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$CH_3Li/TiCl_4$: A NON-BASIC AND HIGHLY SELECTIVE GRIGNARD ANALOGUE

M. T. Reetz,* S. H. Kyung and M. Hüllmann
Fachbereich Chemie der Universität, Hans-Meerwein-Strasse, D-3550 Marburg, Federal Republic of Germany

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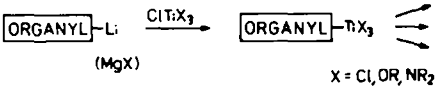
Abstract—Treatment of CH_3Li or CH_3MgCl with $TiCl_4$ results in quantitative formation of CH_3TiCl_3, a non-basic reagent which reacts chemo- and stereoselectively with carbonyl compounds. It is considerably more reactive than the alkoxy analogue $CH_3Ti(OCHMe_2)_3$. This means that selective addition to ketones [which often react sluggishly with $CH_3Ti(OCHMe_2)_3$] in the presence of such a functionality as nitro, cyano and ester groups is possible. Addition to enolizable ketones is smooth. The stereoselectivity is comparable to that observed for $CH_3Ti(OCHMe_2)_3$.

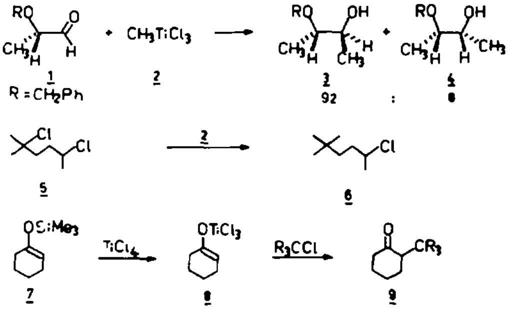
INTRODUCTION

Despite the usefulness of carbanions in organic synthesis, a number of problems remain.[1] In most cases the reagents are very basic and reactive, which means that only a limited number of additional functional groups are tolerated. Furthermore, many carbanions show a low degree of stereoselectivity in reactions with carbonyl compounds.

In 1979–1980 we noticed that certain organotitanium(IV) reagents behave much more selectively than their Li, Mg or Zn counterparts.[2-6] These observations led to the general working hypothesis that titanation of classical carbanions may increase the chemo-, regio- and stereoselectivity in reactions with carbonyl compounds and alkyl halides.[7,8] The type of bond formation is *not* based on typical transition-metal behaviour such as CO insertion, oxidative coupling or β-hydride elimination.[9] Rather, reaction types traditional to carbanion chemistry are involved.

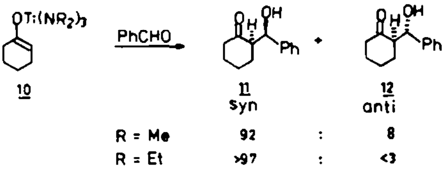


By choosing the proper ligand X at titanium, two parameters can be varied in a predictable way:[8,10] (1) the electronic property, e.g. Lewis acidity; and (2) the steric environment. For example, reagents of the type $RTiCl_3$ are highly Lewis acidic, a property required for chelation-controlled additions to chiral alkoxy carbonyl compounds and for substitution reactions involving S_N1-reactive alkyl halides. Examples are the reactions of the parent compound CH_3TiCl_3 (**2**) with **1**[11] and **5**[4] and the t-alkylation of the trichlorotitanium enolate **8**.[12]



Upon going to organyltitanium alkoxides $RTi(OCHMe_2)_3$ or amides $RTi(NR'_2)_3$, Lewis acidity is reduced drastically, so that the above substitution processes no longer occur.[6,8] In the case of addition to chiral α-alkoxy aldehydes such as **1**, non-chelation control is possible for the first time. Thus, $CH_3Ti(OCHMe_2)_3$ reacts with **1** to form **4** preferentially (**3**:**4** = 8:92).[11] So far, no other methyl-metal reagent has been shown to provide access to the non-chelation-controlled manifold. Titanium enolates having alkoxy or amino groups react similarly.[11]

The size of the amino ligands in $RTi(NR'_2)_3$ often affects the stereoselectivity in reactions with carbonyl compounds. An example is the aldol addition of titanium enolates.[13]



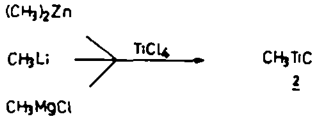
In applying titanium chemistry as delineated here, it is useful to consider certain physical organic aspects such as bond energies, structural parameters and aggregation state.[8,10] For example, the Ti—O bond is very strong (483 kJ mol^{-1}), which means that any reaction leading to such an entity is expected to have a pronounced thermodynamic driving force. It is also short (1.7–1.9 Å) relative to other metal–oxygen bonds (Li—O: 2.0 Å; Mg—O: 2.1 Å; Zr—O: 2.1 Å). This has an important effect on the stereo- and chemoselectivity in reactions involving carbonyl compounds.[8,10]

The present paper is concerned with a simple reaction, namely the chemo- and stereoselective Grignard-type addition of CH_3TiCl_3 (**2**) to aldehydes and ketones. Previously, we had shown that this reagent discriminates effectively between aldehydes and ketones, resulting in complete aldehyde selectivity.[5] In this respect it is similar to $CH_3Ti(OCHMe_2)_3$.[5,8,10,14,15] However, the chemoselective addition of **2** to *ketones* in the presence of additional functional groups remained to be tested. Such a process would be of synthetic value because other methyl-metal reagents often fail to provide acceptable yields of addition products. In fact, even $CH_3Ti(OCHMe_2)_3$ is generally unsuitable for such processes: addition to many ketones is so slow that undesired side reactions involving an additional sensitive functionality compete.[10,15] Thus, a more reactive, but still selective, reagent is needed. We wish to report that CH_3TiCl_3 fills this synthetic gap.

RESULTS AND DISCUSSION

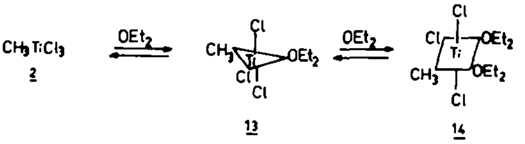
Generation and carbonylophilicity of CH_3TiCl_3

CH_3TiCl_3 can be prepared in dichloromethane by the reaction of $(CH_3)_2Zn$ with $TiCl_4$.[3] Such ether-free solutions are needed for the S_N1 substitutions as well as the chelation-controlled additions described in the introductory remarks. However, for the present purpose, a more convenient procedure is possible. Ethereal solutions of CH_3Li or CH_3MgCl are simply treated with the equivalent amount of $TiCl_4$.[16,17]

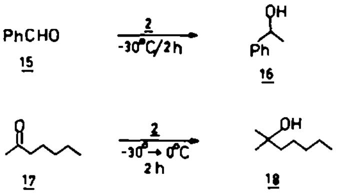


Compound **2** exists in equilibrium with the mono-etherate **13** and the bis-etherate **14**.[18]

Typically, an ethereal solution of CH_3Li (one part) is



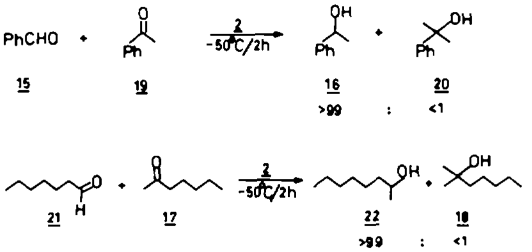
added to $TiCl_4$ (one part) in ether at −78° and the solution allowed to come to about −30°. Titanation is essentially quantitative, as judged by the reactions with carbonyl compounds. For example, addition of benzaldehyde (**15**) or 2-heptanone (**17**) results in quantitative addition. Following aqueous workup, the crude products consist of ~98% of **16** and **18**, respectively.



Addition to aldehydes is quite fast at −30°, unlike the ketone addition reaction. The latter is best performed by letting the temperature come to −5 or 0°. Generally, room temperature should be avoided because tar formation may occur.[16] This is probably due to the fact that the tertiary trichlorotitanium alcoholate undergoes S_N1-like ionization, followed by proton elimination and oligomerization of the olefin. In the above and in the following reactions, the reagent prepared from CH_3Li and $TiCl_4$ is symbolized by **2**, although **13** or **14** (or all three) may actually be the reacting species.[19]

Aldehyde–ketone discrimination

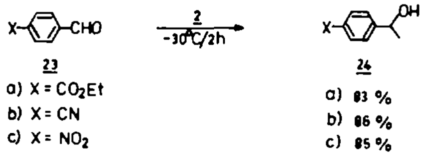
The above observations suggest that the reagent $CH_3Li/TiCl_4/OEt_2$ should react aldehyde-selectively in the presence of ketones, despite the fact that it is considerably more reactive than the alkoxy analogue $CH_3Ti(OCHMe_2)_3$. In fact, we had previously demonstrated aldehyde-selectivity for **2** prepared from dimethylzinc and $TiCl_4$ in dichloromethane.[4] We were therefore not surprised to discover that this also holds for $CH_3Li/TiCl_4$ in ether. Noteworthy is the observation that CH_3Li alone (or CH_3MgCl) reacts almost chemo-randomly;[8,10] in these cases side reactions such as aldol additions involving the ketone and the aldehyde also occur to some extent.



Why are titanium reagents more selective than the Li, Mg *and even* Zr *analogues*? Besides possible electronic effects (e.g. C—metal bond polarity), we believe that steric factors are involved.[8,10] The Ti—O bond is considerably shorter than other metal–oxygen bonds, which means that in the transition state of carbonyl addition, reagent and substrate are tightly together. Thus, small steric differences between two potential acceptor sites are "felt". Even ketone–ketone discrimination is possible (see below).

Reactions of aldehydes having additional functional groups

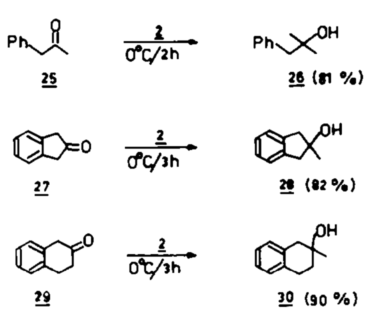
A few aldehydes having an additional functionality were tested. Nitro, cyano or ester groups do not interfere with carbonyl addition. These and similar aldehyde addition reactions are also possible using $CH_3Ti(OCHMe_2)_3$.[8,15] However, it was necessary to show that **2**, being more reactive, performs just as well.



Addition to enolizable ketones

Grignard and alkyllithium reagents are very basic, which means that reactions with readily enolizable ketones fail to provide acceptable yields of addition products. This also applies to the parent methyl compound. In order to test whether titanation with $TiCl_4$ solves this problem, **2** was reacted with ketones **25**, **27** and **29**. In all cases the crude products contained > 90% of the desired adduct. The yields shown in parentheses refer to pure isolated carbinols; the actual isolation was not optimized. The results demonstrate the superiority of CH_3TiCl_3 relative to $CH_3Ti(OCHMe_2)_3$, which reacts with **29** to provide < 20% of **30**.

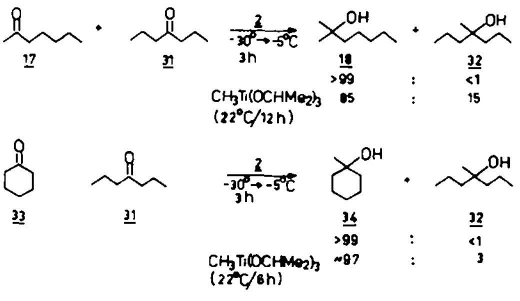
The $CH_3Li/TiCl_4$/ether reagent is cheaper and more readily available than CH_3CeCl_2[20] and $CH_3Zr(OR)_3$,[21] which also react smoothly with enolizable ketones. The $CH_3MgCl/TiCl_4$ combination is just as efficient as $CH_3Li/TiCl_4$. For example, the yield of **30** is 91%. A limitation of the present procedure



pertains to the reaction of **2** with cyclic aryl ketones such as α-tetralone.[16] Addition occurs but a great deal of tar is formed. It should be noted that CH_3Li alone reacts smoothly with α-tetralone, i.e. it poses no enolization problems![8]

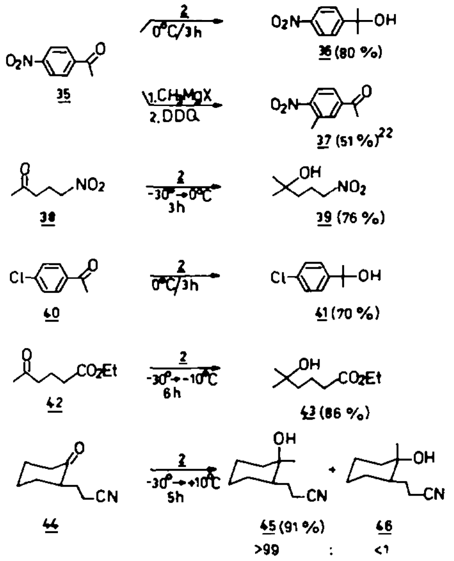
Ketone–ketone discrimination

We have previously shown that $CH_3Ti(OCHMe_2)_3$ is capable of a surprising degree of discrimination between two different ketones, although long reaction times are generally needed and conversion is often mediocre. The following reactions demonstrate that **2** can also distinguish between two different ketone sites. The advantage over $CH_3Ti(OCHMe_2)_3$ has to do with greater reactivity and thus short reaction times as well as better yields (essentially quantitative conversion).



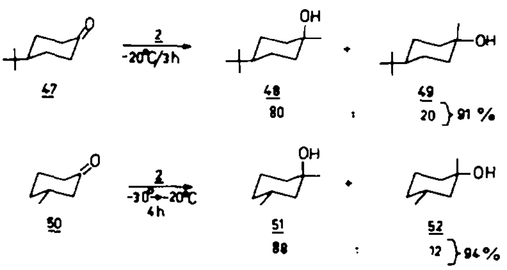
Reactions with ketones having additional functional groups

The following reactions demonstrate that addition to ketones in the presence of such a functionality as nitro, cyano and ester groups poses no problems. Interestingly, CH_3MgX is known to react with the nitro ketone **35** solely at the aryl ring.[22] Thus, titanation of the Grignard reagent with $TiCl_4$ alters the chemical behaviour completely. Here again, it makes no difference whether $CH_3Li/TiCl_4$ or $CH_3MgCl/TiCl_4$ is used. The yield of **36** is essentially identical in both cases. The aliphatic nitro compound **38** also reacts smoothly with **2**. In contrast, $CH_3Ti(OCHMe_2)_3$ affords only 15% of **39** after a reaction time of 2 days at room temperature.[8,15] The reason for this has to do with the fact that competing reactions at the nitro moiety occur, probably deprotonation at the α-position. This problem was originally solved by using the more reactive $(CH_3)_2Ti(OCHMe_2)_2$.[8,15] However, since only one active methyl group is utilized, the present procedure employing $CH_3Li/TiCl_4$ is certainly to be preferred. The pronounced difference between $CH_3Ti(OCHMe_2)_3$ and **2** is also apparent in the reaction of the keto-ester **42**. Whereas the latter affords an excellent yield of **43**, $CH_3Ti(OCHMe_2)_3$ (22°/12 h) leads to 55% of the corresponding lactone.[15] Finally, **44** reacts completely chemo- and stereoselectively. The crude product contains only adduct **45**, which can be isolated in pure form to the extent of 91%. $(CH_3)_2Ti(OCHMe_2)_2$ behaves similarly, but again only one methyl group is utilized.[15]



Equatorial versus axial addition to substituted cyclohexanones

The question of equatorial versus axial addition to cyclic ketones has been addressed on numerous occasions.[23] In the case of six-membered rings, conformationally locked 4-t-butylcyclohexanone (**47**) has often served as a model compound. Of all the reagents tested so far, $CH_3Ti(OCHMe_2)_3$ represents the best choice, the ratio of axial to equatorial alcohol (**48**:**49**) depending upon the reaction conditions (82:18 in the case of CH_2Cl_2 at 22°; 86:14 in ether at 22°; 89:11 in ether at 0°; 94:6 in n-hexane at −15 to 22° over a period of 24 h.[5,8,14,24] Thus, the best result (94:6)[24] is comparable to that observed for $2CH_3Li/LiClO_4$[25] or $CH_3Li/(CH_3)_2CuLi$.[26] The latter reactions require an excess of active methyl groups.

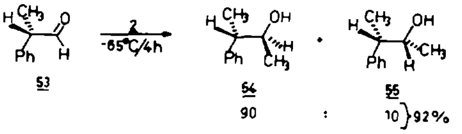


Reagent **2** was reacted with **47** at 0°/3 h, resulting in an isolated yield of 92% of addition products, but the diastereomer ratio **48**:**49** turned out to be a disappointing 71:29. At −20° diastereoselectivity improved to 80:20. Thus, $CH_3Ti(OCHMe_2)_3$ is the reagent of choice.

In the case of 2- and 3-substituted cyclohexanones, **2** can compete effectively with $CH_3Ti(OCHMe_2)_3$. For example, **50** is converted into an 88:12 mixture of **51** and **52**, respectively (isolated yield 94%). This is comparable with the result obtained using $CH_3Ti(OCHMe_2)_3$ (89:11 ratio).[8,24] CH_3MgI delivers a 54:46 product mixture.[23] As noted above, **2** adds to the 2-substituted cyclohexanone **44** with complete chemo- and stereoselectivity. Thus, in all the cases observed so far, equatorial attack is preferred. The traditional explanation is applicable in the present case: 1,3-non-bonded interactions (in the case of axial attack) are more severe than torsional effects (in the case of equatorial attack).[23]

1,2-*Asymmetric induction*

The Cram/anti-Cram problem remains to be solved satisfactorily in a general way. 2-Phenylpropanal (**53**)† has been widely used to study 1,2-asymmetric induction in addition reactions of chiral carbonyl compounds.[27] Following Cram's report that CH_3MgBr forms a 66:34 mixture of **54** and **55**,[27] respectively, other methyl-metal compounds were tested. However, "milder" reagents such as CH_3CdX or CH_3ZnX fail to increase diastereoselectivity (**54**:**55** ≃ 60:40).[28] CH_3Li is slightly better (**54**:**55** 70:30 at $-10°$ and 75:25 at $-60°$).[29]



Titanation of CH_3MgCl or CH_3Li improves the situation considerably. In the early phase of our work in the area of organotitanium chemistry, we showed that $CH_3Ti(OCHMe_2)_3$ leads to an unprecedented diastereomer ratio of 88:12 (at $-40°$) in favour of the Cram product **54**.[5] Later, further improvement was attained by the use of the triphenoxy derivative $CH_3Ti(OPh)_3$ (**54**:**55** = 93:7).[24] In contrast, CH_3TiCl_3 (prepared from dimethylzinc and $TiCl_4$ in dichloromethane) turned out to be somewhat less selective (81:19 diastereomer ratio).[5,24] The THF analogue of **14** (prepared from dimethylzinc and $TiCl_4$ in THF) leads to an 85:15 mixture, but related octahedral complexes are slightly less selective (~ 82:18 ratios).[19] These numbers are all rather similar, which seems to suggest that the octahedral complexes are not the reacting species.[19] Rather, dissociation to the penta-coordinate complex or even the free CH_3TiCl_3 may well precede carbonyl addition.

In view of the above results, we were somewhat surprised to discover that the combination $CH_3Li/TiCl_4/OEt_2$ leads to a **54**:**55** ratio of 90:10 ($-65°$/4 h; 92% yield). This speaks against the involvement of free CH_3TiCl_3. Although mechanistic ambiguities remain to be cleared up (including the possible role of salt effects), participation of **13** seems reasonable. This does not mean that the other two species are not involved to some extent. From a synthetic viewpoint, it is important to note that the THF analogue of **14** is considerably less reactive. For example, $CH_3Li/TiCl_4$ in THF (as the solvent) reacts sluggishly with ketones.[16] THF is a better donor than ether, making the octahedral complex more stable and less prone to dissociate.

CONCLUSIONS

The titanation of CH_3Li or CH_3MgCl in ether is a convenient source of CH_3TiCl_3. It is a non-basic and highly selective Grignard analogue. Its prime virtue relative to the alkoxy analogue $CH_3Ti(OCHMe_2)_3$ pertains to its higher reactivity towards ketones. This makes chemoselective addition to ketones possible in the presence of an additional sensitive functionality, a process that is often inefficient or impossible using CH_3Li, CH_3MgCl or $CH_3Ti(OCHMe_2)_3$. Stereoselectivity of CH_3TiCl_3 is comparable to that of $CH_3Ti(OCHMe_2)_3$, although in certain cases the latter is definitely the reagent of choice. An example is the non-chelation-controlled addition to chiral α-alkoxy aldehydes such as **1**.[11] $CH_3Li/TiCl_4/OEt_2$ is unsuitable for such a reaction; it leads to a 60:40 ratio of **3**:**4**.[16] This again is not in line with the sole involvement of free CH_3TiCl_3. In order to achieve effective chelation control, CH_3TiCl_3 in dichloromethane (free of ether) must be used.[11] Recently, other uses of CH_3TiCl_3 have been reported,[30] including stereoselective reactions of chiral acetals.[31]

EXPERIMENTAL

General information. All reactions were performed in dry flasks under an atmosphere of N_2. Solvents were dried according to standard techniques. Product ratios were determined using a Perkin–Elmer EM 960 gas chromatograph (capillary column), an internal standard being present in the mixture. In all cases, the products were identified by comparison with authentic samples.

Typical procedure for the preparation and reaction of CH_3TiCl_3 (**2**). $TiCl_4$ (1.9 g, 10 mmol) was added by syringe to about 50 ml of cooled ($-78°$) Et_2O, resulting in partial precipitation of the yellow $TiCl_4$-bis-etherate. An ethereal soln of MeLi (10 mmol) was added slowly, which caused a colour change to dark black–purple. The mixture was allowed to come to $-50°$ or $-30°$, and a carbonyl compound was then added (e.g. **15**, **17**, **23**, **27**, **29**, **35**, **40**, **42**, **44**, **47**, **50**, **53**). After reacting for the proper length of time (as indicated in the text), the cold soln (it should not be allowed to reach room temp) was poured into H_2O. In rare cases a TiO_2-containing emulsion may form, in which case a sat soln of NH_4F should be employed. Following usual workup (Et_2O extraction, washing with H_2O, drying over $MgSO_4$), the products were isolated by standard techniques, generally Kugelrohr distillation.

In the case of sensitive polyfunctional molecules (e.g. **38**), it is better to add the cold soln of **2** to an Et_2O soln of the carbonyl component. This reversed mode of addition serves to ensure maximum chemoselectivity. This procedure was applied in competition experiments involving carbonyl pairs. In these cases it is important to use the exact amount of reagent because even a slight excess falsifies the results. For this reason, about 3–5% less of the titanium reagent should be used.

In place of CH_3Li, an ethereal soln of CH_3MgCl can also be employed. In the cases which were tested, no difference relative to $CH_3Li/TiCl_4$ was detected. Also, instead of suspending the $TiCl_4$ in Et_2O and then adding CH_3Li or CH_3MgCl, $TiCl_4$ can be dissolved in CH_2Cl_2 followed by the usual procedure. Several carbonyl additions were performed using both solvents, and no differences in the final result were observed.[16]

Acknowledgements—This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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† Only one enantiomeric form is arbitrarily shown although a racemate was used, leading to racemic products.

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