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Hydrophosphination of Alkoxyalkenes Catalyzed by Transition Metal Complexes

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Abstract—Diphenylphosphine adds to alkyl vinyl ethers in the presence of Ni(II) and Pd(II) complexes with a high regioselectivity, leading to exclusive formation of the corresponding Markownikoff adducts which were isolated as 1-alkoxyalkyl(diphenyl)phosphine oxides via oxidation with hydrogen peroxide.

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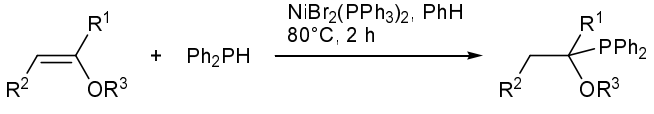
Addition of secondary phosphines to unsaturated compounds underlies one of the most convenient methods for the synthesis of tertiary phosphines having functional groups in the organic radical [1]. However, owing to high strength of the phosphorus–hydrogen bond (E = 77 kcal/mol [2]), secondary phosphines add to alkenes only in the presence of radical initiators [3], strong bases [4], or Brønsted acids [3d, 5]. Usually, these reactions give the corresponding anti-Markownikoff adducts, i.e., the R_2P group adds to the terminal carbon atom of a terminal alkene. It was recently shown that inter- and intramolecular hydrophosphination of alkenes by the action of PH_3 and R_2PH is catalyzed by Pt, Pd, and Ni complexes [1c, 1d, 6], as well as by lanthanide metal complexes [7]. Here, like in radical reactions, the R_2P group always adds at the β-position of terminal alkene.

We previously reported on the addition of diphenylphosphine to styrene and its heteroanalogs, catalyzed by Pd and Ni complexes, and showed that nickel complexes are more efficient catalysts than palladium complexes [8a]. The present article (for preliminary results, see [8b]) describes palladium- and nickel-catalyzed hydrophosphination of nucleophilic alkenes, alkyl vinyl ethers, which leads to formation of 1-alkoxyalkyl(diphenyl)phosphines as potential P,O-ligands.

The known methods of synthesis of these compounds are based on reaction of chloro(diphenyl)phosphine with formaldehyde dialkyl acetals in the presence of a stoichiometric amount of $AlCl_3$ [9], reaction of α-chloro ethers with the Ph_2PCl–$AlCl_3$ complex [10] with subsequent hydrolysis, and alkaline fission of alkoxymethyl(triphenyl)phosphonium salts [11]. These procedures include a number of steps and require strongly acidic or alkaline conditions. The addition of diethylphosphine to methyl vinyl ether [5] and of bis(2-phenylethyl)phosphine to a series of vinyl ethers [3d] in the presence of trifluoroacetic acid or azobis(isobutyronitrile) was reported to afford, respectively, Markownikoff and anti-Markownikoff adducts in a yield not exceeding 60%.

We have found that hydrophosphination of alkyl vinyl ethers is catalyzed by Pd and Ni complexes; however, unlike alkenes having electron-acceptor groups, the addition of diphenylphosphine to vinyl ethers is not catalyzed by zero-valence metal complexes, and it requires the presence of a palladium(II) or nickel(II) complex or salt. As model reaction we used the addition of diphenylphosphine to butyl vinyl ether (**Ia**) (Scheme 1). Table 1 contains the yields of the corresponding adduct (as shown preliminarily, the yield coincided with the conversion determined from the ^{31}P NMR data), depending on the catalyst nature and concentration and temperature. It is seen that various Pd(0) and Ni(0) complexes do not catalyze the

Scheme 1.



Ia–If IIa–IIf

I, **II**, $R^1 = R^2 = H$, R^3 = Bu (**a**), Et (**b**); R^1 = Et, $R^2 = H$, R^3 = Bu (**c**); $R^1 = R^3$ = Me, $R^2 = H$ (**d**); $R^1 = H$, $R^2 = R^3$ = Et (**e**); $R^1 = H$, $R^2R^3 = (CH_2)_3$ (**f**).

Table 1. Addition of diphenylphosphine to butoxyethene (**Ia**) in benzene in the presence of various catalysts[a]

Run no.	Catalyst (mol %)	Temperature, °C (time, h)	Conversion,[b] %
1	$Pd(PPh_3)_4$ (2)	100 (8)	0
2	$Pd(PPh_3)_4$ (5)	120 (8)	<1
3	$PdCl_2(CH_3CN)_2$ (5)	80 (15)	>90
4	$PdCl_2(CH_3CN)_2$ (2)	100 (8)	<50
5[c]	$PdCl_2(PPh_3)_2$ (2)	100 (8)	100
6	$PdCl_2(PPh_3)_2$ (5)	100 (8)	95
7	$Ni(cod)_2$ (5)	120 (8)	0
8	$Ni[P(OEt)_3]_4$ (5)	80 (8)	0
9	$Ni(acac)_2$ (5)	120 (8)	0
10	$NiBr_2(PPh_3)_2$ (2)	80 (2)	100
11	$NiBr_2(PPh_3)_2$ (2)	20 (7 days)	100
12	$NiBr_2$ (2)	80 (2)	100
13	$NiBr_2(PPh_3)_2/Et_3N$ (5/10)	80 (2)	0
14	CF_3COOH (10)	80 (2)	<10
15	HCl (10)	80 (2)	25
16	$Ni(cod)_2$/HCl (5/10)	80 (2)	25
17	$Ni(acac)_2$/HCl (5/10)	80 (2)	100

[a] Amounts of the reactants: **Ia**, 1.65 mmol; Ph_2PH, 1.5 mmol; benzene, 3 ml.
[b] According to the ^{31}P NMR data.
[c] 1.5 equiv of **Ia**.

process (run nos. 1, 2, 7, 8). The reaction is catalyzed by palladium(II) complexes both containing and not containing triphenylphosphine ligand; the triphenylphosphine Pd(II) complex is more active than that containing no Ph_3P ligand. Important factors are also the amount of the catalyst and temperature (run nos. 4 and 5). In the reaction with 1.5 equiv of butyl vinyl ether, the amount of bis(triphenylphosphine)palladium dichloride may be reduced to 2 mol % (run no. 5). Bis(triphenylphosphine)nickel dibromide is even more effective catalyst. It ensures lower reaction temperature (run no. 10) and shorter reaction time at a smaller concentration, as compared to palladium complexes. The reaction with $(Ph_3P)_2NiBr_2$ as catalyst can be performed at room temperature (run no. 11), but in this case the reaction time extends to 7 days.

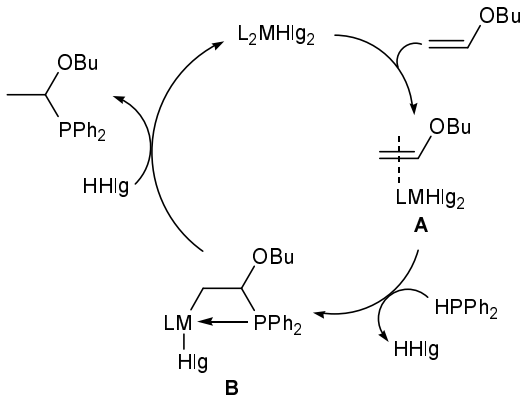
No solvent effect on the reaction rate and yield was revealed. The reaction was equally successful in benzene, tetrahydrofuran, and acetonitrile. Interestingly, nickel(II) bromide catalyzed the hydrophosphination of butyl vinyl ether as effectively as did its complex with triphenylphosphine (cf. run nos. 12 and 14); presumably, the reason is formation in the reaction mixture of highly active $NiBr_2(Ph_2PH)_2$ complex. An analogous palladium complex containing a secondary phosphine as ligand was recently described [12]. On the other hand, halogen-free nickel salt such as nickel(II) acetylacetonate did not catalyze the reaction (run no. 9).

The facts that the reaction does not occur in the presence of Pd(0) and Ni(0) complexes and that palladium and nickel halides [but not $Ni(acac)_2$] are effective catalytic precursors suggest that the crucial factor is participation of hydrogen halide which is likely to be formed via reduction of $PdCl_2$ or $NiBr_2$ with diphenylphosphine [13]. It might be presumed that hydrogen halide liberated during the process is the true catalyst. However, the reaction in the presence of an acid (HCl or CF_3COOH), other conditions being equal, was very slow (run. nos. 14, 15); the same pattern was observed in the system Ni(0)–HHlg (run no. 16).

The above data indicate that hydrophosphination of vinyl ethers which are nucleophilic alkenes follows a mechanism different from that typical of alkenes having electron-withdrawing substituents [6] or aryl- and hetarylethenes [8]. A probable catalytic cycle is shown in Scheme 2. It includes initial activation of the double bond to nucleophilic attack via formation of complex **A**, as in the first stage of the Wacker process. The subsequent addition of diphenylphosphine to activated double bond gives complex **B** and is accompanied by liberation of hydrogen halide. Instead of β-elimination of hydride ion, complex **B** undergoes protonation of the carbon–metal bond, which leads to formation of the final product and initial Ni(II) or Pd(II) complex. Presumably, this reaction path is favored by stabilization of organometallic intermediate **B** via intramolecular coordination of the diphenylphosphino group to the metal atom [14]. Apart from the above stated, the important role of the protolysis stage in the catalytic cycle for hydrophosphination of alkoxyalkenes follows from the absence of catalysis by the $Ni(PPh_3)_2Br_2$ complex in the presence of a tertiary amine (Table 1, run no. 13) and from the presence of catalytic effect in the system nickel(II) acetylacetonate–hydrogen chloride (Table 1, run no. 17); in the latter case, formation of $NiCl_2$ is likely to be responsible for the observed catalytic effect.

It should be noted that, apart from $MHlg_2$, phosphide complexes like $HlgMPPh_2$ or $M(PPh_2)_2$ could also activate double bond to hydrophosphination; these complexes may result from exchange reactions

Scheme 2.



M = Pd, Ni.

between $MHlg_2$ and Ph_2PH. The observed regioselectivity in the hydrophosphination of alkoxyalkenes (i.e., formation of the corresponding Markownikoff adducts) is consistent with the electronic effect of the substituent (alkoxy group).

The optimal conditions for hydrophosphination of butyl vinyl ether include $(Ph_3P)_2NiBr_2$ as catalyst, temperature 80°C, and benzene as solvent. Under these conditions, we performed hydrophosphination of alkoxyalkenes having alkoxy groups at both terminal and internal double-bonded carbon atoms. The results are collected in Table 2. It is seen that substituents only slightly affect the product yield. An exception was cyclic alkyl vinyl ether, 3,4-dihydro-2*H*-pyran (**If**): the reaction with compound **If** required more severe conditions, and the yield was considerably lower.

Phosphines **IIa**–**IIf** are readily oxidized during isolation; therefore, they were converted *in situ* into the corresponding phosphine oxides **IIIa**–**IIIf** by treatment with 30% hydrogen peroxide, and compounds **IIIa**–**IIIf** were isolated and characterized by spectral and analytical data (see Experimental). The structure of **IIIa**–**IIIf** unambiguously follows from their ^{1}H NMR spectra which contained multiplet signals at δ 4.19–4.23, 3.19–3.25, and 3.58–3.64 ppm; the two latter belong to prochiral protons of the OCH_2 group. A doublet of doublets at δ 1.45–1.51 ppm was assigned to the $Ph_2P(O)CHC\mathbf{H}_3$ protons (it was overlapped by the butyl CH_2 signal).

Phosphines **IIa**–**IIf** and phosphine oxides **IIIa**–**IIIf** have been studied poorly. The use of 1-alkoxyalkylphosphines in the Horner–Wittig reaction [15] and stereoselective synthesis of functionally substituted alkenes and as complexones for extraction of uranium and thorium salts from acid solution [16] was reported.

Table 2. Yields of 1-alkoxyalkyl(diphenyl)phosphines **IIa**–**IIf**[a] and phosphine oxides **IIIa**–**IIIf**

Initial ether no.	Yield, %	
	phosphine **II**[b]	phosphine oxide **III**[c]
Ia	98	83
Ib	100	85
Ic	97	80
Id	100	76
Ie	96	70
If[d]	–	40

[a] Ether **Ia**–**If**, 1.65 mmol; Ph_2PH, 1.5 mmol; $(PPh_3)_2NiBr_2$, 2 mol %; benzene, 3 ml; 2 h, 80°C.
[b] According to the ^{31}P NMR data.
[c] Isolated product.
[d] 8 h, 100°C.

Phosphine oxide **IIIf** was used in the synthesis of olive fly pheromone [17]. Furthermore, tertiary phosphines **IIa**–**IIf** possess an asymmetric carbon atom; therefore, they can attract interest as ligands for metal complex catalysis.

Thus we have shown that nucleophilic alkenes, alkoxyalkenes, take up diphenylphosphine according to Markownikoff in the presence of nickel(II) and palladium(II) complexes.

EXPERIMENTAL

All operations with readily hydrolyzable and oxidizable substances and transition metal complexes were performed under dry argon in glassware preliminarily kept in a drying box or flame-dried just before use. Argon was dried by passing through a column charged with phosphoric anhydride. Solvents were dried and purified by standard procedures: petroleum ether, hexane, pentane, benzene, toluene, diethyl ether, and dioxane were refluxed and distilled over metallic sodium, and acetonitrile was distilled over calcium hydride.

Diphenylphosphine [18], 2-butoxy-1-butene (**Ic**) [19], 1-ethoxy-1-butene (**Ie**) [20], tetrakis(triphenylphosphine)palladium(0) [21], tetrakis(triethyl phosphite)nickel(0) [22], bis(cyclooctadienyl)nickel(0) [23], bis(triphenylphosphine)nickel(II) dibromide [24], and bis(triphenylphosphine)palladium(II) dichloride [25] were synthesized by known methods. Butoxyethene (**Ia**), ethoxyethene (**Ib**), and 2-methoxy-1-propene (**Id**) were commercial products (from Aldrich).

The progress of reactions was monitored, and newly synthesized compounds were identified, by ^1H and ^{31}P NMR spectroscopy. The ^1H NMR spectra were measured on a Varian VXR-400 instrument at 400 MHz; the chemical shifts were referenced to tetramethylsilane. The $^{31}P–\{^1H\}$ NMR spectra were obtained on a Varian VXR-400 instrument at 161.9 MHz using $CDCl_3$ as solvent and 85% H_3PO_4 in D_2O as reference.

Reaction of diphenylphosphine with butoxyethene (Ia). *a. In the presence of $Pd(PPh_3)_4$.* A 8-mm NMR ampule was purged with argon and charged with 86 mg (5 mol %) of $Pd(PPh_3)_4$, 279 mg (1.5 mmol) of diphenylphosphine, 208 mg (2.25 mmol) of ether **Ia**, and 3 ml of benzene. The ampule was again purged with argon and sealed, and the mixture was shaken. It was then heated for 8 h at 120°C. The ^{31}P NMR spectrum of the reaction mixture contained only a signal at δ_P –40.6 ppm due to initial diphenylphosphine.

b. In the presence of $Ni[P(OEt)_3]_4$. As described in *a*, a mixture of 54 mg (5 mol %) of $Ni[P(OEt)_3]_4$, 279 mg (1.5 mol) of diphenylphosphine, 208 mg (2.25 mmol) of ether **Ia**, and 3 ml of benzene in a sealed ampule was heated for 8 h at 120°C. The ^{31}P NMR spectrum of the reaction mixture contained only a signal at δ_P –40.6 ppm due to initial diphenylphosphine.

c. In the presence of $PdCl_2(PPh_3)_2$. A 8-mm NMR ampule was purged with argon and charged with 53 mg (5 mol %) of $PdCl_2(PPh_3)_2$, 279 mg (1.5 mmol) of diphenylphosphine, 208 mg (2.25 mmol) of ether **Ia**, and 3 ml of benzene. The ampule was sealed and heated for 8 h at 100°C. The progress of the reaction was monitored by ^{31}P NMR spectroscopy, following change in the intensity of the initial diphenylphosphine signal at δ_P –40.6 ppm. When the reaction was complete, the ^{31}P NMR spectrum contained only one signal at δ_P –5.2 ppm due to 1-butoxyethyl(diphenyl)phosphine (**IIa**).

d. In the presence of $NiBr_2(PPh_3)_2$. Likewise, a mixture of 54 mg (5 mol %) of $NiBr_2(PPh_3)_2$, 279 mg (1.5 mol) of diphenylphosphine, 208 mg (2.25 mmol) of ether **Ia**, and 3 ml of benzene was heated for 2 h at 80°C until the signal of diphenylphosphine disappeared from the ^{31}P NMR spectrum. According to the ^{31}P NMR data, the only phosphorus-containing product was phosphine **IIa**, δ_P –5.2 ppm.

e. In the presence of $NiBr_2(PPh_3)_2$ and triethylamine. A 8-mm NMR ampule was purged with argon and charged with 54 mg (5 mol %) of $NiBr_2(PPh_3)_2$, 279 mg (1.5 mmol) of diphenylphosphine, 208 mg (2.25 mmol) of ether **Ia**, 3 ml of benzene, and 15 mg (10 mol %) of triethylamine. The ampule was sealed and heated for 2 h at 80°C. The ^{31}P NMR spectrum of the mixture contained only a signal at δ_P –40.6 ppm due to initial diphenylphosphine.

f. In the presence of $Ni(acac)_2$ and HCl. A 8-mm NMR ampule was purged with argon and charged with 10 mg (5 mol %) of $Ni(acac)_2$, 279 mg (1.5 mmol) of diphenylphosphine, 208 mg (2.25 mmol) of ether **Ia**, and 3 ml of benzene, and 306 μl of a 2% solution of HCl in benzene (prepared from $ClSiMe_3$ and H_2O in benzene) was added. The ampule was sealed and heated for 2 h at 80°C until the signal of diphenylphosphine disappeared from the ^{31}P NMR spectrum. When the reaction was complete, the ^{31}P NMR spectrum contained only one signal at δ_P –5.2 ppm due to 1-butoxyethyl(diphenyl)phosphine (**IIa**).

1-Butoxyethyl(diphenyl)phosphine oxide (IIIa). A 8-mm NMR ampule was purged with argon and charged with 55 mg (5 mol %) of $Ni(PPh_3)Br_2$, 279 mg (1.5 mmol) of diphenylphosphine, 165 mg (1.65 mmol) of butoxyethene (**Ia**), and 3 ml of benzene. The ampule was sealed and heated for 2 h at 80°C. The ^{31}P NMR spectrum of the mixture contained only one signal at δ_P –5.2 ppm due to 1-butoxyethyl(diphenyl)phosphine (**IIa**). The ampule was cooled and opened, the solution was evaporated, the residue was dissolved in 15 ml of diethyl ether, 2 ml of 30% H_2O_2 was added, and the mixture was stirred until the organic layer turned colorless. The organic layer was separated, washed with water, and dried over $MgSO_4$, and the solvent was distilled off. The residue was dissolved in diethyl ether and subjected to chromatography on Al_2O_3 using diethyl ether as eluent to isolate 380 mg (83%) of phosphine oxide **IIIa** as an oily substance which failed to crystallize. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.83–0.85 t (3H, CH_3), 1.22–1.26 m (2H, CH_2), 1.45–1.51 m (5H, CH_2, CH_3), 3.19–3.25 m (1H), 3.58–3.64 m (1H, OCH_2), 4.19–4.23 m (1H, CHO), 7.45–7.58 m (6H), 7.88–7.92 m (2H), 8.05–8.09 m (2H). ^{31}P NMR spectrum: δ_P 30.0 ppm. Found, %: C 71.35; H 7.45. $C_{18}H_{23}O_2P$. Calculated, %: C 71.52; H 7.61.

1-Ethoxyethyl(diphenyl)phosphine oxide (IIIb). A 8-mm NMR ampule was purged with argon and charged with 55 mg (5 mol %) of $Ni(PPh_3)Br_2$, 279 mg (1.5 mmol) of diphenylphosphine, 122 mg (1.65 mmol) of ethoxyethene (**Ib**), and 3 ml of benzene. The ampule was sealed and heated for 2 h at 80°C. The ^{31}P NMR spectrum of the mixture contained only one signal at

δ_P –6.4 ppm due to 1-ethoxyethyl(diphenyl)phosphine (**IIb**). The mixture was then treated as described above for **IIIa** to isolate 352 mg (85%) of compound **IIIb** as colorless crystals with mp 53–54°C; published data [26]: mp 50–54°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95–0.99 t (3H, CH_3), 1.31–1.36 d.d (3H, CH_3), 3.10–3.17 m (1H), 3.47–3.55 m (1H, OCH_2), 4.02–4.09 m (1H, CHO), 7.24–7.43 m (6H), 7.72–7.75 m (2H), 7.88–7.92 m (2H). ^{31}P NMR spectrum: δ_P 27.0 ppm. Found, %: C 69.88; H 7.13. $C_{16}H_{19}O_2P$. Calculated, %: C 70.07; H 6.93.

1-Butoxy-1-methylpropyl(diphenyl)phosphine oxide (IIIc). A 8-mm NMR ampule was purged with argon and charged with 55 mg (5 mol %) of $Ni(PPh_3)Br_2$, 279 mg (1.5 mmol) of diphenylphosphine, 180 mg (1.65 mmol) of 2-butoxy-1-butene, and 3 ml of benzene. The ampule was sealed and heated for 2 h at 80°C. The ^{31}P NMR spectrum of the mixture contained only one signal at δ_P –1.0 ppm due to phosphine **IIc**. The mixture was then treated as described above for **IIIa** to isolate 396 mg (80%) of phosphine oxide **IIIc** as a colorless oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88–0.92 t (3H, CH_3), 0.95–0.99 t (3H, SH_3), 1.39–1.43 m (2H, CH_2), 1.46 d (3H, CH_3), 1.61–1.65 m (2H, CH_2), 1.82–2.08 m (2H, CH_2), 3.36–3.41 m (1H), 3.45–3.50 m (1H, OCH_2), 7.46–7.51 m (6H), 8.03–8.05 m (2H), 8.17–8.22 m (2H). ^{31}P NMR spectrum: δ_P 29.7 ppm. Found, %: C 72.59; H 8.29. $C_{20}H_{28}O_2P$. Calculated, %: C 72.72; H 8.18.

1-Methoxy-1-methylethyl(diphenyl)phosphine oxide (IIId). A 8-mm NMR ampule was purged with argon and charged with 55 mg (5 mol %) of $Ni(PPh_3)Br_2$, 279 mg (1.5 mmol) of diphenylphosphine, 122 mg (1.65 mmol) of 2-methoxy-1-propene (**Id**), and 3 ml of benzene. The ampule was sealed and heated for 2 h at 80°C. The ^{31}P NMR spectrum of the mixture contained only one signal at δ_P –7.3 ppm due to phosphine **IId**. The mixture was then treated as described above for **IIIa** to isolate 312 mg (76%) of phosphine oxide **IIId** as colorless crystals with mp 153–154°C; published data [26]: mp 151–154°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 d (6H, CH_3), 3.32 s (3H, CH_3), 7.40–7.57 m (6H), 8.05–8.15 m (4H). ^{31}P NMR spectrum: δ_P 31.5 ppm. Found, %: C 69.97; H 6.90. $C_{18}H_{19}O_2P$. Calculated, %: C 70.07; H 6.93.

1-Ethoxybutyl(diphenyl)phosphine oxide (IIIe). A 8-mm NMR ampule was purged with argon and charged with 55 mg (5 mol %) of $Ni(PPh_3)Br_2$, 279 mg (1.5 mmol) of diphenylphosphine, 180 mg (1.65 mmol) of 1-ethoxy-1-butene (**Ie**), and 3 ml of benzene. The ampule was sealed and heated for 2 h at 80°C. The ^{31}P NMR spectrum of the mixture contained only one signal at δ_P –7.8 ppm due to phosphine **IIe**. The mixture was then treated as described above for **IIIa** to isolate 317 mg (70%) of phosphine oxide **IIIe** as colorless crystals with mp 123–124°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.93–0.97 t (3H, CH_3), 1.03–1.07 t (3H, CH_3), 1.44–1.52 m (1H), 1.85–1.96 m (1H, CH_2), 1.63–1.71 m (2H, CH_2), 3.09–3.16 m (1H), 3.45–3.52 m (1H, OCH_2), 3.96–4.01 m (1H, OCH), 7.41–7.56 m (6H), 7.79–7.84 m (2H), 8.02–8.07 m (2H). ^{31}P NMR spectrum: δ_P 28.4 ppm. Found, %: C 71.69; H 7.56. $C_{18}H_{23}O_2P$. Calculated, %: C 71.52; H 7.61.

Diphenyl(tetrahydro-2*H*-pyran-2-yl)phosphine oxide (IIIf). A 8-mm NMR ampule was purged with argon and charged with 55 mg (5 mol %) of $Ni(PPh_3)Br_2$, 279 mg (1.5 mmol) of diphenylphosphine, 139 mg (1.65 mmol) of 3,4-dihydro-2*H*-pyran (**If**), and 3 ml of benzene. The ampule was sealed and heated for 10 h at 100°C. The mixture was then treated as described above for **IIIa** to isolate 171 mg (40%) of phosphine oxide **IIIf** as colorless crystals with mp 155°C; published data [27]: mp 154°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.5–1.70 m (4H, CH_2), 1.96–2.11 m (2H, CH_2), 3.45–3.55 m (1H), 4.10–4.20 m (1H, OCH_2), 4.23–4.31 m (1H, OCH), 7.48–7.57 m (6H), 7.69–8.01 m (4H, C_6H_5). ^{31}P NMR spectrum, δ_P, ppm: 27.7, 28.5 (a mixture of diastereoisomers). Found, %: C 71.28; H 6.58. $C_{17}H_{19}O_2P$. Calculated, %: C 71.32; H 6.58.

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