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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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Infrared Absorption Spectra of Organometallic Compounds of the Ethylene Series

On the cis- and trans-configurations of propenylantimony compounds

(Sb^{III} and Sb^{V})

(Presented by Academician I. V. Obreimov, July 18, 1960)

The present communication is devoted to an investigation of the infrared absorption spectra of the cis- and trans-isomers of propenyl compounds of trivalent and pentavalent antimony. The synthesis of these substances has been described(1). As far as we know from the literature, there are no special studies of cis- and trans-isomerism in organometallic compounds by means of infrared absorption spectra.

In the present work we discuss the results of studying the i.r. absorption spectra of the above-mentioned compounds. A number of communications(2,3) indicate the possibility of identifying cis- and trans-isomers in organic compounds by i.r. absorption bands at 690 cm^{-1} (for cis-) and 960-970 cm^{-1} for trans-configurations; these data apply mainly to disubstituted hydrocarbons of the ethylene series, of the type $R_1 - CH = CH - R_2$ (cis- and trans-).

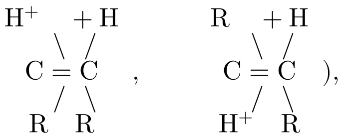
The distinction between configurations according to these works is based in most cases on the presence of a 970 cm^{-1} band in the trans- and its absence in the cis-configurations. We note at once that the calculations of work(4) show a small difference in the frequencies of the absorption bands of out-of-plane vibrations of CH groups for

Fig. 1

double bond (the interval 965-980 cm^{-1} is given for both cis- and trans-configurations, the type of vibrations

Fig. 2

Figure 2: Fig. 2



the authors of that work used experimental data (⁵), from which it is also evident that, for cis- and trans-configurations, the frequencies of the absorption bands associated with out-of-plane vibrations of CH bonds in disubstituted butenes differ very little in practice.

It follows from what has been said that in a number of cases, relying only on the above-mentioned criteria, it is impossible to give a completely unambiguous answer concerning the type of geometrical configuration; and the interpretation of the results obtained with respect to cis-, trans-configurations must be treated with extreme caution.

The infrared absorption spectra were recorded by us on a two-beam IR spectrometer based on the VIKS M-3 spectrometer with a NaCl prism (700–1800 cm^{-1}) and on a single-beam IKS-12 spectrometer with a KBr prism (400–700 cm^{-1}). Liquid substances were recorded in cells of constant thickness (0.016 mm with KBr windows and 0.050 mm with NaCl windows). Solid compounds were pressed with KBr.

Fig. 2

The assignment of the configurations of the stereoisomers under discussion was made by comparing the infrared absorption spectra (⁶) and on the basis of the regularity, previously established by us together with A. N. Nesmeyanov on extensive material, concerning the non-inversion of the configuration of cis-trans ethylene isomers in reactions of electrophilic and homolytic exchange (¹,⁷,⁸). In all the propenyl antimony compounds investigated by us (Sb^{III} and Sb^{V}), a fairly appreciable difference is seen between the cis- and trans-configurations in their infrared absorption spectra (Figs. 1 and 2, Table 1).

For all compounds with trans-configurations (trans arrangement of hydrogens with respect to the double bond), the presence of intense absorption bands in the region 945–970 cm^{-1} is characteristic. If for tri- and pentapropenylantimony the frequency of the out-of-plane vibrations of the CH groups lies at 971 cm^{-1}, then for

halogen derivatives, namely: for dichloro-, dibromo-, and diiodotripropenylantimony the frequency decreases regularly to 945 cm^{-1}; for bromotetrapropenylstibonium the frequency lies in the range 967 cm^{-1} (see Table 1).

Fig. 3. Infrared absorption spectra of cis- and trans-bromopropene. Axes: absorption (%) vs. ν, cm^{-1}.

Figure 3: Fig. 3. Infrared absorption spectra of cis- and trans-bromopropene. Axes: absorption (%) vs. ν, cm^{-1}.

Table 1

Frequencies of propenyl compounds of Sb^{III} and Sb^{V}

$(CH_3CH=CH)_3\cdot$Sbcis-, b.p. 70°/4-5 mm	$(CH_3CH=CH)_3$Sbtrans-, b.p. 82°/5 mm	$(CH_3CH=CH)_3\cdot$SbCl$_2$cis-, m.p. 74-75°	$(CH_3CH=CH)_3$SbCl$_2$trans-, b.p. 160-162°/4 mm	$(CH_3CH=CH)_3\cdot$SbBr$_2$cis-, m.p. 85-86°	$(CH_3CH=CH)_3$SbBr$_2$trans-, b.p. 166-167°/4 mm	$(CH_3CH=CH)_3\cdot$SbJ$_2$cis-, m.p. 122-123°	$(CH_3CH=CH)_3\cdot$SbJ$_2$trans-	$(CH_3CH=CH)_4\cdot$SbBrcis-, m.p. 140-143°	$(CH_3CH=CH)_4\cdot$SbBrtrans-, m.p. 45-48°	$(CH_3CH=CH)_5$Sbcis-, b.p.	$(CH_3CH=CH)_5$Sbtrans, b.p.
1600	1600	1606	1607	1604	1605	1600	1598	1600	1600	1600	1600
1438	1442	1446	1440	1443	1440	1425	1437	1445	1432	1440	1437
1378	1377	1385	1376	1382	1377	1378	1375	1380	1367	1380	1375
1320	1320	1308	1306	1305	1306	1297	1302	1305	1304	1321	1308
1193	1199	1201	1191	1199	1190	1196	1185	1195	1225	1200	1190
1115	1115	–	1109	–	1105	1100	1105	1109	1185	1115	1110
–	1060	1047	1075	1045	1075	–	1065	1048	1062	–	1062
1039	1040	–	1042	–	1041	1040	1039	–	1043	1035	1040
970	971	940	957	939	951	937	945	960	967	970	971
920	935	928	–	925	–	925	–	924	945	920	938
710	720	665	724	–	722	–	718	700	726	–	722
660	655	625	667	663	655	660	660	660	663	660	662
–	610	455	620	818	620	610	615	635	625	–	600
–	–	–	–	452	–	452	–	452	–	–	–

Another essential indication of the trans configuration of the compounds we investigated is the presence in their infrared spectra of absorption bands at 718-726 cm^{-1} (Table 1, Figs. 1 and 2), whereas for the cis configurations these bands are absent.

Fig. 3

For the cis configurations of the compounds investigated, the infrared spectra contain absorption bands at about 920-940 cm^{-1}, of significantly lower intensity than the absorption bands for the trans configurations at 945-970 cm^{-1}. Only cis-tripropenylantimony and cis-pentapropenylantimony have out-of-plane CH-vibration frequencies close to the value for the trans form (970 cm^{-1}), but the intensity of this band in the cis form (estimated from band areas) is approximately three times lower than in the trans configuration. The same picture is observed for propenyl bromide (cis and trans) (see Table 2, Fig. 3): here, for the cis configuration, the intensity of the band at 930 cm^{-1} is also lower than in the trans form, by approximately a factor of three.

For both cis and trans compounds, the infrared spectra contain absorption bands at 655-660 cm^{-1}; for the cis form the intensity of these bands is 2—

2.5 times greater than for the trans- (estimated from the example of tripropenylstibine and the bromide of cis- and trans-propenyl). Among the low-frequency bands one should note the rather intense bands at 452 cm^{-1}, which appear in the IR spectra of the cis compounds of dichloro-, dibromo-, diiodotripropenyl- and bromotetrapropenylstibonium; for the analogous trans compounds there are no absorption bands at 452 cm^{-1}. These bands are also absent both in cis- and in trans-tri- and pentapropenylstibine.

Table 2

Frequencies of propenyl bromide

Cis-, b.p. 57.5–58°	Trans-, b.p. 63.5°	Cis-, b.p. 57.5–58°	Trans-, b.p. 63.5°
1625	1650	1102	1100
	1610	1050	1085
1587	1583	1030	1055
1448	1440	931	1035
1392	1386		930
1305	1299		722
1212		674	675

As for the absorption bands caused by out-of-plane* vibrations of the CH groups at the double bond (1200-1300 cm^{-1}), they are practically indistinguishable in frequency, but between the pairs of bands 1) 1200 cm^{-1} and 2) 1300 cm^{-1} in the cis and trans compounds a different ratio of intensities is observed (intensity at the band maximum).

If for the trans isomers the intensities of the absorption bands at 1300 cm^{-1} are less than at 1200 cm^{-1}, then for the cis compounds, conversely, the absorption bands at 1200 cm^{-1} are less intense than those at 1300 cm^{-1} in the cis. In the region of deformation vibrations of the carbon—hydrogen bonds (1380-1450 cm^{-1}) no substantial differences are observed. The frequency of the double bonds is practically identical for the cis and trans isomers; the absorption bands have approximately the same intensity.

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* Vibrations without displacement out of the plane of the C=C bond.

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

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