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REACTION OF BENZYLIC AND ALLYLIC HALIDES WITH IRON-CARBONYL CLUSTERS

Saburo NAKANISHI, Toshio ODA, Tatsuo UEDA, and Yoshio OTSUJI
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Mozu-Umemachi, Sakai, Osaka 591

The reaction of p-substituted benzyl chlorides [1] with $Fe_3(CO)_{12}$ in benzene gave p-substituted diphenylmethanes [3] as a major product. However, the reaction of [1] with the $Fe_3(CO)_{12}$-pyridine N-oxide (PyNO) reagent system selectively afforded 1,2-diphenylethane derivatives [2]. Allylic halides [5] reacted with $Fe_3(CO)_{12}$ in benzene to give a mixture of three products including 1,5-hexadiene derivatives [7]. While, treatment of [5] with the $Fe_3(CO)_{12}$-PyNO reagent system led to a selective formation of [7]. The role of PyNO in the above reagent system is discussed.

Iron carbonyls are a versatile reagent in organic synthesis.1) They can exist as complexes of diverse structures and often induce unique organic transformations which depend on their structures. However, no systematic information is yet available on their structure-reactivity relationships. We have recently found that treatment of triiron dodecacarbonyl ($Fe_3(CO)_{12}$) with a small amount of PyNO causes an efficient decarbonylation to give a cluster complex which exhibits reactivities different from those of $Fe_3(CO)_{12}$ itself. We now wish to report a characteristic reactivity feature of this complex in the reaction with benzylic and allylic halides.

A solution of 2.0 mmol of $Fe_3(CO)_{12}$ and 0.5 mmol of PyNO in 15 ml of benzene was heated at 80°C for 3 h under N_2 atmosphere. To this solution was added 4.0 mmol of benzyl chloride [1a], and then the resulting mixture was heated for 24 h at the same temperature. After removal of the solvent, the residue was further heated at 150°C for 20 min, and then subjected to a column chromatography on silica gel with hexane-benzene to give 1,2-diphenylethane [2a] in a 50% yield.

The reaction of [1a] with other iron-carbonyl complexes such as $Fe(CO)_5$, $Fe_2(CO)_9$ and two iron-carbonyl ferrates afforded three products: [2a], diphenylmethane [3a] and dibenzyl ketone [4a]. The proportion of these products strongly depended on the structure of the iron-carbonyl complexes used. The results are summarized in Table 1.

$$\underset{[1]}{RC_6H_4CH_2Cl} \xrightarrow{\text{iron complex}} \underset{[2]}{(RC_6H_4CH_2)_2} + \underset{[3]}{RC_6H_4CH_2C_6H_5} + \underset{[4]}{(RC_6H_4CH_2)_2CO}$$

a: R=H, b: $R=CH_3$, c: $R=CH_3O$, d: R=Cl

Table 1. Reaction of Benzyl Chloride with Various Iron-Carbonyl Complexes in Benzene$^{a)}$

Iron Carbonyl	Products, Yield %$^{b)}$		
	[2a]	[3a]	[4a]
$Fe(CO)_5$	0	45	0
$Fe_2(CO)_9$	trace	45	37
$Fe_3(CO)_{12}$	5	71	2
$Fe_3(CO)_{12}$ / PyNO$^{c)}$	74	0	0
$Na_2Fe(CO)_4$$^{d)}$	-	-	38
$Et_3NH[HFe_3(CO)_{11}]$	24	trace	trace

a) A mixture of a given iron-carbonyl complex (2.0 mmol) and benzyl chloride (4.0 mmol) in 15 ml of benzene was heated at 80°C for 24 h. b) The yields were determined by glc, and based on benzyl chloride used. c) $Fe_3(CO)_{12}$ (2.0 mmol) was treated with PyNO (0.5 mmol) at 80°C for 3 h in benzene and then used. d) Data from ref 3.

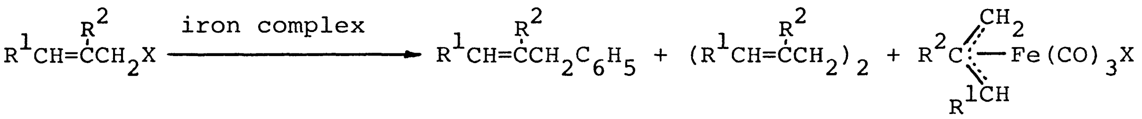
Table 2. Reaction of p-Substituted Benzyl Chloride with $Fe_3(CO)_{12}$$^{a)}$

Halide	mmol	PyNO, mmol	Products, Yield %$^{b)}$		
			[2]	[3]	[4]
[1a]	2.0	0	6	55 (55)	2
	6.0	0	4	66 (198)	0
	17	0	4	58 (247)	0
	2.0	0.5$^{c)}$	69 (35)	0	0
	6.0	0.5$^{c)}$	68 (102)	0	0
	17	0.5$^{c)}$	24 (103)	0	0
[2a]	4.0	0	1	61 (122)	1
	4.0	0.5$^{c)}$	75	0	0
[3a]	4.0	0	2	67 (133)	1
	4.0	0.5$^{c)}$	73	0	0
[4a]	4.0	0	trace	63 (126)	0
	4.0	0.5$^{c)}$	35	0	0

a) A mixture of $Fe_3(CO)_{12}$ (2.0 mmol) and a given amount of p-substituted benzyl chloride in 15 ml of benzene was heated at 80°C for 24 h. b) The yields were determined by glc, and based on benzyl chloride used. The figures in parenthesis are based on $Fe_3(CO)_{12}$ used. c) p-Substituted benzyl chlorides were added after a mixture of $Fe_3(CO)_{12}$ and PyNO was heated at 80°C for 3 h, and then the resulting mixture was heated at the same temperature for 24 h.

The neutral iron-carbonyl complexes, $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, reacted with [1a] to give [3a] which is the benzylation product of benzene as a major product along with small amounts of [2a] and [4a].[2] It must be noticed here that if the reaction of [1a] with $Fe_3(CO)_{12}$ is conducted in THF instead of benzene, [4a] is produced as a major product.[3] The use of $Fe_3(CO)_{12}$-PyNO reagent system caused a remarkable change in the product-distribution: treatment of [1a] with this reagent system led to a selective formation of the reductive coupling product [2a].[4] Such a selectivity in the product-distribution was also observed in the reaction of p-substituted benzyl chlorides with the $Fe_3(CO)_{12}$-PyNO reagent system. The results are shown in Table 2.

The reaction of allylic halides with iron-carbonyl complexes was then studied. The results are summarized in Table 3. In this case, the product-distribution also varied with the structures of iron-carbonyl complexes. Allylic halides have been shown to react with $Fe(CO)_5$ and $Fe_2(CO)_9$ to give allyl iron-carbonyl complexes.[5] However, we found that the reaction of 3-chloro-2-methylpropene [5a] with $Fe_3(CO)_{12}$ gives a mixture of 2-methyl-2-propenylbenzene [6a] and 2,5-dimethyl-1,5-hexadiene [7a] and allyl iron-carbonyl complex [8a]. On the other hand, treatment of [5a] with $Fe_3(CO)_{12}$-PyNO reagent system led to a selective formation of [7a]. Similar results were obtained in the reaction of 3-bromo-1-phenylpropene [5b] with iron-carbonyl complexes.



[5] [6] [7] [8]

a: R^1=H, R^2=CH_3, X=Cl, b: R^1=C_6H_5, R^2=H, X=Br

Table 3. Reaction of Allylic Halides with $Fe_3(CO)_{12}$[a]

Halide	PyNO, mmol	Products, Yield %[b]		
		[6]	[7]	[8]
[5a]	0	15	13	15[d]
	0.5	trace	32	trace
[5b]	0	trace	26	12[d]
	0.5	0	82[c]	0

a) The reactions were carried out under the conditions similar to those described in Table 1. b) The yields were determined by glc, and based on the halides used (4.0 mmol). c) $(C_6H_5CH{=}CHCH_2)_2$, $(CH_2{=}CHCHC_6H_5)_2$ and $C_6H_5CH{=}CHCH_2CH(C_6H_5)CH{=}CH_2$ were obtained in 25, 11, and 64% yields, respectively. d) Isolated yield.

In order to gain insight into the chemical function of PyNO in the above reactions, we studied the reaction of $Fe_3(CO)_{12}$ with PyNO.[6] $Fe_3(CO)_{12}$ (2.0 mmol) was allowed to react with PyNO (0.5 mmol) in benzene at 80°C for 3 h. This reaction gave an air sensitive black solid with evolution of 4.5 moles of carbon monoxide per one mole of $Fe_3(CO)_{12}$ used. The addition of a methylene chloride solution of bis(triphenylphosphine)iminium chloride $[(Ph_3P)_2N]Cl$ to the above reaction mixture gave $[(Ph_3P)_2N]_2[Fe_4(CO)_{13}]$ [9]$^{7)}$ in a 30% yield. These results suggest that $Fe_3(CO)_{12}$ is converted into a tetranuclear carbonyl ferrate which can be formulated as $[Fe_4(CO)_{13}]^{2-}$ upon treatment with PyNO.

Mononuclear carbonyl ferrates such as $Na_2Fe(CO)_4$ and $NaHFe(CO)_4$ are useful reagents in organic synthesis.$^{8)}$ However, the chemical properties of polynuclear carbonyl ferrates have little been elucidated. This investigation indicated that they induce the reductive coupling of benzylic and allylic halides. Further application of polynuclear carbonyl ferrates to organic synthetic reactions now in progress in this laboratory.

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References and Notes

1) For example, see (a) H. Alper, "Transition metal organometallics in organic synthesis" Vol. 1, Academic Press, New York (1976); (b) D. Seyferth, Ed., "New application of organometallic reagents in organic synthesis", Elsevier Scientific Publishing Co., Amsterdam (1976); (c) I. Wender and P. Pino, Ed., "Organic Syntheses via Metal Carbonyls" Vol. 2, John Wiley and Sons, Inc., New York (1977).
2) When the reaction of benzyl chloride with $Fe_3(CO)_{12}$ was carried out in toluene and anisole, o- and p-substituted diphenylmethanes which were produced by benzylation of the aromatic solvents were obtained. In these reactions, the reactivity decreased in the order: anisole $\rangle$ toluene $\rangle$ benzene.
3) I. Rhee, M. Ryang, and S. Tsutsumi, J. Organometal. Chem., 9, 361 (1967).
4) The formation of [2a] is likely to occur by the thermal decomposition of an iron-carbonyl complex which contains benzyl group and which is produced during the course of the reaction. This is suggested by the observation that the NMR spectrum of this complex in benzene exhibited a broad signal at δ 1.22 ppm, which is assignable to the methylene group of $C_6H_5CH_2Fe$. Unfortunately, an attempt to isolate the complex in pure state was unsuccessful because of its instability. The complex gradually decomposed upon standing in a benzene solution even at room temperature.
5) R. F. Heck and C. R. Boss, J. Amer. Chem. Soc., 86, 2580 (1964).
6) Hieber and Lipp have reported that the reaction of 2.0 mmol of $Fe_3(CO)_{12}$ with 10.5 mmol of PyNO in benzene at room temperature for 18 h afforded the tetranuclear ferrate, $Fe(PyNO)_6[Fe_4(CO)_{13}]$: W. Hieber and A. Lipp, Chem. Ber., 92, 2085 (1959).
7) The following analytical and spectral data were obtained for [9]. Found: C,61.02; H,3.60; N,1.78; Fe,13.15%. Calcd. for $C_{85}H_{60}N_2O_{13}P_4Fe_4$: C,61.33; H,3.63; N,1.68; Fe,13.42%. IR (KBr), 1960 cm^{-1}. UVmax (CH_2Cl_2), 510 nm (ε,1058). Cyclic voltammetric data (in CH_3CN, 0.1M Et_4NClO_4, 25°C): E^{ox}=0.75 V; E^{red}=-2.05 V (vs Ag/AgCl).
8) J. P. Collman, Acc. Chem. Res., 9, 209 (1976).

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