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Abstract

Full Text

Chemistry

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ON THE CIS-, TRANS-CONFIGURATIONS OF PROPENYL COMPOUNDS OF $\mathrm{As^{III}}$, $\mathrm{Hg^{II}}$, AND $\mathrm{Sn^{IV}}$

(Presented by Academician A. N. Nesmeyanov, 14 IX 1964)

The present work is a continuation of investigations of the IR absorption spectra of cis-, trans-propenyl organometallic compounds ([1]).

The IR absorption spectra that we obtained for cis- and trans-tripropenylarsine are entirely analogous to the spectra of cis- and trans-tripropenylstibine. As before ([1]), the differences in the spectra of the cis- and trans-configurations pertain to the regions of out-of-plane (920–970 $\mathrm{cm^{-1}}$) and in-plane (1200–1300 $\mathrm{cm^{-1}}$) C—H vibrations. The difference in the spectra of the cis- and trans-configurations is reduced not so much to a difference in the vibration frequencies as to a difference in the intensity ratios of a number of C—H absorption bands.

Fig. 1. IR absorption spectra of the stereoisomers cis- and trans-tripropenylarsine. (Recorded on an IKS-14 in cells with the same layer thickness.) From the spectrum of the cis derivative it is evident that it contains an impurity of the trans stereoisomer.

For trans-tripropenylarsine, the absorption band at 970 $\mathrm{cm^{-1}}$ is considerably more intense than the 922 $\mathrm{cm^{-1}}$ band for the cis isomer.

Again, the absorption band of the in-plane deformation C—H vibration at 1200 $\mathrm{cm^{-1}}$ for the cis compound is less intense than for the trans isomer. For the bands in the region of ~ 1300 $\mathrm{cm^{-1}}$, the opposite picture is observed: the band at 1328 $\mathrm{cm^{-1}}$ is more intense for cis-tripropenylarsine (see Fig. 1).

Table 1

Vibrational frequencies of stereoisomers of tripropenylarsine
(recording range 680–1800 $\mathrm{cm^{-1}}$)

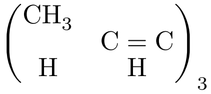
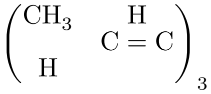
Configuration / compound	Constants	Frequencies
 $\left(\begin{array}{ccc} CH_3 & & \\ & C=C & \\ H & & H \end{array}\right)_3$ Ascis	b.p. 87-88°/18 mm; n_D^{20} 1.5257	ν, cm^{-1} : 687, 747, 922, 970 (trans), 1004, 1040, 1065 (?), 1130, 1210, 1328, 1380, 1440, 1610, 1680
 $\left(\begin{array}{ccc} CH_3 & & H \\ & C=C & \\ H & & \end{array}\right)_3$ Astrans	b.p. 72°/6 mm; n_D^{20} 1.5209	ν, cm^{-1} : 680 (?), 710, 752, 940 (?), 970, 1040, 1070, 1212, 1310, 1334, 1383, 1445, 1620, 1690, 1750

Table 2

Vibrational frequencies of propenyl compounds of Hg^{II}
(recording range 600-1800 cm^{-1})

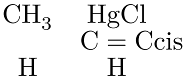
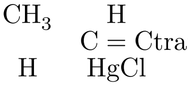
Configuration / compound	Constants and frequencies
 $\begin{array}{ccc} CH_3 & & HgCl \\ & C=C & \\ H & & H \end{array}$cis	m.p. 65.0-65.5°; ν, cm^{-1} : 665, 925, 945, 967 (trans), 1045, 1195, 1315, 1385, 1440, 1615
 $\begin{array}{ccc} CH_3 & & H \\ & C=C & \\ H & & HgCl \end{array}$trans	m.p. 124-125°; ν, cm^{-1} : 662, 710, 943, 970, 1037, 1063, 1082, 1120, 1208, 1307, 1328, 1372, 1440, 1608, 1680, 1750

Table 3

Vibrational frequencies of propenyl compounds of Sn^{IV}
(recording range 680-1700 cm^{-1})

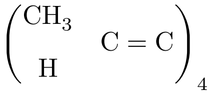
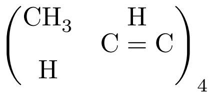
Configuration / compound	Constants	Frequencies
 $\left(\begin{array}{ccc} CH_3 & & \\ & C=C & \\ H & & \end{array}\right)_4$ Sncis	b.p. 91°/4 mm, n_D^{20} 1.5205	ν, cm^{-1} : 920, 980 (trans), 1040, 1208, 1335, 1382, 1450, 1614

Figure 2: IR absorption spectra of cis- and trans-propenylmercury chloride. The spectra were recorded on a UR-10 IR spectrophotometer; the substances were recorded in pellets after pressing with potassium bromide.

Figure 2: Figure 2: IR absorption spectra of cis- and trans-propenylmercury chloride. The spectra were recorded on a UR-10 IR spectrophotometer; the substances were recorded in pellets after pressing with potassium bromide.

Figure 3: IR absorption spectra of cis- and trans-tetrapropenyltin. Recorded on a VIKS M-3 IR spectrophotometer. From the spectrum of the cis derivative it is evident that it contains an admixture of the trans stereoisomer.

Figure 3: Figure 3: IR absorption spectra of cis- and trans-tetrapropenyltin. Recorded on a VIKS M-3 IR spectrophotometer. From the spectrum of the cis derivative it is evident that it contains an admixture of the trans stereoisomer.

Configuration / compound	Constants	Frequencies
 $\left(\begin{matrix} CH_3 & & H \\ & C=C & \\ H & & \end{matrix}\right)_4$ Sntrans	b.p. 84°/1 mm, n_D^{20} 1.5110	ν, cm^{-1} : 712, 934, 980, 1042, 1057, 1207, 1327, 1376, 1450, 1612

In the region of deformation vibrations of the C–H bonds of the CH_3 group (1300–1450 cm^{-1}), no differences are observed in the spectra of the cis- and trans-derivatives of As.

The frequencies of the C=C vibrations for cis- and trans-tripropenylarsine are practically identical (see Table 1).

In studying the IR absorption spectra of cis- and trans-propenylmercury chloride, as well as cis- and trans-tetrapropenyltin, we again observe the same···

Fig. 2. IR absorption spectra of cis- and trans-propenylmercury chloride. Recorded on a UR-10 IR spectrophotometer; the substances were recorded in pellets after pressing with potassium bromide.

Fig. 3. IR absorption spectra of cis- and trans-tetrapropenyltin. (Recorded on a VIKS M-3 IR spectrophotometer.) From the spectrum of the cis derivative it is evident that it contains an admixture of the trans stereoisomer.

the same regularities (see Tables 2 and 3, Figs. 2 and 3) in the ratios of the frequencies and intensities of the absorption bands noted above.

Thus, a distinguishing feature of the IR absorption spectra of the cis and trans configurations of propenyl compounds of As^{III}, Hg^{II}, and Sn^{IV} is not a difference in the frequencies of the bands of the planar (1200–1300 cm^{-1}) and nonplanar

Fig. 4. Schematic representation of the IR absorption spectra of cis and trans stereoisomers of propenyl organometallic compounds. The shaded portions of the figure are the frequency regions in which C—H vibrations lie. The height of the shaded rectangles is the peak intensity of the C—H vibration bands, with the approximate intensity ratio within a spectrum (cis or trans derivative) and between the spectra of the cis and trans isomers observed.

Figure 4: Fig. 4. Schematic representation of the IR absorption spectra of cis and trans stereoisomers of propenyl organometallic compounds. The shaded portions of the figure are the frequency regions in which C—H vibrations lie. The height of the shaded rectangles is the peak intensity of the C—H vibration bands, with the approximate intensity ratio within a spectrum (cis or trans derivative) and between the spectra of the cis and trans isomers observed.

(920-970 cm^{-1}) C—H vibrations of the cis and trans derivatives, but rather a difference in the intensities of the bands of these vibrations.

Summarizing the present work and earlier results ([1]), the following may be noted. Assignment of the geometrical configuration of cis and trans stereoisomers of propenyl compounds of $\mathrm{Sb}^{\mathrm{III}}$, Sb^{V}, $\mathrm{As}^{\mathrm{III}}$, $\mathrm{Hg}^{\mathrm{II}}$, $\mathrm{Sn}^{\mathrm{IV}}$, as well as of a number of other metals (As^{V}, $\mathrm{Bi}^{\mathrm{III}}$, Bi^{V}), from IR absorption spectra is quite possible.

The main difference in the spectra of the cis and trans derivatives should be sought in the difference in the intensities of the absorption bands corresponding to C—H vibrations.

The IR absorption spectra of the cis derivatives of the elements noted by us are similar to one another. The pattern of the IR absorption spectra of the cis derivatives can, in general form, be represented as follows (see Fig. 4). The same applies to the trans derivatives. Figure 4 also gives a schematic pattern of the IR absorption spectra of the trans derivatives.

Fig. 4. Schematic representation of the IR absorption spectra of cis and trans stereoisomers of propenyl organometallic compounds. The shaded portions of the figure are the frequency regions in which C—H vibrations lie. The height of the shaded rectangles is the peak intensity of the C—H vibration bands, with the approximate intensity ratio within a spectrum (cis or trans derivative) and between the spectra of the cis and trans isomers observed.

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Note: Figure translations are in progress. See original paper for figures.