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Synthesis and Steric Structure of Aryloxypropynyl Alcohols of the Phosphinane Series

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Abstract — Phenoxy- and benzyloxypropynyl alcohols of the phosphinane series are synthesized. The steric structure of individual isomers is established by means of ^{1}H and ^{13}C NMR spectroscopy. Stereodirection of the ethynylation of *trans*- and *cis*-2,5-dimethyl-1-phenyl-2-thioxo-λ^5-phosphinane-4-ones is studied.
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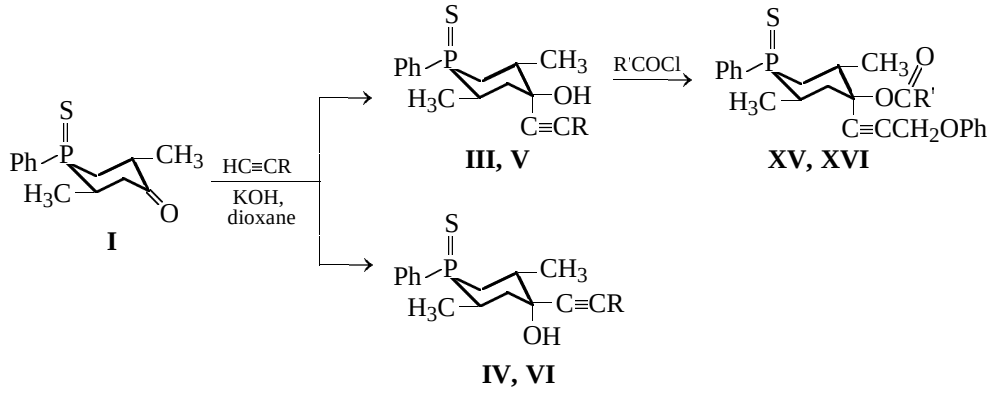
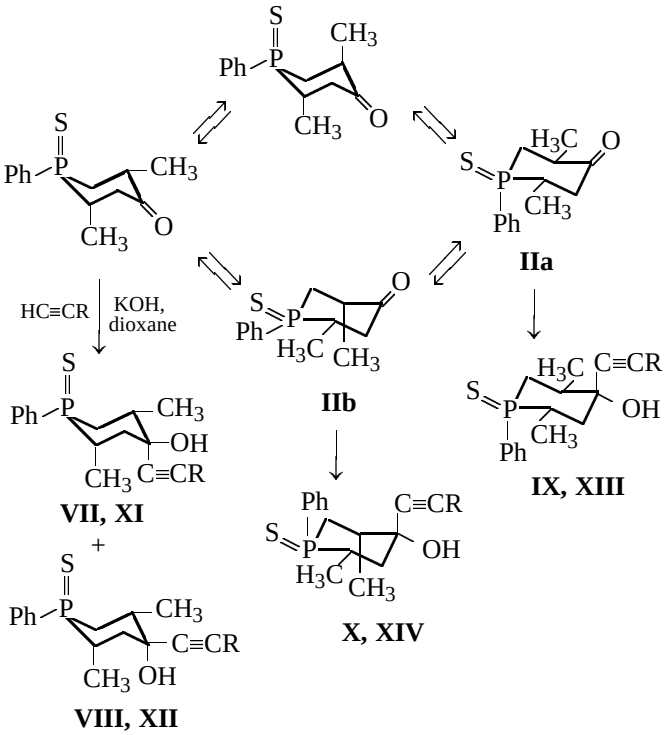
To study stereodirection of the nucleophilic addition of aryloxypropynes by the carbonyl group of stereoisomeric 2,5-dimethyl-1-phenyl-2-thioxo-λ^5-phosphinan-4-ones **I** and **II**, we elucidated optimal conditions for the synthesis and isolation of aryloxypropynyl alcohols of the phosphinane series [1, 2]. The condensation of 1-phenoxy-2-propyne and 1-benzyloxy-2-propyne with individual stereoisomers of ketones **I** and **II** was performed at room temperature in the presence of a tri- and fourfold molar excess of finely ground technical grade potassium hydroxide in anhydrous dioxane. Thin-layer chromatography of the reaction products showed formation of stereoisomeric mixtures of tertiary acetylenic alcohols. The mixtures were separated into individual stereoisomers by fractional crystallization or column chromatography. As a result, individual stereoisomeric acetylenic derivatives 4-hydroxy-2,5-dimethyl-4-(3-phenoxy-1-propynyl)-1-phenyl-λ^5-phosphinane-1-thiones (**III, IV, VIII, IX**) and 4-(3-benzyloxy-1-propynyl)-4-hydroxy-2,5-dimethyl-1-phenyl-λ^5-phosphinane-1-thiones (**V, XI**–**XIII**) were isolated.

By esterification of isomer **III** we synthesized acetate **XV** and propionate **XVI**. The composition and purity of the synthesized aryloxypropynyl alcohols and esters were confirmed by elemental analysis, TLC, and IR spectroscopy. The isomeric composition and physicochemical characteristics of the reaction products are listed in Table 1.

The steric structure of the obtained compounds was established by means of ^{1}H and ^{13}C NMR spectroscopy (Tables 2 and 3). The shapes of signals in the ^{1}H NMR spectra of stereoisomeric acetylenic phosphinanols **III**–**V**, **VIII**, **IX**, and **XI**–**XIII** and esters **XV** and **XVI** are complicated due to additional spin–spin coupling with the phosphorus nucleus. The orientation of the methyl groups was determined from the coupling constants of the protons at C^2 and C^5 with vicinal protons at C^3 and C^6, respectively. Thus, in the spectra of epimers **III** and **V**, the $^3J(H_a^5H_a^6$ and $^3J(H_a^5H_e^6)$ constants are 12.3–13.2 and 2.4–3.0 Hz, respectively, which confirms axial position of H^5 and, consequently, equatorial orientation of the 5-CH$_3$





R = CH_2OPh (**III, IV, VII**–**X**), CH_2OCH_2Ph (**V, VI, XI**–**XIV**); R' = CH_3 (**XV**), CH_2CH_3 (**XVI**).

group. The $^3J(H_a^2H_a^3)$ and $^3J(H_a^2H_e^3)$ constants are 12.5–13.5 and 3.0–3.6 Hz, respectively, providing evidence for axial orientation of H^2 and equatorial orientation of the 2-CH_3 group. Hence, stereoisomeric alcohols **III**–**V** and related esters **XV** and **XVI** are *chair* conformers with *trans*-diequatorial methyl groups.

The OH proton signals in the spectra of epimers **III** and **V** are downfield (δ 2.57 and 2.81 ppm), implying that this group is equatorial. The OH proton of epimer **IV** resonates upfield (δ 1.85 ppm), attesting axial orientation of this group and hence equatorial position of the ethynyl substituent. Similar correlation

Table 1. Physicochemical characteristics of compounds **III**–**V, VIII, IX, XI**–**XIII, XV**, and **XVI**

Comp. no.	Content of isomer in mixtures or yield of ester, %	mp, °C	R_f [a]	ν_{OH}, cm^{-1}	δ_P, ppm	Found, %				Formula	Calculated, %			
						C	H	P	S		C	H	P	S
III	90	110–111	0.32	3350	46.7	68.80	6.72	7.91	8.04	$C_{22}H_{25}O_2PS$	68.75	6.51	8.07	8.33
IV	10	[b]	0.28	3384	–	68.81	6.70	7.93	8.16	$C_{22}H_{25}O_2PS$	68.75	6.51	8.07	8.33
V	74	[b]	0.30	3416	46.5	69.31	6.90	7.83	8.06	$C_{23}H_{27}O_2PS$	69.35	6.78	7.79	8.04
VIII	21	148–149	0.25	3360	44.5	68.83	6.75	7.90	8.21	$C_{22}H_{25}O_2PS$	68.75	6.51	8.07	8.33
IX	52	198–199	0.26	3300	40.6	68.73	6.91	7.91	8.25	$C_{22}H_{25}O_2PS$	68.75	6.51	8.07	8.33
XI	22	121–123	0.29	3352	–	69.23	6.90	7.71	8.07	$C_{23}H_{27}O_2PS$	69.35	6.78	7.79	8.04
XII	30	131–132	0.27	3408	–	69.18	6.93	7.97	8.11	$C_{23}H_{27}O_2PS$	69.35	6.78	7.79	8.04
XIII	35	84–85	0.26	3320	–	69.20	6.91	7.93	8.09	$C_{23}H_{27}O_2PS$	69.35	6.78	7.79	8.04
XV	~100	112–113	0.47	–	–	67.78	6.44	7.02	7.55	$C_{24}H_{27}O_3PS$	67.61	6.34	7.28	7.51
XVI	~100	118–119	0.51	–	–	68.31	6.75	7.03	7.22	$C_{25}H_{29}O_3PS$	68.18	6.59	7.05	7.27

[a] Acetone–hexane, 1 : 2. [b] Oil

Table 2. Parameters of the ^{1}H NMR spectra of compounds **III–V, VIII, IX, XI–XIII, XV**, and **XVI**

Atom	III	IV	V	VIII	IX[a]	XI	XII	XIII	XV	XVI
					δ, ppm					
H_e^2	–	–	–	2.65	–	3.06	2.67	–	–	–
H_a^2	2.56	2.61	2.61	–	2.82	–	–	2.64	2.79	2.80
H_e^3	2.05	2.15	2.09	2.28	2.35	2.22	2.29	2.13	2.86	2.86
H_a^3	2.26	2.43	2.29	2.38	2.48	2.90	2.39	2.30	2.15	2.13
H_a^5	2.42	2.61	2.58	2.23	2.47	–	2.25	2.26	2.46	2.46
H_e^6	1.84	1.78	1.96	2.37	2.65	–	2.36	2.52	1.79	1.79
H_a^6	2.17	2.36	2.36	1.78	1.95	1.79	1.79	1.77	2.27	2.26
C^2CH_3	0.84	0.88	0.93	1.19	1.09	1.06	1.21	1.21	0.84	0.83
C^5CH_3	1.15	1.16	1.22	1.20	1.27	1.32	1.27	1.21	1.10	1.10
CH_2O	4.85	4.72	4.65	4.68	4.89	4.58	4.55	4.62	4.88	4.88
CH_2Ph	–	–	4.34	–	–	4.20	4.17	4.27	–	–
OH	2.57	1.85	2.81	1.70	2.56	–	1.80	2.44	–	–
Ph	6.94–7.73 m	6.93–7.96 m	7.25–7.92 m	6.90–7.85 m	6.93–8.12 m	7.25–7.92 m	7.24–7.87 m	7.25–7.90 m	6.93–7.74 m	6.93–7.74 m
					J_{HH}, Hz					
H^2CH_3	6.6	6.9	6.9	7.2	7.2	7.2	7.2	7.2	6.9	6.6
$H_a^2H_a^3$	12.9	13.5	12.6	–	13.8	–	–	13.2	12.9	12.9
$H_a^2H_e^3$	3.0	3.6	3.3	–	3.9	–	–	3.9	3.3	3.3
$H_e^2H_a^3$	–	–	–	5.1	–	4.8	6.0	–	–	–
$H_e^2H_e^3$	–	–	–	3.9	–	3.0	3.9	–	–	–
$H_a^3H_e^3$	13.2	14.4	13.2	14.4	13.5	14.1	14.4	14.1	13.5	13.2
H^5CH_3	6.3	6.6	6.3	6.6	6.0	6.3	6.6	6.0	6.6	6.3
$H_a^5H_a^6$	12.3	13.2	12.9	13.2	13.5	13.5	13.2	13.5	12.9	13.2
$H_a^5H_e^6$	3.0	2.4	2.7	3.0	2.7	–	3.9	3.0	3.0	3.3
$H_a^6H_e^6$	14.1	13.5	14.1	15.0	13.8	14.7	14.7	13.8	13.5	14.4
					J_{PH}, Hz					
PH_a^2	11.0	13.2	13.2	–	13.5	–	–	13.5	–	–
PH_e^2	–	–	–	13.8	–	–	13.8	–	–	–
PH_e^3	32.7	32.1	32.4	34.2	34.5	30.0	34.2	29.7	32.4	32.4
PH_a^3	8.7	6.0	9.0	9.9	8.1	9.9	12.0	–	9.3	9.0
PH_a^5	10.0	13.2	13.2	–	–	–	–	–	13.2	13.8
PH_e^6	14.7	16.5	15.0	–	11.7	–	11.1	11.4	16.5	16.2
PH_a^6	–	8.7	5.7	8.1	8.1	9.0	7.8	8.1	5.4	5.7
P–2-CH_3	18.0	18.0	18.5	17.4	17.1	17.4	17.1	17.7	18.2	18.3
P–5-CH_3	2.4	2.7	2.4	3.3	3.0	2.4	3.3	2.7	2.4	2.7
P–CH_2O	–	–	–	–	–	–	–	–	3.6	5.1

[a] The ^{1}H and ^{13}C NMR spectra of **IX** were measured in C_5D_5N.

is also observed both with epimers **III** and **IV** and isomers of aryloxypropynyl alcohols of the tetrahydrothiopyran series [3]. Thus, in the spectra of isomer **III** the H_a^3 and H_a^5 signals are shifted upfield by Δδ 0.17–0.19 ppm compared to the respective signals of epimer **IV**, due to the synclinal position of these protons relative to the equatorial hydroxyl group. Epimer **V** was assigned, by analogy of its ^{1}H proton spectrum with that of isomer **III**, a configuration with an equatorial OH group and an axial ethynyl substituent.

In epimers **VIII**, **XI**, and **XII**, the downfield proton signal that appears as a multiplet (δ 2.65–3.06 ppm),

has $^3J(H_e^2H_a^3)$ and $^3J(H_e^2H_e^3)$ constants of 4.8–6.0 and 3.0–3.9 Hz, respectively, which points to equatorial orientation of H^2 and axial orientation of the 2-CH_3 group. The $^3J(H_a^5H_e^6)$ and $^3J(H_a^5H_a^6)$ constants (3.0–3.9 and 13.2–13.5 Hz, respectively) for the H_a^5 signal (multiplet at δ 2.23–2.25 ppm), provide evidence for axial orientation of H^5 and, consequently, equatorial orientation of the 5-CH_3 group.

In the spectra of epimers **VIII**, **XI** and **XII**, the signals of the 2-CH_3 group are shifted downfield to those of epimers **III**–**V** due both to the axial orientation of this group and to its weaker shielding by the phenyl group at phosphorus. The close proton chemical shifts of epimers **VIII** and **XII** points to similar conformations of the rings and orientations of exocyclic substituents in these compounds. The upfield 4-OH proton signals in epimers **VIII** and **XII** (δ 1.70 and 1.80 ppm) suggest that this group is axial and, consequently, the ethynyl substituent is equatorial.

In the ^{1}H NMR spectra of alcohols **IX** and **XIII**, the values of the $^3J(H_a^2H_a^3)$ (13.2, 13.8 Hz), $^3J(H_a^2H_e^3)$ (3.9 Hz) and $^3J(H_a^5H_a^6)$ (13.5 Hz), $^3J(H_a^5H_e^6)$ (2.7, 3.0 Hz) constants point to axial orientation of the H^2 and H^5 protons and equatorial orientation of the 2-CH_3 and 5-CH_3 groups. Equatorial alcohols **IX** and **XIII** differ from alcohols **III** and **V** by steric orientation of substituents at the phosphorus atom, that is, they have the phenyl group axial and the S atom equatorial. The axial orientation of the phenyl group is attested also by the downfield shift of the H_a^3 and H_a^5 axial proton signals, induced by deshielding from the phenyl group. In the spectrum of epimer **IX**, the H_a^3 and H_a^5 proton signals (δ 2.48 and 2.47 ppm) are shifted downfield by Δδ 0.1 and 0.24 ppm, respectively, from those of isomer **VIII** and by Δδ 0.22 and 0.05 ppm from those of epimer **III**. However, the chemical shifts of axial protons at C^3 and C^5 in the spectrum of isomer **IX** remain unchanged. This is obviously due to flattening of the ring near phosphorus in the C^2–P–C^6 fragment. As a result, the axial phenyl group is shifted apart, and H_a^3 and H_a^5 no longer fall into the deshielding area. Based on the fact that the hydroxyl proton in epimers **IX** and **XIII** resonates downfield (δ 2.56 and 2.44 ppm) and by analogy with isomers **III** and **V**, we suggest that the OH group in **IX** and **XIII** is equatorial.

In the spectra of esters **XV** and **XVI**, the H_e^3 proton signal is downfield by Δδ 0.81 ppm from that of alcohol **III**, which results from the replacement of the OH by ester function whose carbonyl group exerts the deshielding effect. This fact provides further evidence for the suggested equatorial orientation of the OH group in **III**.

In the ^{13}C NMR spectra of alcohols **III**–**V**, **VIII**, **IX**, and **XI**–**XIII** and esters **XV** and **XVI** (Table 3), the signals of the 5-CH_3 carbon, $C^{2,5,6}$, and C^3 in **IX** and C^4 in **XI** are doublets due to coupling with phosphorus. The signals were assigned from an analysis of ^{13}C signal multiplicies under incomplete proton decoupling (monoresonance) and J_{PC} constants. Analysis of the carbon chemical shifts gave evidence for the suggested steric structure of the aryloxypropynyl alcohols of the phosphinane series. Methyl carbon signals appear upfield at δ_C 12.85–13.41 (2-CH_3) and 17.07–18.38 ppm (5-CH_3). The downfield doublet with ^3J(P–CH_3) 13.4–15.8 Hz, that corresponds to the P–C^6–C^5–CH_3 dihedral angle of about 180°, is assigned to the carbon atom of the equatorial methyl group at C^5.

In the pair of epimers **III** and **IV**, there is a trend in carbon chemical shifts. The $C^{2,4,5,6}$ signals of **III** appear downfield from those of **IV**. This is probably due to specific orientation of exocyclic substituents at C^4.

The equatorial OH signal makes the signal of the α carbon atom C^4 in alcohol **III** to shift by $\Delta\delta_C$ 3.03 ppm from the respective signal of epimer **IV**. Orientation of the OH group affects substantially the resonance of the γ-carbon atoms C^2 and C^6. The axial OH group exerts a γ-shielding effect and shifts the resonance of these nuclei upfield by Δδ 2.62–3.99 ppm.

The carbon chemical shifts of stereoisomers **III**–**V**, **VIII**, **IX**, and **XI**–**XIII** also depends on steric orientation of substituents at the phosphorus atom. In epimers **IX** and **XIII**, the C^2 and C^6 atoms resonate downfield compared with those in **VIII** and **XII** with an axial sulfur atom. Therewith, C^2 ($\Delta\delta_C$ 4.80–5.16 ppm) is deshielded stronger than C^6 ($\Delta\delta_C$ 3.08–3.42 ppm). Similar relationships can be revealed when comparing the spectra of **IX** and **XIII** with the spectra of their epimers by phosphorus **III** and **V**. The $C^{2,6}$ atoms in epimers **IX** and **XIII** are deshielded (C^2, $\Delta\delta_C$ 3.32–5.99 ppm; C^6, $\Delta\delta_C$ 1.13–1.82 ppm), while in isomers **III** and **V** these atoms are shielded by axial sulfur.

Comparison of the spectra of isomers **IX** and **XIII** and their epimers by the phosphorus and C^2 and C^4 atoms shows that the axial phenyl group deshields C^3 and C^5 and shifts their signals downfield by $\Delta\delta_C$ 0.50–2.14 ppm. In turn, the axial sulfur atom in epimers **VIII** and **XII** shields C^3 and C^5 and shifts their signals upfield. The shielding of C^3 and C^5 ($\Delta\delta_C$ 3.95–

Table 3. Parameters of the ^{13}C NMR spectra, δ_C, ppm (J_{PC}, Hz) of compounds **III**–**V, VIII, IX, XI**–**XIII, XV**, and **XVI**

Comp. no.	2-CH_3	5-CH_3	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	Ph_i	Ph_o	Ph_m	Ph_p
III	12.96 (0)	17.10 (14.6)	31.47 (51.3)	43.49 (0)	72.58 (0)	37.13 (2.0)	36.61 (50.0)	86.32	82.08	55.46	–	156.88	114.67	129.23	121.46
IV	12.94 (0)	17.98 (14.6)	27.48 (51.3)	43.21 (0)	69.55 (0)	36.04 (0)	33.99 (50.1)	89.76	79.74	55.83	–	157.44	114.90	129.47	121.54
V	13.10 (0)	17.16 (15.8)	31.71 (51.3)	43.54 (0)	72.57 (0)	37.18 (2.4)	36.96 (50.0)	85.38	83.10	57.13	71.63	136.77	127.64	128.24	131.53
VIII	12.99 (0)	18.22 (14.6)	32.30 (50.0)	44.43 (0)	68.60 (0)	39.65 (6.1)	35.01 (48.8)	89.46	79.43	55.58	–	157.11	114.59	129.15	121.30
IX	13.40 (0)	18.06 (14.6)	37.46 (50.1)	45.84 (2.4)	71.51 (0)	41.79 (4.8)	38.43 (47.6)	87.60	82.63	55.67	–	157.58	115.20	129.68	121.35
XI	17.60 (0)	18.23 (13.4)	24.35 (50.0)	41.19 (0)	70.33 (4.8)	36.42 (3.6)	26.72 (48.8)	89.47	80.38	57.24	71.70	137.20	128.06	128.45	131.70
XII	13.04 (0)	18.38 (14.6)	32.33 (50.1)	44.64 (0)	68.54 (0)	39.68 (6.1)	35.01 (48.8)	88.71	80.35	56.95	71.58	136.82	127.69	128.13	131.32
XIII	13.41 (0)	17.76 (13.4)	37.13 (48.8)	45.14 (0)	72.18 (0)	40.93 (6.1)	38.09 (47.6)	84.36	84.36	56.92	71.66	136.78	127.85	128.21	127.67
XV	12.85 (0)	17.08 (14.6)	30.77 (51.2)	37.83 (0)	78.42 (0)	36.27 (0)	35.73 (50.0)	84.39	82.37	55.56	–	156.95	114.67	129.24	121.45
XVI	12.85 (0)	17.07 (14.6)	30.72 (51.3)	37.88 (0)	78.15 (0)	36.31 (2.4)	35.70 (50.0)	84.25	82.45	55.53	–	156.90	114.62	129.20	121.38

4.51 ppm) in stereoisomer **XI** is stronger than in its epimer **XIII** that has a different orientation of substituents at phosphorus and of the methyl group at C^2.

Note that comparison of the chemical shifts of the C^3 and C^5 signals in phenoxy- and benzyloxypropynyl alcohols **IX** and **XIII** with those in **III** and **V** that are epimers of the former two compounds by phosphorous only, reveals dependence of the shifts on steric orientation of exocyclic substituents at phosphorus. As shown above, the axial phenyl in epimers **IX** and **XIII** strongly deshields C^3 ($\Delta\delta_C$ 1.60–2.35 ppm) and C^5 ($\Delta\delta_C$ 3.75–4.66 ppm), as compared to epimers **III** and **V** with axial sulfur.

The chemical shifts of the C^4 signals in alcohols **VIII**, **IX** and **XI**–**XIII** depend on steric orientation of exocyclic substituents at C^4. Like with alcohols **III** and **V**, the C^4 signals of epimers **IX**, **XI**, and **XIII** are shifted downfield by $\Delta\delta_C$ 1.79–3.64 ppm from those of isomers **VIII** and **XII**, in agreement with the effect of steric orientation of the OH group.

Noteworthy is a specific dependence of the chemical shifts of the acetylenic carbon atom attached directly to the heteroring C^4 atom on its orientation of the acetylenic moiety, like in aryloxypropynyl alcohols of the tetrahydrothiopyran and tetrahydropyran series [3]. In the pairs of epimers **III** and **IV**, **VIII**, and **IX**, and **XII** and **XIII**, the axial acetylenic atom C^7 resonates upfield by $\Delta\delta_C$ 1.86–4.35 ppm compared to the respective atom in the equatorial acetylenic moiety. In epimer **V** of the benzyloxypropynyl alcohol, the C^7 signal is shifted upfield, like in equatorial alcohol **III** with an axial ethynyl substituent. However, the signal of the axial C^7 atom in epimer **XI** is shifted downfield, due to the effect of the axial 2-CH_3 group.

The revealed correlations between steric structure and ^1H and ^{13}C NMR characteristics allowed us to establish the steric structure of the synthesized individual stereoisomers of aryloxypropynyl alcohols of the phosphinane series and determine the ratio of epimers in the mixtures. These results led us to conclude that the nucleophipic addition of aryloxypropynes occurs stereoselectively by the carbonyl group of stereoisomeric 2,5-dimethyl-1-phenyl-2-thioxo-λ^5-phosphinan-4-ones **I** and **II**. Condensation of unhindered ketone **I** with aryloxypropynes proceeds stereoselectively with preferential formation of equatorial alcohols **III** and **V** in yields of 90 and 74%, respectively. Ethynylation of sterically hindered *cis*-phosphinane **II** gives rise to mixtures of four isomers, in which aryloxypropynyl alcohols **IX** and **XIII** are prevailing (yields 52 and 35%, respectively). The presence of epimers **IX** and **XIII** among the reaction products provides evidence to show that *cis*-ketone **II**

isomerizes into *trans* isomer **IIa** during reaction in alkaline medium at room temperature; the latter undergoes nucleophilic attack on the C=O double bond from the axial side to form equatorial alcohols **IX** and **XIII**.

EXPERIMENTAL

The IR spectra were registered on a Specord M-80 instrument in KBr pellets (*c* 0.25%) and in thin layer. The NMR spectra were registered on a Varian Mercury-300 instrument at 300 (^{1}H) and 75.457 MHz (^{13}C) in $CDCl_3$, internal reference HMDS. Assignment of signals was performed from the C–{^{1}H} NMR spectra. The ^{31}P NMR spectra were recorded on a WP Bruker instrument at 32.44 MHz. The stereoisomeric compositions of the mixtures were assessed from the integral intensities of the methylene proton signals in the ^{1}H NMR spectra and the phosphorus signals in the ^{31}P spectra. Thin-layer chromatography was performed on Silufol UV-254 plates, eluent acetone–hexane (1 : 2). The mixtures were separated by fractional crystallization from an acetone–hexane mixture and by column chromatography on Silpearl silica gel, eluent ethyl acetate–petroleum ether (40–70°C), 1 : 3.

4-Hydroxy-2,5-dimethyl-4-(3-phenoxy-1-propynyl)-1-phenyl-λ^5-phosphinane-1-thiones (III, IV). A solution of 1.98 g (0.015 mol) of 1-phenoxy-2-propyne in 20 ml of dioxane was added dropwise with stirring at room temperature over the course of 0.5 h to a mixture of 60 ml of anhydrous dioxane and 1.68 g (0.03 mol) of finely ground crude KOH, and the resulting mixture was stirred for 3 h. A solution of 2.52 g (0.01 mol) of ketone **I** in 50 ml of dioxane was the added, and the mixture was stirred for 5 h and then treated with 20 ml of water. The aqueous layer was extracted with benzene. The organic extract was washed with water and dried over $MgSO_4$. The solvent was distilled off to obtain 3.15 g (82%) of a mixture of epimeric alcohols **III** and **IV**. Fractional crystallization of the mixture gave 2.02 g (64%) of individual alcohol **III**. The residue (1.13 g) was subjected to column chromatography to isolate 0.057 g (5%) of individual isomer **IV**.

4-Hydroxy-2,5-dimethyl-4-(3-phenoxy-1-propynyl)-1-phenyl-λ^5-phosphinane-1-thiones (VIII, IX) were synthesized similarly. Yield 3.03 g (79%). Fractional crystallization gave 1.39 g (46 %) of epimer IX. Column chromatography of the residue (1.64 g) gave 0.13 g (8%) of isomer **VIII**. Isomeric alcohols **VII** and **X** could not be isolated.

4-(3-Benzyloxy-1-propynyl)-4-hydroxy-2,5-dimethyl-1-phenyl-λ^5-phosphinane-1-thione (V). A solution of 2.19 g (0.015 mol) of 1-benzyloxy-2-propyne in 20 ml of dioxane was added dropwise with stirring at room temperature over the course of 0.5 h to a mixture of 70 ml of anhydrous dioxane and 2.24 g (0.04 mol) of finely ground technical grade KOH, and the resulting mixture was stirred for 3 h. A solution of 2.52 g (0.01 mol) of ketone **I** in 50 ml of dioxane was then added, and the mixture was stirred for 5 h and then treated with 20 ml of water. The aqueous layer was extracted with benzene. The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was removed to obtain 2.95 g (74 %) of a mixture of epimeric alcohols **V** and **VI**. The mixture was subjected to column chromatography to isolate 1.15 g (39%) of isomer **V**. Isomer **VI** could not be isolated individual.

4-(3-Benzyloxy-1-propynyl)-4-hydroxy-2,5-dimethyl-1-phenyl-λ^5-phosphinane-1-thiones (XI–XIII) were synthesized similarly. 3.02 g (76%) of a mixture of epimers **XI**–**XIII** was obtained. Column chromatography of the mixture gave 0.36 g (12%) of epimer **XI**, 0.51 g (17%) of epimer **XII**, and 0.85 g (28%) of isomer **XIII**. Isomer **XIV** could not be isolated individual.

[2,5-Dimethyl-1-phenyl-4-(3-phenoxy-1-propynyl)-2-thioxo-λ^5-phosphinan-4-yl] acetate (XV). A mixture of 0.58 g (0.0015 mol) of alcohol **III** and 10 ml of freshly distilled acetyl chloride was heated at 60–65°C for 1 h. Excess acetyl chloride was then removed in a water-jet-pump vacuum. The residue was dried in an oil-pump vacuum to isolate acetate **XV** in quantitative yield.

[2,5-Dimethyl-1-phenyl-4-(3-phenoxy-1-propynyl)-2-thioxo-λ^5-phosphinan-4-yl] propionate (XVI). A mixture of 0.58 g (0.0015 mol) of alcohol **III** and 10 ml of freshly distilled propionyl chloride was heated at 65–70°C for 1h. Excess acyl chloride was then removed in a water-jet-pump vacuum. The residue was dried in an oil-pump vacuum to isolate acetate **XVI** in quantitative yield.

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