Fig. 1. Ionization energies (IE) and resonance states (RS) of negative molecular ions of dihydropyrans.

coincides with the first IE. As can be seen, the energy distances between the RS and IE coincide within 0.1—0.3 eV limits. This means that the other high-energy resonances are also intershell and result from the excitation of an electron from a deeper OMO to one and the same vacant MO. The closeness of the energies of the first IE, the singlet transitions, and the first high-energy RS of the compounds under study and cyclenes of different structure[6,7] allows one to conclude that the MO responsible for the formation of RS in substituted pyrans is the vacant π^*_{CC}-MO, which, probably, determines also the form of the REC mass spectra in the low-

energy region of electron energies (1—4 eV). In fact, the resonance at 1.4 eV coincides within 0.3—0.5 eV with the position of the form resonance at π^*_{CC} in cyclenes[8] and the resonance at 3—4 eV (See Table 1) differs by only 0.5 eV from the energy of the first triplet electron transition in the same molecules.[6] The latter allows one to attribute it to the usual electron excited feshbach resonance with two coupled electrons on the vacant π^*_{CC}-MO.

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A new method for the synthesis of diorganylvinylphosphine oxides

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Diorganylvinylphosphine oxides were synthesized in 31—38% yields on heating (50 °C) diorganylphosphine oxides with vinyl sulfoxides or divinyl sulfone in the presence of KOH.

Key words: diorganylphosphine oxides, ethyl vinyl sulfoxide, divinyl sulfone, reaction; diorganylvinylphosphine oxides.
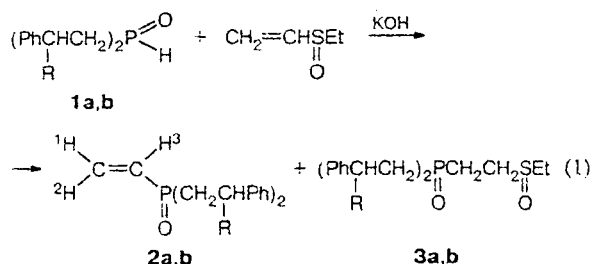
Among the known methods for the synthesis of diorganylvinylphosphine oxides, which are reactive intermediates and semi-products,[1] the reaction of chloro-

diorganylphosphine with oxirane followed by dehydrochlorination of the intermediate 2-chloroethyldiorganylphosphine oxides,[2] as well as oxidation of diorganyl-

vinylphosphines, should be especially noted. Diorganyl-vinylphosphines are usually synthesized from vinyl-magnesium halides and chlorodiorganylphosphines or by the reaction of alkyl ethylenephosphinates with Grignard reagents.[3]
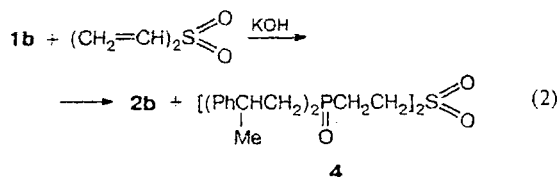
Using bisphenethylphosphine oxide (1a) and bis(2-phenylpropyl)phosphine oxide (1b), which are available now,[4] as examples we showed for the first time that organylvinylphosphine oxides can be obtained by phosphorylation of vinyl sulfoxides or vinyl sulfones with diorganylphosphine oxides.

Thus, heating (50 °C) of phosphine oxides 1a,b with ethyl vinyl sulfoxide in the presence of potassium hydroxide afforded bisphenethylvinylphosphine oxide (2a) and bis(2-phenylpropyl)vinylphosphine oxide (2b) in 31—34% yield (not optimized). The products of the nucleophilic addition of phosphine oxides 1a,b to the vinyl group of the sulfoxide, viz., bisphenethyl[2-(ethyl-sulfinyl)ethyl]- and bis(2-phenylpropyl)[2-(ethylsulfin-yl)ethyl]phosphine oxides (3a,b), which have not been described previously, were also isolated from the reaction mixture.

$$(PhCHCH_2)_2P \underset{R}{\overset{O}{\diagdown H}} + CH_2{=}CHSEt \xrightarrow{\ KOH\ }$$

1a,b

$$\underset{^2H}{\overset{^1H}{\diagdown}} C{=}C \underset{\underset{O \ \ R}{P(CH_2CHPh)_2}}{\overset{H^3}{\diagup}} + (PhCHCH_2)_2PCH_2CH_2SEt \quad (1)$$

2a,b   **3a,b**

R = H (a), Me (b)

Vinylphosphine oxide 2b is also the main product (the yield was 38%) of the reaction of secondary phosphine oxide 1b with divinyl sulfone in the presence of KOH. In this case, the yield of the bis-adduct 4 was 14%.

$$1b + (CH_2{=}CH)_2S \overset{O}{\underset{O}{\diagdown}} \xrightarrow{\ KOH\ }$$

$$\longrightarrow 2b + [(PhCHCH_2)_2PCH_2CH_2]_2S \overset{O}{\underset{O}{\diagdown}} \quad (2)$$

4

Vinylphosphine oxides 2a,b probably result from the elimination of ethanesulfenic acid from adducts 3a,b in the reaction (1) and organosulfinic acids from the products of mono- and bis-addition of phosphine oxide 1b to divinyl sulfone under conditions of the reaction (2). The reason for the easy desulfinylation and desulfonylation in these cases may be the presence of the electron-withdrawing substituent (P=O fragment) in the β-position relative to the sulfinyl or sulfonyl group.[5]

Thus, we have found a new promising approach to the synthesis of vinylphospine oxides. Studies of the preparative potential of the reactions (1) and (2), as well as the scheme of the formation of vinylphospine oxides, are now in progress.

Experimental

^{1}H and ^{31}P NMR spectra were recorded on a Varian VXR-500 S spectrometer (500 MHz) for compounds 2a,b and on a Jeol FX-90Q spectrometer for compounds 3a,b and 4. IR spectra were obtained on a Specord IR-75 instrument.

Reaction of bisphenethylphosphine oxide (1a) with ethyl vinyl sulfoxide. A mixture of phosphine oxide 1a (1.02 g, 4 mmol), ethyl vinyl sulfoxide (0.42 g, 4 mmol), and KOH (0.24 g, 4 mmol) in DMSO (6 mL) was stirred at 50 °C for 3 h. The reaction mixture was diluted with water and extracted with chloroform, and the extracts were washed with water. Crystals precipitated from the chloroform extract were separated, washed with acetone and ether, and dried in vacuo to yield 0.36 g (25%) of bisphenethyl[2-(ethylsulfinyl)ethyl]phosphine oxide (3a), m.p. 102 °C (acetone). Found (%): C, 65.47; H, 7.72; P, 8.27; S, 7.87. $C_{20}H_{27}O_2PS$. Calculated (%): C, 66.29; H, 7.46; P, 8.56; S, 8.84. ^{1}H NMR (CDCl$_3$), δ: 1.32 (t, 3 H, CH$_3$); 2.12 (m, 6 H, CH$_2$P=O); 2.88 (m, 8 H, CH$_2$Ph, CH$_2$SO); 7.25 (m, 10 H, C$_6$H$_5$). ^{31}P NMR, δ: 4.48. IR, v/cm^{-1}: 1150 (P=O); 1050 (O=S), 1020. The filtrate was concentrated in vacuo, the residue was triturated with ether, and ether was distilled off to give 0.37 g (31%) of bisphenethylvinylphosphine oxide (2a), a viscous paraffin-like product. Found (%): C, 75.35; H, 7.24; P, 9.93. $C_{18}H_{21}OP$. Calculated (%): C, 76.04; H, 7.44; P, 10.89. ^{1}H NMR (CDCl$_3$), δ: 1.99—2.11 (m, 4 H, CH$_2$P=O); 2.86—2.94 (m, 4 H, CH$_2$Ph); 6.13 (oct, 1 H, H(3)); 6.24 (oct, 1 H, H(1)); 6.37 (oct, 1 H, H(2)); 7.18—7.28 (m, 10 H, C$_6$H$_5$). ^{31}P NMR, δ: 35.7; $^2J_{H(1)H(2)}$ = 2.2 Hz, $^3J_{H(1)H(3)}$ = 12.6 Hz, $^3J_{H(2)H(3)}$ = 18.3 Hz, $^3J_{PH(3)}$ = 27.8 Hz, $^3J_{PH(1)}$ = 37.7 Hz, $^3J_{PH(2)}$ = 20.5 Hz. IR, v/cm^{-1}: 1150 (P=O).

Reaction of bis(phenylpropyl)phosphine oxide (1b) with ethyl vinyl sulfoxide. A mixture of phosphine oxide 1b (0.57 g, 2 mmol), ethyl vinyl sulfoxide (0.21 g, 2 mmol), and KOH (0.11 g, 2 mmol) in dioxane (6 mL) was stirred at 50 °C for 3 h. Dioxane was distilled off in vacuo and the residue was diluted with chloroform. The chloroform extracts were passed through a filter with calcined potash, chloroform was distilled off, and the residue was washed with ether and dried in vacuo to obtain 0.16 g (21%) of bis(phenylpropyl)[2-(ethylsulfin-yl)ethyl]phosphine oxide (3b). Found (%): C, 67.69; H, 8.08; P, 7.63; S, 8.27. $C_{22}H_{31}O_2PS$. Calculated (%): C, 67.69; H, 7.95; P, 7.95; S, 8.21. ^{1}H NMR (CDCl$_3$), δ: 1.27 (m, 9 H, CH$_3$); 1.87 (m, 6 H, CH$_2$P=O); 2.63 (m, 4 H, CH$_2$SO); 3.16 (m, 2 H, CHPh); 7.25 (m, 10 H, C$_6$H$_5$). ^{31}P NMR, δ: 43.8, 44.2, 45.0 (P). IR, v/cm^{-1}: 1150 (P=O); 1050 (O=S); 1020. The ethereal layer was concentrated and the residue was dried in vacuo to obtain 0.21 g (34%) of bis(phenyl-propyl)vinylphosphine oxide (2b), a viscous paraffin-like product. Found (%): C, 76.95; H, 8.05; P, 10.15. $C_{20}H_{25}OP$. Calculated (%): C, 77.17; H, 7.71; P, 9.97. ^{1}H NMR (CDCl$_3$), δ: 1.27 (m, 6 H, CH$_3$); 1.90 (m, 4 H, CH$_2$P=O); 3.10 (m, 2 H, CHPh); 5.56, 5.70, 5.71 (m, 1 H, H(3)); 5.81, 5.92, 5.94 (m, 1 H, H(1)); 5.96, 6.11, 6.19 (m, 1 H, H(2)); 7.20 (m, 10 H, C$_6$H$_5$). ^{31}P NMR, δ: 32.9, 33.5, 34.1; $^2J_{H(1)H(2)}$ = 2.2—2.5 Hz, $^3J_{H(1)H(3)}$ = 11.9—12.5 Hz, $^3J_{H(2)H(3)}$ = 18.3—19.0 Hz, $^2J_{PH(3)}$ = 27.7—31.0 Hz, $^3J_{PH(1)}$ = 36.8—38.6 Hz, $^3J_{PH(2)}$ = 19.0—20.0 Hz. IR, v/cm^{-1}: 1150 (P=O).

Bis(phenylpropyl)vinylphosphine oxide (2b) and bis{2-[di(phenylpropyl)phosphoryl]ethyl}sulfone (4) were obtained in 38 and 14% yield, respectively. on heating (50 °C) of a mixture of phosphine oxide 1b (4 mmol), divinylsulfone (2 mmol), and KOH (2 mmol) in dioxane (6 mL). Sulfone 4 is a viscous paraffin-like product. Found (%): C, 68.61; H, 8.20; P. 9.35; S, 3.79. $C_{40}H_{52}O_4P_2S$. Calculated (%): C, 69.56; H, 7.54; P, 8.98; S, 4.64. ^1H NMR (CDCl$_3$), δ: 1.30 (m, 12 H, CH$_3$); 1.90 (m, 12 H, CH$_2$P=O); 3.09 (m, 8 H, CHPh, CH$_2$SO$_2$); 7.20 (m, 20 H, C$_6$H$_5$). ^{31}P NMR, δ: 42.6, 44.6, 45.8. IR, v/cm^{-1}: 1150 (P=O); 1310 (O=S=O); 1120.

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Oxygenation of methane with atmospheric oxygen in aqueous solution promoted by H₂O₂ and catalyzed by a vanadate ion—pyrazine-2-carboxylic acid system

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Methane is oxidized in aqueous solution with atmospheric oxygen and hydrogen peroxide in a reaction catalyzed by a NaVO$_3$—pyrazine-2-carboxylic acid system. Methyl hydroperoxide is selectively formed at 50 °C. The turnover number of the catalyst after 24 h amounts to 480, and the yield of methyl hydroperoxide is 24% with respect to H$_2$O$_2$. Formaldehyde and formic acid are mainly formed at 120 °C.

Key words: activation of C—H bond, alkanes, hydroxyl radicals, metallocomplex catalysis, methane, methyl hydroperoxide, formic acid, oxidation, hydrogen peroxide, vanadium complexes, formaldehyde.

The search for new ways of processing methane to obtain valuable chemical products is of great scientific and practical interest due to its considerable reserves, although, on the other hand, methane is the most inert organic compound.[1,2]

Previously, we have shown that hydrocarbons and some other compounds are readily oxidized with atmospheric oxygen in acetonitrile in the presence of hydrogen peroxide and a vanadate anion—pyrazine-2-carboxylic acid (PCA) catalytic system.[3-12] The optimum VO$_3^-$/PCA ratio lies in the 1 : 2 to 1 : 4 range. It has also been shown that under the action of this catalyst H$_2$O$_2$ decomposes under mild conditions to give hydroxyl radicals, which attack the alkane molecules. The alkyl radicals produced add oxygen and are converted into alkyl hydroperoxides. Thus, H$_2$O$_2$ only acts as a promoter and is used in stoichiometric amounts, whereas molecular oxygen is the true oxidant in this reaction.

Since acetonitrile also reacts with hydroxyl radicals, it was of interest to investigate the possibility of oxida-