Heterogenized Homogeneous Catalysts. Hydrogenation of Methyl Sorbate by Polystyrene-Anchored Tricarbonylchromium

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The reaction of a swollen 1% divinylbenzene cross-linked polystyrene with hexacarbonylchromium gave polymer-anchored tricarbonylchromium moieties bonded to the polymer's phenyl rings. Using this heterogenized catalyst, methyl sorbate was converted selectively (96-97%) to (Z)-methyl 3-hexenoate with small amounts of methyl hexanoate and (E)-methyl 2-hexenoate in cyclohexane at 160°C and 500 psi of hydrogen. The product distribution was sensitive to solvent and reaction temperature. No significant hydrogenation of cyclohexene or (E,E,E)-1,5,9-cyclododecatriene occurred at 150°C and 500 psi of hydrogen in 24 hr. This heterogenized homogeneous catalyst system is discussed in relation to known homogeneous hydrogenation catalysts for methyl sorbate.

The anchoring of homogeneous catalysts to polymeric supports has recently attracted increased attention. Such “heterogenized” homogeneous catalysts can exhibit the unique selectivity and reactivity of their homogeneous counterparts while also increasing the ease of separation from the products and facilitating the recycling of the catalysts. However, diffusion into polymer gels can also be a problem. For example, (E)-3-methyl 2,4-hexadienoate as well as methyl hexanoate. No as-

(22) In principal path b could give solvent capture products (e.g., 2-bicyclo-[7.1.0]dec-7-yl-acylate) but none were observed.
(26) We thank the University of Oregon for the use of this instrument.
(27) We thank S. Winston for providing experimental details for the preparation of 1,4,7-cyclononatriene.
(32) Glc analysis before reduction showed essentially the same ratio of ester to hydrocarbon as the alcohol to ester ratio after reduction.
(33) For comparison, the nmr spectrum of bicyclo[3.1.0]hex-2-ene follows: Glc analysis before reduction showed essentially the same ratio of ester to hydrocarbon as the alcohol to ester ratio after reduction.
(34) J. L. Boop, unpublished results in this laboratory.
(35) Other catalysts also give this rearrangement as will be reported more fully in a further paper.
(36) J. L. Boop, unpublished results in this laboratory.
ed out that diffusion into the polymer beads is a rate-limiting factor in the hydrogenation of olefins catalyzed by polystyrene-anchored (PPh₃)₂RhCl.

**Results and Discussion**

A swollen 1% divinylbenzene-styrene resin was complexed with -Cr(CO)₅ groups by refluxing with Cr(CO)₆ in dimethoxyethane under nitrogen. The resulting anchored catalyst 1 (see eq 1) used in this study contained -Cr(CO)₅-bound carbonyl bands was not due to leaching of Cr(CO)₆ or a reaction product was being chemically bound into the resin. To further test this suggestion, the beads were swollen in benzene and toluene and extracted (soxhlet) for BUC.

![Chemical structure](image)

moieties attached to 20–25% of the polymer’s benzene rings and distributed throughout the resin beads.

Methyl sorbate was quantitatively hydrogenated in cyclohexane at 500 psi of hydrogen for 24 hr. The product distribution was a function of temperature. The products were (Z)-methyl 3-hexenoate and distributed throughout the resin beads.

The catalyst conditioning phenomenon was studied by observing the IR spectrum of the polymer before and after its use in the initial reaction. Before use 1 shows intense metal carbonyl stretching frequencies at 1965 and 1880 cm⁻¹. After the initial hydrogenation, a new carbonyl absorption appears at 1635 cm⁻¹. Upon repeated recycling the 1965- and 1880-cm⁻¹ band intensities steadily decreased but the polymer remained catalytically active. The 1635-cm⁻¹ band remained, suggesting that methyl sorbate or a reaction product was being chemically bound into the resin. To further test this suggestion, the beads were swollen in benzene and toluene and extracted (soxhlet) for successive 4-hr periods. The 1635-cm⁻¹ absorption’s intensity remained unchanged. The decrease in the chromium-bound carbonyl bands was not due to leaching of Cr(CO)₆ (or other Cr derivatives) from the polymer because analysis confirmed the per cent Cr remained essentially unchanged during recycling. The presence of an inorganic CO bridging three Cr atoms (which would appear in the 1650-cm⁻¹ range) was ruled out for lack of precedent. Most likely, methyl sorbate is complexed to resin-bound chromium and displaces CO.

The product distribution at 140°, after 24 hr, and 30% conversion, was highly selective for 2 (<93%) and only a trace of 3 (0.2%) and no 4 was observed. Thus, at 140°, the product distribution resembled those obtained at 160°. After much longer reaction periods only small amounts of 3 and 4 were ever observed.

At 150° in cyclohexane at conditions where Cais, et al., reported p-(ethylbenzene)tricarbonylchromium catalyzed a 96% conversion of methyl sorbate in 7 hr, only 50% conversion in 24 hr was obtained using resin 1. This difference in rate can be attributed to diffusion into the resin. This diffusion limitation was expected to be serious in cyclohexane, because it is a poor solvent for swelling styrene-divinylbenzene resins. Significant retardation of the rate of hydroformylation of 1-pentene, catalyzed by anchored (PPh₃)₂RhH(CO), vs. its homogeneous use (at 40–50°), has been observed in this laboratory. Similarly, anchored (PPh₃)₂Ni(CO)₂ catalyzes the cyclooligomerization of butadiene at 112° at a rate about equal to that of the homogeneous catalyst at 90°. In both of those cases, significant

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**Table I**

**Hydrogenation of Methyl Sorbate at 500 psi Catalyzed by Polystyrene-Anchored \( \eta^6 \)-Phenyltricarbonylchromium**

<table>
<thead>
<tr>
<th>React. no.</th>
<th>Methyl sorbate, mmol</th>
<th>Catalyst, mmol</th>
<th>Solvent (15 ml)</th>
<th>Temp, °C</th>
<th>React. time, hr</th>
<th>Total conversion, %</th>
<th>Product distribution, %</th>
<th>(Z)-Methyl 3-hexenoate</th>
<th>(Z)-Methyl 2-hexenoate</th>
<th>Methyl 3-hexanoate</th>
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<td>Cyclohexane</td>
<td>150</td>
<td>24</td>
<td>100</td>
<td>65–58 i</td>
<td>7–21 i</td>
<td>34–40 i</td>
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</tr>
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<td>0.49</td>
<td>Cyclohexane</td>
<td>150</td>
<td>24</td>
<td>100</td>
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<td>7</td>
<td>12</td>
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<tr>
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<td>150</td>
<td>24</td>
<td>100</td>
<td>76</td>
<td>9</td>
<td>15</td>
<td></td>
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<td>100</td>
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<td>Cyclohexane</td>
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<td>10</td>
<td>60</td>
<td>97.4</td>
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<tr>
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<td>100</td>
<td>87.4</td>
<td>5.6</td>
<td>7.0</td>
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</tbody>
</table>

a Millimoles of Cr(CO)₅ units anchored within the resin charged to the reactor. b Runs 2–7 used the same catalyst recycled from run 1. Thus, in run 7 this catalyst was used in runs 1–6 previously. c Catalyst recycled from run 7. d Fresh catalyst used. e Catalyst recycled from run 9. f Catalyst recycled from run 11. g Fresh catalyst used. h Based on total conversion and determined by glc. i Results obtained from several runs spanned the range shown.
rate retardation occurred due to diffusion despite the fact that a good swelling solvent, benzene, was employed.

Dimethylformamide is a good swelling solvent. At 150° complete hydrogenation of methyl sorbate required only 5 hr using anchored catalyst 1. Previously, it had been shown the rate of methyl sorbate hydrogenation, catalyzed by \( \eta^6 \)-benzenetricarbonyl chromium, markedly increased going from nonpolar cyclohexane to more polar methylene chloride.\(^{10}\) Thus, the origin of the rate enhancement observed using DMF with 1 is not clear. Using DMF, the catalyst could not be recovered. After a single 10-hr reaction, the chromium content of 1 was reduced from 8.89% to 4.55%. The greenish-yellow DMF filtrate contained some \( \text{Cr}(\text{CO})_3 \) which could have participated in the catalytic reaction.\(^{14}\) DMF was leaching \( \text{Cr}(\text{CO})_3 \) moieties from the resin by displacing the \( \pi \)-bound phenyl rings. The product distribution changed sharply in DMF. Esters 3 and 4 became the major products (50 and 30%, respectively) and only 20% of the product was 2.

It was necessary to establish that the major product, using cyclohexane as the solvent, was actually the cis isomer 2 rather than the trans isomer. It was the trans isomer which was formed when pentacyanocobaltate(II) was employed.\(^{12}\) This point was not established by Cais.\(^{10}\) The nmr spectrum was not definitive since the coupling constant between the 3- and 4-vinyl protons could not be observed due to the coincidental chemical shifts of these protons. However, the ir spectrum of 2 did not correspond to that published for trans-methyl 3-hexenoate.\(^{12,10}\) Most conclusive was the absence of a strong band in the 970- and 750 cm\(^{-1}\) region indicating the cis isomer had been obtained.

Bis-\( \eta^6 \)-arenetricarbonylchromium compounds such as 5 and 6 greatly enhanced the hydrogenation rate in cyclohexane.\(^{10}\) For example, with \( \text{Cr}(\text{CO})_3 \text{EtCl} \) as the catalyst, 2-hexenoic acid was reduced from 50.8% to 4.55%.

Infrared spectra, recorded on a Beckman IR-33, were obtained in KBr pellets for the cross-linked beads and as thin films for methyl sorbate and its reaction products. Nmr spectra were recorded on a Hitachi-Perkin-Elmer R20B spectrometer using deuteriochloroform as the solvent and TMS as an internal standard.

**Experimental Section**

Chromium hexacarbonyl was purchased from Pressure Chemical Co. and was sublimed prior to use. Methyl sorbate (Pfaltz and Bauer) was purified by distillation at 90° (40 mm) and stored at -12° prior to use. Weekly checks of this material by vpc showed no oligomers were formed during storage. Cyclohexane and dimethoxyethane were dried over calcium hydride and distilled immediately before use. Dimethylformamide was dried over magnesium sulfate, distilled, and stored over Linde 4A molecular sieves. Poly styrene beads, cross-linked with 1% divinylbenzene, were purchased from Bio-Rad, Inc. They had a 12,000-14,000 mol wt exclusion limit when fully swollen in benzene.

In a typical reaction, the Hoke bomb was charged, under nitrogen, with the catalyst, methyl sorbate, and solvent in amounts listed in Table I. After degassing via two freeze–thaw cycles, the bomb was pressurized with 500 psi of hydrogen and placed in a preheated oil bath where it was also shaken for the appropriate time. The bomb was then cooled to room temperature, the excess hydrogen was vented, and the sorbate and products were separated from the catalyst by filtration under nitrogen. The beads were rinsed with 3 x 5 ml of solvent and the rinse was used to wash the beads. The catalyst could then be recycled. After the first and fourth reactions a 10-ml aliquot of the catalyst was removed for chromium analysis. The total filtrate was concentrated and the products were separated by vpc. They eluted in the order methyl hexanoate, \((Z)\)-methyl 3-hexenoate, \((E)\)-methyl 3-hexenoate, \((E,E,E)\)-1,5,9-cyclododecatriene, and unreacted methyl sorbate. The products were identified by comparing their infrared and nmr spectra with published spectra.\(^{11,12}\) The nmr spectra (CCL\(_4\)) follow: methyl hexanoate, 1.09 (3 H, t, CH\(_2\)CH\(_2\)), 1.55 (6 H, CH\(_2\) groups at 3, 4, and 5 positions), 2.35 (2 H, t, CH\(_2\) at C-2 positions), 3.76 (5 H, s, CH\(_2\)).

Other Hydrogenations. Attempts were made to hydrogenate cyclohexene and \((E,E,E)\)-1,5,9-cyclododecatriene at 150° for 24 hr (500 psi of \( \text{H_2} \)) using resin 1 as described for methyl sorbate. No significant hydrogenation was observed.

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**Registry No.** 2, 13894-62-7; 3, 13894-63-8; 4, 106-70-7; chromium hexacarbonyl, 13007-92-6; methyl sorbate, 689-89-4; poly styrene, 9003-53-6.

**References and Notes**

8. W. O. Haag and D. D. Whitenhurst, Proceedings of the Fifth International
A. Reactions of T-2-Methallylnickel Bromide. The general reaction studied is described by eq 1, and the results of this reaction with a wide variety of carbonyl compounds are collected in Table I. The most reactive substrates are a diketones and anthraquinone, which undergo exclusive attack of only one of the carbonyl groups, even in the presence of excess complex, to produce α-keto homooligols in high yield. Phenyl ketones are more reactive than alkyl ketones as evidenced by the requirement of more severe conditions for 2,3-butanedione. In contrast alkylnickel and allylzinc complexes frequently attack both carbonyl groups indiscriminately, lead-