CHEMISTRY LETTERS, pp. 1635-1638, 1986.

# Cyclodimerizations of Alkyl Styryl Ketones and Their Silyl Enol Ethers by Use of Iron Carbonyls

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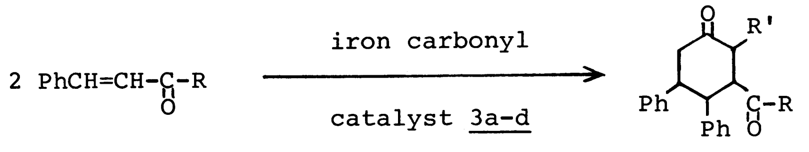
The reaction of alkyl styryl ketones with $Fe_3(CO)_{12}$ gives 3-acyl-4,5-diphenylcyclohexanones in a manner of [2+4] cyclodimerization. ($\eta^4$-Enone)$Fe(CO)_3$ complexes serve as catalyst for this reaction. Silyl enol ethers of the same ketones afford 4-acyl-3,5-diphenylcyclohexanones in the different type of [2+4] cyclodimerization upon treatment with $Fe_3(CO)_{12}$.

In a previous paper, we have reported that the reaction of unenolizable α,β-unsaturated ketones such as benzylideneacetophenone with $Fe_3(CO)_{12}$ in refluxing toluene gives cyclopentene derivatives in high yields.1) This reaction has been interpreted as a deoxygenative [2+3] cyclodimerization of intermediary ($\eta^4$-enone)tricarbonyliron complexes.1) We now report that enolizable α,β-unsaturated ketones such as alkyl styryl ketones and their silyl enol ethers undergo respectively different types of [2+4] cyclodimerizations upon treatment with $Fe_3(CO)_{12}$. Alkyl styryl ketones were converted into 3-acyl-4,5-diphenylcyclohexanones via their tricarbonyliron complexes. It was also found that ($\eta^4$-enone)tricarbonyliron complexes serve as effective catalyst for this conversion. On the other hand, silyl enol ethers of the same ketones were converted into 4-acyl-3,5-diphenylcyclohexanones probably via their iron enolates.

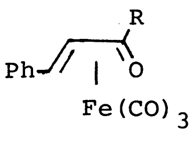
A mixture of methyl styryl ketone (1a; 876 mg, 6 mmol) and $Fe_3(CO)_{12}$ (503 mg, 1 mmol) in dry toluene (10 $cm^3$) was refluxed for 20 h under nitrogen and poured onto $I_2$-benzen solution. The resulting mixture was stirred for 1 h at



$$2\ PhCH{=}CH{-}\overset{\displaystyle O}{\underset{}{C}}{-}R \xrightarrow[\text{catalyst } 3a\text{-}d]{\text{iron carbonyl}}$$

1a; R=Me
1b; R=Et
1c; R=n-Pr
1d; R=i-Pr

2a; R=Me, R'=H
2b; R=Et, R'=Me
2c; R=n-Pr, R'=Et
2d; R=i-Pr, R'=$Me_2$



3a; R=Me
3b; R=Et
3c; R=n-Pr
3d; R=i-Pr

Table 1. Reaction of alkyl styryl ketones with iron carbonyls

| Ketone | Iron carbonyl | Product | Yield/%[a] |
|---|---|---|---|
| 1a | $Fe_3(CO)_{12}$, 2 mmol | 2a | 58 (87) |
| 1a | $Fe_3(CO)_{12}$, 1 mmol | 2a | 62 (186) |
| 1a | $Fe_3(CO)_{12}$, 0.5 mmol | 2a | 52 (312) |
| 1a | $Fe(CO)_5$, 3 mmol | no reaction | |
| 1a | $Fe_2(CO)_9$, 1.5 mmol | 2a | 26 (52) |
| 1b | $Fe_3(CO)_{12}$, 2 mmol | 2b | 90 (135) |
| 1c | $Fe_3(CO)_{12}$, 2 mmol | 2c | 89 (134) |
| 1d | $Fe_3(CO)_{12}$, 2 mmol | 2d | 33 (50) |

a) Isolated yields based on ketones 1 used, and those in parentheses based on iron carbonyls used.

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 benzene gave 543 mg (62%) of 3-acetyl-4,5-diphenylcyclohexanone (2a). In a similar manner, ethyl, propyl, and isopropyl styryl ketones (1b-d) were converted into the corresponding 2-substituted 3-acyl-4,5-diphenylcyclohexanones 2b-d. The results are summarized in Table 1. The structures of the products were assigned from their IR and $^1$H-NMR, $^{13}$C-NMR, and Mass spectral data.[2)]

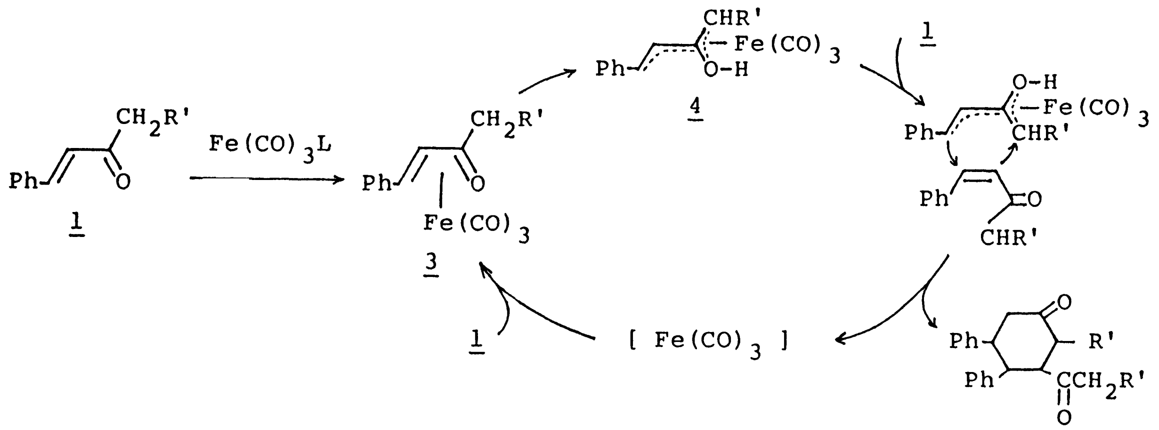
The efficiency of this dimerization reaction depended on iron carbonyl complexes employed. The reaction of 1a with $Fe(CO)_5$ under the similar conditions as above resulted in a quantitative recovery of the starting ketone. $Fe_2(CO)_9$ induced the cyclodimerization of 1a with a lower efficiency. The results are also given in Table 1.

Lewis et al. have reported that the reaction of 1a with iron carbonyls at ambient temperatures affords ($\eta^4$-methylstyrylketone)tricarbonyliron (3a).[3)] We also isolated the iron complexes 3a-d by the reaction of 1a-d with $Fe_3(CO)_{12}$ in toluene at 75 °C for 7 h in good yields. Furthermore, it was found that when degassed toluene solutions of 1a-c (40 mmol) containing a catalytic amount of

Table 2. ($\eta^4$-Enone)tricarbonyliron-catalyzed cyclodimerization of alkyl styryl ketones

| Ketone | Catalyst | Product | Yield / %[a] |
|---|---|---|---|
| 1a | 3a | 2a | 11 (2250) |
| 1b | 3a | 2b | 15 (3000) |
| 1c | 3a | 2c | 14 (2750) |
| 1a | 3b | 2a | 25 (4920) |
| 1b | 3b | 2b | 81 (16200) |
| 1c | 3b | 2c | 60 (11900) |
| 1c | 3c | 2c | 53 (10600) |

a) Yields were determined by GLC and based on ketones 1 used, and those in parentheses based on iron complexes 3 used.

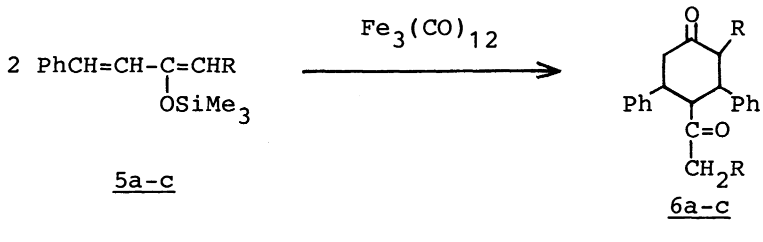


Scheme 1.

($\eta^4$-enone)tricarbonyliron 3a (0.1 mmol) are heated in sealed tubes at 110 °C for 22 h, 2a-c are obtained in good yields. Other ($\eta^4$-enone)tricarbonyliron complexes such as 3b-c also served as catalyst for the conversion of 1a-c to 2a-c. The results are shown in Table 2.

However, complexes $Fe(CO)_4PPh_3$, $Fe(CO)_3(PPh_3)_2$, $Fe(CO)_3[P(OPh)_3]_2$, ($\eta^2$-maleic anhydride)$Fe(CO)_4$, ($\eta^4$-cyclooctadiene)$Fe(CO)_3$, and ($\eta^4$-PhCH=CHCH=CHPh)Fe-$(CO)_3$ were ineffective as catalyst; in the reactions using these iron complexes the substrate enones were recovered unchanged. Barton[4)] and Brookhart[5)] have demonstrated that 3a acts as an efficient transfer agent of $[Fe(CO)_3]$ species towards dienes and other unsaturated compounds. Scheme 1 shows a possible catalytic cycle for the cyclodimerization of enolizable enone 1. A key step is the formation of dienol complex 4[6)] from ($\eta^4$-enone)tricarbonyliron complex 3. The complex 4 may react with 1 to produce cyclohexanone derivative 2 with elimination of $[Fe(CO)_3]$ species.

Table 3. Cyclodimerization of silyl enol ether[a)]

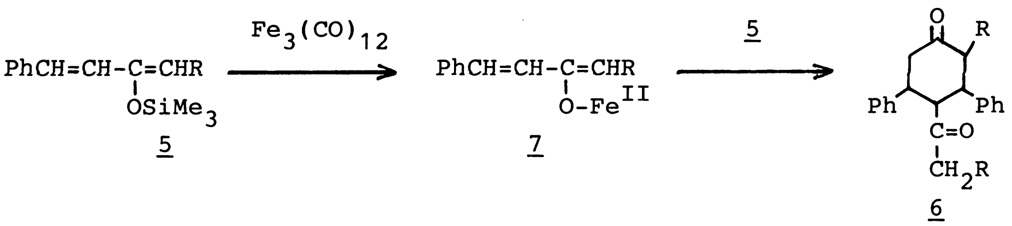


| Silyl enol ether | Product | Yield/%[b)] |
|---|---|---|
| 5a; R=H | 6a | 32 (95) |
| 5b; R=$CH_3$ | 6b | 36 (108) |
| 5c; R=$CH_2CH_3$ | 6c | 32 (96) |

a) A mixture of 5 (6 mmol) and $Fe_3(CO)_{12}$ (1 mmol) in toluene (10 $cm^3$) was stirred at 110 °C for 20 h under nitrogen. b) Isolated yields based on 4 used, and those in parentheses based on $Fe_3(CO)_{12}$ used.

In contrast, the reaction of silyl enol ethers 5a-c, which were derived from 1a-c, with $Fe_3(CO)_{12}$ in refluxing toluene gave 2-substituted 4-acyl-3,5-diphylcyclohexanones 6a-c, that are regioisomers of 2a-c. The results are shown in Table 3. The structures of 6a-c were assigned from their spectral data.$^{7)}$

Nielsen and Dubin have reported that the same type of cyclohexanone derivatives as 6a-c can be obtained from alkyl styryl ketones by a base-catalyzed self-condensation reaction in low yields.$^{8)}$ These results strongly suggest that the cyclodimerization of silyl enol ethers 5 with $Fe_3(CO)_{12}$ proceeds via iron enolate 7 as shown in Scheme 2.



Scheme 2.

References

1) T. Ueda and Y. Otsuji, the preceding paper.

2) Spectral data of 2a: $^{13}$C-NMR ($CDCl_3$) δ(ppm) 31.7($\underline{C}H_3$), 40.7, 41.1($\underline{C}H_2$), 42.9, 44.3, 58.4($\underline{C}H<$), 126.9, 127.1, 127.6, 128.2, 128.6, 128.8(aromatic =$\underline{C}$H-), 140.2, 143.1(aromatic =$\underline{C}<$), 210.5, 210.7($\underline{C}$=O); $^1$H-NMR ($CDCl_3$) δ(ppm) 1.6(s, 3H), 2.4-3.2(m, 4H), 3.4-3.6(m, 3H), 7.0-7.9(10H, ArH); IR (KBr) 1710, 1630 $cm^{-1}$($\nu_{CO}$); MS m/e 292 ($M^+$). The spectral data for 2b-e were also consistent with the assigned structures.

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6) C. H. DePuy, R. L. Parton, and T. Jones, J. Am. Chem. Soc., 99, 4070 (1977); C. H. DePuy, R. N. Greene, and T. E. Schroer, J. Chem. Soc., Chem. Commun., 1968, 1225.

7) Spectral data of 6a: $^{13}$C-NMR ($CDCl_3$) δ(ppm) 33.0($\underline{C}H_3$), 47.8($\underline{C}H_2$), 47.2, 62.0 ($\underline{C}H<$), 127.3, 127.5, 129.0(aromatic =$\underline{C}$H-), 141.1(aromatic =$\underline{C}<$), 207.5, 210.4 ($\underline{C}$=O); $^1$H-NMR ($CDCl_3$) δ(ppm) 1.25(s, 3H), 2.68(broad d, J=6 Hz, 4H), 3.0-3.5 (m, 3H), 7.2(10H, ArH); IR (KBr) 1710, 1670 $cm^{-1}$($\nu_{CO}$); MS m/e 292 ($M^+$). The spectral data for 6b,c were also consistent with the assigned structures.

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(Received July 23, 1986)