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THE REACTION OF ORGANO MONOHALIDES WITH POLYNUCLEAR IRON CARBONYLS IN THE PRESENCE OF OLEFINS

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INTRODUCTION

It is known that reaction of iron pentacarbonyl with organo polyhalides (such as carbon tetrachloride, chloroform) in the presence of olefins leads to telomerization of the olefins[1], and with *gem*-dihalides gives dimeric olefins in good yields[2]. Furthermore, the reaction of iron pentacarbonyl with allyl iodide gives π-allyliron tricarbonyl iodide[3] and with substituted allyl halides gives the corresponding substituted π-allyliron tricarbonyl complexes[4]. However, the reaction of iron pentacarbonyl with other organo monohalides has not yet been reported.

Bauld[5] reported that nickel tetracarbonyl reacted with aryl iodide or aroyl halides at 40 ~ 60° to form benzoylnickel carbonyl halides (C–Ni σ-bond) as intermediate complexes, from whose decomposition the corresponding α-diketone were obtained.

We have found a remarkable difference of reactivities to organo monohalides between nickel tetracarbonyl and iron pentacarbonyl; that is, the reaction of nickel tetracarbonyl with benzyl chloride at 40° in benzene solution led to the recovery of the starting materials and the same reaction at 78° gave bibenzyl (45%), whereas the reaction of iron pentacarbonyl (which has low reactivity to iodobenzene at 30 ~ 60°) with benzyl chloride gave quantitatively the hydrocarbon polymer, $(\text{-}CH_2C_6H_4\text{-})_n$, $n \sim 62$.

On the other hand, both iron pentacarbonyl and nickel tetracarbonyl react with various organolithium compounds at −70° to form the same type of complex, lithium aroyl (or acyl-)iron tetracarbonylate and -nickel tricarbonylate[6], respectively.

This curious behavior of metal carbonyls toward organo monohalides prompted us to study the reaction of organo monohalides with polynuclear iron carbonyls.

We report here that polynuclear iron carbonyls, diiron nonacarbonyl and triiron dodecacarbonyl, whose weak iron–iron and bridging carbonyl bonds can serve as points of attack, are reactive toward organo monohalides. The reactions with benzyl chloride or iodobenzene yield σ-complexes as intermediates from which symmetrical ketones are produced and, when olefins are present in the reaction mixture with the iron carbonyls and the halides, their benzyl adducts are produced.

RESULT AND DISCUSSION

(*A*) *The reactions of benzyl chloride and iodobenzene with polynuclear iron carbonyls*

The reaction of benzyl chloride (0.1 mole) with iron pentacarbonyl (0.1 mole) in tetrahydrofuran (THF) solution proceeded at 30° with evolution of hydrogen chloride and gave quantitatively the hydrocarbon polymer, $(-CH_2C_6H_4)_n$, $n \sim 62$, whose structure was derived from the following results: (*a*) elemental analysis; (*b*) IR spectrum (analogous with *m*-xylene); (*c*) NMR spectrum (showed the presence of four phenyl protons and two methylene protons at τ 3.09, 6.23 ppm); (*d*) UV spectrum (λ_{max} 270.4 mμ); (*e*) molecular weight (5544, calcd. for $(C_7H_6)_{62}$ 5580).

Since, in the case of iron pentacarbonyl, the carbon monoxide insertion product was not isolated and the polymer was the sole product, the reaction of the more reactive diiron nonacarbonyl with benzyl chloride was examined.

Benzyl chloride (0.1 mole) and diiron nonacarbonyl (0.05 mole) in benzene were stirred vigorously at 30° for 50 h; as the reaction proceeded, the color of the reaction mixture changed continuously from gold to dark-brown. The dark-brown residue obtained after solvent removal was distilled to give dibenzyl ketone in 56% yield (based on benzyl chloride reacted). The reaction of triiron dodecacarbonyl (0.03 mole) with benzyl chloride (0.1 mole) in THF solution at 67° gave dibenzyl ketone in a yield of 18% and 1.1 g of another ketone, m.p. 89 ~ 90°.

Hence polynuclear iron carbonyls react quite differently from iron pentacarbonyl with benzyl chloride. This could be due to the formation of reactive iron tetracarbonyl species by the decomposition of polynuclear iron carbonyls. Iodobenzene was unreactive toward iron carbonyls at low temperature (30 ~ 60°) but at 110° in toluene solution, the reaction with triiron dodecacarbonyl gave benzophenone in a yield of 53.3%. Although the mechanism of ketone formation from the reaction of polynuclear iron carbonyls with benzyl chloride and iodobenzene is still open to question, the formation of benzyl- or phenyliron carbonyl halides is assumed to precede ketone formation, based on the facts of ketone formation from lithium aroylnickel tricarbonylate[6], methylcobalt tetracarbonyl[7] and so on (see e.g. ref. 8). The supporting evidence for this assumption is provided by the results of the reaction of benzyl chloride with disodium iron tetracarbonylate in THF at 67°, for the reaction gave dibenzyl ketone in 38% yield via the formation and decomposition of dibenzyliron tetracarbonylate (I).

Thus it would be proper to consider that carbon–iron σ-bonded complexes (II) should be intermediates in the reaction of benzyl chloride or iodobenzene with polynuclear iron carbonyls as seen in eqns. (1) and (2), and the decomposition of the thermally unstable complexes (II) then would give the symmetrical ketones.

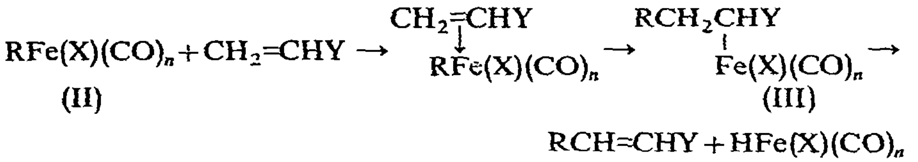
$$2\,PhCH_2Cl + Na_2Fe(CO)_4 \rightarrow \underset{(I)}{(PhCH_2)_2Fe(CO)_4} \rightarrow PhCH_2C(O)CH_2Ph \qquad (1)$$

$$RX + Fe_2(CO)_9 \text{ or } Fe_3(CO)_{12} \rightarrow \underset{(II)}{RFe(X)(CO)_n} \rightarrow RC(O)R \qquad (2)$$

(*B*) *The reaction of benzyl chloride with polynuclear iron carbonyls in the presence of olefins*

Organotransition metal compounds which contain carbon–metal σ-bonds are known to be reactive to unsaturated compounds; thus the addition of carbon–metal σ-bonds to a carbon–carbon double bond has been established by several workers. For example, Heck[9] reported that acylcobalt tetracarbonyls react with butadiene at 0° to give good yields of 1-acylmethyl-π-allylcobalt tricarbonyl, from which 1-acyldienes were obtained in the presence of dicyclohexylethylamine. Evidence for the insertion of an olefinic group between an acyl group and a cobalt atom has been obtained more directly by analyzing the decomposition products of ω-unsaturated acylcobalt tetracarbonyls $[CH_2{=}CH(CH_2)_nCOCo(CO)_4]$[10]. Furthermore, the addition of alkylmanganese tetracarbonyls to polyfluoroolefins[11] and conjugated dienes[12] has been reported.

Since, in the reaction of polynuclear iron carbonyls, benzyl- and phenyliron carbonyl halides (C–Fe; σ-bond) were assumed to be precursors to dibenzyl ketone and benzophenone, respectively, the same reactions in the presence of olefins were expected to give benzylated olefins *via* the decomposition of intermediately formed addition products (III) as shown eqn. 3.



$$\underset{\text{(II)}}{\mathrm{RFe(X)(CO)}_n} + \mathrm{CH_2{=}CHY} \rightarrow \underset{\mathrm{RFe(X)(CO)}_n}{\overset{\mathrm{CH_2{=}CHY}}{\downarrow}} \rightarrow \underset{\text{(III)}}{\underset{\mathrm{Fe(X)(CO)}_n}{\overset{\mathrm{RCH_2CHY}}{|}}} \rightarrow \mathrm{RCH{=}CHY} + \mathrm{HFe(X)(CO)}_n \quad (3)$$

Accordingly the reaction of benzyl chloride (0.1 mole) with triiron dodecacarbonyl (0.03 mole) in the presence of acrylonitrile (0.1 mole) in benzene solution was carried out at 78° for 30 h. Distillation gave 4-phenylbutyronitrile (yield 15.0%) and a minor product believed to be 4-phenylcrotononitrile (1.0%) from the boiling point and CN-frequency (2210 cm^{-1}) and gas chromatographic analysis. The latter was not isolated in the pure state and has not yet been identified. A higher boiling fraction was shown to contain mainly 4-cyano-6-phenyl-n-hexanenitrile [ν(CN) 2260 cm^{-1}] (yield, 3.3%). The minor product [ν(CN) 2210 cm^{-1}) was not isolated in the pure state.

Similar reactions were carried out by using diiron nonacarbonyl or triiron dodecacarbonyl and benzyl chloride in the presence of acrylonitrile or ethyl acrylate and these results are summarized in Table 1.

In each of these reactions, the unsaturated adducts were produced in lower yields than were the saturated adducts.

TABLE 1

REACTIONS OF POLYNUCLEAR IRON CARBONYLS WITH BENZYL CHLORIDE IN THE PRESENCE OF OLEFINS

Iron carbonyl	$CH_2{=}CHY$	*Solvent*	*Product* (%)[a]	
			RCH_2CH_2Y	$RCH_2CH(Y)CH_2CH_2Y$[b]
$Fe_3(CO)_{12}$	$CH_2{=}CHCN$	THF	20.1	4.3
$Fe_2(CO)_9$	$CH_2{=}CHCN$	THF	16.4	2.7
$Fe_3(CO)_{12}$	$CH_2{=}CHCN$	C_6H_6	15.0	3.3
$Fe_3(CO)_{12}$	$CH_2{=}CHCOOEt$	C_6H_6	22.2	4.4
$Fe_3(CO)_{12}$	$CH_2{=}CHCOOEt$	THF	12.0	6.8

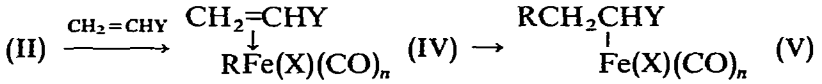
[a] Ultimate yield, based on benzyl chloride reacted. [b] Crude yield.

As for the formation of these addition products, the following two paths would be considered; path (A): olefin–iron π-complexes are initially formed by the interaction of olefin with the polynuclear iron carbonyl, and then benzyl chloride reacts with the π-complexes to produce the adducts; and path (B): σ-complex, formed by the interaction of benzyl chloride with the polynuclear iron carbonyl, reacts with olefins to produce adducts.

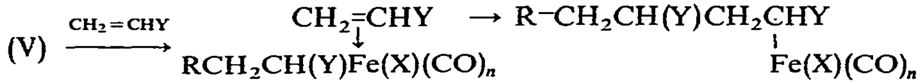
It is well known that good dienophiles, in general, have tend to form π-complexes with iron carbonyls[13]. Hence in our work, the possibility that the interaction of acrylonitrile or ethyl acrylate with the polynuclear iron carbonyls would lead to π-complexes prior to the formation of benzylation products could not be fully neglected, although complexes with ethyl acrylate have not yet been detected and the reaction of the π-complexes with organo halides has not yet been reported. However, path (B) seemed to be more probable from the following experimental results; the reaction of benzyl chloride with disodium iron tetracarbonylate in acrylonitrile under the same conditions gave results quite analogous to those of the above reaction; that is, 4-phenylbutyronitrile (17.5 %) was the main product.

Thus, the whole reaction scheme for the formation of ketones and benzylation products may be described as follows. The reaction of the polynuclear iron carbonyl with organo halides would initially form σ-complexes (II) as intermediates, from which ketones would be obtained (in the absence of an olefin) by decomposition (see eqn. 2).

In the presence of olefins, (II) would be transformed to (V) via (IV) (*cis*-ligand insertion reaction[14]).



$$(\text{II}) \xrightarrow{CH_2=CHY} \underset{RFe(X)(CO)_n}{\overset{CH_2=CHY}{\downarrow}} \ (\text{IV}) \rightarrow \underset{Fe(X)(CO)_n}{\overset{RCH_2CHY}{|}} \ (\text{V})$$



$$(\text{V}) \xrightarrow{CH_2=CHY} \underset{RCH_2CH(Y)Fe(X)(CO)_n}{\overset{CH_2=CHY}{\downarrow}} \rightarrow \underset{Fe(X)(CO)_n}{\overset{R-CH_2CH(Y)CH_2CHY}{|}} \ (\text{VI})$$

Thereafter, the unsaturated adduct would be formed by elimination of the β-proton and iron carbonyl as iron carbonyl hydride (VII);

$$(\text{V}) \longrightarrow RCH{=}CHY + HFe(CO)_nX \quad (\text{VII})$$

$$(\text{VI}) \longrightarrow RCH_2CH(Y)CH{=}CHY + (\text{VII})$$

This elimination process is supported by the following information: the formation of metal–hydride bonds in isomerization of olefins by using metal carbonyls[15], the thermal decomposition of ethylcobalt tetracarbonyl to cobalt carbonylhydride and ethylene[16], and the formation of dienes $[CH_2{=}CH(CH_2)_{n-2}CH{=}CH_2]$ from the ω-unsaturated alkylcobalt tetracarbonyls $[CH_2{=}CH(CH_2)_nCo(CO)_4, n > 4]$[10].

However, in our work, the saturated adducts were the main products. The formation of saturated adducts was accounted for by the fission of the carbon–iron bond in (V) [and (VI)] by the action of hydrogen chloride.*

The mechanism of these reactions is under investigation and detailed descrip-

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* As described above, hydrogen chloride is produced when a small amount of iron pentacarbonyl, formed by the decomposition of polynuclear iron carbonyls[17], reacts with benzyl chloride to give the polymer.

tion of the mechanism and further application of this reaction will be reported shortly.

EXPERIMENTAL

The reaction of benzyl chloride with iron pentacarbonyl and with nickel tetracarbonyl

Into 200-ml four-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser protected from moisture, a gas bubbler and a dropping funnel, was placed 80 ml of THF and, after sweeping the apparatus with dry argon, 12.7 g (0.1 mole) of benzyl chloride was added. A solution of 19.6 g (0.1 mole) of iron pentacarbonyl in 20 ml of anhydrous THF was added via the dropping funnel with stirring over a period of 30 min, while the internal temperature was maintained at 30°. After the addition had been completed, the stirring was continued for a further 30 h; hydrogen chloride was evolved as the reaction proceeded.

The resulting reaction mixture was filtered through magnesium sulfate under reduced pressure and a polymer was obtained after removal of the solvent from the filtrate. The polymer was soluble in boiling benzene or THF but insoluble in ether, acetone, petroleum ether and petroleum benzine. The powdered polymer was treated with boiling water for 3 h in order to remove inorganic material. The hot benzene solution of the polymer was poured into petroleum ether to precipitate yellowish powder. This treatment was repeated four times. [Found: C, 93.06; H, 6.76; mol.wt. in dimethylformamide (v.p. osmometer), 5544: $(C_7H_6)_{62}$ calcd.: C, 93.26; H, 6.71%; mol.wt., 5580.] The IR spectrum was similar with that of *m*-xylene in the region of $800 \sim 600$ cm^{-1}. The NMR spectrum (in carbon tetrachloride) showed the presence of four phenyl protons (τ 3.09 ppm) and two methylene protons (τ 6.23 ppm) and the UV spectrum showed λ_{max} 270.4 mμ in chloroform.

The reaction mixtures obtained from the same reaction carried out in THF at 67° and also gave quantitatively similar polymer.

The reaction of nickel tetracarbonyl (17.0 g, 0.1 mole) with benzyl chloride (12.7 g, 0.1 mole) in benzene solution at 40° for 30 h led to the recovery of starting material, but the same reaction in boiling benzene for 30 h gave a fraction of b.p. $93 \sim 103$°/0.3 mm, 2.0 g (m.p. 52° from ethanol/water), which was identified as bibenzyl (lit. m.p. 51°) by mixing melting point with an authentic sample. This material probably was produced by the reaction of benzyl chloride with metallic nickel formed by the decomposition of nickel tetracarbonyl.

The reaction of benzyl chloride with polynuclear iron carbonyls

Benzyl chloride (12.7 g, 0.1 mole) was allowed to react with diiron nonacarbonyl[18] (18.5 g, 0.05 mole) in 100 ml of benzene solution at 30° for 50 h. The residual oil, obtained by treatment similar to that mentioned above, was distilled under reduced pressure to give a fraction of b.p. $105 \sim 110$°/0.4 mm, 5.5 g.

The infrared spectrum of the fraction showed the presence of a carbonyl group (1730 cm^{-1}) and it was confirmed to be dibenzyl ketone by mixed melting point of its 2,4-dinitrophenylhydrazone (m.p. 111°, from ethanol) with an authentic sample. The results of gas-chromatographic analysis showed that this fraction was mainly dibenzyl ketone, 92.5% (Column, S.E.30, 2.25 m; column temperature, 210°; flow rate of carrier gas (helium), 7 ml per min; retention time of dibenzyl ketone, 5.9

min) (yield 56.0% based on benzyl chloride reacted).

The same reaction of benzyl chloride (12.7 g, 0.1 mole) with triiron dodecacarbonyl[18] (15.1 g, 0.03 mole) was carried out in THF at 67° for 30 h. The residual oil obtained was distilled under reduced pressure to give following fractions; (1) b.p. 106 ~ 110°/0.4 mm, 1.5 g and (2) b.p. 150 ~ 160°/0.3 mm, 1.1 g. The IR spectrum of fraction (1) showed the presence of a carbonyl group (1730 cm^{-1}) and the fraction (1) was confirmed to be dibenzyl ketone (yield 18.0%). Fraction (2) was recrystallized from petroleum ether to give white crystals (m.p. 89 ~ 90°) whose IR spectrum showed the presence of a carbonyl group (1712 cm^{-1}) and whose NMR spectrum showed absorptions at τ 2.90 ppm (14 H, phenyl protons), 6.23, 6.48 and 6.57 (2 H, methylene protons, respectively). (Found: C, 88.12; H, 6.71; mol.wt. in benzene, 298.2. $C_{22}H_{20}O$ calcd.: C, 87.96; H, 6.71%; mol.wt., 300.4.) Thus this material was assumed to be benzyl dibenzyl ketone (substituted position has not yet been confirmed) (yield 8.0%).

The reaction of iodobenzene (10.2 g, 0.05 mole) with triiron dodecacarbonyl (15.1 g, 0.03 mole) was carried out at 78° in benzene solution for 50 h to give 0.5 g of benzophenone (26.3%), which was identified by mixed melting point of its 2,4-dinitrophenylhydrazone (m.p. 232°, from ethyl acetate) with an authentic sample. From the same reaction carried out in refluxing toluene benzophenone was obtained in a yield of 53.3%.

The reaction of benzyl chloride with polynuclear iron carbonyls in the presence of olefins

The reaction of benzyl chloride (12.7 g, 0.1 mole) with triiron dodecacarbonyl (15.1 g, 0.03 mole) in the presence of acrylonitrile (5.4 g, 0.1 mole) was carried out at 78° in benzene for 30 h. The residual oil obtained by treatment similar to that mentioned above was distilled under reduced pressure to give the following fractions; (1) b.p. 75 ~ 79°/0.3 mm, 2.0 g and (2) b.p. 135 ~ 150°/0.3 mm, 1.0 g. The IR spectrum of fraction (1) showed the presence of two cyano groups (2260 strong and 2210 cm^{-1} weak). Fraction (1) was hydrolyzed with aqueous potassium hydroxide, followed by neutralization with 6 *N* hydrochloric acid and by extraction with diethyl ether. The acid was recrystallized from petroleum ether to give white crystals (m.p. 50°), which were identified as 4-phenylbutyric acid (lit. m.p. 51°) by mixed melting point. (Found: C, 73.02; H, 7.32. $C_{10}H_{12}O$ calcd.: C, 73.14; H, 7.37%.) IR spectrum: a carbonyl group (1690 cm^{-1}) and a hydroxy group (3360 cm^{-1}); NMR spectrum: five phenyl protons (τ 2.93 ppm, singlet) and six methylene protons (τ 7.72 ppm, multiplet). Therefore, fraction (1) was mainly 4-phenylbutyronitrile. The results of mixed gas chromatographic analysis with authentic samples showed that this fraction consisted of 4-phenylbutyronitrile (86%) and 4-phenylcrotononitrile (8%) (Column, S.E.30, 2.25 m; column temperature, 170°; rate of flow of the carrier gas He, 10 ml per min; retention time, 4.5 and 5.5 min, respectively) (yield; 4-phenylbutyronitrile, 15.0% and 4-phenylcrotononitrile, 1.0%). Fraction (2) also showed the presence of two cyano groups in the IR spectrum (2260 strong and 2210 cm^{-1} weak). It was hydrolyzed with aqueous potassium hydroxide, and the free acid obtained was treated with thionyl chloride and aniline to give white crystals. This material, recrystallized from toluene, had m.p. 185°. Its IR spectrum showed it to be an amide, 3310 (NH) and 1660 cm^{-1} (CO) and NMR spectrum had absorptions at τ 1.90 (1 H, NH proton), 2.30 (1 H, NH proton), 3.10 (15 H, phenyl protons) and 7.76 ppm (9 H, methylene protons). [Found: C, 78.26; H, 6.50; N, 7.20; mol.wt. in dimethylformamide (v.p. osmometer), 390.9.

$C_{25}H_{26}O_2N_2$ calcd.: C, 77.69; H, 6.78; N, 7.25%; mol.wt., 386.47.] Thus this material was assumed to be 2-β-phenethylglutarodianilide and therefore fraction (2) was mainly 4-cyano-6-phenylhexanenitrile [ν(CN) 2260 cm^{-1}] (crude yield, 3.3%). The minor product of fraction (2) [ν(CN) 2210 cm^{-1}) has not yet been identified.

Same reaction at 67° in THF solution produced 4-phenylbutyronitrile (20.1%) and 4-cyano-6-phenylhexanenitrile (4.3%).

Benzyl chloride (12.7 g, 0.1 mole) reacted with 18.2 g of diiron nonacarbonyl in the presence of acrylonitrile (5.4 g, 0.1 mole) in THF under the same conditions to give 4-phenylbutyronitrile (2.0 g, 16.4%) and 4-cyano-6-phenylhexanenitrile (2.7%).

The reaction of benzyl chloride (12.7 g) with triiron dodecacarbonyl (15.1 g) in the presence of ethyl acrylate (10.0 g) was carried out at 78° in benzene solution for 40 h. The residual oil obtained was distilled under reduced pressure to give the following fractions; (1) b.p. 85 ~ 100°/1.5 mm, 5.0 g, and (2) b.p. 150 ~ 175°/1.7 mm, 1.7 g. The IR spectrum of fraction (1) showed the presence of an ester group (1748, 1160 and 1180 cm^{-1}).

Fraction (1) was hydrolyzed with potassium hydroxide/ethylene glycol and the free acid subsequently obtained was recrystallized from petroleum ether to give white crystals (m.p. 51°), which were identified as 4-phenylbutyric acid by mixed melting point. The results of gas-chromatographic analysis showed that fraction (1) consisted of ethyl 4-phenylbutyrate (86.0%) (Column, S.E.30, 2.25 m; column temperature, 210°; rate of flow of the carrier gas, He, 7 ml per min; retention time, 2.4 min) (yield 22.2%).

Fraction (2) also showed the presence of an ester group (IR spectrum) and was converted to the amide derivative (from aniline and ethylmagnesium bromide in ether). This material was recrystallized from toluene, m.p. 185°, which was assumed to be 2-β-phenethylglutarodianilide by mixed melting point with the amide derivative mentioned above. Therefore, fraction (2) was assumed to be diethyl 2-β-phenethylglutarate (crude yield 4.4%). Same reaction at 67° in THF gave ethyl 4-phenylbutyrate, 2.3 g (12.0%) and diethyl 2-β-phenethylglutarate, 2.0 g (6.8%).

The reaction of benzyl chloride with disodium iron tetracarbonylate

The reaction of benzyl chloride (23.4 g, 0.185 mole) with disodium iron tetracarbonylate, which was prepared by the reaction of triiron dodecacarbonyl (11.3 g, 0.022 mole) with sodium dispersion in THF (sodium 3.1 g, oleic acid one drop in 30 ml of xylene), was carried out at 20 ~ 25° in THF for 10 h. The residual oil was distilled under reduced pressure to give following fractions; (1) b.p. 106 ~ 110°/0.5 mm, 8.0 g and (2) b.p. 159 ~ 170°/0.2 mm, 4.0 g. Fraction (1) was identified as dibenzyl ketone, of which purity was shown to be 92.0% from gas chromatographic analysis (Column, S.E.30, 2.25 m; column temperature, 210°; rate of flow of the carrier gas, He, 7 ml per min; retention time, 5.9 min)(yield 38.0%, based on benzyl chloride used). Fraction (2) was shown to be a hydrocarbon from IR spectrum. (Found: C, 92.02; H, 7.74; mol.wt. in benzene, 284.2. $C_{22}H_{22}$ calcd.: C, 92.26; H, 7.74%; mol.wt., 286.)

The reaction of benzyl chloride with disodium iron tetracarbonylate in the presence of acrylonitrile

Benzyl chloride (15.2 g, 0.12 mole) and acrylonitrile (6.48 g, 0.12 mole) were added to a THF solution of disodium iron tetracarbonylate, which had been prepared by using 1.3 g of sodium (0.06 g-atom), oleic acid (one drop) and 10.1 g of triiron dodecacarbonyl (0.02 mole) in xylene (10 ml). The mixture was stirred vigorously at 30° for 24 h and then at 67° for 12 h. The residual oil obtained from the same treatment was distilled under reduced pressure to give a fraction of b.p. 92 ~ 120°/0.4 mm, 3.5 g. The fraction showed the presence of two cyano groups (2260 strong and 2210 cm^{-1} weak) and was confirmed to contain 4-phenylbutyronitrile, the purity of which was shown to be 85% from gas-chromatographic analysis (theoretical yield 17.5%, based on benzyl chloride used). This material was identified by mixed melting point of its derived acid (m.p. 51°, from water) with an authentic sample. The minor product [ν(CN) 2210 cm^{-1}] has not yet been isolated in the pure state.

Authentic samples

4-Phenylbutyronitrile was prepared from the reaction of 3-phenylpropyl bromide with potassium cyanide in ethanol (b.p. 90 ~ 92°/0.7 mm, n_D^{15} 1.5165).

4-Phenylcrotononitrile was prepared by the reaction of phenylacetaldehyde with cyanoacetic acid in pyridine and piperidine (m.p. 69 ~ 70° from petroleum ether; IR spectrum, CN, 2210 cm^{-1} and monosubstituted benzene ring, 695, 740 cm^{-1}; Found: C, 83.11; H, 6.34; N, 9.96. $C_{10}H_9N$ calcd.: C, 83.91; H, 6.29; N, 9.79%.)

Ethyl 4-phenylcrotonate was prepared by esterification of 4-phenylbutyric acid which was driven from the reaction of phenylacetaldehyde with malonic acid in pyridine. The free acid was recrystallized from petroleum ether, m.p. 92 ~ 93°. (Found: C, 74.40; H, 6.31: $C_{10}H_{10}O_2$ calcd.: C, 74.07; H, 6.16%.)

Ethyl 4-phenylbutyrate was obtained from reduction of ethyl 4-phenylcrotonate using sodium amalgam (b.p. 105 ~ 106°/1.5 mm).

SUMMARY

The reaction of benzyl chloride with mononuclear iron pentacarbonyl quantitatively gave hydrocarbon polymer, $(CH_2C_6H_4)_n$, $n \sim 62$, and the reaction of benzyl chloride or iodobenzene with polynuclear iron carbonyls gave the corresponding symmetrical ketones. The formation of benzyl(or phenyl-)iron carbonyl (σ-complex) is considered to precede ketone formation.

The reaction of benzyl chloride with polynuclear iron carbonyls in the presence of acrylonitrile (or ethyl acrylate) produces 4-phenylbutyronitrile (yield 15.0%) (or ethyl 4-phenylbutyrate, 22.2%), 4-cyano-6-phenylhexanenitrile (yield 3.3%) (or diethyl 2-β-phenethylglutarate 4.4%) and 4-phenylcrotononitrile (1.0%).

The mechanisms of these reactions are discussed.

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