Russian Journal of Organic Chemistry, Vol. 37, No. 12, 2001, pp. 1726–1730. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 12, 2001, pp. 1807–1811.
Original Russian Text Copyright © 2001 by Gusarova, Ivanova, Reutskaya, Arbuzova, Baikalova, Deryagina, Russavskaya, Trofimov.

Dedicated to Academician M.G.Voronkov on occasion of his 80th birthday

Reaction of Tribenzylphosphine Oxide with Aldehydes

N. K. Gusarova, N. I. Ivanova, A. M. Reutskaya, S. N. Arbuzova, L. V. Baikalova, E. N. Deryagina, N. V. Russavskaya, and B. A. Trofimov

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033, Russia

Received March 20, 2001

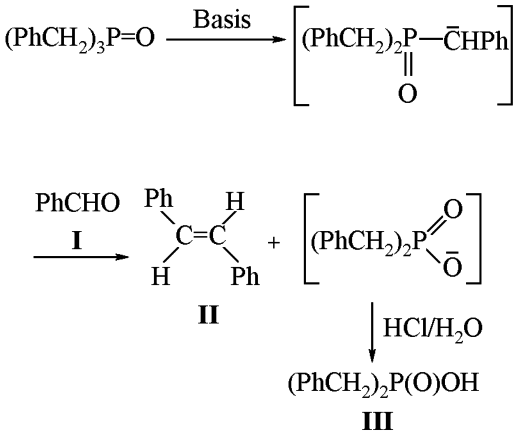
Abstract—Tribenzylphosphine oxide readily and stereoselectively reacts with aliphatic, aromatic, and heteroaromatic aldehydes in the presence of strong bases yielding exclusively (or predominantly) E-isomers of 1-organyl-2-phenylethenes and dibenzylphosphinic acid.

Tertiary phosphine oxides are known to react with aldehydes and ketones under conditions of Horner–Wittig reaction to yield *E*- and *Z*-alkenes [1–7], and previously into the reaction were brought only asymmetric diphenyl(organyl)phosphine oxides of a general formula $Ph_2P(O)CH_2R$ (R = alkyl [4, 8–10], Ph [1, 4], β-aminoalkyl, β-*N*-acylaminoalkyl [11]) containing a diphenylphosphoryl leaving group. The carbanions were generated under the action of strong bases, as potassium *tert*-butylate [2, 6, 7], sodium amide [7], butyl- and phenyllithium [1, 3–5].

We recently published short communications [12, 13] on application in the Horner–Wittig reaction of the symmetrical tribenzylphosphine oxide that was conveniently prepared from the red phosphorus and benzyl chloride [14]. Thus the heating of the tribenzylphosphine oxide to 60–80°C with benzaldehyde, 2,2-dimethylpropanal, or now available [15] 1-methyl- and 1-ethylimidazole-2-carboxaldehydes in a system $NaNH_2$–THF or KOH–DMSO afforded respectively *E*-isomers of 1.2-diphenylethene, 1-(1,1-dimethylethyl)-2-phenylethene, and also 1-(1-methylimidazol-2-yl)- and 1-(1-ethylimidazol-2-yl)-2-phenylethenes [12, 13].

The target of the present study was investigation of the reaction between triphenylphosphine oxides and aldehydes of aliphatic, aromatic, and heteroaromatic series, improvement and extension of the preparative opportunities of the reaction.

By an example of benzaldehyde we studied the influence of reaction (1) conditions (base character, reagents ratio, temperature of the process) on the yield of (*E*)-1,2-diphenylethene (**II**) and dibenzylphosphinic acid (**III**). We used in the reaction superbasic catalytic systems NH_2–THF, *t*-BuOK–DMSO, CsOH–DMSO, KOH–DMSO, NaOH–CsF–DMSO, metallic sodium in THF, and also 60% water solution of KOH in the presence of a phase-transfer catalyst (benzyltriethylammonium chloride, BTAC) (see table). The reactions were carried out in the temperature range 60–105°C.



(1)

The highest yield (88%) of *E*-1,2-diphenylethene was obtained at heating to 58–60°C of tribenzylphosphine oxide and benzaldehyde in the system $NaNH_2$–THF, and the olefination occurred with the same result both at equimolar reagents ratio and at benzaldehyde excess (see table, runs nos. *1* and *2*).

The use of system *t*-BuOK–DMSO, all other things being the same, reduces the yield of (*E*)-1,2-diphenylethene to 56% (see table, run no. 3). Carrying out of reaction (1) at 80°C in systems CsOH–DMSO and KOH–DMSO affords ethene **II** in 51 and 42% yield respectively (see table, runs nos.4 and 5). Further increase of the reaction temperature to 105°C does not increase the efficiency of the process under study (see table, run no. 6). In all runs above cited the tributylphosphine oxide was consumed to 100%.

1070-4280/01/3712-1726$25.00 © 2001 MAIK "Nauka/Interperiodica"

A superbasic system NaOH–CsF–DMSO recently introduced for vinylation of alcohols and oximes with acetylene [16] in reaction between triphenyphosphine oxide and benzaldehyde was not very efficient and was even worse than heterophase superbase KOH–DMSO: the tribenzylphosphine oxide conversion was in this case 75%, and the yield of (*E*)-1,2-diphenylethene and dibenzylphosphinic acid 39 and 61% respectively (see table, cf. run no. 7 with runs nos. 5 and 6).

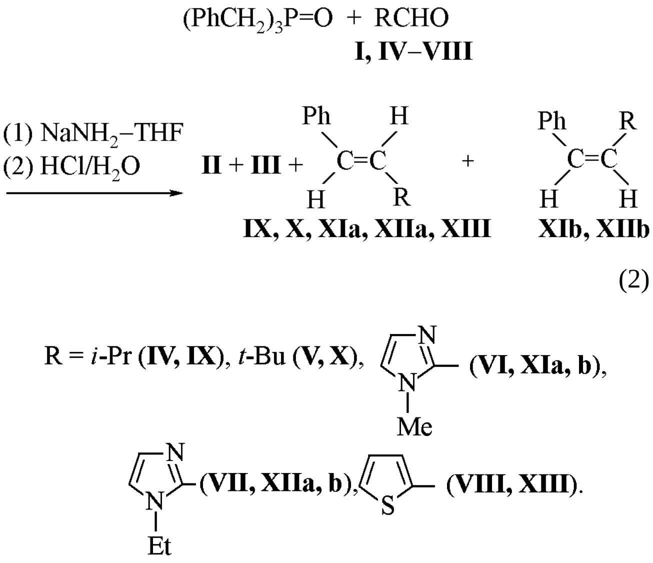
It turned out that the system sodium metal–THF was low-active in reaction (1): at tribenzylphosphine oxide conversion 79% the yield of ethene **I** and acid **III** in this run amounted only to 23 and 28% respectively (see table, run no. 8). The activation of the reaction in question under the conditions of the phase-transfer catalysis (in the system KOH–toluene–BTAC) was also inefficient: the overall yield of the target products reached only 12% at conversion of the initial tribenzylphosphine oxide 36% (see table, run no. 19)

Thus the data obtained evidence that in the synthesis of (*E*)-1,2-diphenylethene and dibenzylphosphinic acid it is feasible to use the catalytic system NH_2–THF at 60°C.

Among the reaction (1) products the ^1H NMR spectra indicated the presence of the benzyl alcohol (yield ~1–5%) arising apparently along Cannizzaro reaction [7].

At the best conditions found for the synthesis of (*E*)-1,2-diphenylethene we brought into the reaction with tribenzylphosphine oxide the other aldehydes: 2-methylpropanal (**IV**), 2,2-dimethylpropanal (**V**), 1-methylimidazole-2-carboxaldehyde (**VI**), 1-ethylimidazole-2-carboxaldehyde (**VI**), and thiophene-2-carboxaldehyde (**VIII**).

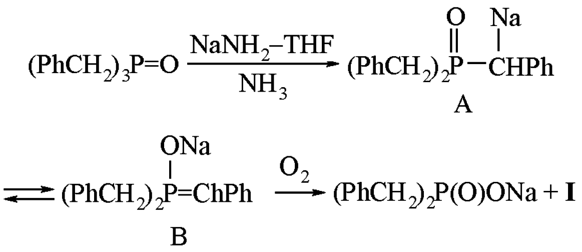
It turned out that aliphatic aldehydes **IV, V**, and thiophene-2-carboxaldehyde (**VIII**) react with tribenzylphosphine oxide stereospecifically to afford *E*-isomers of 1-(1-methylethyl)-2-phenylethene (**IX**), 1-(1,1-dimethylethyl)-2-phenylethene (**IX**), and 1-thiophene-2-phenylethene (**XIII**) respectively in 50–56% yields. Dibenzylphosphinic acid formed therewith in 71–81% yield and was isolated same as in reaction (1) at acidification of the water fraction of the reaction mixture. At the use in reaction (2) of aldehydes from the imidazole series **VI** and **VII** alongside the *E*-isomers 1-(1-methylimidazol-2-yl)-2-phenylethene (**XIa**) and 1-(1-ethylimidazol-2-yl)-2-phenylethene (**XIIa**) were also obtained the corresponding *Z*-isomers **XIb and XIIb**. The overall yield of ethenes **XIa, b** and **XIIa, b** comprised 42 and 52% respectively at the ratio of *E* and *Z* isomers 7.4–6 : 1. The yield of acid **III** was 57–79%. Under conditions of reaction (2) alongside ethenes **IX–XIII** were isolated also (*E*)-1,2-diphenylethene in 5–10% yield with respect to the initial amount of tribenzylphosphine oxide.



(2)

The exclusive or predominant formation of *E*-isomers of 1-organyl-2-phenylethenes **II, IX–XIa, XIIa, XIII** in the studied processes (1) and (2) is consistent with the known *E*-selectivity of the Horner–Wittig reaction [5, 17].

The (*E*)-1,2-diphenylethene may arise in reaction (2) according to scheme (3) including primary deprotonation of the tribenzylphosphine oxide effected by superbases followed by rearrangement of phosphine oxide (A) into a more stable phosphorane (B) that in the presence of oxygen provides sodium dibenzylphosphinate and benzaldehyde. The latter reacts with the tribenzylphosphine oxide to give ethene **II** along reaction (1).



(3)

It turned out actually that the heating of the tribenzylphosphine oxide to 50–60°C in the system

$NaNH_2$–THF provided (*E*)-1,2-diphenylethene and dibenzylphosphinic acid in 15 and 37% respectively. At the deprotonation stage in the ^{31}P NMR spectrum was observed a signal at δ_P 30.1 ppm that may be assigned to phosphorane (B) [18]. This reaction was described before with diphenylbenzylphosphine oxide; it resulted in (*E*)-1,2-diphenylethene and diphenyphosphinic acid [6, 19].

A presumable alternative scheme of (*E*)-1,2-diphenylethene formation via carbene PhCH: generation from tribenzylphosphine oxide at its boiling in xylene (2 h under argon) was not supported by experimental data.

Thus the use as olefinating reagent of the available tribenzylphosphine oxide under conditions of Horner–Wittig reaction provides new opportunities for stereoselective synthesis of 1,2-disubstituted alkenes, in particular, stilbene and its heteroanalogs, promising raw material for production of dyes, optical whiteners, complexing agents, photochemical sensors [20] and drugs (e.g., in the synthesis of milbemycin β_3, vitamine D and its analogs [5]). Besides the reaction of tribenzylphosphine oxide with aldehydes readily furnishes dibenzylphosphinic acids that previously were difficult to obtain: the synthesis that has been previously one of the best is multi-stage and is based on alkylation with benzyl iodide or chloride of fairly expensive and toxic phosphorus iodides [21].

EXPERIMENTAL

^1H and ^{31}P NMR spectra were registered on spectrometer Bruker DPX 400 using respectively HMDS as internal reference and 85% H_3PO_4 as external reference. IR spectra were taken on spectrometer Specord 75IR. All experiments were carried out under inert atmosphere (argon).

Reaction of tribenzylphosphine oxide with benzaldehyde in a system $NaNH_2$–THF (see table, run no. 1). To a heated to 50–60°C solution of 0.7 g (2.2 mmol) of tribenzylphosphine in THF (40 ml) was added 0.26 g (6.6 mmol) of sodium amide, the reaction mixture was stirred at reflux for 1 h (within 10 min the reaction mixture turned bright yellow), and then 0.23 g (2.2 mmol) of aldehyde *I* was added thereto. The mixture was boiled for 1 h more, cooled to room temperature, and diluted with water (35 ml). The reaction products were extracted into ether (3 × 10 ml). The extract was washed with water (2 × 8 ml), dried with potassium carbonate, ether was distilled off, and the residue was dried in a vacuum. We obtained 0.35 g (88%) of (*E*)-1,2-diphenylethene (**II**), mp 122–123°C (from ethanol) (publ. 124°C [3]). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.09 s (2H, =CH), 7.26– 7.46 m (10H, C_6H_5). Found, %: C 92.85; H 6.73. $C_{14}H_{12}$. Calculated, %: C 93.30; H 6.70. Water phases were combined, acidified with 2 N HCl till pH 2–3, and from the solution precipitated colorless crystals that were separated, washed in succession with water, alcohol, ether, and dried in a vacuum. We obtained 0.35 g (65%) of acid **III**, mp 189–190°C (from ethanol) (publ. 191°C [21]). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.85 d (4H, CH_2, $^2J_{HP}$ 16.9 Hz), 7.18–7.28 m (10H, C_6H_5), 9.02 s (1H, OH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 49.9 ppm Found, %: C 67.22; H 6.23; P 12.31. $C_{14}H_{15}O_2P$. Calculated, %: C 68.29; H 6.10; P 13.01.

Reaction of tribenzylphosphine oxide with 2-methylpropanal. In the same way as in the preceding run from 1 g (3 mmol) of tribenzylphosphine oxide, 0.35 g (9 mmol) of sodium amide, and 0.43 g (6 mmol) of 2-methylpropanal (**IV**) in 40 ml of THF was obtained 0.3 g of viscous organic mixture containing according to its ^1H NMR spectrum 79% of (*E*)-1-(1-methylethyl)-2-phenylethene (yield 54%), 9% of (*E*)-1,2 -diphenylethene (yield 5%), and 12% of tribenzylphosphine oxide (conversion 96%). The mixture obtained was washed with small portions of ether, the ether was removed, and the residue was washed with pentane. We obtained as an individual product ethene **IX** (viscous fluid). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.07 d (6H, CH_3, $^3J_{HH}$ 6.65 Hz), 2.43 octet [1H, $C\underline{H}$-$(CH_3)_2$, $^3J_{HCCH}$ 6.65 Hz], 6.17 d.d (1H, =$C\underline{H}$-CH, $^3J_{HC=CH}$ 15.95 Hz), 6.31 d (1H, =$C\underline{H}$-C_6H_5), 7.15–7.35 m (5H, C_6H_5) is in agreement with the published spectrum [22]. Found, %: C 90.62; H 10.05. $C_{11}H_{14}$. Calculated, %: C 90.35; H 9.65. From the water layer was isolated 0.6 g (81%) of acid **III**.

Reaction of tribenzylphosphine oxide with 2,2-dimethylpropanal. In the same way from 1 g (3 mmol) of tribenzylphosphine oxide, 0.35 g (9 mmol) of sodium amide, and 0.39 g (4.5 mmol) of 2,2-dimethylpropanal (**V**) in 40 ml of THF was obtained 0.35 g of viscous organic mixture containing according to its ^1H NMR spectrum 68% of (*E*)-1-(1,1-dimethylethyl)-2-phenylethene (**X**) (yield 50%), 15% of (*E*)-1,2 -diphenylethene (yield 10%), and 17% of tribenzylphosphine oxide (conversion 94%). The mixture obtained was washed with small portions of ether, the ether was removed, and the residue was washed with pentane. We obtained as an individual product ethene **X** (viscous fluid). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.08 s (9H, CH_3), 6.23 d (1H,

=CH, $^3J_{HH}$ 16.22 Hz), 6.29 d (1H, =CH), 7.12–7.36 m (5H, C_6H_5) is in agreement with the published spectrum [23]. Found, %: C 89.49; H 9.34. $C_{12}H_{16}$. Calculated, %: C 90.00; H 10.00. From the water layer was isolated 0.57 g (78%) of acid **III**.

Reaction of tribenzylphosphine oxide with 1-methylimidazole-2-carboxaldehyde. In the same way from 1 g (3 mmol) of tribenzylphosphine oxide, 0.35 g (9 mmol) of sodium amide, and 0.5 g (4.5 mmol) of 1-methylimidazole-2-carboxaldehyde (**VI**) in 40 ml of THF was obtained 0.42 g of viscous organic mixture containing according to its ^1H NMR spectrum 62% of 1-(1-methylimidazol-2-yl)-2-phenylethene (**XI**) (yield 42%), 13% of (*E*)-1,2 -diphenylethene (yield 10%), and 26% of tribenzylphosphine oxide (conversion 90%). The mixture obtained was washed with small portions of ether, the ether was removed, and the residue was washed with pentane and dried in a vacuum. We obtained ethene **XI** (viscous fluid) as a mixture of *E*- and *Z*-isomers (**XIa, b**), *E*:*Z* = 7.4 : 1. ^1H NMR spectrum ($CDCl_3$), δ, ppm, of ethene **XIa**: 3.69 s (3H, CH_3), 6.85 d (1H, H^5, $^3J_{H^5H^4}$ 1.0 Hz), 6.89 d (1H, =CH, $^3J_{HH}$ 16.2 Hz), 7.06 d (1H, H^4), 7.20–7.52 m (5H, C_6H_5), 7.56 d (1H, =CH); of ethene **XIb**: 3.23 s (3H, CH_3), 6.39 d (1H, =CH, $^3J_{HH}$ 12.2 Hz), 6.79 d (1H, H^5, $^3J_{H^5H^4}$ 1.2 Hz), 6.80 d (1H, =CH), 7.20–7.52 m (5H, C_6H_5). The chemical shift of H^4 proton was not determined because of overlapping with the signals of other protons. Acid **III** was isolated from the water layer in amount of 0.42 g (57%).

Reaction of tribenzylphosphine oxide with 1-ethylimidazole-2-carboxaldehyde. In the same way from 1 g (3 mmol) of tribenzylphosphine oxide, 0.35 g (9 mmol) of sodium amide, and 0.56 g (4.5 mmol) of 1-ethylimidazole-2-carboxaldehyde (**VII**) in 40 ml of THF was obtained 0.35 g of viscous organic mixture containing according to its ^1H NMR spectrum 88% of 1-(1-ethylimidazol-2-yl)-2-phenylethene (**XII**) (yield 52%), and 12% of (*E*)-1,2-diphenylethene (yield 7%). The mixture obtained was washed with small portions of ether, the ether was removed, and the residue was washed with pentane and dried in a vacuum. We obtained ethene **XII** (viscous fluid) as a mixture of *E*- and *Z*-isomers (**XIIa, b**), *E* : *Z* = 6 : 1. ^1H NMR spectrum ($CDCl_3$), δ, ppm, of ethene **XIIa**: 1.42 t (3H, CH_3, $^3J_{HH}$ 7.3 Hz), 4.05 q (2H, CH_2), 6.87 d (1H, =CH, $^3J_{HH}$ 15.8 Hz), 6.90 d (1H, H^5, $^3J_{H^5H^4}$ 1.1 Hz), 7.08 d (1H, H^4), 7.20–7.52 m (5H, C_6H_5), 7.59 d (1H, =CH); of ethene **XIIb**: 1.18 t (3H, CH_3, $^3J_{HH}$ 7.3 Hz), 3.65 q (2H, CH_2), 6.37 d (1H, =CH, J_{HH} 12.2 Hz), 6.77 d (1H, =CH), 6.87 d (1H, H^5, $^3J_{H^5H^4}$ 1.1 Hz), 7.20–7.52 m (5H, C_6H_5). C_6H_5). The chemical shift of H^4 proton was not determined because of overlapping with the signals of other protons. Acid **III** was isolated from the water layer in amount of 0.58 g (79%).

Reaction of tribenzylphosphine oxide with thiophene-2-carboxaldehyde. In the same way from 0.7 g (2.2 mmol) of tribenzylphosphine oxide, 0.26 g (6.6 mmol) of sodium amide, and 0.34 g (3 mmol) of thiophene-2-carboxaldehyde (**VIII**) in 40 ml of THF was obtained 0.33 g of crystalline mixture containing according to its ^1H NMR spectrum 70% of (*E*)-1-thienyl-2-phenylethene (**XI**) (yield 56%), 8% of (*E*)-1,2 -diphenylethene (yield 6%), and 22% of tribenzylphosphine oxide (conversion 89%). The mixture obtained was washed with small portions of ether, the ether was removed, and the residue was washed with pentane and dried in a vacuum. We obtained ethene **XI** as an individual compound, mp 108–109°C (publ. 111–112°C [24]). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.91 d (1H, =CH, $^3J_{HH}$ 16.1 Hz), 6.98 d.d (1H, H^4, $^3J_{H^4H^3}$ 3.4, $^3J_{H^4H^5}$ 5.1 Hz), 7.04 d (1H, H^3), 7.16 d (1H, H^5), 7.20 d (1H, =CH), 7.22–7.43 m (5H, C_6H_5). Found, %: C 76.92; H 5.38; S 16.81. $C_{12}H_{10}S$. Calculated, %: C 77.19; H 5.40; S 16.98. From the water layer was separated 0.39 g (72%) of acid **III**.

Transformation of tribenzylphosphine oxide in a system NH_2–THF. To a solution of 0.7 g (2.2 mmol) of tribenzylphosphine oxide in 40 ml of THF heated to 58–60°C was added 0.26 g (6.6 mmol) of sodium amide, and reaction mixture was stirred at reflux for 2 h, cooled, and analyzed by ^{31}P NMR method. The spectrum of the reaction mixture in DMSO-d_6 contained two signals at δ_p, ppm: 41.8 (assigned to tribenzylphosphine oxide by comparison with the spectrum of an authentic sample), and 30.1 that was assigned to phosphorane (B) [reaction (3)] basing on the data of [18]. The reaction mixture was diluted with water (40 ml), the reaction products were extracted into ether (3 × 10 ml), the extract was dried with potassium carbonate, the ether was distilled off, and the residue was dried in a vacuum. We obtained 0.29 g of crystalline residue that according to ^1H NMR spectrum contained 56% of tribenzylphosphine oxide and 44% of (*E*)-1,2-diphenylethene. The mixture obtained was washed with small portions of ether. Thus was separated 0.21 g of tribenzylphosphine oxide (conversion 70%). On removing ether from the ether washings and on recrystallization of the residue from ethanol we obtained

0.06 g (15%) of ethene **II**. From the water layer by the usual procedure was separated 0.2 g (37%) of acid **III**. The NMR spectra of ethene **II** (^{1}H) and acid **III** (^{1}H and ^{1}P) are consistent with the published spectra [3, 21].

REFERENCES

1. Horner, L., Hoffmann, H., Wippel, H.G., and Klahre, G., *Chem. Ber.*, 1959, vol. 92, pp. 2499–2505.
2. Kabachnik, M.I., Medved', T.Ya., and Matrosov, E I., *Dokl. Akad. Nauk SSSR*, 1965, vol. 162, no. 2, pp. 339–342.
3. Buss, A.D., Greeves, N., Mason, R., and Warren, S., *J. Chem. Soc., Perkin Trans. I*, 1987, no. 12, pp. 2569–2577.
4. Buss, A.D. and Warren, S., *J. Chem. Soc., Perkin Trans. I*, 1985, no. 11, pp. 2307–2325.
5. Klayden, J. and Warren, S., *Angew. Chem.*, 1996, vol. 108, no. 3, pp. 261–291.
6. Dombrovskii, A.V. and Dombrovskii, B.A., *Usp. Khim.*, 1966, vol. 35, no. 10, pp. 1771–1787.
7. Vatsuro, K.V. and Mishchenko, G.L., *Imennye reaktsii v organicheskoi khimii* (Personal Reaction in Organic Chemistry), Moscow: Khimiya, 1976, p. 456.
8. Boutagy, J. and Thomas, R., *Chem. Rev.*, 1974, vol. 74, no. 1, pp. 87–99.
9. Amstrong, D.R., Barr, D., Davidson, M.G., Hutton, G., O'Brien, P., Snaith, R., and Warren, S., *J. Organometal. Chem.*, 1997, vol. 529, no. 1, pp. 29–33.
10. Buss, A.D. and Warren, S., *Tetrahedron Lett.*, 1983, vol. 24, no. 36, pp. 3931–3935.
11. Cavalla, D., Cruse, W.B., and Warren, S., *J. Chem. Soc., Perkin Trans. I*, 1987, no. 9, pp. 1883–1898.
12. Gusarova, N.K., Ivanova, N.I., Reutskaya, A.M., Arbuzova, S.N., Trofimov, B.A., *Zh. Org. Khim.*, 1999, vol. 69, no. 11, pp. 1922–1923.
13. Ivanova, N.I., Reutskaya, A.M., Arbuzova, S.N., Baikalova, L.V., Afonin, A.V., Gusarova, N.K., and Trofimov, B.A., *Khim. Geterotsikl. Soed.*, 2000, no. 2, pp. 262–264.
14. Gusarova, N.K., Malysheva, S.F., Arbuzova, S.N., and Trofimov, B.A., *Izv. RAN, Ser. Khim.*, 1998, no. 9, pp. 1695–1702.
15. Baikalova, L.V., Domnina, E.S., Chipanina, N.N., Afonin, A.V., and Shulunova, A.M., *Izv. Russian Akad. Nauk, Ser. Khim.*, 1999, no. 5, pp. 971–975.
16. Trofimov, B.A., Mikhaleva, A.I., Vasil'tsov A.M., Schmidt, E.Yu., Tarasova, O.A., Morozova, L.V., Sobenina, L.N., Preiss, T., and Henkelmann, J., *Synthesis*, 2000, no. 8, pp. 1125–1132.
17. Purdela, D. and Vylchanu, R., *Khimiya organicheskikh soedinenii fosfora* (Chemistry of Phosphorus Organic Compounds), Moscow: Khimiya, 1972.
18. Erastov, O.A. and Nikonov, G.G., *Funktsional'no-zameshchennye fosfiny i ikh proizvodnye* (Functionally Substituted Phosphines and Its Derivatives), Moscow: Mir, 1986, p. 238.
19. Horner, L., Klahre, G., Toscano, G., and Ertel, H., *Chem. Ber.*, 1961, vol. 94, pp. 1987–1996.
20. Simeonov, A., Matsushita, M., Juban, E.A., Thompson, E.H.Z., Hoffman, T.Z., Beuscher, A.E., Taylor, M.J., Wirsching, P., Rettig, W., McCusker, J.K., Stevens, R.C., Millar, D.P., Schultz, P.G., Lerner, R.A., and Janda, K.D., *Science*, 2000, vol. 290, pp. 307–313.
21. Kudryavtseva, L.I. and Feshchenko, H.G., *Zh. Obshch. Khim.*, 1981, vol. 51, no. 2, pp. 478–479; Kudryavtseva, L.I., *Zh. Obshch. Khim.*, 1989, Obshch. Khim., vol. 59, no. 5, pp. 1027–1031.
22. Worm, A.T. and Brewster, J.H., *J. Org. Chem., Obshch. Khim.*, 1970, vol. 35, no. 5, pp. 1715–1716.
23. Seyferth, D. and Singh, G., *J. Am. Chem. Soc.*, 1965, Obshch. Khim., vol. 87, no. 18, pp. 4156–4162.
24. Seus, E.J. and Wilson, C.V., *J. Org. Chem.*, 1961, Obshch. Khim., vol. 26, no. 12, p. 524.