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One-Step Synthesis of [4-(Alkylsulfanyl)buta-1,3-diene-1-yl]-triphenylphosphonium Iodides from Buta-1,3-diene-1,4-diylbis(triphenylphosphonium) Iodide

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Abstract—Buta-1,3-diene-1,4-diylbis(triphenylphosphonium) iodide reacted with alkanethiols at room temperature in the presence of triethylamine to give [4-(alkylsulfanyl)buta-1,3-diene-1-yl]triphenylphosphonium iodides and triphenylphosphine in high yields. Two presumable reaction mechanisms involving ethynylvinyl intermediate (formed via the Hofmann decomposition of the starting diiodide and the initially formed 1,4-adduct with a thiol) were discussed.

Keywords: triphenylphosphonium iodide, thiols, the Hofmann degradation, 1,4-addition

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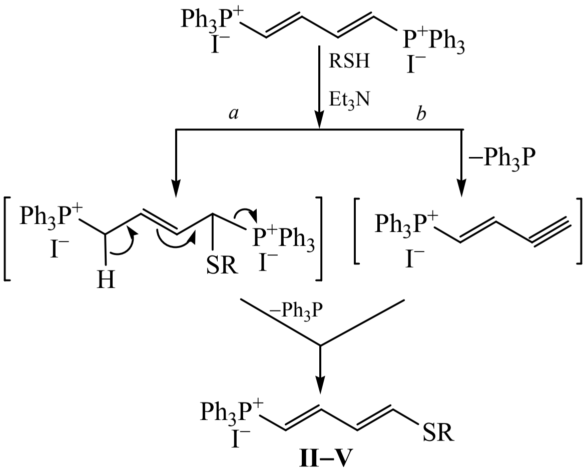
Buta-1,3-diene-1,4-diylbis(triphenylphosphonium) chloride is known to react with dialkylamines in propanol under heating at 80–90°C to form [4-(dialkylamino)buta-1,3-dien-1-yl]triphenylphosphonium chlorides with yields greater than 50% [1]. The reaction included the Hofmann decomposition of the starting dichloride into triphenylphosphine and (but-1-ene-3-yne-1-yl)triphenylphosphonium chloride. The latter reacted further with the secondary amines to give [4-(dialkylamino)buta-1,3-diene-1-yl]phosphonium salts.

In the literature the data on quaternary sulfur-containing buta-1,3-dienylphosphonium salts are scarce. There is only one report describing the conversion of [2-(phenylsulfanyl)buta-1,3-diene-1,4-diyl]bis(triphenylphosphonium) chloride into [3-(phenylsulfanyl)-buta-1,3-diene-1-yl]triphenylphosphonium intermediate using K_2CO_3; further this intermediate is involved into Wittig reaction [2].

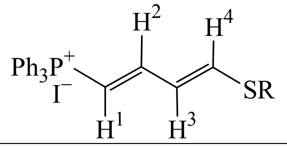
In this work we developed a one-step method for the synthesis of [4-(alkylsulfanyl)buta-1,3-diene-1-yl]triphenylphosphonium iodides **II**–**V** by reacting buta-1,3-diene-1,4-diylbis(triphenylphosphonium) iodide **I** with thiols at room temperature in chloroform in the presence of triethylamine. Probably, triethylamine activated the thiol by deprotonation. The reaction may proceed via the formation of the ethynylvinylphosphonium intermediate as a result of the Hofmann decomposition as in the case of dialkylamines. The resulting

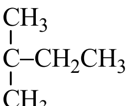
Scheme 1.



R = C_2H_5 (**II**), CH_2CH_2OH (**III**), *tert*-C_5H_{11} (**IV**), C_4H_9 (**V**).

Table 1. IR, ^{1}H, and ^{31}P NMR spectral data of the salts **II**–**V**



Comp. no.	R	δ, ppm (*J*, Hz)	δ_P, ppm	ν, cm^{-1}
II	C_2H_5	1.38 t (3H, $SCH_2C\underline{H}_3$, *J* 7.4), 2.93 q (2H, $SC\underline{H}_2CH_3$, *J* 7.4), 6.74 d.d.d (1H, H^3, J_1 14.7, J_2 10.3, J_3 1.4), 6.89–7.04 m (1H, H^2), 7.14 d.d (1H, H^1, J_1 20.8, J_2 16.0), 7.26 d (1H, H^4, *J* 14.7), 7.69–7.81 m (12H, Ar), 7.86–7.93 m (3H, Ar)	24.35	690, 710, 860, 1460, 1580
III	CH_2CH_2OH	2.95 t (2H, $SC\underline{H}_2CH_2OH$, *J* 7.3), 3.63 t (2H, $SCH_2C\underline{H}_2OH$, *J* 7.3), 4.65 br.s (1H, OH), 6.73 d.d.d (1H, H^3, J_1 14.8, J_2 10.2, J_3 1.5), 6.88–7.02 m (1H, H^2), 7.12 d.d (1H, H^1, J_1 20.9, J_2 15.9), 7.25 d (1H, H^4, *J* 14.8), 7.66–7.8 m (12H, Ar), 7.84–7.91 m (3H, Ar)	24.30	690, 720, 1420, 1460, 1580
IV	 $C(CH_3)_2CH_2CH_3$	0.98 t [3H, $C(CH_3)_2CH_2C\underline{H}_3$, *J* 7.4], 1.39 s [6H, $C(CH_3)_2$], 1.67 q [2H, $C(CH_3)_2C\underline{H}_2CH_3$, *J* 7.4], 6.76 d.d.d (1H, H^3, J_1 14.7, J_2 10.3, J_3 1.4), 6.91–7.05 m (1H, H^2), 7.15 d.d (1H, H^1, J_1 20.7, J_2 16.0), 7.27 d (1H, H^4, *J* 14.7), 7.70–7.82 m (12H, Ar), 7.87–7.94 m (3H, Ar)	24.06	690, 720, 1440, 1480, 1590
V	C_4H_9	0.95 t (3H, $CH_2CH_2CH_2C\underline{H}_3$, *J* 7.4), 1.41–1.52 m (4H, $CH_2C\underline{H}_2C\underline{H}_2CH_3$), 2.63 t (2H, $C\underline{H}_2CH_2CH_2CH_3$, *J* 7.4), 6.75 d.d.d (1H, H^3, J_1 14.7, J_2 10.2, J_3 1.4), 6.9–7.03 m (1H, H^2), 7.13 d.d (1H, H^1, J_1 20.8, J_2 16.0), 7.26 d (1H, H^4, *J* 14.7), 7.73–7.84 m (12H, Ar), 7.86–7.93 m (3H, Ar)	24.36	690, 710, 860, 1460, 1580

intermediate was further reacted with thiols by the 1,4-addition scheme. However, the same reaction products may be obtained through initial 1,4-addition of RSH to the original salt **I** and the subsequent Hofmann decomposition of the formed adduct (Scheme 1).

We have not chosen one among two possible reaction pathways. However, since there are no published data on 1,4-addition to bisphosphonium salts containing 1,4-buta-1,3-diene-1,4-diyl substituent, the *b* direction was preferred (Scheme 1).

We failed to perform the reaction of buta-1,3-diene-1,4-diylbis(tributylphosphonium) bromide with thiols under the same conditions. The reaction resulted in the isomerization of the molecule. Like the reaction of

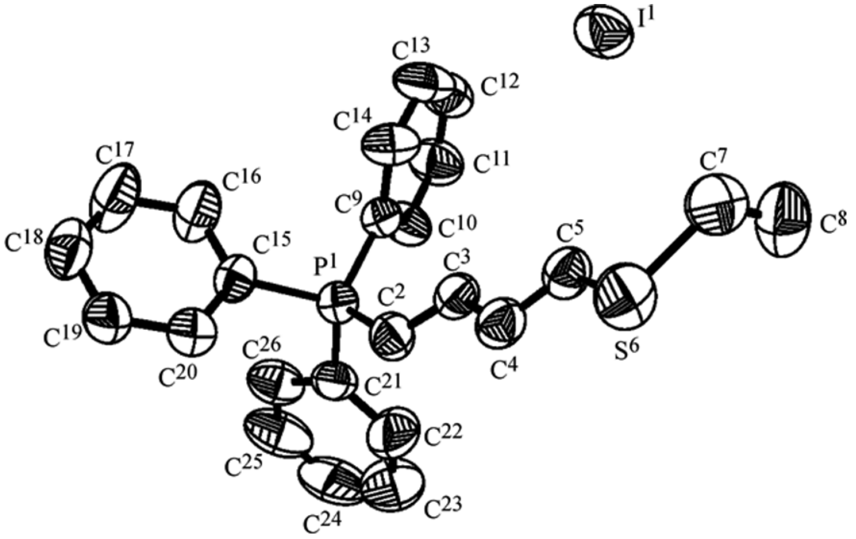


Fig. 1. General view of the molecule of **II**. Thermal ellipsoids are shown with 50% probability.

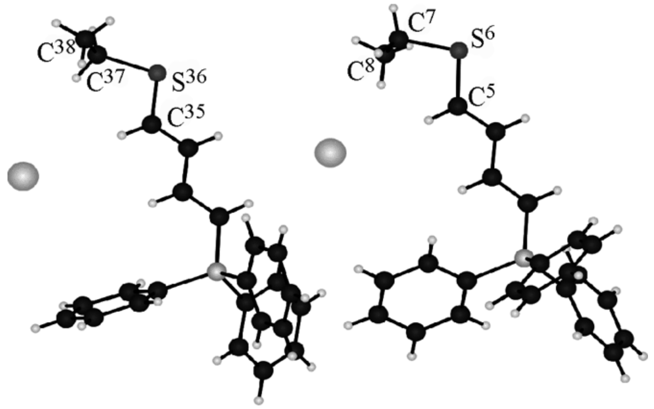


Fig. 2. General view of the symmetrically non-equivalent molecules of **II** with different conformation of ethylsulfanyl moiety.

diphosphonium salt **I** with thiols, ethene-1,2-diyldiphosphonium salts reacted with A–H nucleophile to give the corresponding 2-heteryl-substituted vinylphosphonium salts [3].

Table 2. Main crystallographic parameters of the structure of **II**

Parameter	Value
Formula	$C_{24}H_{24}IPS$
Molecular mass	502.36
Crystal system	Monoclinic
Space group	*P*21/*c*
Z	8
a, *b*, *c*, Å	17.989 (4), 25.782 (5), 10.133 (2)
β, deg	91.28(3)
V, Å^3	4698.4(17)
d_{calc}, g cm^{-3}	1.420
μ(Mo$K_α$), mm^{-1}	1.526
Index ranges	$-25 \le h \le 25$; $-36 \le k \le 0$; $0 \le l \le 14$
Reflections collected, R_{int}	14384 (0.026)
Reflections observed, $I \ge 2σ(I)$	6945
Parameters	489
R_1 [$I \ge 2σ(I)$], wR_2	0.0548, 0.1524

The structure and composition of the obtained compounds were confirmed by the IR, NMR and elemental analysis data (see Table 1). Additionally, the structure of **II** was established by XRD (Fig. 1). According to X-ray diffraction data, in the crystal unit cell there were two independent molecules differing from each other by the conformation of ethylsulfanyl group (Fig. 2). In the first molecule the torsion angle $C^5S^6C^7C^8$ was 68.477(19)°, and the corresponding torsion angle $C^{35}S^{36}C^{37}C^{38}$ in the second molecule was 78.232(18)°.

EXPERIMENTAL

Buta-1,3-diene-1,4-diylbis(triphenylphosphonium) iodide **I** was synthesized by a known method [4].

The IR spectra were recorded on a Specord UR-75 in chloroform. The ^{1}H and ^{31}P NMR spectra were registered on 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 a solvent. Chemical shifts are given with respect to TMS (^{1}H) or 85% H_3PO_4 (^{31}P).

X-Ray diffraction analysis was performed on an automatic diffractometer Enraf Nonius CAD-4 at room temperature (graphite monochromator, Mo$K_α$-irradiation, λ 0.71073 Å, θ/2θ-scanning). The extinction was accounted for by experimental curves of azimuthal scanning (T_{min} 0.39252, T_{max} 0.46941) [5]. All calculations were performed using a SHELXTL software [6]. The structure was solved by the direct method and refined by full-matrix anisotropic approximation for non-hydrogen atoms and by isotropic approximation for the hydrogen atoms. Coordinates of the hydrogen atoms were geometrically determined and refined by a *rider* model. The main crystallographic data and experimental data are reported in Table 2, and full crystallographic data are deposited in the Cambridge Crystallographic Data Centre (CCDC 955844).

Synthesis of compounds II–V. A solution of thiol in 5 mL of chloroform and triethylamine was added to a solution of salt **I** in 15 mL of chloroform. The reaction mixture was stirred at room temperature for 8 h, and then washed with water. The organic layer was dried with $MgSO_4$, and the solvent was removed in a vacuum. The residue was washed with anhydrous ether and recrystallized from ethyl acetate–methylene chloride mixture, 5 : 1.

[4-(Ethylsulfanyl)buta-1,3-diene-1-yl]triphenylphosphonium iodide (II) was obtained from 1 g

(1.2 mmol) of the salt **I**, 0.075 g (1.2 mmol) of ethanethiol, and 0.12 g (1.2 mmol) of triethylamine. Yield 0.42 g (70%), mp 146–147°C. Found, %: C 57.68; H 5.14; I 24.97; P 5.82; S 6.03. $C_{24}H_{24}IPS$. Calculated, %: C 57.37; H 4.78; I 25.30; P 6.18; S 6.37. In addition, 0.24 g (76.3%) of triphenylphosphine (mp 77–79°C) was isolated from the ether extract.

[4-(2-Hydroxyethylsulfanyl)bute-1,3-diene-1-yl]-triphenylphosphonium iodide (III) was obtained from 1 g (1.2 mmol) of salt **I**, 0.094 g (1.2 mmol) of 2-sulfanylethanol, and 0.12 g (1.2 mmol) of triethylamine. Yield 0.44 g (70.8%), mp 154–156°C. Found, %: I 24.18; P 6.24. $C_{24}H_{24}IOPS$. Calculated, %: I 24.52; P 5.98. In addition, 0.22 g (70%) of triphenylphosphine was isolated from the ether extract.

{4-[(2-Methylbut-2-yl)sulfanyl]buta-1,3-diene-1-yl}triphenylphosphonium iodide (IV) was obtained from 1 g (1.2 mmol) of salt **I**, 0.12 g (1.2 mmol) of 2-methylbutanethiol, and 0.12 g (1.2 mmol) of triethylamine. Yield 0.45 g (68.9%), mp 151–153°C. Found, %: I 23.57; P 5.35. $C_{27}H_{30}IPS$. Calculated, %: I 23.35; P 5.69. In addition, 0.23 g (73.2%) of triphenylphosphine was isolated from the ether extract.

[4-(Butylsulfanyl)buta-1,3-diene-1-yl]triphenylphosphonium iodide (V) was obtained from 1 g (1.2 mmol) of salt **I**, 0.11 g (1.2 mmol) of butanethiol, and 0.12 g (1.2 mmol) of triethylamine. Yield 0.5 (78.6%), mp 149–150°C. Found, %: I 23.74; P 6.13. $C_{26}H_{28}IPS$. Calculated, %: I 23.96; P 5.85. In addition, 0.26 g (82.7%) of triphenylphosphine was isolated from the ether extract.

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