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Reactions of But-2-yne-1,4-diylbis(triphenylphosphonium) Dihalides with SH- and NH-Nucleophiles

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Abstract—But-2-yne-1,4-diylbis(triphenylphosphonium) diiodide reacts with 2-sulfanylethan-1-ol in the presence of triethylamine to form a 1 : 1 adduct. Under similar conditions, ethane-, butane- and 2-methylbutane-1-thiols form [4-(alkylsulfanyl)buta-1,3-dien-1-yl]triphenylphosphonium iodides, probably via β-cleavage of the original salt involving vinylethynyl intermediate. Features of the reaction of but-2-ynebisphosphonium salt with 3,5-dimethylpyrazole, hydrazine and its derivatives have been studied.

Keywords: but-2-yne-1,4-diylbis(triphenylphosphonium) diiodide, alkanethiol, hydrazine, hydrazone, 3,5-dimethylpyrazole

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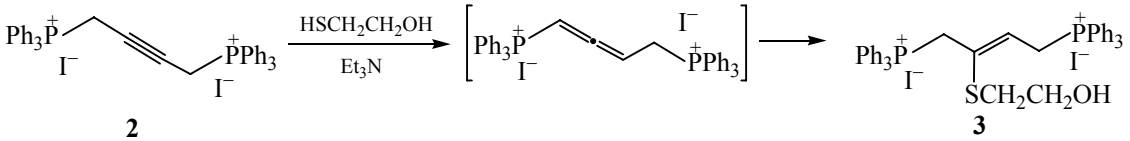
An unusual pathway of buta-1,3-diene-1,4-diylbis (triphenylphosphonium) diiodide **1** reaction with alkanethiols has been recently revealed. The reaction has occurred at room temperature in chloroform in the presence of an equimolar amount of triethylamine to form [4-(alkylsulfanyl)buta-1,3-dien-1-yl]triphenylphosphonium diiodides and triphenylphosphine [1]. It has been found that thiolate anions generated from alkanethiols and triethylamine are involved into the β-cleavage of salt **1** to give triphenylphosphine and ethynylvinyl intermediate.

It was of interest to study the interaction of but-2-yne-1,4-diylbis(triphenylphosphonium) diiodide **2**, a structural isomer of phosphonium salt **1**, with alkanethiols. The similar salts containing acetylene moiety have been shown to undergo prototropic isomerization yielding bisphosphonium salts with conjugated diene group under the action of diethylamine, benzylamine, and even phenol at room temperature [2]. Probably, in the case of phenol the hydroxyl hydrogen has reacted with acetylene bond, the phenolate anion being involved in the prototropy. The prolonged incubation of the reaction mixture has resulted in the formation of dienebisphosphonium benzylamine salt but not diethylamine. Addition reactions of but-2-ynebisphosphonium salts with less basic reagents (aniline, *N*-methylaniline, and thiophenol) at room temperature occur via nucleophilic attack directly at the electrophilic triple bond [2].

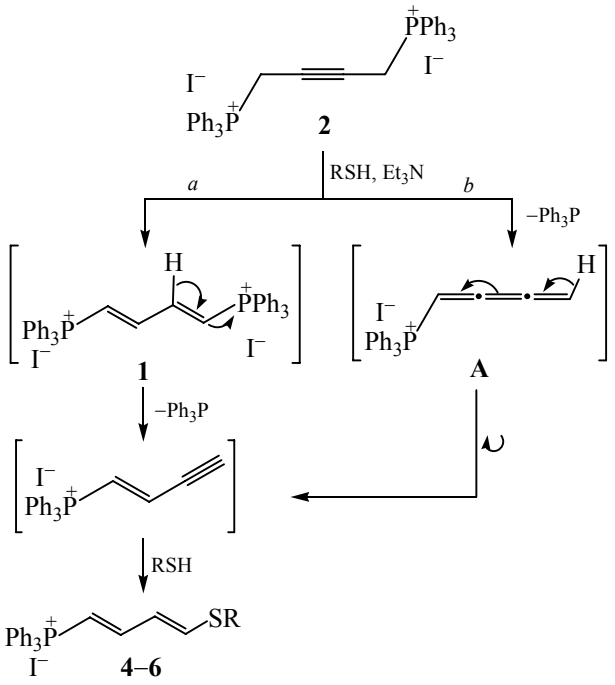
Diiodide **2** reacted with 2-sulfanylethan-1-ol in the presence of an equimolar amount of triethylamine in a mixture of chloroform and methanol at 5°C to form the adduct **3** in yield of about 70%. The reaction proceeded probably via prototropic acetylene group isomerization into the allene {but not 1,3-diene one, as 1,3-dienebisphosphonium salt reacted with sulfanylethanol to form [4-(2-hydroxyethylsulfanyl)buta-1,3-diene-1-yl]triphenylphosphonium iodide [1]} (Scheme 1).

Scheme 1.



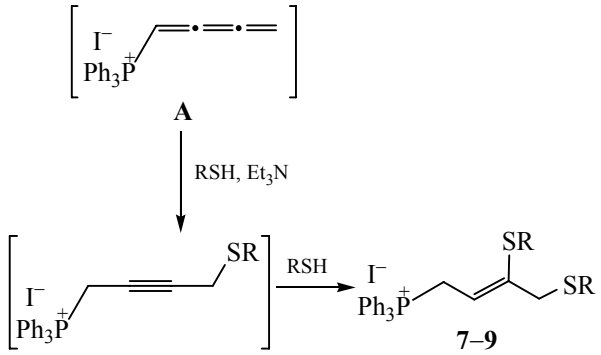
2 **3**

Scheme 2.



R = Et (**4**), Bu (**5**), *i*-C_5H_{11} (**6**).

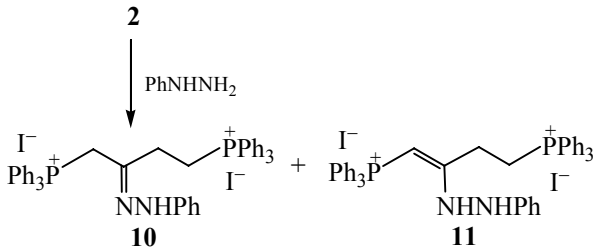
Scheme 3.



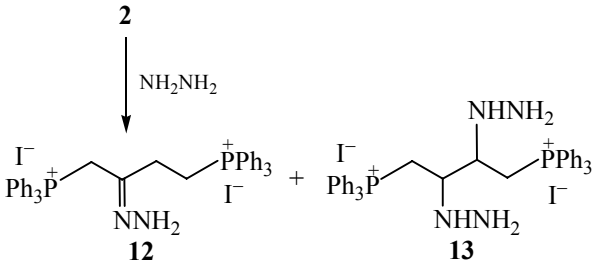
The reactions with ethane-, butane- and 2-methylbutanethiols afforded a complex mixture of phosphorus-containing compounds under the same conditions; 4-(alkylsulfanyl)buta-1,3-diene-1-yltriphenylphosphonium iodides **4**–**6** were isolated in yields of 30, 24, and 46%, respectively, along with the accompanying triphenylphosphine. Formation of the phosphonium salts proceeded probably according to one of the alternative pathways: *a* or *b* (Scheme 2).

The reaction pathway *a* included initial double prototropic isomerization of phosphonium salt **2** into phosphonium salt **1** under the action of thiolate anions and formation of adducts **4**–**6** [1]. In the case of reaction pathway *b*, 1,4-splitting of salt **2** occurred initially to form the phosphonium intermediate **A** with a butatriene bond system, followed by addition of alkanethiol.

Scheme 4.



Scheme 5.

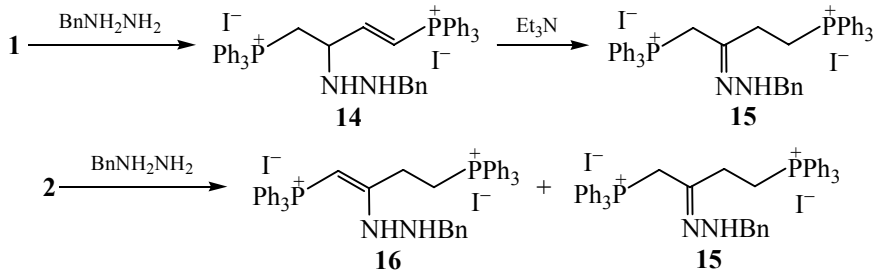


^{1}H NMR spectra of the reaction mixture contained the proton signals characteristic of 3,4-bis(alkylsulfanyl)but-2-enyl(triphenyl)phosphonium halides **7**–**9** at 4.65 ($PC\underline{H}_2CH$) and 3.4 (CH_2S) ppm. Compounds **7**–**9** (they were not isolated in pure form) were probably formed via double nucleophilic addition of alkanethiols to butatriene intermediate **A** (Scheme 3).

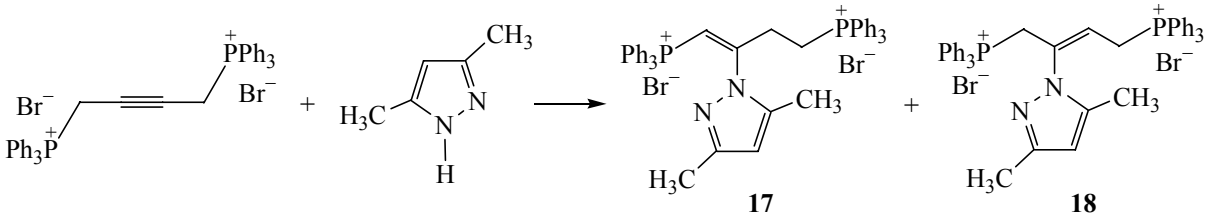
Phenyl-, benzyl- and unsubstituted hydrazines were used as nitrogen nucleophiles in the reactions with phosphonium salt **2**. Bisphosphonium salt **1** reacted with phenylhydrazine to form 2-(2-phenylhydrazinylidene)butane-1,4-diylbis(triphenylphosphonium) diiodide in a high yield [3]. The reaction of salt **2** with phenylhydrazine at heating in chloroform afforded a mixture (≈1 : 2) of 2-(2-phenylhydrazinylidene)butane-1,4-diylbis(triphenylphosphonium) diiodide **10** and 2-(2-phenylhydrazinyl)but-1-ene-1,4-diylbis(tri-phenylphosphonium) diiodide **11** in total yield of 65% (Scheme 4).

Interaction of phosphonium salt **2** with 60% aqueous hydrazine resulted in the formation of the target hydrazone **12** with yield of only 22% and bis-adduct **13** in 43% yield. The bis-adduct formation has been observed in the reaction of salt **1** with hydroxylamine [4, 5]. Probably, salt **2** reacted with hydrazine after the double prototropic isomerization of salt **1** (Scheme 5).

Scheme 6.



Scheme 7.



The reaction of phosphonium salt **1** with 2 equivalents of benzylhydrazine in chloroform at 5°C led to the formation of adduct **14** in yield of ≈80%. Treating of compound **14** with triethylamine at room temperature gave 2-(2-benzylhydrazinylidene)butane-1,4-diylbis(triphenylphosphonium) diodide **15** as a product of double prototropic isomerization. Compound **15** and its isomer **16** were prepared via the reaction of phosphonium salt **2** with benzylhydrazine in a mixture of chloroform and methanol at –5°C (Scheme 6).

The reaction of bromide analog of phosphonium salt **2** with 3,5-dimethylpyrazole at room temperature led to the formation of two isomeric bisphosphonium salts **17** and **18**. The reaction probably proceeded according to the scheme proposed in [2] via direct nucleophilic attack at the triple bond (Scheme 7).

The attempt to perform similar reaction with iodide **2** failed. ^{1}H and ^{31}P NMR spectra of the reaction mixture contained the signals assigned to the product of prototropic isomerization of phosphonium salt **2** and to triphenylphosphine oxide formed probably via attack of triethylamine at the positively charged phosphorus atom of **2** followed by fragmentation of the carbon chain.

In summary, the results revealed the similarity of the reactions of bisphosphonium salts **1** and **2** with the studied nucleophiles.

EXPERIMENTAL

IR spectra were recorded using a Specord UR-75 instrument in chloroform. ^{1}H and ^{31}P NMR spectra were registered using a Varian Mercury-300 spectrometer [300.077 (^{1}H) and 121.47 MHz (^{31}P)] at 303 K using a DMSO-d_6–CCl_4 mixture (1 : 3) as solvent. Chemical shifts are reported relative to TMS (^{1}H) and 85% H_3PO_4 (^{31}P).

But-2-yne-1,4-diilbis(triphenylphosphonium) diiodide and dibromide were prepared according to known methods [6].

2-(2-Hydroxyethylsulfanyl)but-2-ene-1,4-diylbis (triphenylphosphonium) diiodide (3). 0.094 g (1.2 mmol) of 2-sulfanylethanol and 0.12 g (1.2 mmol) of triethylamine were added at 5°C to a solution of 1 g (1.2 mmol) of but-2-yne-1,4-diylbis(triphenylphosphonium) diiodide **2** in a chloroform–methanol mixture (2 : 1). The reaction mixture was stirred at 5°C during 8 h, and then washed with water. The organic layer was dried with $CaCl_2$, and the solvent was removed in vacuum. The residue was washed sequentially with anhydrous diethyl ether and benzene, and then crystallized from ethyl acetate–methylene chloride mixture, 5 : 1. Yield 0.68 g (69.8%), mp 200–202°C. IR spectrum, ν, cm^{-1}: 3080, 1570, 740, 710, 680. ^{1}H NMR, δ, ppm: 2.6 t (2H, $SC\underline{H}_2CH_2OH$, J = 7.3 Hz), 3.22 t (2H, $SCH_2C\underline{H}_2OH$, J = 7.3 Hz), 3.45 br.s (1H, OH), 4.77 d.d.d (2H, $P^+C\underline{H}_2CH$, ^{1}J = 16.0, ^{2}J = 6.8, ^{3}J = 6.8 Hz), 5.11 d.d (2H, P^+CH_2, ^{1}J = 15.3,

^2J = 2.5 Hz), 6.0–6.11 m (1H, $P^+CH_2C\underline{H}$), 7.6–7.98 m (15H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 26.26 d and 26.86 d (J = 11.2 Hz). Found, %: P 6.45; I 28.12. $C_{42}H_{40}I_2OP_2S$. Calculated, %: P 6.83; I 27.97.

Reactions of phosphonium salt 2 with alkanethiols were performed similarly.

a. Reaction of 1 g (1.2 mmol) of salt **2**, 0.07 g (1.2 mmol) of ethanethiol and 0.12 g (1.2 mmol) of triethylamine gave 0.24 g (30%) of 4-(ethylsulfanyl) buta-1,3-diene-1-yltriphenylphosphonium iodide **4** [1] after recrystallization from ethyl acetate–isopropanol mixture (4 : 1). In addition, 0.26 g (62%) of triphenylphosphine was isolated from the ethereal extract, mp 77–79°C.

b. Reaction of 1.3 g (1.6 mmol) of salt **2**, 0.14 g (1.6 mmol) of butane-1-thiol and 0.16 g (1.6 mmol) of triethylamine gave 0.2 g (23.6%) of 4-(butylsulfanyl)-buta-1,3-dien-1-yltriphenylphosphonium iodide **5** [1] after recrystallization from ethyl acetate–isopropanol mixture (4 : 1). In addition, 0.24 g (57%) of triphenylphosphine was isolated from the ethereal extract.

c. Reaction of 1.3 g (1.6 mmol) of salt **2**, 0.17 g (1.6 mmol) of 3-methylbutane-1-thiol and 0.16 g (1.6 mmol) of triethylamine gave 0.4 g (46%) of 4-[(3-methylbut-1-yl)sulfanyl]buta-1,3-diene-1-yltriphenylphosphonium iodide **6** [1] after recrystallization from ethyl acetate–isopropanol mixture (4 : 1). In addition, 0.27 g (64.4%) of triphenylphosphine was isolated from the ethereal extract.

2-(2-Phenylhydrazinylidene)butane-1,4-diylbis(triphenylphosphonium) diodide (10) [3] and 2-(2-phenylhydrazinyl)but-1-ene-1,4-diylbis(triphenylphosphonium) diiodide (11). A mixture of 1 g (1.2 mmol) of salt **2** and 0.26 g (2.4 mmol) of phenylhydrazine in 15 mL of chloroform was refluxed during 12 h. The reaction mixture was washed with water; the organic layer was dried with $CaCl_2$ and concentrated. The residue was sequentially washed with anhydrous diethyl ether and anhydrous benzene and dried in vacuum to yield 0.62 g (55.1%) of a mixture of compounds **10** and **11** in a ratio of 1 : 2.

2-(2-Phenylhydrazinyl)but-1-ene-1,4-diylbis(triphenylphosphonium) diodide (11). ^1H NMR spectrum, δ, ppm: 2.7–2.81 m (2H, $P^+CH_2C\underline{H}_2$), 4.2–4.35 m (2H, $P^+C\underline{H}_2CH_2$), 5.09 br.s (2H, $N\underline{H}N\underline{H}Ph$), 7.18–7.59 m (6H, P^+CH=, $NHNH\underline{Ph}$), 7.6–8.05 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 19.28, 29.15. Found, %: P 6.23; I 27.42. $C_{46}H_{42}I_2N_2P_2$. Calculated, %: P 6.61; I 27.09.

2-Hydrazinylidenebutane-1,4-diylbis(triphenylphosphonium) diodide (12) and 2,3-dihydrazinylbutane-1,4-diylbis(triphenylphosphonium) diodide (13). 0.17 g (3.2 mmol) of 60% aqueous hydrazine solution was added at 0°C to a solution of 1.3 g (1.6 mmol) salt **2** in 15 mL of chloroform. The reaction mixture was incubated at that temperature for 4 h, and then washed with water. The organic layer was dried with $CaCl_2$, and the solvent was removed in vacuum. The residue was sequentially washed with anhydrous ether and anhydrous benzene and dried in vacuum. Fractional recrystallization from ethyl acetate–isopropyl alcohol (4 : 1) gave 0.3 g (22%) of compound **12** and 0.62 g (43.3%) of salt **13**.

2-Hydrazinylidenebutane-1,4-diylbis(triphenylphosphonium) diodide (12). Mp 222–224°C. ^1H NMR spectrum, δ, ppm: 2.52–2.64 m (2H, $P^+CH_2C\underline{H}_2$), 4.2–4.36 m (2H, $P^+C\underline{H}_2CH_2$), 5.34 d (2H, $P^+C\underline{H}_2C$=N, J = 14.2 Hz), 6.01 br.s (2H, NNH_2), 7.6–7.98 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 28.38, 30.15. Found, %: P 6.83; I 29.72. $C_{40}H_{38}I_2N_2P_2$. Calculated, %: P 7.19; I 29.47.

2,3-Dihydrazinylbutane-1,4-diylbis(triphenylphosphonium) diodide (13). ^1H NMR spectrum, δ, ppm: 1.30 br.s and 1.58 br.s. (4H, $NHN\underline{H}_2$), 3.60–3.71 m (2H, $C\underline{H}N$), 3.83–4.00 m (4H, $P^+C\underline{H}_2CH$), 6.08 d and 6.20 d (2H, $N\underline{H}NH_2$), 7.4–8.0 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 30.04, 30.21. Found, %: P 6.61; I 28.78. $C_{40}H_{42}I_2N_4P_2$. Calculated, %: P 6.94; I 28.41.

3-(2-Benzylhydrazinyl)but-1-ene-1,4-diylbis(triphenylphosphonium) diodide (14) was prepared similarly from 1 g (1.2 mmol) of salt **1** and 0.3 g (2.4 mmol) of benzylhydrazine. Yield 0.78 g (68.6%), mp 165–168°C. ^1H NMR spectrum, δ, ppm: 3.0–3.12 m (4H, $N\underline{H}N\underline{H}C\underline{H}_2Ph$), 3.6–3.72 m (1H, $C\underline{H}NH$), 3.98 d.d.d (1H, $P^+CH^AH^B$, ^1J = 15.6, ^2J = 11.5, ^3J = 6.2 Hz), 4.62 d.d.d (1H, $P^+CH^AH^B$, ^1J = 15.6, ^2J = 13.5, ^3J = 6.2 Hz), 6.52–6.71 m (1H, P^+CH=$C\underline{H}$), 7.04–7.4 m (5H, $CH_2\underline{Ph}$), 7.56 d.d (1H, $P^+C\underline{H}$=CH, ^1J = 24.4, ^2J = 14.8 Hz), 7.62–7.98 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 22.76, 28.21. Found, %: P 6.38; I 27.01. $C_{47}H_{44}I_2N_2P_2$. Calculated, %: P 6.51; I 26.68.

2-(2-Benzylhydrzinylidene)butane-1,4-diylbis(triphenylphosphonium) diodide (15). *a.* A mixture of 1g (1.1mmol) of salt **14** and 0.11 g (1.1 mmol) of triethylamine in 10 mL of chloroform was stirred at room temperature during 12 h. After the solvent removal, the residue was sequentially washed with

anhydrous diethyl ether and anhydrous benzene, dried in vacuum, and recrystallized from ethyl acetate–isopropyl alcohol mixture (4 : 1). Yield 0.76 g (66.7%), mp 204–207°C. ^{1}H NMR spectrum, δ, ppm: 2.65–2.77 m (2H, $P^+CH_2C\underline{H}_2$), 3.67 d (2H, $C\underline{H}_2Ph$, J = 1.3 Hz), 4.23–4.39 m (2H, $P^+C\underline{H}_2CH_2$), 5.37 d (2H, $P^+C\underline{H}_2C{=}N$, J = 14.3 Hz), 6.69 br.s (1H, $N\underline{H}CH_2Ph$), 6.81–6.9 m (2H, H^o), 7.11–7.18 m (3H, $H^{p,m}$), 7.54–8.0 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 28.23, 30.12. Found, %: P 6.79; I 26.92. $C_{47}H_{44}I_2N_2P_2$. Calculated, %: P 6.51; I 26.68.

b. 0.15 g (1.2 mmol) of benzylhydrazine was added at 5°C to a solution of 1 g (1.2 mmol) salt **2** in 15 mL of chloroform–methanol mixture. The reaction mixture was stirred at 5°C during 8 h and then washed with water. The organic layer was dried with $CaCl_2$, and the solvent was removed in vacuum. The residue was sequentially washed with anhydrous diethyl ether and anhydrous benzene and dried in vacuum to yield 0.62 g (55.1%) of a mixture of compounds **15** and **16** in a ratio of 1 : 1.

2-(2-Benzylhydrzinyl)but-1-ene-1,4-diylbis(triphenylphosphonium) iodide (16). ^{1}H NMR spectrum, δ, ppm: 3.07–3.18 m (2H, $P^+CH_2C\underline{H}_2$), 4.05 s (2H, $C\underline{H}_2Ph$), 4.41–4.59 m (2H, $P^+C\underline{H}_2CH_2$), 4.72 br.s (2H, $N\underline{H}N\underline{H}CH_2Ph$), 7.19–7.24 m (6H, $P^+C\underline{H}{=}$, $CH_2\underline{Ph}$), 7.64–8.1 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 18.91, 30.8. Found, %: P 6.35; I 27.12. $C_{47}H_{44}I_2N_2P_2$. Calculated, %: P 6.51; I 26.68.

2-(3,5-Dimethylpyrazol-1-yl)but-1-ene-1,4-diylbis-(triphenylphosphonium) bromide (17) and 2-(3,5-dimethylpyrazol-1-yl)but-2-ene-1,4-diylbis(triphenylphosphonium) bromide (18). A mixture of 0.8 g (1.1 mmol) of but-2-yne-1,4-diylbis(triphenylphosphonium) dibromide and 0.1 g (1.1 mmol) of 3,5-dimethylpyrazole in 15 mL of chloroform was stirred at room temperature during 9 h. Chloroform was removed in vacuum, and the residue was sequentially washed with anhydrous diethyl ether and anhydrous benzene and dried in vacuum to yield 0.7 g (77.8%) of a mixture of compounds **17** and **18** in a ratio of 1 : 4.

2-(3,5-Dimethylpyrazol-1-yl)but-1-ene-1,4-diylbis-(triphenylphosphonium) bromide (17). ^{1}H NMR spectrum, δ, ppm: 1.9 s and 1.95 s (6H, $2CH_3$), 3.18–3.3 m (2H, $P^+CH_2C\underline{H}_2$), 4.27–4.48 m (2H, $P^+C\underline{H}_2CH_2$), 5.64 s (1H-pyrazole), 6.31–6.4 m (1H, $P^+C\underline{H}{=}$), 7.56–7.98 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 26.41 d and 27.09 d (J = 12.5 Hz).

2-(3,5-Dymethypyrazol-1-yl)but-2-ene-1,4-diylbis-(triphenylphosphonium) bromide (18). ^{1}H NMR spectrum, δ, ppm: 1.79 s and 1.84 s (6H, $2CH_3$), 5.12 d.d.d (2H, $P^+C\underline{H}_2CH{=}$, ^1J = 16.1, ^2J= 6.9, ^3J = 5.2, Hz), 5.4 d.d (2H, $P^+C\underline{H}_2C{=}$, ^1J = 15.3, ^2J= 2.4 Hz), 5.43 s (1H-pyrazole), 5.52–5.63 m (1H, $P^+CH_2C\underline{H}{=}$), 7.56–7.98 m (30H, Ph_3P^+). ^{31}P NMR spectrum, δ_P, ppm: 25.56 d and 27.92 d (J = 9.0 Hz). Found, %: P 7.73; Br 19.61. $C_{45}H_{42}Br_2N_2P_2$. Calculated, %: P 7.45; Br 19.23.

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