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Preliminary communication

Friedel–Crafts chemistry of dieneiron tricarbonyl complexes. Acetylation of 1-silylated and 1,4 disubstituted dienes

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Abstract

In contrast to simple olefinic or to aromatic compounds bearing a silyl group attached to an sp^2 carbon, trimethyl-silylated dieneiron tricarbonyl complexes, do not undergo *ipso*-substitution reactions unless there is an alkyl group in the 4 position. This allows synthesis of acylated dienes that still retain the Me_3Si substituent. In one case an unusual 1,1-diacylation was observed during an attempted single acetylation. 1,4-Disubstituted dieneiron tricarbonyl complexes were found to give good yields of stable acylated complexes under the usual Friedel–Crafts conditions.

Electrophilic acylation of dieneiron tricarbonyl complexes leads primarily to *cis*-dienone complexes [1]. We recently investigated the acylation of 2-silylated diene complexes and described the novel 1,4-bis-acylation reactions they undergo [2]. No acylation products resulting from an *ipso*-replacement of the silyl group were observed during the first or the second acylation of these complexes. Moreover, the presence of a silicon atom in the molecule did not seem to be necessary for bis-acylation, and iron tricarbonyl complexes of other dienes, such as isoprene, were later found to give similar results, showing that bis-acylation is a quite general reaction [3].

Since terminal diene acylation was always observed even with 2-silylated diene complexes, our interest turned next to the acylation of 1-silylated diene complexes. We report hence that *ipso*-substitution is only observed if the second terminal position of the 1-silylated diene unit is also substituted.

The butadienic complex Ia [4] and the analogous isoprenic complex Ib, obtained from 1-trimethylsilyl-3-methylbutadiene [5] by complexation with nonacarbonyldiiron, were treated in dichloromethane at 0 °C with the 1/1 acetyl chloride/aluminium chloride Perrier complex. The *cis*-dienone complexes IIa and IIb [6*],

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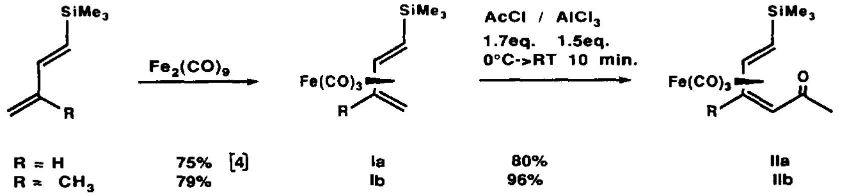
* This and other references marked with asterisks indicate notes occurring in the list of references.

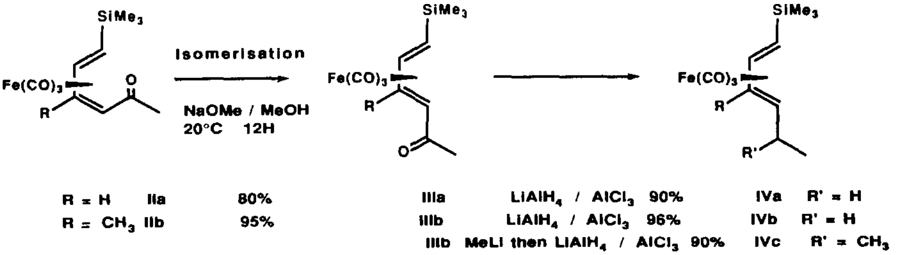
still bearing the silyl substituent, were obtained in high yields as the sole acetylated products (Scheme 1).



Scheme 1.

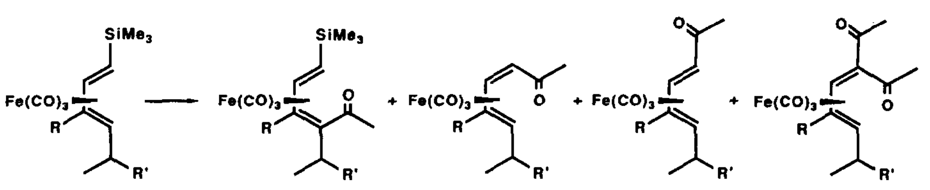
After isomerisation [7*] to the *trans*-dienones IIIa and IIIb and decomplexation, 4-acyl-1-silyldienes are obtained in good yields [8*]. These products cannot be obtained by direct acylation of 1-silylated dienes because desilylation is the usual process with uncomplexed dienes [9].

Since acylation of compounds Ia and Ib proceeded at the unsubstituted end of the complexed silylated butadiene unit, it was decided to lock that position with a *trans*-alkyl substituent. Complexes IIIa and IIIb were reduced with alanes [10*] to the ethylated complexes IVa and IVb. The isopropyl substituted complex VIc was similarly obtained by treatment of complex IIIb with methyllithium followed by reduction with alanes (Scheme 2).



Scheme 2.

Compound IVb after acetylation with an excess of Perrier complex (AcCl/$AlCl_3$), and aqueous work-up, yielded a mixture of four products which were chromatographically separated and fully characterized [6*]. The less polar complex, Vb, still bearing the silyl substituent, arose from the *endo*-acylation at the alkyl substituted end position of the diene complex IVb. Complexes VIb and VIIb resulted from the acetyldesilylation (*ipso*-substitution), as expected. Complex VIIIb, another product of *ipso*-substitution, isolated in 13% yield, is a diacetylated compound having both acetyl groups on the same carbon atom. We checked that the formation of this unusual 1,1-diacylated product did not result from the acetylation of complexes VIb or VIIb under the conditions of monoacylation. The ratio of acylation at position 1 (*ipso*-substitution: VIb, VIIb and VIIIb) to that at position 4 (Vb) was approximatively 1.5/1. This ratio was almost the same for acetylation of IVa, though no diacetylated complex was isolated in this case. When complex IVc was acetylated a mixture of only two products, VIc and VIIc, was obtained in 93% overall yield (Scheme 3). Their formation resulted from the sole *ipso*-substitution reaction and no



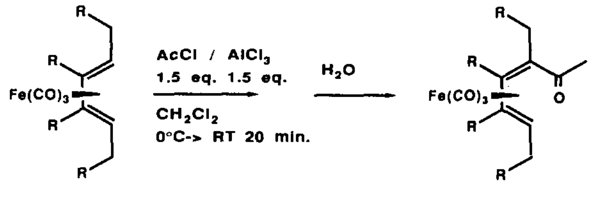
R=R'=H	IVa	97 %	Va 40 %	VIa 45 %	VIIa 13 %	
R=CH$_3$,R'=H	IVb	97 %	Vb 34 %	VIb 19 %	VIIb 31 %	VIIIb 13 %
R=R'=CH$_3$	IVc	93 %		VIc 69 %	VIIc 24 %	

Conditions :					
1.0 eq. IVa	3.0 eq. AcCl	3.0 eq. AlCl$_3$	CH$_2$Cl$_2$	35 min.	0°C -> RT
1.0 eq. IVb	1.5 eq. AcCl	1.5 eq. AlCl$_3$	CH$_2$Cl$_2$	15 min.	0°C -> RT
1.0 eq. IVc	1.5 eq. AcCl	1.5 eq. AlCl$_3$	CH$_2$Cl$_2$	10 min.	0°C -> RT

Scheme 3.

acylation occurred at the more sterically hindered carbon 4 position bearing the isopropyl substituent.

It should be noted that we rapidly obtained complexes such as Va and Vb bearing three substituents at the end positions of the diene unit. It has been reported that 1,4-disubstituted butadiene complexes do not give isolable acylated complexes in Friedel–Crafts reaction [11]. This is obviously not the case here, and so we checked whether the behaviour we observed depended on the presence of a silyl group. This was found not to be the case, since under the usual conditions we obtained the analogous trisubstituted dieneiron complexes IX, X from unsilylated starting materials (Scheme 4). This points to novel synthetic possibilities involving use of the Friedel–Crafts chemistry of complexed dienes.



R = H		IX	66%
R = CH$_3$		X	82%

Scheme 4.

We conclude that the normal Friedel–Crafts acylation at the unsubstituted end of an iron tricarbonyl complexed diene is the preferred reaction even where there is a silyl substituent at the other terminal position. However, *ipso*-substitution can be observed if the complex has an substituent at the other end of the diene unit, and this reaction becomes the sole process for larger groups.

References

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6 Analytical and spectral data for IIb, Vb, VIb, VIIb and VIIIb:

IIb: yellow crystals recrystallized from ether–hexane, m.p. 38–39° C; $\nu_{\text{max.}}$ (CCl_4): 2050, 1990 and 1980 cm^{-1} ($Fe(CO)_3$), 1665 cm^{-1} (C=O); δ($CDCl_3$) ^1H: 5.49 (1H, d, *J* 11.4 Hz), 3.20 (1H, s), 2.22 (3H, s), 2.12 (3H, s), 1.03 (1H, d, *J* 11.4 Hz), 0.15 (9H, s); found: C, 48.7; H, 5.6; calcd.: C, 48.46; H, 5.63%.

Vb: yellow crystals recrystallized from ether/hexane, m.p. 61–62° C; $\nu_{\text{max.}}$ (CCl_4): 2050, 1992 and 1970 cm^{-1} ($Fe(CO)_3$), 1665 cm^{-1} (C=O); δ($CDCl_3$) ^1H: 5.34 (1H, d, *J* 11.6 Hz), 2.0–2.4 (2H), 2.27 (3H, s), 2.13 (3H, s), 1.01 (3H, t, *J* 7.4 Hz), 0.49 (1H, d, *J* 11.6 Hz), 0.12 (9H, s); found C, 51.4; H, 6.3; calcd.: C, 51.43; H, 6.33%.

VIb: yellow crystals recrystallized from ether/hexane, m.p. 42–43° C; $\nu_{\text{max.}}$ (CCl_4): 2050, 1987 and 1980 cm^{-1} ($Fe(CO)_3$), 1665 cm^{-1} (C=O); δ($CDCl_3$) ^1H: 5.14 (1H, d, *J* 6.3 Hz), 2.91 (1H, d, *J* 6.3 Hz), 2.16 (3H, s), 2.10 (3H, s), 1.5–2.2 (2H), 1.13 (3H, t, *J* 7.2 Hz); found: C, 51.8; H, 5.2; calcd.: C, 51.83; H, 5.08%.

VIIb: yellow liquid; $\nu_{\text{max.}}$ (CCl_4) 2055, 1992 and 1975 cm^{-1} ($Fe(CO)_3$), 1680 cm^{-1} (C=O); δ($CDCl_3$) ^1H: 5.70 (1H, d, *J* 8.0 Hz), 2.17 (3H, s), 2.13 (3H, s), 1.5–2.0 (2H), 1.31 (1H, m), 1.14 (3H, t, *J* 7.2 Hz), 1.12 (1H, d, *J* 8.0 Hz); found: C, 52.0; H. 5.3; calcd.: C, 51.83; H, 5.08%.

VIIIb: yellow crystals recrystallized from ether/hexane, m.p. 71–72° C; $\nu_{\text{max.}}$ (CCl_4): 2065, 2010 and 1985 cm^{-1} ($Fe(CO)_3$), 1695 and 1675 cm^{-1} (C=O); δ ($CDCl_3$) ^1H: 5.88 (1H, s), 2.24 (3H, s), 2.16 (3H, s), 2.03 (1H, m), 1.95 (3H, s), 1.5–2.0 (2H), 1.11 (3H, t, *J* 7.0 Hz); found: C, 52.6; H, 5.0; calcd.: C, 52.53; H, 5.04%.

7 The *cis*-dienone complexes II are completely isomerized to the corresponding *trans*-dienone complexes III, either by treatment with methanolic sodium methoxide or by dissolution in acetyl chloride followed by quenching with ice-water (cf. ref. 2).

8 Treatment of IIIb with H_2O_2/NaOH [12] yielded 1-trimethylsilyl 3-methyl hexa 3,5-diene 5-one (80%) $\nu_{\text{max.}}$ (CCl_4): 1680 cm^{-1} (C=O), 1590 and 1575 cm^{-1} (C=C); δ($CDCl_3$) ^1H: 6.49 (1H, d, *J* 19 Hz), 6.40 (1H, d, *J* 19 Hz), 6.15 (1H, broad s), 2.20 (3H, s), 2.19 (3H, m), 0.09 (9H, s).

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10 The reduction with alanes follows litterature procedure [11a,b].

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