Basic hydrolysis of 1,4-bis(triphenylphosphonio)buta-1,3-diene dihalides

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Basic hydrolysis of 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride with 10% NaOH gave isomeric 4-diphenylphosphoryl-4-phenylbut-1(2)-enes and 1-diphenylphosphoryl-1-phenylbuta-1,3-diene, the products of anionotropic migration of a phenyl group from the P atom to the α-position. Hydrolysis with Na_2CO_3 afforded only the diene product. In both cases, triphenylphosphine and triphenylphosphine oxide were isolated as secondary products. Dehydrochlorination of 2-chloro-1,4-bis(triphenylphosphonio)but-2-ene dibromide with triphenylphosphine was proposed as a new convenient route to 1,4-bis(triphenylphosphonio)buta-1,3-diene dibromide.

Key words: basic hydrolysis, anionotropic rearrangements, phosphonium salts, dienes, 1,4-bis(triphenylphosphonio)buta-1,3-diene dihalides, phosphine oxides.

1,4-Bis(triphenylphosphonio)buta-1,3-diene salts are known[1] to add nucleophiles A—H independently at both of their C=C bonds. In addition, basic hydrolysis reactions are widely known for triphenylphosphonium salts containing a vinyl group activated with an electron-withdrawing substituent. The hydrolysis is accompanied by anionotropic migration of the phenyl substituent to the α-position of the vinyl group[2,3] (the reaction intermediate is a pentacovalent phosphorus compound resulting from an attack of a hydroxy ion on the phosphonium center). The study of the behavior of such bisphosphonium salts in basic hydrolysis reactions is of certain interest for possible implementation of this migration in both fragments Ph_3P^+—CH=CH, which would afford 1,4-diphosphorylbutadienes.

It turned out that 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (**1a**) reacts with a triple molar excess of ~10% aqueous NaOH even at room temperature to give triphenylphosphine (40%, identified as methyl(triphenyl)phosphonium iodide upon treatment with excess MeI), triphenylphosphine oxide (46%), isomeric 4-diphenylphosphoryl-4-phenylbut-2(1)-enes (**3** and **4**) (total yield 17%, **3** : **4** = 9 : 1), and 1-diphenylphosphoryl-1-phenylbuta-1,3-diene (**5**) (31%). Apparently, the basic hydrolysis of salt **1a** follows two main pathways (*a*) and (*b*) (Scheme 1).

Pathway *a* (see Scheme 1) involves an initial attack of hydroxy ions on either phosphonium center. Subsequent transformations give buta-1,3-dienyl(triphenyl)phosphonium chloride (**2**) and triphenylphosphine oxide. Phosphonium salt **2** undergoes *in situ* anionotropic migration of a phenyl group to the α-position, thus yielding a mixture of two known isomeric phosphine oxides **3** and **4** (earlier,[4] they have been obtained by basic hydrolysis of prepared salt **2**).

Pathway *b* involves initial β-cleavage leading to triphenylphosphine and a phosphonium salt containing a vinylacetylene fragment. Anionotropic migration of a phenyl group to the α-position in this fragment is accompanied by isomerization, which ultimately gives compound **5**.

We also studied basic hydrolysis of salt **1a** with aqueous Na_2CO_3. The hydrolysis products were triphenylphosphine (49%), triphenylphosphine oxide (46%), and phosphine oxide **5** (40%). The absence of rearrangement products **3** and **4** can be explained by a slower direct attack of OH^- ions on the phosphonium center of salt **1a** because of their lower concentration in aqueous Na_2CO_3 compared to NaOH.

To the best of our knowledge, no phosphonium salts with a vinylacetylene fragment have been documented. Apparently, this is due to their instability. The formation of an acetylene intermediate in the β-cleavage has been assumed[5] in the study of a reaction of 1,2-bis(triphenylphosphonio)ethene dichloride (related to salt **1**) with triethylamine in methanol, which gives a β-methoxyvinyl(triphenyl)phosphonium salt.

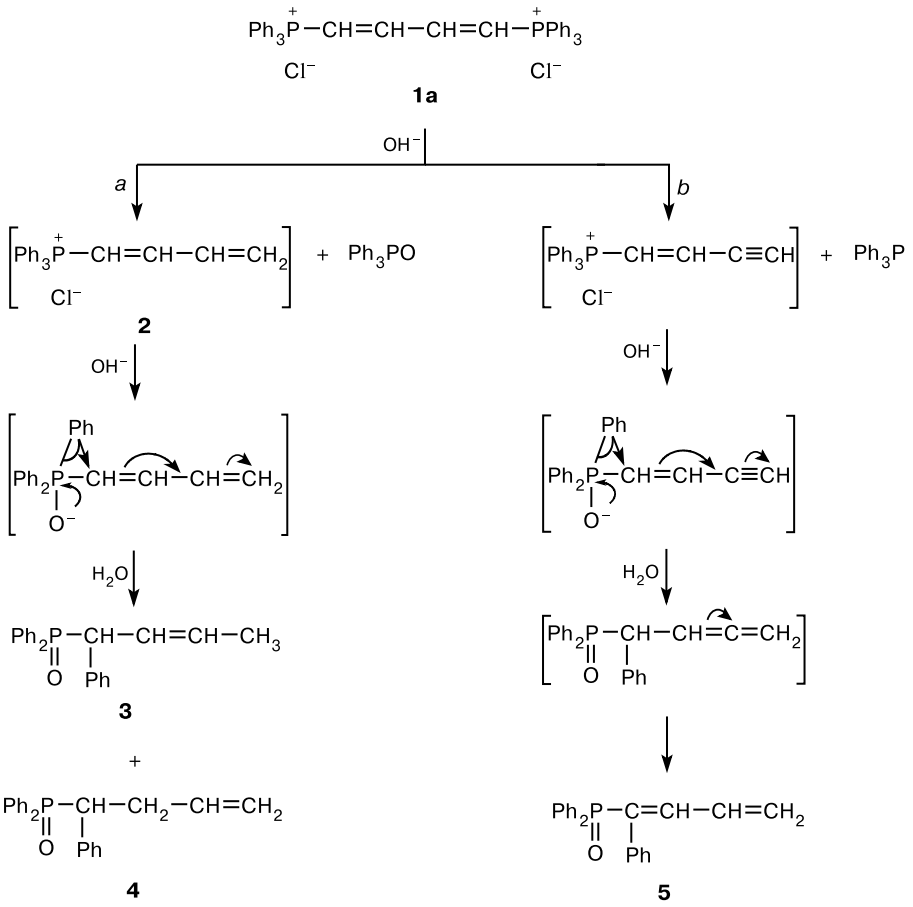
Note that rearranged phosphine oxide **5** has been obtained earlier[6] in 7% yield by hydrolysis of analogous dibromide **1b** under the action of a 20-fold excess of an alcoholic alkali (the proposed[6] pathway of this reaction is shown in Scheme 2).

A reaction of this salt with an equimolar amount of NaOH under phase-transfer conditions (CH_2Cl_2—H_2O)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 548—552, March, 2010.

1066-5285/10/5903-0560

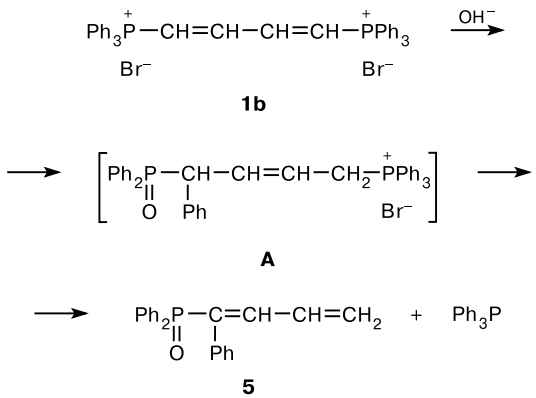
Scheme 1



afforded compound **A** in 70% yield. Under the same conditions, the latter reacts with an equimolar amount of NaOH to give phosphine oxide **5** (40%) and triphenylphosphine (32%).[6]

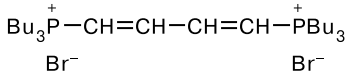
To discover the actual pathway for the formation of product **5** under our experimental conditions, we studied a reaction of salt **1a** with an equimolar amount of ~10% NaOH at room temperature. The reaction gave triphenylphosphine oxide (47%) and isomeric rearrangement products **3** and **4** (total yield 51%); 44% of the starting salt remained intact.

Scheme 2



A comparison of the literature data[6] on the basic hydrolysis of salt **1a** with our data revealed that the reaction outcome depends on the molar ratio of the reagents and the solvent. This is also evidenced by the data on the basic hydrolysis of 1,4-bis(triphenylphosphonio)but-2-ene dihalides under different conditions.[4,7]

In contrast to salt **1a**, the hydrolysis of related 1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (**6**) with ~10% aqueous NaOH was accompanied by strong resinification. Only tributylphosphine (28%) and tributylphosphine oxide (43%) were isolated from the reaction mixture and identified. Resinification was not avoided in the hydrolysis of salt **6** with 10% aqueous Na_2CO_3 at 80—90 °C. The reaction products were tributylphosphine



(45%) and tributylphosphine oxide (43%). Note that at a lower temperature, half of the starting salt was recovered. The fact itself of resinification in the basic hydrolysis of salt **6** provides indirect evidence for the formation of a vinylacetylene intermediate since both this compound and an unsaturated product of its basic hydrolysis (vinylacetylene) strongly tend to polymerize.

According to our data on the hydrolysis of salts **1a** and **6** under the action of both aqueous NaOH and aqueous Na_2CO_3, a main reaction pathway of their hydrolysis seems to involve β-elimination leading to earlier unknown phosphonium salts with an enyne substituent. For isolation of these intermediates, we studied reactions of salts **1a** and **6** with softer bases such as triethylamine and *N*,*N*-dimethyl-*N*-allylamine.

We found that salt **1a** is inert to either amine at both room temperature and when heated in chloroform. Heating of salt **1a** in a tube with an excess of triethylamine in DMF yielded triphenylphosphine (75%), triethylamine hydrochloride (58%), and a large amount of resin. Apparently, it is the enyne-containing phosphonium salt resulting from β-elimination that undergoes resinification, rather than vinylacetylene, a product of its basic reduction. Otherwise, triphenylphosphine oxide would be detected among the reaction products.

A similar pattern was observed in a reaction of salt **1a** with *N*,*N*-dimethyl-*N*-allylamine under the same conditions. Triphenylphosphine was obtained in ~61% yield.

We attempted to obtain a β-elimination product by the action of KF on phosphonium salt **1a**. However, the reaction did not occur even when the mixture was heated in DMSO at 150 °C for several hours.

Reactions of the *cis*-isomer of salt **6** with these amines gave its *trans*-isomer only (^{1}H NMR).

Salt **1a** was prepared in one step by heating triphenylphosphine with 2,3,4-trichlorobut-1-ene in a sealed tube.[8] Longer heating of the components in toluene at 110 °C raised the yield of salt **1a** to 87%.

Salt **1a** can be obtained in two ways: (1) isomerization of diphosphonium salts containing a but-2-ynylene fragment under the action of amines[9] and (2) a reaction of triphenylphosphine with butenoyl bromide.[10] We developed an alternative method for the synthesis of salt **1b** by heating 2-chloro-1,4-bis(triphenylphosphonio)but-2-ene dibromide (**7**) with an equimolar amount of triphenylphosphine in toluene at 70 °C. Apparently, the reaction involves prototropic isomerization and dehydrochlorination (Scheme 3). Triphenylphosphine is completely recovered.

Experimental

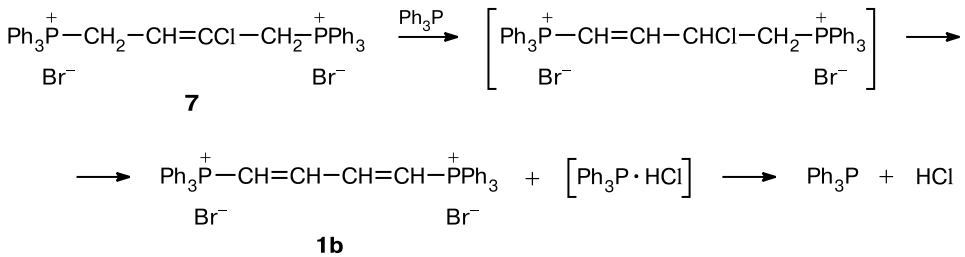
^{1}H and ^{31}P NMR spectra were recorded on a Mercury-300 Varian spectrometer (300.077 MHz (^{1}H)) at 303 K with $SiMe_4$ as the internal standard. The starting salts **1a** and **6** were prepared according to a known procedure;[8,11] their physicochemical parameters agree with the literature data.

Reaction of 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (1a) with aqueous NaOH. ***A.*** A solution of NaOH (0.36 g, 9 mmol) in water (6 mL) was added to 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (**1a**) (2 g, 3.1 mmol). The reaction mixture was stirred for 4 h and the product was extracted with benzene. The benzene extracts were combined and dried with $MgSO_4$. To identify triphenylphosphine, the solution was kept with iodomethane (0.5 g, 3.5 mmol) for 24 h. The precipitate that formed was filtered off, thoroughly washed with anhydrous ether, and dried to give methyl(triphenyl)phosphonium iodide (0.5 g, 1.24 mmol), m.p. 183 °C. Its mixture with the authentic sample did not depress the melting point. Found (%): I, 31.7. $C_{19}H_{18}IP$. Calculated (%): I, 31.43. The filtrate was concentrated and the viscous residue (0.9 g) was recrystallized from ethanol—chloroform. The yield of triphenylphosphine oxide was 0.4 g (46%), m.p. 154 °C. Its mixture with the authentic sample did not depress the melting point. The mother liquor was concentrated and the residue was dried to give a solid (0.5 g) containing a 9 : 1 mixture (0.18 g, 17%) of isomeric 4-diphenylphosphoryl-4-phenylbut-2-ene (**3**) and 4-diphenylphosphoryl-4-phenylbut-1-ene (**4**) and 1-diphenylphosphoryl-1-phenylbuta-1,3-diene (**5**) (0.32 g, 31%) (^{1}H and ^{31}P NMR).

Compound 3. ^{1}H NMR ($CDCl_3$), δ: 1.60 (m, 3 H, =CH—C<u>H</u>$_3$); 4.15 (dd, 1 H, —C<u>H</u>(Ph)—CH=, $^2J_{P,H} = {}^3J_{H,H} = 8.68$ Hz); 5.44 (m, 1 H, =C<u>H</u>—CH$_3$); 5.88 (m, 1 H, —C<u>H</u>=CH—CH$_3$); 7.15—7.95 (m, 15 H, <u>Ph</u>$_2$P(O)—CH(<u>Ph</u>)—). ^{31}P NMR ($CDCl_3$), δ: 32.65 (s, 1 P).

Compound 4. ^{1}H NMR ($CDCl_3$), δ: 2.65, 2.85 (both m, 1 H each, —C<u>H</u>$_2$—CH=); 3.45 (m, 1 H, —C<u>H</u>(Ph)—CH$_2$); 5.45 (m, 3 H, —C<u>H</u>=C<u>H</u>$_2$); 7.15—7.95 (m, 15 H, <u>Ph</u>$_2$P(O)—CH(<u>Ph</u>)—). ^{31}P NMR ($CDCl_3$), δ: 36.30 (s, 1 P).

Scheme 3



The ^{1}H and ^{31}P NMR spectra of compound **5** fully agree with those for its sample obtained from salt **1a** and aqueous Na_2CO_3.

B. A solution of NaOH (0.31 g, 7.75 mmol) in water (2.8 mL) was added to a suspension of salt **1a** (5 g, 7.72 mmol) in water (5 mL). The reaction mixture was stirred for 4 h and the product was extracted with benzene. The benzene extracts were combined and dried with $MgSO_4$. For detection of triphenylphosphine, iodomethane (1.5 g, 10.5 mmol) was added and the solution was left for 24 h. Formation of a precipitate virtually was not observed. The benzene solution was filtered off and concentrated. The resulting waxy solid (2.3 g) was recrystallized from ethanol—chloroform to give triphenylphosphine oxide (1 g, 47%), m.p. 154 °C. Its mixture with the authentic sample did not depress the melting point. The mother liquor was concentrated and the residue was dried to give a solid (1.3 g) consisting of a ~9 : 1 mixture of isomeric 4-diphenylphosphoryl-4-phenylbut-2-ene (**3**) and 4-diphenylphosphoryl-4-phenylbut-1-ene (**4**) (total yield 51%) (^{1}H and ^{31}P NMR).

The product from the aqueous layer was extracted with chloroform; the extract was dried with $MgSO_4$ and concentrated to give the starting salt **1a** (2.2 g, 44%). Its spectroscopic and physicochemical parameters fully agree with those of the authentic sample.

Reaction of 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (1a) with aqueous Na_2CO_3. A solution of Na_2CO_3 (1.3 g, 12.4 mmol) in water (30 mL) was added to a suspension of salt **1a** (2 g, 3.1 mmol) in water (20 mL). The reaction mixture was stirred at 50—55 °C for 2 h and the product was extracted with benzene. The benzene extract was dried with $MgSO_4$ and concentrated. The resulting viscous mass (1.2 g) was thoroughly triturated with hexane. The hexane extracts were combined and concentrated. The residue was dried *in vacuo* to give triphenylphosphine (0.4 g, 49%), m.p. 74—76 °C. Its mixture with the authentic sample did not depress the melting point.

The hexane-insoluble residue was filtered off and dried to give a solid (0.8 g), which was recrystallized from ethanol—chloroform. The yield of triphenylphosphine oxide was 0.4 g (46%), m.p. 154 °C. Its mixture with the authentic sample did not depress the melting point. The mother liquor was concentrated to give 1-diphenylphosphoryl-1-phenylbuta-1,3-diene (**5**) (0.4 g, 40%). ^{1}H NMR ($CDCl_3$), δ: 5.36 (m, 1 H, —CH=C$\underline{H}_2$); 5.53 (m, 1 H, —CH=C$\underline{H}_2$); 6.35 (dddd, 1 H, —C$\underline{H}$=CH$_2$, $^4J_{P,H}$ = = 1.8 Hz, J_1 = 10.9 Hz, J_2 = 16.9 Hz, J_3 = 10.1 Hz); 7.07 (dd, 1 H, —C(Ph)=C$\underline{H}$—, $^3J_{P,H}$ = 18.9 Hz, $^3J_{H,H}$ = 10.9 Hz); 6.95—7.95 (m, 15 H, $\underline{Ph}_2$P(O)—C($\underline{Ph}$)=). ^{31}P NMR ($CDCl_3$), δ: 33.65 (s, 1 P).

The product from the aqueous layer was extracted with chloroform. The starting salt (0.2 g, 0.3 mmol) was isolated from the extract.

Reaction of 1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (6) with aqueous NaOH. A solution of NaOH (0.4 g, 10 mmol) in water (30 mL) was added to salt **6** (2 g, 3.2 mmol). The reaction mixture was stirred under argon at 35—40 °C for 2 h; then the product was extracted with ether. The ethereal extracts were combined, dried with $MgSO_4$, and kept with iodomethane (0.5 g, 3.5 mmol) for 24 h. The precipitate that formed was separated, thoroughly washed with ether, and dried to give tributyl(methyl)phosphonium iodide (0.3 g, 0.87 mmol), m.p. 123 °C. Its mixture with the authentic sample did not depress the melting point. The mother liquor was evaporated to dryness and the residue was dried *in vacuo* to give tributylphosphine oxide (0.3 g, 44%). Its ^{1}H and ^{31}P NMR spectra fully agree with those of the authentic sample.

On the extraction with ether, the insoluble viscous resinous mass contained in the water phase was separated and dried over P_2O_5 to give resin (1.2 g).

Reaction of 1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (6) with aqueous Na_2CO_3. A solution of Na_2CO_3 (1.4 g, 13 mmol) in water (20 mL) was added to salt **6** (2 g, 3.2 mmol). The reaction mixture was stirred under argon at 80—90 °C for 2 h and the product was extracted with benzene. The benzene extracts were combined, dried with $MgSO_4$, and kept with iodomethane (0.5 g, 3.5 mmol) for 24 h. The precipitate that formed was separated, thoroughly washed with ether, and dried to give tributyl(methyl)phosphonium iodide (0.25 g, 0.73 mmol), m.p. 123 °C. Its mixture with the authentic sample did not depress the melting point. The benzene solution was concentrated and the residue was dried to give tributylphosphine oxide (0.3 g, 43%). The product from the aqueous layer was extracted with chloroform; the starting salt **6** (1 g, 1.6 mmol) was isolated from the extract.

The insoluble viscous resinous mass contained in the water phase was separated and dried over P_2O_5 to give resin (0.5 g).

Reaction of 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (1a) with triethylamine. Triethylamine (1.2 g, 12 mmol) was added to a suspension of salt **1a** (2 g, 3.1 mmol) in anhydrous DMF (30 mL). The reaction mixture was heated at 80—90 °C in a sealed tube for 12 h. Then the tube was opened and the DMF-insoluble precipitate was separated, washed with ether, and dried to give triethylamine hydrochloride (0.25 g, 58%), m.p. 253 °C. Its mixture with the authentic sample did not depress the melting point. The solution was concentrated and a resinous residue (1.2 g) was thoroughly washed with ether. The ethereal extracts were combined and concentrated to give triphenylphosphine (0.6 g, 75%), m.p. 74—76 °C. Its mixture with the authentic sample did not depress the melting point.

Reaction of 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (1a) *N*,*N*-dimethyl-*N*-allylamine. *N*,*N*-Dimethyl-*N*-allylamine (2 g, 25 mmol) was added dropwise to a suspension of salt (**1a**) (2 g, 3.1 mmol) in anhydrous DMF (30 mL). The reaction mixture was heated at 80—90 °C in a sealed tube for 12 h and subjected to the work-up described in the preceding entry. The yield of triphenylphosphine was 0.5 g (61.3%).

Reaction of *cis*-1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (*cis*-1b) with triethylamine. A solution of the salt *cis*-**1b** (2 g, 3.2 mmol) in acetonitrile (15 mL) was added dropwise to triethylamine (2.5 g, 25 mmol). The reaction mixture was stirred for 5 h, kept for 24 h, and then concentrated. The residue was washed with anhydrous ether, dried *in vacuo*, and recrystallized from ethyl acetate to give *trans*-1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (1.7 g, 85%), m.p. 213 °C. Found (%): Br, 26.32. $C_{28}H_{58}Br_2P_2$. Calculated (%): Br, 25.97. ^{1}H NMR ($CDCl_3$), δ: 1.00 (t, 18 H, CH_3, J = 6.9 Hz); 1.56 (m, 24 H, C$\underline{H}_2$C$\underline{H}_2$CH$_3$); 2.51 (m, 12 H, PCH_2); 7.54 (dd, 2 H, CH=CH, J_1 = 18.5 Hz, J_2 = 16.0 Hz); 8.43 (dd, 2 H, PCH=, J_1 = 16.0 Hz, J_2 = 13.0 Hz). ^{31}P NMR ($CDCl_3$), δ: 32.8 (s, 2 P).

Reaction of *cis*-1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (*cis*-1b) with (*N*,*N*-dimethyl)allylamine. A solution of the salt *cis*-**1b** (2 g, 3.2 mmol) in acetonitrile (15 mL) was added dropwise to (*N*,*N*-dimethyl)allylamine (2.12 g, 25 mmol). The reaction mixture was stirred for 5 h, kept for 24 h, and subjected to the work-up described in the preceding entry. The yield of *trans*-**1b** was 1.6 g (80%).

Reaction of 2,3,4-trichlorobut-1-ene with triphenylphosphine. A solution of 2,3,4-trichlorobut-1-ene (18.3 g, 0.115 mol) in toluene (30 mL) was added to a solution of triphenylphosphine (60 g, 0.23 mol) in anhydrous toluene (120 mL). The reaction mixture was stirred at 110 °C for 48 h. The solvent was decanted and the residue was thoroughly washed with anhydrous ether, dried *in vacuo*, and recrystallized from chloroform. The yield of 1,4-bis(triphenylphosphonio)buta-1,3-diene dichloride (**1**) was 65 g (87%). Found (%): Cl, 10.53. $C_{40}H_{34}Cl_2P_2$. Calculated (%): Cl, 10.97. Its physicochemical parameters fully agree with the literature data.[8]

Reaction of 2-chloro-1,4-bis(triphenylphosphonio)but-2-ene dibromide (7) with triphenylphosphine. A solution of triphenylphosphine (0.35 g, 1.33 mmol) in toluene (10 mL) was added to a suspension of salt **7** (1 g, 1.3 mmol) prepared from triphenylphosphine and 1,4-dibromo-2-chlorobut-2-ene in anhydrous toluene (15 mL). The reaction mixture was stirred at 70 °C for 6 h. The solvent was decanted and the precipitate was thoroughly washed with ether and dried *in vacuo* to give a powder (0.8 g), which was recrystallized from chloroform. The yield of 1,4-bis(triphenylphosphonio)buta-1,3-diene dibromide (**1b**) was 0.75 g (77%), m.p. 295 °C. Found (%): Br, 21.6. $C_{40}H_{34}Br_2P_2$. Calculated (%): Br, 21.74. ^{1}H NMR ($CDCl_3$), δ: 7.80 (m, 30 H, C_6H_5); 8.25 (dd, 2 H, $P^+CH{=}C\underline{H}$, $^3J_{P,H}$ = 21.6 Hz, $J_{H,H}$ = 14.7 Hz); 9.15 (dd, 2 H, $P^+CH{=}$, $^2J_{P,H}$ = 24.4 Hz, $J_{H,H}$ = 14.8 Hz). ^{31}P NMR ($CDCl_3$), δ: 23.8 (s, 2 P). The organic extracts were combined and concentrated to give triphenylphosphine (0.33 g), m.p. 74—76 °C. Its mixture with the authentic sample did not depress the melting point.

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Received February 10, 2009;
in revised form October 20, 2009