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Reactions of Elemental Phosphorus and Phosphine with Electrophiles in Superbasic Systems: XIV.[1] Phosphorylation of 2-Vinylnaphthalene with Elemental Phosphorus and Phosphines in the KOH–DMSO System

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Abstract — Elemental phosphorus (red or white) reacts with 2-vinylnaphthalene while heating at 90–96°C in the superbasic KOH–DMSO system to form 2-(2-naphthyl)ethylphosphine, 2-(2-naphthyl)ethylphosphinic acid, bis[2-(2-naphthyl)ethyl]phosphine, bis[2-(2-naphthyl)ethyl]phosphine oxide, and tris[2-(2-naphthyl)ethyl]-phosphine oxide in a total yield of up to 40%. Selective conditions for preparing the tertiary phosphine oxide from white phosphorus and 2-vinylnaphthalene in 58% yield were found. Phosphine and (2-phenylpropyl)-phosphine add to 2-vinylnaphthalene in the KOH–DMSO system to form, under certain conditions, corresponding secondary phosphines in high yields.

In [2], using styrene and α-methylstyrene as examples, we showed that phosphide and phosphinite ions generated from red phosphorus in superbasic systems comprising an alkali metal hydroxide and a polar aprotic solvent react with the weakly electrophilic double bond of arylalkenes at 60–65°C to form corresponding primary, secondary, and tertiary phosphines and/or their oxidized derivatives in a total yield of 48% [2]. Conditions (85–125°C, KOH–HMPA or KOH–DMSO) for preparing tris(2-phenylethyl)-phosphine oxide in 60–65% yield from styrene and elemental (red or white) phosphorus were developed. Phosphine adds to styrene and α-methylstyrene to form, under certain conditions (atmospheric pressure, 60–65°C, KOH–DMSO), bis(2-phenylethyl)- and bis-(2-phenylpropyl)phosphines in good yield (63–79%) [8–10].

In the present work we, for the first time, accomplished and investigated phosphorylation of 2-vinylnaphthalene with elemental phosphorus and phosphines. The aim of this work was to prepare new phosphines and phosphine oxides with bulky radicals, which hold promise as ligands for chlorine substitution in chloroarenes and C–C, C–N, and C–O bond formation [11].

We found that heating (90–96°C, 7 h) of red phosphorus and 2-vinylnaphthalene (10 : 1 molar ratio) in the KOH–DMSO system in the presence of a little water (for neutralization of carbanions formed) leads to a mixture of 2-(2-naphthyl)ethylphosphine (**I**), 2-(2-naphthyl)ethylphosphinic acid (**II**), bis[2-(2-naphthyl)-ethyl]phosphine (**III**), bis[2-(2-naphthyl)ethyl]phosphine oxide (**IV**), and tris[2-(2-naphthyl)ethyl]phosphine oxide (**V**). The yields of these compounds are 6%, 5%, <1.2%, and 6%, respectively (see table, exp. no. 1). Under similar conditions, white phosphorus reacts with 2-vinylnaphthalene to give the same set of organophosphorus compounds **I**–**V**, but the total yield of the products is two times higher than in the case of red phosphorus. The yield of primary phosphine **I** (6%) and phosphinic acid **II** (6%) practically does not alter, while the yield of secondary phosphine **III** and phosphine oxide **IV**, as well as tertiary phosphine oxide **V** considerably increases (6%, 8%, and 14%, respectively; see table, exp. no. 2).

The example of white phosphorus was used to show that the effectiveness and, especially, selectivity of reaction (1) can be increased by significantly increasing (five times) the initial content of 2-vinylnaphthalene in the reaction mixture. Under this conditions, the main phosphorylation products are tris[2-(2-naphthyl)ethyl]phosphine (**VI**) and phosphine oxide **V**, formed in a 1 : 5 ratio with a total yield of 63% (see

[1] For communication XIII, see [1].

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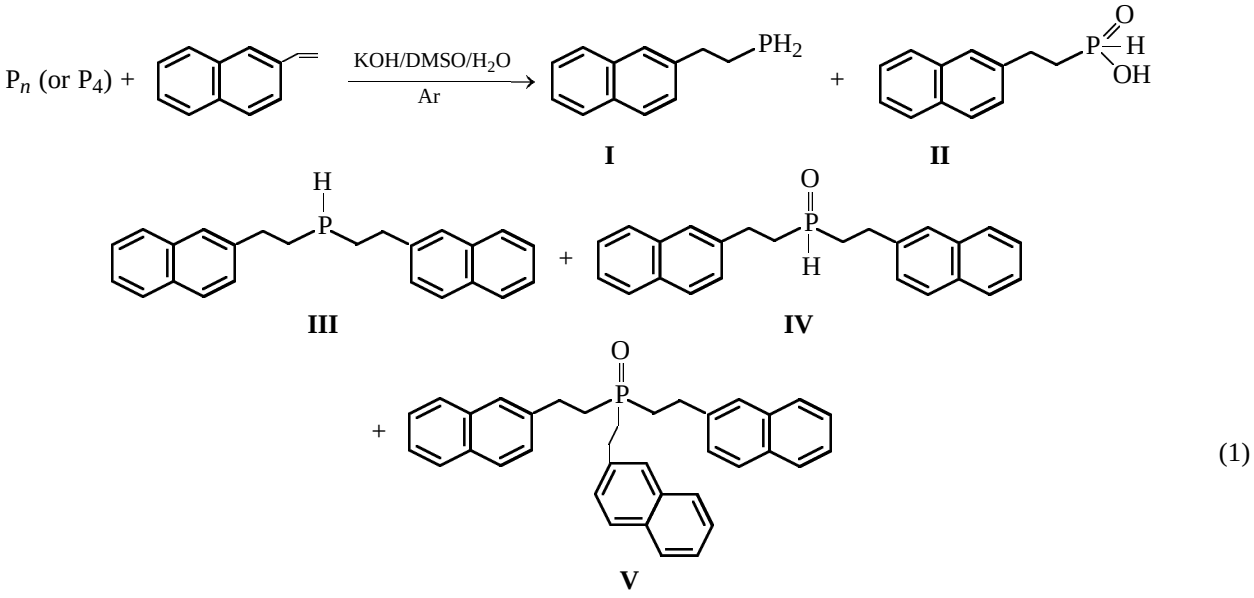
Reaction of 2-vinylnaphthalene with elemental phosphorus and phosphine in the KOH–DMSO system[a]

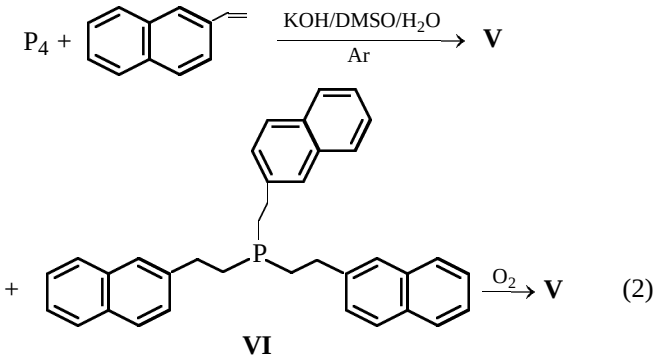
Exp. no.	Phosphorylation agent, g (mol)	2-Vinylnaphthalene, g (mol)	KOH, g (mol)	H_2O, ml	Reaction time, h	Yield[b], %				
						I	**II**	**III**	**IV**	**V**
1	P_{red}, 3.1 (0.1)	1.5 (0.01)	10 (0.18)	4.3	7.0	6	5	<1	2	6
2[c]	P_4, 3.1 (0.1)	1.5 (0.01)	10 (0.18)	4.3	7.0	6	6	6	8	14
3[c]	P_4, 0.5 (0.016)	1.23 (0.008)	1.6 (0.03)	0.7	4.0	[d]	[d]	[d]	[d]	52[e]
4	PH_3[f]	1.25 (0.008)	15 (0.27)	8	3.5	[d]	[d]	75	[d]	[d]

[a] Reaction temperature 90–96°C, amount of DMSO 50–70 ml. [b] The yield was calculated per taken 2-vinylnaphthalene whose conversion in exp. nos. 1–4 was almost 100%. [c] Hydroquinone, 0.01 mol, was added. [d] Does not form. [e] Phosphine **VI** was formed in 11% yield (^{31}P NMR data). [f] Phosphine was generated from 7 g of red phosphorus, 40 g of 50% aqueous KOH, and 40 ml of dioxane and supplied to the reaction mixture at a rate of 20–25 ml/min.



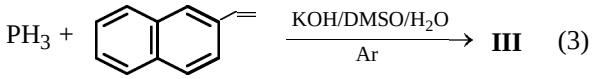
(1)

table, exp. no. 3). Treatment of this mixture with oxygen gave phosphine oxide **V** in 58% yield.



(2)

Phosphine generated from red phosphorus and potassium hydroxide in aqueous dioxane adds to 2-vinylnaphthalene at atmosheric pressure and 90–96°C to form secondary phosphine **III** in 75% yield at a complete conversion of 2-vinylnaphthalene (see table, exp. no. 4). The reaction is accomplished by vigorously passing the phosphine through the superbasic KOH–DMSO–H_2O system simultaneously slowly adding 2-vinylnaphthalene to a heated reaction mixture.



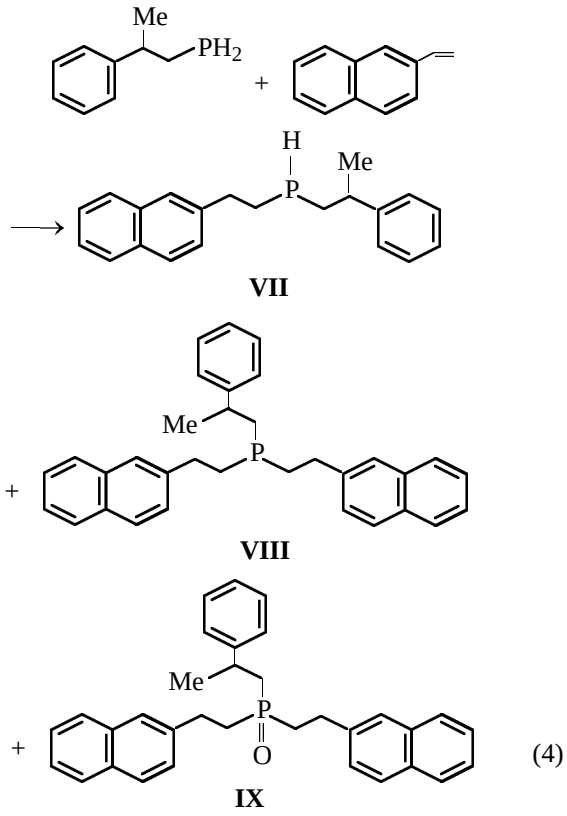
(3)

Reaction (3) performed at a lower temperature (65–68°C) results is a lower yield of phospine **III**, and the conversion of 2-vinylnaphthalene decreases to 19% and 22%, respectively.

Bubbling of air through a chloroform solution of secondary phosphine **III** for 24 h at room temperature gave phosphine oxide **IV** in quantitative yield.

2-Phenylpropylphosphine prepared from α-methyl-

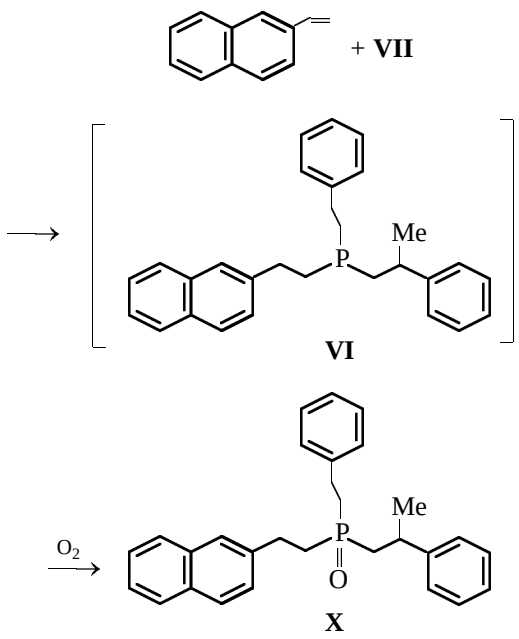
styrene and phosphine [12] readily adds to 2-vinylnaphthalene, when equimolar amounts of these reagents are heated at 95–98°C in the superbasic KOH–DMSO system, providing the unsymmetrical [2-(2-naphthyl)ethyl](2-phenylpropyl)phosphine (**VII**) as the main product and small amounts of bis[2-(2-naphthyl)ethyl](2-phenylpropyl)phosphine (**VIII**) and its oxide **IX**.



(4)

With the purpose of preparing an unsymmetrical tertiary phosphine (or phosphine oxide) with bulky radicals, that is potential synthons for preparing optically active phosphorus-containing ligands [13], we performed nucleophilic addition of secondary phosphine **VII** to styrene by heating at 80°C equimolar amounts of the reagents in the KOH–DMSO system. The reaction product was [2-(2-naphthyl)ethyl](2-phenylethyl)(2-phenylpropyl)phosphine oxide (**X**), yield 95% (considering 76% conversion of the starting phosphine **VII**). The expected [2-(2-naphthyl)-ethyl](2-phenylethyl)(2-phenylpropyl)phosphine was not found in the reaction mixture, evidently because of its easy oxidation.

Hence, the reactions of 2-vinylphosphine with elemental phosphorus and phosphines permit to obtain formerly unknown phosphines and phosphine oxides with bulky radicals, promising ligands for metal complex catalysts. Comparative analysis of our present



(5)

and published [2, 8] data shows that 2-vinylnaphthalene is slightly less reactive in these reactions than styrene.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer. The ^{1}H NMR spectra were obtained on a Bruker DPX-400 spectrometer. The ^{31}P NMR spectra were measured on a Jeol FX-90Q spectrometer in $CDCl_3$. All experiments were carried out under argon. Phosphine was obtained as a phosphine–hydrogen mixture obtained by the procedure in [8].

Bis[2-(2-naphthyl)ethyl]phosphine (III) (see table, exp. no. 4). A solution of 1.25 g of 2-vinylnaphthalene in 8 ml of DMSO was added dropwise at 90–93°C with stirring over the course of 1.5 h to a mixture of 15 ml of KOH, 50 ml of DMSO, and 8 ml of water, saturated with phosphine. Phosphine was continuously bubbled through the reaction mixture. The heating (90–93°C) and bubbling of phosphine was continued for an additional 1 h, after which the bubbling of phosphine was discontinued, and the mixture was heated under argon for 1 h at 90–93°C, cooled, diluted with water, and extracted with ether. The ethereal extracts were washed with water, dried over potassium carbonate, the ether was removed, and the residue was dried in a vacuum to obtain 1.04 g (75%) of phosphine **III** as light yellow crystals, mp 90–92°C (from ether). IR spectrum: ν(P–H) 2290 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.01 m (4H, CH_2P), 2.95 m (4H, CH_2), 7.24-7.80 m (14H, $C_{10}H_7$).

^{31}P NMR spectrum, δ_P, ppm: –70.8 d ($^1J_{PH}$ 198 Hz). Found, %: C 85.25; H 6.93; P 7.34. $C_{24}H_{23}P$. Calculated, %: C 84.18; H 6.77; P 9.05.

Bis[2-(2-naphthyl)ethyl]phosphine oxide (IV). A solution of 0.5 g of bis[2-(2-naphthyl)ethyl]phosphine (**III**) in 5 ml of chloroform was kept at room temperature for 24 h with constant bubbling of air. The chloroform was then removed, and the residue was washed with ether to obtain 0.5 g (96%) of phosphine oxide **IV** as white crystals, mp 140–142°C (from ether). IR spectrum, ν, cm^{-1}: 2300 (P–H), 1160 (P=O). ^{1}H NMR spectrum, δ, ppm: 2.12 m (4H, CH_2P), 3.08 m (4H, CH_2), 7.20–7.80 m (14H, $C_{10}H_7$). ^{31}P NMR spectrum, δ_P, ppm: 30.5 ($^1J_{PH}$ 432 Hz). Found, %: C 80.18; H 6.72; P 8.48. $C_{24}H_{23}PO$. Calculated, %: C 80.43; H 6.47; P 8.64.

Tris[2-(2-naphthyl)ethyl]phosphine oxide (V) (see table, exp. no. 3). A solution of 1.6 g of KOH n .7 ml of H_2O was added dropwise with stirring to a solution of 0.5 g of white phosphorus, 1.23 g of 2-vinylnaphthalene, and 0.01 g of hydroquinone in 50 ml of DMSO. The reaction mixture was heated for 4 h at 95–96°C, cooled, diluted with water, and extracted successively with ether and chloroform. The ethereal extracts were washed with water, dried over potassium carbonate, the ether was removed, and the residue was dried in a vacuum to obtain 0.47 g of a product containing, according to ^{31}P NMR data, 66% of tris[2-(2-naphthyl)ethyl]phosphine oxide (**V**) (δ_P 46.0 ppm) and 34% of tris[2-(2-naphthyl)ethyl]phosphine (**VI**) (δ_P –27.4 ppm). The yields of compounds **V** and **VI** were 24 and 11%, respectively. The chloroform extract was dried with potassium carbonate, the chloroform and DMSO were removed at reduced pressure, and the residue was washed with ether to give 0.38 g (28%) of phosphine oxide **V**.

The mixture of phosphine **VI** and phosphine oxide **V**, obtained from the ethereal extract, was dissolved in chloroform, and air was bubbled through the resulting solution for 24 h at room temperature. The chloroform was removed, and the residue was washed with ether and dried in a vacuum to give 0.41 g (30%) of phosphine oxide **V** as a white powder, mp 216–218°C (from ether). IR spectrum: ν(P=O) 1170 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 2.15 m (6H, CH_2), 3.08 m (6H, CH_2), 7.22–7.80 m (21H, $C_{10}H_7$). Found, %: C 84.28; H 6.58; P 5.63. $C_{36}H_{33}OP$. Calculated, %: C 84.35, H 6.49; P 6.04.

Reaction of 2-vinylnaphthalene with white phosphorus (see table, exp. no. 2). A solution of 10 g of KOH in 4.3 ml of H_2O was added dropwise with stirring to a mixture of 3.1 g of white phosphorus, 1.5 g of 2-vinylnaphthalene, and 0.01 g of hydroquinone in 60 ml of DMSO. The reaction mixture was heated for 7 h at 95–96°C, cooled, diluted with water, and extracted successively with ether and chloroform. The ethereal extracts were washed with water, dried with potassium carbonate, the ether was removed, and the residue was dried in a vacuum to obtain 0.4 g of a product containing, according to ^{31}P NMR data, 42% of 2-(2-naphthyl)ethylphosphine (**I**) (δ_P –139.1 ppm, $^1J_{PH}$ 198 Hz), 24% of bis[2-(2-naphthyl)ethyl]phosphine (**III**), 12% of bis[2-(2-naphthyl)ethyl]phosphine oxide (**IV**), and 22% of tris[2-(2-naphthyl)ethyl]phosphine oxide (**V**). The yields of compounds **I**, **III**–**V** were 6, 6, 4, and 8%, respectively.

The chloroform extract was dried with potassium carbonate, and the chloroform and DMSO were removed at reduced pressure to obtain 0.17 g of a product containing, according to ^{31}P NMR data, 52% of bis[2-(2-naphthyl)ethyl]phosphine oxide (**IV**) and 48% of tris[2-(2-naphthyl)ethyl]phosphine oxide (**V**). The yields of compounds **IV** and **V** were 4 and 6%.

The aqueous layer was treated with 30% aqueous HCl to pH 4–5, extracted with ether, the ethereal extracts were dried with potassium carbonate, the ether was removed, and the residue was dried in a vacuum to obtain 0.13 g (6%) of 2-(2-naphthyl)ethylphosphinic acid (**II**). ^{1}H NMR spectrum, δ, ppm: 1.84 m (2H, CH_2P), 2.94 m (2H, CH_2), 7.52–7.87 m (7H, $C_{10}H_7$). ^{31}P NMR spectrum, δ_P, ppm: 33.1 ($^1J_{PH}$ 557 Hz).

[2-(2-Naphthyl)ethyl](2-phenylpropyl)phosphine (VII). A solution of 0.46 g of 2-vinylphosphine in 2 ml of DMSO was added dropwise with stirring at 95–96°C over the course of 40 min to a mixture of 3.5 g of KOH, 2.3 ml of water, and 0.45 g of (2-phenylpropyl)phosphine in 10 ml of DMSO. The reaction mixture was heated for an additional 30 min at 95–96°C, cooled, diluted with water, and extracted with ether. The ethereal extracts were washed with water, dried over potassium carbonate, the ether was removed, and the residue was dried in a vacuum to obtain 0.89 g of a product containing, according to ^{31}P NMR data, 83% of [2-(2-naphthyl)ethyl](2-phenylpropyl)phosphine (**VII**) (δ_P –76.6 ppm, $^1J_{PH}$ 202 Hz), 7% of bis[2-(2-naphthyl)ethyl](2-phenylpropyl)phosphine (**VIII**), and 10% of bis[2-(2-naphtyl)ethyl](2-phenylpropyl)phosphine oxide (**IX**) (δ_P 46 ppm). The product was dissolved in ether, the resulting solution was filtered, and the ether was removed to obtain 0.74 g (82%) of [2-(2-naphthyl)ethyl](2-phenylpropyl)-phosphine (**VII**) as a viscous liquid. IR spectrum: ν(PH) 2300 cm^{-1}. ^{1}H NMR spectrum, δ, ppm: 1.30–1.40 m (3H, CH_3), 1.75–2.00 m (4H, CH_2P), 2.78–2.84 m (2H, CH_2), 7.10–7.70 m (12H, C_6H_5, $C_{10}H_7$).

Found, %: C 82.00; H 7.60; P 9.90. $C_{21}H_{23}P$. Calculated, %: C 82.35; H 7.52; P 10.13.

[2-(2-Naphthyl)ethyl](2-phenylethyl)(2-phenylpropyl)phosphine oxide (X). A solution of 0.1 g of styrene in 2 ml of DMSO was added with stirring at 60°C to a mixture of 2.3 g of KOH, 1.5 ml of H_2O, and 0.3 g of [2-(2-naphthyl)ethyl](2-phenylpropyl)-phosphine in 7 ml of DMSO. The reaction mixture was heated for 2 h at 80°C, cooled, diluted with water, and extracted with ether. The ethereal extracts were washed with water, dried over potassium carbonate, the ether was distilled off, and the residue was dried in a vacuum to obtain 0.43 g of a product containing, according to ^{31}P NMR data, 82% of [2-(2-naphthyl)-ethyl](2-phenylethyl)(2-phenylpropyl)phosphine oxide (**IX**) (δ_P 45.5 ppm) and 18% of [2-(2-naphthyl)ethyl]-(2-phenylpropyl)phosphine (**VII**) (δ_P –76.6 ppm, $^1J_{PH}$ 202 Hz). The product was washed with ether and dried in a vacuum to give 0.31 g (95%) of [2-(2-naphthyl)ethyl](2-phenylethyl)(2-phenylpropyl)phosphine oxide (**X**) as a viscous liquid. Conversion of secondary phosphine **VII** 76%. IR spectrum: ν(P=O) 1150 cm^{-1}. ^1H NMR spectrum, δ, ppm: 1.30–1.50 m (3H, CH_3), 1.78–2.20 m (6H, CH_2P), 2.80–3.15 m (4H, CH_2), 3.30 m (1H, CH_2), 7.12–7.70 m (17H, C_6H_5, $C_{10}H_7$). Found, %: C 82.16; H 7.55; P 7.03. $C_{29}H_{31}PO$. Calculated, %: C 81.69; H 7.28; P 7.28.

REFERENCES

1. Gusarova, N.K., Sukhov, B.G., Malysheva, S.F., Kazantseva, T.I., Smetannikov, Yu.V., Tarasova, N.P., and Trofimov, B.A., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, pp. 768–770.
2. Arbuzova, S.N., Gusarova, N.K., Malysheva, S.F., Brandsma, L., Albanov, A.I., and Trofimov, B.A., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 1, pp. 56–60.
3. Trofimov, B.A., Malysheva, S.F., Rakhmatulina, T.N., Gusarov, A.V., and Gusarova, N.K., *Zh. Obshch. Khim.*, 1991, vol 61, no 9, pp. 56–60.
4. Dmitriev, V.I., Kazantseva, T.I., Gusrova, N.K., and Trofimov, B.A., USSR Inventor's Certificate 1 759 841, 1990; *Byull. Izobret.*, 1992, no. 33.
5. Trofimov, B.A., Rakhmatulina, T.N., Gusarova, N.K., and Malysheva, S.F., *Usp. Khim.*, 1991, vol. 60, no. 12, pp. 2619–2632.
6. Trofimov, B.A., Gusarova, N.K., and Brandsma, L., *Main Group Chem. News*, 1996, vol. 4, no. 1, pp. 18–24.
7. Gusarova, N.K., Brandsma, L., Arbuzova, S.N., Malysheva, S.N., and Trofimov, B.A., *Zh. Obshch. Khim.*, 1996, vol. 32, no. 2, pp. 269–276.
8. Trofimov, B.A., Brandsma, L., Arbuzova, S.N., Malysheva, S.F., and Gusarova N.K., *Tetrahedron Lett.*, 1994, vol. 35, no. 41, pp. 7647–7650.
9. Gusarova, N.K., Malysheva, S.F., Arbuzova, S.N., and Trofimov, B.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 9, pp. 1695–1702.
10. Trofimov, B.A., Arbuzova, S.N., and Gusarova, N.K., *Usp. Khim.*, 1999, vol. 68, no. 3, pp. 240–253.
11. Stürmer, R., *Angew. Chem.*, 1999, vol. 111, no. 22, pp. 3509–3510.
12. Gusarova, N.K., Arbuzova, S.N., Malysheva, S.F., Khil'ko, M.Ya., Tatarinova, A.A., Gorokhov, V.G., and Trofimov, B.A., *Izv. Ross. Akad. Nauk, Ser Khim.*, 1995, no. 8, pp. 1597–1598.
13. Brunner, H., *J. Organomet. Chem.*, 1986, vol. 300, no. 1, pp. 39–56.