

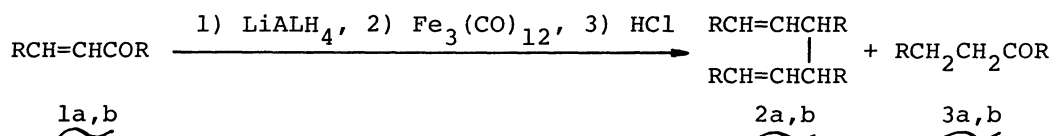
REDUCTIVE DIMERIZATION OF α,β -UNSATURATED KETONES
BY $\text{LiAlH}_4\text{-Fe}_3(\text{CO})_{12}\text{-HCl}$ REAGENT SYSTEM

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Aromatic α,β -unsaturated ketones were converted into 1,5-hexadiene derivatives by use of $\text{LiAlH}_4\text{-Fe}_3(\text{CO})_{12}\text{-HCl}$ reagent system.

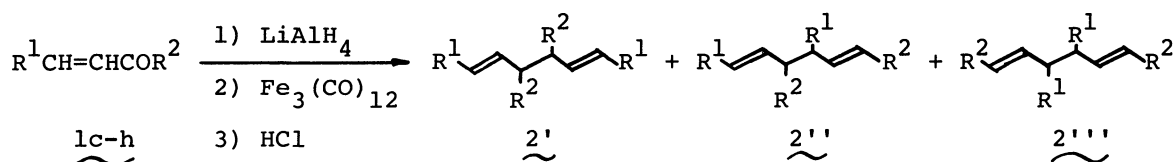
Iron carbonyls have been used as a versatile reagent for organic syntheses. They can effect deoxygenation of organic compounds, such as epoxides,¹⁾ amine oxides,²⁾ oximes,³⁾ and nitro compounds,⁴⁾ but the deoxygenation of ketones can not be achieved with this reagent. We now report that the reaction of α,β -unsaturated ketones with $\text{LiAlH}_4\text{-Fe}_3(\text{CO})_{12}\text{-HCl}$ reagent system causes reductive dimerization accompanied by deoxygenation to give 1,5-hexadiene derivatives.


A solution of benzylideneacetophenone 1a (8.0 mmol) and LiAlH_4 (4.0 mmol) in THF (30 ml) was stirred at -10°C for 30 min under argon. $\text{Fe}_3(\text{CO})_{12}$ (2.0 mmol) was added to this solution, and the resulting mixture was heated at 60°C for 15 h, and then treated with 3N HCl (15 ml) for 3 h at the same temperature. The mixture was extracted with benzene (50 ml). The extract was washed with water, dried (MgSO_4) and evaporated. The residue was subjected to a column chromatography (silica gel) to give 1,3,4,6-tetraphenyl-1,5-hexadiene 2a and 1-benzoyl-2-phenyl-ethane 3a in 78 and 4% yields, respectively. The products were identified by their elemental analyses, ir, nmr, and mass spectra.



Similarly, 1,3,4,6-tetra(2-furyl)-1,5-hexadiene 2b was obtained from 1,3-di(2-furyl)-2-propen-1-one 1b in a 75% yield together with a trace amount of 1,3-di(2-furyl)-1-propanone 3b. Yields of products varied with the change in a molar ratio of reagents. The maximal yield of 2 was obtained when the molar ratio of the ketones : LiAlH_4 : $\text{Fe}_3(\text{CO})_{12}$ was 4 : 2 : 1. For the above dimerization, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$ were also effective, but the efficiency decreased in the order : $\text{Fe}_3(\text{CO})_{12} > \text{Fe}_2(\text{CO})_9 > \text{Fe}(\text{CO})_5$. Application of this reaction is limited to aromatic α,β -unsaturated ketones. For example, treatment of 4-phenyl-3-buten-2-one gave 1-phenyl-1-butene by the reduction of the carbonyl group.

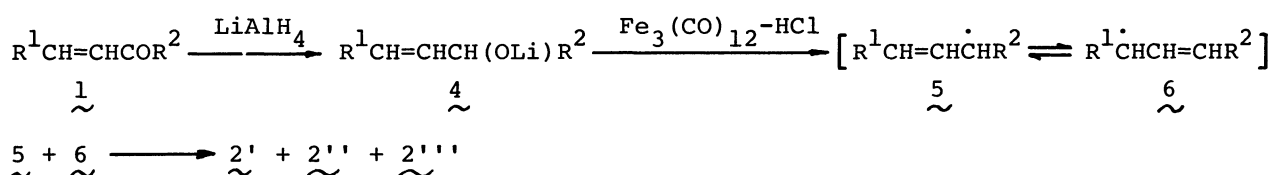
Similar treatment of substituted benzylideneacetophenone 1c-h afforded three isomers of 1,5-hexadiene derivatives 2c-h as major products. The results are given in Table.

Table. Formation of 1,5-Hexadiene Derivatives from α,β -Unsaturated Ketones

Ketone	Total Yield of Diene, % ^{a)}	Isomer Distribution ^{b)}		
		2'	2''	2'''
lc : p-CH ₃ C ₆ H ₄	76	43	37	20
ld : p-CH ₃ OC ₆ H ₄	71	26	63	11
le : C ₆ H ₅	59	14	57	29
lf : p-ClC ₆ H ₄	47	24	52	24
lg : C ₆ H ₅	51	~0	~0	>99
lh : 	59	>99	~0	~0

a) Isolated yields based on 1 used. b) Isomer distribution was determined by GLC analysis of the methyl esters of succinic acid derivatives which were derived by the oxydation of a mixture of 2', 2'' and 2''' with KMnO₄.

The first step of the above reactions appears to be the reaction of α,β -unsaturated ketones with LiAlH₄ to give α,β -unsaturated alcohols,⁵⁾ which then undergo the reductive dimerization with Fe₃(CO)₁₂-HCl to afford 1,5-hexadiene derivatives.⁶⁾ The results of Table suggest that allylic radicals (5 and 6) are involved as intermediates in these reactions. An advantage of the method reported in this paper is that the reactions can be carried out in a single flask under mild conditions.



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References and Notes

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- 3) A. Dondoni and G. Barbaro, J. Chem. Soc., Chem. Comm., 761 (1975).
- 4) J. M. Landesberg, L. Katz, and C. Olsen, J. Org. Chem., 37, 930 (1972).
- 5) Treatment of 1a with 0.5 molar LiAlH₄ in THF at -10°C gave almost quantitatively 1-hydroxy-1,3-diphenyl-2-propene.
- 6) Fe(powder)-HCl in place of Fe₃(CO)₁₂-HCl also effects the similar reductive dimerization, but with less satisfactory results : in this case, the yield of 2a was 9%.

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