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Synthesis and Properties of *tert*-Butylphenylmethylene(chloro)phosphorane

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Abstract—The synthesis and properties of *tert*-butylphenylmethylene(chloro)phosphorane were described. The prepared chlorophosphorane reacted with alcohols and phenol with the formation of the corresponding phosphonium salts. Its reaction with carbonyl compounds led to the formation of 2-chloro-1,2λ^5-oxaphosphetanes, which rearranged providing 2-chloroalkylphosphine oxides or alkenylphosphine oxides.

Keywords: 1,2λ^5-oxaphosphetanes, alkylidenphosphoranes, phosphine oxides, alkenylphosphine oxides

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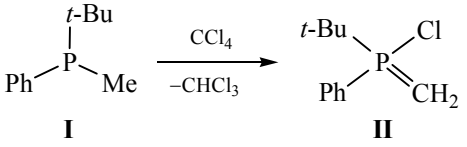
The reactions of phosphorus ylides with carbonyl compounds are of great practical importance [1–6]. An interesting type of the phosphorus ylides are practically accessible and highly reactive *P*-halogen alkylidenphosphoranes [5–8]. In the course of our investigations on the chemistry of *P*-halogen ylides [7–10], we synthesized unsymmetrically substituted *tert*-butylphenylmethylene(chloro)phosphorane **II** by the reaction of *tert*-butylphenyl(methyl)phosphine **I** with tetrahalomethane in diethyl ether at –70°C. Ylide **II** proved to be comparatively stable and can be isolated by vacuum distillation.



I **II**

The structure of *tert*-butylphenylmethylene(chloro)-phosphorane **II** was confirmed by the data of NMR spectroscopy. Thus, chemical shift δ_P 93.5 ppm distinctively indicated phosphonium nature of the phosphorus atom involved into the P=C→P$^+$–C$^-$ group. In the ^{13}C NMR spectrum the doublet signal at 23 ppm with the coupling constant of spin-spin interaction of 95 Hz was observed that corresponded to the carbanion nature of the carbon atom.

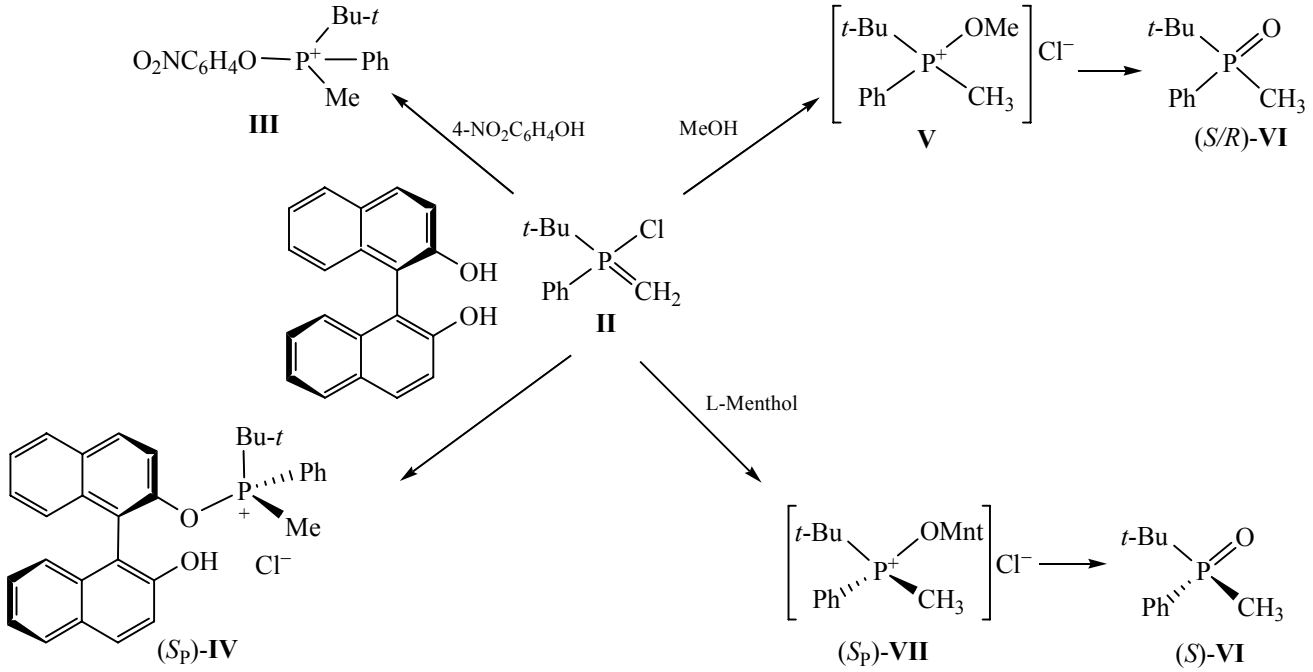
Ylide **II** can easily add alcohols and phenols to the P=C bond with the formation of the corresponding phosphonium salts **III** and **V**. Ylide **II** is also interesting as an active chiral reagent for asymmetric synthesis. Thus, the reaction of ylide **II** with chiral phenol BINOL and L-menthol proceeded stereoselectively with the formation of scalemic phosphonium salts **IV** and **VII** (Scheme 1).

Methoxyphosphonium salt **VII**, whose formation we succeeded to register by the means of ^{31}P NMR spectroscopy (δ_P = 90 ppm), at room temperature converted to phosphine oxide (*S*)-**VI**. The comparison of the angle of optical rotation of the phosphine oxide prepared by us with the value described earlier [12] allowed the establishment of its absolute configuration as well as absolute configuration of the alkoxyphosphonium salt.

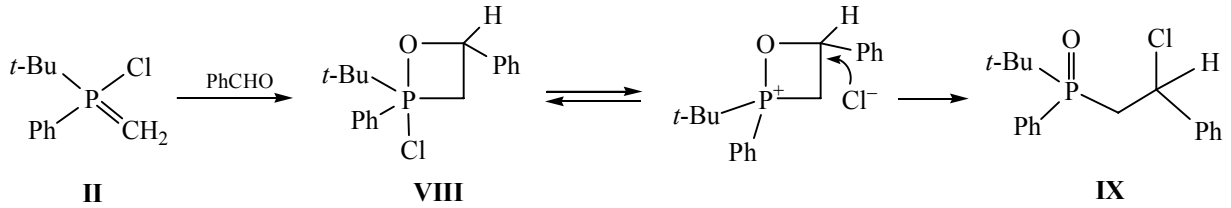
tert-Butylphenylmethylene(chloro)phosphorane **II** also reacted with carbonyl compounds. The reaction with benzaldehyde proceeded at cooling providing stable at low temperature chlorooxaphosphetane **VIII** which at temperature about 0°C rearranged into 2-chlorooxaphosphine oxide **IX** (Scheme 2).

As we showed earlier [7, 8], 2-chlorooxaphosphetanes might be easily ionized at P–Cl bond with the formation of the corresponding cyclic oxyphos-

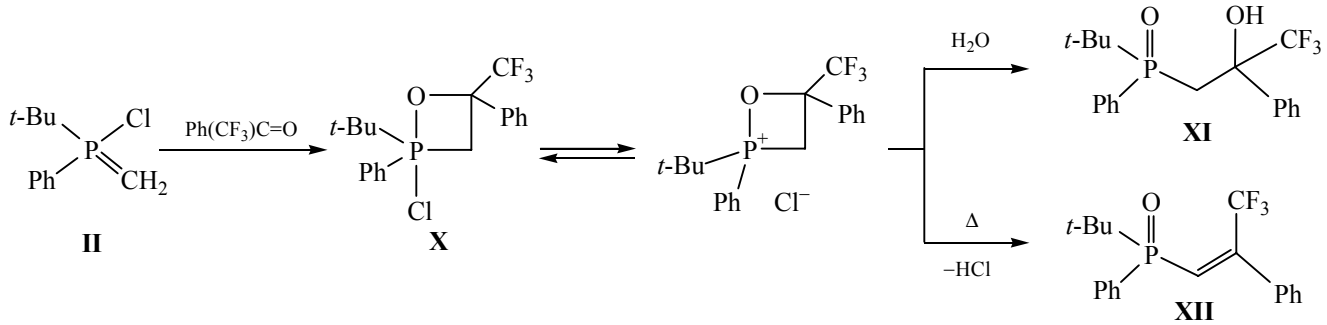
Scheme 1.



Scheme 2.



Scheme 3.



phonium salts, which underwent 2-chlorooxaphosphetane→2-chlorooxyphosphine oxide rearrangement as a result of the attack of chloride ion on the β-carbon atom.

The reaction of P-halogenylide **II** with trifluoroacetophenone led to the formation of 2-chlorooxaphosphetane **X** stable at room temperature. The latter can be easily hydrolyzed under air humidity condition with the formation of 2-hydroxyalkylphosphine oxide **XI**; the thermolysis of **X** provided the corresponding alkenylphosphine oxide **XII** (Scheme 3).

In the mass spectrum of 2-chlorooxaphosphetane **X** the peak of molecular ion was observed that indicated the covalent character of the P–Cl bond. It was found that the chemical shift of phosphorus in **X** depended on the polarity of the solvent. Thus, in nonpolar solvents

(diethyl ether, pentane) the signals of δ_P were in the strong field of the ^{31}P NMR spectrum (from –3 to 10 ppm) that corresponded to the pentacoordinated state of the phosphorus atom [5]. In polar solvents and especially in the presence of Lewis acids like $AlCl_3$ the values of δ_P were shifted downfield. For example, for compound **IV** the chemical shift of phosphorus, δ_P was as follows (ppm): 9 (pentane), 22 (CH_2C1_2), 30 ($CHC1_3$), 35 (CH_3CN), 45 ($CHC1_3$ + $A1C1_3$, traces). With the increase in amount of aluminum chloride up to equimolar level the value of δ_P 100 ppm was registered for 2-chlorooxaphosphetane **VII** that was in accordance with the values of chemical shifts for the known alkoxyphosphonium salts [5, 6] and apparently indicated complete ionization of chlorophosphorane with the formation of phosphonium salt **XVI**. The dependence of the chemical shift value of phosphorus in 2-chlorooxaphosphetanes on the solvent polarity and on the presence of Lewis acid is in accordance with the published data showing that chlorophosphoranes are able to be ionized with the formation of phosphonium structures. Herewith in the ^{31}P NMR spectrum the resultant signal is registered due to fast exchange in the phosphorus coordination P(V) ⇄ P(IV). The value of δ_P is shifted downfield proportionally to the increase in the phosphonium structure content, which in its turn depends on the solvent polarity [10].

The structure of 2-halogen-1,2λ^5-oxaphosphetane **X** was confirmed by ^1H NMR spectroscopy. A significant downfield shift of δ value of oxaphosphetane ring protons (4.5–6.35 ppm) is worth a special attention. In the ^1H NMR spectra of the compounds possessing asymmetric carbon atom C^4 the magnetic nonequivalence of protons CH^aH^b in the four-membered ring became apparent because the geminal spin-spin interaction arose between them. Each of the signals CH^a and CH^b was the double doublet with the coupling constant with phosphorus nucleus $^2J_{PH}$ = 20–22 Hz and a constant of geminal interaction $^2J_{HH}$ = 16–17 Hz.

In summary, chloro(*tert*-butyl)phenyl(methylene) phosphorane **II** was found to be highly reactive compound that participated in the reaction of asymmetric synthesis, [2+2]-cycloaddition with carbonyl compounds with the formation of 2-chloro-1,2λ^5-oxaphosphetanes, which then were converted to β-substituted tertiary phosphine oxides or alkenylphosphine oxides.

EXPERIMENTAL

NMR spectra were recorded on a Varian VXR-300 instrument operating at 300 (^1H), 60 (^{13}C), 225.8 (^{19}F), and 126.16 (^{31}P) MHz with TMS as a reference. Mass spectra were registered on an Agilent 1100 LC/MSD spectrometer. The reagents, silica gel, and plates Poligram SIL G/UV254 used in the work were purchased from commercial suppliers Fluka and Merck. The starting methyl(*tert*-butyl)phenylphosphine **I** was synthesized by the known method [14].

***tert*-Butylphenylmethylene(chloro)phosphorane (II)**. Carbon tetrachloride (4 mL) was added dropwise under inert atmosphere to a cooled to –78°C solution of methyl(*tert*-butyl)phenylphosphine **I** (3.6 g, 0.02 mol) in 5 mL of anhydrous diethyl ether. Then temperature was increased to ambient, and the mixture was stirred for 20 min. The precipitate and solvent were removed, and the residue was distilled in vacuum. Yield 3 g (70%), bp 45–50°C (0.008 mmHg). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.58 d (9H, CH_3, $^3J_{PH}$ 15.0 Hz), 2.48 d (2H, PCH_2, $^2J_{PH}$ 20.0 Hz), 7.47 m and 7.49 m (5H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.20 d (P=CH_2, $^2J_{PC}$ 95.0 Hz), 27.6 d (CH_3, $^3J_{PC}$ 15.0 Hz), 41.90 d (PC, $^1J_{PC}$ 45.0 Hz), 124.01, 124.89, 126.94, 131.8, 132.0. ^{31}P NMR spectrum ($CDCl_3$): δ_P 93.50 ppm. Found, %: C 62.14; H 7.79; P 14.03. $C_{11}H_{16}ClP$. Calculated, %: C 61.54; H 7.51; P 14.43.

***tert*-Butyl(methyl)(4-nitrophenoxy)(phenyl)phosphonium chloride (III).** A solution of 4-nitrophenol (0.02 mol) in minimal amount of THF was added at cooling (–70°C) to a solution of chloro(*tert*-butyl)-phenyl(methylene)phosphorane **II** (2.1 g, 0.01 mol) in 10 mL of diethyl ether. The precipitate formed was filtered off and washed with a little of diethyl ether. Yield 0.27 g (75%), decomposes upon heating. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.71 d (9H, CH_3, $^3J_{PH}$ 18.0 Hz), 3.10 d (3H, CH_3, $^2J_{PH}$ 10.0 Hz), 8.50 d.d (4H, C_6H_4), 7.75 m and 8.50 m (C_6H_5). ^{31}P NMR spectrum ($CDCl_3$): δ_P 93.50 ppm. Found, %: C 58.12; H 6.02; P 8.50. $C_{17}H_{21}ClNO_3P$. Calculated, %: C 57.72; H, 5.98; P 8.76.

***tert*-Butyl[2'-hydroxy-(1,1'-binaphth-2-yl)oxy]-(methyl)(phenyl)phosphonium chloride (*S*)-IV**. A solution of (*R*)-BINOL (3.1 g, 0.11 mol) in THF was added at cooling (–78°C) to a solution of *tert*-butyl-phenylmethylene(chloro)phosphorane **II** (2.1 g, 0.01 mol) in anhydrous toluene. The mixture was stirred at this temperature for 10 min. The precipitate formed was filtered off and washed with anhydrous ether (2 × 20 mL). Yield 0.46 g (90%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.84 d (9H, CH_3, $^3J_{PH}$ 20.0 Hz), 3.18 d (3H, $^2J_{PH}$ 15.0 Hz), 5.50 s (OH), 7.00–7.50 m (5H, C_6H_5), 8.80 m (12H, $C_{10}H_{12}$). ^{13}C NMR spectrum

($CDCl_3$), δ_C, ppm: 9.1 d ($^1J_{PC}$ 55.0 Hz), 24.5 d (J_{PC} 15.0 Hz), 35.2 d (J_{PC} 42.0 Hz), 116.0, 122.5, 127.0, 128.3, 130.4, 131.4, 132.5, 134.6, 150.5, 154. ^{31}P NMR spectrum ($CDCl_3$): δ_P 93.7, 94.6 ppm (3 : 1). Found P, %: 6.09. $C_{31}H_{30}ClO_2P$. Calculated P, %: 6.18.

***tert*-Butylmethylphenylphosphine oxide (*S*/*R*)-VI**. Methanol (0.4 mL, 0.01 mol) was added dropwise to a solution of *tert*-butylphenylmethylene(chloro)-phosphorane **II** (1.05 g, 0.005 mol) in 5 mL of diethyl ether at –70°C. Then the reaction mixture was stirred at room temperature for 30 min and kept for the following 30 min without stirring. After removing the solvent the residue was distilled in a vacuum and additionally purified by re-precipitation with methanol from methylene chloride solution. Yield 0.65 g (65%), bp 90 °C (0.05 mmHg), mp 97°C (mp 98–99°C [12–14]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 d (9H, CH_3C, $^3J_{PH}$ 14.9 Hz), 1.66 d (3H, CH_3, $^2J_{PH}$ 12.2 Hz), 7.47–7.37 m (3H, ArH), 7.69–7.62 m (2H, ArH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 47.75 ppm.

***tert*-Butylmethylphenylphosphine oxide (*S*)-(–)-VI** was prepared similarly from *tert*-butylphenyl-methylene(chloro)phosphorane **II** (2.1 g, 0.01 mol) and L-menthol (1.7 g, 0.11 mol). Yield 1.5 g (75%), bp 90°C (0.1 mmHg), mp 97°C (mp 98–99°C [12–14]), $[\lambda]_D^{20}$ –10 (*c* = 2, MeOH). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 d (9H, CH_3C, $^3J_{PH}$ 14.9 Hz), 1.66 d (3H, CH_3, $^2J_{PH}$ 12.2 Hz), 7.47–7.37 m (3H, ArH), 7.69–7.62 m (2H, ArH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 47.75 ppm.

***tert*-Butyl(2-chloro-2-phenylethyl)(phenyl)phos-phine oxide (IX).** Benzaldehyde (0.02 mol) was added at cooling (–70°C) to a solution of *tert*-butylphenyl-methylene(chloro)phosphorane **II** (2.1 g, 0.01 mol) in 10 mL of diethyl ether. After removing the precipitate and the solvent, the residue was recrystallized from a mixture hexane–Et_2O at –70°C. Yield 75%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10 d (9H, CH_3, $^3J_{PH}$ 15.0 Hz), 2.71 d.d (1H, PCH, $^2J_{HP}$ = $^3J_{HH}$ = 10.0 Hz), 2.95 d.d (1H, PCH, $^2J_{HP}$ = $^3J_{HH}$ = 10.0 Hz), 5.42 d (1H, CHPh, $^3J_{HH}$ 10.0 Hz), 7.3–7.6 m (5H,C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.7 ($PCCH_3$), 32.8 d (PC, $^1J_{PC}$ 66.0 Hz), 34.9 d (PCH_2, $^1J_{PC}$ 57.0 Hz), 57.2, 127.5, 127.8, 131.2, 131.5, 130.9, 131.5, 132.3 d (PCC, $^2J_{CP}$ 25.0 Hz), 140.1. ^{31}P NMR spectrum ($CDCl_3$): δ_P 57.90, 58.33 ppm (10:1). Mass spectrum (70 eV): *m*/*e* 320 $[M]^+$. Found, %: C 67.27; H 6.89; P 9.54. $C_{18}H_{22}ClOP$. Calculated, %: C 67.39; H 6.91; P 9.66.

2-*tert*-Butyl-2-chloro-2,4-diphenyl-4-trifluoro-methyl-1,2λ^5-oxaphosphetane (X). Trifluoromethyl phenyl ketone (0.02 mol) was added at cooling (–70°C) to a solution of *tert*-butylphenylmethylene(chloro)-phosphorane **II** (2.1 g, 0.01 mol) in 10 mL of diethyl ether. The reaction mixture was allowed to warm up to room temperature. The precipitate was filtered off, the filtrate was evaporated. The residue (yield 95% by NMR data) was recrystallized from hexane at –70°C. Yield 2 g (50%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.76 d (9H, CH_3, $^3J_{PH}$ 20.0 Hz), 5.16 m and 5.23 m (2H, PCH_2), 7.20–7.60 m (5H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.7 d (PC, $^2J_{PC}$ 15.0 Hz), 40.8, 52.5 d (PC, $^1J_{PC}$ 61.0 Hz), 91 dq ($^2J_{CP}$ 10.0 Hz, $^2J_{CF}$ 25.0 Hz), 127.0 q (CF_3, J_{CF} 270.0 Hz), 125.4, 129.2, 130.4, 131.8, 140.5. ^{31}P NMR spectrum ($CDCl_3$): δ_P 2.99, 4.93 ppm (4 : 1). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 78.4, 78.3. Mass spectrum (70 eV): *m*/*e* 388 $[M]^+$. Found, %: C 58.85; H 5.49; P 7.91. $C_{19}H_{21}ClF_3OP$. Calculated , %: C 58.70; H 5.44; P 7.97.

***tert*-Butyl(phenyl)(3,3,3-trifluoro-2-hydroxy-2-phenylpropyl)phosphine oxide (XI)**. An open flask with the solution of 2-*tert*-butyl-2-chloro-2,4-diphenyl-4-trifluoromethyl-1,2λ^5-oxaphosphetane **X** (1.8 g, 0.0048 mol) in 10 mL of hexane was placed into the desiccator on the bottom of which water was poured to form a thin layer. The formed colorless product of the reaction insoluble in hexane was filtered off and additionally purified by column chromatography eluting with a mixture ethyl acetate–chloroform, 1 : 1. Yield 1.2 g (65%), colorless crystals, mp 149–152 °C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 d (9H, CH_3, $^3J_{PH}$ 15.0 Hz), 2.60 t (1H, CH_2, $^2J_{PH}$ 15.0 Hz), 2.80 t (1H, CH_2, $^2J_{PH}$ 15.0 Hz), 6.8 m (1H, OH), 7.4–7.6 m (10H, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 23.4, 27.1 d ($^1J_{PC}$ 62.0 Hz), 33.5 d (*J* 65.0 Hz), 82.0, 125.0 q ($^1J_{CF}$ 275.0 Hz), 128.0, 129.0, 130.0, 132.0, 133.0, 144.0. ^{31}P NMR spectrum ($CDCl_3$): δ_P 52.5 ppm. ^{19}F NMR spectrum ($CDCl_3$): δ_F 82.16 ppm. Found, %: C 61.73; H 5.99; P 8.11. $C_{19}H_{22}F_3O_2P$. Calculated, %: C 61.62; H 5.99; F 15.39; P 8.36.

***Z*-*tert*-Butyl(phenyl)(3,3,3-trifluoro-2-phenylprop-1-en-1-yl)phosphine oxide (XII)**. Oxaphosphetane **X** was heated at 149–150°C to the end of hydrogene chloride emission. Then the reaction mixture was cooled and the product was isolated by column chromatography on silica gel eluting with hexane–ethyl acetate mixture (10 : 1). Yield 35%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.50 d (9H, CH_3, $^3J_{HH}$ 15.0 Hz), 6.90 d.d (1H, CH=, $^2J_{PH}$ 25.0 Hz, $^4J_{HF}$ 1.0 Hz), 7.30–7.60 m (10H, C_6H_5). ^{31}P NMR spectrum

($CDCl_3$): δ_P 32.0 ppm. ^{19}F NMR spectrum ($CDCl_3$): δ_F –68.1 ppm. Mass spectrum (70 eV): *m*/*e* 352 $[M]^+$. Found, %: C 64.66; H 5.62; P 8.91. $C_{19}H_{20}F_3OP$. Calculated, %: C 64.77; H 5.72; P 8.79.

REFERENCES

1. Hoffmann, R.W., *Angew. Chem. Int. Ed*., 2001, vol. 40, no. 8, p. 1411. DOI: 10.1002/1521-3773.
2. Vedejs, E., and Marth, C.F., *J. Am. Chem. Soc*., 1990, vol. 112, no. 10, p. 3905. DOI: 10.1021/ja00166a026.
3. Maryanoff, B.E., Reitz, A.B., Mutter, M.S., Inners, R.R., and Almond, H.R., Jr., *J. Am. Chem. Soc.*, 1985, vol. 107, no. 4, p. 1068. DOI: 10.1021/ja00290a058.
4. Maryanoff, B.E., Reitz, A.B., Graden, D.W., and Almond, H.R., Jr., *Tetrahedron Lett*., 1989, vol. 30, no. 11, p. 1361. DOI: 10.1016/S0040-4039(00)99465-6.
5. Kolodiazhnyi, O.I., *Phosphorus Ylides. Chemistry and Application in Organic Synthesis*, Weinheim; New York; Chichester: J. Wiley-VCH, 1999.
6. Kolodiazhnyi, O.I., *Khimiya ilidov fosfora* (Chemistry of Phosphorus Ylides), Kiev: Naukova Dumka, 1994.
7. Kolodiazhnyi, O.I., *Russ. Chem. Rev*., 1991, vol. 60, no. 4, p. 391.
8. Kolodiazhnyi, O.I., *Tetrahedron Lett*., 1985, vol. 26, no. 4, p. 439. DOI: 10.1016/S0040-4039(00)61905-6.
9. Kolodiazhnyi, O.I., *Tetrahedron Lett*., 1981, vol. 22, no. 13, p. 1231. DOI: 10.1016/S0040-4039(01)90282-5.
10. Kolodiazhnyi, O.I., *Zh. Obshch. Khim.,* 1986, vol. 56, no. 2, p. 253.
11. Vedejs, E., Marth, C.F., and Ruggeri, R., *J. Am. Chem. Soc*., 1988, vol. 110, no. 12, p. 3940. DOI: 10.1021/ja00220a036.
12. Kyba, E.P., *J. Am. Chem. Soc*., 1976, vol. 98, no. 16, p. 4805. DOI: 10.1021/ja00432a020.
13. Wolfe, B., and Livinghouse, T., *J. Am. Chem. Soc*., 1998, vol. 120, no. 20, p. 5116. DOI: 10.1021/ja973685k.
14. Bergin, E., O'Connor, C.T., Robinson, S.B., McGarrigle, E.M., O'Mahony, C.P., and Gilheany, D.G., *J. Am. Chem. Soc*., 2007, vol. 129, no. 31, p. 9566. DOI: 10.1021/ja072925l.