

terium substitution. No deuterium-hydrogen exchange was detectable by nmr in a solution of dibenzoylmethide and tetra-*n*-butylammonium perchlorate in d_6 -DMSO indicating that no deuteration occurs prior to electrolysis.

Spectra may be obtained by electrolysis of dibenzoylmethane in THF at -60° or by electrolysis of dibenzoylmethane in DMSO containing 0.1 *M* tetra-*n*-butylammonium dibenzoylmethide at room temperature. These spectra are different than any so far reported for this system (benzil,¹ acetophenone, 1-phenyl-1,2-propanedione⁶) but unambiguous analyses of the spectra have not been attained. Definite assignment must await further studies now in progress.

Experimental Section

A Sargent Model XV polarograph with a Sargent IR compensator was used with a three electrode polarographic cell.^{2a} The reference electrode was an aqueous saturated calomel electrode. The potentiostat for controlled potential coulometry was a Wenking Model 61 RS. The working electrode in the controlled potential electrolysis cell^{2a} was a 30 cm² mercury pool. Cyclic voltammetric instrumentation was of conventional¹⁰ design. The working electrode for cyclic voltammetry was a hanging mercury drop electrode (Model E410, Brinkmann Instruments) used in the polarographic cell mentioned above. The esr spectrometer was a Varian E-3. A Varian electrolytic cell was used for generation of radicals in the microwave cavity. The computer program for simulation of esr spectra was similar to that employed by Stone and Maki.¹¹

Reagent grade DMSO was stirred over calcium hydride for at least 12 hr and distilled at reduced pressure just before use. Tetra-*n*-butylammonium perchlorate (Matheson) was used as received except for the cyclic voltammetric studies where it was recrystallized from ethyl acetate and vacuum dried. The dibenzoylmethide ion was prepared as its tetra-*n*-butylammonium salt.^{2a} The 2-*t*-butyl-1,3-diphenyl-1,3-propanedione was prepared by a procedure analogous to the reported synthesis of 3-*t*-butyl-2,4-pentanedione:¹² mp 124.5–125°; nmr (CCl₄) δ 1.15 (s, 9, CH₃), 5.22 (s, 1, methine), 7.38 (m, 6, aromatic), 7.92 (m, 4, aromatic). *Anal.* Calcd for C₁₉H₂₀O₂: C, 81.40; H, 7.19. Found: C, 81.59; H, 7.23. The 2,2-dimethyl-1,3-diphenyl-1,3-propanedione was prepared as described previously:¹³ mp 97.5–98° (99°);¹³ nmr (CDCl₃) δ 1.67 (s, 6, CH₃), 7.33 (m, 6, aromatic), 7.85 (m, 4, aromatic).

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Production of Linear Acids or Esters by the Platinum-Tin-Catalyzed Carbonylation of α Olefins

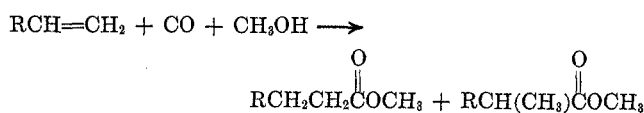
L. J. KEHOE AND R. A. SCHELL

Research Laboratories, Ethyl Corporation,
Ferndale, Michigan 48220

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The carbonylation reaction of olefins in the presence of metal carbonyls or carbonyl precursors to form acids or esters was developed by Reppe and his coworkers.¹ For example, the reaction of ethylene with CO and water in the presence of nickel salts or nickel carbonyl

yields propionic acid. When olefins larger than ethylene are reacted, the products consist of large amounts of branched isomers, in addition to the desired linear product, *i.e.*



Furthermore, these reactions are generally carried out at temperatures above 150°, and a variety of other side reactions including polymerization, isomerization, and reduction can compete with the carbonylation.

Recent reports describe successful olefin carbonylation under relatively mild conditions which can avoid many of these competing reactions. Both palladium^{2,3} and platinum⁴ complexes were found to be catalytically active below 100°. However, none of these systems, as described, offers the combination of excellent yields and a high degree of product linearity. While systems for the formation of highly linear aldehydes^{5,6} or alcohols⁷ from α olefins are known, the purpose of this note is to describe a catalyst system that will effect rapid conversion of α olefins to highly linear acids or esters.

Jenner and Lindsey⁴ found that a platinum salt-tin salt couple catalyzed the formation of esters from olefins at relatively low temperatures. However, their work was limited to olefins with less than six carbon atoms, and very high pressures (~800–1000 atm) with long reaction times (usually 10–16 hr) were necessitated. Additionally, propylene, the only straight chain, α monoolefin reported, gave a product mixture containing approximately equal amounts of methyl *n*-butyrate and methyl isobutyrate.

By utilizing a solvent such as acetone, methyl isobutyl ketone or 1,2-dimethoxyethane, and carefully controlling the reaction conditions, it has now been found that a H₂PtCl₆-SnCl₂ couple will catalyze carbonylation of olefins such as dodecene-1, in the presence of methanol, to highly linear (~85%) esters in 1 hr at 200 atm. The system has also been extended to acid synthesis under essentially the same conditions, by substituting water for the methanol. A typical reaction was carried out at 90° and 3000 psig of CO, with 1 mol % of H₂PtCl₆ and 5 mol % of SnCl₂ as catalyst, and acetone as solvent. Dodecene-1 conversion was 100% and product yield approximately 80% regardless of whether H₂O or methanol was utilized in the reaction. A small amount of olefin reduction occurred (2–4% of the olefin), but isomerization of the α olefin to internal olefins (mostly the 2-isomer) was the only major competing reaction. The acid (or ester) product was composed of approximately 85% of the straight chain isomer and 15% branched isomers. A mass spectral study showed that 80% of the branched product was the 2-methyl isomer.

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TABLE I
 CARBONYLATION OF OLEFINS

Reaction	Olefin	Amt, mmol	H source	Time, hr	% conversion ^a	% yield ^b	% linearity
I	Propylene	250	CH ₃ OH	2	80	100	67
II	1-Hexene	250	CH ₃ OH	1	98	85	83
III	1-Hexene	250	H ₂ O	2	93	88	83
IV	1-Dodecene	268	CH ₃ OH	1	100	76	83
V	1-Dodecene	268	H ₂ O	2	100	74	86
VI	1-Tetradecene	268	CH ₃ OH	1	98	81	82
VII	Dodecenes ^c	268	H ₂ O	5	5	Mixture of products	
VIII	3-Heptene	250	CH ₃ OH	2	10	Mixture of products	
IX	2-Ethyl-1-hexene	250	CH ₃ OH	5	86	22	Compd 1 ^d + 9 other alcohols
X	1,7-Octadiene	250	CH ₃ OH	2	100	64 diester 35 mono- ester	71 66 65
XI	1-Dodecene + dodecenes ^c	268 268	CH ₃ OH	2	56	88	65

^a Conversion (*via vpc*) = moles of olefin consumed/mole of olefin charged. ^b Yield (*via vpc*) = moles of product/mole of olefin consumed. ^c Randomized dodecenes, see Experimental Section. ^d Compound 1, CH₃(CH₂)₃C(OH)(Et)CH₃.

The results of the reaction of a number of olefins with acetone as a solvent are summarized in Table I. The reaction rates for ester formation tended to be faster than those for acid formation, and thus the shorter reaction times for the former. The carbonylation catalyzed by the platinum-tin catalyst appears to be general for hydrocarbon α olefins which contain hydrogen on the 2-carbon atom. Reactions I-VI demonstrate the high yields and excellent linearity that can be achieved with this system, propylene being the only α olefin that gave a product with linearity of less than 80%.

Internal olefins, however, were relatively inert to carbonylation under these conditions. Both 3-heptene and a mixture of randomized dodecenes gave very low conversions, and a mixture of products. The lower reactivity of the internal olefins suggested that it might be possible to react selectively α olefins from a mixture of isomers. Indeed, with a 50:50 mixture of 1-dodecene and random dodecene, approximately 50% of the olefin was carbonylated after 2 hours. However, the product linearity was less than expected. The attempted reaction of 2-ethyl-1-hexene was interesting, for when an ethyl group was substituted for the hydrogen on the 2-carbon of 1-hexene, olefin isomerization and hydration in typical Markovnikov fashion became the almost exclusive reaction. Protonation of the 1-carbon by chloroplatinic acid to give the tertiary carbonium ion is apparently much more rapid than carbonylation with this olefin.

The reaction with 1,7-octadiene indicates that the platinum-tin carbonylation system is applicable to terminal dienes, but the product distribution and linearity are complicated by the presence of the second double bond. The product mix was about 2:1 diester to unsaturated monoester. In both products the linearity dropped to near 70% from the 85% level found with monoolefins. A second problem was that the remaining double bond in the monoester was isomerized internally, indicating that any further carbonylation of the remaining olefin could yield only branched product.

The H₂PtCl₆-SnCl₂ couple has shown reactivity as a hydrogenation catalyst.^{8,9} In the carbonylation work it offers the same advantage of ease of catalyst formation. Several other platinum compounds were found to catalyze carbonylation in the presence of SnCl₂, however only K₂PtCl₆ gave a rate of reaction comparable to H₂PtCl₆. The related palladium complex K₂PdCl₆ showed very little catalytic activity. Rather surprisingly, (Ph₃P)₂PtCl₂ gave only a trace of products with added SnCl₂. This is a catalyst that Bailar and Itatani used so successfully in selective olefin hydrogenation work.¹⁰

While the mechanism of the reaction is not completely understood, several comments are made here to aid in the understanding of this catalyst system. Neither H₂PtCl₆ nor SnCl₂ function individually. Previous work utilizing a H₂PtCl₆-SnCl₂ catalyst system for olefin hydrogenation has noted this same phenomenon.⁸ Formation of a Pt-SnCl₃ complex apparently occurs. The SnCl₃⁻ ligand, a strong π acceptor and a mild σ donor, modifies the platinum metal atom and enhances coordination of hydride or of olefin, thus triggering catalysis. The maximum rate of olefin carbonylation occurs for molar Sn:Pt ratios of 5 or greater. This is in contrast to Pietropaolo and co-workers¹¹ finding that the rate of ethylene absorption on PtCl₄²⁻ promoted by SnCl₃⁻ was highest for Sn:Pt ratios lower than 5. However, similar to our findings, Bailar and Itatani¹⁰ noted higher reaction rates with Sn:Pt ratios higher than 5 in their olefin hydrogenation work.

It was found that water activates the K₂PtCl₆-SnCl₂ catalyst. In the ester syntheses this water requirement was usually satisfied by the water of hydration present on the SnCl₂·2H₂O. Under completely anhydrous conditions however, no reaction occurred.

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For example, an attempted ester preparation using K_2PtCl_6 and anhydrous $SnCl_2$ with dimethoxyethane solvent gave no product, while the same reaction repeated with water added gave the desired carbonylation. Apparently a platinum hydride, which is a presumed intermediate in the catalysis, was formed by the interaction with water. This is another example of the formation of platinum hydrides from water, a reaction which has been noted previously.¹²

Experimental Section

Material.— $(Ph_3P)_2PtCl_2$ was prepared by the reported method.¹³ Randomized dodecene was prepared by refluxing 1-dodecene with $PdCl_2$ for 16 hr. Vpc analysis of this random mixture showed 1-isomer = 2%, 2-isomer = 30%, 3-isomer = 24%, 4-isomer = 9%, other isomers = 34%. All other materials were best commercial grade used as purchased.

Typical Procedure for Acid Formation.—A 600 ml Magnedrive autoclave (Autoclave Engineers) was charged with 45 g (268 mmol) of 1-dodecene, 9 g (500 mmol) of water, 150 ml of acetone, 1.3 g (2.5 mmol) of $H_2PtCl_6 \cdot 6H_2O$, and 2.8 g (12.5 mmol) of $SnCl_2 \cdot 2H_2O$. The autoclave was sealed, flushed with carbon monoxide, and finally pressured to about 2000 psig with carbon monoxide. Stirring was begun and the autoclave was quickly heated to 90° and the pressure then adjusted to 3000 psi with more carbon monoxide. Reaction times were 1 or 2 hr depending on the rate of pressure drop.

Typical Procedure for Ester Formation.—This procedure was identical with that for acid synthesis, with 32 g (1 mol) of methanol substituted for water.

Analysis of Products.—The ester products were determined by vpc analysis of the recovered solutions. A Perkin-Elmer Model 9000 instrument was used. A 10 ft column packed with Carbowax 20M and Diatoport S was found to be suitable for analysis of the esters. A 150 ft capillary column coated with

Carbowax 1540 gave a good separation of the isomerized olefins. Authentic samples of the linear products were available for use as standards. The individual products were trapped as they emerged from the chromatograph and were identified by mass spectrometric and nmr analysis. The acid products were esterified by BF_3 -methanol reagent and analyzed as the methyl esters.

Catalysis by Other Platinum Group Catalysts.—The typical procedure for ester formation was repeated with several platinum compounds substituted for $H_2PtCl_6 \cdot 6H_2O$. A reaction utilizing 0.8 g (2.5 mmol) of $PtCl_2$ gave a 78% yield (100% conversion) of ester after 6 hr, 0.7 g (2.5 mmol) of $PtCl_2$ gave a 95% yield (30% conversion) after 6 hr, 1.2 g (2.5 mmol) of K_2PtCl_6 gave a 76% yield (100% conversion) after 1 hr, 2.0 g (2.5 mmol) of $(Ph_3P)_2PtCl_2$ gave a trace of ester after 6 hr, and 1 g (2.5 mmol) of K_2PdCl_6 gave a trace of ester after 2 hr.

Changing the Sn:Pt Ratio.—The typical procedure for acid formation when repeated using 1.7 g (7.5 mmol) of $SnCl_2 \cdot 2H_2O$ (Sn:Pt = 3) gave a 69% yield (35% conversion) of acid while 4.5 g (20 mmol) of $SnCl_2 \cdot 2H_2O$ (Sn:Pt = 8) gave a 70% yield (100% conversion) of acid.

Solvents Other Than Acetone.—The procedure for ester formation was repeated with three solvents, methyl isobutyl ketone, 1,2-dimethoxyethane, and tetrahydrofuran, substituted for acetone. No major difference in reactivity was noted.

Effect of Water on Catalytic Activity of K_2PtCl_6 .—The procedure for ester formation was repeated utilizing 45 g (268 mmol) of dodecene-1, 32 g (1 mol) of methanol, 150 ml of 1,2-dimethoxy ethane, 1.2 g (2.5 mmol) of K_2PtCl_6 , and 2.3 g (12.5 mmol) of anhydrous $SnCl_2$. Careful vpc analysis of the product mixture found no esters. This procedure was then repeated with 1.8 g (100 mmol) of water added. Vpc analysis indicated a 72% yield (32% conversion) of ester.

Registry No.—Propylene, 115-07-1; 1-hexene, 592-41-6; 1-dodecene, 112-41-4; 1-tetradecene, 1120-36-1; 2-ethyl-1-hexene, 1632-16-2; 1,7-octadiene, 3710-30-3.

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