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The Stereochemistry of Hydrogenation with Tris(triphenylphosphine)chlororhodium

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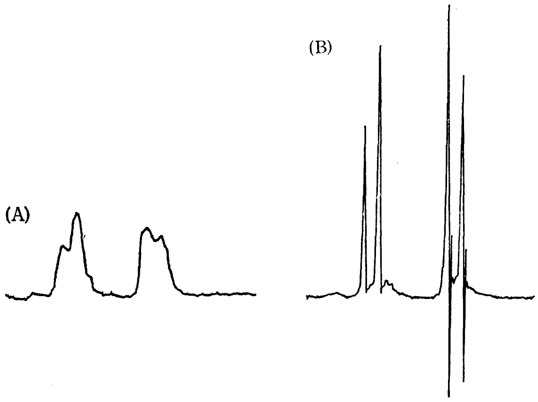
Wilkinson and his co-workers have shown that tris(triphenylphosphine)chlororhodium is an efficient catalyst for the hydrogenation of alkenes and alkynes.[1] The stereochemistry of the addition of hydrogen to the olefinic bond has been investigated only by Wilkinson and his co-workers[1] and by Birch and Walker.[2] Wilkinson and his co-workers confirmed, by a study of the IR spectrum, that the deuteration of maleic acid proceeded to give mainly *meso*-1,2-dideuterosuccinic acid; this means that the hydrogenation occurs with the *cis* addition of hydrogen to the double bond. Birch and Walker found that the deuteration of 22-dihydroergosteryl acetate occurred in a *cis* fashion.

In order to obtain further evidence on the stereochemistry of the addition of hydrogen, several olefinic compounds were deuterated and the steric configuration of the products were examined by the NMR procedure. The following olefins were used as substrates; *trans*-benzalacetophenone, *trans*-benzalpinacolone, methyl *trans*-cinnamate, *trans*-crotononitrile, and *trans*-cinnamonitrile. Deuteration was performed in benzene at an ordinary pressure and temperature. The products were separated from the complex catalyst by alumina chromatography and were subjected to NMR.

TABLE 1. CHEMICAL SHIFT AND COUPLING CONSTANT OF DEUTERATION PRODUCTS WITH $RhCl(PPh_3)_3$

trans-Olefin	d_2-Product	–CHD–CHD– δ (ppm)	–CHD–CHD– J (Hz)
Methyl Cinnamate	Methyl β-Phenylpropionate	2.55 2.93	5.46
Benzalacetophenone	Diphenylpropanone	3.04 3.17	4.86
Benzalpinacolone	Dimethylphenylpentanone	2.67 2.79	5.11
Cinnamonitrile	Phenylpropionitrile	2.33 2.71	6.60
Crotononitrile	Butyronitrile	1.57 2.24	6.56

The NMR spectrum of methyl β-phenylpropionate-d_2, the reduction product from methyl *trans*-cinnamate, showed that its ethylene moiety resonated at δ: 2.55 and 2.93 as a broad doublet. The vicinal coupling constant, J_{HH}, was approximately 6.5 Hz. In order to confirm the coupling constant, the double resonance of the deuterium atom was performed. The spectrum of –CHD–CHD– obtained was a sharp AB-type doublet whose coupling constant was 5.46 Hz. The spectra were shown in Fig. 1. In the NMR spectrum of phenylpropionitrile-d_2 from *trans*-cinnamonitrile, the signal of the ethylene moiety appeared at δ: 2.33 and 2.71; in shape it was a broad doublet, and their vicinal coupling constant was 6.60 Hz.



(A) Undecoupled Spectrum (B) Deuterium Decoupled Spectrum

Fig. 1. The NMR spectra of ethylene part of methyl β-phenylpropionate-d_2.

In spite of our expectation that the spectra of the ethylene parts of diphenylpropanone-d_2, the reduction product from *trans*-benzalacetophenone, and of dimethylphenylpentanone-d_2, from *trans*-benzalpinacolone, being an AB-type signal, the former compound showed the signal at around δ: 3.00, and the latter, at around 2.75 as a multiplet. In order to examine these spectra in detail, the double resonance of the deuterium atoms of these compounds was performed. As a consequence,

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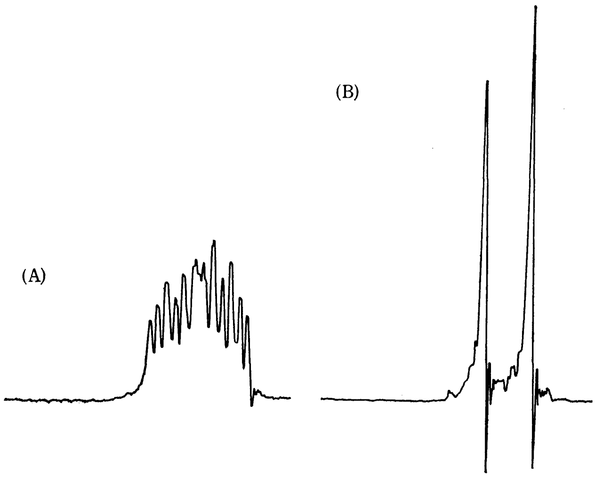
[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, **1966**, 1711; F. H. Jardine, J. A. Osborn, and G. Wilkinson, *ibid., A*, **1967**, 1574.

[2] A. J. Birch and K. A. M. Walker, *Tetrahedron Lett.*, **1966**, 4939.

we obtained the coupling constants of these AB-type signals as 4.86 Hz in diphenylpropanone-d_2 and 5.11 Hz in dimethylphenylpentanone-d_2 accompanying the unidentified peaks.

The deuterium decoupling of the complicated spectra of butyronitrile-d_2 obtained from *trans*-crotononitrile showed signals which were a sharp doublet at δ: 2.24 and an A_3B-type octet at 1.57. The coupling constant of the signal at δ: 2.24, which corresponds to the methine proton, α to the cyano group, was 6.56 Hz. The spectra are shown in Fig. 2.



(A) Undecoupled spectrum (B) Deuterium decoupled spectrum

Fig. 2. The NMR spectra of methylene proton α to the cyano group of butyronitrile

The NMR spectra of methyl β-phenylpropionate-d_2 and phenylpropionitrile-d_2 were also measured at low and high temperatures. When the temperature was decreased to −55, −70, −80, and −90°C, the spectra showed no significant change in the shape of the signals as the coupling constant of the protons of the ethylene moiety. On the other hand, when the spectra of methyl β-phenylpropionate-d_2 were measured at a high temperature, those signals became broad at 100°C, but again became sharp at 150°C. In this case, no significant change in the coupling constant of the methylene protons of the ethylene moiety was observed.

Jackmann reported[3] that the vicinal coupling constants of the *erythro* and the *threo* isomers of *p*-methoxycinnamic acid dibromides were found to be 11.6 and 9.9 Hz respectively. He also reported that in a typical case it could perhaps be assumed that the J_{AB} in the *erythro* isomer is essentially in the range above 10 Hz, while that in the *threo* isomer is essentially in the range below 5 Hz.

Whitesides and his co-workers[4] confirmed, from a measurement study of dimethylbutane derivatives, that J_{trans} is normally 10—14 Hz and that J_{gauche} is 4—6 Hz.

When the spectra of methyl β-phenylpropionate-d_2 were measured at several points of the temperature, the width of the signal of the ethylene protons showed a temperature dependence at high temperatures. The signal became broader at 100°C than at room temperature. A further increase of the temperature made the signal sharp. This fact shows that the compounds used in the present study seem to take a fixed conformation at room temperature. As the temperature is elevated, a restricted rotation around the carbon-carbon single bond may occur; a high rate of interconversion is inferred at 150°C.

These results show that all of the diastereoisomers of open-chain compounds which were obtained in the present study by deuteration with tris(triphenylphosphine)chlororhodium may be assumed to be *threo* isomers. Therefore, deuteration occurs to the olefinic double bond in a *cis* fashion, supporting the results of Wilkinson and his co-workers and of Birch and Walker.

Experimental

Materials. The methyl *trans*-cinnamate was prepared from commercial *trans*-cinnamic acid by esterification. The *trans*-benzalacetophenone was prepared by the Claisen-Schmidt condensation of benzaldehyde and acetophenone with a 1.7 mol solution of sodium hydroxide in aqueous ethanol.[5] The *trans*-benzalpinacolone was obtained from benzaldehyde and pinacolone as the above unsaturated ketone.[6] The *trans*-crotononitrile was separated from commercial isomeric mixture by preparative gas chromatography. The *trans*-cinnamonitrile was prepared by the dehydration of cinnamaldoxime in boiling acetic anhydride.[7] All the olefinic compounds agreed in physical constants with the samples earlier prepared and were checked by studying their NMR and IR spectra.

Hydrogenation. In a typical experiment, a 80 mg portion of tris(triphenylphosphine)chlororhodium in 5.0 m*l* of benzene was presaturated with deuterium for 2 hr, and then the substrate (0.01 mol) in 5.0 m*l* of benzene was added, through a side-arm entry port, to the reaction flask. After the reaction flask had been stirred for 24 hr, the complex catalyst was removed by alumina-column chromatography and the solvent was distilled off.

NMR Spectra. The NMR spectra were measured with a JNM-C-60HL apparatus at 60 MHz and a JNM-PS-100 apparatus at 100 MHz. Simultaneous decoupling was accomplished at 14.349152 MHz using JNM-PS-100. The samples were examined at approximately 20% (w/v) in CCl_4. TMS was used as the internal standard. The low-temperature NMR was measured at approximately 5% (w/v) in CS_2 while at high temperatures the samples were in a neat condition.

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[3] L. M. Jackmann and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed., Pergamon Press, Oxford, London (1969), p. 291.

[4] G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, **89**, 1135 (1967).

[5] E. P. Kohler and H. M. Chadwell, "Org. Syntheses," Coll. Vol. I, (1941) p. 71.

[6] G. A. Hill and G. M. Braumann, *ibid.*, Coll. Vol. I, (1941) p. 74.

[7] E. Pozner, *Ann. Chem.*, **389**, 117 (1912).