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Preliminary communication

The reaction of $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ with sulfoxides

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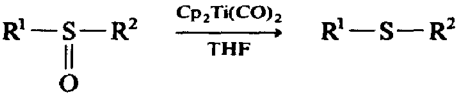
Abstract

Sulfoxides are reduced by $(\eta\text{-}C_5H_5)_2Ti(CO)_2$ to give sulfides in high yield while sulfones and phosphine oxides do not react.

The deoxygenative coupling of aromatic aldehydes by $Cp_2Ti(CO)_2$, where Cp = C_5H_5, to give pinacols and olefin has been reported [1]. Deoxygenation of sulfoxides to sulfides is also of current interest. A number of reagents such as $HSiCl_3$ [2], Si_2Cl_6 [3,4], P_2S_5 [5], PCl_5/enamine [6], and $(CF_3CO)_2O$/NaI [7] have been reported to convert sulfoxides to sulfides in varying yields. A number of low-valent transition metal reagents such as $CrCl_2$ [8], $TiCl_4$/Zn [9] or LiH [10] or $NaBH_4$ [11], $MoCl_3$/Zn [12], $CoCl_2/NaBH_4$ [13], $K_3W_2Cl_9$ [14] and others have received much attention as deoxygenating agents as well.

We have found that $Cp_2Ti(CO)_2$ readily deoxygenates sulfoxides (**1**) to sulfides (**2**) in high yield.



$$\underset{\text{(1)}}{R^1{-}\underset{\underset{O}{\|}}{S}{-}R^2} \xrightarrow[\text{THF}]{Cp_2Ti(CO)_2} \underset{\text{(2)}}{R^1{-}S{-}R^2}$$

(**1**) (**2**)

$Cp_2Ti(CO)_2$ was prepared and purified by the literature procedure [15] and kept as a solution in THF at room temperature. In a typical procedure a solution of *p*-tolylsulfoxide (0.29 g, 1.25 mmol) and $Cp_2Ti(CO)_2$ (1.2 mmol) in THF (7.0 ml) was refluxed under nitrogen for 2 h. During the reaction, the red-brown solution became a suspension with a dark-blue precipitate. After cooling and opening to air, the reaction mixture, now a suspension of a pale yellow precipitate, was filtered. The filtrate was concentrated and chromatographed on a silica gel column. Elution with CH_2Cl_2 gave pure *p*-tolylsulfide (0.25 g, 93%). When a solution of *p*-tolylsulfoxide (0.58 g, 2.5 mmol) and $Cp_2Ti(CO)_2$ (1.25 mmol) was refluxed under nitrogen in

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Table 1

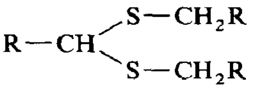
Reduction of sulfoxides with $Cp_2Ti(CO)_2$ [a]

	Sulfoxide		Molar ratio $1/Cp_2Ti(CO)_2$	Temperature	Time (h)	Sulfide (**2**) yield [b]
	R^1	R^2				
1a	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	1/1	reflux THF	2	93
	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	2/1	reflux THF	2	91
1b	p-ClC_6H_4	p-ClC_6H_4	1/1	reflux THF	2	94
	p-ClC_6H_4	p-ClC_6H_4	2/1	reflux THF	2	91
1c	C_6H_5	C_6H_5	1/1	reflux THF	2	91
	C_6H_5	C_6H_5	2/1	reflux THF	4	96
	C_6H_5	C_6H_5	2/1	room temp.	40	96
1d	CH_3	CH_3	2/1	reflux THF	2	74 [c]
1e	n-C_3H_7	n-C_3H_7	1/1	reflux THF	2	81 [c]
1f	n-C_4H_9	n-C_4H_9	1/1	reflux THF	6	89
1g	$C_6H_5CH_2$	$C_6H_5CH_2$	1/1	reflux THF	6	93
1h	C_6H_5	CH_2=CH–	2/1	40 °C	5	80

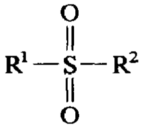
[a] All products were identified by comparison (IR and NMR) with authentic samples. [b] Yield of products isolated by column chromatography. [c] Yield determined by GC or NMR.

THF (13 ml) for 2 h, a stable yellow suspension formed and p-tolylsulfide was obtained (91%) after the same work-up procedure. The identifies of the sulfide products were confirmed via spectroscopic comparison with an authentic sample.

Both aliphatic and aromatic sulfoxides are readily deoxygenated when treated with $Cp_2Ti(CO)_2$ in THF under nitrogen in the temperature range 25° to refluxing THF. As shown in Table 1, the isolated yield of the sulfide product is generally high. The high yield and purity of the product is of interest with respect to the mechanism of this reaction. The reduction of sulfoxide to sulfide is not accompanied by Pummerer rearrangement product (**3**) which has sometimes been observed with the use of several other reagents [2,6,7]. This rearrangement is usually facilitated by the presence of a strong acid [2,6,7] hence the absence of **3** suggests that $Cp_2Ti(CO)_2$ does not behave as a strong acid in this case. In addition benzyl mercaptan, which is occasionally formed during reduction of benzyl sulfoxide (**1g**) under other conditions [13], could not be detected by TLC. While the most efficient reduction of sulfoxide is obtained using 1 mole equivalent of $Cp_2Ti(CO)_2$, only 0.5 mole equivalent is required. This indicates greater reducing capacity than simple oxidation of Ti^{II} to Ti^{IV} would suggest. The formal similarity of these reactions to the reduction of amine oxides by metal carbonyls to give amine complexes and CO_2 is noted. Finally $Cp_2Ti(CO)_2$ is a mild reductant; sulfones (**4**) and phosphine oxides (**5**) are inert under these reaction conditions.



(**3**)



$$R^1-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-R^2$$

(**4**)

$(R)_3P{=}O$

(**5**)

The reducing agent, $Cp_2Ti(CO)_2$, is a well characterized species [15,16] and the reduction is carried out under homogeneous reaction conditions. For many other low valent transition metal reagents [9–12], the exact nature of the starting material is not well characterized and the reaction is done under heterogeneous reaction conditions. The reactivity of $Cp_2Ti(CO)_2$ was followed by infrared spectroscopy. During the reaction carbon monoxide was released there being no evidence in the IR spectra of the presence of a monocarbonyl intermediate. In the absence of sulfoxide the reaction gave a dark blue precipitate after refluxing for 4 h suggesting the possibility that THF is also a possible oxidant for $Cp_2Ti(CO)_2$. For all the sulfoxides studied here, when the reaction was carried out with a ratio of Ti reagent to sulfoxide of 1/1, the corresponding sulfide and an air-sensitive blue titanium-containing species was obtained; whereas with a ratio of Ti/sulfoxide of 1/2, the sulfide and a yellow titanium-containing polymer was obtained. The latter was similar to that which formed upon exposure of the 1/1 ratio reaction to air.

The IR spectrum of the yellow polymer displayed bands consistent with the presence of the C_5H_5 ligand and Ti–O–Ti linkages. Elemental analysis indicated that the polymer had not retained two cyclopentadienyl rings per titanium [17]. This was further confirmed by the isolation of cyclopentadiene in the volatile distillate from the reaction mixture. A blue colour is characteristic of reduced cyclopentadienyloxotitanium complexes which are easily oxidized to give yellow oxotitanium(IV) polymers [17–19]. Further investigation will be necessary before a reasonable mechanism can be suggested. Nevertheless, present results indicate that $Cp_2Ti(CO)_2$ is an effective agent for the deoxygenation of sulfoxides. The reaction also suggests a possible route to early transition metal oxo complexes via the use of mild, non-protic [20] oxygen transfer reagents.

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