Tetrahedron Letters No.16, pp. 1919-1923, 1968. Pergamon Press. Printed in Great Britain.

ORGANOMETALLIC STUDIES, XXIV. (1). SELECTIVE HYDROGENATION OF CONJUGATED OLEFINS CATALYZED BY ARENE CHROMIUM TRICARBONYL COMPLEXES.

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(Received in UK 2 January 1968)

The current interest in homogeneous catalysis (3) prompts us to report some preliminary results on the remarkable effectiveness of arenechromium tricarbonyl complexes as catalysts in the selective hydrogenation of conjugated olefins.

Methyl sorbate (methyl 2,4-hexadienoate) was chosen as substrate in the reduction studies because the resulting hydrogenation products can be readily determined by gas chromatography (4). The data collected in Table 1 show that methyl 3-hexenoate is the major reduction product (5) and it is obtained in conversion yields as high as 99%. It is of interest to note that the reduction of sorbic acid with $Co(CN)_6^{-3}$ has been reported (6) to yield mainly 2-hexenoic acid and the reduction of methyl sorbate catalyzed by iron carbonyl complexes (4) yields a mixture of methyl 2-, 3- and 4- hexenoate as well as methyl hexanoate.

The high selectivity of the arenechromium tricarbonyl complexes in these hydrogenation reactions does not appear to be greatly affected by variation of the arene moiety. On the other hand, as shown in Table 1, the rate of hydrogenation is enhanced by the presence of electron withdrawing substituents in the benzene moiety of the complexes. Similarly the cyclohepta-

Table 1

Hydrogenation[a] of Methyl Sorbate with Arene $Cr(CO)_3$ Catalysts[b].

No.	Arene Ligand in Catalyst	Reaction time hr	Product Composition[c] Methyl Sorbate	Methyl 3-Hexenoate	Methyl 2-Hexenoate	Methyl Hexanoate
1.	Benzene[d]	8	0.4	93.9	3.6	2.1
1a.	Benzene[d,e]	0.5	0.0	91.8	3.1	5.1
2.	Toluene	7	0.0	93.6	5.3	1.1
3.	Ethylbenzene	7	4.8	90.1	5.1	0.0
4.	Anisole	6	88.4	11.6	0.0	0.0
4a.	Anisole[f]	6	11.6	85.0	3.4	0.0
5.	Methyl benzoate	2	0.0	98.9	0.1	1.1
6.	Chlorobenzene	2	0.0	95.7	0.1	4.3
7.	1,4-Diphenylbutadiene	2	0.0	95.3	1.8	2.9
8.	3-Carbomethoxyanisole	1	0.9	96.0	2.2	0.9
9.	Cycloheptatriene	0[g]	0.0	87.8	2.9	9.3

[a] Hydrogenations were carried out in a Magne Stir autoclave (300 ml) with glass insert, fitted with a valve system for collecting reaction samples. [b] Unless otherwise stated, the reaction conditions were 19mM methyl sorbate and 1mM of catalyst in 90ml. cyclohexane at 150° temperature and 700 psi pressure. [c] Analysis by gas-liquid chromatography with a glass column (72x0.25 in.) packed with Chromosorb W coated with 15% diethylene glycol succinate, at 85°, a nitrogen flow of 45 ml per min., on a Packard Model 871 instrument provided with a hydrogen flame detector and integrator. [d] The reaction temperature was 165°. [e] The reaction solvent was methylene chloride. [f] The reaction solvent was acetone. [g] The zero-time sample was collected as soon as reaction temperature was attained (approximately 15 min after charging the autoclave).

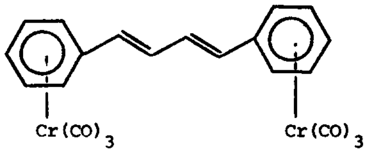
triene ligand (7) appears to be more effective than the benzene ligand.

Polarity of the solvent (8) seems to have a strong effect on the efficacity of the catalyst; as shown for the pairs of experiments 1, 1a and 4, 4a in Table 1.

Rate curves for the hydrogenation reaction, using the more active catalysts such as chlorobenzenechromium tricarbonyl, show that the disappearance of methylsorbate and the appearance of methyl 3-hexenoate approach a reciprocal relationship. The relatively less active catalysts, such as benzenechromium tricarbonyl, in cyclohexane as solvent, show an induction period after which the rate curves exhibit the same type of reciprocal relationship as mentioned above.

It is important to note that hydrogenation takes place without decomposition of the arenechromium tricarbonyl complexes. Infrared analyses showed that the concentration of these complexes remained essentially constant during the reaction.(7)

Of particular interest is the result that the presence of two $Cr(CO)_3$ moieties per molecule of complex greatly improves the efficiency of the catalyst. Thus, with catalytic amounts (0.25 mmoles) of complexes such as I (9) and II (10) we obtained methyl 3-hexenoate in conversion yields of 99%, and better, in about 15 min., the time needed to bring the autoclave conditions to 160° and 700 psi. With compound II as catalyst and much milder reaction conditions (115° and 70 psi) it took less than 30 minutes to obtain methyl 3-hexenoate in a conversion yield of 99%.



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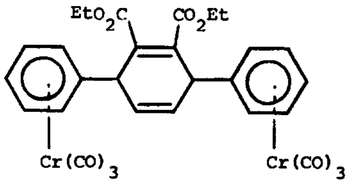

II

The catalytic activity of arene $Cr(CO)_3$ complexes was also tested on dienoic and trienoic fatty acid esters. With a mixture of dienoic fatty acid esters derived from dehydrated methyl ricinolate (11) the conjugated dienes (12) (71%) were completely reduced (13) to monoene (14). The non-conjugated dienes (24%) in the mixture were unaffected.

The major product (71%) from the catalytic hydrogenation [methyl benzoate-$Cr(CO)_3$ catalyst] of methyl β-eleostearate (methyl 9 _trans_, 11 _trans_, 13 _trans_ - octadecatrienoate) consisted of unconjugated dienes (approximately equal amounts of the 9,12 - and 10,13 - isomers),(17). The same catalytic reduction, with similar results, has been carried out directly on tung oil. This may provide a method for changing the structure of what is principally a paint oil into a mixture of the constituents normally found in edible oils.

We believe that the high selectivity of arenemetal carbonyl complexes in homogeneous catalysis should prove useful in the reduction of various types of conjugated olefins. The further scope of this reaction and its mechanism is currently under investigation.

This work has been supported in part by a P.L. 480 grant, U.S.D.A. Project UR-A10-(40)-34.

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(4) E.N. Frankel, N. Maoz, A. Rejoan and M. Cais, Abstracts of 3rd International Symposium on Organometallic Chemistry, Munich, Germany, Aug.29 - Sep.1, 1967.

(5) The analysis of the products was carried out by glc [A.F. Mabrouk, H.J. Dutton and J.C. Cowan, _J. Amer. Oil Chem. Soc._, _41_, 153 (1964)],

ir and nmr and a comparison with authentic samples. We wish to thank the U.S.D.A., Northern Regional Research Laboratory, Peoria, Illinois for a supply of authentic methyl 2-,3- and 4- hexenoates.

(6) B. De Vries, *J. Catalysis*, *1*, 489 (1962).

(7) The concentration of cycloheptatrienechromium tricarbonyl was rapidly decreased at 120° and 700 psi. Similarly, the molybdenum analog, which also proved active as a homogeneous catalyst, appeared to be even more readily decomposed during reduction.

(8) In benzene solution only 3% reduction of methyl sorbate occurred with 5 mole percent $C_6H_6Cr(CO)_3$ after 4 hrs at 175° and 700 psi. Raising the temperature to 187–189° for another 3 hrs resulted in only 11% conversion of methyl sorbate into methyl 3-hexenoate. It is possible that ligand exchange between the catalyst complex and the solvent interferes with hydrogenation of the substrate.

(9) M. Cais and M. Feldkimel, *Tetrahedron Letters*, *13*, 444 (1961).

(10) M. Cais and N. Narkis, unpublished results.

(11) We wish to thank Victor Wolf company, Manchester, England for a gift sample.

(12) The conjugated diene in the starting material is mainly methyl *cis* 9 - *trans* 11 - octadecadienoate.

(13) Reaction conditions: 19 mmoles dienes + 1 mmole $C_6H_6Cr(CO)_3$ in 90 ml cyclohexane at 175° and 700 psi.

(14) The products (15) consist mainly of a mixture of methyl 9 - *cis* and 10 - *cis* octadecenoate. This result seems to indicate a stereoselective reduction of the 11-12 *trans* double bond in the starting conjugated diene (12).

(15) The hydrogenated products were fractionated by reverse phase chromatography through a rubber column. The diene and monoene fractions were then analyzed by glc, ir and ozonolysis to determine location of double bond (16). We thank V.L. Davison and R.L. Hoffman (Northern Regional Research Laboratory) for their assistance with these analyses.

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(17) The other products: 18.5% monoene (principally the 10- and 12- isomers), 7.5% conjugated dienes and 3.0% trienes (in which two double bonds are conjugated and one is isolated).