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Allylation of Acyl Halides Adjacent to (η^4-Diene)Fe(CO)3 Fragment with Allylsilanes

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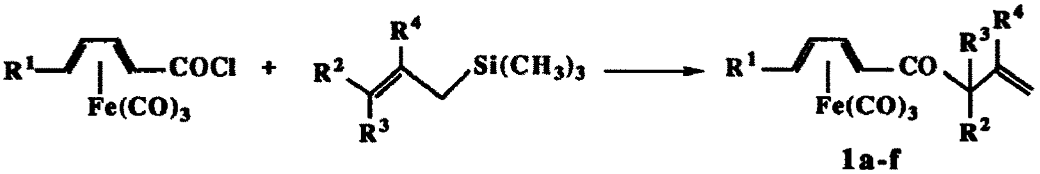
Abstract: Acyl halides adjacent to (η^4-diene)Fe(CO)$_3$ group react with allyltrimethylsilanes without catalyst to give the corresponding allyl ketones in high yields.

(η^4-Diene)Fe(CO)$_3$ complexes having carbonyl group have been shown to be versatile reagents in organic synthesis,[1] and several synthetic routes to the complexes such as Friedel-Craft type acylation[2] of diene complexes and palladium-catalyzed acylation[3] of 2-stannylated diene complexes have been developed. However, (η^4-2,4-hexadienoic acid)Fe(CO)$_3$ complex and its analog have little been utilized because solubility of these complexes is poor in most organic solvents and transformation of the carboxyl group of the complexes into other functional groups is relatively restricted. In the context of a program dealing with the use of the (η^4-diene)Fe(CO)$_3$ complexes in organic synthesis, we have found a remarkable effect of (η^4-diene)Fe(CO)$_3$ group on the allylation of acyl halides with allylsilanes. Allylation of acyl halides with allylsilanes is an useful method for the preparation of β,γ-unsaturated carbonyl compounds.[4] In this paper, we wish to report a novel route to (η^4-diene)Fe(CO)$_3$ complexes containing β,γ-unsaturated acyl groups via allylation of acyl halides with allylsilanes.



1a-f

To a suspension of (η^4-2,4-hexadienoic acid)Fe(CO)$_3$ (1.0 mmol) in dichloromethane (20 ml) was added oxalyl chloride (2.0 mmol). The mixture was stirred at r.t. for 3 h. The complex dissolved completely and was converted into the acyl chloride during the procedure. After removal of the excess oxalyl chloride and the solvent, dichloromethane (20 ml) was added to the residue. Allyltrimethylsilane (1.2 mmol) was added to the solution at -60 °C. The resulting mixture was stirred at -60 °C for 3 h and then gradually warmed to r.t. All compounds were isolated after usual work-up by column chromatography on silica gel.[5] Several examples of allylation reaction are shown in Table.

The remarkable features of the reaction are: 1) Although acyl halides generally react with allylsilanes in the presence of Lewis acid as activating agent, the present reaction proceeds under neutral conditions without Lewis acid, indicating that (η^4-diene)Fe(CO)$_3$ fragment activates the acyl group for the allylation reaction. 2) Carbon-carbon bond formation takes place only at γ-position of allylsilanes in usual fashion. 3) The reaction of sterically hindered allylsilanes such as prenyl-, 2-octenyl- and cinnamyltrimethylsilanes gave the corresponding ketones in low yield. However, the yields can be improved in the presence of AlCl$_3$ without decomposition of the complexes. 4) This allylation reaction provides a route to (η^4-diene)Fe(CO)$_3$ complexes bearing β,γ-unsaturated acyl groups, and 1,3-butadienyl allyl ketones can be obtained via decomplexation of the (η^4-diene)Fe(CO)$_3$ fragment.[6] 5) The iron carbonyl fragment serves as not only activating agent on the allylation reaction but also protecting reagent of 1,3-butadiene group in the reaction.

Table. Reaction of Acyl Chlorides with Allylsilanes

Complex R^1	Allylsilane R^2	R^3	R^4	Yield of 1 / %[a)]		Complex R^1	Allylsilane R^2	R^3	R^4	Yield of 1 / %[a)]	
CH_3	H	H	H	**1a**	86	CH_3	C_6H_5	H	H	**1d**	89[b)]
CH_3	H	H	CH_3	**1b**	87	CH_3	C_5H_{11}	H	H	**1e**	67
CH_3	CH_3	CH_3	H	**1c**	23	CH_3	C_5H_{11}	H	H	**1e**	89[b)]
CH_3	CH_3	CH_3	H	**1c**	70[b)]	C_6H_5	H	H	H	**1f**	83
CH_3	C_6H_5	H	H	**1d**	60						

a) Isolated yields. b) In the presence of AlCl$_3$.

The complexes **1d** and **1e** consist of 1:1 mixture of the complexes having R and S configulation at the chiral carbon. The reaction of chiral (2S)-(η^4-2,4-hexadienoic acid)Fe(CO)$_3$[7] with cinnamyltrimetyl-silane and 2-octenyltrimetylsilane was carried out to give a mixture of diastereomers in 1 : 1 ratio in each case, indicating no asymmetric induction.

References and Notes

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4. a) Calas, R.; Dunogues, J.; Pillot, J.-P.; Biran, C.; Pisciatti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 145. b) Ojima, I.; Kumagai, M.; Miyazawa, Y. *Tetrahedron Lett.* **1977**, 1385.
5. The indicated structures are in good agreement with elementary analysis and the spectroscopic data. In a typical example, **1a**: Yellow oil. IR (Neat): ν=2056, 1972 (C=O), 1678 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$): δ=6.00-5.78 (1H, m, CH=), 5.79 (1H, dd, J=8.4, 4.8 Hz, CH=), 5.24 (1H, dd, J=8.0, 4.8 Hz, CH=), 5.23-5.10 (2H, m, CH$_2$=), 3.11 (2H, d, J=6.8 Hz, CH$_2$), 1.61-1.48 (1H, m, CH=), 1.48 (3H, d, J=5.3 Hz, CH$_3$), 1.25 (1H, d, J=8.1 Hz, CH=). ^{13}C NMR (CDCl$_3$): δ=218.33 (C=O), 203.27 (C=O), 131.20, 118.75, 88.92, 81.27, 59.34, 52.49 (CH=), 47.70 (CH$_2$), 19.11 (CH$_3$).
6. Treatment of **1a** with cerium ammonium nitrate in methanol gave 1,3-pentadienyl allyl ketone in 95 % yield.
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