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1-Trimethylsiloxyallylic Iron Complexes as a β-Acylcarbanion Equivalent

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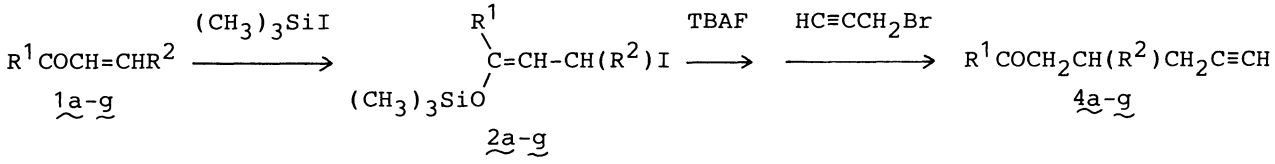
3-Iodo-1-trimethylsiloxypropenes, which were derived by the reaction of α,β-unsaturated ketones and esters with iodotrimethylsilane, gave (η^3-1-trimethylsiloxyallylic)$Fe(CO)_2NO$ complexes upon treatment with tetrabutylammonium tricarbonylnitrosylferrate. These allylic iron complexes reacted regioselectively with 2-propynyl bromide, giving the corresponding 4-pentynyl ketone and 5-hexynoic ester derivatives.

Recently, β-acylcarbanions (homoenolates) have emerged as valuable intermediates in organic synthesis.[1-2] Several methods have been developed for the generation of these intermediates or their synthetic equivalents. An approach to the generation of these intermediates is the desilylative ring cleavage of siloxycyclopropanes with metal salts.[3] The other approach is based on the preparation of heteroatom-substituted allylic carbanions.[4-5] Previously, we have reported that the reaction of (η^3-allylic)$Fe(CO)_2NO$ complexes with allylic and acyl halides gives 1,5-dienes and β,γ-unsaturated ketones, respectively, as major products.[6] These results imply that the allylic ligands in the iron complexes behave as allylic anions. We now report that (η^3-1-trimethylsiloxyallylic)$Fe(CO)_2NO$ complexes, which can be derived readily from α,β-unsaturated ketones or esters, react regioselectively with an electrophilic reagent at 3-position of the allylic ligands in the complexes, thus the complexes may be utilized as a synthetic equivalent of β-acylcarbanions.

Treatment of phenyl vinyl ketone (1a, 2.0 mmol) with iodotrimethylsilane (2.2 mmol) in CH_2Cl_2 (10 cm^3) at room temperature for 2 h gave 3-iodo-1-trimethylsiloxy-1-phenylpropene (2a) in 95% yield.[7] The iron complex n-$Bu_4NFe(CO)_3NO$ (TBAF, 2.0 mmol) in CH_2Cl_2 (2.5 cm^3) was added to the above solution, without isolation of 2a, and then the mixture was stirred at room temperature for 2 h under argon atmosphere. After removal of solvent under reduced pressure, dimethylformamide(DMF, 10 cm^3) was added as solvent, then 2-propynyl bromide (4.0 mmol) as an alkylating

agent under argon atmosphere. The resulting mixture was warmed at 75 °C for 15 h, cooled and extracted with ether (30 cm^3). The extract was washed successively with dil hydrochloric acid, aqueous $NaHSO_3$ solution and water, then dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed on silica-gel. Elution with hexane/ethylacetate(97.5/2.5) gave 4-pentynyl phenyl ketone (4a) in 81% yield. Further elution with hexane/ethylacetate(95/5) gave phenyl vinyl ketone (1a) in 19% yield.



Similarly, α,β-unsaturated ketones and esters (1b-g) were converted into 3-iodo-1-trimethylsiloxypropenes (2b-g) by treating with iodotrimethylsilane in CH_2Cl_2.[7] The iodo compounds thus prepared were allowed to react with TBAF without isolation, and then with 2-propynyl bromide in a similar manner as above. Work-up of the reaction mixtures gave 4-pentynyl ketones (4b-e) and 5-hexynoic esters (4f-g). No other products were detected in the reaction mixtures. The

Table 1. Preparation of 4-Pentynyl Ketones and 5-Hexynoic Esters Promoted by TBAF[a)]

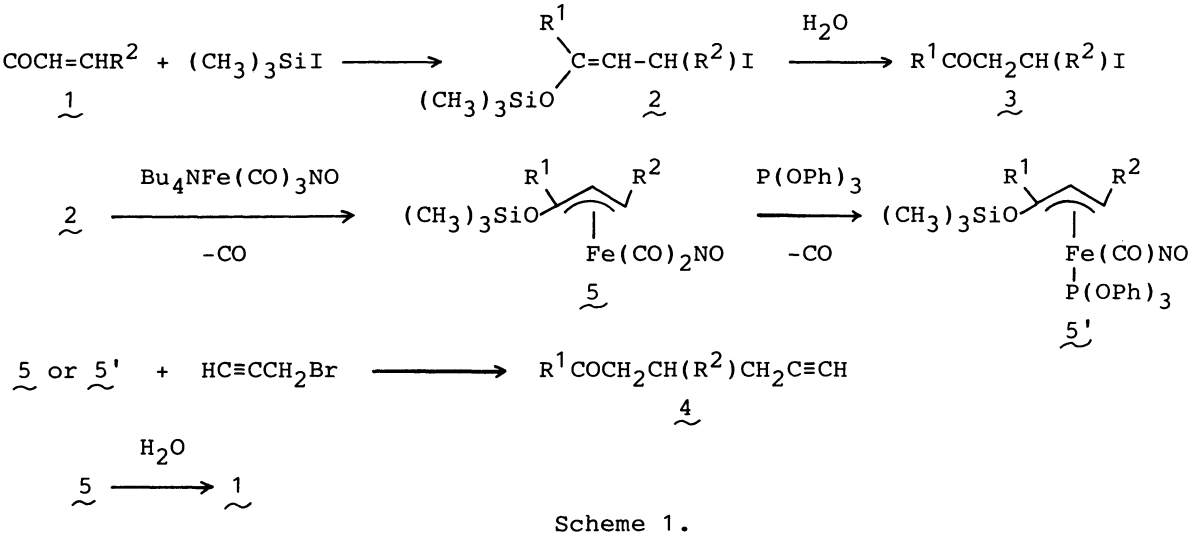
Run	Substrate		Additive	Yield of product/%[b)]
	R^1	R^2		4
1	1a: C_6H_5	H	None	81
2	1b: p-$CH_3C_6H_4$	H	None	35
3	1b:		$P(OPh)_3$	83
4	1c: p-ClC_6H_4	H	None	66
5	1c:		$P(OPh)_3$	87
6	1d: C_2H_5	H	None	27
7	1d:		$P(OPh)_3$	58
8	1e: -$(CH_2)_3$-		None	32
9	1e:		$P(OPh)_3$	56
10	1f: C_6H_5O	H	None	12
11	1f:		$P(OPh)_3$	50
12	1g: CH_3O	C_6H_5	None	30
13	1g:		$P(OPh)_3$	62

a)Substrate(1): 2.0 mmol, Iodotrimethylsilane: 2.2 mmol, TBAF: 2.0 mmol, 2-Propynyl bromide: 4.0 mmol, Solvent: DMF(10 cm^3), Temp: 75 °C, Time: 15 h. b)Yields based on substrate used.

results are summarized in Table 1. The structures of the products were confirmed by their elemental analyses and also from their spectral data.[8)]

The yields of 4a-g were considerably improved by adding triphenylphosphite to the reaction mixtures after treatments of 2a-g with TBAF. The results are also given in Table 1.

A remarkable feature of the above sequence of reactions is that the alkynyl group in 2-propynyl bromide which is usually regarded as an electrophile is introduced into the β-position of α,β-unsaturated ketones and esters with high regioselectivity. A plausible mechanism accounting for all the experimental results is presented in Scheme 1.



Scheme 1.

A key intermediate of the reactions is (η^3-1-trimethylsiloxyallylic)$Fe(CO)_2NO$ complexes (5). The siloxyallylic ligands are formally regarded as heteroatom-substituted carbanions and behave as nucleophiles. Therefore, 5 may be viewed as a synthetically equivalent synthon for β-acylcarbanions.

Although the iron complexes 5 were not identified by isolation due to high sensitivities to moisture and air, the formation of 5 in the course of the reactions was supported by the following experiments. Treatment of 2a (2.0 mmol) with TBAF (2.0 mmol) in CH_2Cl_2 (10 cm^3) at 20 °C for 15 h under argon atmosphere, followed by hydrolysis with dil hydrochloric acid, gave quantitatively 1a. During this reaction, one equiv of CO to TBAF was evolved. On the other hand, the hydrolysis of 2a without added TBAF gave quantitatively 2-iodoethyl phenyl ketone (3a). A more strong support for the formation of 5 was furnished by taking an IR spectrum of the reaction mixture that was obtained by treating 2a with TBAF in CH_2Cl_2. The IR spectrum showed the following bands characteristic of the iron complex; ν_{CO} 2060, 1980 cm^{-1}; ν_{NO} 1745 cm^{-1}; ν_{OSi} 870 cm^{-1}.

Detailed mechanism and synthetic applications of the reactions reported here are now under investigation.

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8)4a: Oil; IR(neat) 3300, 2100, 1680 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.84-2.00(3H, m, ≡CH and $CH_2\underline{CH}_2CH_2$), 2.14-2.40(2H, m, ≡CCH_2), 3.04(2H, t, J=6.9 Hz, $COCH_2$), 7.30-7.38(3H, m, aromatic H), 7.74-7.88(2H, m, aromatic H).

4b: Oil; IR(neat) 3300, 2100, 1690 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.90-1.99(3H, m, ≡CH and $CH_2\underline{CH}_2CH_2$), 2.11-2.45(2H, m, ≡CCH_2), 2.41(3H, s, p-CH_3), 3.04(2H, t, J=6.9 Hz, $COCH_2$), 7.14(2H, d, J=8.4 Hz, aromatic H), 7.78(2H, d, J=8.4 Hz, aromatic H).

4c: Oil; IR(neat) 3300, 2100, 1690 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.85-1.99(3H, m, ≡CH and $CH_2\underline{CH}_2CH_2$), 2.00-2.30(2H, m, ≡CCH_2), 3.04(2H, t, J=6.9 Hz, $COCH_2$), 7.33(2H, d, J=8.0 Hz, aromatic H), 7.84(2H, d, J=8.0 Hz, aromatic H).

4d: Oil; IR(neat) 3300, 2100, 1740 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.06(3H, t, J=6.9 Hz, $CH_2\underline{CH}_3$), 1.63-1.98(3H, m, ≡CH and $CH_2\underline{CH}_2CH_2$), 2.00-2.58(6H, m, ≡CCH_2 and 2x $COCH_2$).

4e: Oil; IR(neat) 3300, 2100, 1710 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.66-1.80(5H, m), 1.92-2.38(7H, m, ≡CH, ≡CCH_2, and 2x $COCH_2$).

4f: Oil; IR(neat) 3300, 2100, 1750 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.92-2.02(3H, m, ≡CH and $CH_2\underline{CH}_2CH_2$), 2.21-2.33(2H, m, ≡CCH_2), 2.54(2H, t, J=6.9 Hz, $COCH_2$), 7.03-7.10(5H, m, aromatic H).

4g: Oil; IR(neat) 3300, 2100, 1725 cm^{-1}; ^1H NMR($CDCl_3$) δ=1.93(1H, t, J=2.4 Hz, ≡CH), 2.42-2.54(2H, m, ≡CCH_2), 2.60-2.78(3H, m, PhCH and $COCH_2$), 3.50(3H, s, CO_2CH_3), 7.02-7.20(5H, m, aromatic H).

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