Organylthiochloroacetylenes: III. Nucleophilic Addition of Di(2-phenylethyl)phosphine Oxide to Alkylthiochloroacetylenes: Configuration and Conformation of Adducts


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Abstract—Alkylthiochloroacetylenes regio- and stereospecifically react with di(2-phenylethyl)phosphine oxide in dioxane at 20–22°C in the presence of potassium hydroxide to form 1-chloro-2-(alkylthio)vinyl[di(2-phenylethyl)]phosphine oxides in a 78–85% yield. According to IR and 1H and 31P NMR data, dielectrometric measurements, and quantum-chemical calculations, the obtained adducts have the Z configuration and exist mainly in the sp,sp conformation.

Organylthiochloroacetylenes react with secondary and tertiary phosphines following the nucleophilic substitution pattern to give alkylthioethynylphosphonium chlorides and products of their further transformations [1–3]. Here we report new data on the reactivity of (alkylthio)chloroacetylenes I and II toward P-containing nucleophiles with di(2-phenylethyl)phosphine oxide III as example. Compound III can be readily prepared from styrene and red phosphorus (or phosphine) [4, 5].

Acetylenes I and II react with secondary phosphine oxide III under mild conditions (room temperature, 5–8 h, dioxane). At the equimolar amounts of the reactants and potassium hydroxide, the reaction yields monoadducts. According to IR, 1H, and 31P NMR data, dielectrometric measurements, and quantum-chemical calculations, the products were identified as Z-1-chloro-2-(alkylthio)vinyl[di(2-phenylethyl)]phosphine oxides IV and V.

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\text{RSC\equiv\text{Cl} + \text{HPR}_2 \xrightarrow{\text{KOH}} \text{C=\text{C-Cl}} + \text{HPR}_2 \text{P=O}}
\]

\[
\text{I, II \rightarrow III \rightarrow IV, V}
\]

R = Et (I, IV), n-Pr (II, V); R’ = CH₂CH₂Ph.

The reaction does not occur in the absence of potassium hydroxide. Complete conversion of phosphine oxide III can be achieved in the presence of no less than 15 wt % of KOH relative to the starting reactants. Under these conditions the yield of IV and V reaches 78–85%. This fact agrees with the data that a considerable amount (15 wt %) of alkali metal hydroxide is required to effect the nucleophilic addition of secondary phosphine oxides to the multiple bond of electrophilic alkenes [6–8].

The IR spectra of IV and V contain the absorption bands of stretching vibrations of the C=C (1520 cm⁻¹), =C–H (3010, 3070 cm⁻¹), and P=O (1170 cm⁻¹) bonds [9]. Their 1H NMR spectra, along with the signals of the alkylthio group and aliphatic protons of substituents at phosphorus, contain the signal with \( \delta_p \) 7.15–7.25 ppm belonging to the multiplet of phenyl protons and overlapping with the signal of the ethenyl proton. 31P NMR spectra of the products obtained contain a single phosphorus signal at \( \delta_p \) 48–49 ppm, which proves that this reaction is regio- and stereoselective. Its regioselectivity agrees with the published data about the preferred addition of nucleophiles to organylthiochloroacetylenes at the C\(_{sp}\) atom bound to chlorine [10].

Theoretically compounds IV and V can have several rotamers originating from the internal rotation about the C–P and C–S bonds. The conformational isomerism of such molecules was studied with model regio- and stereoisomers VI–VIII as examples. Their formation is hypothetically possible in the course of nucleophilic addition of dimethylphosphine oxide.

1 For communication II, see [1].
to methylthiochloroacetylene. According to ab initio calculations (HF/6–31G*), only ten of the twelve theoretically probable forms of these compounds correspond to the energy minimum (Scheme 1).

The following designations were accepted: sp, syn-periplanar; ap, anti-periplanar; sc, syn-clinal; and ac, anti-clinal. For each conformer the first symbol characterizes the rotation about the C=S bond (\( \theta_1 \) angle), and the second, about the C=P bond (\( \theta_2 \) angle).

Their energy characteristics and also the dihedral angles \( \theta_1 \) and \( \theta_2 \) are presented in the table. These are the conformers of the Z and E isomers of 1-chloro-2-(methylthio)vinyl(dimethyl)phosphine oxide VIa–VId and VIIa–VIIId and the Z isomer of 2-chloro-1-(methylthio)vinyl(dimethyl)phosphine oxide VIIa and VIIb. Among the stable structures obtained we should note the two most stable geometric isomers VIa and VIIia separated from each other by an energy gap of 3 kcal mol\(^{-1}\). Z Isomer VI has two axes of internal rotation and therefore forms four rotamers, two of which are the most stable: VIa and VIIb (Scheme 1, table). Conformer VIa corresponds to the global energy minimum, which evidently determines the regioselectivity of the reaction. Its calculated geometric parameters (bond lengths, Å, and bond angles, deg) are given in Scheme 2. The maximal range of their variations in the series of structures under consideration is ~0.02 Å and ~6.0°, respectively. At the same time, the P=O bond length varies in the range 1.471–1.479(5) Å established for phosphine oxides by electron diffraction [11].

Rotamer VIa is characterized by the planar arrangement of all heavy atoms. The difference in the total energies of conformers VIa and VIIb is 3.9 kcal mol\(^{-1}\). The structure of the second conformer (sp, sp), as well as that of the first one (ap, sp), is planar with respect to the heavy atoms. This as a specific feature as compared to stable conformers of vinyl thioethers. For example, vinyl methyl sulfide has two conformers, the most stable sp, and the next one ac, with the dihedral angle of the CSC=C fragment within the range 90° < \( \varphi < 150° \) [12].

Ishmaeva [13] explained the relative stability of rotamers of \( \alpha \)-substituted vinylphosphonates from the viewpoint of electrostatic interactions and the preference of forms with the antiparallel direction of the C\( \text{sp}^2\)-Cl and P=O dipoles. Such a conclusion fully agrees with the relative stability of syn-periplanar conformers VIa, VIIb, VIIia, and VIIib (\( \theta_2 \approx 0° \)), and this trend does not break in the presence of the terminal SCP=O group in VIIia. At the same time, analysis of data for the anti forms (90° ≤ \( \theta_2 \) ≤ 180°) (see table)