Journal of Organometallic Chemistry, 268 (1984) C1—C6
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIONS OF $Cp_2Ti(CO)_2$ WITH ALDEHYDES AND KETONES

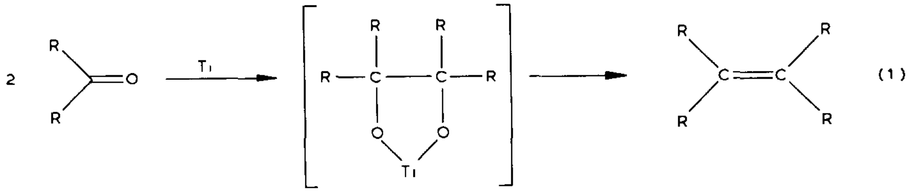
T.L. CHEN*, T.H. CHAN** and ALAN SHAVER**
Department of Chemistry, McGill University, Montreal, Quebec, H3A 2K6 (Canada)

(Received December 12th, 1984)

Summary

Aromatic aldehydes are coupled by $Cp_2Ti(CO)_2$ to give pinacols and olefins in good yields. Aliphatic aldehydes react to give mainly the corresponding alcohols. Aromatic ketones give a mixture of products.

Reductive coupling of carbonyl compounds to pinacols and olefins by low-valent titanium reagents has been found to be a useful reaction [1] (eq. 1). The titanium reagents are generally prepared by metal or hydride reduction of titanium halides (e.g. $TiCl_3/LiAlH_4$, $TiCl_3/K$ or Li or Zn or Mg) [2—4]. The nature of the titanium compound is not well defined. Furthermore, the reaction is usually conducted under heterogeneous conditions with a large excess of the titanium reagent which renders the study of the reaction rather difficult.



Homogeneous reactions of carbonyl compounds with low valent titanium complexes of well-defined structures have been studied. Thus, Corey [5] has demonstrated that $(\pi\text{-}C_6Me_6)TiAl_2Cl_6$ is effective in converting carbonyl compounds to pinacols but not to olefins. On the other hand, $(\pi\text{-}C_6H_6)_2Ti$ is effective in the reductive coupling of ketones to olefins [6], but the reac-

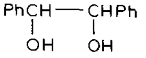
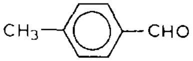
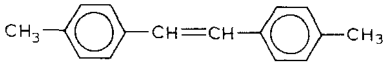
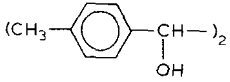
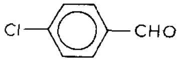
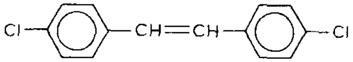
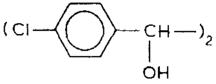
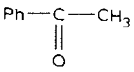
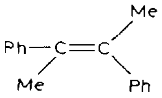
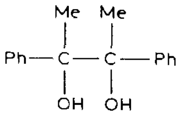
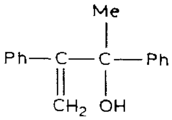
(Continued on p. C4)

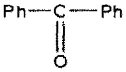
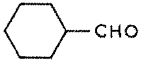
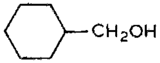
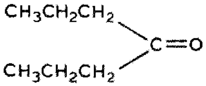
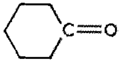
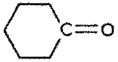
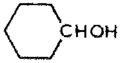
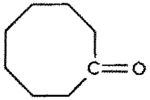
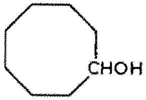
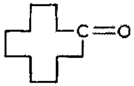
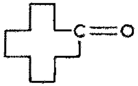
---

*Visiting scientist from Institute of Applied Chemistry, Academia Sinica, Peoples' Republic of China.
**Authors to whom correspondence should be addressed.

TABLE 1

REACTIONS OF CARBONYL COMPOUNDS WITH $Cp_2Ti(CO)_2$

Carbonyl compound	Ratio titanium reagent/carbonyl	Reflux time (h) THF	Products (%)[a]		
PhCHO	2/1	3	PhCH=CHPh (25)	 $PhCH(OH)-CH(OH)Ph$ (50)	
		5	(80)		
		10	(98)		
	2/1	5	 (58)		
		10	(99)		
	2/1	5	 (28)	 (41)	
		10	(59)	(10)	
	4/1	10	(88)		
 $Ph-C(=O)-CH_3$	2/1	30	 (17) (III)	 $PhC(Me)(OH)-C(Me)(OH)Ph$ (57) (II)	 $PhC(=CH_2)-C(Me)(OH)Ph$ (3) (IV)

 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}Ph}$	2/1	05	Ph_2CHOH (72) (V)	Ph_2CH_2 (3) (VI)	
		5	(55)	(28)	$Ph_2CHCHPh_2$ (VII)
		30	(26)	(44)	(17)
	2/1	30	 (75)		
$C_7H_{15}CHO$	2/1	22	$C_7H_{15}CH_2OH$ (46)		
		48	(43)		
	2/1	30	$(CH_3CH_2CH_2)_2C{=}O$ (16)	$(CH_3CH_2CH_2)_2CHOH$ (22)	
	2/1	30	 (35)	 (45)	
	2/1	30	 (46)	 (34)[b]	
	2/1	30	 (47)	 (30)	
	4/1	30	(34)	(37)	

[a] Isolated yield. [b] Yield determined by GC.

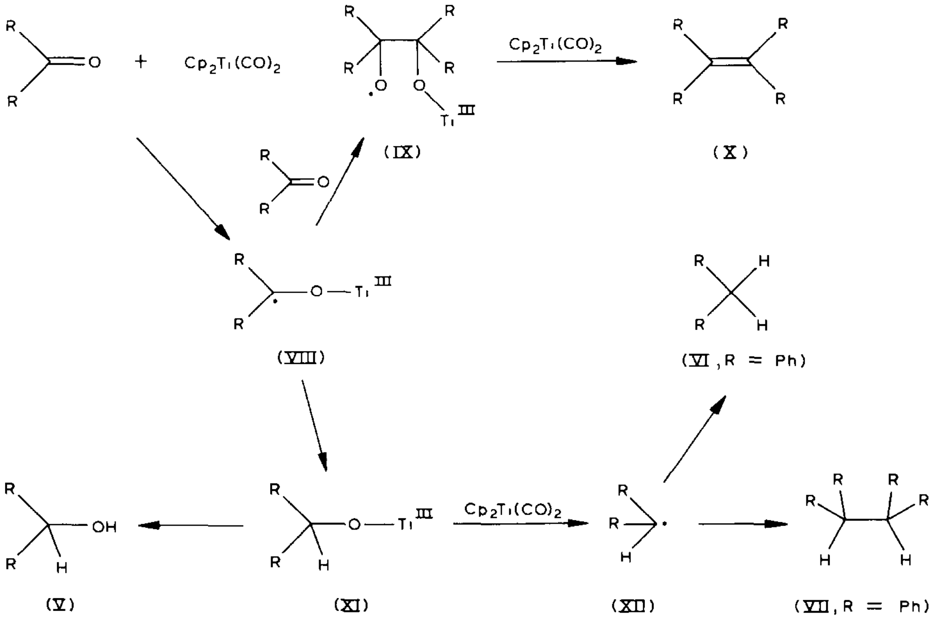
tion appears not to proceed through the pinacol intermediate. We wish to report here the reaction of carbonyl compounds with di-η^5-cyclopentadienyldicarbonyltitanium(II) (I, $Cp_2Ti(CO)_2$).

$Cp_2Ti(CO)_2$ was prepared and purified by the literature procedure [7]. A tetrahydrofuran (THF) solution of I (0.1 *M*) can be kept at room temperature for a reasonable period of time (1 week) without obvious diminution of activity. The reaction of I with diethyl ketomalonate has previously been reported [8]. The typical experimental conditions for the reactions reported here involved refluxing a mixture of aldehyde or ketone (1.25 mmol) and $Cp_2Ti(CO)_2$ (2.5 mmol) in 15 ml THF for 5—30 h under N_2. During this time the colour of the solution changes from dark red to very dark blue and a dark precipitate forms. The cooled reaction mixture was poured into 50 ml water and left overnight. The solution was extracted with ether. The organic solution was washed, dried ($MgSO_4$) and evaporated to give the crude products which were purified by column chromatography over silica gel to yield olefin (eluted by hexane/CH_2Cl_2 3/1) and alcohol (eluted by CH_2Cl_2). The structure of the product was identified by spectroscopic comparison with an authentic sample.

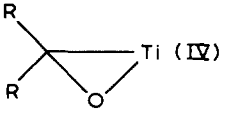
We found that I is an effective reagent for the reductive coupling of aromatic aldehydes (Table 1). With a ratio of Ti reagent to aldehyde of 2/1, after 10 h of reflux, excellent yield of the corresponding olefin can be obtained. If the reflux time was shortened, or the amount of titanium reagent reduced, pinacol was obtained as the other product at the expense of olefin. This indicates clearly that in the reductive coupling of aromatic aldehydes, the pinacol structure is the intermediate to olefin. Acetophenone behaves somewhat similarly to the aromatic aldehydes in giving a mixture of pinacols (*meso* and *dl*, II) and olefins (*cis* and *trans*, III) together with IV which is clearly derived from the pinacol II. Benzophenone, on the other hand, reacted with I to give a mixture of products V, VI and VII without any significant amount of benzpinacol or tetraphenylethylene. The distribution of V, VI and VII with respect to reaction time was revealing. In the initial stage of the reaction, only diphenylmethanol (V) was formed. As reaction was allowed to proceed longer, diphenylmethane (VI) was formed together with tetraphenylethane (VII) at the expense of V. Aliphatic aldehydes and ketones (Table 1) reacted with I to give mainly the corresponding alcohols although the ketones also gave polymeric by-products. The ester methyl benzoate remained unchanged after 30 h or reflux in THF with I.

The reactivity of I in refluxing THF in the absence of a carbonyl compound was followed by infrared spectroscopy. The solution became dark blue after 30 h reflux whereupon it was evaporated to dryness. The residue was extracted with hexane to give a red solution whose infrared spectrum in the carbonyl region displayed the peaks of I only. The dark residue polymerized benzaldehyde under the above reaction conditions. It is reasonable to conclude that the blue precipitate is not the active component leading to the observed products. Complex I or an intermediate species, which is stabilized by THF, is implicated [9].

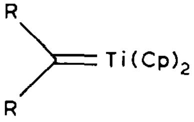
Scheme 1 shows a reasonable reaction course which can account for the above products. For aromatic aldehydes the postulated radical intermediate



VIII could dimerize to give the pinacol structure IX and thence to the observed olefin X. For benzophenone or for aliphatic aldehydes, because of steric or electronic reasons, dimerization may not be competitive with the alternative possibility of hydrogen abstraction to give a titanium alkoxide XI. In the case of benzophenone, further reduction of XI could give the diphenylmethyl radical XII which accounts for the formation of diphenylmethane (VI) and tetraphenylethane (VII). That V and VI are likely formed via a radical intermediate such as VIII and not by either a metallocycle XIII or a metal carbene XIV during hydrolytic workup is based on the following experiment. Quenching of the reaction mixture of benzophenone and I with D_2O gave V, VI and VII with no evidence of deuterium incorporation at the methine hydrogens [9]. While further studies on the nature of the proposed intermediate are necessary the results reported here demonstrate the reactivity of I with aldehydes and ketones.



(XIII)



(XIV)

Acknowledgements. We thank NSERC of Canada and FCAC of Quebec for financial support. The award of a fellowship by Academia Sinica to TLC is gratefully acknowledged.

References

1 J.E. McMurry and M.P. Fleming, J. Am. Chem. Soc., 96 (1974) 4708.
2 A.L. Baumstark, E.J.H. Bechara, and M.J. Semigran, Tetrahedron Lett., (1976) 3265.
3 T. Mukaiyama, T. Sato, and J. Hanna, Chem. Lett., (1973) 1041.
4 S. Tyrlik, and I. Wolochowicz, Bull. Soc. Chem. Fr., (1973) 2147.
5 E.J. Corey, R.L. Danheiser, and S. Chandrasekaran, J. Org. Chem., 41 (1976) 260.
6 H. Ledon, I. Ikatchenko, and D. Young, Tetrahedron Lett., (1979) 173.
7 B. Demerseman, G. Bouquet, and M. Bigorgne, J. Organomet. Chem., 101 (1975) C24.
8 M. Pasquali, C. Floriani, A. Chiesi-Villa, and C. Guastini, J. Am. Chem. Soc., 101 (1979) 4740.
9 The source of hydrogen could be the solvent or the reagents. In attempts to use THF-d_8 as solvent for the reaction, the reagent $Cp_2Ti(CO)_2$ was evaporated to dryness from the THF solution, followed by addition of THF-d_8. However, the course of reaction with benzophenone was changed drastically giving mainly polymeric products.