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Studies of the Organic Reactions of Metal Carbonyls. XVII.[*1] The Reaction of Potassium Iron Carbonylates with Allyl Halide and Its Derivatives

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The reactions of potassium iron carbonylates ($K_2Fe(CO)_4$, $KHFe(CO)_4$ and $K_2Fe_2(CO)_8$) with allyl halide and its derivatives have been studied. Allyl halide and its derivatives react readily with these carbonylates in ethyl alcohol at 30°C to give the corresponding and isomerized olefins. The reaction of allyl chloride in hydrous ethyl alcohol gives propylene in a good yield and 1,5-hexadiene as a by-product. In dry ethyl alcohol, the yield of propylene decreases. The reaction of *trans*-1-chloro-2-butene gives *trans*-2-butene (the major product), *cis*-2-butene, and 1-butene. The reaction of 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene gives 2-methyl-2-butene (the major product), 3-methyl-1-butene, and 2-methyl-1-butene. These reactions are considered to proceed *via* σ- and π-allyl iron carbonyl complexes.

Previous work in this laboratory has shown that potassium iron carbonylates, mainly $KHFe(CO)_4$, react with isoprene in alcohol to give three different monoolefins, and that the yields and the distribution of these monoolefins are remarkably affected by the reaction conditions (the solvents and the atmosphere).[1)]

The present study deals with the reactions of iron carbonylates, mainly $K_2Fe(CO)_4$, with allyl halide compounds. The results obtained here indicate that allyl halide compounds react with the iron carbonylates to give σ- and π-allylic iron carbonyl complexes, which then decompose in such polar solvents as alcohol and water to the corresponding olefin and isomerized olefins.

Experimental

Three potassium iron carbonylates, $KHFe(CO)_4$, $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$, were prepared according to the method described in a previous paper.[2)] A 50 m*l* portion of a 0.011 M $KHFe(CO)_4$, $K_2Fe(CO)_4$, or 0.0055 M $K_2Fe_2(CO)_8$ solution was used in each run.

Materials. 1-Chloro-3-methyl-2-butene (A) and 3-chloro-3-methyl-1-butene (B) were prepared by bubbling hydrogen chloride into isoprene at −10°C. These products were fractionated by vacuum distillation into two fractions.[*2] The allyl halides, *trans*-1-chloro-2-butene, 3-chloro-2-methyl-1-propene, iron pentacarbonyl, and the other compounds employed in this study were all commercial products.

Reaction Procedure. To the solution of the potassium iron carbonylate, a certain amount of allyl halide or its derivatives was added, and then the mixture was agitated vigorously at 30°C under an atmospheric pressure of nitrogen or carbon monoxide. After a certain reaction time, the reaction flask was connected with a cold trap immersed in liquid nitrogen and fitted with a vacuum pump. The gases in the reaction flask were collected in the trap at 30 mmHg. The trap was allowed to warm to room temperature and then heated to 80°C, and the gas evolved was submitted to analysis. The liquid reaction mixture was analyzed at the same time.

Analytical Procedures. The reaction products were gas-chromatographed. For the gaseous products, a column packed with active carbon (0.3 cmϕ, 3 m) or a column packed with dimethylsulfolan (0.3 cmϕ, 5 m) was used. For the liquid products, a Golay R 45 column (0.25 mmϕ, 45m) and a column packed with SE 30 on a chromasorb were used.

Results and Discussion

The Reactions of $K_2Fe(CO)_4$ and $K_2Fe_2(CO)_8$ with Allyl Halides. Table 1 summarizes the results of these reactions, which were carried out under an atmosphere of carbon monoxide or nitrogen at 30°C. $K_2Fe(CO)_4$ reacts readily with allyl chloride, while the light-brown reaction mixture immediately turns dark red, and then yellow brown. As the reaction products, propylene (the major product) and 1,5-hexadiene are obtained.

[*1] Part XVI: This Bulletin, **42**, 206 (1969). Presented at the Symposium on Organometallic Compounds, Tokyo, October, 1968.

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

2) Y. Takegami, Y. Watanabe, H. Masada and I. Kanaya, *ibid.*, **40**, 1456 (1967).

[*2] One, A 79%, B 21%; the other, A 17%, B 83%.

TABLE 1. THE REACTION OF $KHFe(CO)_4$, $K_2Fe(CO)_4$ AND $K_2Fe_2(CO)_8$ WITH ALLYL HALIDES AT 30°C

Exp. No.	Allyl halide	Reaction conditions*				Products**	
		Iron carbonylate	Solvent	H_2O Content	Atmosphere	Propylene	1,5-Hexadiene
1	Allyl chloride***	$K_2Fe(CO)_4$	EtOH	1	N_2	1.90	0.18
2	Allyl chloride****	$K_2Fe(CO)_4$	EtOH	0	N_2	1.00	0.15
3	Allyl chloride	$K_2Fe(CO)_4$	EtOH	1	CO	1.75	0.13
4	Allyl chloride	$KHFe(CO)_4$	EtOH	1	CO	1.31	0.18
5	Allyl chloride	$K_2Fe_2(CO)_8$	EtOH	1	CO	1.22*****	0.15*****
6	Allyl bromide	$K_2Fe(CO)_4$	EtOH	1	CO	0.75	0.16
7	Allyl iodide	$K_2Fe(CO)_4$	EtOH	1	CO	0.84	0.19
8	Allyl chloride	$K_2Fe(CO)_4$	THF	0	N_2	0.42	0
9	Allyl chloride	$K_2Fe(CO)_4$	Benzene	0	N_2	0.27	0.02

* 1 atm, 3—4 hr, allyl halide 3.0 mol/mol-$Fe(CO)_4^{2-}$

** mol/mol-$Fe(CO)_4^{2-}$

*** CO_2 (0.43 mol/mol-$Fe(CO)_4^{2-}$) and CO (0.81 mol/mol-$Fe(CO)_4^{2-}$) were evolved.

**** CO_2 (0.07 mol/mol-$Fe(CO)_4^{2-}$) and CO (0.67 mol/mol-$Fe(CO)_4^{2-}$) were evolved.

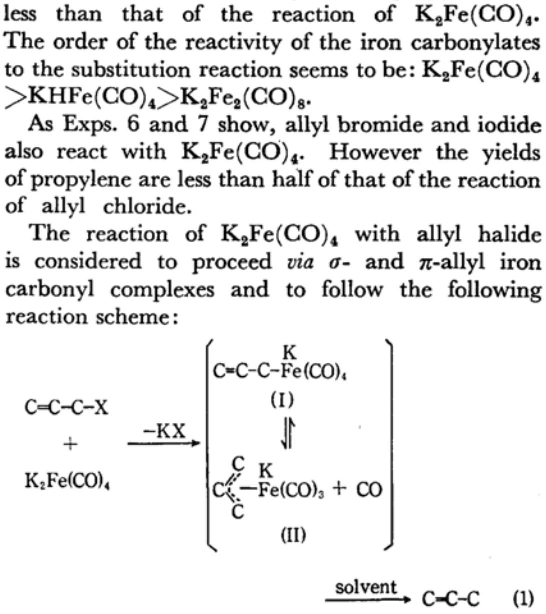
***** mol/g-atm Fe

The yield of propylene amounts to about 2 mol*3 in hydrous ethyl alcohol (Exp. 1). However, in dry ethyl alcohol the yield of propylene decreases to 1 mol (Exp. 2). In both cases the yield of 1,5-hexadiene is almost 0.2 mol. Comparing Exp.1 with Exp. 3, the nitrogen atmosphere seems to be little more favorable to the production of propylene than the carbon monoxide atmosphere. Under carbon monoxide some side reactions, such as a carbonylation reaction, occur. The infrared spectrum of the reaction mixture treated with an alcoholic solution of iodide and hydrogen chloride has a band at 1738 cm^{-1} characteristic of an ester, indicating that some acyl-iron carbonyl complex is formed.

$KHFe(CO)_4$ and $K_2Fe_2(CO)_8$ also react with allyl chloride to give propylene and 1,5-hexadiene (Exps. 4 and 5), but the yields of propylene are less than that of the reaction of $K_2Fe(CO)_4$. The order of the reactivity of the iron carbonylates to the substitution reaction seems to be: $K_2Fe(CO)_4 > KHFe(CO)_4 > K_2Fe_2(CO)_8$.

As Exps. 6 and 7 show, allyl bromide and iodide also react with $K_2Fe(CO)_4$. However the yields of propylene are less than half of that of the reaction of allyl chloride.

The reaction of $K_2Fe(CO)_4$ with allyl halide is considered to proceed *via* σ- and π-allyl iron carbonyl complexes and to follow the following reaction scheme:



(1)

In the first step, $K_2Fe(CO)_4$ reacts with allyl halide to give the σ-allyl complex (I). This complex seems then to be converted to the π-allyl complex (II) with an evolution of carbon monoxide. These complexes may be unstable in an alcoholic solution, thus abstracting hydrogen from the solvent and giving propylene in a good yield. This reaction scheme is supported by the fact that, under nitrogen, a considerable amount of carbon monoxide evolves (Exps. 1 and 2).

When 1 mol of water is present in the reaction system, a considerable amount of carbon dioxide also evolves (Exp. 1). Thus, the water present in the system is more favorable to the formation of propylene and carbon dioxide. This fact seems to indicate that the water acts as one of the hydrogen sources and that a reaction between the water and carbon monoxide occurs to give hydrogen and carbon dioxide:

$$H_2O + CO \rightarrow 2(H) + CO_2 \qquad (2)$$

This reaction mechanism is, however, not yet completely clear.

In dry tetrahydrofuran and in dry benzene the iron carbonylate is less reactive and the yield of propylene decreases to lees than half of that in dry ethyl alcohol (Exps. 8 and 9). These solvents are unsuitable for this reaction because the iron carbonylate is insoluble in benzene and only slightly soluble in THF. In these solvents, the formation of 1,5-hexadiene is also retarded.

The Reaction of *trans*-1-Chloro-2-butene and 3-Chloro-2-methyl-1-propene. The results of the reactions are summarized in Table 2. All of the reactions were carried out at 30°C in ethyl alcohol. *trans*-1-Chloro-2-butene reacts with $K_2Fe(CO)_4$ to give *trans*-2-butene (the major product), *cis*-2-butene, and 1-butene. The yield of the

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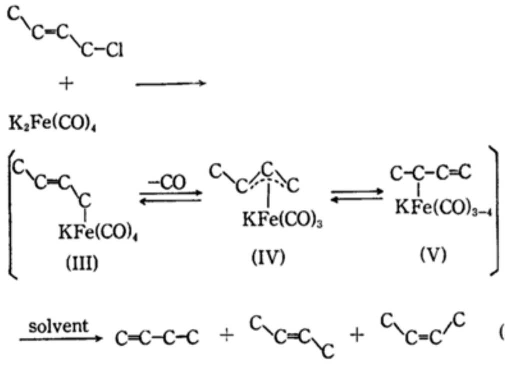
*3 Hereafter mol means mole per mole of $Fe(CO)_4^{2-}$.

TABLE 2. THE REACTION OF $K_2Fe(CO)_4$ WITH THE DERIVATIVES OF ALLYL HALIDE IN ETHYL ALCOHOL AT 30°C

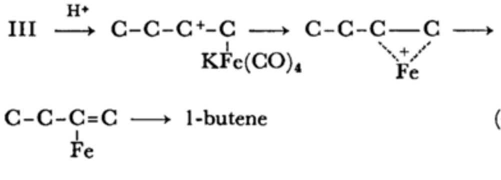
		Reaction conditions****			Products**				
Exp. No.	Reagent	H_2O Content*	Atmos-phere	Reaction time (min)	1-Butene	*cis*-2-Butene	*trans*-2-Butene	2-Methyl-propene	Total yield of mono-olefins
10	*trans*-1-Chloro-2-butene	1	CO	10	0.16 (21)	0.14 (19)	0.44 (60)		0.74
11	*trans*-1-Chloro-2-butene	1	CO	60	0.15 (18)	0.15 (19)	0.51 (63)		0.81
12	*trans*-1-Chloro-2-butene	1	CO	240	0.20 (18)	0.20 (18)	0.72 (64)		1.12
13	*trans*-1-Chloro-2-butene	0	N_2	60	0.19 (19)	0.18 (19)	0.60 (62)		0.97
14	*trans*-1-Chloro-2-butene	0	N_2	4(d)***	0.17 (15)	0.16 (15)	0.78 (70)		1.11
15	3-Chloro-2-methyl-1-propene	1	N_2	180				1.75	

* mol/mol-$Fe(CO)_4^{2-}$
** mol/mol-$Fe(CO)_4^{2-}$ ( ): mol%, total monoolefins at each run=100%
*** (d): day
**** 3.0 mol/mol-$K_2Fe(CO)_4$

olefins amounts to 1.1 mol. The distribution of these monoolefins is approximately independent of the atmosphere, the presence of water, and the reaction time (10—240 min). After 4 days (Exp. 14), however, the percentage of *trans*-2-butene increases to 70%, while those of 1-butene and *cis*-2-butene decrease to 15% and 15% respectively, showing that under these conditions the isomerization among the butenes slowly occurs. This reaction is considered to proceed *via* σ- and π-allyl iron carbonyl complexes and to follow the following reaction scheme:

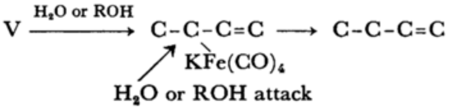

(3)

Thus, two σ-allylic compleexs (III and V) and one π-allylic complex (IV) are possible. For the formation of 1-butene, two routes from the complexes III and V are probable.
From the complex III:



$$\mathrm{III} \xrightarrow{H^+} \mathrm{C{-}C{-}}\underset{\mathrm{KFe(CO)_4}}{\mathrm{C^+}}\mathrm{{-}C} \longrightarrow \mathrm{C{-}C{-}}\underset{\mathrm{Fe}}{\mathrm{C{-}\overset{+}{}{-}C}} \longrightarrow \mathrm{C{-}C{-}}\underset{\mathrm{Fe}}{\mathrm{C}}\mathrm{{=}C} \longrightarrow \text{1-butene} \tag{4}$$

From the complex V:



$$\mathrm{V} \xrightarrow{H_2O \text{ or } ROH} \underset{\nearrow\ \mathrm{KFe(CO)_4}}{\mathrm{C{-}C{-}C{=}C}} \longrightarrow \mathrm{C{-}C{-}C{=}C} \tag{5}$$
H_2O or ROH attack

The π-allylic structure can reasonably be considered to be more stable than the σ-allyl structures. σ-Allyl manganese carbonyl has been suggested to decompose in the presence of an acid to give propylene in a way similar to that of Eq.(4).[3] In this case the reaction was carried out in a neutral or a rather basic solution. Moreover, it is safe to conclude that the complex III is more stable and more dominant than the complex V, which has a structure with larger steric hindrance. Accordingly, the route (5) is more probable for the formation of 1-butene. The complexes III and V seem to give 2-butene and 1-butene respectively. This consideration is supported by the facts that the percentages of 2-butenes are larger than that of 1-butene and that the isomerization among the the butenes occurs slowly under the conditions employed.

3-Chloro-2-methyl-1-butene also reacts with $K_2Fe(CO)_4$ to give 2-methylpropene in a good yield (Exp. 15).

The Reaction of 1-Chloro-3-methyl-2-butene and 3-Chloro-3-methyl-1-butene. The results of the reactions are summarized in Table 3. All of the reactions were carried out in ethyl alcohol at 30°C.

As Table 3 shows, 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene react with $K_2Fe(CO)_4$ and $KHFe(CO)_4$ to give three different

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[3] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, **1963**, 189.

TABLE 3. THE REACTION OF $K_2Fe(CO)_4$ AND $KHFe(CO)_4$ WITH 1-CHLORO-3-METHYL-2-BUTENE AND 3-CHLORO-3-METHYL-1-BUTENE IN ETHYL ALCOHOL

		Reaction conditions				Products		
						Distribution of monoolefins (%)		
Exp. No.	Reagent	mol ratio Reagent/ $Fe(CO)_4^{2-}$	H_2O Content*	Reaction time**	Yield of mono-olefins*	3-Methyl-1-butene (A)	2-Methyl-1-butene (B)	2-Methyl-2-butene (C)
21	1-Chloro-3-methyl-2-butene	1	0	1.5	0.64	20	1	79
22	1-Chloro-3-methyl-2-butene	1	0	2(d)	0.59	5	5	90
23	1-Chloro-3-methyl-2-butene	3	1	1.5	0.98	7	7	86
24	1-Chloro-3-methyl-2-butene	3	0	1.5	0.82	5	5	90
25*	1-Chloro-3-methyl-2-butene	3	0	1.5	0.98	5	7	88
26	3-Chloro-3-methyl-1-butene	1	0	1.5	0.55	18	3	79
27	3-Chloro-3-methyl-1-butene	3	1	1.5	1.29	9	7	84
28	3-Chloro-3-methyl-1-butene	3	1	2(d)	1.23	9	6	85
29	3-Chloro-3-methyl-1-butnee	3	0	1.5	1.07	9	6	86

* mol/mol-$Fe(CO)_4^{2-}$

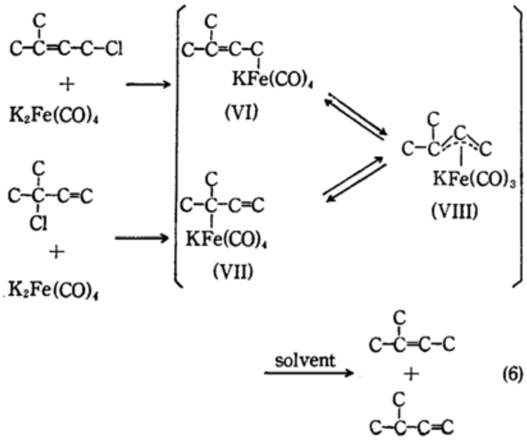
** hr, (d): day

*** $KHFe(CO)_4$ used

monoolefins, 2-methyl-2-butene (C), 3-methyl-1-butene (A), and 2-methyl-1-butene (B). At a high mole ratio ($RX/Fe(CO)_4^{2-}=3.0$), the distribution of the olefins is almost independent of the reaction conditions (the atmosphere, the presence of water, and the reaction time 1.5 hr —2 day). Under these conditions the olefin C is predominant, its percentage amounting to 85—90%; the olefins seem to be almost in an equilibrium because the distribution of the olefins remains unchanged with an increase in the reaction time.

When the mole ratio is 1.0 (Exps. 21 and 26), the olefins A and C predominate in the initial stage of the reactions. In this case the percentage of the olefin A amounts to 20%.

Judging from the similarity between the reactions of 1-chloro-3-methyl-2-butene and 3-chloro-3-methyl-1-butene, these reactions seems to have the same intermediates. Thus, the following reaction scheme seems reasonable:



(6)

In these cases, two σ-allyl complexes and one π-allyl complex are possible. The complex VI may be more stable than the complex VII because the tertiary structure of the latter has a larger steric hindrance. Accordingly, the equilibrium between them may be much more favorable to the complex VI. Thus, starting with even 3-chloro-3-methyl-1-butene under the conditions employed, the complex VI seems to be readily formed, giving the olefin C as the major product. The formation of the π-complex VIII is supported by the evolution of carbon monoxide.

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