coordinate complex. Although it cannot be disproven at this point, it seems highly unlikely that scission of the metal–methyl bond fortuitously occurs at the same temperature at which dmpe dissociates and that it is this scission which initiates the decomposition of **2** and **3**.[11]

The above data suggest that the more highly alkylated complexes, $[M(CH_3)_6]^-$ and $[M(CH_3)_7]^{-2}$ (M = Nb or Ta), should show enhanced thermal stability due to the greater coordination number of the metal. Indeed, a diethyl ether solution of "$[TaCH_3)_7]^{2-}$" (**4**) prepared from $Ta(CH_3)_3Cl_2$ and 4 mol of methyllithium at −78° remains pale yellow in color after 1 hr at 35° while a solution of "$[Nb(CH_3)_7]^{2-}$" (**5**) shows no signs of decomposition after 1 hr at 0°. The temperature-dependent ^1H nmr spectrum of **4** in tetrahydrofuran indicates that at least two polymethyl tantalum species and methyllithium are in equilibrium; only one broad methyl group resonance is found just below TMS at 60° (100 MHz). Lability of the methyl group(s) is also suggested by the reaction of **4** and **5** with dmpe to yield **2** and **3**, respectively. The proposed anionic polymethyl complexes should be compared with those known for Ti,[12a] Zr,[12b] and Cr.[12c,d]

---

[11] At this time the precise description of metal–carbon bond cleavage in transition metal alkyl complexes is much debated (see M. C. Baird, *J. Organometal. Chem.*, **64**, 289 (1974)). Here only the apparent distinction between initiation of decomposition by ligand dissociation and initiation by metal–carbon bond scission is made.

[12] (a) H. J. Berthold and G. Groh, *Z. Anorg. Allg. Chem.*, **372**, 292 (1970); (b) K. H. Thiele, K, Milowski, P. Zdunneck, J. Müller, and H. Rau, *Z. Chem.*, **12**, 186 (1972); (c) E. Kurras and J. Otto, *J. Organometal. Chem.*, **4**, 114 (1965); (d) J. Krausse and G. Marx, *ibid.*, **65**, 215 (1974).

R. R. Schrock,* P. Meakin
Contribution No. 2138, Central Research Department
E. I. du Pont de Nemours and Co., Experimental Station
Wilmington, Delaware 19898

Received April 25, 1974

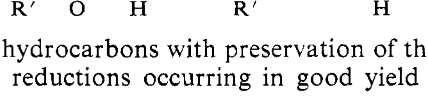
Direct Conversion of Aldehydes, Esters, and 1,2-Oxides to Alkanes with Carbon Skeleton Preservation

Sir:

Remarkable for its facile, reversible binding of molecular nitrogen as a reducible ligand, the titanocene system $[(C_5H_5)_2Ti]_{1-2}$[1,2] also effects the catalytic hydrogenation of olefins[2] and the reductive decyanation of alkyl nitriles.[3] We now report the titanium-based, direct conversion of aldehydes, esters, and 1,2-oxides to

$$RCHO \longrightarrow RCH_3$$

$$RCOOR' \longrightarrow RCH_3(+R'OH)$$



saturated hydrocarbons with preservation of the carbon skeleton,[4] reductions occurring in good yield at room temperature. Although this type change can be realized through the Wolff–Kishner (basic) or Clemmensen (acidic) reaction on aldehydes, the corresponding transformations with esters and 1,2-oxides[5] are, as far as we know, not precedented.

The procedure is illustrated with dodecanal, the carbonyl compound selected for various studies on the aldehyde reaction. In a glove box or Schlenk apparatus rigorously free of oxygen,[6] 2.5 g (10 mmol) of recrystallized ($CHCl_3$) titanocene dichloride, 0.5 g (22 mmol) of fine sodium sand, 12 ml of dry, deoxygenated benzene (purified by distillation from sodium benzophenone ketyl), and a 1-in. Teflon stirring bar were added to a 50-ml round-bottomed flask. The mixture was stirred at the highest possible speed until the supernate turned a dark green (10–48 hr) and then was immediately filtered with benzene washing through a glass frit, thereby being freed from NaCl, unreacted sodium, and insoluble polymeric titanium species (CAUTION: the gray-black residue warms up and can ignite upon exposure to air). To the dark greenish filtrate[7] was added 36.8 mg (0.2 mmol) of dodecanal. After being stirred 72 hr, 5 ml of degassed water was added to the mixture while maintaining inert atmosphere conditions; over the course of 4–8 hr, the reaction mixture turned a dark purple. The benzene was removed under reduced pressure, and the product was extracted with petroleum ether. Drying, concentration, and silica gel chromatography yielded 24.1 mg of pure dodecane (71%), characterized by gas chromatography (gc) and mass spectrometry. About 15–20% dodecanol was formed concurrently.

In experiments with molar ratios of starting titanocene dichloride–dodecanal less than 10:1, much less total product is recoverable. At temperatures either lower or higher than ambient, considerably more alcohol and much less alkane are generated.

By means of the outlined procedure, decanal and 2-methylundecanal were converted in similar yield to decane and 2-methylundecane, respectively. Ketones afforded much less hydrocarbon (7–25%) and correspondingly larger amounts of alcohol (up to 74%) and starting materials (Table I).

When subjected to the above conditions, many esters are reduced to hydrocarbons in acceptable yields (see Table I). Although in poorer yields, dodecanoyl chloride (18–45%), dodecanoic acid (2%), and lithium dodecanoate (25%) were transformed to dodecane.

1,2-Oxides are reduced to alkanes (Table I) under the same conditions used for aldehydes and esters. Also, as single case examples, nonane (27%) and dodecane (98%) were formed respectively from nonyl isocyanide and dodecyl bromide. Dodecane is produced from both dodecyl mercaptan (20%) and didodecyl sulfide (11–13%). Only starting material was recovered when reduction was attempted with alcohols, alkoxides, or acyclic ethers.

That the reagent employed in the described reactions

---

[1] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Åkermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969); (b) E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *ibid.*, **92**, 5151 (1970); (c) J. E. Bercaw, R. H. Narvich, L. G. Bell, and H. H. Brintinger, *ibid.*, **94**, 1219 (1972).

[2] E. E. van Tamelen, W. Cretney, N. Klaentschi, and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 481 (1972).

[3] E. E. van Tamelen, H. Rudler, and C. Bjorklund, *J. Amer. Chem. Soc.*, **93**, 7113 (1971).

[4] For the preparation of alkanes through aldehyde or acyl chloride decarbonylation, see J. Tsuji and K. Ihno, *Synthesis*, **1**, 157 (1969).

[5] For two-electron reductions of epoxides to alkenes, see K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Amer. Chem. Soc.*, **94**, 6538 (1972), and references cited therein.

[6] Catalytic amounts of oxygen inhibit this reaction and for obvious reasons, nitrogen must also be excluded.

[7] A brown color indicates incomplete reduction and a yellow color reflects oxygen contamination of the reaction mixture, which then should not be used.

Table I. Reduction of Carbonyl Compounds and 1,2-Oxides

Starting material	Product	% yield[a]
	Aldehydes and Ketones	
Dodecanal	Dodecane	71[b]
	Dodecanol	15–20
Decanal	Decane	61
	Decanol	11
2-Methylundecanal	2-Methylundecane	44
trans-2-Decenal	Decane	0–22
	1-Decene	0
	Decanol	0–5
p-Methoxybenzaldehyde	*p*-Cresol methyl ether	0
2-Undecanone	Undecane	3–20
	2-Undecanal	48–72
6-Dodecanone	Dodecane	7–25
	6-Dodecanol	32–70
2-Adamantanone	2-Adamantanol	72–74
	Esters	
Methyl dodecanoate	Dodecane	66
	Dodecanol	9
Ethyl dodecanoate	Dodecane	64–69
	trans-2-Dodecene	0–4
	Dodecanol	9–14
Decyl dodecanoate	Dodecane	58
	trans-2-Dodecene	2
	Dodecanol	7
	Decanol	70
Methyl *trans*-2-decenoate	Decane	3–35
	1-Decene	0
	Decanol	0–2
γ-Decalactone	4-Decanol	60
Methyl *trans*-myrtanoate	*trans*-Pinane	17
	trans-Myrtanol	28
Methyl 1-adamantanecarboxylate	1-Methyladamantane	0
	Adamantylcarbinol	35–64
Methyl 5β-cholanate	5β-Cholane	56[b]
Methyl *p*-isopropylbenzoate	*p*-Isopropylbenzyl alcohol	82
	Oxides	
1-Decene oxide	Decane	68–81
	1-Decanol	4–9
trans-2-Decene oxide	Decane	58
2-Methyl-1-undecene oxide	2-Methylundecane	52
α-Pinene oxide	*cis*-Pinane	10

[a] Product identity and yields were determined by gc and mass spectral methods. [b] Yields also based on isolated product.

is extraordinary is revealed by reduction attempts with other transition metal species. No dodecane (or dodecene) was formed from dodecanal when the following systems were assayed: $(C_5H_5)_2MoH_2$, $(C_5H_5)_2MoH_2$–isoprene,[8] TiH_2, VH, Na, VCl_{2-3}–Na, $MoCl_{3-4}$–Na. A few per cent of alkane was detected after reaction with $(C_5H_5)_2MoH_2$ with a catalytic amount of HCl, $(C_5H_5)_2TaH_3$ (80°),[9] or $Fe(acac)_3$–Na.

Various observations signify that the reduction of aldehydes and esters to alkanes involves olefin intermediates. Interruption of a dodecanal reaction after 3 hr revealed 10–15% 1- and 2-dodecene with 37–44% dodecane. As reaction time increased, the yield of dodecane became optimal while the amount of olefin approached zero. Olefin reduction during the overall reaction is consistent with the separate conversion of 1-decene by the usual titanocene preparation to decane in 76–89% yield. When a dodecanal reduction was carried out starting with $(C_5H_5)(C_5D_5)TiCl_2$, highly deuterated decane (d_1–d_{16}) was formed (as evidenced by gc and mass spectral data), thereby revealing extensive exchange of titanocene deuterium, presumably with hydrogen of intermediate olefin. Further, when an aliquot removed after 3 hr from a dodecanal reaction was quenched with D_2O, *ca.* 50% of the dodecane contained two deuteriums (mass spectral), while remaining alkane and 1-dodecene possessed deuterium at *ca.* natural abundance levels. However, reactions quenched with D_2O after 72 hr featured substantially less deuterium incorporation. No deuterium was transferred to hydrocarbon product from benzene-d_6 solvent. The foregoing results indicate the formation of intermediate titanium-bound olefin, which can be converted to alkane by D_2O–H_2O or by hydride from cyclopentadienide ligands. Similar deuterium labeling results were secured with ethyl dodecanoate, thus suggesting that with esters initial reduction to the aldehyde level is followed by steps identical with those involved in reductions starting with aldehydes. In keeping with the suggested scheme, no hydrocarbon was formed from aldehydes and esters which would not be expected to form olefins, including aromatic aldehydes and 1-adamantane carboxylic acid methyl ester. Although the driving force for the conversion of aldehyde to olefin must be formation of the titanium–oxygen bond by a reactive titanocene species, the exact mechanism of deoxygenation has not been established. That epoxide deoxygenation conforms to the pattern is revealed through D_2O quenching of the 1-decene oxide reaction after 3 hr, whereupon 1-decene, 2-decene, and decane emerged with deuterium levels at or slightly above natural abundance.

$$RR'CHCOOR'' \longrightarrow RR'CHCHO \longrightarrow$$
$$RR'C{=}CH_2 + [(C_5H_5)_2Ti]_n \rightleftharpoons RR'C{=}CH_2\cdot[(C_5H_5)_2Ti]_n \longrightarrow RR'CHCH_3$$

Acknowledgment. Financial support was provided by NIH Grant GM13797.

---

[8] These conditions are believed to produce a molybdenocene intermediate: B. R. Francis, M. L. H. Green, and G. G. Roberts, *Chem. Commun.*, 1290 (1971); M. L. H. Green and P. J. Knowles, *J. Chem. Soc. A*, 1508 (1971).

[9] In refluxing benzene, $(C_5H_5)_2TaH_3$ evolves H_2 to give an intermediate isoelectronic with titanocene: E. K. Barefield, G. W. Parshall, and F. N. Tebbe, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

(10) National Science Foundation Fellow, 1971–1974.

E. E. van Tamelen,* J. A. Gladysz[10]
Department of Chemistry, Stanford University
Stanford, California 94305

Received May 11, 1974

Structure and Properties of Hydrogen Bonds between the Electronegative Atoms of the Second and Third Rows

Sir:

We report a systematic electronic structure theory study of the hydrogen bond in the hydride dimers involving the atoms N, O, F, P, S, and Cl. Dimerization energies, geometry, dipole moments, and force constants were obtained for 38 dimers, the majority of which have not heretofore been investigated. Complete results are given in Table I and interrelations be-