BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1417—1422 (1968)

The Benzylation and Phenylation Reactions of Unsaturated Compounds Using Organo Monohalides and Polynuclear Iron Carbonyl

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(Received December 23, 1967)

The reaction of iodobenzene and benzyl halides (Cl, Br and I) with $Fe_3(CO)_{12}$ (mole ratio; $Fe_3(CO)_{12}/R-X=1/3$) gave the corresponding symmetrical ketones (18—55.2%). The increasing order of the reactivity of the organo halides to $Fe_3(CO)_{12}$ was as follows: iodobenzene< benzyl chloride<benzyl bromide<benzyl iodide. In the reaction of benzyl chloride with $Fe_3(CO)_{12}$, when two-thirds of the $Fe_3(CO)_{12}$ had been used, or moles equal to benzyl chloride, the yields of the ketones were increased to 87% (total yield). The same reaction in the presence of olefin produced benzylation or phenylation products of the olefin; for example, the reaction of benzyl iodide with $Fe_3(CO)_{12}$ in the presence of acrylonitrile (in tetrahydrofuran) gave 4-phenylbutyronitrile (30.2%) and 4-cyano-6-phenylhexanonitrile (10.0%). When olefin with a higher coordinating ability to iron carbonyl was used, the yields of the benzylated adducts of the olefin decreased, while when the more reactive organo halide was used, the yields increassed. Thus, it was postulated that organo halide reacted with $Fe_3(CO)_{12}$ to form the σ-complex, benzyl(or phenyl)iron carbonyl halide, as an intermediate to the benzylation (or phenylation) products. The benzylation and phenylation reactions proceeded smoothly in a polar solvent (dimethylformamide or ethanol) to give high yields. The benzylation of phenylacetylene did not occur in benzene, but in a polar solvent it proceeded, giving 1,3-diphenylpropane and -propene. The mechanistic aspects of these reactions are discussed below.

In a previous paper,[1] we reported that organo monohalide (benzyl chloride and iodobenzene) reacted with polynuclear iron carbonyls, triiron dodecacarbonyl [$Fe_3(CO)_{12}$], and diiron nonacarbonyl [$Fe_2(CO)_9$], to form the σ-complex as an intermediate, from whose decomposition the corresponding symmetrical ketone was produced, while when olefin was present in the reaction, its benzylated adduct was obtained.

In this paper, we wish to report on our study of several factors which affect the above benzylation reaction; the reactivity of organo monohalide to $Fe_3(CO)_{12}$, the coordinating ability of olefin to $Fe_3(CO)_{12}$, the remarkable solvent effect, and the effect of the mole ratio between organo monohalide and $Fe_3(CO)_{12}$.

Results and Discussion

A) The Reaction of Organo Monohalide with $Fe_3(CO)_{12}$ in the Presence of Olefin.

The Effect of the Coordinating Ability of Olefin. The reaction of iodobenzene (0.05 mol) with $Fe_3(CO)_{12}$

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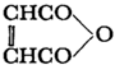
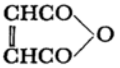
[1] I. Rhee, M. Ryang and S. Tsutsumi, *J. Organometal. Chem.*, **9**, 361 (1967).

TABLE 1. REACTION OF ORGANO MONOHALIDE WITH $Fe_3(CO)_{12}$ (mole ratio 1 : 1/3)

R-X	Solvent	Temp. °C	Convn.[c)] %	Products, %[a)]		
				R-R	RCOR	$RCOCH_2C_6H_4$-R[b)]
PhI	Toluene	110	30	Trace	20.0	—
$PhCH_2Cl$	THF	67	50	Trace	18.0	11.1
$PhCH_2Br$	THF	67	80	12.7	26.4	25.0
$PhCH_2I$	THF	40—45	100	37.6	55.2	—

a) Theoretical yield, based on organo halide used.
b) Crude yield.
c) Based on moles of organo halide used.

TABLE 2. REACTION OF ORGANO HALIDE WITH $Fe_3(CO)_{12}$ IN THE PRESENCE OF OLEFIN
(mole ratio; R-X : $Fe_3(CO)_{12}$: CH_2=CHY = 0.05 : 0.015 : 0.05)

R-X	Solvent	Temp. °C	CH_2=CHY	Convn.[c)] %	Products, %[a)]	
					RCH_2CH_2Y and RCH=CHY	$RCH_2CH(Y)$-CH_2CH_2Y[b)]
PhI	Toluene	110	CH_2=CHPh[d)]	18	3.0	—
PhI	Toluene	110	CH_2=$CHCO_2Et$[e)]	0	—	—
PhI	Toluene	110	CH_2=CHCN[e)]	0	—	—
$PhCH_2Cl$	THF	67	CH_2=CHPh[d)]	50	4.0	—
$PhCH_2Cl$	THF	67	CH_2=$CHCO_2Et$	35	20.0	6.8
$PhCH_2Cl$	THF	67	CH_2=CHCN	30	18.7	4.0
$PhCH_2Cl$	THF	67		0	—	—
$PhCH_2Br$	THF	67	CH_2=CHCN	50	24.0	8.5
$PhCH_2I$	THF	40—45	CH_2=CHCN	60	30.2	10.0
$PhCH_2I$	THF	40—45		30	9.6	—

a) Theoretical yield, based on organo halide used.
b) Crude yield.
c) Based on moles of organo halide used.
d) In this reaction, polymerization of styrene proceeded predominantly and dimer and ketone were also produced (see experimental section).
e) Even in THF as solvent, the reaction did not occur.

(0.015 mol) in refluxing toluene gave benzophenone in a 20% yield. In the presence of acrylonitrile, however, iodobenzene did not react with $Fe_3(CO)_{12}$ in refluxing toluene and all the iodobenzene was recovered. The results are extremely interesting in contrast with those in the case of benzyl chloride, which reacted with $Fe_3(CO)_{12}$ in the presence of acrylonitrile [in tetrahydrofuran (THF)] at 67°C to give benzylated adducts of the olefin in a 22.7% yield.[*1] Furthermore, when styrene was used as an olefin, iodobenzene reacted with $Fe_3(CO)_{12}$ to give *trans*-stilbene in a low yield.

These results stimulated us to study the reactions of iodobenzene and benzyl halides (Cl, Br and I) with $Fe_3(CO)_{12}$ in the presence of some olefins (styrene, ethyl acrylate, acrylonitrile and maleic anhydride). The coordinating ability of the above olefins decreases in the following order: maleic anhydride > acrylonitrile > ethyl acrylate > styrene.[*2]

[*1] All yields in this paper are theoretical yields based on the organo halide used.

[*2] The order was assumed by considering the ease of formation and the stability of the olefin-iron carbonyl π-complex; for example, maleic anhydride - iron tetracarbonyl[2)] is produced in a 78% yield by the reaction of maleic anhydride with $Fe_2(CO)_9$, and it is relatively stable in air. Acrylonitrile - iron tetracarbonyl[3)] is obtained in a 3% yield from the reaction of acrylonitrile with $Fe_2(CO)_9$, decomposes at 60°C, and is unstable at room temperature. However, the unstable π-complexes of ethyl acrylate and styrene are first obtained by a reaction between the olefins and iron pentacarbonyl under UV irradiation.[4)]

2) R. B. King, "Organometallic Syntheses," Vol. I, Academic Press, New York (1965), p. 130.

3) S. F. A. Kettle and L. E. Orgel, *Chem. Ind. (London)*, **1960**, 49; M. R. Tuter and A. R. Tturmoore, *Proc. Chem. Soc.*, **1961**, 466.

4) E. Koerner von Gustorf, M. C. Henry and C. D. Pietro, *Z. Naturforsch.*, **21** b, 42 (1966).

TABLE 3. EFFECT OF MOLE RATIO OF $Fe_3(CO)_{12}$ TO ORGANO HALIDE

R-X	$Fe_3(CO)_{12}$/R-X[c]	Products, %[a]		
		R-R	RCOR	$RCOCH_2C_6H_4$-R[b]
PhI	1/3	Trace	20.0	—
PhI	2/3	Trace	53.3	—
$PhCH_2Cl$	1/3	Trace	18.0	11.1
$PhCH_2Cl$	2/3	5.4	45.1	25.0
$PhCH_2Cl$	1	5.4	52.0	35.0

a) Theoretical yield, based on organo halide used.
b) Crude yield.
c) Mole ratio.

First, the results of the reactions of iodobenzene and benzyl halides with $Fe_3(CO)_{12}$ are summarized in Table 1.

The reactivity of organo halide to $Fe_3(CO)_{12}$ increased in the following order: iodobenzene$<$benzyl chloride$<$benzyl bromide$<$benzyl iodide.

The results of the same reaction in the presence of olefin are summarized in Table 2.

As may be seen in Table 2, the yields of benzyl adducts of olefins increase in parallel with the increasing order of reactivity of the halide. By comparing Table 1 with Table 2, it can easily be found that the addition of olefin to the reaction system between halide and $Fe_3(CO)_{12}$ markedly affected the reactivity of the halide to $Fe_3(CO)_{12}$; for example, iodobenzene, which reacted with $Fe_3(CO)_{12}$ to give benzophenone in a 20% yield, did not react at all with $Fe_3(CO)_{12}$ in the presence of acrylonitrile. When olefin was present, each conversion of organo halides decreased; furthermore, when the coordinating ability of olefin became stronger, the conversion of the halide was suppressed more (Tables 1 and 2).

The Effect of the Solvent. As has been mentioned, iodobenzene did not react with $Fe_3(CO)_{12}$ in the presence of acrylonitrile or ethyl acrylate in toluene or THF, but when dimethylformamide (DMF) was used as a solvent at 100°C, the reaction proceeded well, giving phenylated products of the olefins: in the case of acrylonitrile, hydrocinnamonitrile (18%) and cinnamonitrile (5%), and in the case of ethyl acrylate, ethyl hydrocinnamate (22%) and ethyl cinnamate (9%). These results indicate that, in this reaction, the solvent plays a very important role. A similar tendency was also observed in the reaction of benzyl chloride. That is, when DMF was used as the solvent instead of THF, the reaction of benzyl chloride (0.05 mol) with $Fe_3(CO)_{12}$ (0.015 mol) at 80°C gave the increased yields of the dibenzyl ketone (40%) and the benzyl *p*-benzylbenzyl ketone (crude yield, 12%). When acrylonitrile was present in the above reaction, benzylated adducts, 4-phenylbutyronitrile and 4-cyano-6-phenylhexanonitrile, were obtained in yields of 35.8 and 12.1% (in THF, 18.7 and 4.0%) respectively.

When refluxing ethanol was the solvent, the reaction of benzyl chloride (0.05 mol) with $Fe_3(CO)_{12}$ (0.015 mol) gave ethyl benzyl ether (20%), ethyl phenylacetate (3.3%), and dibenzyl (8%). The same reaction in the presence of acrylonitrile produced ethyl benzyl ether (7.8%), ethyl phenylacetate (3.6%), dibenzyl (6.6%), and 4-phenylbutyronitrile (44.8%). Thus, the yields of the benzylation and phenylation products of olefins were much increased by using a polar solvent.

The Effect of the Mole Ratio of Organo Halide-Iron Carbonyl. In the reaction described above, $Fe_3(CO)_{12}$ has been used in the ratio of one-third of a mole to one of the organo halide, on the basis of the assumption that the halide reacts with each iron atom of $Fe_3(CO)_{12}$. On the other hand, when the ratio is two-thirds of a mole to one or when $Fe_3(CO)_{12}$ and the halide are equal, the yields of the products were markedly increased (Table 3).

Therefore, it was expected that if olefin were added to this reaction system, the yields of the adducts would increase. In truth, the reaction of benzyl chloride (0.05 mol) with $Fe_3(CO)_{12}$ (0.033 mol) in the presence of acrylontirile (0.05 mol) in THF at 67°C for 30 hr gave increased yields of 4-phenylbutyronitrile (26.2%) and 4-cyano-6-phenylhexanonitrile (crude yield, 10%).

B) The Reaction of Benzyl Chloride with $Fe_3(CO)_{12}$ in the Presence of the Acetylenic Compound. It is well-known[5] that the metal-carbon σ-bonding complex undergoes insertion reactions readily with a large variety of acetylenes; also, the σ-complex, derived from the reaction between benzyl chloride and $Fe_3(CO)_{12}$, may be assumed to react with an acetylenic compound. Thus, the reaction of benzyl chloride (0.067 mol) with $Fe_3(CO)_{12}$ (0.023 mol) in the presence of diphenylacetylene (0.056 mol) was carried out in refluxing benzene under argon for 30 hr. From the residual oil obtained after the removal of the solvent under reduced pressure, the following

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[5] R. F. Heck, "Advances in Chemistry Series 49, Am. Chem. Soc." Washington D. C. (1965), pp. 194—201 and references cited therein.

products were given: diphenylmethane[*3] (8%), dibenzyl (3.3)%, dibenzyl ketone (12.1%), $Fe_2(CO)_6(PhC\equiv CPh)_2$ (43.3%, based on the diphenylacetylene used), and $Fe(CO)_4(PhC\equiv CPh)_2$ (6.8%). However, the expected benzylation product of diphenylacetylene was not isolated. Similarly, from the same reaction using phenylacetylene, the benzylated adduct was not obtained. On the other hand, when ethanol was used as the solvent, the same reaction gave 1,3-diphenylpropane and -propene in low yields (total yield, 2%). Furthermore, when DMF was the solvent, the former and the latter were produced in yields of 5.4 and 3.6% respectively. Thus, the insertion reaction of an acetylenic compound into a carbon-metal bond is markedly affected by the solvent polarity, although the reason for this is not yet clear.

C) Mechanistic Aspects. We have proposed that organo halide reacts with $Fe_3(CO)_{12}$ to yield the σ-complex, benzyliron carbonyl halide, as an intermediate, whose decomposition then produces the dibenzyl ketone, while when olefin is present, the σ-complex reacts with the olefin to give the benzylated products of olefin. Herein, the formation of the σ-complex was postulated as preceding the benzylation.

However, although iodobenzene reacted with $Fe_3(CO)_{12}$ in toluene to give benzophenone (20%), which was assumed to be produced by the decomposition of the σ-complex, iodobenzene did not react with $Fe_3(CO)_{12}$ in the presence of acrylonitrile and all the iodobenzene was recovered. Furthermore, in the case of benzyl halide, the presence of an olefin which has a strong coordinating ability resulted in a decreased conversion of benzyl halide. These results indicate that the olefin acts as an inhibitor of the reaction of halide with $Fe_3(CO)_{12}$. This inhibiting action may be interpreted in terms of the formation of an olefin-iron carbonyl π-complex prior to the formation of the σ-complex.

It is well known that π-complexes between iron carbonyl and acrylonitrile or maleic anhydride are easily formed under our reaction conditions.[2,3] Thus, the formations of the π-complex and the σ-complex are competitive with each other, and therefore, if a more reactive halide or a olefin of a lower coordinating ability is used, the conversion of the halide should be increased, and *vice versa*. For example, benzyl chloride reacted with $Fe_3(CO)_{12}$ in the presence of acrylonitrile to give benzylated adducts, and in the same reaction using maleic anhydride instead of acrylonitrile, all the benzyl chloride was recovered, while benzyl iodide reacted with $Fe_3(CO)_{12}$ not only in the presence of acrylonitrile, but also in the presence of maleic anhydride, to give benzylated adducts of the olefins.

The information reported about the reaction of the π-complex with organo halide is as follows; the reaction of bis-acrylonitrile nickel with allyl halide results in the formation of bis-(1-cyano-4-pentenyl)nickel, $(CH_2{=}CHCH_2CH_2CHCN)_2Ni$, while benzyl chloride or iodobenzene reacts a little with bis-acrylonitrile nickel,[6] but the reaction of π-allylnickel bromide with alkyl (aryl) halide does not occur in benzene or THF.[7]

The reaction of π-olefin - metal carbonyl with organo halide, however, has not yet been reported, and it was assumed that the π-complex was unreactive to halide in nonpolar solvents (THF, toluene, and benzene). Supporting evidence for our assumption was provided by the results of the reaction of benzyl chloride with a maleic anhydride-iron tetracarbonyl complex,[*4] for the reaction did not proceed and all the benzyl chloride was recovered.

In the presence of an acetylenic compound, no benzylation product was yielded in a nonpolar solvent, so the iron carbonyl reacted predominantly with an acetylenic compound with a very strong coordinating ability, thus forming several previously-known iron complexes.[8] However, when ethanol or DMF was the solvent, benzyl chloride reacted with $Fe_3(CO)_{12}$ in the presence of phenylacetylene to give its benzylated adducts, 1,3-diphenylpropane and -propene.

Similarly, aroylnickel carbonyl halide does not react with acetylenic compound in benzene or THF,[9] but when water is the solvent, it reacts with acetylene to yield the adduct with acetylene, 3-benzoylpropionic acid.[10]

A similar interesting solvent effect was observed in the reaction between organo halide and $Fe_3(CO)_{12}$ in the presence of an olefin. In toluene iodobenzene did not react with $Fe_3(CO)_{12}$ in the presence of acrylonitrile, but when DMF was used as the solvent, it reacted well with $Fe_3(CO)_{12}$ to give phenylated adducts of the olefin. Hence, the insertion reaction of an unsaturated compound into a carbon-metal σ-bond is markedly affected by the solvent polarity. During the course of our study, Corey and Semmelhack reported that the π-allylnickel bromide complex, which did not

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[*3] It has been assumed that diphenylmethane was produced from a Friedel-Crafts type reaction between benzyl chloride and benzene by the action of iron carbonyl chloride, although it has not yet been isolated.

6) M. Dubini and F. Montino, *J. Organometal. Chem.*, **6**, 188 (1966).

7) E. J. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2755 (1967).

[*4] This π-complex was synthesised by the reaction of maleic anhydride with $Fe_2(CO)_9$ and was purified by recrystallization from acetone.[2]

8) W. Hübel und E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959).

9) E. Yoshisato, M. Ryang and S. Tsutsumi, unpublished observation.

10) G. P. Chiusoli, S. Merzoni and G. Mondelli, *Tetrahedron Letters*, **1964**, 2777.

react with alkyl halide in benzene or THF, reacted smoothly in DMF to give coupling products in high yields.[7] As for the solvent effect of DMF, they suggested that dimeric π-allylnickel bromide became monomeric π-allylnickel bromide by the coordination of DMF, and that the latter reacted with alkyl halide. However, in our work, the olefin-iron carbonyl π-complex is monomeric.[2,3] Therefore, our results can evidently not be explained in terms of their explanation.

The solvent effect and the precise mechanism of these reactions are now under investigation; a detailed description of the mechanism and further applications of this reaction will be reported in due course.

Experimental

The Reaction of Organo Monohalide with $Fe_3(CO)_{12}$. The reaction and the identification of the product were carried out according to the method described in a previous paper.[1]

The Reaction of Organo Monohalide with $Fe_3(CO)_{12}$ in the Presence of Olefin. Most of these reactions were carried out in a method similar to that described in the previous paper. Only a typical reaction will be described here.

The reaction of iodobenzene (10.2 g, 0.05 mol) with $Fe_3(CO)_{12}$ (8.1 g, 0.015 mol) in the presence of styrene (5.2 g, 0.05 mol) was carried out in refluxing toluene for 30 hr under an atmosphere of argon. The resulting reaction mixture was filtered through magnesium sulfate under reduced pressure, and, after the removal of the solvent from the filtrate, the residual oil thus obtained was distilled to give a fraction (bp 45—172°C/0.7 mmHg, 0.7g) and a large quantity of a polymer. The fraction was then chromatographed on silica gel; the subsequent elution of the first band with petroleum ether gave white crystals after the removal of the solvent. This material was recrystallized from ethanol (mp 70.5°C) and confirmed to be biphenyl (3.5%) by a mixed-melting point determination with an authentic sample. The elution of the second band with petroleum ether gave *trans*-stilbene (3.0%) (mp 124°C, from petroleum ether). Elution with benzene showed the presence of a carbonyl group (ν_{CO} 1680 cm^{-1}); after the removal of the benzene, it was identified as benzophenone (8.4%) by a mixed-melting point determination of its 2,4-dinitrophenylhydrazone (mp 232°C, from ethyl acetate) with an authentic sample. The theoretical yields of the products were determined by vpc analysis. [Column, S.E. 30, 2.25 m; column temperature, 230°C; flow rate of carrier gas (helium), 7 m*l*/min; internal standard, dibenzyl; retention times, 2.8, 6.0 and 8.5 min respectively.] A large quantity of a polymeric material was assumed to be a polymer of styrene, but it was not examined.

The reaction of benzyl chloride (6.4 g, 0.05 mol) with $Fe_3(CO)_{12}$ (8.1 g, 0.015 mol) in the presence of styrene (5.2 g, 0.05 mol) was carried out at 67°C in THF (100 m*l*) for 30 hr. The residual oil obtained by a treatment similar to that described above was distilled under reduced pressure to give the following fractions: (1) bp 90—108°C/0.3 mmHg, 1.2 g, and (2) bp 150—190°C/0.3 mmHg, 0.8 g. The results of vpc analysis showed the fraction (1) to be a mixture of the following materials: dibenzyl (1.7%), 1,3-diphenylpropane (1.8 %), 1, 3-diphenylpropene (2.2%), and dibenzyl ketone (17.0%) [Column, S. E. 30, 2.25 m; column temperature, 230°C; flow rate of carrier gas (helium), 7 m*l*/min; flame ionization detector; retention times, 4.8, 6.8, 8.2 and 9.7 min respectively]. The fraction (2) has not yet been identified.

The reaction of benzyl iodide (10.9 g, 0.05 mol) with $Fe_3(CO)_{12}$ (8.1 g, 0.015 mol) in the presence of maleic anhydride (4.7 g, 0.05 mol) was carried out at 40—45°C in THF for 30 hr. The residue after the removal of the THF *in vacuo* was dissolved in benzene and filtered through magnesium sulfate. The mother liquors were then chromatographed on silica gel after the benzene had been removed under reduced pressure. The product of elution with petroleum ether was confirmed by vpc to be unreacted benzyl iodide (7.6 g). The product of elution with benzene was hydrolyzed with 6 N hydrochloric acid and then extracted with benzene; the resulting free acid was recrystallized from water to give 1.0 g of white crystals (mp 161°C). This material was then assumed to be benzylsuccinic acid (9.6%). [Found: C, 62.97; H, 5.83%; mol wt (in the neutralization equivalent method), 209.8. Calcd for $C_{11}H_{12}O_4$: C, 63.10: H, 5.80%; mol wt, 208]. Therefore, the product of elution with benzene was mainly the anhydride of benzylsuccinic acid.

With DMF as the Solvent, the Reaction of Organo Halide with $Fe_3(CO)_{12}$ in the Presence of Olefin. The reaction of iodobenzene (9.6 g, 0.044 mol) with $Fe_3(CO)_{12}$ (7.4 g, 0.014 mol) in the presence of ethyl acrylate (5.0 g, 0.05 mol) was carried out at 100°C in DMF (100 m*l*). After the reaction had continued for 30 hr, the reaction mixture was hydrolyzed with 6 N hydrochloric acid and then extracted with diethyl ether. The residual oil obtained after the removal of the solvent was distilled under reduced pressure to give the following fractions: (1) bp 78—100°C/0.7 mmHg, 2.4 g, and (2) bp 150—220°C/0.6 mmHg, 1.9 g. The fraction (1) showed the presence of ester groups (1740, 1100—1300 cm^{-1}) and was found by vpc to be a mixture of ethyl hydrocinnamate (22%) and ethyl cinnamate (9%) [Column, S. E. 30 (5%), 2.25 m; column temperature, 180°C; flow rate of carrier gas (helium), 10 m*l*/min; flame ionization detector; retention times, 2.3 and 3.4 min]. The fraction (2) also showed the presence of an ester group, but has not yet been identified. The other reactions and the identification of the product were carried out according to the methods described above.

With Ethanol as the Solvent, the Reaction of Benzyl Chloride with $Fe_3(CO)_{12}$ in the Presence of Acrylonitrile. The reaction (at 80°C) and treatment were carried out by a method similar to that described in the case of DMF; the following fractions were thus obtained; (1) bp 60—70°C/25 mmHg, 1.2 g, and (2) bp 80—90°C/0.9 mmHg, 4.2 g. Vpc analysis showed 44% of the fraction (1) to be ethyl benzyl ether (7.8%), while the fraction (2) was found to be a mixture of ethyl phenylacetate (3.6%), dibenzyl (6.6%), and 4-phenylbutyronitrile (44.8%) [Column, S.E. 30 (5%); column temperature, 210°C; flow rate of carrier gas (helium), 10 m*l*/min; flame ionization detector; retention times, 1.6, 2.1, 4.2, and 3.0 min respectively].

The Reaction of Benzyl Chloride with $\mathrm{Fe_3(CO)_{12}}$ in the Presence of an Acetylenic Compound. The reaction of benzyl chloride (8.6 g, 0.067 mol) with $\mathrm{Fe_3(CO)_{12}}$ (11.6 g, 0.023 mol) in the presence of diphenylacetylene (10.0 g, 0.056 mol) was carried out for 30 hr in refluxing benzene. The residual oil obtained after the removal of the benzene *in vacuo* under an atmosphere of argon was dissolved in hot acetic acid (70 m*l*). The red crystals (6.7 g) crystallized from this solution were recrystallized from acetic acid (mp 197—199°C). This material was identified as a known π-complex, $\mathrm{Fe_2(CO)_6(PhC{\equiv}CPh)_2}$ (IR: ν_{CO} 2020, 1993, 1969, 1950 and 1905 cm^{-1}; NMR: τ 3.2 ppm; Found: C, 63.85; H, 3.25%. Calcd for $\mathrm{Fe_2C_{34}H_{20}O_6}$: C, 64.15; H, 3.14%), an identification which agreed with the data of Ref. 8 (43.2%). The residual oil remaining after the removal of acetic acid from the filtrate was chromatographed on silica gel. Orange crystals were obtained from elution with benzene; they were recrystallized from ethanol, mp 184—186°C (Found: C, 74.01; H, 3.59%. Calcd for $\mathrm{FeC_{32}H_{20}O_4}$: C, 73.25; H, 3.81%). This material was identified as $\mathrm{Fe(CO)_4(PhC{\equiv}CPh)_2}$ by the agreement with the data of Ref. 8 (6.8%). The products of all the other elutions were distilled together *in vacuo* under argon to give the following fractions: (1) bp 53—60°C/12 mmHg, 3.6 g, and (2) bp 100—130°C/3 mmHg, 4.0 g. The fraction (1) was confirmed to be unchanged benzyl chloride, while the fraction (2) was found by vpc to be a mixture of diphenylmethane (8%), dibenzyl (3.3%), and dibenzyl ketone (12.1%).

In the presence of phenylacetylene, the same reaction gave diphenylmethane (26%), dibenzyl (4.4%), dibenzyl ketone (5.5%), and $\mathrm{Fe_2(CO)_6(PhC{\equiv}CH)_2}$, the data of all of which agreed with that in Ref. 8. The other complex was not examined.

With ethanol as the solvent, the same reaction was carried out and the residual oil obtained after the removal of the ethanol *in vacuo* was distilled under argon. From the fraction thus obtained, the following products were identified by vpc: ethyl benzyl ether (32.8%), ethyl phenylacetate (2%), dibenzyl (0.5%), ethyl cinnamate (6.6%, based on the phenylacetylene used), 1,3-diphenylpropane (1.5%), 1,3-diphenylpropene (0.5%), and the dibenzyl ketone (1%). [Column, S.E. 30; column temperature, 230°C; flow rate of carrier gas (helium), 5 m*l*/min; flame ionization detector; retention times, 4.1, 5.4, 11.5, 9.2, 16.5, 19.6 and 21.1 min]. No other complexes were examined.

From the same reaction with DMF as the solvent, dibenzyl (3.2%), 1,3-diphenylpropane (5.4%) and 1,3-diphenylpropene (3.6%) were obtained.

The Reaction of Benzyl Chloride with Maleic Anhydride-Iron Tetracarbonyl. The reaction of benzyl chloride (3.2 g, 0.025 mol) with maleic anhydride-iron tetracarbonyl (6.4 g, 0.025 mol), which had been obtained by the reaction[2)] of maleic anhydride with $\mathrm{Fe_2(CO)_9}$, was carried out for 30 hr in refluxing THF (60 m*l*). The resulting reaction mixture was filtered through magnesium sulfate *in vacuo*, and, after the removal of THF from the filtrate, unchanged benzyl chloride (2.9 g) was recovered by distillation under reduced pressure; the residue (6.0 g) was dried *in vacuo* and was confirmed from its IR to be the starting π-complex.

Authentic Samples. *Ethyl Cinnamate* was prepared from the reaction of cinnamic acid with ethanol, n_{D}^{20} 1.5597 (lit., n_{D}^{20} 1.55982).

Ethyl Hydrocinnamate was obtained from the reduction of ethyl cinnamate using a sodium amalgam, n_{D}^{20} 1.4955 (lit., n_{D}^{20} 1.49542).

1,3-Diphenylpropene was prepared by a Wittig reaction using benzyl iodide, triphenylphosphine, *n*-butyllithium, and phenylacetaldehyde (mp 56°C, from ethanol; lit., mp 57°C).

1,3-Diphenylpropane was afforded by the reduction of 1,3-diphenylpropene using palladium black, n_{D}^{20} 1.5697 (lit., n_{D}^{20} 1.5694).

Cinnamonitrile was prepared by the reaction of benzaldehyde with cyanoacetic acid in pyridine and piperidine (bp 89°C/1.8 mmHg).

Hydrocinnamonitrile was obtained by the reaction of β-phenethyl bromide with potassium cyanide (bp 114°C/8 mmHg).