

Figure 1. Nmr (100 MHz, CDCl_3 , room temperature) of I.

with hydrazine hydrate (11.6 mmol) in ethanol (100 ml) for 6 hr. The resulting oil was air sensitive and easily dehydrogenated upon the usual work-up. Distillation at 145–155° (3 mm), followed by column chromatography on silica gel, afforded I (50% yield) as colorless prisms of mp 59–60° (*n*-hexane):⁵ ir (Nujol) 3055, 1575, 1538, 1070, 887, 841, 810, 769, 710 cm^{-1} ; *m/e* 190 (M^+).

The nmr spectrum of I is shown in Figure 1. The multiplet (4 H) at δ 3 due to benzylic protons clearly shows that the octamethylene chain resides at the one side of the aromatic ring at room temperature. The situation remained unchanged up to 200°. The 2 H signal at δ -0.3 is due to each one of methylene protons on C_1 and C_5 being shielded by both the diamagnetic ring current of pyridazine and the magnetic anisotropy of nitrogen atoms. The 2 H signal at δ 0.5 is ascribed to the counterpart of C_1 and C_5 methylene protons which are less susceptible to these effects. The signal at δ -0.3 disappeared at -72° and at lower temperature a new 1 H peak at δ -1.75 appeared (Figure 2). The dynamic change is understood in terms of the conformational equilibrium of $\text{Ia} \rightleftharpoons \text{Ib}$. At room temperature there exists a rapid equilibrium between the two enantiomeric conformers due to the pseudorotation of the saturated chain, which is gradually frozen at lower temperature. The energy barrier of the conformational change at the coalescence temperature was estimated to be 9.2 kcal/mol, a remarkably larger value than that of cyclooctane (7.7 kcal/mol).⁷

The aromatic proton of I absorbed at δ 7.12 (Figure 1) or at relatively higher field compared with that of 3,6-dimethylpyridazine (II) (δ 7.20).⁸ The strain of the pyridazine ring of I is evidenced by its uv spectra: $\lambda_{\text{max}}^{\text{EtOH}}$ (ϵ) 267 (1260), 314 nm (413); $\lambda_{\text{max}}^{\text{n-hexane}}$ (ϵ) 270 (1260), 337 nm (442). The benzenoid absorption ($^1\text{L}_b$) of I as compared with that of II⁹ experienced a

(5) The new compound gave satisfactory elemental analysis and/or correct molecular peak in its exact mass spectrum.

(6) This indicates that the space surrounded by the octamethylene chain is not wide enough for the pyridazine ring to rotate, although the -CH=CH- moiety of [8]paracyclophane is replaced by -N=N-.

(7) (a) The value is naturally smaller than that of 4-[8]paracyclophanes (ca. 12 kcal/mol) (ref 1d) but should be deemed to be large for 12-membered ring compound; (b) F. A. L. Anet and J. S. Hartman, *J. Amer. Chem. Soc.*, **85**, 1204 (1963).

(8) The recorded chemical shift of II is δ 7.5 (neat) (D. G. Farnum, R. J. Alaimo, and J. M. Dunston, *J. Org. Chem.*, **32**, 1130 (1967)). The paramagnetic shift of the ring protons in I is due to the strain caused by octamethylene chain. The effect by a short bridging is seen in S. Fujita, T. Kawaguchi, and H. Nozaki, *Tetrahedron Lett.*, 1119 (1971).

(9) $\lambda_{\text{max}}^{\text{EtOH}}$ (ϵ) 258 (1835), 312 nm (325); $\lambda_{\text{max}}^{\text{n-hexane}}$ (ϵ) 259 (1560), 263 (1568), 341 nm (319).

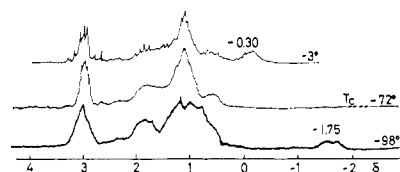


Figure 2. Temperature-dependent nmr (60 MHz, Freon 11) of I.

9–11-nm bathochromic shift and a hypochromic effect due to the bridging. In contrast, no apparent wavelength difference was observed with respect to the $n-\pi^*$ absorption (>300 nm) of both compounds I and II, although the ϵ of I was larger than that of II. Apparently the strain due to bridging releases I from the forbiddenness of the $n-\pi^*$ transition. The smaller bathochromic shift in I (337 (*n*-hexane)–314 (EtOH) = 23 nm) than II (341 (*n*-hexane)–312 (EtOH) = 29 nm) is ascribed to the octamethylene chain, which is forced to solvate on the one side of the pyridazine ring intramolecularly in I.

Oxidation of I with 1 equiv of perbenzoic acid gave pyridazinophane monoxide (III).^{5,10,11} This is a chiral ansa compound.

(10) Bp 140–150° (0.1 mm); ir (neat) 3060, 1584, 1553, 1370, 1330 cm^{-1} ; mass spectral, *m/e* 206 (M^+), 189 ($\text{M}^+ - \text{OH}$); nmr (CCl_4) δ -0.3 to +0.1 (m, 2 H) 0.1–2.2 (m, 10 H), 2.3–2.5 (m, 1 H), 2.74 (t, 2 H), 3.48 (double t, $J = 12.5, 4.5$ Hz, 1 H), 6.86 (d, $J = 7.7$ Hz, 1 H), 7.37 (d, $J = 7.7$ Hz, 1 H).

(11) This is in contrast to the chemical behavior of [7](2,6)pyridinophane which is resistant to oxidation (ref 2g). It is suggested that the success or failure of oxidizing heterophanes depends on the dynamic behavior of the bridging chain.

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Received May, 3, 1974

Pentamethyl Complexes of Niobium and Tantalum

Sir:

The known examples of mononuclear neutral binary methyl complexes of the transition metals are $\text{Ti}(\text{CH}_3)_3$,¹ $\text{Zr}(\text{CH}_3)_4$,² $\text{Cr}(\text{CH}_3)_4$,³ and $\text{W}(\text{CH}_3)_6$.⁴ (Dimethylmanganese⁵ is probably polymeric.) Pentamethyltantalum has now been prepared and isolated and is reported here along with the remarkably stable dmpe adducts ($\text{dmpe} = (\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$), $\text{Ta}(\text{CH}_3)_5\text{-}(\text{dmpe})$ and $\text{Nb}(\text{CH}_3)_5(\text{dmpe})$.

The addition of 2 mol of methyl lithium (in diethyl ether) to a diethyl ether solution of yellow $\text{Ta}(\text{CH}_3)_5\text{Cl}_2$ ⁶ at -78° produced a homogeneous yellow solution. Lithium chloride was precipitated upon warming to 0° and the color of the solution deepened slightly. The solution was filtered after 0.5 hr and the ether removed

(1) (a) K. Clauss and C. Beermann, *Angew. Chem.*, **71**, 627 (1959); (b) H. J. Berthold and G. Groh, *Z. Anorg. Allg. Chem.*, **319**, 230 (1963).

(2) H. J. Berthold and G. Groh, *Angew. Chem.*, **78**, 495 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 516 (1966).

(3) (a) W. Kruse, *J. Organometal. Chem.*, **42**, C39 (1972); (b) W. Mowat, A. J. Shortland, N. J. Hill, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 770 (1973).

(4) A. J. Shortland and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 872 (1973).

(5) (a) C. Beermann and K. Clauss, *Angew. Chem.*, **71**, 627 (1959); (b) R. Riemschneider, H. G. Kassahn, and W. Schneider, *Z. Naturforsch. B*, **15**, 547 (1960).

(6) (a) G. L. Juvinall, *J. Amer. Chem. Soc.*, **86**, 4202 (1964); (b) G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 961 (1973).

in vacuo. Extraction with pentane followed by filtration and removal of the pentane *in vacuo* gave $\text{Ta}(\text{CH}_3)_5$ (**1**) in approximately 50% yield as a volatile yellow oil (analysis, Br < 0.3%, Cl < 0.2%, Li < 0.1%; mass spectrum, $\text{Ta}(\text{CH}_3)_4^+$ at m/e 241; ^1H nmr in toluene- d_6 at -10° singlet at τ 9.18. Hydrolysis with HCl-ethanol gives 4.5–5.0 mol of methane. Accurate molecular weight studies and analyses for C, H, and Ta were precluded due to the instability of the compound). Pentamethyltantalum (as a pure liquid or in aliphatic hydrocarbons) decomposes readily and apparently autocatalytically at 25° to give methane as the only detectable gaseous product (mass spectral analysis) along with what is assumed to be tantalum metal (as a mirror *in vacuo*) and unidentified black residues. However, the original ethereal solution is considerably more stable toward thermal decomposition; it has not been determined if coordination of diethyl ether (*cf.* $\text{M}(\text{CH}_3)_4$, $\text{M} = \text{Ti}^1$ or Zr^2) or possibly of halide is responsible for the enhanced stability. The existence of **1** is further substantiated by its reaction with 1 mol of dmpe to yield a white, light-sensitive adduct, $\text{Ta}(\text{CH}_3)_5(\text{dmpe})$ (**2**), which can be completely characterized. The addition of dmpe to the original ethereal solution believed to contain **1** produces **2** in virtually quantitative yield based on $\text{Ta}(\text{CH}_3)_3\text{Cl}_2$.

The analogous reaction of 3 mol of methyl lithium with $\text{Nb}(\text{CH}_3)_2\text{Cl}_3$ in diethyl ether at -78° produces some lithium chloride. Decomposition sets in upon warming the solution to *ca.* -50° ; an insoluble black solid and a colorless ethereal solution result. However, if 1 mol of dmpe is added at -78° , yellow $\text{Nb}(\text{CH}_3)_5(\text{dmpe})$ (**3**) is formed and may be isolated in high yield. Like **2**, **3** is indefinitely stable at room temperature under nitrogen. The data available at this time do not allow any conclusions to be drawn concerning the existence or stability of $\text{Nb}(\text{CH}_3)_5$.

The nmr spectra of **2** and **3** are indicative of stereochemical nonrigidity. The low temperature limit (-18°) 220-MHz ^1H nmr spectrum for a 9% solution of $\text{Ta}(\text{CH}_3)_5(\text{dmpe})$ in toluene- d_6 consists of two doublets due to the methyl (τ 9.20, $J = 7$ Hz) and methylene (τ 8.84, $J = 12.5$ Hz) protons of the dmpe ligand and three resonances in the ratio of 1:2:2 assigned to three types of methyl ligands (τ 8.27, singlet, $J_{\text{H}-^{31}\text{P}}$ small; τ 9.08, nonfirst-order multiplet, $J_{\text{HP}_1} + J_{\text{HP}_2} = 12$ Hz; and τ 10.23, triplet, $J = 10$ Hz, respectively). As the temperature is raised, the resonances assigned to the five methyl ligands at first broaden and eventually coalesce into a triplet with $J \approx 5.5$ Hz at 100° . That part of the 22.63-MHz $^{13}\text{C}\{^1\text{H}\}$ nmr spectrum of **2** assigned to the methyl carbons (-76.6 , -60.3 , and -44.7 ppm upfield from TMS in toluene- d_6) is quite similar and is shown as a function of temperature in Figure 1. Because of the large chemical shift separations in this case, the high temperature limit triplet could not be reached before the sample decomposed. These results are consistent with an idealized pentagonal bipyramidal structure in which the two phosphorus nuclei and three of the methyl groups (two sets, A and BB') lie in the pentagonal plane, and the third set (CC) is located axially.⁸ The intra-

(7) G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 2313 (1972).

(8) We have also considered the capped trigonal prism, the capped octahedron, and the tetragonal base-trigonal base as alternative idealized structures⁹ to the pentagonal bipyramid. In the absence of accidental

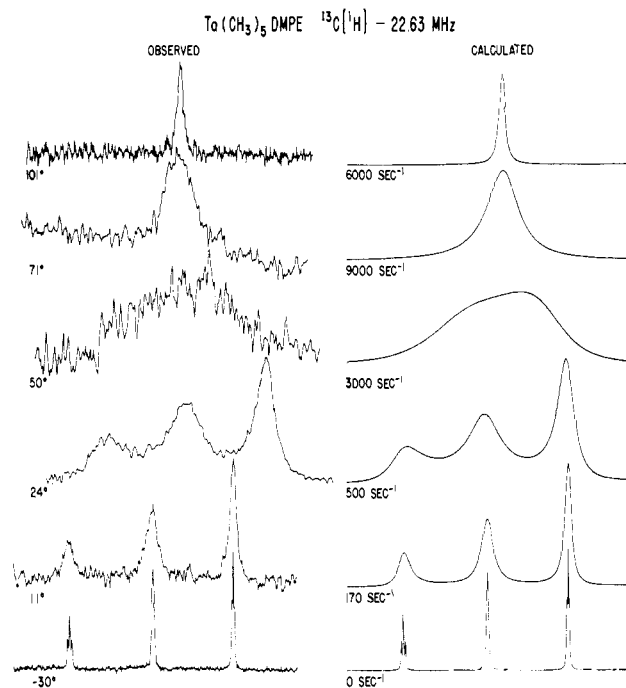
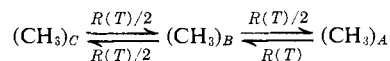


Figure 1. Observed and calculated 22.63-MHz Fourier mode proton noise decoupled ^{13}C nmr spectra for a solution of $\text{Ta}(\text{CH}_3)_5$ DMPE in toluene- d_6 as a function of temperature in the range -30 to 100° .

molecular equilibration of all methyl groups occurs with $\Delta G_{298}^\ddagger = 13.7$ kcal mol $^{-1}$. The calculation was made employing a first-order three-site approximation and the model



Although the chemical shifts of the methyl resonances are strongly dependent upon the concentration of **2**, the exchange rates were observed to be independent of concentration. The temperature-dependent ^1H and $^{13}\text{C}\{^1\text{H}\}$ nmr spectra for $\text{Nb}(\text{CH}_3)_5(\text{dmpe})$ are very similar to those described for the tantalum complex, but, in this case, line broadening effects resulting from incomplete quadrupolar relaxation of the niobium spin (^{93}Nb 100% natural abundance spin = 9/2) prevent a complete lineshape analysis ($\Delta G_{298}^\ddagger \approx 13.4$ kcal mol $^{-1}$).

The decomposition of **2** in toluene begins to occur at a significant rate at 110° . At this temperature the methyl resonance in the ^1H nmr spectrum is a singlet and free dmpe is observed to exchange with coordinated dmpe. These results are taken as direct evidence¹⁰ that the lowest energy intra- or intermolecular decomposition pathways are available only if metal coordination sites are made available by dissociation of (in this case) at least one end of the bidentate dmpe from the seven-

equalities in chemical shifts and coupling constants these idealized structures are not consistent with the low temperature limit nmr spectra.

(9) E. L. Muettterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

(10) (a) The isolability and thermal stability of adducts of $\text{Ti}(\text{CH}_3)_4$,^{10b,c} have provided indirect evidence that strongly coordinating, particularly bidentate, ligands block decomposition pathways in this case. The existence of a large number of alkyl complexes containing relatively nonlabile auxiliary ligands such as $\pi\text{-C}_3\text{H}_5$, CO, etc., is now generally accepted to be due simply to the nonavailability of "vacant" metal coordination sites.^{10d} (b) K. H. Thiele and J. Müller, *Z. Anorg. Allg. Chem.*, **362**, 113 (1968). (c) J. Müller and K. H. Thiele, *ibid.*, **362**, 120 (1968). (d) G. Wilkinson, *Pure Appl. Chem.*, **30**, 627 (1972).

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 “[Ta(CH₃)₇]²⁻” (**4**) prepared from Ta(CH₃)₃Cl₂ and 4 mol of methyllithium at -78° remains pale yellow in color after 1 hr at 35° while a solution of “[Nb(CH₃)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).

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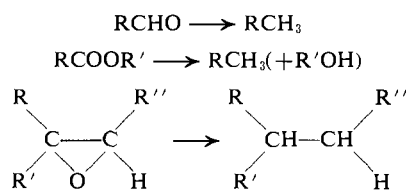
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Direct Conversion of Aldehydes, Esters, and 1,2-Oxides to Alkanes with Carbon Skeleton Preservation

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 olefins² and the reductive decyanation of alkyl nitriles.³ We now report the titanium-based, direct conversion of aldehydes, esters, and 1,2-oxides to



saturated hydrocarbons with preservation of the carbon skeleton,⁴ reductions occurring in good yield at room

(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).

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-oxides⁵ 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 (CHCl₃) 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 filtrate⁷ 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

(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.