cyclic ketone.[2] Elemental analysis was made of all compounds.[2]

cis-**2,5-Dibenzylcyclopentanone.**—Hydrogenation of 2,5-dibenzylidenecyclopentanone[2] in EtOAc over 10% Pd/C gave a mixture of saturated ketone and alcohol (ir). Chromatography on silica gel gave an oil which later crystallized on standing in an open dish, mp 39–40° (lit.[5] mp 39°).

trans-**2,5-Dibenzylcyclopentanone.**—Isomerization of the cis isomer in methanolic KOH after Cornubert, *et al.*,[5] gave the trans isomer, mp 54–55° (lit.[5] mp 58°). By tlc ($C_6H_6/CHCl_3$, 95:5) this material was free of the cis isomer.

cis-**2,6-Dibenzylcyclohexanone.**—Crystallization of the crude mixture from hydrogenation (10% Pd/C in EtOAc) of 2,6-dibenzylidenecyclohexanone[2] from MeOH gave the cis isomer, mp 119–122° (lit.[3] mp 122°).

trans-**2,6-Dibenzylcyclohexanone.**—The trans isomer was isolated from the mother liquor from crystallization of the cis isomer, after several batches of cis isomer were removed, mp 55° (lit.[3] mp 55°).

cis- **and** *trans*-**2,7-Dibenzylcycloheptanone.**—Hydrogenation of 2,7-dibenzylidenecycloheptanone[2] (10% Pd/C in EtOAc) gave an oil which failed to crystallize. Chromatography of 1 g of the oil on a 2-cm column using 60 g of 75–325 mesh silica gel and C_6H_6 eluent gave first the cis isomer, followed by the trans. Neither isomer was ever obtained as a solid.

trans-**2,8-Dibenzylcyclooctanone.**—Crystallization of the crude mixture from hydrogenation (10% Pd/C in EtOAc) of 2,8-dibenzylidenecyclooctanone[2] from MeOH gave the trans isomer, mp 82–83°.

cis-**2,8-Dibenzylcyclooctanone.**—Isomerization of trans isomer was carried out using 0.1 *M* NaOEt in EtOH,[2] yielding cis isomer, mp 84–85°. These were not the same compounds by mixture melting point, ir, and nmr.

Lithium Aluminum Hydride Reductions.—Each isomeric ketone (50 mg) was reduced with 50 mg of $LiAlH_4$ in anhydrous Et_2O by standard procedures.

Equilibration of Isomers.—One gram of one isomer of each pair was dissolved in 0.1 *M* NaOEt in EtOH and stirred at room temperature. Samples were analyzed at 24-hr intervals until no change in concentration was seen. The samples of the cycloheptanones had to be reduced to the alcohols with $NaBH_4$ before analysis. This was done by adding 50 mg of $NaBH_4$ to the aliquot, allowing it to stand overnight, and extracting into Et_2O after acidifying with 1 *N* HCl.

Vapor Phase Chromatography.—The cyclooctanones were separated on a 5 ft × 0.25 in. o.d. glass column packed with 3% OV-225 on Chromosorb W-AW-DMCS. The cyclohexanones were separated on a 5 ft × 0.25 in. o.d. glass column packed with 3% OV-17 on Chromosorb W-AW-DMCS. The alcohols obtained from the ketones were separated on the OV-225 column. The two alcohols from the *cis*-2,5-dibenzylcyclopentanone were separable but the alcohol from the trans isomer had the same retention time as one of the alcohols from the cis ketone.

Registry No.—**1a,** 34403-27-5; **1b,** 34403-28-6; **2a,** 7382-09-4; **2b,** 7382-10-7; **3a,** 34403-31-1; **3b,** 34410-06-5; **4a,** 34403-32-2; **4b,** 34403-33-3.

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Noble Metal Catalysis. I. Synthesis of Succinates from Olefins

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Dialkyl succinates[1] can be prepared in good yields by the oxidative carbonylation of olefins in the presence of alcohols with a palladium redox system, according to eq 1.

$$C_2H_4 + 2CO + {}^1/_2O_2 + 2ROH \longrightarrow RO_2CCH_2CH_2CO_2R + H_2O \quad (1)$$

The palladium redox system is somewhat similar to the one used in acetaldehyde synthesis[2] but optimum results are achieved by restricting both the amounts of excess hydrogen ion and chloride ion. Both iron and copper chlorides were shown to be useful as redox reagents for palladium, according to the following equations (for copper).

$$PdCl_2 + 2CO + CH_2{=}CH_2 + 2ROH \longrightarrow RO_2CCH_2CH_2CO_2R + Pd^0 + 2HCl \quad (2)$$

$$2CuCl_2 + Pd^0 \longrightarrow Cu_2Cl_2 + PdCl_2 \quad (3)$$

$$Cu_2Cl_2 + 2HCl + {}^1/_2O_2 \longrightarrow 2CuCl_2 + H_2O \quad (4)$$

However, it was quickly found that palladium chloride with either cupric chloride or ferric chloride alone gave a very poor catalyst system for succinate synthesis. The problem was found to be due to the presence of hydrogen chloride generated by eq 2. To the extent that eq 2 and 3 are faster than 4, then large amounts of cupric chloride give large amounts of hydrogen chloride. It was found that, when cuprous chloride was added, the excess chloride ion could be tied up. In the iron system, ferrous chloride was more effective than even a mixture of ferrous and ferric chlorides.

The oxidation of ferrous chloride by air was already known to be much faster in alcohols than in water and to increase in rate with increasing molecular weight of the alcohol.[3] The presence of water or small amounts of mineral acid in the solution reduced the rate of oxidation considerably. The rate of oxidation was related to the square of the concentration of ferrous chloride. The reaction was thought to be eq 5. Some oxidation

$$2FeCl_2 + {}^1/_2O_2 \longrightarrow FeCl_3 + FeOCl \quad (5)$$

of the ethanol solvent to acetaldehyde and ethyl acetate was also observed.

The acid–base effect is illustrated in Table I, where it is seen that in the synthesis of methyl succinate the addition of small amounts of sodium acetate (organic bases such as pyridine are also effective) increases the yield of succinate and decreases the yield of carbon dioxide, the chief by-product. On the other hand, hydrogen chloride has just the opposite effect.

TABLE I

EFFECT OF ACID AND BASE[a]

Acid or base	Wt, of acid or base, g	Mol of product produced: Methyl succinate	Carbon dioxide	Other
	0	0.17	0.17	Methyl formate, 0.02
Sodium acetate	3	0.22	0.10	
37% Hydrochloric acid	1	0.04	0.26	Methyl formate, 0.02 Methylal, 0.1

[a] At 300 psig CO, 700 psig C_2H_4, methanol to 400 ml in a 0.5-gal stirred titanium autoclave with 1 g of $PdCl_2$, 10 g of $FeCl_2 \cdot 4H_2O$, and oxygen addition to 125–175 psig in increments at 85°.

The other product produced along with the succinate

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(1) D. M. Fenton, U. S. Patents 3,481,845; 3,397,225; 3,397,226.

(2) J. Smidt, *Angew. Chem.*, 176 (1959).

(3) J. R. Pound, *J. Phys. Chem.*, **43**, 955, 969 (1939).

is water. Although small amounts of water do not prevent succinates from forming, water definitely increases the production of carbon dioxide, as seen in Table II.

TABLE II

EFFECT OF ADDITION OF ORTHOFORMATE[a]

Wt of methyl orthoformate, g	Mol of product produced		
	Methyl succinate	Carbon dioxide	Other
0	0.17	0.17	Methyl formate, 0.02
100	0.33	0.068	
200	0.18	0.0044	
200[b]	0.24[b]	0.0088	Ethyl acetate, 0.19

[a] At 300 psig CO, 700 psig C_2H_4, methanol to a total of 400 ml in a 0.5-gal stirred titanium autoclave with 1 g of $PdCl_2$, 10 g of $FeCl_2 \cdot 4H_2O$, and oxygen addition to 125–175 psig in increments at 85°. [b] The corresponding ethyl esters and ethyl alcohol.

Alkyl orthoformates can be added to suppress the carbon dioxide formation. In this way yields of succinate of over 90% based upon both ethylene and carbon monoxide are achieved.

Although eq 1 shows the need for 2 mol of carbon monoxide for 1 mol of ethylene, it was shown that slightly higher partial pressures of ethylene to carbon monoxide give better yields of succinates, as shown in Table III, for butyl succinate. Also, lower yields of carbon dioxide are produced at lower CO/C_2H_4 ratios. However, at still lower CO/C_2H_4 ratios, instead of succinates, acrylates are produced. However, with the same carbon monoxide–ethylene ratio using the ferrous system without excess chloride ion, succinates were made (Tables I and II). Thus the product distribution depends significantly on the CO/C_2H_4 ratio. This dependence on CO/C_2H_4 ratio was previously noted for the synthesis of acrylic acid[4] starting from ethylene and carbon monoxide, according to eq 6,

TABLE III

EFFECT OF CHANGES IN THE CARBON MONOXIDE–ETHYLENE RATIO[a]

Pressure, psig			
Carbon monoxide	Ethylene	CO/C_2H_4	Wt of butyl succinate product, g
300	700	0.43	0[b]
500	750	0.67	26
500	400	1.25	23
800	500	1.60	12

[a] 1 g of $PdCl_2$, 5 g of $CuCl_2$, 5 g of LiCl, and 400 ml of butanol, at 125–150° in a 0.5-gal stirred steel autoclave with 150–200 psig oxygen added in increments. [b] 15 g of butyl acrylate produced.

$$CH_2{=}CH_2 + CO + {}^1/_2O_2 \longrightarrow CH_2{=}CHCO_2H \qquad (6)$$

using a similar palladium redox catalyst with an acetic acid solvent. Here β-acetoxypropionic acid was also produced, particularly at higher temperatures and pressures and also at higher CO/C_2H_4 ratios. However, succinic acid was not a significant product.

Other olefins may also be used in place of ethylene. The results of two of these runs are shown in Table IV.

TABLE IV

USE OF OTHER OLEFINS[a]

Olefin	Wt, g: Olefin	Wt, g: Ethyl orthoformate	Pressure, psig carbon monoxide	Wt of products, g
Propylene	238	200	600	Diethyl methylsuccinate, 30 Ethyl crotonate, 30
1-Octene	100	100	700	Diethyl hexylsuccinate, 22

[a] 1 g of $PdCl_2$, 5 g of $CuCl_2$, 5 g of LiCl, and enough ethanol to make 600 ml of liquid, in a 0.5-gal stirred steel autoclave at 125–150° with 100–200 psig oxygen.

Experimental Section

The reactions were carried out in 0.5-gal stirred autoclaves made of either steel or titanium. The steel autoclaves exhibited some corrosion and so titanium was preferred. The catalyst and liquids were charged to the autoclave and ethylene (where used) and carbon monoxide were added to the desired pressures. Stirring was commenced and the autoclave was heated to the desired temperature. Oxygen was then added (controlled from behind a suitable barracade) in 10-psig increments. In almost all cases an immediate exotherm was noted and cooling water was circulated to bring the temperature under control. Pressure drops were noted. Oxygen was added until 150–200 psi had been added or until the reaction slowed down. In those cases where no noticeable reaction occurred no more than 40 psi of oxygen was added. After oxygen addition, the autoclave was cooled to room temperature and the gases were collected and analyzed by gas chromatography. The liquid was weighed and analyzed by gas chromatography and occasionally by distillation.

Registry No.—Palladium chloride, 7647-10-1; sodium acetate, 127-09-3; hydrochloric acid, 7647-01-0; methyl orthoformate, 34405-39-5; carbon monoxide, 630-08-0; ethylene, 74-85-1.

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Effect of α-Methyl Substitution in the Beckmann and Schmidt Rearrangement of 1-Hydrindanones[1]

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In this paper we report the results of a study of (1) the Beckman rearrangement on the oximes of *cis*- and *trans*-1-hydrindanones (**1**), *cis*- and *trans*-8-methyl-1-hydrindanones (**4**), *cis*- and *trans*-2,8-dimethyl-1-hydrindanones (**8**), and 16-methylestrone 3-methyl ether (**13**); and (2) the Schmidt reaction on *cis*- and *trans*-**8**. *cis*- and *trans*-**1**,[3] *cis*- and *trans*-**4**[4–6] and **13** are known compounds, and the oximes of the former, respectively

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[2] Graduate Research Assistant (1963–1967) on grants[1] supported by NIH; taken entirely from the Ph.D. Thesis of M. A. Stemniski, Fordham University, New York, N. Y., 1967.

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