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DEOXYGENATION REACTIONS WITH BIS (BENZENE) TITANIUM

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Low valent titanium compounds have attracted much interest in the last few years, chiefly for the intermolecular reductive coupling of ketones to pinacols[1,2], and alkenes[1,3] and of allyl alcohols to dienes[4,5] and for the deoxygenation of oximes and nitro compounds[1].

These reactions generally need a large excess of the titanium compounds and of the reducing agent. Furthermore, only in few cases was the nature of the titanium compound discussed and ascertained. Thus, Corey[2] has demonstrated that $(\pi\text{-}C_6Me_6)TiAl_2Cl_6$ is effective for the reductive coupling of carbonyl compounds to pinacols. Tyrlik[6] points out that titanium and magnesium act together for reductive coupling reactions of ketones with $TiCl_4$-Mg slurries. However, the presence of Lewis acids ($TiCl_4$, $TiCl_3$, AlX_nH_{3-n}, $MgCl_2$,...) and their opportunity to activate the carbonyl groups through coordination was never considered.

We wish to report our preliminary results on the use of the well defined zerovalent titanium complex, bis (benzene) titanium[7], for these reactions. Heating a THF solution of $(\pi\text{-}C_6H_6)_2Ti$[†] **1**, with representative oxygen-containing compounds (Table) leads to effective deoxygenation and generally C-C coupling in good yields. Substrate/**1** ratio of 0.5 was considered to be a reasonable excess according to the high sensitivity of **1** towards hydrolysis and oxidation.

The formation of alkynes from α-diketones could represent a new synthetic procedure since the starting diketones are easily obtained from the corresponding ketones[8] and since there is no by-product.

In the reductive coupling of ketones, the intermediacy of pinacols was not observed. This contrasts with the experiments of Mc Murry who suggested that the pinacol deoxygenation is the rate determining step in the reductive coupling of ketones. Although the α-glycol reduction is feasible, the reaction conditions used (120°C, 4.5hrs instead of 80°C, 2hrs) are far more stringent.

Allyl and benzyl alcohols are deoxygenated and lead to olefins only. With the reac-

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[†] THF does not react with **1**.

TABLE

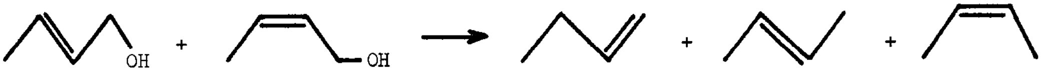
Substrate	Reagent and Conditions	Products (% yield)
Benzophenone, 0.5mM	$(PhH)_2Ti$, 1mM; THF, 20mL; 75°C/2hrs	Tetraphenylethylene (100)
Acetone, 1mM	$(PhH)_2Ti$, 2mM; THF, 40mL; 80°C/3hrs	Tetramethylethylene (100)
Benzophenone, 1mM	$Ti^{a)}$, 5.4ma.g; THF, 40mL; 80°C/18hrs	Tetraphenylethylene (100)
Benzil, 0.25mM	$(PhH)_2Ti$, 0.5mM; THF, 20mL; 80°C/2hrs	Diphenylacetylene (96)
Epoxypropane	$(PhH)_2Ti$, 1mM; THF, 20mL; 80°C/2hrs	Propene (100)
Butan-2,3-diol, 0.5mM	$(PhH)_2Ti$, 1mM; THF, 20mL; 80°C/2hrs	Small conversion to butenes
Allyl alcohol, 1mM	$(PhH)_2Ti$, 2mM; THF, 20mL; 80°C/2hrs	Propene (100)
Benzyl alcohol, 0.5mM	$(PhH)_2Ti$, 1mM; THF, 20mL; 80°C/2hrs	Toluene (100)
But-2-enol$^{b)}$, 0.25mM	$(PhH)_2Ti$, 0.5mM; THF, 40mL; 75°C/5hrs	But-1-ene (70); *trans*-but-2-ene (20); *cis*-but-2-ene (10)
But-2-enol$^{b)}$, 5mM	$TiCl_4/Li$, 1mM/50ma.g; THF 50mL; 75°C/6hrs	But-1-ene (25); *trans*-but-2-ene (50); *cis*-but-2-ene (25)
Pent-1-en-3-ol, 0.5mM	$(PhH)_2Ti$, 0.4mM; THF, 20mL; 90°C/4hrs	Pent-1-ene (75); *trans*-pent-2-ene (15); *cis*-pent-2-ene (10)
Pent-1-en-3-ol, 5mM	$TiCl_4/Li$, 12mM/50ma.g.; THF, 30ml; 110°C/24hrs	Pent-1-ene (30), *trans*-pent-2-ene (50); *cis*-pent-2-ene (20)

a) Obtained as a by-product in the synthesis of bis(toluene)titanium and thoroughly washed with toluene

b) *trans*: 90%; *cis*: 10%

tion conditions used, no coupling products are observed. However, the use of THF which is a good H donor can quench any radical species. Thus, if the reaction is performed in diethylene glycol diethylether, bibenzyl is also formed (toluene/bibenzyl = 3.8). When excess benzene is used as reaction medium, the bibenzyl content increases again (toluene/bibenzyl = 1.4). However in all instances, the formation of the reduction product is favoured contrary to the results of Mc Murry[5] who observed mainly the coupled products.

With alkyl substituted allyl alcohols, different product distributions are observed. Thus, a 90:10 mixture of *trans*- and *cis*-but-2-enol, **2**, **3** quantitatively leads to a mixture of 70% but-1-ene **4**, 20% *trans*-but-2-ene **5** and 10% *cis*-but-2-ene **6**. The formation of but-1-ene could be explained through the intermediacy of either two rapidly equilibrating radicals or an intermediate **7** which proceeds from the insertion of a titanium species into the O-H bond:

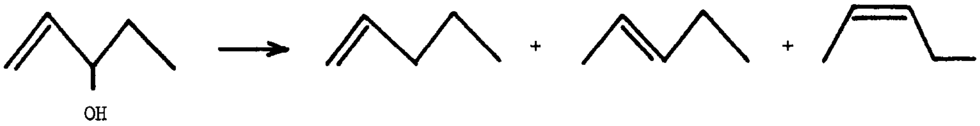


2 **3** **4** **5** **6**

7

With the isomer **3**, an intermediate corresponding to **7** could not lead to **5**, owing to the steric hindrance and 1,2 H transfer (or H capture from solvent) is only observed.

The 1,2- *vs* the 1,4-transfer seems to be highly dependent on the allyl alcohol substitution. Thus, pent-1-en-3-ol **8** leads to a 75:15:10 mixture of pent-1-ene **9**, *trans*-pent-2-ene **10** and *cis*-pent-2-ene **11**.



8 **9** **10** **11**

It is interesting to note that the $TiCl_4$/Li couple leads to different isomer ratios. Thus, with the same mixture of **2** and **3**, a 25:50:25 ratio of **4**, **5**, **6**, and with **8**, a 30:50:20 ratio of **9**, **10**, **11** are observed.

Further experiments with other substituted and/or deuterated allyl alcohols and different solvents are needed to provide more precise insight into the mechanism of these peculiar deoxygenation reactions.

Finally, the formation of alkenes from epoxides parallels the work of Sharpless[9] and Green[10] using low-valent molybdenum and tungsten compounds. The lack of reactivity between **1** and saturated alcohols could explain the sluggish reaction with glycols.

The nature of the titanium species involved in these reactions is presently not clear. No titanium dioxide is observed before the reaction work up. It is noteworthy that titanium powder obtained through the vaporisation procedure also acts for the reductive coupling of benzophenone.

Further studies to answer these questions are in progress.

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