Reactions of tertiary phosphines with (3-chlorobuta-1,3-dienyl)(trimethyl)ammonium chloride

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Tributylphosphine reacts with (3-chlorobuta-1,3-dienyl)(trimethyl)ammonium chloride to give 1,2,4-tris(tributylphosphonio)but-3-en-1-ide dichloride; triethylphosphine reacts in a similar way. Triphenylphosphine is inert to the above ammonium salt; whereas an analogous tris(triphenylphosphonium) derivative can be obtained from (3,4-dichlorobut-2-enyl)-(trimethyl)ammonium chloride.

Key words: tributylphosphine, triphenylphosphine, phosphonium derivatives, dienes, nucleophilic substitution, ammonium derivatives.

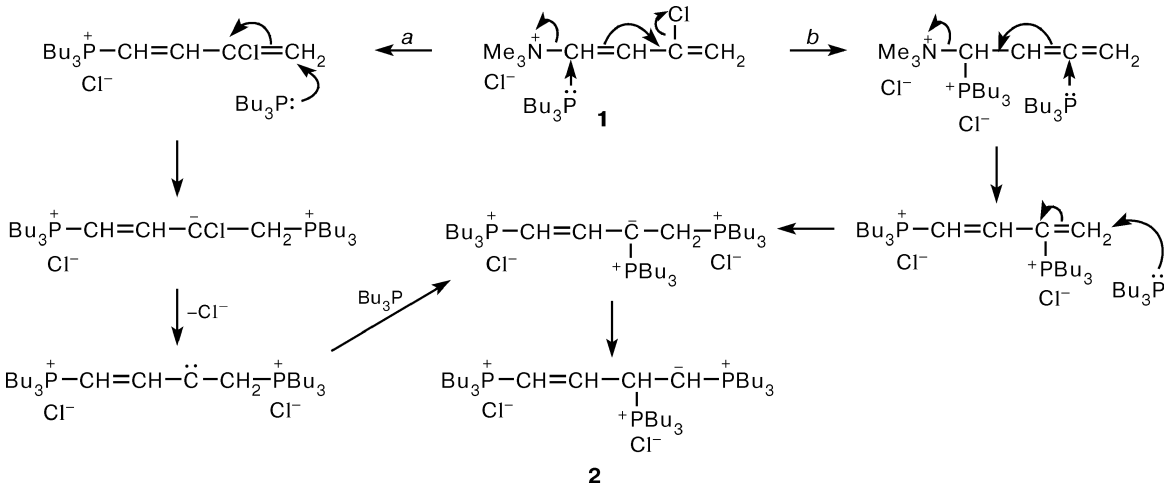
It is known[1—3] that trialkyl(vinyl)ammonium salts, in contrast to structurally similar sulfonium and phosphonium salts, are inert in nucleophilic addition reactions because the N atom has no *d* orbitals (the *d* orbitals of atoms of the higher periods can participate in their resonance stabilization). In addition, various rearrangements of base-generated ammonium ylides are widely known.[4] Recently,[5] we have found that triphenylphosphine and pyridine easily react with vinylpyridinium halides to give nucleophilic addition products.

In connection with this, it was interesting to study reactions of conjugated dienylammonium salts with phosphorus nucleophiles.

We studied (3-chlorobuta-1,3-dienyl)(trimethyl)ammonium chloride (**1**). Its reaction with tributylphosphine even at room temperature gave fairly stable 1,2,4-tris-(tributylphosphonio)but-3-en-1-ide dichloride (**2**) in high yield (Scheme 1).

Apparently, ylide **2** results either from direct nucleophilic displacement of trimethylamine by tributylphos-

Scheme 1



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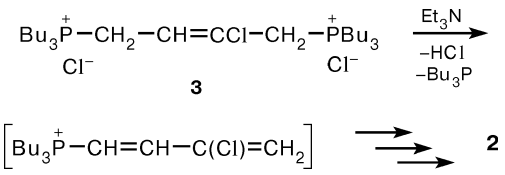
phine (see Scheme 1, pathway *a*) or from anomalous nucleophilic displacement of the Cl atom at the α-sp^2-hybridized C atom in salt **1** (see Scheme 1, pathway *b*). The formation of 1,4-bis(tributylphosphonio)buta-1,3-diene dichloride as a reaction intermediate is less probable (earlier,[6] we have demonstrated that tributylphosphine does not add to the double bonds of such a dibromide). The possibility of pathway *a* for this reaction is partially confirmed by data from another experiment (Scheme 2). Treatment of salt **3** with triethylamine gave compound **2** along with tributyl(3-chlorobuta-1,3-dienyl)phosphonium chloride and some unidentified products (^{31}P NMR).

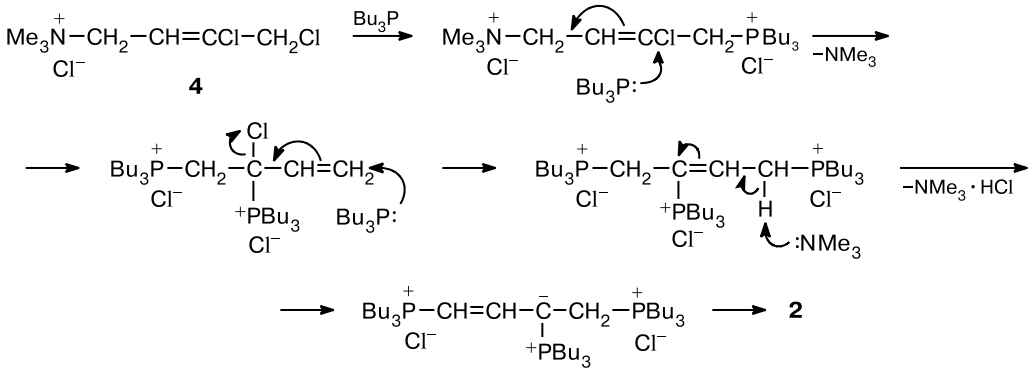
Scheme 2



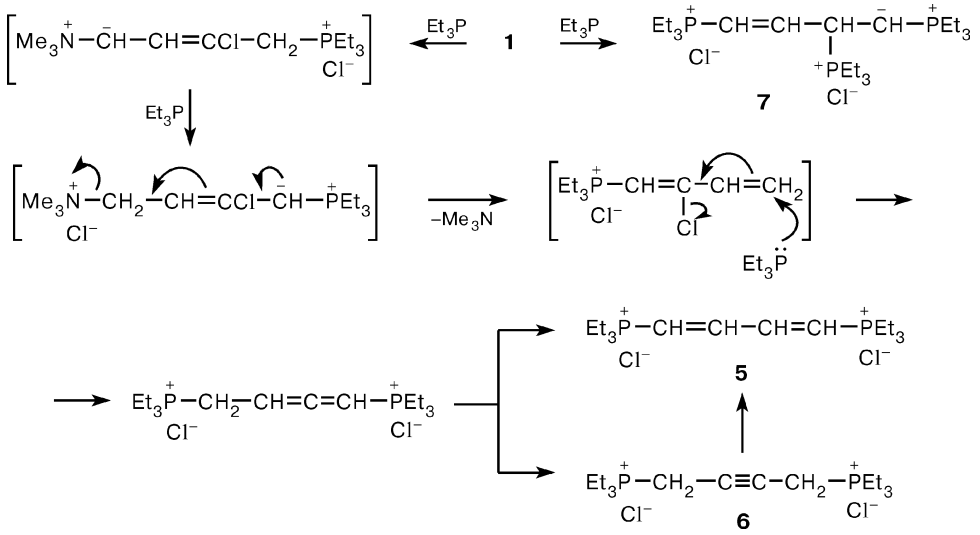
Compound **2** was also obtained in high yield by a reaction of (3,4-dichlorobut-2-enyl)(trimethyl)ammonium chloride (**4**) with a double molar excess of tributylphosphine (Scheme 3). Trimethylamine hydrochloride (44%) was another reaction product. It should be noted that the use of a triple molar excess of tributylphosphine in the same reaction did not increase the yield of the final product. Apparently, the reaction proceeds through the formation of a mixed ammonium phosphonium salt. Plausible initial 1,4-dehydrochlorination to ammonium salt **1** seems to be very unlikely because highly nucleophilic tributylphosphine is a weak base.

We also studied reactions of ammonium salt **1** with triethyl- and triphenylphosphines (Scheme 4). The former reaction yielded a mixture of 1,4-bis(triethylphosphonio)-buta-1,3-diene dichloride (**5**) and 1,4-bis(triethylphosphonio)but-2-yne dichloride (**6**), which were identified

Scheme 3



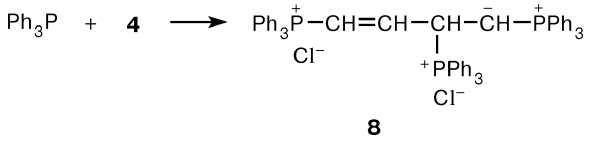
Scheme 4



using ^{1}H and ^{31}P NMR spectroscopy. In addition, tris(triethylphosphonio) ylide **7** (a homolog of ylide **2**) was isolated. Apparently, the formation of ylide **7** follows the same scheme as in the case of ylide **2**. A possible pathway to salts **5** and **6** is shown in Scheme 4 involving initial addition of triethylphosphine to the terminal C atom of the diene system in salt **1** followed by transylidation and decomposition. The intermediate (2-chlorobuta-1,3-dienyl)phosphonium salt reacts with a second triethylphosphine molecule according to the anomalous nucleophilic substitution pattern to give an allene-containing diphosphonium salt which isomerizes *in situ* into salts **5** and **6**.

Unlike trialkyl analogs, triphenylphosphine is inert to salt **1**, yet easily reacting with salt **4**. The resulting tris(triphenylphosphonio) ylide **8** (^{31}P NMR) is structurally similar to compound **2** (Scheme 5). Unfortunately, the ^{1}H NMR spectrum of compound **8** is not very informative because of its complicated pattern. Trimethylamine hydrochloride was also isolated from the reaction products. In this case, as in the reaction of tributylphosphine with salt **4**, the use of a triple molar excess of phosphine did not increase the yield of the target product.

Scheme 5



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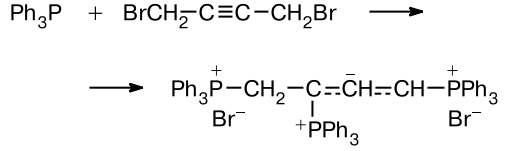
The reaction with triphenylphosphine, in contrast to that with tributylphosphine, unambiguously proceeds through the formation of a mixed ammonium phosphonium salt, following the pattern cited above for the tributylphosphonium derivative.

Note that a reaction of triphenylphosphine with 1,4-dibromobut-2-yne[7] yields trisphosphonium salt **9** (Scheme 6) with different parameters of the ^{31}P NMR spectrum. Its cationic part is isomeric to that of compound **8** (see Scheme 3).

Scheme 6



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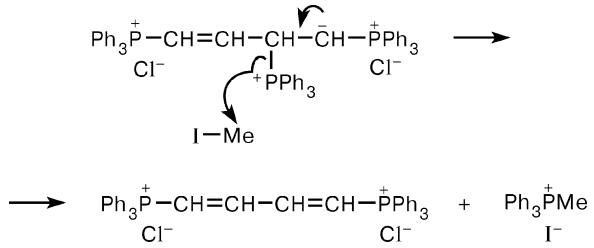
We showed qualitatively that trisphosphonium salt **8** completely decomposes under the action of iodomethane to give a mixture of compounds. Small amounts of methyl(triphenyl)phosphonium iodide and a dienediphosphonium salt were isolated and identified. Scheme 7 displays a possible pathway to these compounds.

Scheme 7



Phosphonio ylide **2** is more stable than trisphosphonio ylide **8** in reactions with iodomethane and phenylacetyl chloride.

Hence, one can suggest that tributyl- and triethylphosphines react with ammonium salt **1** according to the anomalous or direct nucleophilic substitution at its α-sp^2-hybridized C atom.

Experimental

^{1}H, ^{13}C, 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 **1** and **3** were prepared according to a known procedure.[6] Their physicochemical parameters agree with the literature data. The yields of trisphosphonio ylides were calculated with respect to phosphine.

Reaction of (3-chlorobuta-1,3-dienyl)(trimethyl)ammonium chloride (1) with tributylphosphine. A solution of (3-chlorobuta-1,3-dienyl)(trimethyl)ammonium chloride (1.3 g, 7 mmol) in methanol (30 mL) was added dropwise under argon to tributylphosphine (2.8 g, 14 mmol). The reaction mixture was stirred for 4 h and left for two days. The solvent was removed and the residue was thoroughly washed with anhydrous ether and dried *in vacuo*. The resulting solid (3.2 g) was recrystallized from chloroform—ethyl acetate to give salt **1** (0.6 g). The mother liquor was concentrated to give 1,2,4-tris(tributylphosphonio)but-3-en-1-ide dichloride (**2**) (2.4 g, 72%). Found (%): Cl, 9.51; P, 12.62. $C_{40}H_{85}Cl_2P_3$. Calculated (%): Cl, 9.74; P, 12.75. ^{1}H NMR ($CDCl_3$), δ: 0.97 (m, 27 H, CH_3); 1.43—1.72 (m, 36 H, CH_2CH_2); 2.40—2.90 (m, 18 H, PCH_2); 4.69 (m, 1 H, $PC^-H(1)$); 5.76 (m, 1 H, CH(2)); 7.78 (ddd, 1 H, CH(3), J_1 = 18.9 Hz, J_2 = 16.7 Hz, J_3 = 3.8 Hz); 7.98 (ddd, 1 H, CH(4), J_1 = 18.9 Hz, J_2 = 16.7 Hz, J_3 = 4.2 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.56 (3 C, CH_3); 13.66 (3 C, CH_3); 13.69 (3 C, CH_3); 18.29 (d, 3 C, PCH_2, $^1J_{P,C}$ = 42.3 Hz); 19.55 (d, 3 C, PCH_2, $^1J_{P,C}$ = 44.3 Hz); 19.76 (d, 3 H, PCH_2, $^1J_{P,C}$ = 48.4 Hz); 23.95—24.49 (m, 18 C, $PCH_2C\underline{H}_2C\underline{H}_2$); 31.54 (ddd, 1 C, PC^-H, $^1J_{P,C}$ = 42.5 Hz, $^2J_{P,C}$ = 18.4 Hz, $^4J_{P,C}$ = 2.0 Hz); 53.58 (ddd, 1 C, PCH, $^1J_{P,C}$ = 96.2 Hz, $^2J_{P,C}$ = 43.9 Hz, $^3J_{P,C}$ = = 2.5 Hz); 151.53 (m, 1 C, =CH); 118.49 (ddd, 1 C, =CHP, $^1J_{P,C}$ = 72.8 Hz, $^3J_{P,C}$ = 10.4 Hz, $^4J_{P,C}$ = = 2.9 Hz). ^{31}P NMR ($CDCl_3$), δ: 31.10 (d, 1 P, $J_{P,P}$ = 5.8 Hz); 43.18 (d, 1 P, $J_{P,P}$ = = 38.1 Hz); 44.60 (dd, 1 P, J_1 = 38.1 Hz, J_2 = 5.8 Hz).

Reaction of *E,Z*-1,4-bis(tributylphosphonio)buta-1,3-diene dibromide with tributylphosphine. A solution of *E,Z*-1,4-bis(tri-

butylphosphonio)buta-1,3-diene dibromide (0.36 g, 0.6 mmol) in acetonitrile (15 mL) was added dropwise under argon to tributylphosphine (0.12 g, 0.6 mmol). The reaction mixture was stirred for 5 h, left for 24 h, and then concentrated. The residue was washed with anhydrous ether, dried *in vacuo*, and recrystallized from ethyl acetate to give *E*,*E*-1,4-bis(tributylphosphonio)buta-1,3-diene dibromide (0.3 g, 83%), m.p. 213 °C. Found (%): Br, 26.04. $C_{28}H_{58}Br_2P_2$. 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, $C\underline{H}_2C\underline{H}_2CH_3$); 2.51 (m, 12 H, PCH_2); 7.54 (dd, 2 H, C=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 (3,4-dichlorobut-2-enyl)(trimethyl)ammonium chloride (4) with tributylphosphine. A solution of (3,4-dichlorobut-2-enyl)(trimethyl)ammonium chloride (**4**) (1.3 g, 6 mmol) in methanol (30 mL) was added dropwise under argon to tributylphosphine (2.4 g, 12 mmol). The reaction mixture was stirred for 3 h, left for 24 h, and then concentrated. The residue was diluted with chloroform and the precipitate that formed was filtered off. The filtrate was concentrated and the residue was washed with anhydrous ether and dried *in vacuo*. The resulting viscous solid (3 g) was worked up as described above to give salt **4** (0.6 g), trimethylamine hydrochloride (0.25 g, 44%), and trisphosphonio ylide **2** (2.4 g, 82%).

Reaction of 3-chloro-1,4-bis(tributylphosphonio)but-2-ene dibromide (3) with triethylamine. Triethylamine (0.45 g, 4.4 mmol) was added dropwise to a solution of compound **3** (3.4 g, 4.4 mmol) in chloroform (20 mL). The reaction mixture was stirred at −5 °C for 8 h and then concentrated. The residue was washed with ether, dried, and recrystallized from chloroform—ethyl acetate to give the starting salt (1.4 g, 1.8 mmol). The mother liquor was concentrated and a powdery solid (1.9 g) was isolated. According to ^{31}P NMR data, the solid contained compound **2** and unidentified reaction products.

Reaction of (3-chlorobuta-1,3-dienyl)(trimethyl)ammonium chloride (1) with triethylphosphine. A solution of salt **1** (1.1 g, 6 mmol) in methanol (10 mL) was added dropwise under argon to a solution of triethylphosphine (1.45 g, 12 mmol) in methanol (10 mL). The reaction mixture was left at 6 °C for 24 h and then concentrated. The residue was thoroughly washed with anhydrous ether and dried *in vacuo*. The resulting solid (2.5 g) was recrystallized from chloroform—ethyl acetate to give a powdery solid (1.3 g). According to ^{1}H NMR data, the latter consisted of salt **6** (0.3 g, 0.83 mmol) and salt **5** (1 g, 2.78 mmol). The filtrate was concentrated and the residue was washed with anhydrous ether and dried *in vacuo* to give trisphosphonio ylide **7** (1.2 g, 2.51 mmol).

Compound **5**. Found (%): Cl, 19.77. $C_{16}H_{34}Cl_2P_2$. Calculated (%): Cl, 19.65. ^{1}H NMR (DMSO-d_6), δ: 1.1 (m, 18 H, CH_3); 2.5 (m, 12 H, $C\underline{H}_2CH_3$); 7.14 (dd, 2 H, J_1 = 18.5 Hz, J_2 = = 16.0 Hz), 7.95 (dd, 2 H, J_1 = 16.0 Hz, J_2 = 13.0 Hz). ^{31}P NMR (DMSO-d_6), δ: 39.0 (s, 2 P).

Compound **6**. ^{1}H NMR (DMSO-d_6), δ: 1.1 (m, 18 H, CH_3); 2.35 (m, 12 H, $C\underline{H}_2CH_3$); 3.46 (d, 4 H, PCH_2, $^2J_{P,H}$ = 10.5 Hz). ^{31}P NMR (DMSO-d_6), δ: 43.18 (s, 2 P).

Compound **7**. Found (%): Cl, 14.67; P, 19.28. $C_{22}H_{49}Cl_2P_3$. Calculated (%): Cl, 14.88; P, 19.50. ^{31}P NMR (DMSO-d_6), δ: 37.40 (d, 1 P, $J_{P,P}$ = 6.5 Hz); 48.70 (d, 1 P, $J_{P,P}$ = 41.0 Hz); 51.0 (dd, 1 P, $J_{P(1),P}$ = 41.0 Hz, $J_{P(2),P}$ = 6.5 Hz).

Reaction of (3,4-dichlorobut-2-enyl)(trimethyl)ammonium chloride (4) with triphenylphosphine. A solution of compound **4** (1.5 g, 7 mmol) in methanol (20 mL) was added dropwise to a solution of triphenylphosphine (1.8 g, 7 mmol) in methanol (30 mL). The reaction mixture was stirred for 3 h, left for 3 days, and then concentrated. The residue was washed with anhydrous ether, dried *in vacuo*, and concentrated to give triphenylphosphine (0.6 g, 2.3 mmol). Water and chloroform were added to the resulting hygroscopic powder (2.7 g) and the aqueous layer was separated and concentrated. Recrystallization of the residue from ethyl acetate—isopropyl alcohol gave trimethylamine hydrochloride (0.1 g). The chloroform extract was dried over $MgSO_4$ and concentrated. The residue was washed with anhydrous ether and dried *in vacuo*. The yield of 1,2,4-tris(triphenylphosphonio)but-3-en-1-ide dichloride (**8**) was 1 g (47%). Found (%): Cl, 7.69; P, 10.17. $C_{58}H_{49}Cl_2P_3$. Calculated (%): Cl, 7.81; P, 10.23. ^{31}P NMR ($CDCl_3$), δ: 23.0 (d, 1 P, $J_{P,P}$ = 7.8 Hz); 28.55 (d, 1 P, $J_{P,P}$ = 43.0 Hz); 36.2 (dd, 1 P, J_1 = 43.0 Hz, J_2 = 7.8 Hz).

Reaction of ylide 2 with phenylacetyl chloride. A solution of phenylacetyl chloride (0.17 g, 1.1 mmol) in chloroform (5 mL) was added dropwise to a solution of ylide **2** (0.8 g, 1.1 mmol) in chloroform (10 mL). The mixture was refluxed for 4 h, kept at room temperature for 48 h, and then concentrated. The residue was washed with anhydrous ether and dried *in vacuo* to give ylide **2** (0.8 g, 1.1 mmol).

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