ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 5, pp. 1088–1092. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © M.Zh. Ovakimyan, G.Ts. Gasparyan, A.S. Bichakhchyan, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 5, pp. 791–795.

Special Features of Alkaline Hydrolysis of 4-Substituted Buta-1,3-dienetriphenylphosphonium Salts

M. Zh. Ovakimyan, G. Ts. Gasparyan, and A. S. Bichakhchyan

R&D Center of Organic and Pharmaceutical Chemistry, National Academy of Sciences of Armenia, Institute of Organic Chemistry, ave. Azatutyan 26, Yerevan, 0014 Armenia
e-mail: marlena.ovakimyan @rambler.ru

Received January 15, 2015

Abstract—Alkaline hydrolysis of triphenylphosphonium salts containing 4-*S*-, *N*-, and *O*- substituted buta-1,3-diene group has been studied. 4-*S*-substituted phosphonium salts are hydrolyzed with formation of the corresponding diphenyl-1-phenyl-4-alkylsulfanylphosphoryl compounds, the products of anionotropic migration of the phenyl group. Under the same conditions, the 4-*N*- and *O*-substituted buta-1,3-diene phosphonium salts form triphenylphosphine oxide as the major product along minor diphenyl-4-*N*- or diphenyl-4-*O*-substituted buta-1,3-diene phosphine oxides.

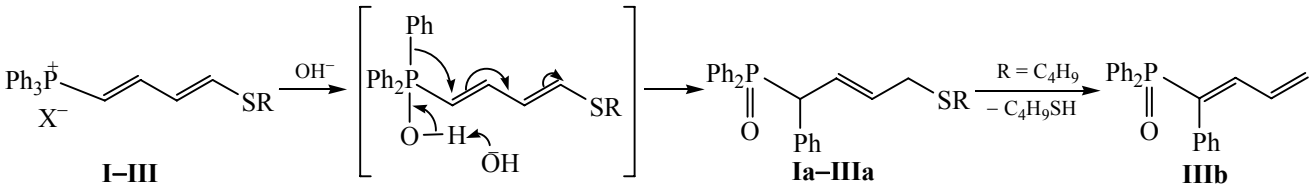
Keywords: alkaline hydrolysis, anionotropic migration, phosphonium salt, diphenyl phosphoryl compound, triphenylphosphine oxide

DOI: 10.1134/S1070363215050151

We have recently worked out a convenient synthesis of [4-(alkylsulfanyl)buta-1,3-dien-1-yl]-triphenylphosphonium salts (**I–IV**) via reaction of buta-1,3-diene-1,4-diylbis(triphenylphosphonium) halides with alkanethiols in the presence of equimolar amount of triethylamine [1]. The obtained phosphonium salts are of both fundamental and applied interest from the viewpoint of the occurring anionotropic migration of the phenyl group. Such a rearrangement has been realized earlier for triphenylbuta-1,3-dienylphosphonium bromide with 10-fold excess of 25% aqueous NaOH on a boiling water bath [2].

Herein, aiming to investigate the effect of alkylsulfanyl group in the δ-position of the buta-1,3-diene system of triphenylphosphonium salts **I–IV** on the course of the rearrangement, we studied the alkaline hydrolysis following the procedure described in [2]. The alkaline hydrolysis of salts **I** and **II** resulted in diphenyl(1-phenyl-4-alkylsulfanylbut-2-enyl)phosphine oxides (**Ia** and **IIa**), the products of α-anionotropic migration of the phenyl group, in 68 and 77.6% yield, respectively. In the case of salt **III**, the product of the 1,4-splitting, diphenyl(1-phenylbuta-1,3-dienyl)phosphine oxide (**IIIb**), was formed along with phosphine oxide **IIIa**. Similar result was observed in case of the alkaline hydrolysis of the same phosphonium salt with potassium *tert*-butoxide in THF at –5 to –10°C. The reasons for different behavior of the structurally similar phosphine oxides **Ia–IIIa** have not been evident and therefore require further investigation (Scheme 1).

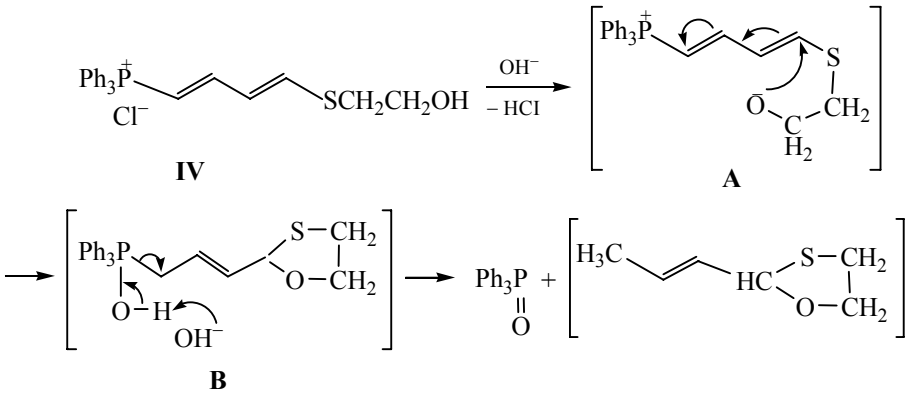
Scheme 1.



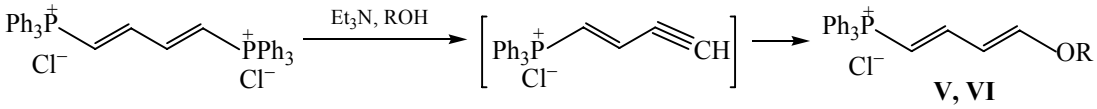
I–III **Ia–IIIa** **IIIb**

R = C_2H_5, X = I (**I**); R = $C(CH_3)_2C_2H_5$, X = Cl (**II**); R = C_4H_9, X = Cl (**III**).

Scheme 2.

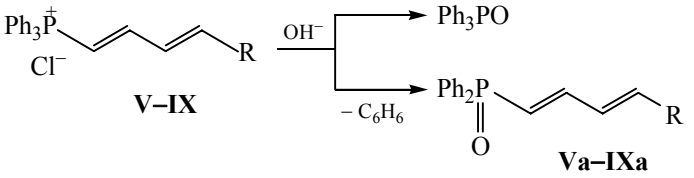


Scheme 3.



R = C_2H_5 (**V**), C_3H_7 (**VI**).

Scheme 4.



R = OC_2H_5 (**V, Va**), OC_3H_7 (**VI, VIa**), $N(C_2H_5)$ (**VII, VIIa**), $N(C_3H_7)_2$ (**VIII, VIIIa**), N⟨ ⟩ (**IX, IXa**).

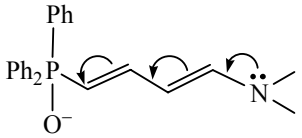
On the contrary to phosphonium salts **I–III**, in the case of salt **IV** containing 2-hydroxyethyl group at the sulfur atom, triphenylphosphine oxide was obtained as the only phosphorus-containing product in 82% yield. The reaction apparently proceeded via the intermediate formation of *O*-phosphobetaine (**A**) that was further transformed into phosphonium salt (**B**) containing an easily ionizable anionic β,γ-unsaturated group under the reaction conditions (Scheme 2).

In order to study the effect of functional δ-substituent of buta-1,3-diene system of triphenylphosphonium salt on the alkaline hydrolysis reaction, we further synthesized [4-(alkoxy)buta-1,3-dien-1-yl]triphenylphosphonium chlorides (**V** and **VI**) via reaction of buta-1,3-dien-1,4-diylbis(triphenylphosphonium) dichloride with ethanol and propanol, the yield being of 43.9 and 45.7%, respectively, and degree of the starting salt regeneration being of 44 and 41%, respectively; the reaction was similar to that of [4-(alkylsulfanyl)buta-1,3-dien-1-yl]triphenylphosphonium salts preparation. Lower yields of the obtained salts were apparently due to lower reactivity of alkoxide anions as compared to that of thiolate and amide anions (Scheme 3).

Alkaline hydrolysis of salts **V** and **VI** yielded triphenylphosphine oxide as the major product along with negligible amounts of diphenyl(4-alkoxybuta-1,3-dienyl)phosphine oxides **Va** and **VIa**. The hydrolysis reaction proceeded similarly (other conditions being the same) in the cases of [4-(dialkylamino)buta-1,3-dien-1-yl]triphenylphosphonium salts **VII–IX** [3], yielding triphenylphosphine oxide as the major product and the corresponding diphenylphosphoryl compounds containing 4-(dialkylamino)buta-1,3-dienyl group **VIIa–IXa** in low yields. Formation of phosphine oxides **Va–IXa** from the structurally similar triphenylphosphonium

salts **V–IX** apparently included anionization of the phenyl group in the intermediate containing pentavalent phosphorus atom (Scheme 4).

Such a different behavior of phosphonium salts **I–III** and **V–IX** in the alkaline hydrolysis was apparently due to stronger conjugation of nitrogen and, to a lesser extent, oxygen lone-electron pair (as compared with that of sulfur) with the π-electron conjugated bond system, thus preventing migration of the phenyl anion in the pentavalent phosphorus intermediate.



The suggestion was supported by the downfield shift of the α-protons signals of 4-*S*-alkylbuta-1,3-dienylphosphonium salts (δ ≈ 7.1 ppm) compared to those of 4-*N*-alkylbuta-1,3-dienylphosphonium salts (δ ≈ 5.7 ppm). On the other hand, the same effect favored the hydrolysis followed by anionization of the formed β,γ-unsaturated group yielding triphenylphosphine oxide (the case of phosphonium salt **IV**). Unfortunately, we failed to isolate and identify the phosphorus-free product of the alkaline hydrolysis of phosphonium salts **IV–IX**.

To conclude, the presence of alkylthio group in δ-position of the buta-1,3-diene system of triphenylphosphonium salts did not prevent anionotropic migration of the phenyl group, whereas the reaction practically did not occur in the cases of similar dialkylamino- and alkoxybuta-1,3-diene phosphonium salts.

EXPERIMENTAL

^{1}H, ^{13}C and ^{31}P NMR spectra were registered with a Varian Mercury-300 spectrometer [300.077 (^{1}H), 75.46 (^{13}C), and 121.47 MHz (^{31}P)] at 303 K, using the DMSO-d_6-CCl_4 1 : 3 mixture as solvent. Chemical shifts are reported relative to TMS (^{1}H) and 85% H_3PO_4 (^{31}P).

Diphenyl-(1-phenyl-4-ethylsulfanylbut-2-enyl)-phosphine oxide (Ia). 2.4 g (15 mmol) of 25% aqueous NaOH was added to 0.75 g (1.5 mmol) of salt **I**, and the reaction mixture was heated on a boiling water bath during 0.5 h. Then the reaction mixture was cooled to ambient, extracted with benzene (3 × 10 mL), the combined extracts were dried over $CaCl_2$, the solvent was removed in vacuum, and the residue was crystallized from the hexane–benzene 4 : 1 mixture to obtain 0.4 g (68%), mp 152–153°C. ^{1}H NMR spectrum, δ, ppm: 0.93 t (3H, $SCH_2C\underline{H}_3$, *J* 7.3 Hz), 1.93 q (3H, $SC\underline{H}_2CH_3$, *J* 7.3 Hz), 2.93 d.d.d (2H, $=CHC\underline{H}_2S\cdot C_2H_5$, *J* 7.0, 2.4, 1.0 Hz), 4.66 d.d (1H, C<u>H</u>Ph, *J* 9.3, 8.3 Hz), 5.43 d.t.d (1H, $=C\underline{H}CH_2SC_2H_5$, *J* 15.0, 3.5, 7.3 Hz), 5.81 d.d.d.t (1H, $C\underline{H}=CHCH_2SC_2H_5$, *J* 15.0, 9.3, 7.0, 1.0 Hz), 7.04–7.99 m [15H, P(O)<u>Ph</u>$_2$, CH<u>Ph</u>], 7.04–7.16 m (3H), 7.22–7.35 m (5H), 7.45–7.54 m (3H), 7.55–7.63 m (2H), 7.91–7.99 m (2H). ^{13}C NMR spectrum, δ_C, ppm: 13.7 (CH_3), 22.9 ($\underline{C}H_2CH_3$), 32.3 ($\underline{C}H_2CH=CH$), 49.0 d (CH, *J* 64.9 Hz), 126.0, 127.2–127.8 m, 128.9 d (2C, *J* 5.9 Hz), 130.3–130.5 m, 130,6 d (*J* 2.5 Hz), 130.9 d (2C, *J* 8.4 Hz), 131.8, 133.1, 136.1 d (*J* 6.1 Hz). The signals in the ^{1}H and ^{13}C NMR spectra were assigned basing on the 2D NMR and HMQC spectra. ^{31}P NMR spectrum: δ_P 34.43 ppm. Found, %: C 73.82; H 6.05; P 8.14. $C_{24}H_{25}OPS$. Calculated, %: C 73.47; H 6.38; P 7.91.

Diphenyl{1-phenyl-4-[(2-methylbutan-2-yl)sulfanyl]but-2-enyl}phosphine oxide (IIa) was obtained similarly from 0.87 g (1.9 mmol) of salt **II** and 3.1 g (19 mmol) of 25% aqueous NaOH. Yield 0.64 g (77.6%) mp 160–161°C. ^{1}H NMR spectrum, δ, ppm: 0.82 t [3H, $SC(CH_3)_2CH_2C\underline{H}_3$, *J* 7.3 Hz], 1.08 s [6H, $SC(C\underline{H}_3)_2CH_2CH_3$], 1.4 q [2H, $SC(CH_3)_2C\underline{H}_2CH_3$, *J* 7.3 Hz], 2.94 d.d.d (2H, $=CHC\underline{H}_2S$–, *J* 7.1, 2.3, 1.1 Hz), 4.59 d.d (1H, C<u>H</u>Ph *J*9.2, 8.3 Hz), 5.42 d.t.d (1H, $=C\underline{H}CH_2S$–, *J* 15.1, 3.4, 7.3 Hz), 5.84 d.d.d. t ($C\underline{H}=CHCH_2S$–, *J* 15.1, 9.4, 7.0, 1.1 Hz), 7.03–7.98 m [15H, P(O)<u>Ph</u>$_2$, CH<u>Ph</u>], 7.03–7.15 m (3H), 7.21–7.36 m (5H), 7.42–7.53 m (3H), 7.54–7.62 m (2H), 7.90–7.98 m (2H). ^{31}P NMR spectrum: δ_P 34.53 ppm. Found, %: C 74.22; H 7.49; P 7.38. $C_{27}H_{31}OPS$. Calculated, %: C 74.65; H 7.14; P 7.14.

Diphenyl(1-phenyl-4-butylsulfanyl-but-2-enyl)-phosphine oxide (IIIa) and diphenyl(1-phenylbuta-1,3-dienyl)phosphine oxide (IIIb). *a*. Prepared similarly from 0.75 g (1.7 mmol) of salt **III** and 2.74 g (17 mmol) of 25% aqueous NaOH. Yield 0.55 g (**IIIa** : **IIIb** ≈ 1 : 1). **Diphenyl(1-phenyl-4-butylsulfanyl-but-2-enyl)-phosphine oxide (IIIa).** ^{1}H NMR spectrum, δ, ppm: 0.92 t [3H, $SCH_2(CH_2)_2C\underline{H}_3$, *J* 7.2 Hz], 1.22–134 m [4H, $SCH_2(C\underline{H}_2)_2CH_3$], 1.98 t [2H, $SC\underline{H}_2(CH_2)_2CH_3$, *J* 7.2 Hz], 2.91 d.d.d (2H, $=CHC\underline{H}_2SC_4H_9$, *J* 7.2, 2.5, 1.0 Hz), 4.67 d.d (1H, C<u>H</u>Ph, *J*9.3, 8.2 Hz), 5.44 d.t.d (1H, $=C\underline{H}CH_2SC_4H_9$, *J* 15.0, 3.5, 7.2 Hz), 5.79 d.d.d. t ($C\underline{H}=CHCH_2SC_4H_9$, *J* 15.0, 9.5, 7.1, 1.0 Hz), 7.06–8.0 m [15H, P(O)<u>Ph</u>$_2$, CH<u>Ph</u>]. ^{31}P NMR spectrum: δ_P 34.51 ppm. **Diphenyl(1-phenylbuta-1,3-dienyl)phos-**

phine oxide (IIIb). ^{1}H NMR spectrum, δ, ppm: 4.83–4.90 m (1H, –CH=C$\underline{H}_2$), 4.96–5.05 m (1H, –CH=C$\underline{H}_2$), 6.28 d.d.d.d (1H, –C$\underline{H}$=CH$_2$, *J* 16.9, 10.9, 10.1, 1.8 Hz), 7.07 d.d [1H, –C(Ph)=C$\underline{H}$, *J* 18.9, 10.9 Hz], 7.06–8.0 m [15H, P(O)$\underline{Ph}_2$, CH$\underline{Ph}$]. ^{31}P NMR spectrum: δ_P 30.93 ppm.

b. 0.34 g (3.0 mmol) of potassium *tert*-butoxide was added to a vigorously stirred suspension of 0.66 g (1.5 mmol) of salt **III** in 15 mL of THF under dry nitrogen stream at –5 to –10°C, and the mixture was incubated at that temperature during 3 h and filtered. The filtrate was extracted twice with anhydrous THF. The solvent was removed in vacuum from the combined THF extracts; the residue was washed with anhydrous diethyl ether and dried in vacuum. Yield 0.6 g (**IIIa** : **IIIb** ≈1 : 2).

Alkaline hydrolysis of [4-(2-hydroxyethylsulfanyl)-buta-1,3-dien-1-yl]triphenylphosphonium chloride (IV) was performed as described for compound **I**. 0.48 g (82.2%) of triphenylphosphine oxide was obtained with mp 155–156°C, showing no depression of melting point when mixed with a reference sample.

(4-Ethoxybuta-1,3-dien-1-yl)triphenylphosphonium chloride (V). 1.06 g (23 mmol) of ethanol and 0.16 g (1.5 mmol) of triethylamine were added to 1 g (1.5 mmol) of buta-1,3-dien-1,4-diylbis(triphenylphosphonium)chloride in 20 mL of chloroform; the reaction mixture was stirred at 35–40°C during 10 h and washed with water; the organic layer was dried with $CaCl_2$; the solvent was removed in vacuum; the residue was washed with anhydrous ether, dried in vacuum, and purified by re-precipitation. Yield 0.26 g (43.9%). ^{1}H NMR spectrum, δ, ppm: 1.32 t (3H, CH$_2$C$\underline{H}_3$, *J* 7.2 Hz), 4.02 q (2H, C$\underline{H}_2$CH$_3$, *J* 7.2 Hz), 6.09 d.d (1H, C$\underline{H}$=CHO, *J* 12.7, 11.2 Hz), 6.83–7.05 m (2H, P$^+$C$\underline{H}$=C$\underline{H}$), 7.21 d (1H, CH=C$\underline{H}$O, *J* 13.3 Hz), 7.52–7.82 m (15H, Ph_3P^+). ^{31}P NMR spectrum: δ_P 24.1 ppm. Found, %: Cl 9.34. $C_{24}H_{24}ClOP$. Calculated, %: Cl 8.99. Regenerated 0.44 g (44%) of the starting phosphonium salt. 0.17 g (43.3%) of triphenylphosphine oxide was obtained from the ethereal extracts; mp 74–76°C, no depression of melting point when mixed with a reference sample.

(4-Propoxybuta-1,3-dien-1-yl)triphenylphosphonium chloride (VI) was obtained similarly from 1 g (1.5 mmol) of buta-1,3-dien-1,4-diylbis(triphenylphosphonium) chloride, 1.4 g (23 mmol) of propanol, and 0.16 g (1.5 mmol) of triethylamine. Yield 0.28 g (45.7%). ^{1}H NMR spectrum, δ, ppm: 1.12 t (3H, CH$_2$CH$_2$C$\underline{H}_3$, *J* 7.3 Hz), 1.29–1.37 m (3H, CH$_2$C$\underline{H}_2$CH$_3$), 3.92 q (2H, C$\underline{H}_2$CH$_2$CH$_3$, *J* 7.3 Hz), 6.1 d.d (1H, C$\underline{H}$=CHO, *J* 12.6, 11.3 Hz), 6.8–7.02 m (2H, P$^+$C$\underline{H}$=C$\underline{H}$), 7.2 d (1H, CH=C$\underline{H}$O, *J* 13.3 Hz), 7.5–7.8 m (15H, Ph_3P^+). ^{31}P NMR spectrum: δ_P 24.18 ppm. Found, %: Cl 8.23. $C_{25}H_{26}ClOP$. Calculated, %: Cl 8.69. Regenerated 0.41 g (41%) of the starting phosphonium salt. 0.19 g (48.3%) of triphenylphosphine was obtained from the ethereal extracts; mp 74–76°C, no depression of melting point when mixed with a reference sample.

Alkaline hydrolysis of (4-ethoxybuta-1,3-dien-1-yl)triphenylphosphonium chloride (V). The experiment was performed as described for phosphonium salts **I–IV**. 0.54 g (69.4%) of triphenylphosphine oxide (mp 155–156°C) and 0.12 g (14.4%) of diphenyl (4-ethoxybuta-1,3-dienyl)phosphine oxide (**Va**) were obtained from 1.12 g (2.8 mmol) of salt **V** and 4.6 g (28 mmol) of 25% aqueous NaOH. ^{1}H NMR spectrum, δ, ppm: 1.3 t (3H, CH$_2$C$\underline{H}_3$, *J* 7.3 Hz), 3.89 q (2H, C$\underline{H}_2$CH$_3$, *J* 7.3 Hz), 5.72 d.d (1H, C$\underline{H}$=CHO, *J* 13.1, 10.8 Hz), 6.08 d.d (1H, P$^+$C$\underline{H}$=CH, *J* 24.0, 16.1 Hz), 6.92 d (1H, CH=C$\underline{H}$O, *J* 13.1 Hz), 7.01–7.17 m (1H, P$^+$CH=C$\underline{H}$), 7.4–7.63 m (10H, Ph_2P). ^{31}P NMR spectrum: δ_P 26.01 ppm. Found, %: C 72.87; H 6.05; P 10.12. $C_{18}H_{19}O_2P$. Calculated, %: C 72.48; H 6.38; P 10.40.

Alkaline hydrolysis of (4-propoxybuta-1,3-dien-1-yl)triphenylphosphonium chloride (VI) was performed similarly. 0.78 g (71.9%) of triphenylphosphine oxide (mp 155–156°C, no depression of melting point when mixed with a reference sample) and 0.14 g (11.5%) of diphenyl(4-propoxybuta-1,3-dienyl)phosphine oxide (**VIa**) were obtained from 1.6 g (3.9 mmol) of salt **VI** and 6.3 g (39 mmol) of 25% aqueous NaOH. ^{1}H NMR spectrum, δ, ppm: 0.99 t (3H, CH$_2$CH$_2$C$\underline{H}_3$, *J* 7.2 Hz), 1.62–1.75 m (2H, CH$_2$C$\underline{H}_2$CH$_3$), 3.8 t (2H,C$\underline{H}_2$CH$_2$CH$_3$, *J* 7.2 Hz), 5.73 d.d (1H, C$\underline{H}$=CHO, *J* 13.0, 10.9 Hz), 6.06 d.d (1H, PC$\underline{H}$=CH, *J* 23.9, 15.9 Hz), 6.91 d (1H, CH=C$\underline{H}$O, *J* 13.0 Hz), 7.02–7.18 m (1H, PCH=C$\underline{H}$), 7.38–7.62 m (10H, Ph_2P). ^{31}P NMR spectrum: δ_P, 26.24 ppm. Found, %: C 72.74; H 6.35; P 10.12. $C_{19}H_{21}O_2P$. Calculated, %: C 73.08; H 6.73; P 9.94.

Alkaline hydrolysis of [4-(diethylamino)buta-1,3-dien-1-yl]triphenylphosphonium chloride (VII) was performed similarly. 0.5 g (74.9%) of triphenylphosphine oxide (mp 155–156°C) and 0.1 g (12.8%) of diphenyl(4-diethylaminobuta-1,3-dienyl)phosphine oxide (**VIIa**) were obtained from 1 g (2.4 mmol) of

salt **VII** and 3.84 g (24 mmol) of 25% aqueous NaOH. ^{1}H NMR spectrum, δ, ppm: 1.18 t (6H, $CH_2C\underline{H}_3$, *J* 7.1 Hz), 3.8 q (4H, $C\underline{H}_2CH_3$, *J* 7.1 Hz), 5.12 d.d (1H, C<u>H</u>=CHN, *J* 12.9, 11.2 Hz), 5.46 d.d (1H, PC<u>H</u>=CH, *J* 24.2, 16.3 Hz), 6.65 d (1H, CH=C<u>H</u>N, *J* 12.8 Hz), 6.86 d.d.d (1H, PCH=C<u>H</u>, *J* 18.8, 16.0, *J* 10.9 Hz), 7.39–7.72 m (10H, Ph_2P). ^{31}P NMR spectrum: δ_P 28.02 pm. Found, %: C 74.03; H 7.65; P 9.28. $C_{20}H_{24}NOP$. Calculated, %: C 73.85; H 7.38; P 9.54.

Alkaline hydrolysis of [4-(dipropylamino)buta-1,3-dien-1-yl]triphenylphosphonium chloride (VIII) was performed similarly. 0.33 g (74.2%) of triphenylphosphine oxide (mp 155–156°C) and 0.1 g (17.7%) of diphenyl(4-dipropylaminobuta-1,3-dienyl)phosphine oxide (**VIIIa**) were obtained from 0.7 g (1.6 mmol) of salt **VIII** and 2.49 g (16 mmol) of 25% aqueous NaOH. ^{1}H NMR spectrum, δ, ppm: 0.89 t (6H, $CH_2CH_2C\underline{H}_3$, *J* 7.2 Hz), 1.50–1.62 m (4H,$CH_2C\underline{H}_2CH_3$), 2.92–3.1 m (4H,$C\underline{H}_2CH_2CH_3$), 5.1 d.d (1H, C<u>H</u>=CHN, *J* 13.0, 10.9 Hz), 5.47 d.d (1H, PC<u>H</u>=CH, *J* 24.4, 16.2 Hz), 6.63 d (1H, CH=C<u>H</u>N, *J* 12.8), 6.89 d.d.d (1H, PCH=C<u>H</u>, *J* 18.6, 16.2, 10.9 Hz), 7.35–7.70 m (10H, Ph_2P). ^{31}P NMR spectrum: δ_P 28.48 ppm. Found, %: C 74.42; H 8.25; P 9.13. $C_{22}H_{28}NOP$. Calculated, %: C 74.79; H 7.93; P 8.78.

Alkaline hydrolysis of [4-(piperidyl)buta-1,3-dien-1-yl]triphenylphosphonium chloride (IX) was performed similarly. 0.36 g (71.9%) of triphenylphosphine oxide (mp 155–156°C) and 0.1 g (16.5%) of diphenyl(4-piperidylbuta-1,3-dienyl)phosphine oxide (**IXa**) were obtained from 0.8 g (1.8 mmol) of salt **IX** and 2.95 g (18 mmol) of 25% aqueous NaOH. ^{1}H NMR spectrum, δ, ppm: 1.52–1.68 m (6H, $C_5H_{10}N$), 3.04–3.18 m (4H, NCH_2), 5.24 d.d (1H, C<u>H</u>=CHN, *J* 13.0, 10.7 Hz), 5.5 d.d (1H, PC<u>H</u>=CH, *J* 23.9, 16.1 Hz), 6.57 d (1H, CH=C<u>H</u>N, *J* 13.0 Hz), 6.84 d.d.d (1H, PCH=C<u>H</u>, *J* 18.2, 16.1, 10.7 Hz), 7.38–7.63 m (10H, Ph_2P). ^{31}P NMR spectrum: δ_P 27.71 ppm. Found, %: C 75.12; H 7.33; P 9.48. $C_{21}H_{24}NOP$. Calculated, %: C 74.78; H 7.12; P 9.20.

REFERENCES

1. Ovakimyan, M.Zh., Gasparyan, G.Ts., Bichakhchyan, A.S., Pogosyan, A.S., Kinoyan, F.S., Tamazyan, R.A., and Aivasyan, A.G., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 3, p. 496. DOI: 10.1134/S1070363214031141.
2. Brophy, J.J., Freeman, K.L., and Gallagher, M.J., *J. Chem. Soc. (C)*, 1968, p. 2760. DOI: 10.1039/S39680002760.
3. Movsisyan, M.L., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 3, p. 496. DOI: 10.1134/S1070363211030297.