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SYNTHESIS OF CONJUGATED DIENES FROM π-ALLYLIC COMPLEXES OF PALLADIUM (II) CHLORIDE AND OLEFINS.

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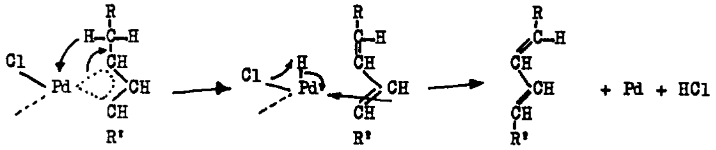
It is known (1,2) that olefins react with palladium (II) chloride at temperatures between 80°C and 100°C, to give π-allylic complexes as follows:

$$2\ C_nH_{2n} + 2\ PdCl_2 \rightleftarrows (C_nH_{2n}PdCl_2)_2 \underset{+HCl}{\overset{-HCl}{\rightleftarrows}} (C_nH_{2n-1}PdCl)_2$$

We have now found that, when π-allylic complexes of olefins C_nH_{2n} with $n \geqslant 4$ are heated without solvents under high vacuum, conjugated dienes are obtained.

The reaction mechanism is possibly as follows:



As an example, we report here the results obtained with π-allylic-2-octenyl-palladium (II) chloride.

When this compound is heated to 160°C and 10^{-2} mm Hg, metallic palladium, hydrogen chloride and a distillate, which is a mixture of unsaturated hydrocarbons, are obtained in almost quantitative yields.

The average molecular weight of this distillate is 112 (osmometric; calc. for C_8H_{14}: 110); the U.V. absorption spetrum shows a band at 228 mμ ($\lg \varepsilon = 4.205$) as expected for symmetric di-alkyl-substituted conjugated dienes.

The I.R. spectrum shows absorption bands at:

1605 cm^{-1} which can be assigned to $\nu_{C=C}$ of conjugated double bonds;
1660 cm^{-1} " " " " " $\nu_{C=C}$ for cis-isomers;
987 cm^{-1} " " " " " δ_{C-H} for trans-conjug.-isomers;
965 cm^{-1} " " " " " δ_{C-H} for trans-isomers;
895 cm^{-1} " " " " " δ_{C-H} for vinyl-conjug.-isomers;
708 cm^{-1} " " " " " δ_{C-H} for cis-isomers;

and a ratio methyl/methylene groups about 1.3.

Gas-chromatography analysis (Squalane on Chromosorb W, 2m, Ø 4 mm, 140°C, Perkin-Elmer 116 E) shows three peaks: one, in lower percentage, corresponds to trans-cis-2-octene, the other two, which are predominant, are in the ratio 2:1 and are to be attributed to 2-4 and 1-3 dienic hydrocarbons.

A sample of 2.6 mg of this mixture absorbs 9.64 cm^3 (N.T.P.) of H_2 on 5% palladium-on-charcoal: this corresponds to a composition of about 12% mono-olefinic C_8-hydrocarbons and 88% of dienic ones.

As revealed by I.R. spectra, these dienes are a mixture of cis-trans isomers, in which the trans-isomers prevail.

We find that this cis-trans ratio for the present dienes depends on the experimental conditions of thermal decomposition.

Generally, quantitative yields are obtained when the reaction is carried out in high vacuum with immediate removal of the hydrocarbons, whereas at one nitrogen atm, the reaction course is the same, but some polymerization occurs most likely by a cationic mechanism.

REFERENCES

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