Cyclodimerization of Benzylideneacetophenone and Its Derivatives by Use of Triiron Dodecacarbonyl

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The reaction of benzylideneacetophenone and its derivatives with $Fe_3(CO)_{12}$ in refluxing toluene gives 1-aroyl-2,4,5-triaryl-cyclopentene derivatives via (η^4-enone)tricarbonyliron complexes. The mechanistic feature of this reaction is presented.

Iron carbonyls have been shown to activate or stabilize various kinds of unsaturated organic compounds through the formation of their iron complexes.[1] These complexes often induce unique transformations.[2] However, the reactivity and synthetic utility of iron carbonyl complexes of α,β-unsaturated ketones have so far been little elucidated, although the complexes can readily be prepared from the ketones and iron carbonyls. We now report that treatment of benzylideneacetophenone and its derivatives with $Fe_3(CO)_{12}$ in refluxing toluene affords 1-aroyl-2,4,5-triarylcyclopentene derivatives in high yeilds. This reaction is formally regarded as a deoxygenative [2+3] cyclodimerization of α,β-unsaturated ketones and proceeds via a bimolecular interaction between two molecules of the iron complexes.

A mixture of benzylideneacetophenone (<u>1a</u>; 624 mg, 3 mmol) and $Fe_3(CO)_{12}$ (503 mg, 1 mmol) in dry toluene (10 cm^3) was stirred for 20 h at 110 °C under argon atmosphere, and poured onto I_2-benzen solution. The resulting mixture was stirred for 2 h at room temperature, and then washed successively with 10% aqueous NaOH, water, 10% HCl, and water. The organic layer was dried over Na_2SO_4 and evaporated. Chromatography of the residue on silica gel with toluene gave 432 mg (72%) of 1-benzoyl-2,4,5-triphenylcyclopentene (<u>2a</u>).

In a similar manner, the substituted benzylideneacetophenones <u>1-e</u> were converted into the corresponding cyclopentene derivatives <u>2b-e</u>. The results are

$$2\ Ar^1CH=CH-\underset{\underset{O}{||}}{C}Ar^2 \xrightarrow{Fe_3(CO)_{12}}$$

<u>1</u>   <u>2</u>

a; $Ar^1=C_6H_5$, $Ar^2=C_6H_5$ b; $Ar^1=p\text{-}ClC_6H_4$, $Ar^2=C_6H_5$

c; $Ar^1=p\text{-}CH_3C_6H_4$, $Ar^2=C_6H_5$ d; $Ar^1=p\text{-}CH_3OC_6H_4$, $Ar^2=C_6H_5$
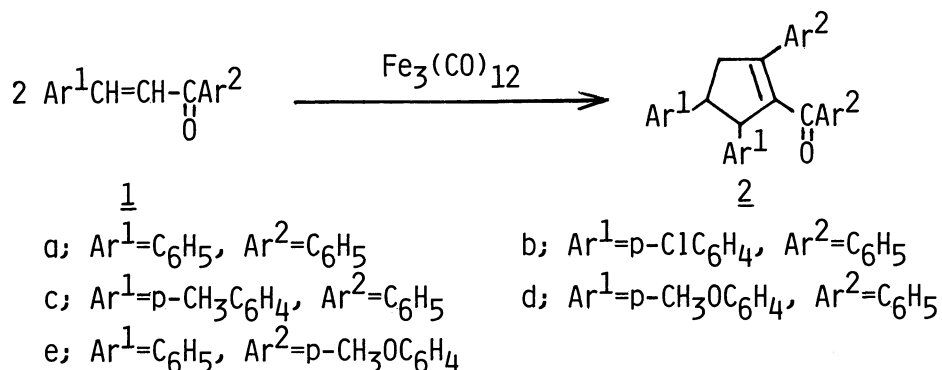
e; $Ar^1=C_6H_5$, $Ar^2=p\text{-}CH_3OC_6H_4$

Table 1. Reaction of substituted benzylideneacetophenones with $Fe_3(CO)_{12}$

Substrate		Yield/% [a]	Product mp/°C	UV λ_{max}/nm (ε) [b]
1a	2a	108 (72)	122-123	247(21000), 351(280)
1b	2b	98 (65)	145-146	246(23000), 352(280)
1c	2c	104 (69)	169-170	247(22000), 351(270)
1d	2d	87 (58)	135-136	246(29000), 351(360)
1e	2e	83 (55)	183-184	266(26000)

a) Isolated yields based on $Fe_3(CO)_{12}$ used, and those in parentheses based on 1 used. b) In cyclohexane.

summarized in Table 1. The products were identified from their UV, IR, ^{1}H-NMR, ^{13}C-NMR, and Mass spectral data.[3]

Yields of the products varied with molar ratios of the substrate enones to $Fe_3(CO)_{12}$ in the reactant mixtures; indeed, in the reaction of 1a with $Fe_3(CO)_{12}$, the yields of 2a based on $Fe_3(CO)_{12}$ reached a maximum value of 150% when the molar ratio $[1a]/[Fe_3(CO)_{12}] > 3$ (Fig. 1). This result indicates that 1a reacts with $Fe_3(CO)_{12}$ in a 3:1 molar ratio to produce 1.5 molar amount of 2a.

The efficiency of the reaction depended strongly on the nature of iron carbonyls. The reaction of 1a with $Fe(CO)_5$ under the similar conditions resulted in a quantitative recovery of the substrate. $Fe_2(CO)_9$ induced the cyclodimerization of 1a, but with lower efficiency; the yeild of 2a in this reaction based on one atom equiv of Fe reduced to one half the value that was obtained by use of $Fe_3(CO)_{12}$ (Fig. 2).
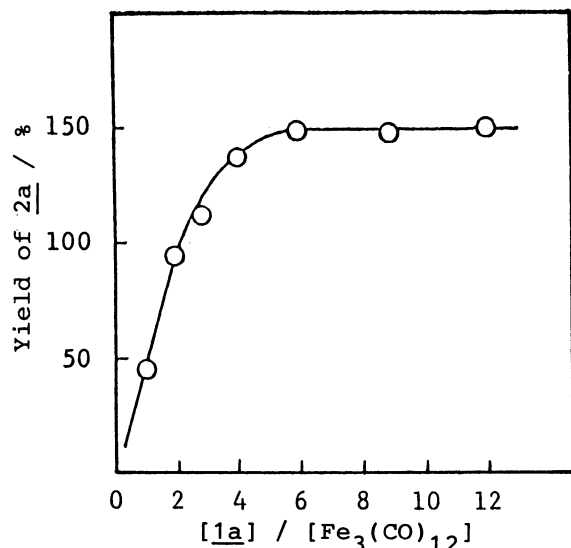
Fig. 1. Variation of yield of 2a with the change in the molar ratio $[1a]$ / $Fe_3(CO)_{12}$: $Fe_3(CO)_{12}$; 1 mmol, toluene; 10 cm^3. Stirred at 110 °C for 20 h under argon atmosphere. Yields were based on $Fe_3(CO)_{12}$ used.
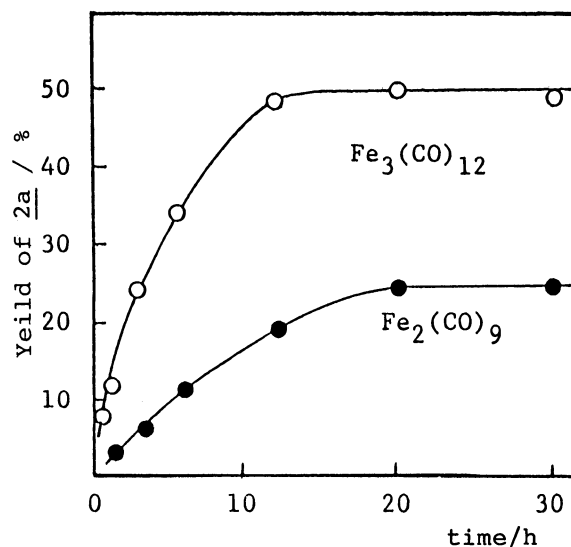
Fig. 2. Reaction of 1a with $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$: 1a; 6 mmol, $Fe_3(CO)_{12}$; 1 mmol, $Fe_2(CO)_9$; 1.5 mmol, toluene; 10 cm^3. Heated at 110 °C under argon atomsphere. Yields were based on one atom equiv of Fe used.

On the other hand, when the reactions of <u>1a-e</u> (18 mmol) with $Fe_3(CO)_{12}$ (6 mmol) were carried out in dry toluene (30 cm^3) at 75 °C for 8 h under argon atomsphere, (η^4-enone)tricarbonyliron complexes <u>3a-e</u> were obtained in 55-72% yeilds.[4) These iron complexes were converted into <u>2a-e</u> in almost quantitative yeilds with evolution of CO by refluxing in toluene.

$$Ar^1CH=CH-\underset{O}{\overset{\|}{C}}Ar^2 \xrightarrow{Fe_3(CO)_{12}} \underset{\underset{\underline{3}}{Fe(CO)_3}}{Ar^1\diagup\!\!/ \overset{Ar^2}{\underset{|}{\diagdown}}O} \xrightarrow{\triangle} \underset{\underline{2}}{Ar^1\diagup\!\!\diagup\overset{Ar^2}{\diagdown}\underset{Ar^1}{\diagdown}\underset{O}{\overset{\|}{C}}Ar^2}$$

$$\underline{1}$$

Table 2. The conversion of (η^4-enone)tricarbonyliron complexes into cyclopentene derivatives[a)]

(η^4-Ar^{1}CH=CHCOAr^2)Fe(CO)$_3$	Product	Yield/%[b)]
<u>3a</u>; Ar^1=C$_6$H$_5$, Ar^2=C$_6$H$_5$	<u>2a</u>	94
<u>3b</u>; Ar^1=p-ClC$_6$H$_4$, Ar^2=C$_6$H$_5$	<u>2b</u>	90
<u>3c</u>; Ar^1=p-CH$_3$C$_6$H$_4$, Ar^2=C$_6$H$_5$	<u>2c</u>	93
<u>3d</u>; Ar^1=p-CH$_3$OC$_6$H$_4$, Ar^2=C$_6$H$_5$	<u>2d</u>	92
<u>3e</u>; Ar^1=C$_6$H$_5$, Ar^2=p-CH$_3$OC$_6$H$_4$	<u>2e</u>	92

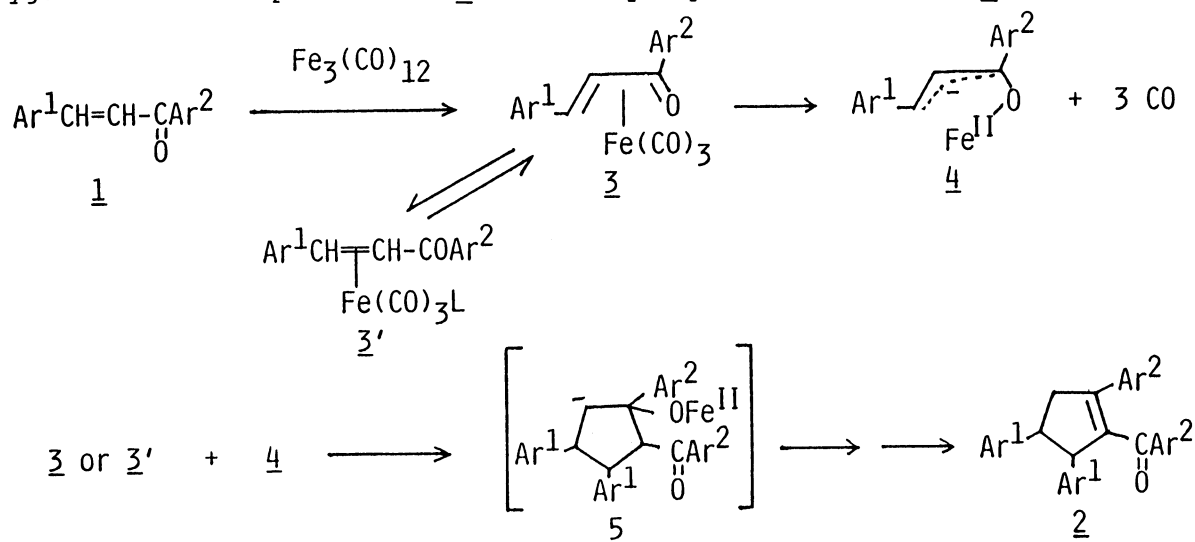a) Complexes <u>3</u> (1 mmol) were refluxed in toluene (10 cm^3) for 8 h under argon atomsphere. b) Yeilds based on <u>3</u> used.

When a 1:1 mixture of iron complex <u>3a</u> and uncomplexed enone <u>1d</u> was heated in toluene for 8 h, <u>2a</u> was obtained as a sole product with a quantitative recovery of <u>1d</u>. However, when a 1:1 mixture of iron complexes <u>3a</u> and <u>3d</u> was heated under the similar conditions, two crossed coupling products <u>2f</u> and <u>2g</u> were obtained together with homocoupling products <u>2a</u> and <u>2d</u>. These results strongly suggest that <u>2a-e</u> are formed by a bimolecular reaction between two molecules of the respective iron complexes <u>3a-e</u>, but not by the reaction of the iron complex with an uncomplexed enone.

$$\underset{\underset{\underline{3a}}{Fe(CO)_3}}{Ph\diagup\!\!/\overset{Ph}{\underset{|}{\diagdown}}O} + Ar^1CH=CH-\underset{O}{\overset{\|}{C}}Ph \longrightarrow \underset{\underline{2a}}{Ph\diagup\!\!\diagup\overset{Ph}{\diagdown}\underset{Ph}{\diagdown}\underset{O}{\overset{\|}{C}}Ph}$$

$$\underset{\underline{1d}}{}$$

$$\underset{\underset{\underline{3a}}{Fe(CO)_3}}{Ph\diagup\!\!/\overset{Ph}{\underset{|}{\diagdown}}O} + \underset{\underset{\underline{3d}}{Fe(CO)_3}}{Ar^1\diagup\!\!/\overset{Ph}{\underset{|}{\diagdown}}O} \longrightarrow$$

$$\underset{\underline{2a}}{Ph\diagdown\overset{Ph}{\diagdown}\underset{Ph}{\diagup}CPh} + \underset{\underline{2d}}{Ar^1\diagdown\overset{Ph}{\diagdown}\underset{Ar^1}{\diagup}CPh} + \underset{\underline{2f}}{Ph\diagdown\overset{Ph}{\diagdown}\underset{Ar^1}{\diagup}CPh} + \underset{\underline{2g}}{Ar^1\diagdown\overset{Ph}{\diagdown}\underset{Ph}{\diagup}CPh}$$

$$Ph=C_6H_5, \quad Ar^1=p-CH_3OC_6H_4$$

A possible mechanistic pathway for the above cycloaddition reaction is shown in Scheme 1.

A key step of this reaction is the generation of allylic anion **4** by electron-transfer from **3** and/or **3'** (**3'** exists in equilibrium with **3** at a high temperature[5]) to the enone ligand in the complex with elimination of three molecules of CO.[6] The anion thus generated undergoes a [2+3] cycloaddition by interaction with **3** and/or **3'**, giving anionic cycloadduct **5**. The elimination of oxygen as anionic species from **5** affords cyclopentene derivative **2**.

$Ar^1CH=CH-\underset{\underset{O}{\|}}{C}Ar^2$ $\xrightarrow{Fe_3(CO)_{12}}$ $Ar^1\diagup\!\!\!\diagup\overset{Ar^2}{\underset{Fe(CO)_3}{|}}\diagdown O$ $\longrightarrow$ $Ar^1\diagup\!\!\!\diagup\overset{Ar^2}{\underset{Fe^{II}}{-}}\diagdown O$ $+$ 3 CO

1   **3**   **4**

$Ar^1CH\underset{\underset{Fe(CO)_3L}{|}}{=}CH-COAr^2$

3'

3 or **3'** $+$ **4** $\longrightarrow$ $\left[Ar^1\underset{Ar^1}{\diagup\!\!\diagdown}\overset{\overset{Ar^2}{OFe^{II}}}{\underset{\underset{O}{\|}}{C}Ar^2} \right]$ $\longrightarrow$ $\longrightarrow$ $Ar^1\underset{Ar^1}{\diagup\!\!\diagdown}\overset{Ar^2}{\underset{\underset{O}{\|}}{C}Ar^2}$

5   **2**

Scheme 1.

References

1) R. B. King, "The Organic Chemistry of Iron," Academic Press, New York (1978), Vol. 1.

2) H. Alper, "Organic Syntheses with Iron Pentacarbonyl," in "Organic Syntheses via Metal Carbonyl," ed by I. Wender and P. Pino, John Wiley and Sons, Inc., New York (1977), Vol. 2, pp. 545-593; J. P. Collman and L. S. Hegedus, "Principles and Application of Organotransition Metal Chemistry," University Science Books, Mill Valey, Calif. (1980).

3) Spectral data of **2a**: ^{13}C-NMR (CDCl$_3$) δ(ppm) 44.6($\underline{C}H_2$),52.9, 63.6($\underline{C}H<$), 135.2, 136.4(=$\underline{C}<$), 126.4, 127.2, 127.7, 128.0, 128.1, 128.3, 128.7, 132.7(aromatic =$\underline{C}H$-), 138.8, 141.9, 143.1, 145.6(aromatic =$\underline{C}<$), 195.8($>\underline{C}$=O); ^1H-NMR (CDCl$_3$) δ(ppm) 2.9-3.8(m, 3H), 4.4-4.6(m, 1H), 7.0-7.6(20H, ArH); IR (KBr) 1630 cm^{-1} (ν_{CO}); MS m/e 400 (M$^+$). The spectral data for **2b-e** were also consistent with the assigned structures.

4) For formation of (η^4-enone)tricarbonyliron complexes, see: J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, J. Organomet. Chem., **39**, 329 (1972).

5) A. Vessires and P. Dixneuf, Tetrahedron Lett., **1974**, 1499.

6) Quantitative analysis of the gas evolved during the reactions revealed that three molar amounts of CO were liberated with formation of one molar amount of **2**. Prolonged heating of the reaction mixture, about three molar amounts of CO evolved too slowly with a mirror of iron metal.