Magnesium- and Titanium-induced Reductive Coupling of Carbonyl Compounds: Efficient Syntheses of Pinacols and Alkenes

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Finely dispersed magnesium on graphite was found to be a totally selective single-electron transfer reagent of general utility for the reduction of various kinds of carbonyl and dicarbonyl compounds to pinacols, a reaction quite compatible with a number of functional groups. Similarly, titanium on graphite proved to be a universally applicable reducing agent for the efficient conversion of pinacols, carbonyl and dicarbonyl compounds into alkenes and cycloalkenes respectively and for the cyclization of oxo alkanoates to enol ethers, facilitating and unifying the highly useful McMurry reaction. The practicability of the presently known carbonyl coupling methods is discussed in the light of these results.

The acyloin condensation of esters,[1] pinacol coupling,[2] and the closely related McMurry reduction[3,4] of carbonyl compounds to alkenes constitute a very important group of carbon–carbon-bond forming reductions. With rare exceptions[5] these reactions proceed by dimerizations of carbonyl radical anions formed by single electron transfer from a variety of metals, metal salts, metal complexes, or nonmetallic reagents (see Tables) under various conditions. While sodium is almost exclusively used for acyloin condensations[1] and while McMurry reactions are essentially limited to titanium reagents,[6] there is, however, a considerable variety of pinacolization procedures listed below reflecting the continuous search for ever more efficiency and higher selectivity. The classical pinacolizations which use amalgams of sodium,[2] magnesium,[2] or aluminium[7] by and large give unsatisfactory yields because of sluggish reactions, of two-electron transfer, and of alkene-forming reductions, or even complete failure. Magnesium amalgam, for example, does not reduce aryl ketones[2] and aluminium amalgam is quite inefficient in reducing benzaldehyde.[7] In contrast newer pinacolization reagents such as $Fe_3(CO)_{12}$/pyridine,[8] hexamethyldisilane/tetrabutylammonium fluoride (TBAF),[9] $[Fe_4S_4(SPh)_4]^{2-}[Bu_4N_2]^{2+}$/BuLi,[10a] Yb,[10b] $[TiCp_2(CO)_2]$,[11] $TiCl_3$/HCl,[12] or $TiCl_3$/OH⁻[13] only reduce aromatic carbonyl compounds, and some are even restricted to aromatic aldehydes,[8,9] $TiCl_3$/H⁺ needs electron-withdrawing functions to be successful which, in turn, proved to be deleterious in pinacolizations with hexamethyldisilane/TBAF; all of them, however, produce alcohols and/or alkenes as by-products.

Although the simple Mg/MgI_2 reagent[14] turned out to be most useful for the reduction of aryl ketones, Ce/I_2, $Ce/TiCl_4$, or Rieke-Ce, despite low reaction rates, proved to be of wider applicability,[15] whilst SmI_2 was not only the first reagent to allow pinacolizations of aromatic as well as aliphatic carbonyl compounds, but also favourably compatible with a variety of functional groups.[16] However, its coupling rates for aliphatic educts are remarkably low and only a single, low-yield intramolecular pinacolization is reported.[16]

Among the various single-electron transfer reductions for the different kinds of carbonyl compounds, the most interesting are those induced by titanium reagents, which under appropriate conditions cause pinacolization[17–21] as well as alkene coupling reactions.[3,4]

However, as outlined below, several aspects such as preparation of reagents, educt and reagent reactivity, as well as selectivity of product formation are still puzzling and called for a detailed investigation.

(1) In contrast to active titanium metal, which invariably forms alkenes from all kinds of carbonyl compounds,[22] pinacols,[23,24] and epoxides,[24] low-valent titanium species which by and large convert aryl carbonyl compounds into alkenes,[19] give preferential pinacol formation from alkyl and cycloalkyl carbonyl compounds.[19]

(2) Active titanium metal reagents, so called Rieke-titanium, suitable for McMurry reactions,[25] can be obtained directly from $TiCl_3$ only. Its reduction is generally performed by metals such as Li,[26–28] Na,[26] K,[22,23,26] Mg,[18,26] Zn-Cu-couple[22] or by $LiAlH_4$,[24,29,30] which, when employed in equimolar amounts, produces monovalent titanium salts.[26] In this context, the use of a tertiary amine as part of this reagent[31] is noteworthy. [See below (5) and (6)].

(3) The reduction of titanium trichloride is assumed to be a two-step reaction with the Ti^{III} to Ti^{II} conversion being rate determining, thus allowing the coexistence of Ti^{III} and Ti^0, but not that of Ti^{III} and Ti^{II}.[26] In contrast the reduction of titanium tetrachloride by Mg,[14] Mg/Hg,[20,21] Zn,[19,32,33] Zn–Cu-couple[34] or $LiAlH_4$[35] forms only low-valent, preferably di-valent titanium, which generally resists further reduction, as proved by the preferable formation of pinacols from aliphatic carbonyl compounds.[19,20,21]

(4) Even to a greater extent than in classical pinacolizations[7,14] low-valent titanium reagents tend to form olefinic by-products.[17,21] This over-reduction was, in fact, to be expected from these reducing agents.

(5) Surprisingly, however, these titanium tetrachloride derived species, independent of their preparation, become genuine alkene-forming McMurry reagents when employed in the presence of equimolar amounts of a tertiary amine.[32–35] For this as well as for the titanium trichloride/$LiAlH_4$/amine combination[31] [see above (2)] no plausible explanations exist.

(6) Considering the fact that in some cases the same McMurry procedure is applied to greatly differing coupling problems there is, in turn, no obvious reason for the various reagent preparations described for the same type of reduction. This discrepancy is exemplified by the cyclization procedures used for either diketones[22] or keto esters[31] by two reagent combinations as far apart as $TiCl_3$/Zn–Cu-couple/THF[22] or $TiCl_3$/$LiAlH_4$/triethylamine/dimethoxyethane[31] despite completely analogous mechanisms of these reductions.[31]

With respect to pinacolization none of the reagents presently known are totally satisfactory and even the generally favoured[21] titanium-induced pinacolizations, because of their limited selectivity,[17,21,11] are to be met with caution. As to the McMurry reaction, assumed to proceed by a single mechanism,[3,4] there is hardly good reason for the various different

Table 1. Pinacolization of carbonyl and dicarbonyl compounds (yield %)

Starting material	Product	Mg-graphite	Al (Hg)[a]	Mg (Hg)	Mg/MgI₂[b]	Ce/I₂[c]	SmI₂[d]	TiCl₄ Zn	TiCl₄ Mg (Hg)	Others
(1)	(2)	91	32	0[h]	99.6	0				0[Fe₃(CO)₁₂][g,p]
(37)	(3)	86			o					
(4)	(5)	78	21—38	Low[i]		88	95	91[f]		0 [Fe₃(CO)₁₂][g,q]
(7)	(8)	93	Low		0	94	95	98[f]	84[e]	88 [Fe₃(CO)₁₂][g]
(12)	(13)	65[j]		16.5						
(14)	(15)	84	55	35[b]		95		24[e]	93[e]	
(17)	(18)	82	31—40			84			95[e]	
(20)	(21)	87					85		80[e]	
(23)	(24)	66[k,l]								
(26)	(27)	48[k,m]							32[e,n]	
(29)	(30)						32			
(32)	(33)	89[k,l]								
(35)	(36)	54[k,l] 74[k,l]								10[Na(Hg)][b]

[a] Ref. 7. [b] Ref. 2. [c] Ref. 15. [d] Ref. 16. [e] Ref. 20. [f] Ref. 19. [g] Ref. 8. [h] J. Böeseken, W. D. Cohen, Z. Chem., 1915, 1, 1375. [i] J. M. Johlin, J. Am. Chem. Soc., 1917, 39, 292. [j] Pentan-3-ol as by-product (20%). [k] High dilution technique. [l] cis:trans Ratio undetermined. [m] cis:trans Ratio = 3:2. [n] cis-Diol only. [o] Tetraphenylthiiran only. [p] 97% With Yb.[10b] [q] 73% With Yb.[10b].

titanium preparations and the various conditions described. Thus, a totally selective and generally applicable pinacolization and a unified McMurry procedure would facilitate and improve the applicability of these most useful carbonyl couplings.

Results and Discussion

The considerably higher reactivity of metal-graphite combinations as compared to Rieke-metals[25] has recently led to noteworthy improvements in various metal-induced reductions.[36-38] These results encouraged us to reinvestigate the whole field of carbonyl coupling reactions in order to clarify the cause of inconsistencies and to improve pinacolization[38] as well as the McMurry reaction.[39]

Pinacolization.—The use of magnesium-graphite in this context was indicated by its notorious single-electron transfer (s.e.t.) potential observed in Grignard[40] and Barbier[41] reactions. The results compared in Table 1 demonstrate the general applicability of magnesium-graphite[38] in inter- and intra-molecular pinacol condensations, due to the particularly high s.e.t. potential of magnesium in this form,[38] rendering amalgamation obsolete. All products were found to be completely free of alkene by-products, invariably observed with reducing agents such as Al/Hg,[21] Mg/MgI₂,[14] and all low-valent titanium-induced pinacolizations.[11,17,19-21] Interestingly, aluminium-graphite turned out to be a very poor pinacol coupling agent. The ready conversion of thio-benzophenone (37) into tetraphenylethylene (3) by magnesium-graphite shows an only gradual difference in the reactivities of active magnesium and titanium,[22] also indicated by the sluggish reaction of magnesium-graphite with keto esters as compared to titanium.[31]

With the exception of the nitro and chlorine functions magnesium-graphite reductions are quite well compatible with various functional groups and give very good results with sterically crowded educts as shown in Table 2. Although the very low rate of SmI₂ pinacolizations of aliphatic ketones and the poor yield of intramolecular reductions reduce the scope of this reagent, its functional group compatibility is superior.[16] Attempts to avoid the obvious formation of the Grignard reagent of p-chlorobenzaldehyde (50) by using solvents such as diethyl ether or diglyme invariably led to the formation of p-

Table 2. Results of a comparative investigation of the functional group compatibility of selected pinacolization reagents (Yield %)

R	RC₆H₄CO₂H	[RC₆H₄CH(OH)]₂
OMe	(42)	(43)
NMe₂	(44)	(45)
CN	(46)	(47)
F	(48)	(49)
Cl	(50)	(51)
NO₂	(52)	(53)

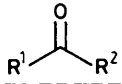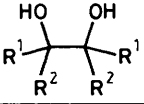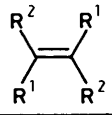| Starting material	Product	Mg-graphite	SmI₂[16]	Hexamethyldisilane/ fluoride[9]	Ce/I₂[15]
(10)	(11)	90[a]	95		
(42)	(43)	93[b,d]	90	87	82
(44)	(45)	81	90	61	
(46)	(47)	86[e]	95		91
(48)	(49)	68[c]			
(50)	(51)	0		90	
(52)	(53)	0	95	Low	

[a] 74% with Mg/MgI₂². [b] 54% with Mg/MgI₂². [c] p-Fluorobenzyl alcohol as by-product (20%). [d] 99% With Yb.[10b] [e] 58% With Yb.[10b].
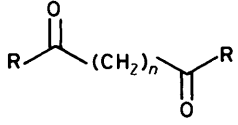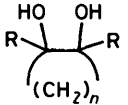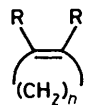
Table 3. Optimal conditions for the formation of titanium-graphite from TiCl₃/3C₈K and its reaction with cyclohexanone (14) (molar ratio 2:1)[39]
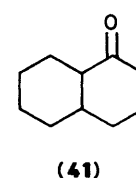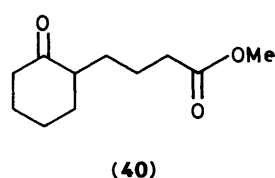
Reduction time (h)	Reaction time (h)	(15) (%)	(16) (%)
0.25	10	84	0
0.5	10	40	40
1.0	10	5	80
1.5	10	0	83
3.0	10	0	80
6.0	10	0	72

chlorobenzyl alcohol. Thus, magnesium-graphite-induced pinacolizations are restricted to tetrahydrofuran (THF) as solvent.

McMurry Reactions.—As shown in Table 3, the optimal time for the reduction of TiCl₃ by C₈K[39,42] is considerably shorter than that with potassium[26] or other reducing metals,[26] and the rate for the coupling reaction of cyclohexanone (14) as an

R^1	R^2	$R^1\!-\!\overset{O}{\overset{\|}{C}}\!-\!R^2$	$R^1\!-\!\overset{HO}{\underset{R^2}{\overset{\|}{C}}}\!-\!\overset{OH}{\underset{R^2}{\overset{\|}{C}}}\!-\!R^1$	$\overset{R^2}{\underset{R^1}{C}}\!=\!\overset{R^1}{\underset{R^2}{C}}$
Ph	Ph	(1)	(2)	(3)
Ph	Me	(4)	(5)	(6)
Ph	H	(7)	(8)	(9)
$C_6H_2Me_3$ - 2,4,6	H	(10)	(11)	
Et	Et	(12)	(13)	
-(CH$_2$)$_5$-		(14)	(15)	(16)
-(CH$_2$)$_4$-		(17)	(18)	(19)
$CH_3(CH_2)_6$-	H	(20)	(21)	(22)

n	R	$R\!-\!\overset{O}{\overset{\|}{C}}\!-\!(CH_2)_n\!-\!\overset{O}{\underset{\|}{C}}\!-\!R$	$R\!-\!\overset{HO}{\overset{\|}{C}}\!-\!\overset{OH}{\underset{(CH_2)_n}{\overset{\|}{C}}}\!-\!R$	$\overset{R\quad R}{\underset{(CH_2)_n}{C\!=\!C}}$
2	Ph	(23)	(24)	(25)
4	H	(26)	(27)	(28)
4	Ph	(29)	(30)	(31)
10	Ph	(32)	(33)	(34)

(35)

(36)

(37)

(38)

(39)

(40)

(41)
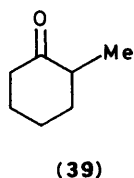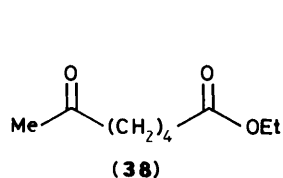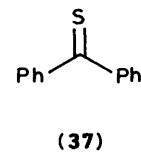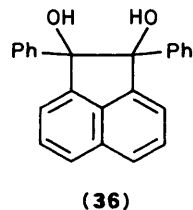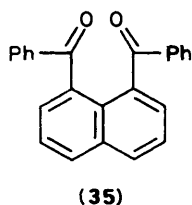
appropriate example is also higher with titanium-graphite than with Rieke-titanium.[26] Incomplete reduction of TiCl$_3$ gives a high yield of pinacol owing to the presence of low-valent titanium.[18]

Table 4 depicting the results of McMurry reactions employing titanium-graphite compared with literature data, shows the general applicability of this reagent to all kinds of carbonyl to alkene couplings. The TiCl$_3$/3C$_8$K reagent [39.42] allows the intramolecular cyclization of keto esters without needing a tertiary amine.[31] Interestingly, methyl 4,6-O-benzylidene-α-D-gluco-pyranoside, a vicinal diol,[23] completely resisted deoxygenation by zero-valent as well as low-valent titanium reagents.

Table 5 summarizes the results of an investigation by reagents derived from TiCl$_4$ and different reducing agents under different conditions; it shows the invariable and preferential formation of low-valent titanium reagents [20.32.35] forming pinacols from aliphatic carbonyl compounds.[19.20.21] However, independent of the reducing agent employed, the addition of pyridine to such reagents changes their reactivity by forming genuine McMurry reagents.[32,35] The tertiary amine as part of these reagents, thought to avoid pinacol-pinacone rearrangement,[35] in fact causes disproportionation with formation of active titanium metal.[39] This two-step method presently seems to be the only one allowing the complete reduction of TiCl$_4$ in solution.

Experimental

General Methods.—All melting points (Tottoli) are uncorrected; n.m.r. spectra were recorded at 60 or 90 MHz (Hitachi/Perkin-Elmer R24B and Bruker WH 90) in $CDCl_3$ as solvent with $SiMe_4$ as internal standard unless stated otherwise; i.r. spectroscopy was performed on a Beckman IR 33 instrument with a film of the corresponding product on a NaCl plate; for t.l.c. precoated silica gel sheets (Merck Nr. 5554) were used, and Merck silica gel (230—240 mesh) served for column chromatography. In all experiments graphite samples supplied by Lonza AG, Basle, Switzerland (HSAG 9) were employed, although this is the least critical part in these investigations.

Pinacolizations Induced by Magnesium-graphite: General Procedure.—Graphite (3.0 g, 250 mmol) degassed at 150—160 °C for 20 min was mechanically stirred under argon in a two-necked flask in the presence of potassium (1.2 g, 31 mmol) at 150 °C until the black mixture had turned bronze coloured. This appearance turned out to be critical for the quality of the

Table 4. Inter- and intra-molecular alkene-forming coupling of carbonyl compounds employing titanium-graphite under optimized conditions

Starting material	Product	Reaction time (h)	Yield (%)	Literature procedures[a]
(1)	(3)	2	87	K, 0.6/16 h, 80%;[b] Mg, 1.5/—,[c] 67%[d]
(4)	(6)	10	86	Li, 1/16 h, 94%[b]
(7)	(9)	3	95	Li, 1/16 h, 97%;[b] $LiAlH_4$, —[c]/4 h, 85%[e]
(14)	(16)	10	83	K, 0.6/16 h, 85%;[b] Li, 40/20 h, 80%[f]
(20)	(22)	3	96	
(23)	(25)	14[g]	70	$LiAlH_4$, 0.25/120 h, 40—61%;[h] Zn/Cu, 1/42 h, 87%[b]
(26)	(28)[i]	14[g]	96[i]	
(29)	(31)	14[g]	87	$LiAlH_4$, 0.25/24 h, 35%;[h] Zn/Cu, 1/42 h, 95%[b]
(32)	(34)	14[g]	89	$LiAlH_4$, 0.25/144 h, —[c,h]
(38)	(39)	14[g]	77[j]	
(40)	(41)	14[g]	91[j]	$LiAlH_4/NEt_3$, 1.5/27 h, 80%[k]

[a] Refers to: reducing agent, reduction/reaction time (h), yield (%). [b] Ref. 22. [c] Unreported. [d] Ref. 18. [e] Ref. 29. [f] Ref. 21. [g] High dilution technique. [h] Ref. 30. [i] Isolated as *trans*-1,2-dibromocyclohexane. [j] After hydrolysis of the intermediate enol ether. [k] Ref. 31.

Table 5. Inter- and intra-molecular coupling of carbonyl compounds employing reagents from $TiCl_4$ by different reducing agents

Starting material	Reducing agent	Reduction time (h)	Reaction time (h)	Additive	Product (%)
(1)	C_8K	1.5	2.0		(3) (80%)
(7)	C_8K	0.5	1.0		(9) (95%)
(7)	Mg (Hg)	a	0.5[b]		(8) (84%)[c]
(14)	C_8K	0.5	2.0		(15) (60%)
(14)	C_8K	0.5	12.0		(15) (55%)
(14)	C_8K	6.0	2.0		(15) (40%)
(14)	Zn/Ag-graphite	0.5	2.0		(15) (93%)
(14)	Mg (Hg)	a	0.5[b]		(15) 93%)[c]
(14)	Mg (Hg)	1.0	4.5	Pyridine	(16) (66%)
(14)	C_8K	1.5	4.5	Pyridine	(16) (75%)
(17)	C_8K	0.5	1.0		(18) (50%), (19) (20%)
(20)	C_8K	0.5	0.25		(21) (91%)
(29)	C_8K	1.5	14.0[d]		(31) (84%)

[a] Unreported. [b] At 0 °C. [c] Ref. 20. [d] High dilution technique.

Table 6. Physical properties of pinacols from magnesium-graphite induced carbonyl coupling reactions

Product	M.p. (°C)	Lit. m.p. (°C)	^1H N.m.r. data
(2)	180—182	182[b]	6.9—7.35 (20 H, m, Ph), 3.0 (2 H, br s, OH)[c]
(5)	120—123	121—122[b]	7.0—7.4 (10 H, m, Ph), 2.4 (2 H, br s, OH),[c] 1.60 (s, *meso*, Me), 1.50 (s, ±, Me); ± : *meso* = 3:1
(8)	94—96	139—140(*meso*), 122—123(±)[b]	6.9—7.4 (10 H, m, Ph), 4.80 (*meso*), 4.70(±) (2 H, s, PhC*H*OH), 4.0 (2 H, br s, OH);[c] ± : *meso* = 3:1
(11)	117—121	214—215(*meso*), 160—161(±)[d]	6.4—7.2 (4 H, m, Ar), 5.4—5.8 (2 H, m, C*H*OH), 1.9—2.8 (18 H, m, Me, OH)[j,k]
(13)	25—28	27—28[d]	2.7 (2 H, br s, OH),[c] 1.8—2.0 (20 H, m, Et)
(15)	124—125	124—125[e]	2.05 (2 H, br s, OH),[c] 1.8—1.9 (20 H, m, CH_2)
(18)	108—112	111—112[e]	2.1 (2 H, br s, OH),[c] 1.7—1.9 (16 H, m, CH_2)
(21)	58—60	53—54,[k,f] 132(*meso*), 70.5(±)	3.3—3.6 (2 H, br, OH),[c] 2.20—2.35 (2 H, m, C*H*OH), 1.10—1.45 (24 H, m, CH_2), 0.8 (6 H, vt, Me)[k]
(24)	122—123[l]		7.10 (10 H, br s, Ph), 3.45 (2 H, br s, OH),[c] 2.50 (4 H, m, CH_2)[l]
(27)[m]	98—99(*cis*)	99—101(*cis*)[b]	*cis* 3.8 (2 H, m, C*H*OH), 3.0 (2 H, br s, OH)[c]
	101—104(*trans*)	105(*trans*)[b]	1.0—1.8 (8 H, m, CH_2), *trans* 4.25 (2 H, br s, OH),[c] 3.35 (2 H, m, C*H*OH), 1.1—2.15 (8 H, m, CH_2)
(30)	Oil[l]	73.2—73.9(*cis*)[g]	7.33 (10 H, br s, Ph), 4.8 (2 H, br s, OH),[c] 1.75—1.95 (8 H, m, CH_2)
(33)	71—75[l]		7.25 (10 H, br s, Ph), 3.25 (2 H, br s, OH),[c] 1.2—1.9 (20 H, m, CH_2)[d]
(36)	136—138[l]	173.5—175.6(*cis*)[d]	6.5—8.7 (16 H. m, Ar), 5.9 (2 H, br s, OH)[c]
(43)	106—108	172(*meso*) 133—135(±)[h]	6.7—7.1 (8 H, m, Ar), 4.6 (s, *meso*, C*H*OH) 4.55 (s, ±, C*H*OH), 3.7 (6 H, s, Me), 2.8—3.0 (2 H, br s, OH);[c] ± : *meso* = 3:1
(45)	98—100	178—179(*meso*) 112—113(±)[i]	6.4—7.2 (8 H, m, Ar), 4.55 (s, *meso*, C*H*OH) 4.50 (s, ±, C*H*OH), 2.85 (s, *meso*, NMe_2), 2.75 (s, ±, NMe_2), 2.25 (2 H, br s, OH);[c] ± : *meso* = 2:1
(47)	201—203		7.2—8.0 (8 H, m, Ar), 5.4—5.7 (2 H, br s, OH),[c] 4.5—4.8 (2 H, m, C*H*OH)[j,k]
(49)	108—109		6.7—7.1 (8 H, m, Ar), 4.70 (s, *meso*, C*H*OH), 4.55 (s, ±, C*H*OH), 3.3 (br s, *meso*, OH),[c] 2.9 (br s, ±, OH);[c] ± : *meso* = 3:1

[a] All compounds gave i.r. absorptions at 3 600—3 250 cm^{-1}; ± : *meso* assignment according to Seebach *et al.*, ref. *h.* [b] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 62nd edn., CRC Press, Boca Raton, Florida, 1981. [c] Disappears on addition of D_2O. [d] Ref. 2. [e] Ref. 20. [f] I. Marszak, M. Koulkes, R. Epsztein, and S. Holand, *Bull. Soc. Chim. Fr.,* 1967, 1895. [g] W. D. Hoffman, W. E. McEwen, and J. Kleinberg, *Tetrahedron,* 1959, 5, 293. [h] D. Seebach, H. A. Oei, and H. Daum, *Chem. Ber.,* 1977, 110, 2316. [i] M. J. Allen, *J. Org. Chem.,* 1950, 15, 435. [j] In $(CD_3)_2SO.$ [k] ± : *meso* Ratio undetermined. [l] *cis : trans* Ratio undetermined. [m] *cis : trans* = 3:2.

Table 7. Physical properties of alkenes and cyclanones obtained by titanium-graphite induced carbonyl coupling reactions

Product	M.p. (°C)	Lit. m.p. (°C)	[1]H N.m.r. data
(3)	204—205	207—209 [a]	7.0 (s, Ph)
(6)	103—106	107(trans), 67—68(cis) [b]	7.1—7.4 (10 H, m, Ph), 2.15 (s, trans, Me), 1.9 (s, cis, Me); cis:trans = 1:20
(9)	126—127	124—125 [b]	7.2—7.6 (10 H, m, Ph), 7.1 (2 H, s, H olef.)
(16)	52—54	52—54 [a]	2.2 (8 H, m), 1.5 (12 H, m)
(19)	Oil	Oil [a]	2.1 (8 H, m), 1.6 (8 H, m)
(22)	c		5.4 (2 H, m, H olef.), 2.42 (4 H, m), 1.38 (20 H, m, CH_2), 0.95 (6 H, m, Me)
(25)	50—52	50.5—52 [f]	7.1—7.6 (10 H, m, Ph), 2.75 (4 H, s, CH_2)
(28) [d]	d.e		4.45 (2 H, m, CHBr), 1.4—2.7 (8 H, m, CH_2)
(31)	47—48	47—48 [f]	7.1 (10 H, br s, Ph), 2.35 (4 H, m), 1.90 (4 H, m)
(34)	82—84	82—84	7.1 (10 H, br s, Ph), 2.35—2.7 (4 H, m), 1.5 (14 H, br s)
(39)	g		1.4—2.5 (9 H, m), 1.0 and 1.1 (3 H, s, Me) [h]
(41)	i		0.9—2.4 (m) [j]

[a] Ref. 22. [b] 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 62nd ed., CRC press, Boca Raton, Florida, 1981. [c] B.p. (0.3 Torr) = 76—80 °C (Kugelrohr); n_D^{20} 1.4454. [d] Isolated as trans-1,2-dibromocyclohexane. [e] B.p. (2.0 Torr) = 56—59 °C (Kugelrohr); n_D^{20} 1.5449 (lit.,[b] 1.5445). [f] Ref. 20. [g] B.p. (18 Torr) = 61—68 °C; n_D^{20} 1.4470 (lit.,[b] n_D^{25} 1.4483). [h] I.r. 1 710s cm^{-1}; δ_{13C}:213.62(carbonyl). [i] B.p. (1.3 Torr) = 78—79 °C; n_D^{20} 1.4926. [j] I.r. 1 705s cm^{-1}; δ_{13C}:214.09(carbonyl); cis:trans ratio undetermined.

resulting C_8K. After cooling and introduction of THF (30 ml) by syringe, anhydrous $MgCl_2$ (1.46 g, 15.3 mmol) was added in one portion causing immediate boiling; the mixture was then heated for 30 min to complete the reduction. For intermolecular pinacolizations, solutions of educt (12 mmol) in THF (20 ml) were added under argon with stirring during a period of 15 min at ambient temperature; stirring was then continued until the starting material had disappeared (t.l.c.). For intramolecular pinacolizations the starting material (6 mmol) in THF (40 ml) was added over different periods of time (4—6 h) to achieve high dilution. For work-up, reaction mixtures were filtered through a short pad of silica gel which was then washed with THF several times; the combined filtrate and washings were evaporated to dryness and the resulting residue chromatographed on a silica gel column. Yields and physical properties are given in the appropriate Tables. Under these conditions thiobenzophenone (37) formed tetraphenylethylene (3) exclusively.

McMurry Reactions Induced by Titanium-graphite: Unified Procedure.—$TiCl_3$ (1.58 g, 10.2 mmol) was added in one portion with stirring to bronze-coloured C_8K (31 mmol) in THF (30 ml) under argon at ambient temperature; the mixture was then treated under reflux for 1.5 h until the reduction was complete. For intermolecular McMurry couplings the carbonyl compound (5 mmol) in THF (15 ml) was added at reflux temperature over a period of 15 min and the reaction brought to completion in the periods of time given in Table 4. For intramolecular alkene couplings, the dicarbonyl compound (2.5 mmol) in THF (40 ml) was added under the same conditions as described above over periods of at least 6 h. Work-up was performed as described in pinacolizations induced by magnesium-graphite. Yields and properties of the alkenes thus obtained are compiled in Tables 4 and 7.

Carbonyl Coupling Reactions Induced by Low-valent Titanium: General Procedure.—$TiCl_4$ (1.47 g, 7.7 mmol) was added dropwise via a syringe with stirring to bronze-coloured C_8K (31 mmol) in THF (30 ml) at 0 °C under argon and the mixture refluxed for various periods of time (see Table 5). All samples thus obtained were found to be equivalent for the following reductions of carbonyl compounds. The condensations of carbonyl or dicarbonyl compounds as well as the work-up were performed under the same conditions as those described for McMurry reactions. The results and properties of the products are shown in Tables 5—7.

Disproportionations of Low-valent Titanium Induced by Tertiary Amine with Formation of Zero-valent Titanium.—Reagent samples obtained from either $TiCl_4$ (1.47 g)/$4C_8K$ or $TiCl_4$ (1.47 g)/$2Mg(Hg)$ [20] in THF (30 ml) were each combined with an equimolar amount of pyridine (0.6 g, 7.5 mmol) and refluxed for 1 h after which the colour of the latter sample had turned from green to grey. Reactions with the resulting mixtures each with cyclohexanone (14) (0.37 g, 3.5 mmol) as an example invariably and exclusively led to the formation of cyclohexylidenecyclohexane (16) in yields of 0.23 g (75%) and 0.19 g (66%), respectively, proving the presence of active titanium metal.

Note added in proof. For very recent applications of low-valent titanium-based pinacolizations see: J. Nakayama, S. Yamaoka, and M. Hoshino, *Tetrahedron Lett.*, 1988, 1161; J. Nakayama, F. Murai, M. Hoshino, and A. Ishii, *ibid.*, 1988, 1399; Y. Handa and J. Inanaga, *ibid.*, 1987, 5717.

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