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FORMATION AND CHARACTERIZATION OF TRICHLOROTITANIUM ENOLATES

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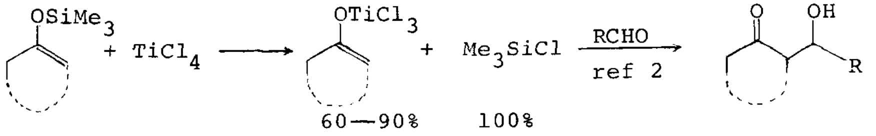
Summary: The reaction of enol silyl ethers with $TiCl_4$ gives trichlorotitanium enolates, which are unique with their relatively electron deficient double bonds.

Despite extensive research about the enolate anion, relatively little has been known for the properties of transition metal enolates.[1] We report in this communication the preparation and the characterization of titanium enolates and, in the following, their aldol reaction.[2]

Reddish trichlorotitanium enolates readily form in better than 90% NMR yield (except 1b and 7b formed in 60—70% yield) by the reaction of the corresponding enol silyl ethers and 1 equiv of $TiCl_4$ at 20—35 °C in a halomethane solvent. The enolate formation in the cyclohexanone series is rapid and completes within 5 to 15 min; 5a reacted most rapidly within a few minutes and the substituted ones more slowly. Interestingly, the reaction of 3a, being stereospecific, completed within a few minutes, while that of 4a took 2 h for 50% conversion at ca. 30 °C, giving a 1:1 mixture of 3b and 4b. During the course of the latter reaction, the isomeric ratio remained virtually unchanged. Of the two stereoisomers of the enol silyl ethers of 3-pentanone, only the Z-isomer afforded the titanium enolate in good yield. The stability of the titanium enolate (as formed in $CDCl_3$ under nitrogen and kept at 20—30 °C) depends greatly on the structure of substrates: The cyclopentanone enolate appears to decompose as it forms, the cyclohexanone enolate 5b remains stable for less than 10 min, enolates, 1b, 6b, 7b, and 8b, for some hours, and the most stable ones, 3b (isolable as a brown solid) and 4b, for an order of a few days.



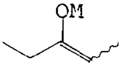
Enol silyl ethers react with $SnCl_4$ to afford α-stannyl ketones.[3] The formation of metal enolates in the reaction with $TiCl_4$ is therefore highly intriguing. The enolate structure of the products was generally deduced from their ^1H NMR spectra (Table 1). The triplet of the vinyl protons in the cyclohexanone series closely resembles in shape that of the respective starting materials. This stands in contrast to the appearence of a doublet of doublets with α-stannyl[3] and α-mercurio[4] ketones. Additional information concerning the structure comes from the presence of a single methyl resonance in the ^{1}H NMR spectrum of 6b; the corresponding metallo ketone 9 shows two non-equivalent methyl groups owing to the chiral center generated by the attachment of the metal to the carbon atom. Without the crucial olefinic proton, the enolate structure of 8b could only be ascertained by ^{13}C NMR analysis. The spectrum of 8b is clearly incompatible with the metallo ketone formulation. The α-stannyl ketone 9 shows its carbonyl carbon at a very low field: 215.9 (s), 67.4 (d), 46.9 (s), 40.4 (t), 30.6 (t), 25.1 (q), 23.0 (t).

The NMR signals of the olefinic protons and carbons of the titanium enolate appear exceptional as an enol derivative.[5] The olefinic carbon signals of 6b, for instance, appear at 181.1 and 114.8 ppm, while the signals of the silyl ether 6a are located at 157.0 and 101.4 ppm. The lithium enolates generally exhibit their carbon signals at much higher fields.[6] The trichlorotitanium group thus exerts a significant electron withdrawing effect instead of an electron release usually expected for a metal atom.

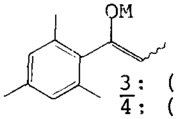
Among other metal chlorides examined thus far, $SbCl_5$ and $TeCl_4$ reacted with enol silyl ethers to give α-metallo ketones. Studies on the mechanism and the possible reasons of the metal-dependent dichotomy in the reaction of enol silyl ethers with metal salts are under way.

a series: M = $SiMe_3$

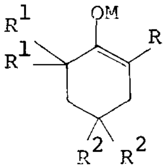
b series: M = $TiCl_3$



1: (Z)
2: (E)



3: (Z)
4: (E)



	R	R^1	R^2
5:	H	H	H
6:	H	Me	H
7:	H	H	Me
8:	Me	H	H

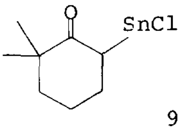


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Table I. NMR Spectra ($CDCl_3$) of Trichlorotitanium Enolates

Compd No.	^{1}H NMR (multiplicity, J)	^{13}C NMR (multiplicity)
1b	4.67 (q, 7), 2.30 (qq, 1.5, 7) 1.76 (dq, 1.5, 7), 1.10 (t, 7)	175.4 (s), 108.7 (d)
3b	4.94 (q, 7), 2.05 (d, 7)	169.4 (s), 139.4 (s), 136.8 (s), 132.4 (s), 128.4 (d), 113.6 (d), 21.1 (q), 20.1 (q), 11.4 (q)
4b	5.90 (q, 7), 1.45 (d, 7)	
5b	5.88 (br t)	
6b	5.56 (t, 4.5), 1.27 (s)	181.1 (s), 114.8 (d), 38.7 (t), 37.1 (s), 26.9 (q), 24.3 (t), 18.8 (t)
7b	5.70 (br t, 4)	
8b	1.90 (m)	170.1 (s), 120.7 (s), 29.7 (t), 28.9 (t), 23.9 (t), 23.0 (t), 22.1 (t), 16.6 (q)

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