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LETTERS TO THE EDITOR

Synthesis of Brominated Allenic, 1-3-Butadienyl, and Cyclobutenyl Diphenylphosphine Oxides

A. S. Bogachenkov and B. I. Ionin

St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia
e-mail: borisionin@mail.ru

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It is known that the halogenation of allenic phosphine oxides leads to the formation of stable phospholene salts [1, 2]. Allenic phosphine oxides are intermediates in the synthesis of cyclobutenyl phosphine oxides [3]. In this work we found that the reaction of the brominated allenic diphenylphosphine oxide **I**, **II** with bromine occurs via the intermediate formation of unstable phospholene salts. The latter easily eliminate hydrogen bromide to afford 1,2-dibromo-3-*tert*-butyl(phenyl)-1,3-butadien-1-yldiphenylphosphine oxides **III**, **IV**, which isomerized into the corresponding cyclobutenes **V**, **VI** when refluxed in toluene. These compounds contain the bromine atoms both at the double bond and at the saturated carbon atom. Therefore they are of interest to study further transformations of cyclobutene carbocycles.

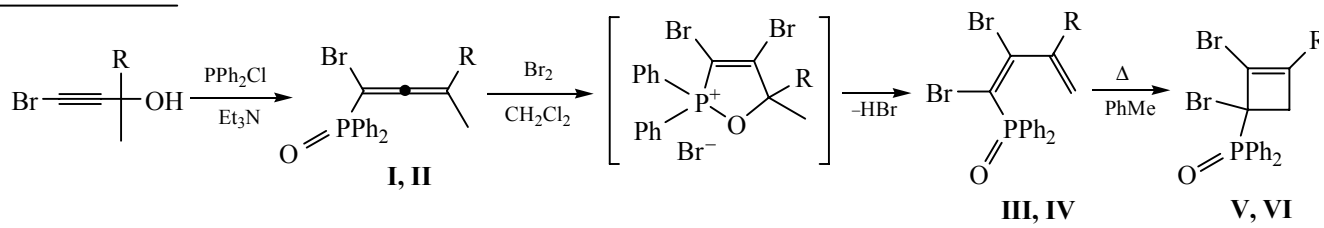
Allenes **I**, **II** were prepared by addition of diphenylchlorophosphine to a cooled (–10°C) mixture of the corresponding γ-bromopropargyl alcohol and triethylamine in dichloromethane [2]. The product was isolated by the recrystallization from diethyl ether. Then, according to the procedure [2], to a solution of the allene in dichloromethane cooled to 0°C was slowly added a solution of the equivalent amount of bromine in dichloromethane, maintaining the temperature between 0–4°C. The temperature was gradually raised to room temperature, and the solvent was removed under a reduced pressure. The residue, yellow oil, was chromatographed on a silica gel column eluting with a dichloromethane–methanol mixture (from 99:1 to 97:3). The target dienes **III**, **IV** were recrystallized from diethyl ether. The latter quantitatively isomerized into cyclobutenes **V**, **VI** under reflux for 30 min in toluene.

All the obtained phosphine oxides are colorless crystalline substances with the melting points above 100°C. Compound **III**, whose melting starts at 98.5°C, is gradually transformed into a cyclic isomer **V**. This fact was confirmed by the thin layer chromatography.

The structure of compounds obtained was proved by the ^{13}C, ^{1}H, ^{31}P NMR spectra.

The results of studying the reactions of dienes and brominated cyclobutenyl phosphine oxides will be published later. In particular, we found that these compounds can be used for the synthesis of the phosphorus-containing heterocyclic structures.

The ^{13}C, ^{1}H, ^{31}P NMR spectra were registered on a Bruker Avance instrument operating at 400.13 (^{1}H), 100.61 (^{13}C), 161.98 MHz (^{31}P) with internal reference TMS or external 85% phosphoric acid in D_2O. $CDCl_3$ was used as a solvent. The melting points were measured on a Koeffler heating block (VEB Wägetechnik Rapido, PHMK 81/2969). The column chromatography was performed on a Merck Silica Gel 60 (40–



R = *t*-Bu (**I, III, V**); Ph (**II, IV, VI**).

63 mesh). The R_f values were determined in a dichloromethane–methanol system (98:2).

1-Bromo-3,4,4-trimethyl-1-diphenylphosphoryl-1,2-pentadiene (I). Yield 60%, mp 119–120°C, R_f 0.41. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.81 s [9H, C(C$\underline{H}_3$)$_3$], 1.67 d (=CC$\underline{H}_3$), 7.43–7.56 m (6H, 2 *p*-H, 4 *m*-H), 7.75 d.d (2H, 2 *o*-H, $^3J_{HH}$ 7.0, $^3J_{HP}$ 12.3), 7.79 d.d (2H, 2 *o*-H, $^3J_{HH}$ 7.2, $^3J_{HP}$ 12.2). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 14.24 d (=C$\underline{C}$H$_3$, $^4J_{CP}$ 4.0), 28.20 [C($\underline{C}$H$_3$)$_3$], 34.37 d [$\underline{C}$(CH$_3$)$_3$, $^4J_{CP}$ 3.4], 81.85 d (=CBr, $^1J_{CP}$ 119.2), 120.64 d (=$\underline{C}$CH$_3$, $^3J_{CP}$ 9.4), 128.39 d (2 *m*-C, $^3J_{CP}$ 12.8), 128.44 d (2 *m*-C, $^3J_{CP}$ 12.1), 130.20 d (*ipso*-C, $^1J_{CP}$ 111.1), 131.00 d (*ipso*-C, $^1J_{CP}$ 111.1), 131.74 d (2 *o*-C, $^2J_{CP}$ 10.1), 132.00 d (2 *o*-C, $^2J_{CP}$ 9.4 Hz), 132.21 s (2 *p*-C), 205.04 d (=C=, $^2J_{CP}$ 13.5). ^{31}P NMR spectrum: δ_P 26.5 ppm.

1-Bromo-3-phenyl-1-diphenylphosphoryl-1,2-pentadiene (II). Yield 56%, mp 132–133°C, R_f 0.40. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.01 d (=CC$\underline{H}_3$), 7.23 d.d [2H, 2 *o*-H, C(Ph), $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.5], 7.29–7.36 m [3H, 1 *p*-H, 2 *m*-H, C(Ph)], 7.37–7.55 m [6H, 2 *p*-H, 4 *m*-H, P(Ph)], 7.76 d.d [2H, 2 *o*-H, P(Ph), $^3J_{HH}$ 7.1, $^3J_{HP}$ 12.3], 7.78 d.d [2H, 2 *o*-H, P(Ph), $^3J_{HH}$ 7.2, $^3J_{HP}$ 12.2]. ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 16.06 d (=C$\underline{C}$H$_3$, $^4J_{CP}$ 4.0), 83.35 d (=CBr, $^1J_{CP}$ 114.4), 111.71 d (=$\underline{C}$CH$_3$, $^3J_{CP}$ 10.1), 126.58 s [2 *o*-C, Ph(C)], 128.42 d [2 *m*-C, Ph(P), $^3J_{CP}$ 12.1], 128.49 d [2 *m*-C, Ph(P), $^3J_{CP}$ 12.1], 128.69 s [2 *m*-C, Ph(C)], 128.91 [*p*-C, Ph(C)], 130.21 d [*ipso*-C, Ph(P), $^1J_{CP}$ 110.4], 130.34 d [*ipso*-C, Ph(P), $^1J_{CP}$ 110.4], 131.74 d [2 *o*-C, Ph(P), $^2J_{CP}$ 9.4 Hz], 131.81 d [2 *o*-C, Ph(P), $^2J_{CP}$ 9.4 Hz], 132.35 d [2 *n*-C, Ph(P), $^4J_{CP}$ 1.7 Hz], 133.22 d [*ipso*-C, Ph(C), $^4J_{CP}$ 4.7], 208.12 d (=C=, $^2J_{CP}$ 13.2). ^{31}P NMR spectrum: δ_P 25.9 ppm.

1,2-Dibromo-3-*tert*-butyl-1-diphenylphosphoryl-1,2-pentadiene (III). Yield 85%, R_f 0.63. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.37 s [9H, C(C$\underline{H}_3$)$_3$], 4.99 s (1H, =C$\underline{H}_2$), 5.15 s (1H, =C$\underline{H}_2$), 7.41–7.46 m (2H, 2 *m*-H), 7.50–7.55 m (3H, 1 *p*-H, 2 *m*-H), 7.58–7.63 m (1H, 1 *p*-H), 7.662 d.d (1H, 1 *o*-H, $^3J_{HH}$ 8.3, $^3J_{HP}$ 12.5), 7.665 d.d (1H, 1 *o*-H, $^3J_{HH}$ 8.3, $^3J_{HP}$ 12.6), 7.879 d.d (1H, 1 *o*-H, $^3J_{HH}$ 8.1, $^3J_{HP}$ 12.3), 7.882 d.d (1H, 1 *o*-H, $^3J_{HH}$ 8.2, $^3J_{HP}$ 12.4). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 30.92 [C($\underline{C}$H$_3$)$_3$], 35.54 [$\underline{C}$(CH$_3$)$_3$], 117.59 (=CH$_2$), 121.66 d [=C(Br)P, $^1J_{CP}$ 88.9], 128.16 d (2 *m*-C, $^3J_{CP}$ 12.8), 128.62 d (2 *m*-C, $^3J_{CP}$ 12.1), 130.73 d (*ipso*-C, $^1J_{CP}$ 109.7), 131.20 d (*ipso*-C, $^1J_{CP}$ 109.7), 132.06 d (2 *o*-C, $^2J_{CP}$ 10.8), 132.27 d (2 *o*-C, $^2J_{CP}$ 11.4), 132.42 (2 *p*-C), 145.58 d [$\underline{C}$=C(Br)P, $^2J_{CP}$ 14.8], 157.24 d ($\underline{C}$=CH$_2$, $^3J_{CP}$ 2.0). ^{31}P NMR spectrum: δ_P 26.9 ppm.

1,2-Dibromo-3-phenyl-1-diphenylphosphoryl-1,2-pentadiene (IV). Yield 79%, mp 138–139.5°C, R_f 0.54. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 5.33 s (1H, =C$\underline{H}_2$), 5.51 s (1H, =C$\underline{H}_2$), 7.30–7.34 m [3H, 1 *p*-H, 2 *m*-H, C(Ph)], 7.36–7.44 m [6H, 2 *o*-H, C(Ph); 4 *m*-H, P(Ph)], 7.49–7.53 m [2H, 2 *p*-H, P(Ph)], 7.76 d.d (4H, 4 *o*-H, P(Ph), $^3J_{HH}$ 7.9, $^3J_{HP}$ 11.9). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 118.41 (=CH$_2$), 122.06 d [=C(Br)P, $^1J_{CP}$ 87.5], 126.78 [2 *o*-C, Ph(C)], 128.35 [2 *m*-C, *p*-C, Ph(C)], 128.42 d [4 *m*-C, Ph(P), $^3J_{CP}$ 15.1], 129.78 d [*ipso*-C, Ph(P), $^1J_{CP}$ 105.6], 131.57 d [*ipso*-C, Ph(P), $^1J_{CP}$ 105.6], 132.09 d [4 *o*-C, Ph(P), $^2J_{CP}$ 10.1], 132.31 [2 *p*-C, Ph(P)], 135.94 [*ipso*-C, Ph(C)], 143.28 d [$\underline{C}$=C(Br)P, $^2J_{CP}$ 16.1], 146.49 ($\underline{C}$=CH$_2$). ^{31}P NMR spectrum: δ_P 26.5 ppm.

1,2-Dibromo-3-*tert*-butyl-1-diphenylphosphoryl-cyclobut-2-ene (V). Yield 98%, mp 184.5–186°C, R_f 0.38. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.90 s [9H, C(C$\underline{H}_3$)$_3$], 3.03 d.d (1H, PCC$\underline{H}_2$, $^2J_{HH}$ 12.3, $^3J_{HP}$ 2.3), 3.32 d.d (1H, PCC$\underline{H}_2$, $^2J_{HH}$ 12.3, $^3J_{HP}$ 5.0), 7.43–7.61 m (6H, 2 *p*-H, 4 *m*-H), 7.93 d.d (2H, 2 *o*-H, $^3J_{HH}$ 7.3, $^3J_{HP}$ 10.3), 7.97 d.d (2H, 2 *o*-H, $^3J_{HH}$ 7.2, $^3J_{HP}$ 11.2). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 26.98 [C($\underline{C}$H$_3$)$_3$], 33.76 [$\underline{C}$(CH$_3$)$_3$], 43.80 (CH$_2$), 57.35 d [C(Br)P, $^1J_{CP}$ 72.4], 108.35 d [=$\underline{C}$C(CH$_3$)$_3$, $^3J_{CP}$ 5.0], 128.25 d (2 *m*-C, $^3J_{CP}$ 12.1), 128.31 d (2 *m*-C, $^3J_{CP}$ 12.1), 128.67 d (*ipso*-C, $^1J_{CP}$ 103.6), 129.91 d (*ipso*-C, $^1J_{CP}$ 103.6), 132.47 d (2 *o*-C, $^2J_{CP}$ 9.1), 132.56 (2 *p*-C), 132.64 d (2 *o*-C, $^2J_{CP}$ 9.1), 158.00 d [=CBr, $^2J_{CP}$ 11.1]. ^{31}P NMR spectrum: δ_P 31.5 ppm.

1,2-Dibromo-3-phenyl-1-diphenylphosphoryl-cyclobut-2-ene (VI). Yield 96%, mp 140–141°C, R_f 0.45. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.39 d.d (1H, PCC$\underline{H}_2$, $^2J_{HH}$ 11.7, $^3J_{HP}$ 1.0), 3.88 d.d (1H, PCC$\underline{H}_2$, $^2J_{HH}$ 11.7, $^3J_{HP}$ 4.9), 7.35–7.60 m [5H, C(Ph); 6H, 2 *p*-H, 4 *m*-H, P(Ph)], 7.94 d.d (2H, 2 *o*-H, $^3J_{HH}$ 8.0, $^3J_{HP}$ 11.0), 8.08 d.d (2H, 2 *o*-H, $^3J_{HH}$ 8.5, $^3J_{HP}$ 10.4). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 44.03 (CH$_2$), 58.09 d [C(Br)P, $^1J_{CP}$ 72.7], 110.00 d (=$\underline{C}$Ph, $^3J_{CP}$ 6.0), 126.49 [2 *o*-C, Ph(C)], 128.21 d [2 *m*-C, Ph(P), $^3J_{CP}$ 13.1], 128.37 d [2 *m*-C, Ph(P), $^3J_{CP}$ 12.1], 128.50 [2 *m*-C, *p*-C, Ph(C)], 129.08 [*ipso*-C, Ph(P), $^1J_{CP}$ 104.6], 130.26 [*ipso*-C, Ph(P), $^1J_{CP}$ 104.6], 132.35 d [2 *o*-C, Ph(P), $^2J_{CP}$ 10.1], 132.63 [2 *p*-C, Ph(P)], 133.25 d [2 *o*-C, Ph(P), $^2J_{CP}$ 10.1], 138.84 [*ipso*-C, Ph(C)], 145.64 d [=CBr, $^2J_{CP}$ 12.1]. ^{31}P NMR spectrum: δ_P 30.0 ppm.

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