

## Hydrogenative deoxygenation of organic compounds: Direct conversion of amides to alkanes

(titanocene/reduction/carbonyl compounds)

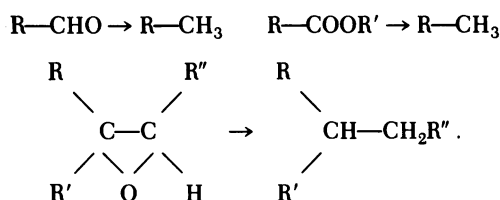
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**ABSTRACT** Through the use of  $(\text{Cp}_2\text{TiH})_x$  or  $(\text{Cp}_2\text{Ti})_{1-2}$ , in which Cp is  $\text{C}_5\text{H}_5$  (cyclopentadienyl ligand), it is possible to effect not only the previously known direct reduction of aldehydes and esters to alkanes but also the one-step conversion to alkane of amides derived from selected primary aromatic amines.

As disclosed previously (1), it is possible by means of a titanium reagent to carry out in good yield and with carbon skeleton preservation the direct reduction of aliphatic aldehydes, esters, and 1,2-oxides to saturated hydrocarbons, the last two reactions being unprecedented.



We now report that not only the above one-step reductions but also that of an ordinary amide to alkane, another apparently heretofore unrecorded type of transformation,



can be accomplished by means of a modified reducing system using the storable species  $(\text{Cp}_2\text{TiH})_x$ , a known progenitor of titanocene,  $(\text{Cp}_2\text{Ti})_{1-2}$  (2, 3). Cp represents  $\text{C}_5\text{H}_5$  (cyclopentadienyl ligand).

In an endeavor to develop a titanocene-based reducing system less capricious and more convenient than that resulting from the action of sodium sand of titanocene dichloride in benzene as described (1), various modifications and alternatives were investigated. It was determined that utilization of metals (K, Na/K alloy, Li, Mg, Ca or Na/naphthalene) and solvents (toluene, hexane, dioxane, ether, hexamethylphosphoramide, 1,2-dimethoxyethane, or tetrahydrofuran) other than those in the original recipe offered no improvement. Also, both the relatively stable  $(\text{CpTi-}\mu\text{-H})_2\text{C}_{10}\text{H}_8$  (4) as well as the more reactive  $\text{Cp}_3\text{Ti}_2(\text{C}_5\text{H}_4)$  (5) were incapable of reducing ester or aldehyde to alkane—transformations characteristic of the prototype system. However, it was discovered that the use of either  $(\text{Cp}_2\text{TiH})_x$  (2) or  $(\text{Cp}_2\text{Ti})_{1-2}$  prepared from the former led to reduction results that paralleled qualitatively and roughly quantitatively those already reported from this laboratory (1) (see above), thereby fully corroborating that earlier study and providing a more reliable and practical procedure based upon an accessible, storable reagent. Because  $(\text{Cp}_2\text{TiH})_x$  in solution is

a spontaneous precursor of genuine titanocene (2), the present body of results supports the idea that the latter species is intimately connected with the reduction processes.

As an expansion of the earlier studies (1), quantities of  $(\text{Cp}_2\text{TiH})_x$  were deployed for reductive attack on a variety of organic substances. Extensive experimentation revealed that optimal yields of alkane result when the reduction is conducted with 50–100 mol of reagent in benzene or diethyl ether at ambient temperatures for 4 hr or more. Formation is best managed through quenching with an acid, such as concentrated  $\text{H}_2\text{SO}_4$  (reductions in ether) or anhydrous maleic acid (reductions in benzene), which removes cyclopentadienyl titanium compounds from benzene or toluene solutions as an insoluble red complex. Use of the former method was preferred because of the greater solvating power of ether and the elimination of olefinic by-products after formation. By these means, the yields of *n*-dodecane from ethyl dodecanoate, dodecanal, and dodecene 1,2-oxide can reach 85%, 35%, and 60%, respectively. In addition to the virtual duplication of other earlier conversions (1), the new reagent permitted formation of hydrocarbon from *n*-dodecanoic anhydride (64%), methyl dodecanon-3-ate (20%), and methyl dodecyl sulfoxide (72%). The reagent was without action on the ethylene acetal and ketal derived from dodecanal and 2-dodecanone, respectively; dodecyl tetrahydropyranol ether; methyl  $\alpha$ -methoxy dodecanoate; and dimethyl alkylmalonates.

In regard to reduction of the acyl moiety in amides, the yield of alkane is greatly dependent on the nature of the amine from which the amide is derived (see Table 1), being greater than zero only when primary and aromatic, and then only in that category represented by aniline and relatively minor modifications thereof. The fate of the original nitrogenous moiety could not be determined, in keeping with the observation that in separate experiments various amines could not be recovered after being deliberately subjected to the reaction conditions normally employed for the amide reductions. Although benzene is serviceable as a solvent in the reduction of other carbonyl compounds, use of benzene led to zero yields of alkane in all amide examples investigated. In successful amide cases, yields of alkane were generally optimal when *ca.* 50 mol of reagent [ab  $(\text{Cp}_2\text{TiH})_1$ ] was employed, the best example (40% dodecane) being that of dodecanotoluidide, detailed below.

A kinetic/product survey revealed that under normal reduction conditions initial rapid consumption of dodecanotoluidide (or ethyl dodecanoate) is followed by slower concurrent evolution of dodecene and dodecane, with ultimate disappearance of olefin and emergence of alkane as the exclusive product, results that parallel those obtained with dodecanal (1). These findings, taken together with other results and conclusions pre-

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Abbreviation: Cp, cyclopentadienyl ligands ( $\text{C}_5\text{H}_5$ )

Table 1. Reduction of anilides  $n\text{-C}_{11}\text{H}_{23}\text{CONR}_1\text{R}_2 \rightarrow n\text{-C}_{12}\text{H}_{26}$ 

R <sub>1</sub>	R <sub>2</sub>	Yield, %
H	C <sub>6</sub> H <sub>5</sub>	24*
H	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	40
H	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	36
H	2,4-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	24†
H	H	0
H	CH <sub>3</sub>	0
H	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	0
H	2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	0‡
H	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	0‡
H	C <sub>6</sub> F <sub>5</sub>	0‡
CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	0
CH <sub>3</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	0

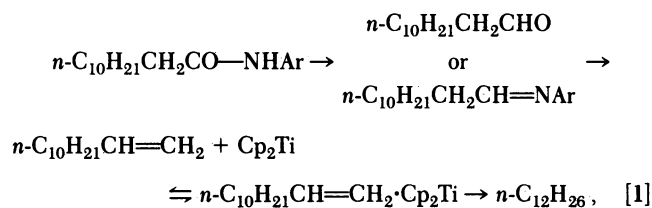
Reagent [as (Cp<sub>2</sub>TiH)<sub>1</sub>] (100 mol) in (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O at room temperature for 4–6 hr.

\* Amide recovered, 30%.

† Reagent [as (Cp<sub>2</sub>TiH)<sub>1</sub>], 200 mol.

‡ Amide recovered, 100%.

sented earlier, suggest pathway 1 for the reduction of amides to alkanes,



with new hydrogen in the final product emanating from the cyclopentadienide ligands and water used in the formation of reaction product, as determined in other cases (1).

## EXPERIMENTAL

In a glovebox with a purified helium atmosphere, 3.2 mg (0.011 mmol) of dodecanotoluidide was dissolved in 30 ml of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O (previously distilled from sodium/benzophenone under argon) in a 50-ml round-bottomed flask equipped with a magnetic stirrer. To the solution was added standardized  $n\text{-C}_{13}\text{H}_{28}$  as an internal standard and 0.200 g (1.10 mmol) of (Cp<sub>2</sub>TiH)<sub>x</sub>, which was prepared by the method of Marvich and Brintzinger (2). The contents of the loosely capped flask were stirred inside the drybox for as long as 72 hr, following which the reaction was quenched with about 0.1 ml of concentrated H<sub>2</sub>SO<sub>4</sub>. After a few minutes, evolution of gas stopped, whereupon the reaction mixture was exposed to the open atmosphere and, thus, was oxidized by aeration. After disappearance of the initial blue color and centrifugation of the murky brown mixture, the resulting clear, colorless solution was washed with 10% (wt/vol) NaOH to remove residual H<sub>2</sub>SO<sub>4</sub> and was dried with brine and K<sub>2</sub>CO<sub>3</sub>. Analysis was carried out on both 10/Carbowax 20 M and 3/OV-17, and the dodecane product (40%) was identified by gas chromatographic and mass spectrophotometric comparison with authentic material.

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