Russian Chemical Bulletin, International Edition, Vol. 50, No. 11, pp. 2095—2100, November, 2001

Organic Chemistry

Cross-coupling of *E*,*E*-1,4-diiodobuta-1,3-diene with nucleophiles catalyzed by Pd or Ni complexes: a new route to functionalized dienes

I. G. Trostyanskaya, D. Y. Titskiy, E. A. Anufrieva, A. A. Borisenko, M. A. Kazankova,★ and I. P. Beletskaya★

Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 3618. E-mail: kazank@org.chem.msu.ru; beletska@org.chem.msu.ru

E,*E*-1,4-Diiodobuta-1,3-diene can enter into cross-coupling reactions with carbon- or other element-centered nucleophiles in the presence of Pd or Ni complexes as catalysts. Convenient procedures were developed for the stereoselective synthesis of *E*,*E*-1,4-dialkenylbuta-1,3-dienes, dienyl-1,4-bisphosphonates, *E*,*E*-1,4-bis(diphenylphosphino)buta-1,3-diene, *E*,*E*-1,4-diphenylbuta-1,3-diene, and *E*,*E*-1,4-bis(thiophenyl)buta-1,3-diene.

Key words: *E*,*E*-1,4-diiodobuta-1,3-diene, alkynes, phosphines, phosphonates, palladium and nickel complexes, catalysis.

Functionalized butadienes are of considerable interest in the preparative chemistry because they are widely used in important organic syntheses, such as the Diels—Alder reactions,[1—3] heteroannelation of 1,3-dienes,[4,5] *etc.*, for the regio- and stereoselective preparation of various carbo- and heterocyclic systems, including useful biologically active compounds and analogs of natural substances.[6—9] 1,4-Dihalobutadienes have a particularly high synthetic potential.[10—14] These compounds are precursors of 1,4-dienyl dianions generated upon the halogen—metal exchange. These transformations of 1,4-dihalobutadienes and, in particular, 1,4-diiodobutadienes provide the basis for the synthesis of most of metallacyclopentadiene derivatives (siloles, germoles, stannoles, phospholes,[15,16] *etc.*) and 1,1′-diheteroferrocenes.[17,18] At the same time, 1,4-dihalobutadienes can be used as synthetic equivalents of 1,4-dienyl dications in cross-coupling with various nucleophilic reagents catalyzed by transition metal complexes. However, this type of transformations of 1,4-dihalobutadienes has not been adequately explored[19,20] and only a few examples of the cross-coupling reactions of monoiodobuta-1,3-dienes were reported.[21—23]

Recently, a procedure has been developed for the synthesis of the previously unavailable *E*,*E*-1,4-diiodobuta-1,3-diene (**1**). This procedure is based on the Pt^{IV}-catalyzed reaction of acetylene with the iodide ion in the presence of iodine.[24,25]

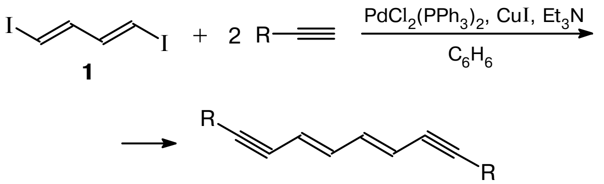
It should be noted that *Z*,*Z*-1,4-diiodobuta-1,3-diene has been prepared previously according to a three-stage procedure from 1,4-dichloro-2-butyne[10] and has been detected upon pyrolysis of 1,2-diiodocyclobutene at 120 °C.[26]

In the present study, we examined cross-coupling of 1,4-diiodobuta-1,3-diene (**1**) with a series of carbon- and other element-centered nucleophiles catalyzed by Pd or Ni complexes, which gave rise to new $C_{sp^2}—C_{sp}$ and C_{sp^2}-heteroatom bonds.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 2003—2007, November, 2001.

Cross-coupling of *E*,*E*-1,4-diiodobuta-1,3-diene (**1**) with terminal alkynes is of interest as a route to polyunsaturated compounds, including biologically active substances (for example, pheromones[27,28]), because these reactions allow one to insert the four-carbon unsaturated fragment into the molecule in one step.

The reactions of 1,4-diiodobuta-1,3-diene with two equivalents of terminal alkynes according to Sonogashira,[29] unlike analogous reactions of 1,4-diiodo-1,2,3,4-tetraethylbuta-1,3-diene with hex-1-yne,[30] proceeded smoothly under mild conditions (~20 °C, 30 min) to give the corresponding *E*,*E*-1,4-dialkynylbuta-1,3-dienes (**2a—c**) in quantitative yields.

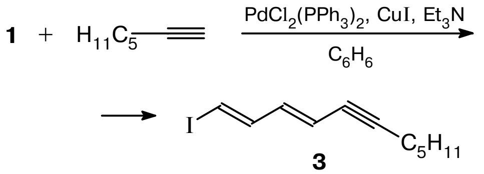


1

2a—c

R = Ph (**a**), Me_3Si (**b**), C_5H_{11}-*n* (**c**)

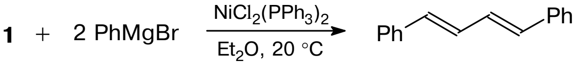
The reaction of **1** with hept-1-yne can be performed in several steps. Within 20 min after the addition of 4 mol.% of bis(triphenylphosphino)palladium chloride and copper iodide to a mixture of equimolar amounts of compound **1**, hept-1-yne, and triethylamine in benzene at 20 °C, diene **3** was obtained in 80% yield as a result of the replacement of one iodine atom in diene **1**, whereas heating of diiododiene **1** with 2 equivalents of heptyne at 70 °C for 3 h in the presence of the same catalytic system afforded the corresponding dienediyne **2c** in 95% yield.



3

Octa-3,5-diene-1,7-diynes **2a—c** are heavy oils, which are readily polymerized at room temperature but are stable upon storage at low temperature or in solution. Their compositions and structures were confirmed by the data from elemental analysis and IR spectroscopy and by the ^1H and ^{13}C NMR spectra. Cross-coupling of **1** with alkynes proceeded stereoselectively with complete retention of the configurations of the double bonds.

The reaction of *E*,*E*-1,4-diiodobuta-1,3-diene (**1**) with phenylmagnesium bromide in the presence of bis(triphenylphosphino)nickel dichloride (5 mol.%) also proceeded smoothly. At 20 °C, the reaction in ether was completed in 1.5 h to produce diene **4** in 89% yield.

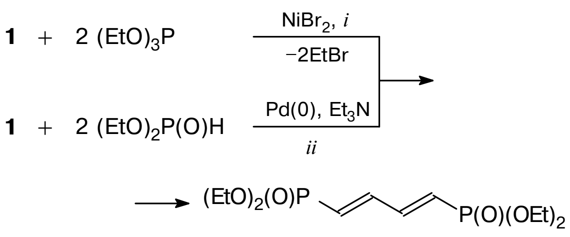


4

Previously, *E*,*E*-1,4-diphenylbuta-1,3-diene (**4**) has been prepared in ~60% yield by the Horner—Wittig reaction of cinnamaldehyde with diethyl benzylphosphonate.[31] This compound finds many applications, for example, in cycloaddition reactions[32,33] and as a component of catalytic systems based on Zr or Ti, which are used in polymerization of olefins.[34,35]

Dienylphosphonates are of considerable synthetic interest as dienophiles or Michael acceptors and the possibility of their application in the organic synthesis has been examined extensively in recent years.[36] Thus 1,3-dienylphosphonates proved to be useful intermediates in the Diels—Alder reactions for the preparation of bi- and polycyclic systems[37] and in the synthesis of biologically active compounds.[38] In addition, some of these compounds possess biological activities by themselves.[39] At the same time, dienylphosphonates are difficultly accessible compounds due to which they are of limited synthetic usefulness and the syntheses of these compounds are few in number.[40—43]

We found that tetraethyl *E*,*E*-buta-1,3-diene-1,4-diyldiphosphonate (**5**) can be prepared in one step either by the Arbuzov reaction of 1,4-diiodobuta-1,3-diene (**1**) with triethyl phosphite catalyzed by a zero-valent nickel complex[44—46] and or by cross-coupling of diethylphosphorous acid with diiododiene **1** in the presence of tetrakis(triphenylphosphino)palladium (10 mol.%).[46—48]

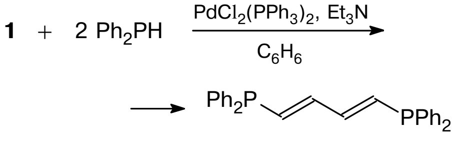


5

i. 110 °C, 15 min *ii*. 20 °C, 1.5 h.

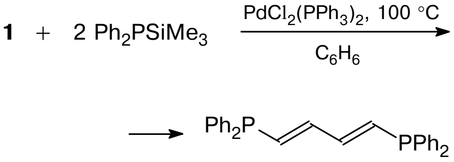
Diene-1,4-diylbisphosphonate **5** occurs as a viscous oil. After removal of the solvent and keeping *in vacuo* with the use of an oil pump for the purpose of removing low-boiling impurities, spectrally pure compound **5** was obtained. Its ^{31}P NMR spectrum has the only signal at δ_P 17.68. The reaction proceeded stereoselectively with retention of the configuration of the double bond to give phosphonate **5** in quantitative yield. The structure of **5** was confirmed by the ^{31}P, ^{13}C, and ^1H spectroscopic data. It should be noted that the procedure developed by us allows one to substantially simplify the synthesis of this compound, which has been prepared previously[49] in 60% yield from 1,4-dibromobut-2-ene according to a multistage procedure.

Previously, we have proposed[50] the Pd-catalyzed synthesis of alkenylphosphines from alkenyl halides and secondary phosphines. In the present study, we examined the possibility of the application of this procedure to the synthesis of new types of tertiary phosphines, in particular, of *E*,*E*-1,4-bis(diphenylphosphino)buta-1,3-diene (**6**).



6

The addition of bis(triphenylphosphino)palladium dichloride (5 mol.%) to a mixture of 1,4-diiodobuta-1,3-diene (**1**), diphenylphosphine, and thriethylamine in benzene was accompanied by the exothermic effect. After 30 min, the ^{31}P NMR spectrum of the reaction mixture had the only signal at δ_P −12.88 corresponding to 1,4-bis(diphenylphosphino)buta-1,3-diene (**6**), whereas the signal at δ_P −41.6 of the initial diphenylphosphine disappeared. Diphosphine **6** was isolated in high yield (Table 1). Its composition and structure were confirmed by the data from elemental analysis and ^1H, ^{13}C, and ^{31}P NMR spectroscopy. An analogous reaction of **1** with trimethylsilyldiphenylphosphine in the presence of $PdCl_2(PPh_3)_2$ proceeded under substantially more drastic conditions and was completed in 9 h upon heating at 90—100 °C.



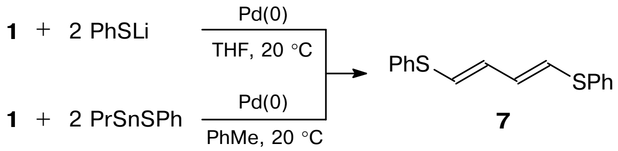
6

The newly synthesized diphosphine **6** exists as pale-yellow crystals, which are stable upon storage under an inert atmosphere.

Buta-1,3-diene-1,4-dithiols are precursors in the synthesis of an important class of analogs of natural biologically active compounds, *viz.*, thiarubrines, belonging to the class of 1,2-dithiynes (1,2-dithiacyclohexadienes).[51,52]

1,4-Di-*RS*-substituted buta-1,3-dienes can be prepared by the nucleophilic addition of thiols to 1,4-disubstituted diynes.[53,54]

We devised a new procedure for the synthesis of 1,4-di(arylthio)butadienes based on *E*,*E*-diiodobuta-1,3-dienes. The reaction of **1** with the lithium salt of thiophenol in THF in the presence of tetrakis(triphenylphosphino)palladium (4 mol.%) gave rise to *E*,*E*-1,4-bis(phenylthio)buta-1,3-diene (**7**) in 90% yield.



7

The reaction of **1** with tripropylphenylthiostannane catalyzed by the tetrakis(triphenylphosphino)palladium complex (at room temperature) afforded 1,4-bis(phenylthio)buta-1,3-diene (**7**) in somewhat lower yield (82%). In both cases, the nucleophilic substitution and cross-coupling proceeded with complete retention of the configuration of the double bond.

To summarize, we developed a procedure for the synthesis both of the known and new types of 1,4-difunctionalized butadienes based on cross-coupling of *E*,*E*-1,4-diiodobutadiene with various nucleophiles, which gave rise to C_{sp^2}—C_{sp^2}/C_{sp} and C_{sp^2}—heteroatom bonds. Investigations on the use of the catalytic reactions of 1,4-diiodobutadienes with nucleophiles with the aim of introducing other functional groups (−NR_2, −OR, *etc.*) are being continued.

Experimental

All reactions and operations associated with the synthesis, isolation, and generation of trivalent phosphorus compounds, organometallic compounds, or their complexes in the reaction mixtures were carried out under an atmosphere of dry argon. The solvents were dried according to standard procedures: benzene, toluene, THF, diethyl ether, and light petroleum ether were refluxed over sodium in the presence of benzophe-

Table 1. Reaction conditions and products of cross-coupling of *E*,*E*-1,4-diiodobuta-1,3-diene with nucleophilic reagents

Reagent	Catalyst	Base	Solvent	*T*/°C	τ/h	Product	Yield (%)
Ph—≡	$PdCl_2(Ph_3P)_2$, CuI	Et_3N	PhH	20	0.5	**2a**	98
Me_3Si—≡	$PdCl_2(Ph_3P)_2$, CuI	Et_3N	PhH	20	0.5	**2b**	98
$H_{11}C_5$—≡	$PdCl_2(Ph_3P)_2$, CuI	Et_3N	PhH	70	3	**2c**	95
$H_{11}C_5$—≡	$PdCl_2(Ph_3P)_2$, CuI	Et_3N	PhH	70	0.3	**3**	80
PhMgBr	$NiCl_2(Ph_3P)_2$	Et_2O	PhH	20	1.5	**4**	89
$(EtO)_2P(O)H$	$[(EtO)_3P]_4Pd$	Et_3N	PhMe	60	1.5	**5**	94
$(EtO)_3P$	$[(EtO)_3P]_4Ni$	Et_3N	PhMe	110	0.25	**5**	95
Ph_2PH	$PdCl_2(Ph_3P)_2$	PhH	Et_3N	20	0.5	**6**	93
Ph_2PSiMe_3	$PdCl_2(Ph_3P)_2$	PhH	Et_3N	90—100	9	**6**	95
Pr_3SnSPh	$(Ph_3P)_4Pd$	PhH	Et_3N	20	24	**7**	82
PhSH	$(Ph_3P)_4Pd$	THF	Et_3N	20	2	**7**	90

none. The course of the reactions was monitored and the resulting compounds were identified by IR spectroscopy (NaCl, in a thin layer), ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and thin-layer chromatography (Silufol).

The IR spectra were recorded on an IKS-22 spectrometer. The ^{1}H NMR spectra were measured on a Varian VXR-400 instrument (400 MHz). The ^{31}P NMR spectra were recorded on Varian FT-80 (32.4 MHz) and Varian VXR-400 (162 MHz) instruments with 85%H_3PO_4 as the external standard. The ^{13}C NMR spectra were measured on a Varian VXR-400 instrument (100.6 MHz). The chemical shifts are given in the δ scale relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). Bis(triphenylphosphino)palladium dichloride,**[55]** tetrakis(triphenylphosphino)palladium,**[56]** and bis(triphenylphosphino)nickel dichloride**[57]** were synthesized according to known procedures. *E*,*E*-1,4-Diiodobuta-1,3-diene,**[24]** phenylacetylene,**[58]** trimethylsilylacetylene,**[59]** hept-1-yne**[60]**, diphenylphosphine,**[61]** triethyl phosphite,**[62]** diethyl phosphite,**[63]** and tripropylphenylthiostannane**[64]** were prepared according to procedures developed previously.

Reactions of *E*,*E*-1,4-diiodobuta-1,3-diene (1) with terminal alkynes (general procedure). Copper(I) iodide (8 mol.%) was added to a solution of diene **1** (1 mmol), the corresponding terminal alkyne (2 mmol), triethylamine (2 mmol), and bis(triphenylphosphino)palladium dichloride (4 mol.%) in benzene (2 mL). The reaction mixture was stored at 20—80 °C for 0.5—3 h until precipitation of triethylamine hydroiodide ceased. After completion of the reaction (TLC control, benzene—light petroleum ether, 1 : 2), the salt was filtered off and washed with light petroleum ether. The solvent was distilled off *in vacuo*, the residue was dissolved in benzene, and light petroleum ether was added until the solution became turbid. Then the reaction mixture was stored at 0 °C to achieve more complete precipitation of the amine salt. The precipitate of the salt was filtered off and the solvent was distilled off *in vacuo*. The residue was kept *in vacuo* with the use of an oil pump for 2 h.

1,8-Diphenylocta-3,5-diene-1,7-diyne (2a) was prepared from phenylacetylene at 20 °C (30 min) in quantitative yield as an oil. Found (%): C, 94.70; H, 5.50. $C_{20}H_{14}$. Calculated (%): C, 94.49; H, 5.51. IR, ν/cm^{-1}: 2250 (C≡C); 1600 (C=C). ^{1}H NMR ($CDCl_3$), δ: 5.87 (m, 2 H, =CH—C≡), 6.68 (m, 2 H, =HC—CH=); 7.37 (m, 10 H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 87.14, 92.33 (—C≡C—); 111.58 (=$\underline{C}$—C≡); 138.63 (=C—C=); 121.28, 126.45, 129.62, 130.58 (C_6H_5).

1,8-Bis(trimethylsilyl)octa-3,5-diene-1,7-diyne (2b). From trimethylsilylacetylene, 20 °C, 30 min, quantitative yield, oil. IR, ν/cm^{-1}: 2150 (C≡C); 1590 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.18 (s, 18 H, Me_3Si); 5.67 (m, 2 H, =CH—C≡); 6.58 (m, 2 H, =CH—CH=). ^{13}C NMR ($CDCl_3$), δ: −0.20 (H_3C—Si); 99.36 (≡$\underline{C}$—Si); 103.99 (≡$\underline{C}$—C=); 113.70 (=$\underline{C}$—C≡); 141.19 (=$\underline{C}$—$\underline{C}$=).

Octadeca-8,10-diene-6,12-diyne (2c). From hept-1-yne, 70 °C, 3 h, 95% yield, oil. IR, ν/cm^{-1}: 2250 (C≡C), 1580 (C=C). ^{1}H NMR ($CDCl_3$), δ: 0.87 (t, 1.36 m, 1.53 m, 2.27 m (11 H, Me(CH_2)$_4$); 6.50 (m, 2 H, =CH—C≡); 6.96 (m, 2 H, =CH—CH=). ^{13}C NMR ($CDCl_3$), δ: 12.08 (Me); 17.29, 20.61, 26.16, 27.82 (CH_2)$_4$; 77.97, 92.92 ($\underline{C}$≡$\underline{C}$); 111.17 (=$\underline{C}$—C≡); 142.71 (=$\underline{C}$—$\underline{C}$=).

1-Iodoundeca-1,3-dien-5-yne (3). From hept-1-yne, 20 °C, 20 min, 80% yield, oil. ^{1}H NMR ($CDCl_3$), δ: 0.89 (t, 3 H, Me); 1.29, 1.51, and 2.28 (all m, 8 H, CH_2); 6.39 (m, 1 H, =CH—C≡); 6.47 (m, 1 H, HC=C—C≡); 6.93 (m, 1 H, =CHI); 7.01 (m, 1 H, —CH=CI). ^{13}C NMR ($CDCl_3$), δ: 13.93 (Me); 19.63, 22.17, 28.25, 31.04 (CH_2)$_4$; 77.25 (≡$\underline{C}$—C=); 79.28 (IC=); 93.42 (≡$\underline{C}$—CH_2); 111.17 (=$\underline{C}$—C≡); 137.51 (—$\underline{C}$=CI); 137.68 (=$\underline{C}$—$\underline{C}$=).

The reaction of *E*,*E*-1,4-diiodobuta-1,3-diene (1) with phenylmagnesium bromide. An ethereal solution containing phenylmagnesium bromide (0.4 g, 2.2 mmol) was added with intense stirring to a solution of compound **1** (0.306 g, 1 mmol) and bis(triphenylphosphino)nickel dichloride (0.037 g, 5 mol.%) in ether (2 mL). The reaction mixture was stirred at ~20 °C for 1.5 h and then pyridine (0.16 g, 2 mmol) was added. The precipitate that formed was filtered off and the solvent was distilled off from the filtrate *in vacuo*. The residue was dissolved in ether (10 mL), and light petroleum ether (5 mL) was added. The precipitate that formed was filtered off and the solvents were distilled off *in vacuo*. *E*,*E*-1,4-Diphenylbuta-1,3-diene (**1**)**[65]** was obtained in a yield of 0.183 g (89%), m.p. 150—151 °C. ^{1}H NMR ($CDCl_3$), δ: 6.69 and 6.98 (both m, 4 H, —CH=CH—CH=CH—); 7.45 (m, 10 H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 102.67 (=$\underline{C}$—C_6H_5); 137.33 (=$\underline{C}$—$\underline{C}$=), 126.36, 127.15, 128.73, 132.80 (C_6H_5).

The reaction of *E*,*E*-1,4-diiodobuta-1,3-diene (1) with triethyl phosphite. Compound **1** (0.459 g, 1.5 mmol) and triethyl phosphite (0.498 g, 3 mmol) were added to the tetrakis(triethyl phosphite)nickel complex (0.072 g, 6.7 mol.%), which was prepared from triethyl phosphite (0.082 g, 0.5 mmol) and nickel bromide (0.022 g, 0.1 mmol). The mixture was rapidly heated to 110 °C until distillation of ethyl iodide started. After 15 min, EtI was distilled off in quantitative yield (0.468 g, 0.24 mL). The ^{31}P NMR spectrum of the reaction mixture had the only signal at δ_P. The residue was treated with a mixture of benzene and light petroleum ether (1 : 1) and the solvent was distilled off *in vacuo*. Tetraethyl *E*,*E*-buta-1,3-diene-1,4-diyldiphosphonate (**5**)**[79]** was obtained in a yield of 0.465 g (95%), b.p. 162 °C ($4.5 \cdot 10^{-2}$ Torr), $n^{20}{}_D$ 1.4664. ^{1}H NMR ($CDCl_3$), δ: 1.33 (t, 12 H, Me); 4.10 (dq, 8 H, CH_2O); 6.10 (m, 2 H, =CH—P); 7.11 (m, 2 H, =CH—C). ^{13}C NMR ($CDCl_3$), δ: 14.42 ($\underline{Me}$); 60.10 ($\underline{C}H_2O$); 123.00 (d, =$\underline{C}$H—P, $^1J_{CP}$ = 189.13 Hz); 143.52 (m, P—C=$\underline{C}$—$\underline{C}$=C—P).

The reaction of *E*,*E*-1,4-diiodobuta-1,3-diene (1) with diethylphosphorous acid. Triethylamine (0.292 g, 2.88 mmol, 0.4 mL) was added to a solution of compound **1** (0.391 g, 1.27 mmol), diethylphosphorous acid (0.397 g, 2.88 mmol, a 20% excess), and tetrakis(triphenylphosphino)palladium (0.138 g, 10 mol.%) in toluene (2 mL). The reaction mixture warmed up spontaneously to 60 °C and a precipitate formed. The reaction was completed in 1.5 h. The ^{31}P NMR spectrum had the only signal at δ_P 17.68 corresponding to diphosphonate **5**. The precipitate was filtered off, the solvent was distilled off from the filtrate *in vacuo*, and the residue was stored at 40—50 °C (2 Torr) for 1 h. Tetraethyl *E*,*E*-buta-1,3-diene-1,4-diyldiphosphonate (**5**) was obtained in a yield of 0.395 g (94%), b.p. 162 °C ($4.5 \cdot 10^{-2}$ Torr), $n^{20}{}_D$ 1.4664.

The reaction of *E*,*E*-1,4-diiodobuta-1,3-diene (1) with diphenylphosphine. A solution of compound **1** (0.341 g, 1.1 mmol), triethylamine (0.225 g, 2.2 mmol), and diphenylphosphine (0.415 g, 2.2 mmol) in benzene (3 mL) was placed in a tube. Then bis(triphenylphosphino)palladium dichloride (0.031 g, 4.4 mol.%) was added and the tube was sealed. The reaction mixture spontaneously warmed up and the reaction was completed in 30 min. ^{31}P NMR: δ_P −12.88. After completion of the reaction, the precipitate was filtered off and washed with a 1 : 1 benzene—light petroleum ether mixture (5 mL). The solvent was distilled off from the filtrate *in vacuo*. The solid crystalline precipitate was stored at 40—45 °C (1 Torr) for 1 h. *E*,*E*-1,4-Bis(diphenylphosphino)buta-1,3-diene (**6**) was obtained in a yield of 0.394 g (93%), m.p. 142—142.5 °C.

Found (%): C, 78.75; H, 5.74. $C_{28}H_{24}P_2$. Calculated (%): C, 79.61; H, 5.76. ^{1}H NMR ($CDCl_3$), δ: 6.40 (m, 2 H, =CH—CH=); 7.31 (m, 20 H, C_6H_5); 7.65 (m, 2 H, =$\underline{C}$HP). ^{13}C NMR ($CDCl_3$), δ: 128.45 (d, $^4J_{PC}$ = 4.0 Hz); 128.60 (d, $^3J_{PC}$ = 23.1 Hz); 133.15 (d, $^2J_{PC}$ = 18.1 Hz); 137.29 (d, C_6H_5P, $^1J_{CP}$ = 9.1 Hz); 133.50 (dd, P—C=$\underline{C}$—$\underline{C}$=C—P, $^2J_{CP}$ = 18.11 Hz, $^3J_{PC}$ = 3.5 Hz); 142.75 (dd, P—$\underline{C}$=C—C=$\underline{C}$—P, $^1J_{CP}$ = 24.14 Hz, $^4J_{PC}$ = 12.0 Hz).

The reaction of *E,E*-1,4-diiodobuta-1,3-diene (1) with diphenyl(trimethylsilyl)phosphine. A solution of compound **1** (0.306 g, 1 mmol) in benzene (2.5 mL) was placed in a tube. Then diphenyl(trimethylsilyl)phosphine (0.516 g, 2 mmol) and bis(triphenylphosphino)palladium dichloride (0.028 g, 4 mol.%) were added and the tube was sealed. The reaction mixture was heated at 90—100 °C for 9 h. After completion of the reaction, the solvent was distilled off *in vacuo*. The target product was extracted from the crystalline precipitate with a 1 : 1 benzene—light petroleum ether mixture. *E,E*-1,4-Bis(diphenylphosphino)buta-1,3-diene (**6**) was obtained in a yield of 0.398 g (95%), m.p. 142—142.5 °C.

The reaction of *E,E*-1,4-diiodobuta-1,3-diene (1) with thiophenol. Lithium thiophenoxide (0.26 g, 2.13 mmol), which was prepared from thiophenol (0.23 g, 2.13 mmol) in THF (2 mL) and butyllithium in hexane (0.138 g, 1.2 mL, 1.78 mol L^{-1}, 2.16 mmol), was added to a solution of compound **1** (0.306 g, 1 mmol) and tetrakis(triphenylphosphino)palladium (0.046 g, 4 mol.%) in benzene (5 mL). The reaction mixture was stored at 20 °C for 2 h. After completion of the reaction (TLC control, ethanol—dichloromethane, 1 : 1), the solvent was distilled off *in vacuo* and the residue was recrystallized from light petroleum ether. *E,E*-1,4-Bis(phenylthio)buta-1,3-diene (**7**) was obtained in a yield of 0.24 g (90%), m.p. 56.3—57.2 °C. Found (%): C, 70.95; H, 5.23; S, 23.82. $C_{16}H_{14}S_2$. Calculated (%): C, 71.11; H, 5.19; S, 23.70. ^{1}H NMR ($CDCl_3$), δ: 6.29 (m, 2 H, =CHS); 7.22 (m, 2 H, =CH—CH=); 7.30 (m, 10 H, C_6H_5). ^{13}C NMR ($CDCl_3$), δ: 125.67 (=$\underline{C}$S); 130.44 (=$\underline{C}$—$\underline{C}$=); 127.04, 127.36, 128.96, 136.90 (C_6H_5).

The reaction of *E,E*-1,4-diiodobuta-1,3-diene (1) with tripropyl(phenylthio)stannane. A solution of compound **1** (0.3 g, 1 mmol), tripropyl(phenylthio)stannane (0.7 g, 1.96 mmol), and tetrakis(triphenylphosphino)palladium (0.057 g, 5 mol.%) in toluene (2 mL) was kept at 20 °C for 24 h (the completion of the reaction was determined by TLC). Then the reaction mixture was intensively washed three times with a solution of potassium fluoride. The precipitate that formed was filtered off, the solvent was evaporated from the filtrate, and the crystalline precipitate was recrystallized from hexane. *E,E*-1,4-Bis(phenylthio)buta-1,3-diene (**7**) was obtained in a yield of 0.22 g (82%), m.p. 56—57 °C.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 0003-32747), by the Program "Leading Scientific Schools" (Project No. 0015-97406), and by the Program "Integration of the Higher School and Basic Research" (AO115).

References

1. F. Fringuelli and A. Jaliccni, *Dienes in the Diels-Alder Reaction*, Wiley, New York, 1990.
2. M. Lautens, W. Klute, and W. Tam, *Chem. Rev.*, 1996, **96**, 49.
3. T.-Y. Luh and K.-T. Wong, *Synthesis*, 1993, 349.
4. R. C. Larock and L. Guo, *Synlett*, 1995, 465.
5. S. V. Gagnier and R. C. Larock, *J. Org. Chem.*, 2000, **65**, 1525.
6. G. Desimoni, G. Tacconi, A. Barco, and G. P. Pollini, *Natural Products Synthesis through Pericyclic Reaction*, American Chemical Society, Washington DC, 1983.
7. J. Barluenga, A. Suarez-Sobrino, and L. A. Lopez, *Aldrichimica Acta*, 1999, **32**, 4.
8. X. Chen and G. Millar, *Synthesis*, 2000, 113.
9. S. A. Kozmin and V. H. Raval, *J. Am. Chem. Soc.*, 1999, **121**, 9562.
10. A. J. Ashe III and F. Drone, *Organometallics*, 1985, **4**, 1478.
11. S. L. Buchwald and R. B. Nielson, *J. Am. Chem. Soc.*, 1989, **111**, 2870.
12. I. L. Reich, C. L. Haile, and H. J. Reich, *J. Org. Chem.*, 1978, **43**, 2402.
13. S. Yamaguchi, R.-Z. Jin, K. Tamao, and F. Sato, *J. Org. Chem.*, 1998, **63**, 10060.
14. F. Sato, H. Urabo, and S. Okamoto, *Chem. Rev.*, 2000, **100**, 2835.
15. J. Dubac, A. Laporterie, and G. Manuel, *Chem. Rev.*, 1990, **90**, 215.
16. F. Mathey, *Chem. Rev.*, 1988, **88**, 429.
17. A. J. Ashe III, S. Al-Ahmad, S. Pilotek, and D. B. Puranik, *Organometallics*, 1995, **14**, 2689.
18. A. J. Ashe III, J. W. Kamf, and S. M. Al-Tawell, *J. Am. Chem. Soc.*, 1992, **114**, 372.
19. E. Block, Ch. Guo, M. Thiruvazhi, and R. J. Toscano, *J. Am. Chem. Soc.*, 1994, **116**, 9403.
20. E. P. Serebryakov, A. A. Vasil´ev, D. Yu. Titskii, and I. P. Beletskaya, *Mendeleev Commun.*, 2000, 168.
21. Y. Pazos and A. R. de Lera, *Tetrahedron Lett.*, 1999, **40**, 8287.
22. Y. Thibonnet, M. Abarbri, J.-L. Parrain, and A. Duchene, *Synlett*, **1997**, 771.
23. J. K. Stille and J. H. Simpson, *J. Am. Chem. Soc.*, 1987, **109**, 2138.
24. S. A. Mitchenko, V. P. Ananikov, J. P. Beletskaya, and Yu. A. Ustynyuk, *Mendeleev Commun.*, **1997**, 130.
25. V. P. Ananikov, S. A. Mitchenko, J. P. Beletskaya, S. E. Nefedov, and Y. L. Eremenko, *Inorg. Chem. Commun.*, 1998, 411.
26. G. Maier, M. Hoppe, K. Lanz, and H. P. Reisenauer, *Tetrahedron Lett.*, 1984, **25**, 5645.
27. J. H. Tumlinson, M. M. Brennan, R. E. Doolittle, E. R. Mitchell, A. Brabham, B. E. Mazemenos, A. H. Baumhouer, and D. M. Jackson, *Arch. Insect Biochem. Physiol.*, 1989, **10**, 255.
28. F. Teller, *Bioorg. Med. Chem. Lett.*, 1991, **1**, 635.
29. K. Sonogashira, in *Comprehensive Organic Synthesis*, Eds. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, **3**, 521.
30. R. Harra, Y. Liu, W. H. Sun, and T. Takahashi, *Tetrahedron Lett.*, 1997, **38**, 4103.
31. W. H. Atwell, D. R. Weyenberg, and H. Gilman, *J. Org. Chem*, 1967, **32**, 885.
32. J. Breu, P. Hoecht, U. Rohr, J. Schatz, and J. Sauer, *Eur. J. Org. Chem*, 1998, 2864.
33. V. V. Zuev, E. E. Kever, and Yu. N. Sazonov, *Vysokomol. Soedin., Sers. A and B*, 1999, **41**, 134 [*Russ. Polym. Sci., Sers. A and B*, 1999, **41** (Engl. Transl.)].
34. US Pat. 5491246; *Chem. Abstr.*, 1996, **124**, 290563d.
35. US Pat. 5470993; *Chem. Abstr.*, 1995, **123**, 257778j.
36. T. Minami and G. Motoyoshiya, *Synthesis*, 1992, 333.
37. T. Okauchi, T. Kakiuchi, N. Kitamura, T. Utsunomiya, J. Ichikawa, and T. Minami, *J. Org. Chem*, 1997, **62**, 8419.

38. X. Huang, Ch. Zhang, and X. Lu, *Synthesis*, 1995, 769.
39. D. E. C. Corbridge, *Phosphorus 2000. Chemistry*, *Biochemistry and Technology*, Elsevier, Amsterdam, 2000, 1285.
40. L.-B. Han and M. Tanaka, *J. Am. Chem. Soc.*, 1996, **118**, 1571.
41. A. N. Pudovik and I. V. Konovalova, *Zh. Obshch. Khim.*, 1961, **31**, 1580 [*J. Gen. Chem. USSR*, 1961, **31** (Engl. Transl.)].
42. V. S. Tsivunin, G. K. Kamai, and S. V. Fridland, *Zh. Obshch. Khim.*, 1966, **36**, 436 [*J. Gen. Chem. USSR*, 1966, **36** (Engl. Transl.)].
43. Y. Shen, G. F. Jiang, and J. Sun, *J. Chem Soc.*, *Perkin Trans. 1*, 1999, 3495.
44. P. Tavs and H. Weitkamp, *Tetrahedron*, 1970, **26**, 5529.
45. M. L. Honig and D. J. Martin, *Phosphorus*, 1974, **4**, 63.
46. M. A. Kazankova, I. G. Trostyanskaya, S. V. Lutsenko, and I. P. Beletskaya, *Tetrahedron Lett.*, 1999, **40**, 569.
47. K. S. Petrakis and T. L. Nagabhushan, *J. Am. Chem. Soc.*, 1987, **109**, 2831.
48. T. Hirao, T. Masunga, N. Yamada, J. Ohshiro, and T. Agawa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 909.
49. A. N. Pudovik, I. V. Konovalova, and E. A. Ishmaeva, *Zh. Obshch. Khim.*, 1963, **33**, 2509 [*J. Gen. Chem. USSR*, 1963, **33** (Engl. Transl.)].
50. M. A. Kazankova, E. A. Chirkov, A. N. Kochetkov, I. V. Efimova, and I. P. Beletskaya, *Tetrahedron Lett.*, 1999, **40**, 573.
51. F. Freeman, D. S. H. Kim, and E. Rodriguez, *Sulfur Rep.*, 1989, **9**, 207.
52. F. Freeman, *Heterocycles*, 1990, **31**, 701.
53. M. Korreda and W. Yang, *J. Am. Chem. Soc.*, 1994, **116**, 10793.
54. D. E. Bierer, J. M. Dener, L. G. Dubenko, R. E. Gerber, J. Litvak, S. Peterli, P. Peterli-Roth, T. V. Truong, G. Mao, and B. E. Bauer, *J. Med. Chem.*, 1995, **38**, 2628.
55. H. Hatani and J. C. Beilar, *J. Am. Chem. Soc.*, 1967, **44**, 147.
56. D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.
57. L. M. Venanzi, *J. Chem. Soc.*, **1958**, 719.
58. T. H. Vaughn, *J. Am. Chem. Soc.*, 1934, **56**, 2064.
59. M. F. Shostakovskii, N. V. Komarov, and O. G. Yarosh, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 101 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1966, **15** (Engl. Transl.)].
60. B. Bachman and A. J. Hill, *J. Am. Chem. Soc.*, 1934, **56**, 2730.
61. N. Gee, R. A. Shaw, and B. C. Smith, *Inorg. Synth.*, 1967, **9**, 19.
62. P. T. Milobedzki and A. Sachnowski, *Chem. Zentralbl.*, 1918, **1**, 911.
63. H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 1945, 380.
64. E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1965, 1192.
65. R. N. Mc Donald and T. W. Cambell, *Org. Synth.*, 1960, **40**, 36.

Received April 3, 2001;
in revised form May 28, 2001