# Titanium Enolates from Epoxides and Bis(pentamethylcyclopentadienyl)dimethyltitanium(IV)

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Typical epoxides such as cyclohexene oxide and *cis-* and *trans*-but-2-ene oxide are converted to titanium enolates by heating at 80 °C with the title compound.

Epoxides appear to be ideal substrates for organometallic complexes of the early transition metals, considering the Lewis base and strained nature of the former and the Lewis acid and oxyphilic nature of the latter. Nevertheless, this chemistry is relatively undeveloped aside from the preparation of aminols,[1] chlorohydrins,[2] azidohydrins,[1,3] *etc.*[1] by Ti-mediated nucleophilic ring opening. We report the reaction of the titanium–methylene complex $(\eta^5\text{-}C_5Me_5)_2Ti{=}CH_2$ (**1**) [generated *in situ* by thermolysis of the dimethyl compound (**2**)[4]] with epoxides (**3**) to afford titanium enolates (**4**).

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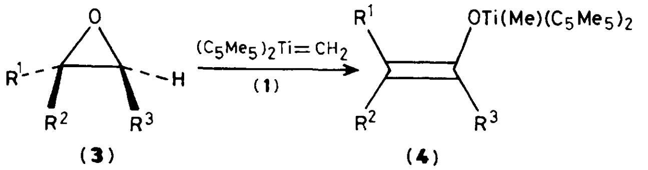
**Table 1.** Reaction of (**2**) with butanone and butene oxides at 80 °C.

| | % Product | | | |
|---|---|---|---|---|
| Substrate | (**4b**) | (**4c**) | (**4d**) | $10^6 k/\mathrm{s}^{-1}$ |
| Butan-2-one | 18 | 37 | 43 | 7.2 |
| 1,2-Epoxybutane (**3b**) | 21 | 11 | <0.5 | 6.7 |
| *cis*-But-2-ene oxide (**3c**) | 18 | 26 | 15 | 7.5 |
| *trans*-But-2-ene oxide (**3d**) | 19 | 10 | 4 | 7.2 |



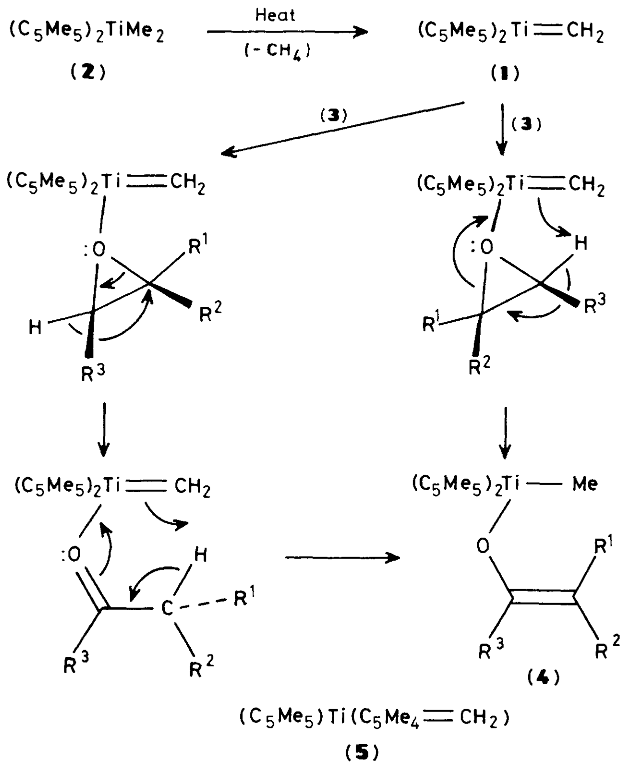
(**3**) (**4**)

a; $R^1 = H$, $R^2R^3 = (CH_2)_4$
b; $R^1 = R^2 = H$, $R^3 = Et$
c; $R^1 = H$, $R^2 = R^3 = Me$
d; $R^1 = R^3 = Me$, $R^2 = H$
e; $R^1 = H$, $R^2 = R^3 = Pr$
f; $R^1 = R^3 = Pr$, $R^2 = H$
g; $R^1 = H$, $R^2 = Et$, $R^3 = Bu$
h; $R^1 = Et$, $R^2 = H$, $R^3 = Bu$

For example, when an equimolar mixture of (**2**) and cyclohexene oxide (**3a**) was heated at 80 °C in $[^2H_8]$toluene, a reaction took place which consumed (**2**) with the first-order rate constant of $7.2 \times 10^{-6}\ s^{-1}$ to yield 56% of the Ti enolate (**4a**) of cyclohexanone, which was identified by its $^1H$ and $^{13}C$ n.m.r. spectra‡ and protonation to cyclohexanone. In the absence of substrate, (**2**) is converted *via* (**1**) to pentamethylcyclopentadienyl(tetramethylfulvene)methyltitanium-(IV), (**5**), as described by Bercaw *et al.*,[4] at approximately the same rate ($k$ $8 \times 10^{-6}\ s^{-1}$). We also observe (**5**) in our reaction mixtures; in fact, the mass balances (**4**) + (**5**) are *ca.* 100%. Within experimental error (~10%) the rate of disappearance of (**2**) is independent of epoxide structure (*vide infra*).

The product distribution from butan-2-one[5] is significantly different from the product distributions from 1,2-epoxybutane or *cis*- or *trans*-but-2-ene oxide (Table 1); thus the free ketone does not appear to be an intermediate. Rearrangement of epoxides to the corresponding ketones has been observed for transition metal complexes.[6] The yields were measured by integration of the $^1H$ n.m.r. spectra (run in $[^2H_8]$toluene),‡ and the stereochemistries of the enolates were assigned on the basis of the nuclear Overhauser enhancement (n.O.e.) effects observed in the vinyl H resonances when the Ti-bound Me group was irradiated.[7]

The more sterically demanding substrates *cis*- (**3e**) and *trans*-oct-4-ene oxide (**3f**) gave the same *ca.* 1 : 1 mixture of regioisomeric *E*-enolates (**4e**) and (**4g**) [40 and 25% total yields from (**3e**) and (**3f**), respectively, after 96 h].§ In contrast, octan-4-one yielded the same ratio of regioisomers as well as the corresponding stereoisomers (**4f**) and (**4h**). [After 96 h at 80 °C, the yields of (**4e**—**h**) were 36, 3, 32, and 2%, respectively].¶



Scheme 1

Styrene oxide is deoxygenated to styrene under our conditions. The deoxygenation of epoxides by reduced Ti complexes has been reported.[8]

A mechanism consistent with the information above is shown in Scheme 1, in which the first step (elimination of methane) is rate-limiting. Rapid complexation of the epoxide to the co-ordination site thus created makes subsequent H abstraction from substrate competitive with H abstraction from a pentamethylcyclopentadienyl ligand [*vide supra* (**5**)]. Rearrangement of complexed epoxide to complexed ketone followed by intramolecular H transfer (*cf.* 1,5-sigmatropic reaction) yields the enolate. The rearrangement of 1,2-epoxybutane to butan-2-one derivatives suggests that some special feature must be involved to overcome the usual tendency to break the C–O bond to the more substituted C (carbonium ion character control). A concerted complexed-epoxide to enolate conversion cannot be ruled out in some cases [*e.g.*, (**3b**)]. Regioisomeric Ti-enolates do not equilibrate rapidly under the reaction conditions, unless an excess of the corresponding ketone is used.[5]

Titanium enolates have also been prepared by the reaction of $(\eta^5\text{-}C_5H_5)_2TiCH_2$ with acid chlorides[9] and with hindered ketones,[10] by the reaction of lithium enolates with $(\eta^5\text{-}C_5H_5)_2\text{-}TiMeCl$, $(\eta^5\text{-}C_5H_5)_2TiCl_2$,[11] or $TiCl_4$,[12] and by the reaction of trimethylsilyl enol ethers with $TiCl_4$.[13] Considering the variety of transition metal–methylene complexes known,[14] we believe

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‡ Diagnostic resonances: cyclohexanone enolate vinyl $^1H$ $\delta$ 4.32 (t, $J$ 3.8 Hz); olefinic $^{13}C$ $\delta$ 95.4 (*C*=C–O). 161.2 (C=*C*–O). Butan-2-one enolates: *E* vinyl $^1H$ $\delta$ 4.13 (q, $J$ 6.9 Hz), *Z* vinyl $^1H$ $\delta$ 3.91 (q, $J$ 6.4 Hz), *least substituted* vinyl $^1H$ $\delta$ 3.79 (s), 3.67 (s).

§ With 2 equiv. of (**2**) at 80 °C, the yields from both substrates were 40%; the ratio of regioisomers remained essentially the same.

¶ When the reaction was run with a deficit (0.92 equiv.) of octan-4-one at 100 °C for 22 h,[5] <0.5% of the *Z*-isomers (**4f**) or (**4h**) was detected. The yields of (**4e**) and (**4g**) were ~45% each.

that these preliminary results point towards a new area for investigation of some scope.

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