

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 $\text{Fe}_3(\text{CO})_{12}$ gives 3-acyl-4,5-diphenylcyclohexanones in a manner of [2+4] cyclodimerization. $(\eta^4\text{-Enone})\text{Fe}(\text{CO})_3$ 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 $\text{Fe}_3(\text{CO})_{12}$.

In a previous paper, we have reported that the reaction of unenolizable α,β -unsaturated ketones such as benzylideneacetophenone with $\text{Fe}_3(\text{CO})_{12}$ in refluxing toluene gives cyclopentene derivatives in high yields.¹⁾ This reaction has been interpreted as a deoxygenative [2+3] cyclodimerization of intermediary $(\eta^4\text{-enone})\text{tricarbonyliron}$ 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 $\text{Fe}_3(\text{CO})_{12}$. Alkyl styryl ketones were converted into 3-acyl-4,5-diphenylcyclohexanones via their tricarbonyliron complexes. It was also found that $(\eta^4\text{-enone})\text{tricarbonyliron}$ 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 $\text{Fe}_3(\text{CO})_{12}$ (503 mg, 1 mmol) in dry toluene (10 cm³) was refluxed for 20 h under nitrogen and poured onto I₂-benzen solution. The resulting mixture was stirred for 1 h at

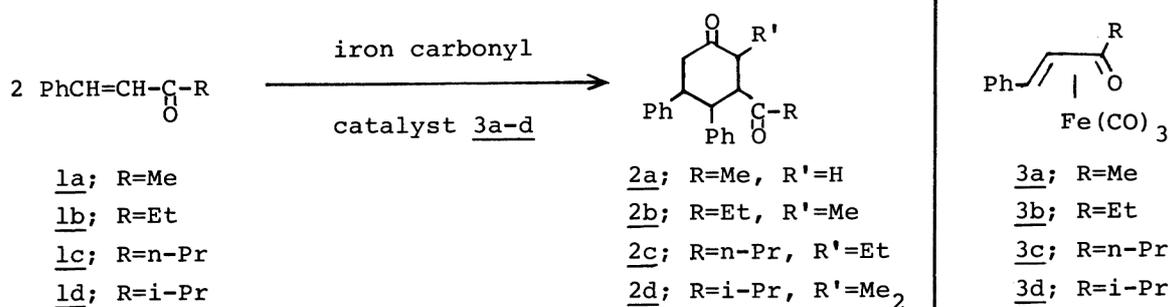


Table 1. Reaction of alkyl styryl ketones with iron carbonyls

Ketone	Iron carbonyl	Product	Yield/% ^{a)}
<u>1a</u>	Fe ₃ (CO) ₁₂ , 2 mmol	<u>2a</u>	58 (87)
<u>1a</u>	Fe ₃ (CO) ₁₂ , 1 mmol	<u>2a</u>	62 (186)
<u>1a</u>	Fe ₃ (CO) ₁₂ , 0.5 mmol	<u>2a</u>	52 (312)
<u>1a</u>	Fe(CO) ₅ , 3 mmol	no reaction	
<u>1a</u>	Fe ₂ (CO) ₉ , 1.5 mmol	<u>2a</u>	26 (52)
<u>1b</u>	Fe ₃ (CO) ₁₂ , 2 mmol	<u>2b</u>	90 (135)
<u>1c</u>	Fe ₃ (CO) ₁₂ , 2 mmol	<u>2c</u>	89 (134)
<u>1d</u>	Fe ₃ (CO) ₁₂ , 2 mmol	<u>2d</u>	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 Na₂SO₄ 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 ¹H-NMR, ¹³C-NMR, and Mass spectral data.²⁾

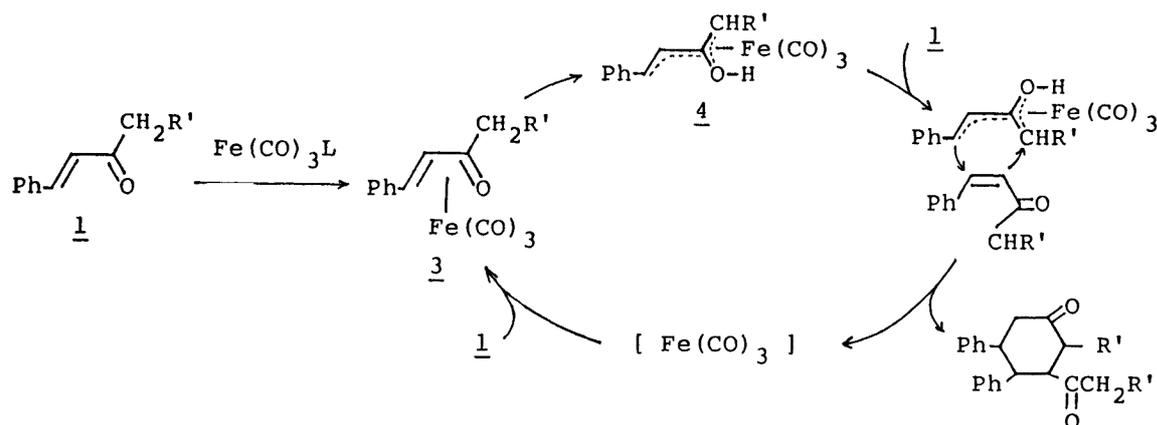
The efficiency of this dimerization reaction depended on iron carbonyl complexes employed. The reaction of 1a with Fe(CO)₅ under the similar conditions as above resulted in a quantitative recovery of the starting ketone. Fe₂(CO)₉ induced the cyclodimerization of 1a with a lower efficiency. The results are also given in Table 1.

Lewis et al. have reported that the reaction of 1a with iron carbonyls at ambient temperatures affords (η⁴-methylstyrylketone)tricarbonyliron (3a).³⁾ We also isolated the iron complexes 3a-d by the reaction of 1a-d with Fe₃(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. (η⁴-Enone)tricarbonyliron-catalyzed cyclodimerization of alkyl styryl ketones

Ketone	Catalyst	Product	Yield / % ^{a)}
<u>1a</u>	<u>3a</u>	<u>2a</u>	11 (2250)
<u>1b</u>	<u>3a</u>	<u>2b</u>	15 (3000)
<u>1c</u>	<u>3a</u>	<u>2c</u>	14 (2750)
<u>1a</u>	<u>3b</u>	<u>2a</u>	25 (4920)
<u>1b</u>	<u>3b</u>	<u>2b</u>	81 (16200)
<u>1c</u>	<u>3b</u>	<u>2c</u>	60 (11900)
<u>1c</u>	<u>3c</u>	<u>2c</u>	53 (10600)

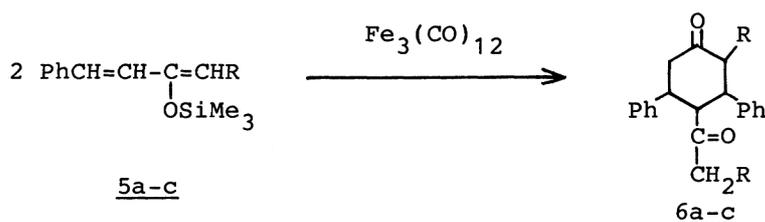
a) Yields were determined by GLC and based on ketones 1 used, and those in parentheses based on iron complexes 3 used.



(η^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 (η^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 $\text{Fe}(\text{CO})_4\text{PPh}_3$, $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, $\text{Fe}(\text{CO})_3[\text{P}(\text{O}Ph)_3]_2$, (η^2 -maleic anhydride) $\text{Fe}(\text{CO})_4$, (η^4 -cyclooctadiene) $\text{Fe}(\text{CO})_3$, and (η^4 - $\text{PhCH}=\text{CHCH}=\text{CHPh}$) $\text{Fe}(\text{CO})_3$ were ineffective as catalyst; in the reactions using these iron complexes the substrate enones were recovered unchanged. Barton⁴⁾ and Brookhart⁵⁾ have demonstrated that 3a acts as an efficient transfer agent of $[\text{Fe}(\text{CO})_3]$ 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 4⁶⁾ from (η^4 -enone)tricarbonyliron complex 3. The complex 4 may react with 1 to produce cyclohexanone derivative 2 with elimination of $[\text{Fe}(\text{CO})_3]$ species.

Table 3. Cyclodimerization of silyl enol ether^{a)}

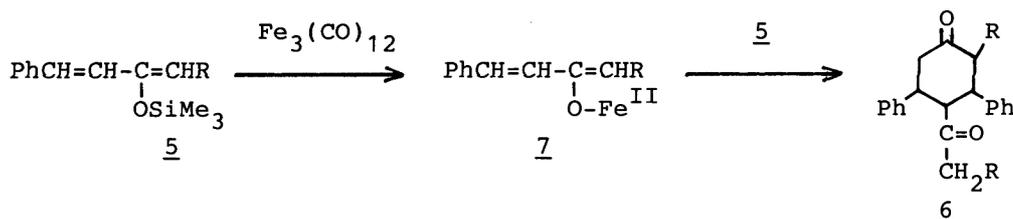


Silyl enol ether	Product	Yield/% ^{b)}
<u>5a</u> ; R=H	<u>6a</u>	32 (95)
<u>5b</u> ; R=CH ₃	<u>6b</u>	36 (108)
<u>5c</u> ; R=CH ₂ CH ₃	<u>6c</u>	32 (96)

a) A mixture of 5 (6 mmol) and $\text{Fe}_3(\text{CO})_{12}$ (1 mmol) in toluene (10 cm³) was stirred at 110 °C for 20 h under nitrogen. b) Isolated yields based on 4 used, and those in parentheses based on $\text{Fe}_3(\text{CO})_{12}$ used.

In contrast, the reaction of silyl enol ethers 5a-c, which were derived from 1a-c, with $\text{Fe}_3(\text{CO})_{12}$ in refluxing toluene gave 2-substituted 4-acyl-3,5-diphenylcyclohexanones 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 $\text{Fe}_3(\text{CO})_{12}$ 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($\underline{\text{CH}}_3$), 40.7, 41.1($\underline{\text{CH}}_2$), 42.9, 44.3, 58.4($\underline{\text{CH}}\leq$), 126.9, 127.1, 127.6, 128.2, 128.6, 128.8(aromatic $=\underline{\text{CH}}-$), 140.2, 143.1(aromatic $=\underline{\text{C}}\leq$), 210.5, 210.7($\underline{\text{C}}=\text{O}$); ^1H -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} (ν_{CO}); MS m/e 292 (M^+). The spectral data for 2b-e were also consistent with the assigned structures.
- 3) J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organomet. Chem.*, **39**, 329 (1972).
- 4) D. H. R. Barton, A. A. L. Gunatilaka, T. Nakanishi, H. Patin, D. A. Widdowson, and B. R. Worth, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 821.
- 5) C. R. Graham, G. Scholes, and M. Brookhart, *J. Am. Chem. Soc.*, **99**, 1180 (1977).
- 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($\underline{\text{CH}}_3$), 47.8($\underline{\text{CH}}_2$), 47.2, 62.0($\underline{\text{CH}}\leq$), 127.3, 127.5, 129.0(aromatic $=\underline{\text{CH}}-$), 141.1(aromatic $=\underline{\text{C}}\leq$), 207.5, 210.4($\underline{\text{C}}=\text{O}$); ^1H -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} (ν_{CO}); MS m/e 292 (M^+). The spectral data for 6b,c were also consistent with the assigned structures.
- 8) A. T. Nielsen and H. J. Dubin, *J. Org. Chem.*, **28**, 2120 (1963).

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