Atom-Economic, Solvent-Free, High Yield Synthesis of 2-(Pyrrol-1-yl)propyldiorganylphosphines

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Abstract: Free-radical addition of secondary phosphines to 1-isopropenylpyrroles (AIBN, 65 °C) proceeds with 100% regioselectivity to give 2-(pyrrol-1-yl)propyldiorganylphosphines in 89–92% isolated yields. This constitutes a highly efficient, atom-economic, solvent-free ('green') synthesis of new promising ligands for metal complex catalysts, and potent building blocks for designing of drugs and advanced materials.

Key words: free-radical addition, 1-isopropenylpyrroles, phosphorylation, regioselectivity, P,N-ligands, green chemistry

1-Isopropenylpyrroles **1a–c**, now readily available thanks to an efficient and convenient method for their synthesis through isopropenylation of corresponding 1*H*-pyrroles with propyne and (or) allene in the superbase system KOH/DMSO,[1] represent reactive building blocks for organic synthesis and prospective monomers. At the same time, available data on the reactivity of 1-isopropenylpyrroles are limited to just one brief communication concerning their interaction with thiols in the presence of radical initiators giving anti-Markovnikov adducts.[2] In the present work, to gain a better understanding of the synthetic potential of 1-isopropenylpyrroles and to further develop the synthesis of tertiary phosphines by free-radical addition reactions of diverse alkenes,[3] we have studied the free-radical reaction of 1-isopropenylpyrroles with secondary phosphines, now directly prepared from elemental phosphorus and electrophiles in superbase systems.[4] Dialkylphosphinyl radicals are nucleophilic[5] and the double bond in *N*-vinylpyrroles is electron-rich due to the p-π conjugation,[6] hence the electron-donating methyl group at the α-position of the ethenyl moiety is to be an additional electronically unfavorable factor, let alone its anticipated steric interference. Therefore, a preparatively meaningful result of the addition of dialkylphosphines to 1-isopropenylpyrroles, a new family of substituted *N*-vinylpyrroles, was far from being predictable despite positive data for unsubstituted *N*-vinylpyrroles.[7] Meanwhile, to harness this reaction would be a principal contribution to the targeted synthesis of phosphines with pyrrole substituents and an unsymmetrical carbon atom, capable of resolving to enantiomers. Such a reaction would open a straightforward atom-economic ('green') approach to the synthesis of a new family of phosphorus-containing pyrroles, promising chelating P,N(π)-ligands for metal complex catalysts of a new generation,[8] as well as reactive intermediates for the design of drugs and advanced materials.

1-Isopropenylpyrroles **1a–c** were found to add diorganylphosphines **2a–c** regiospecifically in the presence of a radical initiator, azoisobutyronitrile (AIBN), at 65 °C to form 2-(pyrrol-1-yl)propyldiorganylphosphines **3a–e** in 89–92% yield (Scheme 1, Table 1).

1	R¹	R²	R³
a	Me	Me	H
b	$(CH_2)_4$		Me
c	$(CH)_4$		H

2	R⁴
a	$PhCH_2$
b	$Ph(CH_2)_2$
c	$2\text{-}Py(CH_2)_2$

3	R¹	R²	R³	R⁴
a	Me	Me	H	$PhCH_2$
b	Me	Me	H	$Ph(CH_2)_2$
c	Me	Me	H	$2\text{-}Py(CH_2)_2$
d	$(CH_2)_4$		Me	$Ph(CH_2)_2$
e	$(CH)_4$		H	$Ph(CH_2)_2$

Scheme 1

Table 1 Hydrophosphination of 1-Isopropenylpyrroles with Secondary Phosphines[a]

Entry	Reactants (mmol) 1-Isopropenylpyrrole **1**	$(R^4)_2PH$ **2**	Time (h)	Product **3**	Yield (%)[b]
1	**1a** (3.0)	**2a** (3.0)	288	**3a**	91
2	**1a** (2.4)	**2b** (2.3)	21	**3b**	92
3	**1a** (2.1)	**2c** (2.0)	160	**3c**	89
4	**1b** (2.2)	**2b** (2.1)	317	**3d**	89
5	**1c** (3.3)	**2b** (3.3)	48	**3e**	89

[a] All experiments were carried out under argon at 65 °C with AIBN as an initiator (1–5 wt%).

[b] Isolated yields.

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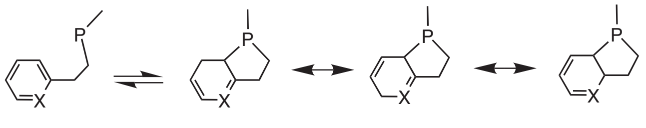
As anticipated, the reaction conditions have proven to be, for some pairs, substantially different (Table 1) from those found for unsubstituted *N*-vinylpyrroles:[7] in the former case, up to 13 days (instead of 41 h) is required for the completion of the reaction which is uncommon for AIBN-initiated radical additions.

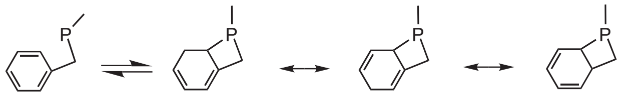
At the same time, the reaction of isopropenylpyrrole **1a** with bis(2-phenylethyl)phosphine **2b** requires just 21 hours for its completion, whereas full conversion of dibenzylphosphine (**2a**) and bis[2-(pyridin-2-yl)ethyl]phosphine (**2c**) is attained in 288 and 160 hours, respectively (Table 1), thus implying unusually strong structural effects. The reactivity of the phosphines in this process drops in the following order: **2b** > **2c** > **2a**.

Apart from steric hindrances, this fact can likely be explained by a lower stability of the dibenzylphosphinyl radical generated from dibenzylphosphine, as compared to the corresponding bis(2-phenylethyl)- and bis[2-(pyridin-2-yl)ethyl]phosphinyl radicals, for which a through space stabilization with the formation of a five-membered ring is conceivable (Scheme 2), as, e.g., it is observed for the intermediate radicals formed in the *N*-vinylindole and -carbazole radical polymerization.[9]



Scheme 2

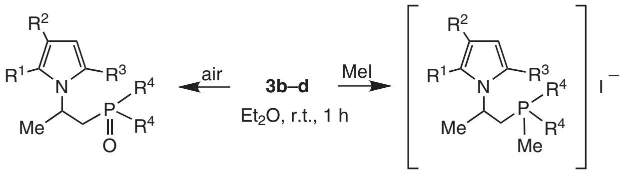
In the case of dibenzylphosphinyl radical, such stabilization may be realized, if any, only in a strained, hence, less favorable four-membered structure (Scheme 3).



Scheme 3

Comparative analysis of the hydrophosphination of isopropenylpyrroles **1a**–**c** with the phosphine **2b** indicates (Table 1) that 1-isopropenyl-2,3-dimethylpyrrole (**1a**) is the most reactive species in this reaction, while the least reactive is 1-isopropenyl-2-methyl-4,5,6,7-tetrahydroindole (**1b**). This agrees with spatial structures of the pyrroles **1a**–**c** and may be rationalized by steric hindrances.

Some preliminary information concerning the properties of the polyfunctional compounds synthesized has been obtained on phosphines **3b**–**d**. Thus, methylation of **3b**–**d** with MeI proceeds under mild conditions (r.t., 1 h) to quantitatively afford the phosphonium iodides **4b**–**d** (Scheme 4). When exposed to air, phosphines **3b**,**c** quantitatively oxidize to phosphine oxides **5b**,**c** (Scheme 4). Under analogous conditions, conversion of the phosphine **3d** to phosphine oxide **5d** is just 10%.



5b–d **4b–d**

Scheme 4

In summary, the addition of secondary phosphines to 1-isopropenylpyrroles represents a straightforward atom-economic non-metal-catalyzed ('green') approach to C–P bond formation thus contributing to both pyrrole and phosphine chemistry, especially to the hydrophosphination of heteroethenes (vinyl ethers,[10] alkyl vinyl sulfides and selenides,[11] divinyl sulfide,[12] *N*-vinylpyrroles[7]) under free-radical conditions. Unlike *N*-vinylpyrrole-derived phosphines,[7] phosphines **3** containing an asymmetrical carbon atom can be resolved to enantiomers by common procedures and, therefore, are prospective chiral hemilabile ligands for enantioselective processes.[13] The synthesis of such ligands is usually complicated and requires the use of organometallic compounds and aggressive highly toxic phosphorus halides.[14]

Diorganyl-2-(1-pyrrolyl)propylphosphines 3a–e; General Procedure

A mixture of secondary phosphine **2**[4d,15] and 1-isopropenylpyrrole (**1**)[1] was heated at 65 °C in the presence of AIBN (1–5 wt% of the total mass of reactants) in a sealed ampoule (reaction scale and time are given in Table 1). The reaction was monitored using ^{31}P NMR by disappearance of signal of the starting secondary phosphine **2** in the –70 ppm to –48 ppm region and appearance of new resonance in the –32 ppm to –20 ppm interval, corresponding to tertiary phosphine **3** (for ^{31}P monitoring, the ampoule was unsealed and a probe of the reaction mixture was taken for analysis). The crude product, a viscous undistillable liquid, was purified by column chromatography (Al_2O_3, Et_2O) to give the phosphine **3** (oil). Spectral characteristics of compounds **3**–**5** are given in Table 2. All experiments were carried out under argon.

[2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis(phenylmethyl)phosphine (3a)

Yield: 91%; light-yellow oil.

Anal. Calcd for $C_{23}H_{28}NP$: C, 79.06; H, 8.08; N, 4.00; P, 8.86. Found: C, 79.21; H, 8.24; N, 3.80; P, 8.75.

[2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis(2-phenylethyl)phosphine (3b)

Yield: 92%; light-yellow oil.

Anal. Calcd for $C_{25}H_{32}NP$: C, 79.54; H, 8.54; N, 3.71; P, 8.20. Found: C, 79.65; H, 8.45; N, 3.84; P, 8.06.

[2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis[2-(2-pyridinyl)ethyl]phosphine (3c)

Yield: 89%; light-yellow oil.

Anal. Calcd for $C_{23}H_{30}N_3P$: C, 72.80; H, 7.97; N, 11.07; P, 8.16. Found: C, 72.99; H, 8.08; N, 10.93; P, 7.95.

Table 2 Spectral Data of Compounds **3–5**[a]

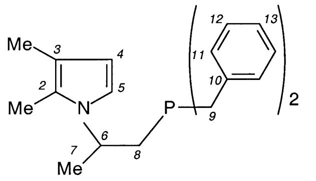
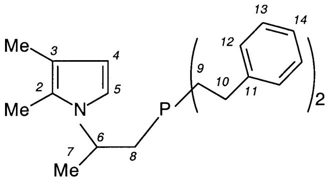
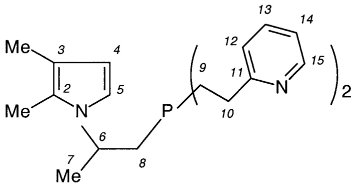
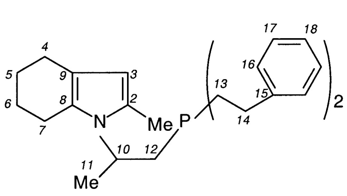
Product	Structure	NMR, δ, *J* (Hz) ^{1}H	^{13}C	^{31}P[b]
3a[c]		1.28 (d, 3 H, C^7-H, $^3J_{6,7}$ = 6.7), 1.73–1.78 (m, 2 H, C^8-H), 2.06 (s, 3 H, C^3-CH_3), 2.13 (s, 3 H, C^2-CH_3), 2.37, 2.52, 2.63, 2.75 (d, 4 H, C^9-H, $^2J_{H,H}$ = 13.4), 3.91–3.97 (m, 1 H, C^6-H), 5.95 (d, 1 H, C^4-H, $^3J_{4,5}$ = 2.9), 6.55 (d, 1 H, C^5-H), 7.07–7.32 (m, 10 H, $C^{11–13}$-H)	9.32 and 9.52 (C^3-CH_3), 10.93 and 11.12 (C^2-CH_3), 22.39 and 22.49 (C^7, $^3J_{P,C}$ = 9.4), 34.71, 34.88 (C^9, $^1J_{P,C}$ = 17.1), 36.08 (C^8, $^1J_{P,C}$ = 20.1), 49.37 and 49.77 (C^6, $^2J_{P,C}$ = 20.1 and 21.0), 108.42 and 108.51 (C^4), 113.71 and 113.84 (C^5), 117.77 (C^3), 123.67 ($C^{2,}$), 125.44 and 125.58 (C^{13}), 128.06 and 128.09 (C^{11}), 128.69 and 128.91 (C^{12}), 137.42 and 137.47 (C^{10}, $^2J_{P,C}$ = 27.8 and 28.7)	–20.58
3b		1.47 (d, 3 H, C^7-H, $^3J_{6,7}$ = 6.7), 1.51−1.80 (m, 6 H, $C^{8,9}$-H), 2.0 (s, 3 H, C^3-CH_3), 2.13 (s, 3 H, C^2-CH_3), 2.61−2.70 (m, 4 H, C^{10}-H), 4.20−4.23 (m, 1 H, C^6-H), 5.95 (d, 1 H, C^4-H, $^3J_{4,5}$ = 2.8), 6.55 (d, 1 H, C^5-H), 7.09−7.27 (m, 10 H, $C^{12–14}$-H)	9.95 (C^3-CH_3), 11.38 (C^2-CH_3), 23.00 (C^7, $^3J_{P,C}$ = 8.6), 28.81 and 29.38 (C^9, $^1J_{P,C}$ = 15.1), 32.15 and 32.29 (C^{10}, $^2J_{P,C}$ = 14.7), 36.96 (C^8, $^1J_{PC}$ = 16.8), 50.05 (C^6, $^2J_{P,C}$ = 19.0), 108.95 (C^4), 114.17 (C^5), 114.37 (C^3), 123.94 (C^2), 125.94 and 126.03 (C^{14}), 128.13, 128.43, 128.48, 128.73 ($C^{12,13}$), 142.66 (C^{11}, $^3J_{P,C}$ = 9.9)	–31.29
3c		1.46 (d, 3 H, C^7-H, $^3J_{6,7}$ = 6.6), 1.60–1.84 (m, 6 H, $C^{8,9}$-H), 1.98 (s, 3 H, C^3-CH_3), 2.12 (s, 3 H, C^2-CH_3), 2.81−2.89 (m, 4 H, C^{10}-H), 4.21−4.25 (m, 1 H, C^6-H), 5.91 (d, 1 H, C^4-H, $^3J_{4,5}$ = 2.9), 6.55 (d, 1 H, C^5-H), 7.05−7.09 (m, 4 H, $C^{12,14}$-H), 7.50−7.51 (m, 2 H, C^{13}-H), 8.47 (m, 2 H, C^{15}-H)	9.57 (C^3-CH_3), 11.05 (C^2-CH_3), 22.73 (C^7, $^3J_{P,C}$ = 8.1), 26.41 and 26.89 (C^9, $^1J_{P,C}$ = 14.6 and 13.7), 34.07 and 34.13 (C^{10}, $^2J_{P,C}$ = 14.6), 36.59 (C^8, $^1J_{P,C}$ = 17.1), 49.62 (C^6, $^2J_{P,C}$ = 18.8), 108.52 (C^4), 113.80 (C^5), 117.80 (C^3), 120.75 and 120.80 (C^{14}), 122.14 and 122.19 (C^{12}), 123.50 (C^2), 135.91 and 135.98 (C^{13}), 148.81 and 148.87 (C^{15}), 161.56 (C^{11}, $^3J_{P,C}$ = 11.1)	–31.38
3d[d]		1.51 (d, 3 H, C^{11}-H, $^3J_{10,11}$ = 7.2), 1.64–1.82 (m, 10 H, $C^{5,6,12,13}$-H), 1.96 (s, 3 H, C^2-CH_3), 2.42–2.48 (m, 4 H, $C^{4,7}$-H), 2.57–2.76 (m, 4 H, C^{14}-H), 4.28–4.31 (m, 1 H, C^{10}-H), 5.62 (s, 1 H, C^3-H), 7.15–7.21 (m, 10 H, $C^{16–18}$)	11.88 and 11.65 (C^2-CH_3), 21.87, 22.55, 23.37, 23.48 ($C^{4–7}$), 23.42 (C^{11}, $^3J_{P,C}$ = 11.0), 27.30 and 27.98 (C^{13}, $^1J_{P,C}$ = 14.6 and 14.1), 31.67 and 31.92 (C^{14}, $^1J_{P,C}$ = 13.7), 34.10 (C^{12}, $^1J_{P,C}$ = 14.6), 49.53 and 49.76 (C^{10}, $^2J_{P,C}$ = 23.1 and 22.7), 107.95 (C^3), 113.84 (C^2), 115.95 (C^9), 125.52 and 125.72 (C^{18}), 126.18 (C^8), 127.80, 128.03, 128.09, 128.32 ($C^{16,17}$), 142.18 and 142.24 (C^{15}, $^3J_{P,C}$ = 10.0 and 10.7)	–28.66

Table 2 Spectral Data of Compounds **3–5**[a] (continued)

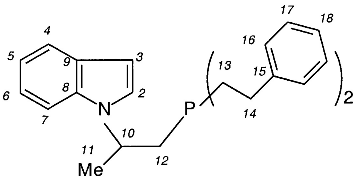
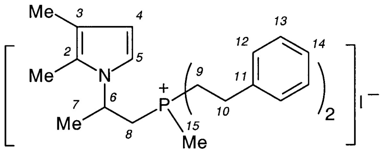
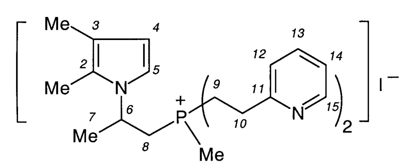
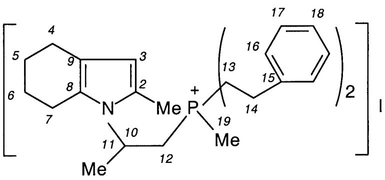
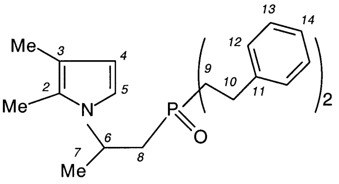
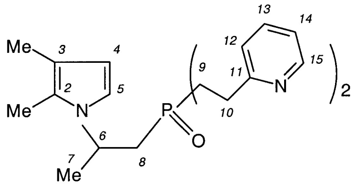
Product	Structure	NMR, δ, *J* (Hz)		
		^{1}H	^{13}C	^{31}P^b
3e		1.43–1.59 (m, 4 H, C^{13}-H), 1.58 (d, 3 H, C^{11}-H, $^3J_{10,11}$ = 7.3), 1.88 and 2.07 (m, 2 H, C^{12}-H), 2.52–2.62 (m, 4 H, C^{14}-H), 4.59–4.63 (m, 1 H, C^{10}-H), 6.49 (d, 1 H, C^3-H, $^3J_{2,3}$ = 3.2), 6.97–7.16 (m, 13 H, C$^{2,5,6,16–18}$-H), 7.17 (d, 1 H, C^7-H, $^3J_{6,7}$ = 7.0), 7.21 (d, 1 H, C^4-H, $^3J_{4,5}$ = 7.0)	22.47 (C^{11}, $^3J_{P,C}$ = 8.5), 29.09 and 29.46 (C^{13}, $^1J_{P,C}$ = 14.2), 32.32 and 32.39 (C^{14}, $^2J_{P,C}$ = 14.1), 35.94 (C^{12}, $^1J_{P,C}$ = 17.2), 50.63 (C^{10}, $^2J_{P,C}$ = 18.5), 101.98 (C^3), 109.95 (C^7), 119.75 (C^6), 121.43 (C^4), 121.69 (C^5), 124.30 (C^2), 126.28 and 126.31 (C^{18}), 128.38, 128.41, 128.74 (C^{16,17}), 129.01 (C^9), 135.70 (C^8), 142.78 (C^{15}, $^3J_{P,C}$ = 8.5)	–31.79
4b		1.48 (d, 3 H, C^7-H, $^3J_{6,7}$ = 5.8), 1.79 (d, 3 H, C^{15}-H, $^1J_{P,H}$ = 13.4), 1.91 (s, 3 H, C^3-CH$_3$), 2.09 (s, 3 H, C^2-CH$_3$), 2.31–2.71 (m, 4 H, C^9-H), 2.80–2.89 (m, 4 H, C^{10}-H), 3.11–3.50 (m, 2 H, C^8-H), 4.42 (m, 1 H, C^6-H), 5.93 (s, 1 H, C^4-H), 6.65 (s, 1 H, C^5-H), 7.16–7.27 (m, 10 H, C$^{12–14}$-H)	5.37 (C^{15}, $^1J_{P,C}$ = 49.7), 10.25 (C^3-CH$_3$), 11.16 (C^2-CH$_3$), 21.91 and 22.34 (C^9, $^1J_{P,C}$ = 44.9 and 45.8), 24.84 (C^7, $^3J_{P,C}$ = 14.1), 27.48 and 27.51 (C^{10}, $^2J_{P,C}$ = 7.3 and 7.5), 29.22 (C^8, $^1J_{P,C}$ = 48.4), 46.82 (C^6, $^2J_{P,C}$ = 7.3), 110.91 (C^4), 115.66 (C^5), 116.34 (C^3), 122.97 (C^2), 127.25 (C^{14}), 128.14 and 128.26 (C^{12}), 128.88 and 128.93 (C^{13}), 137.96 and 138.0 (C^{11}, $^3J_{P,C}$ = 12.9 and 11.2)	30.28
4c		1.53 and 1.54 (d, 3 H, C^7-H, $^3J_{6,7}$ = 6.4), 1.70 (d, 3 H, C^{16}-H, $^2J_{P,H}$ = 13.6), 1.92 (s, 3 H, C^3-CH$_3$), 2.17 (s, 3 H, C^2-CH$_3$), 2.61–2.95 (m, 6 H, C^{8,9}-H), 3.16–3.47 (m, 4 H, C^{10}-H), 4.56–4.57 (m, 1 H, C^6-H), 5.90 (d, 1 H, C^4-H, $^3J_{4,5}$ = 2.4), 6.67 (d, 1 H, C^5), 7.17–7.20 (m, 2 H, C^{14}-H), 7.38–7.41 (m, 2 H, C^{12}-H), 7.64–7.68 (m, 2 H, C^{13}-H), 8.46 and 8.47 (d, 2 H, C^{15})	6.10 (C^{16}, $^1J_{P,C}$ = 51.0), 10.27 (C^3-CH$_3$), 11.0 (C^2-CH$_3$), 20.46 and 20.55 (C^9, $^1J_{P,C}$ = 49.7), 25.20 (C^7, $^3J_{P,C}$ = 13.7), 29.84 (C^{10}, $^2J_{P,C}$ = 5.1), 30.20 (C^8, $^1J_{P,C}$ = 50.0), 46.91 (C^6, $^2J_{P,C}$ = 9.0), 110.90 (C^4), 115.63 (C^5), 116.27 (C^3), 122.55 (C^{14}), 123.31 (C^2), 123.84 and 123.88 (C^{12}), 137.50 (C^{13}), 148.76 (C^{15}), 157.40 and 157.52 (C^{11}, $^3J_{P,C}$ = 8.6)	31.67
4d		1.54 (d, 3 H, C^{11}-H, $^3J_{10,11}$ = 4.5), 1.64–1.74 (m, 4 H, C^{5,6}-H), 1.80 (d, 3 H, C^{19}-H, $^2J_{P,H}$ = 13.8), 2.15 (s, 3 H, C^2-CH$_3$), 2.20–2.40 (m, 8 H, C^{4,7,13}-H), 2.50–2.75 (m, 2 H, C^{12}-H), 2.80–2.95 (m, 4 H, C^{14}-H), 4.50 (m, 1 H, C^{10}-H), 5.61 (s, 1 H, C^3), 6.97–7.37 (m, 10 H, C$^{16–18}$-H)	5.94 (C^{19}, $^1J_{P,C}$ = 49.9), 13.70 (C^2-CH$_3$), 22.16 and 23.03 (C^{13}, $^1J_{P,C}$ = 45.7 and 46.3), 23.54, 23.68 (C$^{4–7}$), 23.61 (C^{11}, $^3J_{P,C}$ = 13.6), 28.05 (C^{14}, $^2J_{P,C}$ = 12.9), 28.62 (C^{12}, $^1J_{P,C}$ = 48.4), 46.23 (C^{10}, $^2J_{P,C}$ = 5.9), 107.94 (C^3), 120.0 (C^2), 126.22 (C^{8,9}), 127.50 and 127.59 (C^{18}), 128.20 and 128.43 (C^{16}), 129.10 and 129.21 (C^{17}), 137.93 and 138.02 (C^{15}, $^3J_{P,C}$ = 12.0)	30.20

Table 2 Spectral Data of Compounds **3–5**[a] (continued)

Product	Structure	NMR, δ, *J* (Hz)		
		^{1}H	^{13}C	^{31}P[b]
5b[e]		1.49 (d, 3 H, C^7-H, $^3J_{6,7}$ = 6.8), 1.97 (s, 3 H, C^3-CH_3), 1.80–2.15 (m, 6 H, $C^{8,9}$-H), 2.21 (s, 3 H, C^2-CH_3), 2.61–2.85 (m, 4 H, C^{10}-H), 4.63–4.67 (m, 1 H, C^6-H), 5.95 (d, 1 H, C^4-H, $^3J_{4,5}$ = 2.8), 6.52 (d, 1 H, C^5), 7.01–7.22 (m, 10 H, C^{12-14})	9.69 (C^3-CH_3), 11.26 (C^2-CH_3), 24.65 (C^7, $^3J_{P,C}$ = 9.9), 27.66 and 27.69 (C^{10}, $^2J_{P,C}$ = 17.4 and 17.1), 28.86 and 30.88 (C^9, $^1J_{P,C}$ = 62.1 and 63.0), 36.75 (C^8, $^1J_{P,C}$ = 62.5), 45.67 (C^6, $^2J_{P,C}$ = 3.9), 110.21 (C^4), 113.81 (C^5), 114.59 (C^3), 124.50 (C^2), 126.32 and 126.50 (C^{14}), 127.94 and 128.06 (C^{12}), 128.49 and 128.69 (C^{13}), 140.71 and 140.75 (C^{11}, $^3J_{P,C}$ = 12.8)	45.06
5c[e]		1.45 (d, 3 H, C^7-H, $^3J_{6,7}$ = 6.8), 1.56–1.70 (m, 4 H, C^9-H), 1.88 (s, 3 H, C^3-CH_3), 2.08–2.27 (m, 2 H, C^8-H), 2.17 (s, 3 H, C^2-CH_3), 2.76–3.15 (m, 4 H, C^{10}-H), 4.60–4.67 (m, 1 H, C^6-H), 5.84 (d, 1 H, C^4-H, $^3J_{4,5}$ = 2.4), 6.48 (d, 1 H, C^5-H), 6.96–7.28 (m, 4 H, $C^{12,14}$-H), 7.50–7.53 (m, 2 H, C^{13}-H), 8.38–8.44 (m, 2 H, C^{15}-H)	9.30 (C^3-CH_3), 10.85 (C^2-CH_3), 24.10 (C^7, $^3J_{P,C}$ = 9.4), 26.28 and 28.20 (C^9, $^1J_{P,C}$ = 63.8 and 64.7), 29.50 and 29.52 (C^{10}, $^2J_{P,C}$ = 24.4), 36.45 (C^8, $^1J_{P,C}$ = 62.6), 45.36 (C^6, $^2J_{P,C}$ = 3.9), 109.55 (C^4), 113.48 (C^5), 113.97 (C^3), 121.05 and 121.19 (C^{14}), 122.14 and 122.46 (C^{12}), 124.13 (C^2), 136.10 and 136.25 (C^{13}), 148.66 and 148.88 (C^{15}), 159.65 and 159.80 (C^{11}, $^3J_{P,C}$ = 13.9 and 15.8)	45.60

[a] ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 100.69 and 161.98 MHz, respectively) in $CDCl_3$.

[b] ^{31}P NMR for **5d**: δ = 49.02.

[c] Nonequivalence of all protons in P–C^8H_2 and P(C^9H_2)$_2$ fragments in the ^{1}H NMR spectrum is caused by the presence of a chiral center (C^6). Splitting of signals of CH_3 groups (at C^2, C^3 and C^6 carbon atoms) in the ^{13}C NMR spectrum is likely to occur due to the 'propeller' asymmetry of the phosphorus atom in the phosphine **3a** (analogous to tribenzylamine[16]). The possibility of such diastereomerism is being studied.

[d] Splitting of signals of the atoms C^2 and C^{10} and methyl groups attached thereto in the ^{13}C NMR spectrum may be explained by hindered rotation about the N–C^{10}, C^{10}–C^{12} and C^{12}–P bonds owing to the steric effect of methyl groups at C^2 and C^{10}.

[e] IR spectra (Specord IR-75 spectrometer, KBr) of phosphine oxides **5b**,**c** contain an absorption band at 1150 cm^{-1} (P=O).

[2-(2-Methyl-4,5,6,7-tetrahydro-1*H*-indol-1-yl)propyl]bis(2-phenylethyl)phosphine (3d)
Yield: 89%; light-yellow oil.

Anal. Calcd for $C_{28}H_{36}NP$: C, 80.54; H, 8.69; N, 3.35; P, 7.42. Found: C, 80.56; H, 8.73; N, 3.49; P, 7.23.

[2-(1*H*-Indol-1-yl)propyl]bis(2-phenylethyl)phosphine (3e)
Yield: 89%; light-yellow oil.

Anal. Calcd for $C_{27}H_{30}NP$: C, 81.17; H, 7.57; N, 3.51; P, 7.75. Found: C, 81.10; H, 7.61; N, 3.68; P, 7.61.

Methyl [2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis(2-phenylethyl)phosphonium Iodide (4b)
Yield: 97%; mp 186–188 °C (EtOH).

Anal. Calcd for $C_{26}H_{35}INP$: C, 60.12; H, 6.79; I, 24.43; N, 2.70; P, 5.96. Found: C, 60.35; H, 7.05; I, 24.39; N, 2.94; P, 5.68.

Methyl [2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis[2-(2-pyridinyl)ethyl]phosphonium Iodide (4c)
Yield: 97%; mp 110–111 °C (Et_2O).

Anal. Calcd for $C_{24}H_{33}IN_3P$: C, 55.28; H, 6.38; I, 24.34; N, 8.06; P, 5.94. Found: C, 55.52; H, 6.46; I, 24.16; N, 8.17; P, 5.83.

Methyl [2-(2-Methyl-4,5,6,7-tetrahydro-1*H*-indol-1-yl)propyl]bis(2-phenylethyl)phosphonium Iodide (4d)
Yield: 97%; mp 180–181 °C (EtOH).

Anal. Calcd for $C_{29}H_{39}INP$: C, 62.25; H, 7.03; I, 22.68; N, 2.50; P, 5.54. Found: C, 61.98; H, 6.86; I, 22.96; N, 2.77; P, 5.67.

Methyl [2-(2-Methyl-4,5,6,7-tetrahydro-1*H*-indol-1-yl)propyl]bis(2-phenylethyl)phosphonium Iodide (4d)
Yield: 97%; mp 180–181 °C (EtOH).

Anal. Calcd for $C_{29}H_{39}INP$: C, 62.25; H, 7.03; I, 22.68; N, 2.50; P, 5.54. Found: C, 61.98; H, 6.86; I, 22.96; N, 2.77; P, 5.67.

[2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis(2-phenylethyl)phosphine Oxide (5b)
Yield: 96%; light-yellow oil.

Anal. Calcd for $C_{25}H_{32}NOP$: C, 76.31; H, 8.20; N, 3.56; P, 7.87. Found: C, 76.05; H, 8.00; N, 3.34; P, 7.60.

[2-(2,3-Dimethyl-1*H*-pyrrol-1-yl)propyl]bis[2-(2-pyridinyl)ethyl]phosphine Oxide (5c)
Yield: 96%; yellow oil.

Anal. Calcd for $C_{23}H_{30}N_3OP$: C, 69.85; H, 7.65; N, 10.63; P, 7.83. Found: C, 69.65; H, 7.55; N, 10.44; P, 7.58.

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References

(1) (a) Trofimov, B. A.; Tarasova, O. A.; Mikhaleva, A. I.; Kalinina, N. A.; Sinegovskaya, L. M.; Henkelmann, J. *Synthesis* **2000**, 1585. (b) Trofimov, B. A.; Tarasova, O. A.; Shemetova, M. A.; Afonin, A. V.; Klyba, L. V.; Baikalova, L. V.; Mikhaleva, A. I. *Zh. Org. Khim.* **2003**, *39*, 437; *Russ. J. Org. Chem.* **2003**, *39*, 408.

(2) Trofimov, B. A. *Curr. Org. Chem.* **2002**, *6*, 1121.

(3) Valentine, D. H. Jr.; Hillhouse, J. H. *Synthesis* **2003**, 2437.

(4) (a) Trofimov, B. A.; Gusarova, N. K.; Brandsma, L. *Main Group Chem. News* **1996**, *4*, 18; *Chem. Abstr.* **1996**, *125*, 142810n. (b) Gusarova, N. K.; Malysheva, S. F.; Arbuzova, S. N.; Trofimov, B. A. *Russ. Chem. Bull.* **1998**, *47*, 1645. (c) Trofimov, B. A.; Arbuzova, S. N.; Gusarova, N. K. *Russ. Chem. Rev.* **1999**, *68*, 215. (d) Malysheva, S. F.; Arbuzova, S. N. In *Sovremenniy organicheskiy sintez (Modern Organic Synthesis)*; Rakhmankoulov, D. L., Ed.; Chemistry: Moscow, **2003**, 160–177.

(5) Nonhebel, D. C.; Walton, J. C. *Free-Radical Chemistry, Structure and Mechanism*; University Press: Cambridge, **1974**.

(6) Trofimov, B. A. In *The Chemistry of Heterocyclic Compounds, Pyrroles*, Vol. 48; Jones, R. A., Ed.; Wiley: New York, **1992**, 131–298.

(7) Trofimov, B. A.; Malysheva, S. F.; Sukhov, B. G.; Belogorlova, N. A.; Schmidt, E. Yu.; Sobenina, L. N.; Kuimov, V. A.; Gusarova, N. K. *Tetrahedron Lett.* **2003**, *44*, 2629.

(8) (a) Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, **1999**. (b) Brunner, H.; Limmer, S. *J. Organomet. Chem.* **1991**, *417*, 173. (c) Roucoux, A.; Suisse, I.; Devocelle, M.; Carpentier, J. F.; Agbosson, F.; Mortreux, A. *Tetrahedron: Asymmetry* **1996**, *7*, 379. (d) Clarke, M. L.; Cole-Hamilton, D. J.; Slavin, M. Z.; Woollins, J. D. *Chem. Commun.* **2000**, 2065. (e) Jang, H.-Y.; Seo, H. H. J. W.; Chung, Y. K. *Tetrahedron Lett.* **2000**, *41*, 5083. (f) Guo, R.; Li, X.; Wu, J.; Kwok, W. H.; Chen, J.; Choi, M. C. K.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 6803. (g) Braunstein, P.; Naud, F. *Angew. Chem. Int. Ed.* **2001**, *40*, 680.

(9) Priola, A.; Gatti, G.; Cesca, S. *Makromol. Chem.* **1979**, *180*, 1.

(10) Malysheva, S. F.; Gusarova, N. K.; Belogorlova, N. A.; Nikitin, M. V.; Gendin, D. V.; Trofimov, B. A. *Zh. Obshch. Khim.* **1997**, *67*, 63; *Russ. J. Gen. Chem.* **1997**, *67*, 58.

(11) Trofimov, B. A.; Gusarova, N. K.; Malysheva, S. F.; Ivanova, N. I.; Sukhov, B. G.; Belogorlova, N. A.; Kuimov, V. A. *Synthesis* **2002**, 2207.

(12) Trofimov, B. A.; Gusarova, N. K.; Malysheva, S. F.; Sukhov, B. G.; Belogorlova, N. A.; Kuimov, V. A.; Al'pert, M. L. *Sulfur Lett.* **2003**, *26*, 63.

(13) Chelucci, G.; Orrù, G.; Pinna, G. A. *Tetrahedron* **2003**, *59*, 9471.

(14) (a) Cozzi, P. G.; Zimmermann, N.; Hilgraf, R.; Schaffner, S.; Pfaltz, A. *Adv. Synth. Catal.* **2001**, *143*, 450. (b) Gurevich, P. A.; Yaroshevskaya, V. A. *Chem. Heterocycl. Comp.* **2000**, *36*, 1361. (c) Moloy, K. G.; Petersen, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 7707.

(15) Trofimov, B. A.; Brandsma, L.; Arbuzova, S. N.; Malysheva, S. F.; Gusarova, N. K. *Tetrahedron Lett.* **1994**, *35*, 7647.

(16) Potapov, V. M. *Stereokhimia (Stereochemistry)*; Khimia: Moscow, **1988**.