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# Heterogenized homogeneous catalysts. Hydrogenation of methyl sorbate by polystyrene-anchored tricarbonylchromium

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## 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  $\eta^6$  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° 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° 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 and glass supports has recently attracted increased attention.<sup>1–8</sup> 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 play an important role in reactions using supported catalysts. In this paper we report the use of cross-linked polystyrene-anchored  $-\text{Cr}(\text{CO})_3$  moieties in selective methyl sorbate hydrogenations.

Methyl sorbate (methyl 2,4-hexadienoate) was chosen as a model substrate (1) because of its relation to commercially important dienolic and trienolic fatty acid esters, (2) because the resulting hydrogenation products can be analyzed readily by gas chromatography, and (3) because its hydrogenation has been previously studied using a variety of catalysts.<sup>9–12</sup> Hydrogenation of methyl sorbate, catalyzed by pentacarbonyliron,<sup>9</sup> gave a mixture of methyl 2-, 3-, and 4-hexenoate as well as methyl hexanoate. No as-

signment of the geometrical isomeric distribution was given. Cais, *et al.*,<sup>10</sup> and Frankel and Butterfield<sup>11</sup> showed a wide variety of  $\eta^6$ -arenetricarbonylchromium derivatives would selectively catalyze hydrogenation to methyl 3-hexenoate, but assignment of the geometrical isomer was not given. The same authors showed that  $\eta^6$ -arenetricarbonylchromium-catalyzed hydrogenations of dienes proceeded by 1,4-addition<sup>13</sup> and that isomerization of methyl 3-hexenoate to the 2-isomer occurred by a 1,3-hydrogen shift. The room temperature hydrogenation of sorbic acid by pentacyanocobaltate(II) gave (*E*)-2-hexenoic acid (82%), (*E*)-3-hexenoic acid (17%), and (*E*)-4-hexenoic acid (1%).<sup>12</sup> In methanol the selectivity to (*E*)-2-hexenoic acid increased to 96%.

$\eta^6$ -(Ethylbenzene)tricarbonylchromium is a good electronic model for polystyrene-anchored tricarbonylchromium. Using it at 150° and 700 psi of hydrogen, methyl sorbate gave 90.1% methyl 3-hexenoate.<sup>10</sup> The product distribution in this study was different from that which we found using the heterogenized analog. Grubbs<sup>14</sup> has point-

Table I  
Hydrogenation of Methyl Sorbate at 500 psi Catalyzed by Polystyrene-Anchored  $\eta^6$ -Phenyltricarbonylchromium

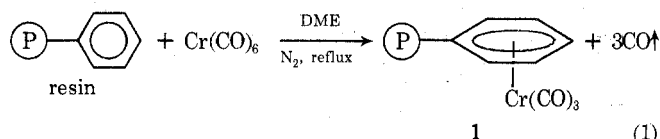
React. no.	Methyl sorbate, mmol	Catalyst, mmol <sup>a</sup>	Solvent (15 ml)	Temp, °C	React. time, hr	Total conversion, %	Product distribution, % <sup>h</sup>		
							(Z)-Methyl 3-hexenoate	(E)-Methyl 2-hexenoate	Methyl hexanoate
1	15.2	0.51	Cyclohexane	150	24	100	65–58 <sup>i</sup>	7–2 <sup>i</sup>	34–40 <sup>i</sup>
2 <sup>b</sup>	15.2	0.49	Cyclohexane	150	24	100	80	7	12
3 <sup>b</sup>	15.2	0.49	Cyclohexane	150	24	100	76	9	15
4 <sup>b</sup>	15.2	0.49	Cyclohexane	150	24	100	80	5	15
5 <sup>b</sup>	15.2	0.48	Cyclohexane	150	24	100	79	5	16
6 <sup>b</sup>	15.2	0.48	Cyclohexane	150	24	100	82	4	14
7 <sup>b</sup>	15.2	0.51	Cyclohexane	140	24	33	99.8	0.2	0
8 <sup>c</sup>	15.2	0.51	Cyclohexane <sup>c</sup>	160	24	100	96.5	2.0	0.7
9 <sup>d</sup>	15.2	0.51	Cyclohexane <sup>d</sup>	160	24	100	97.2	2.0	0.8
10 <sup>e</sup>	15.2	0.51	Cyclohexane <sup>e</sup>	160	24	100	97.4	1.8	0.8
11	15.2	0.51	DMF	150	10	100	20	50	30
12 <sup>f</sup>	15.2	0.51	DMF <sup>f</sup>	150	24	0	0	0	0
13 <sup>g</sup>	15.2	0.51	DMF <sup>g</sup>	150	5	100	70.7	23.6	5.7
14	15.2	0.51	Cyclohexane	150	10	60	97.4	2.7	0
15	76.0	0.51	Cyclohexane	150	48	100	87.4	5.6	7.0

<sup>a</sup> Millimoles of  $\text{Cr}(\text{CO})_3$  units anchored within the resin charged to the reactor. <sup>b</sup> Runs 2–7 used the same catalyst recycled from run 1. Thus, in run 7 this catalyst was used in runs 1–6 previously. <sup>c</sup> Catalyst recycled from run 7. <sup>d</sup> Fresh catalyst used. <sup>e</sup> Catalyst recycled from run 9. <sup>f</sup> Catalyst recycled from run 11. <sup>g</sup> Fresh catalyst used. <sup>h</sup> Based on total conversion and determined by glc. <sup>i</sup> Results obtained from several runs spanned the range shown.

ed out that diffusion into the polymer beads is a rate-limiting factor in the hydrogenation of olefins catalyzed by polystyrene-anchored  $(\text{PPh}_3)_3\text{RhCl}$ .

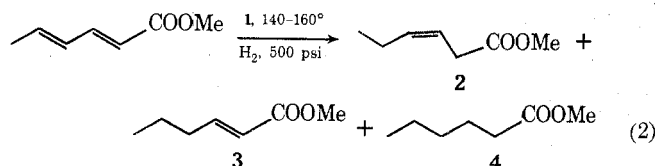
### Results and Discussion

A swollen 1% divinylbenzene–styrene resin was complexed with  $-\text{Cr}(\text{CO})_3$  groups by refluxing with  $\text{Cr}(\text{CO})_6$  in dimethoxyethane under nitrogen. The resulting anchored catalyst 1 (see eq 1) used in this study contained  $-\text{Cr}(\text{CO})_3$



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

Methyl sorbate was quantitatively hydrogenated in cyclohexane or DMF solvents containing swollen beads of 1 at 140–160° and 500 psi of hydrogen for 24 hr. The product distribution was a function of temperature. The products were (Z)-methyl 3-hexenoate (2), (E)-methyl 2-hexenoate (3), and methyl hexanoate (4) (eq 2). At 160° the selectivity



to (Z)-methyl 3-hexenoate (2) was 96–98% which was higher than that observed using the  $\eta^6$ -ethylbenzene analog. At 150°, the selectivity was significantly lower with 2 (74–81%) still the major product. The product distribution at 150° was different in the initial reaction, but upon recycling the distribution stabilized to a different value. Once conditioned, the catalyst performs in a uniform manner for several recycling operations. Representative sample runs are given in Table I.

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  $\text{cm}^{-1}$ . After the initial hydrogenation, a new carbonyl absorption appears at 1635  $\text{cm}^{-1}$ . Upon repeated recycling the 1965- and 1880- $\text{cm}^{-1}$  band intensities steadily decreased but the polymer remained catalytically active. The 1635- $\text{cm}^{-1}$  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- $\text{cm}^{-1}$  absorption's intensity remained unchanged. The decrease in the chromium-bound carbonyl bands was not due to leaching of  $\text{Cr}(\text{CO})_6$  (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- $\text{cm}^{-1}$  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 (<99%) 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.

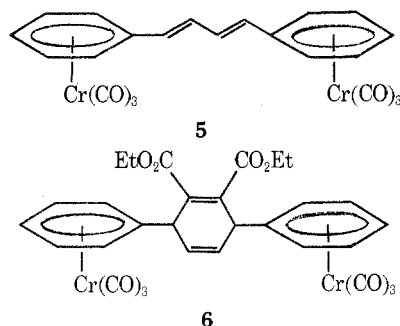
At 150° in cyclohexane at conditions where Cais, *et al.*,<sup>10</sup> had reported  $\eta^6$ -(ethylbenzene)tricarbonylchromium catalyzed a 95% conversion of methyl sorbate in 7 hr, only 50% conversion in 24 hr was obtained using resin 1. This difference in rate can be attributed to diffusion into 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  $(\text{PPh}_3)_3\text{RhH}(\text{CO})$ , *vs.* its homogeneous use (at 40–50°), has been observed in this laboratory.<sup>15</sup> Similarly, anchored  $(\text{PPh}_3)_2\text{Ni}(\text{CO})_2$  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

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  $\eta^6$ -benzenetricarbonylchromium, markedly increased going from nonpolar cyclohexane to more polar methylene chloride.<sup>10</sup> Thus, the origin of the rate enhancement observed using DMF with 1 is not clear. Using DMF, the catalyst could not be recycled. 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 (DMF)<sub>3</sub>Cr(CO)<sub>3</sub> which could have participated in the catalytic reaction.<sup>16</sup> DMF was leaching -Cr(CO)<sub>3</sub> 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.<sup>12</sup> This point was not established by Cais.<sup>10</sup> 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.<sup>12,16</sup> Most conclusive was the absence of a strong band in the 970-cm<sup>-1</sup> region where the *trans* isomer absorbs. Bands at 700 and 750 cm<sup>-1</sup> were present indicating the *cis* isomer had been obtained.

Bis- $\eta^6$ -arenetricarbonylchromium compounds such as 5 and 6 greatly enhanced the hydrogenation rate in cyclohex-



ane.<sup>10</sup> For example, with 6 a 99% conversion of methyl sorbate to 2 was obtained at 115° and 70 psi *vs.* the 150° and 700 psi of hydrogen required using  $\eta^6$ -benzenetricarbonylchromium.<sup>10</sup> Apparently, this special rate effect cannot be operative in resin 1 despite the fact that this resin must have phenyl-bound Cr(CO)<sub>3</sub> moieties in close proximity. The origin of this special effect may be in the conjugative interactions between rings in 5 and 6 rather than their relative proximity to one another.

### 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. Polystyrene 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.

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.

Vpc curves were recorded on a Varian Aerograph Model 90-P. An 8-ft column consisting of 15% SE-30 or 20% Carbowax 20M deposited on Chromosorb P (non-acid-washed) at 180° was used to effect efficient product separation.

The stainless steel Hoke bomb, 150-ml capacity, used in these reactions was scraped clean, treated with mineral acids and organic solvents, and dried prior to each series of runs.

**Preparation of Polystyrene-Anchored Tricarbonylchromium.** A Strohmeier reactor, equipped with a 250-ml reaction flask containing a magnetic stirring bar, was charged with 4.0 g of cross-linked beads, 4.0 g of Cr(CO)<sub>3</sub>, and 150 ml of dimethoxyethane.<sup>17</sup> After refluxing the mixture under nitrogen for 48 hr, the reaction was cooled to room temperature and filtered under nitrogen onto a sintered glass frit to collect the polymer beads. The beads were repeatedly swollen with benzene and collected by filtration in order to remove non-polymer-bound chromium complexes. After a final wash with petroleum ether (bp 30–60°), the beads were dried *in vacuo* for 48 hr. The presence of only polystyrene tricarbonylchromium moieties was confirmed by the infrared spectrum which showed two carbonyl stretching frequencies at 1965 and 1880 cm<sup>-1</sup>. Elemental analysis showed 8.89% Cr, corresponding to *ca.* one Cr(CO)<sub>3</sub> unit for each four aromatic rings. The beads could be stored under nitrogen indefinitely. The beads occasionally had a green cast due to surface oxidation of the chromium during the above preparation. This in no way affected their activity or the results.

**Hydrogenation of Methyl Sorbate.** 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 solvent and products were separated from the catalyst by filtration under nitrogen. The bomb was rinsed with 3 × 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-mg 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 2-hexenoate, and unreacted methyl sorbate. The products were identified by comparing their infrared and nmr spectra with published spectra.<sup>11,12</sup> The nmr spectra (CCl<sub>4</sub>) follow: methyl hexanoate,  $\delta$  0.9 (3 H, t, CH<sub>3</sub>CH<sub>2</sub>), 1.55 (6 H, m, CH<sub>2</sub> groups at 3, 4, and 5 positions), 2.35 (2 H, t, CH<sub>2</sub> at 2 positions), 3.76 (3 H, s, CH<sub>3</sub>O); methyl 3-hexenoate,  $\delta$  0.94 (3 H, t, CH<sub>3</sub>CH<sub>2</sub>), 2.05 (2 H, m, CH<sub>2</sub> at C-5), 3.05 (2 H, d, 7 H<sub>2</sub>, CH<sub>2</sub> at C-2), 3.60 (3 H, s, CH<sub>3</sub>O), and 5.5 (2 H, br t, *J* = 6–8 Hz, *cis* vinyl H's at C-3 and C-4 where *J*<sub>3-4</sub>  $\approx$  0 due to almost identical chemical shifts); methyl 2-hexenoate,  $\delta$  1.0 (3 H, t, CH<sub>3</sub>CH<sub>2</sub>), 1.5 (2 H, m, CH<sub>2</sub>), 2.2 (2 H, m, CH<sub>2</sub>), 4.0 (3 H, s, CH<sub>3</sub>O), 6.1 (1 H, d, 2-vinyl H, *J*<sub>2,3</sub> = 16 Hz), and 7.2 (1 H, m, 3-vinyl H).

**Other Hydrogenations.** Attempts were made to hydrogenate cyclohexene and (*E,E,E*)-1,5,9-cyclododecatriene at 150° for 24 hr (500 psi of H<sub>2</sub>) 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; polystyrene, 9003-53-6.

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## Reaction of $\pi$ -Allylnickel Bromide Complexes with Ketones and Aldehydes. Synthesis of $\alpha$ -Methylene- $\gamma$ -butyrolactones

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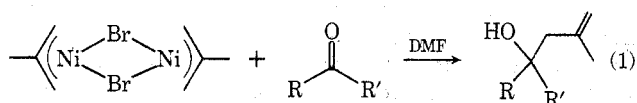
$\pi$ -Allylnickel bromide complexes react with ketones and aldehydes to produce homoallylic alcohols.  $\alpha$  diketones are the most reactive substrates, leading to  $\alpha$ -keto homoallylic alcohols. Aldehydes and alicyclic ketones including some steroidal ketones are also reactive, while aliphatic acyclic ketones and  $\alpha,\beta$ -unsaturated ketones react only sluggishly under forcing conditions. With conjugated ketones exclusive 1,2 attack results, even in the presence of added CuI. The reaction of  $\alpha$ -(2-carbethoxyallyl)nickel bromide with ketones and aldehydes leads to  $\alpha$ -methylene- $\gamma$ -butyrolactones. Other carbonyl functional groups such as acid chlorides, esters, and amides, as well as nitriles and epoxides, are relatively unreactive. Thus  $\pi$ -allylnickel bromide complexes are less reactive and more selective than the corresponding allylzinc reagents toward carbonyl compounds, and are of potential synthetic utility.

$\pi$ -Allylnickel halide complexes are becoming increasingly useful as carbon-carbon bond forming reagents for organic synthesis, and have been the subject of two recent reviews.<sup>1,2</sup> They react with a variety of organic halides under mild conditions to replace the halogen with the allyl group.<sup>3</sup> Complexes containing functional groups such as carbethoxy<sup>4</sup> or methoxy<sup>5</sup> in the allyl portion are readily prepared, and react similarly to produce more highly functionalized products.  $\pi$ -Allylnickel bromide complexes react with quinones under very mild (DMF,  $-50^\circ$ ) conditions to produce allylquinones in what is formally a 1,4 addition of the allyl complex to the quinone.<sup>6</sup> In contrast, other normally reactive carbonyl compounds such as benzaldehyde and cyclopentanone require considerably more vigorous (DMF,  $50^\circ$ ) conditions to react, forming homoallylic alcohols, while benzophenone and methyl benzoate are unreactive.<sup>3</sup>

In an attempt to clarify some of the features of the reaction of  $\pi$ -allylnickel halide complexes with quinones, we initiated a general study of the interaction of these complexes with a variety of simple as well as conjugated carbonyl compounds. Our results indicate that these complexes are generally reactive toward ketones and aldehydes to produce fair to excellent yields of homoallylic alcohols under mild conditions. They are significantly less reactive than the corresponding allyllithium, -magnesium, or -zinc reagents, and offer a high degree of selectivity among normally quite reactive carbonyl compounds.<sup>7</sup>

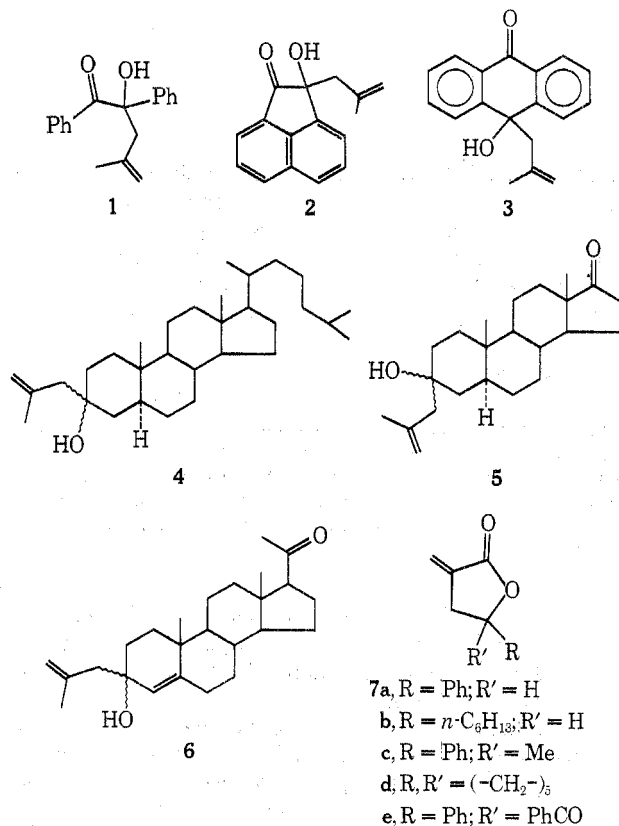
### Results and Discussion.

**A. Reactions of  $\pi$ -2-Methallylnickel Bromide.** The general reaction studied is described by eq 1, and the re-



sults of this reaction with a wide variety of carbonyl compounds are collected in Table I. The most reactive sub-

strates are  $\alpha$  diketones and anthraquinone, which undergo exclusive attack of only one of the carbonyl groups, even in the presence of excess complex, to produce  $\alpha$ -keto homoallylic alcohols (1, 2, and 3) 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 allylmagnesium and allylzinc complexes frequently attack both carbonyl groups indiscriminately, lead-