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Reactions of Potassium Iron Carbonylate with Olefins and Alkyl Halides*1

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Potassium iron carbonylate, $KHFe(CO)_4$, reacted with ethyl acrylate, crotonate, 3-butenoate, styrene, and α-olefins at 40—70°C under an atmosphere of carbon monoxide. Methylmalonate was selectively obtained from the acrylate by treatment of the reaction mixture with an alcoholic iodine and hydrogen chloride solutions. Dipotassium iron carbonylate, $K_2Fe(CO)_4$, reacted with β-bromopropionate to give mainly methylmalonate. Isomerization of β-ethoxycarbonylpropionyliron carbonylate to the α-isomer occurred readily in contrast to isomerization of acylcobalt carbonyl. Both crotonate and 3-butenoate gave ethylmalonate as a major product and methylsuccinate and glutarate as minor ones. The results suggest that α-ethoxycarbonylbutyliron carbonylate is more predominant than the corresponding β- and γ-isomers in equilibrium state. This is in striking contrast to the case of acylcobalt carbonyl. Styrene yielded two isomeric aldehydes, α- and β-phenylpropionaldehydes. Ethyl caproate and enanthate were obtained from 1-pentene and 1-hexene, respectively in poor yield.

Some of the present authors demonstrated that cobalt hydrocarbonyl reacted with ethyl acrylate to give, selectively, α-ethoxycarbonylpropionylcobalt carbonyl which readily isomerized to β-isomer.[1] Styrene also reacted similarly with cobalt hydrocarbonyl. In the present work, carbonylation of olefins with iron carbonylate and the isomerization of the intermediate alkyl- or acyliron complexes were investigated in detail. The effect of the functional groups on the isomerization was examined in order to estimate the reaction mechanism. The difference of reactivity between the iron and cobalt complexes was clarified.

Experimental

Preparation of Potassium Iron Carbonylate, $KHFe(CO)_4$ and $K_2Fe(CO)_4$. An alcoholic solution of potassium iron carbonylate was prepared by Krumholz's method.[2] A 200 m*l* three-necked flask, fitted with a 50 m*l* dropping funnel, a gas inlet and a rubber stopple, was connected with a 500 m*l* gas buret and the atmosphere was then replaced with dry carbon monoxide.

A 1N alcoholic potassium hydroxide solution (33 m*l* or 44 m*l*) and iron pentacarbonyl (1.5 m*l*, 11 mmol) were syringed into the flask and then stirred for a few hours at room temperature to give a brown solution of potassium iron carbonylate.

Materials. Ethyl acrylate, ethyl crotonate, styrene, 1-pentene, 1-hexene, ethyl α- and β-bromopropionates, β-phenylpropionate, diethyl methylmalonate, diethyl succinate, ethyl caproate, and ethyl enanthate were commercial reagents. Iron pentacarbonyl was obtained from the Strem Chemicals Inc., bp 102°C. Diethyl ethylmalonate, diethyl methylsuccinate, and diethyl glutarate were prepared by the usual esterification of the corresponding carboxylic acids. Ethyl 3-butenoate was obtained from allyl cyanide[3] (bp 118—119°C, lit, 119°C). α-Phenylpropionaldehyde was obtained from acetophenone.[4] Starting materials were distilled before use and purity was checked by gas chromatography.

Reaction Procedures. To a solution of potassium iron carbonylate prepared as described above, olefin (33 mmol) or alkyl halide (22 mmol) was added with a syringe. The mixture was then stirred vigorously at 25—65°C under an atmosphere of carbon monoxide. After a certain reaction time, a 7N alcoholic hydrogen chloride solution (5—7 m*l*) and 50 m*l* of a saturated benzene solution of iodine were added dropwise into the reacting mixtures at room temperature; stirring was continued until gas evolution ceased. Sodium thiosulfate (5 g) was then applied to remove excess

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1) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, This Bulletin, **37**, 1190 (1964).

2) P. Krumholz and H. M. Stettiner, *J. Amer. Chem. Soc.*, **71**, 3035 (1949).

3) E. Rietz, "Organic Syntheses," Coll. Vol. III, (1955), p. 851.

4) C. F. H. Allen and J. VanAllen, *ibid.*, Coll. Vol. III, (1955), p. 733.

iodine. After 50 ml of water was added to the solution, the reaction products were extracted three times with 50 ml of benzene and dried over anhydrous magnesium sulfate overnight. The solution was concentrated to about 5% weight by distillation and then subjected to analysis.

Analytical Procedures. The reaction products were gas-chromatographed with a Shimadzu Model GC-3AH on a column, 3 m long, 3 mm in diameter, filled with Apiezon L or Carbowax on cerite at 150—180°C and at the carrier-gas (hydrogen) flow rate of 70 ml/min. Isomeric esters and aldehydes were confirmed and determined by direct comparison with authentic samples. The infrared spectra were measured with a Nippon Bunko Model DS-301 spectrophotometer on NaCl cells.

Results and Discussion

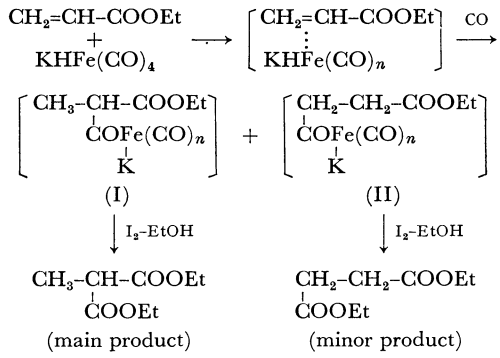
Reaction of $KHFe(CO)_4$ with Ethyl Acrylate. Results are summarized in Table 1. As shown

Table 1. Reaction of ethyl acrylate with potassium iron carbonylate, $KHFe(CO)_4$

Exp. No.	Reaction conditions[a] Temp. (°C)	Time (hr)	CO absorbed[b]	Yield of esters[b]	Distribution of isomers[c] (%) *iso*-Ester	*n*-Ester
1	25	30	0.76	0.14	100	0
2	40	14	1.00	0.16	100	0
3	50	4	1.00	0.59	96	4
4	50	6	1.00	0.22	84	16
5[d]	50	6	1.00	0.30	91	9
6	50	10	1.00	0.26	92	8
7	60	1	0.44	0.88	97	3
8	60	1.5	0.91	0.84	97	3
9	60	3	1.00	0.68	95	5

a) $KHFe(CO)_4$: 11 mmol (EtOH solution), Ethyl acrylate: 33 mmol
b) mol/mol $KHFe(CO)_4$
c) *iso*-Ester: Diethyl methylmalonate, *n*-Ester: Diethyl succinate
d) Methyl acrylate was used instead of ethyl acrylate.

in Scheme 1, ethyl acrylate reacted with potassium iron tetracarbonylate to give two isomeric diesters upon treatment with an alcoholic iodine and hydrogen chloride solutions. These diesters can be derived from the corresponding acyliron complexes, *i. e.*, α- and β-ethoxycarbonylpropionyliron carbonylates (I) and (II), as was proved in the case of acylcobalt carbonyls.[5] Diethyl methylmalonate was afforded as the main product and diethyl succinate as a minor one. Carbonylation of ethyl acrylate took place at temperatures above 25°C and an almost quantitative yield of esters was obtained for 1—1.5 hr at 60°C (Expts. 7 and 8). The consumption of potassium iron carbonylate was estimated by means of carbon monoxide absorption as in the case of cobalt hydrocarbonyl.[1] The absorption volume, however, was not always proportional to the yield of esters. The intermediate acyliron complexes seemed to decompose with a prolonged reaction time. The yield of the derived esters decreased in these cases (Expts. 3—7).



Scheme 1

At 25—40°C methylmalonate only was obtained, while at higher temperatures a small amount of succinate was also obtained (Expts. 3—9). The distribution of the esters was scarcely affected by reaction time and temperature. This implies that the potassium iron carbonylate gives selectively α-ethoxycarbonylpropionyliron carbonyl (I) in the same way as cobalt hydrocarbonyl,[1] but the branched acyliron complex (I) is not converted to the β-isomer (II) so readily as the corresponding acylcobalt complex. From these results, we see that the isomerization of the acyliron complexes is apparently different from that of two acylcobalt complexes between which the equilibrium lies well toward the side of the β-isomer. The following experiments were carried out in order to examine the equilibrium of isomerization.

Reaction of Dipotassium Iron Carbonylate, $K_2Fe(CO)_4$, with Ethyl α- and β-Bromopropionates. Results are shown in Table 2 and Scheme 2. The reaction of α- or β-bromopropionate with dipotassium iron carbonylate was carried out at 30—50°C under an atmosphere of carbon monoxide. The usual treatment resulted in the formation of two isomeric esters, diethyl methylmalonate and diethyl succinate in both reactions.

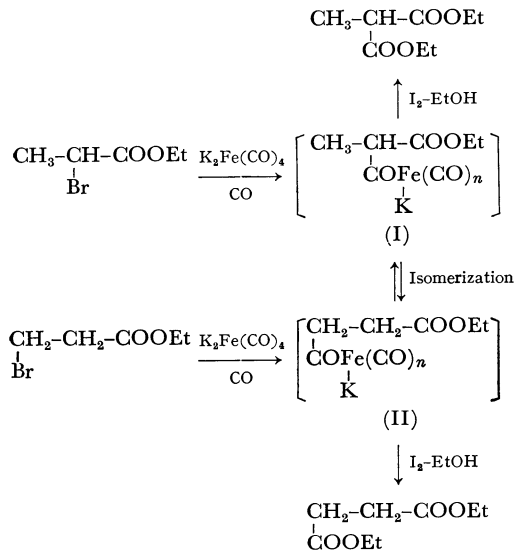
It is interesting that methylmalonate was predominantly obtained from the reaction of ethyl β-bromopropionate, while the same product was given from ethyl α-bromopropionate at 30—50°C (Expts. 10—17). The percentage of isomerization of the intermediate complexes (I and II) was estimated by the distribution of the derived esters. In the case of α-bromopropionate, the percentage of isomerization to the β-complex (II) was only

5) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **84**, 2499 (1962).

Table 2. Reaction of ethyl α- and β-bromopropionates with dipotassium iron carbonylate, $K_2Fe(CO)_4$

Exp. No.	Substrate	Reaction conditions: Temp. (°C)	Reaction conditions: Time (hr)	CO absorbed[b]	Yield of esters[c]	Isomerization[d] (%)
10[e]	Ethyl α-bromopropionate	30—50	15+2	0.45	0.45	2
11	Ethyl α-bromopropionate	30—50	15+6	0.44	0.52	2
12	Ethyl α-bromopropionate	60	7	0.50	0.34	6
13	Ethyl β-bromopropionate	30—50	15+2	1.00	0.11	94
14	Ethyl β-bromopropionate	30	10	0.31	0.20	81
15	Ethyl β-bromopropionate	30	25	0.77	0.39	95
16	Ethyl β-bromopropionate	40	1.3	0.30	0.30	66
17	Ethyl β-bromopropionate	40	8	1.00	0.20	81

a) $K_2Fe(CO)_4$: 11 mmol (EtOH solution), Ethyl α- and β-bromopropionates: 22 mmol
b) mol/mol $K_2Fe(CO)_4$
c) Diethyl succinate and diethyl methylmalonate, mol/mol $K_2Fe(CO)_4$
d) In the case of α-bromopropionate: Diethyl succinate/Total Esters × 100
In the case of β-bromopropionate: Diethyl methylmalonate/Total Esters × 100
e) The reaction was carried out in two stages, first at 30°C for 15 hr and then at 50°C for 2 hr.



Scheme 2

2—6%, whereas in the case of β-bromopropionate the percentage of isomerization to the α-complex (I) amounted to 95% (Expts. 13—17). Accordingly, isomerization of the straight-chained complex (II) to the branched complex (I), occurs more readily than the reverse isomerization and the equilibrium between these complexes lies far to the side of the branched isomer. Ethyl acrylate was not afforded under the conditions employed and therefore dehydrobromination of α- and β-bromopropionates would not occur in the reaction system.

Reaction of Ethyl Crotonate and Ethyl 3-Butenoate with Potassium Iron Carbonylate, $KHFe(CO)_4$. Results are shown in Table 3. The reactions of ethyl crotonate and its homolog were carried out to confirm a similar isomerization. Ethyl crotonate was carbonylated with potassium iron carbonylate to afford mainly diethyl ethylmalonate (A) and other isomers, diethyl methylsuccinate (B) and diethyl glutarate (C) as by-products (Expts. 18—25). Ethyl 3-butenoate gave the same products as in the case of ethyl crotonate and the distribution of products was similar in both reactions (Expts. 26 and 27). As shown in Scheme 3, isomers (A, B and C) may be derived from the corresponding α-, β- and γ-ethoxycarbonylacyliron carbonylate (III, IV and V), respectively.

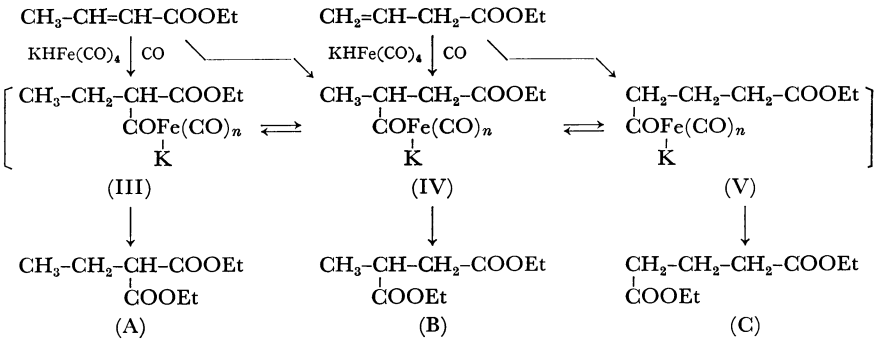
The distribution of isomers shown in Table 3 implies that the intermediates, iron complexes (III, IV and V), were isomerized to each other at 60—70°C, and that the equilibrium was favorable to α-isomer (III). The results are consistent with those of the reaction of the ethyl acrylate or the alkyl halides with respect to isomer equilibrium.

Reaction of Potassium Iron Carbonylate with Styrene. Results are summarized in Table 4 and Scheme 4. Styrene reacted with potassium iron carbonylate to give two isomeric aldehydes, α- and β-phenylpropionaldehydes, instead of expected esters, α- and β-phenylpropionates. Tollen's reagent test for the products was positive. The infrared spectra had bands at 1725, 2708, 2800 cm^{-1}, characteristic of aldehydes. They were identified with those of authentic samples. The carbonylation of styrene occurred at 40—65°C, and the yield of aldehydes was not more than 50% in all runs. The poor yield seems to be partly due to instability of the intermediate complexes. These aldehydes may be readily formed with reduction of the α- and β-phenylpropionyliron carbonyls (VI and VII) as shown in Scheme 4. The mechanism is supported by the fact that *n*-propyl iodide reacted with the iron carbonylate to give *n*-butyraldehyde in good

Table 3. Reaction of ethyl crotonate, and ethyl 3-butenoate with potassium iron carbonylate

Exp. No.	Reaction conditions[a] Temp. (°C)	Time (hr)	CO absorbed[b]	Yield of esters[c]	Distribution of esters[d] (A)	(B)	(C)
	Ethyl Crotonate						
18	60	3	0.11	0.02	100	0	0
19	60	5	0.30	0.65	95	5	0
20	60	7	0.45	0.26	93	7	0
21	60	8.5	0.61	0.35	91	9	0
22	60	9.5	1.00	0.23	91	9	0
23	60	10.5	1.00	0.18	86	14	0
24	70	1.5	0.31	0.54	89	7	4
25	70	3.5	1.00	0.19	73	14	13
	Ethyl 3-Butenoate						
26	60	5.5	0.60	0.37	92	5	3
27	60	7	1.00	0.35	80	13	7

a) $KHFe(CO)_4$: 11 mmol (EtOH solution), Ethyl Crotonate or Ethyl 3-Butenoate: 33 mmol
b) mol/mol $KHFe(CO)_4$
c) Diethyl ethylmalonate(A), Diethyl methylsuccinate(B), and Diethyl glutarate(C); mol/mol $KHFe(CO)_4$
d) (A), (B) or (C)/Total Esters × 100



Scheme 3

Table 4. Reaction of styrene with potassium iron carbonylate

Exp. No.	Reaction conditions[a] Temp. (°C)	Time (hr)	CO absorbed[b]	Products[c] Ethylbenzene	Total aldehydes	Distribution of aldehydes[d] (%)
28	40	10	0.32	0.04	0.05	11
29	40	35	1.00	0.09	0.28	11
30	55	5	0.35	0.05	0.07	13
31	55	10	0.76	0.10	0.16	18
32	55	15	1.00	0.18	0.39	21
33	55	20	1.00	0.22	0.50	21
34	65	3	0.66	0.12	0.09	20
35	65	6	1.00	0.10	0.27	26
36	65	10	1.00	0.24	0.24	28

a) $KHFe(CO)_4$: 11 mmol (EtOH solution), Styrene: 33 mmol
b) mol/mol $KHFe(CO)_4$
c) Aldehydes: α- and β-phenylpropionaldehydes, mol/mol $KHFe(CO)_4$
d) β-Phenylpropionaldehyde/Total Aldehydes × 100

yield.[6]

The distribution of β-phenylpropionaldehyde was already attained to 11—13% in the initial stage of the reaction, while in the case of ethyl acrylate or ethyl crotonate, the corresponding β-isomer was not observed initially. The discrepancy may be explained as follows. Potassium iron carbonylate attacked both the α- and β-carbons of styrene, whereas it carbonylated selectively the α-carbon of ethyl acrylate in the early stage.

In general, the distribution of acylmetal carbonyl isomers was affected by the following two factors: (1) the direction of addition of metal carbonylate to a carbon-carbon double bond and (2) the isomerization of intermediate alkyl- or acylmetal carbonyls.[1] The latter factor affected particularly the distribution of products in the case of ethyl acrylate and its homologs.

The reactions of dipotassium iron carbonylate with α- and β-bromoethylbenzenes were carried

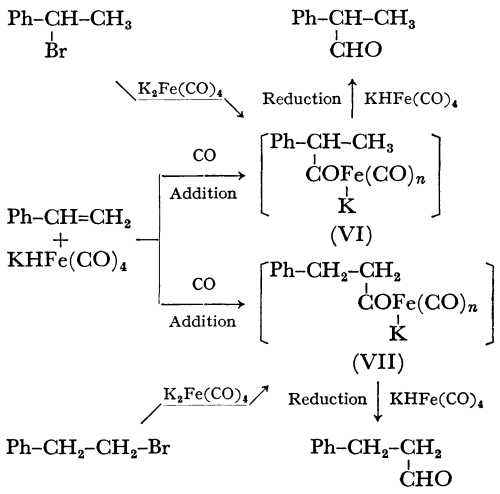
6) Y. Takegami, Y. Watanabe, H. Masada and I. Kanaya, This Bulletin, **40**, 1456 (1967).

Table 5. Reaction of α- and β-bromoethylbenzenes with dipotassium iron carbonylate

Exp. No.	Substrate	Conditions[a] Temp. (°C)	Conditions[a] Time (hr)	CO absorbed[b]	Products[c] Ethylbenzene	Products[c] Total aldehydes	Isomerization[d] (%)
37	α-Bromoethylbenzene	40	35	0.77	0.30	0.51	0
38	α-Bromoethylbenzene	65	3	0.30	0.33	0.07	3
39	α-Bromoethylbenzene	65	6	0.33	0.42	0.08	2
40	β-Bromoethylbenzene	40	35	1.00	0.18	0.30	0
41	β-Bromoethylbenzene	65	3	0.72	0.13	0.18	1
42	β-Bromoethylbenzene	65	6	1.00	0.25	0.11	3

a) $K_2Fe(CO)_4$: 11 mmol(EtOH solution), α- and β-Bromoethylbenzenes: 11 mmol
b) mol/mol $K_2Fe(CO)_4$
c) Aldehydes: α- and β-Phenylpropionaldehydes, mol/mol $K_2Fe(CO)_4$
d) In the case of α-bromoethylbenzene: β-Phenylpropionaldehyde/Total Aldehydes × 100
In the case of β-bromoethylbenzene: α-Aldehyde/Total Aldehydes × 100

out to examine the isomerization of α- and β-phenylpropionyliron complexes (VI and VII). The results are summarized in Table 5. Such an isomerization as from VI to VII or from VII to VI was scarcely observed. Thus it seems that the distribution of aldehydes corresponds to the direction of the addition of iron carbonylate to styrene. α-Phenylpropionaldehyde should be derived from α-phenylpropionyliron carbonylate alone as well as in the case of β-phenylpropionaldehyde (Scheme 4).

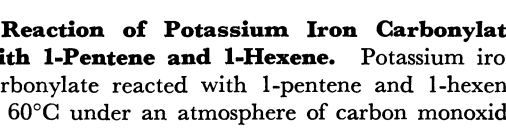


Scheme 4

Reaction of Potassium Iron Carbonylate with 1-Pentene and 1-Hexene. Potassium iron carbonylate reacted with 1-pentene and 1-hexene at 60°C under an atmosphere of carbon monoxide as shown in Table 6. Ethyl enanthate was obtained as a carbonylation product of 1-hexene. The yield of ester was invariably low under various conditions. Most of 1-hexene was readily reduced into *n*-hexane in the reaction system. Similarly 1-pentene was carbonylated with the iron carbonylate to give ethyl caproate in a yield less than 1%, whereas in the case of cobalt hydrocarbonyl, ethly caproate and ethyl α-methylvalerate were obtained in good yield under milder conditions.[7]

At room temperature carbonylation of α-olefin with potassium iron carbonylate could not occur. At higher temperatures, the α-olefin may be readily reduced into *n*-paraffin instead of carbonylation.

Discussion of Acyliron Carbonyls. The reaction of ethyl acrylate was followed by infrared spectra in order to prove the participation of acyliron carbonyls as reaction intermediates. After ethyl acrylate had been carbonylated and the complex formed neutralized with dilute alcoholic hydrogen chloride solution, excess acrylate and solvent were evaporated to dryness at 0°C in a high vacuum. The iron complex was extracted with cold benzene under carbon monoxide atmosphere to give a dark red solution and subjected to analysis immediately. The infrared spectrum in benzene contained coordinated carbonyl bands at 2118(w), 2005(vs) and 1967(s) cm^{-1}, an ester carbonyl band at 1742(s) cm^{-1}, the acyliron carbonyl bands at 1678(m) and 1710(m) cm^{-1}. The sample was then treated with an alcoholic iodine solution. The vapor phase chromatogram showed the presence of 97% of diethyl methylmalonate and 3% of diethyl succinate. Ethyl acrylate and its polymer were not detected by infrared spectra and chromatography. Thus the acyliron carbonyls (I′, II′) are suggested to be intermediate complexes in this reaction.



Triphenylphosphine complexes of acyliron carbonylates were scarcely obtained in the usual way on account of the cleavage to iron carbonyl triphenylphosphine, $Fe(CO)_4PPh_3$. Our suggestion of acyl-

7) Y. Takegami, Y. Watanabe, H. Masada and T. Mitsudo, This Bulletin, **42**, 206 (1969).

Table 6. Reaction of potassium iron carbonylate with 1-pentene and 1-hexene

Exp. No.	Substrate	Reaction conditions[a]		CO absorbed[b]	Products	
		Temp. (°C)	Time (hr)		Ester[b] (%)	*n*-Paraffin[c] (%)
43[d]	1-Pentene	25—60	4+20	~0	0.3	—
44	1-Hexene	60	10	~0	0.2	64
45	1-Hexene	60	25	~0	0.2	69
46[e]	1-Hexene	60	10	~0	0.2	50

a) $KHFe(CO)_4$: 11 mmol (EtOH solution), 1-Pentene or 1-Hexene: 33 mmol
b) mol/mol $KHFe(CO)_4 \times 100$; Ester: Ethyl caproate (1-Pentene), Ethyl enanthate (1-Hexene)
c) *n*-Paraffin: *n*-Hexane, mol/mol Hexene × 100
d) The reaction was carried out in two stages, first at 25°C for 4 hr and then at 60°C for 20 hr.
e) Benzene was used as solvent.

iron complexes is strongly supported. Heck and Breslow[8] showed the infrared spectrum of the mixture of α- and β-methoxycarbonylpropionylcobalt tricarbonyl triphenylphosphines, which contained carbonyl bands at 1740(vs) and 1670(m) cm^{-1}. We have elucidated the fact that the α-methoxycarbonylpropionylcobalt complex had bands at 1743(m) and 1706(s) cm^{-1}, while the β-isomer had bands at 1745(s) and 1675(s) cm^{-1} assigned to an ester and acylcobalt carbonyls, respectively. On the other hand, maleyliron tetracarbonyl has a doublet in the 1665 cm^{-1} region due to the absorption of the ketonic groups of the organic ligands.[9] The spectrum of ethoxymalonyliron dicarbonyl(nitrosyl)triphenylphosphine contains acyl and ester bands at 1689 and 1754 cm^{-1}, which are similar to the bands observed in the case of acyliron complex (I').[10]

The results are summarized as follows. Potassium iron carbonylate reacted with unsaturated carboxylic esters and styrene to give carbonylated products under an atmosphere of carbon monoxide at 40—65°C. On the other hand, α-olefin was scarcely carbonylated under these conditions. Cobalt hydrocarbonyl reacted readily with various acrylates and styrene to give the branched-chain complexes mainly at 0°C for several hours.[1]

β-Ethoxycarbonylpropionyliron carbonyl was easily isomerized to the α-isomer and the reverse isomerization hardly occured, whereas α-ethoxycarbonylpropionylcobalt carbonyl completely isomerized to the β-isomer in a few hours at 25°C.[1] It is concluded that the isomeric equilibrium of acyliron complexes lies well towards the side of the α-isomer, in contrast to that of acylcobalt complexes. The isomerization of acyliron complexes was greatly affected by the functional groups in the olefins and alkyl halides. For example, ethoxycarbonylpropionyliron carbonyl was easily isomerized, while phenylpropionyliron carbonyl was scarcely isomerized. The electronic effect of the ethoxycarbonyl group[11] as well as the isomeric equilibrium of acyliron complexes promotes the isomerization of the iron complexes.

8) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 4026 (1961).
9) W. Hübel, "Organic Syntheses *via* Metal Carbonyls," Vol. I, ed. by I. Wender and P. Pino, Interscience Publishers, New York, N. Y. (1968), p. 325.
10) F. M. Chaudhari, G. R. Knox and P. L. Pauson, *J. Chem. Soc., C*, **1967**, 2255.
11) S. Suga, H. Masada, H. Suda, Y. Takegami and Y. Watanabe, This Bulletin, **42**, 2920 (1969).