organic synthesis, especially in the field of natural products and bioactive compounds [1–4]. Over the past two decades, the transformations from allenes have been well conducted including intramolecular and intermolecular trifluoromethylation [5,6], hydroallylation [7], hydroarylation [8], hydrocyanation [9], as well as hydroamination [10]. Due to its unique electronic and structural arrangement, the highly chemo-, regio- and stereoselective functionalization of the different C═C bonds is appealing but challenging [11,12]. Diphenylphosphorylallenes, as one of the most important functionalized allene chemicals, have attracted more attention. Ma and co-workers have reported the elegant studies using diphenylphosphorylallenes as starting materials such as iodohydroxylation [13], selenohydroxylation [14], hydroformylation-hydrogenation [15], semihydrogenation [16], and so on [17]. Our group previously developed the methyltrioxorhenium-catalyzed selective dihydroxylation [18], palladium-catalyzed regio- and stereoselective hydroarylation [19], and $CuBr_2$/TBHP-promoted selective dibromination and bromohydroxylation of diphenylphosphorylallenes [20].

2-Bromo-substituted allyl bromides are also versatile building blocks and have found broad applications in organic synthesis. Traditionally, they are obtained by bromination of 2-bromo-substituted allyl alcohols with CBr_4/PPh_3 [21] or Br_2/PPh_3 [22]. Alternatively, the direct dibromination of allenes may provide another useful pathway to access 2-bromo-substituted allyl bromides [23]. Ivanov and co-workers [23b] reported the treatment of bifunctionalized allenes containing alkoxycarbonyl and phosphine oxide

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groups with bromine, affording the dibromination products in moderate yields (Scheme 1a). Nevertheless, the scope of examined substrates is rather limited. Recently we reported the dibromination and bromohydroxylation of 1,2-allenylic diphenyl phosphine oxides, affording the corresponding allyl bromides and alcohols in a cooperative $CuBr_2$ and TBHP system [20]. Although the bromohydroxylation products were obtained in good to excellent yields, the yields of dibromination products were not acceptable in a practical organic synthesis (Scheme 1b). Herein, we wish to report an efficient and highly stereoselective dibromination of diphenylphosphorylallenes with a cooperative NBS and TBHP system to afford 2-bromo-substituted allyl bromides (Scheme 1c).

2. Experimental section

2.1. General information

All solvents were purified and dried according to standard methods prior to use. NMR spectra were recorded on a Bruker Ascend HD 500 spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics micrOTOF II spectrometer. Melting points were determined on a WRS-3 apparatus.

2.2. General procedure for the synthesis of compound **2**

A solution of allene (0.25 mmol), NBS (1.5 mmol), and TBHP (0.5 mmol, 5.5 M in decane) in THF (1 mL) was mixed in a reaction tube at room temperature. When the reaction was completed, as monitored by TLC (eluent: petroleum ether/ethyl acetate = 3/1), the resulted mixture was quenched with saturated ammonium chloride (10 mL) and extracted with dichloromethane (2 × 20 mL). The combined organic layer was dried over $MgSO_4$. Filtration, concentration, and purification by flash chromatography on silica gel afforded pure products.

2.2.1. *(E)-(2,3-Dibromoprop-1-en-1-yl)diphenylphosphine oxide (**2a**) [20]*

White solid, m.p. 92–93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.68 (m, 4 H), 7.60–7.55 (m, 2 H), 7.53–7.48 (m, 4 H), 6.66 (d, J = 18.5 Hz, 1H), 5.02 (d, J = 1.0 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8 (d, J_{PC} = 3.6 Hz), 132.4 (d, J_{PC} = 2.6 Hz), 131.8 (d, J_{PC} = 107.4 Hz), 131.1 (d, J_{PC} = 9.9 Hz), 128.9 (d, J_{PC} = 11.6 Hz), 128.2 (d, J_{PC} = 86.6 Hz), 33.6 (d, J_{PC} = 4.5 Hz).

2.2.2. *(E)-(3,4-Dibromobut-2-en-2-yl)diphenylphosphine oxide (**2b**) [20]*

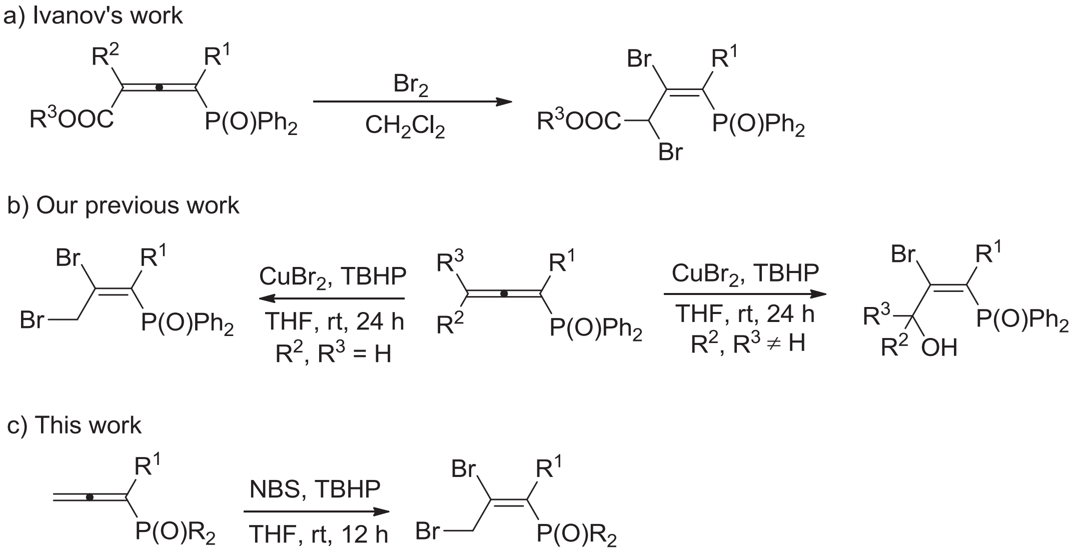
Colorless liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.66 (m, 4 H), 7.62–7.56 (m, 2 H), 7.54–7.48 (m, 4 H), 5.26 (s, 2 H), 1.82 (d, J = 12.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2 (d, J_{PC} = 14.4 Hz), 132.5 (d, J_{PC} = 2.6 Hz), 131.8 (d, J_{PC} = 10.0 Hz), 130.9 (d, J_{PC} = 105.6 Hz), 128.8 (d, J_{PC} = 12.6 Hz), 35.9 (d, J_{PC} = 4.5 Hz), 24.5 (d, J_{PC} = 10.8 Hz).

2.2.3. *(E)-(1,2-Dibromopent-2-en-3-yl) diphenylphosphine oxide (**2c**) [20]*

White solid, m.p. 121–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.66 (m, 4 H), 7.62–7.56 (m, 2 H), 7.54–7.48 (m, 4 H), 5.17 (s, 2 H), 2.32–2.20 (m, 2 H), 0.58 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0 (d, J_{PC} = 14.5 Hz), 137.8 (d, J_{PC} = 80.4 Hz), 132.5 (d, J_{PC} = 1.8 Hz), 132.0 (d, J_{PC} = 10.0 Hz), 131.1 (d, J_{PC} = 104.8 Hz), 128.7 (d, J_{PC} = 12.6 Hz), 36.4 (d, J_{PC} = 4.5 Hz), 30.2 (d, J_{PC} = 9.9 Hz), 11.2.

2.2.4. *(E)-(1,2-Dibromohex-2-en-3-yl) diphenylphosphine oxide (**2d**) [20]*

White solid, m.p. 126–127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.66 (m, 4 H), 7.62–7.56 (m, 2 H), 7.54–7.48 (m, 4 H), 5.15 (s, 2 H), 2.20–2.10 (m, 2 H), 1.02–0.92 (m, 2 H), 0.56 (t, J = 7.5 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0 (d, J_{PC} = 14.4 Hz), 137.0 (d, J_{PC} = 80.3 Hz), 132.5 (d, J_{PC} = 1.8 Hz), 132.0 (d, J_{PC} = 10.0 Hz), 131.2 (d, J_{PC} = 103.8 Hz),



Scheme 1 Dibromination of allenyl phosphine oxides.

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