DOI: 10.1002/chem.201102867

Pivaloylmetals (*t*Bu-COM: M = Li, MgX, K) as Equilibrium Components

R. Knorr,* G. Böhrer, B. Schubert, and P. Böhrer[a]

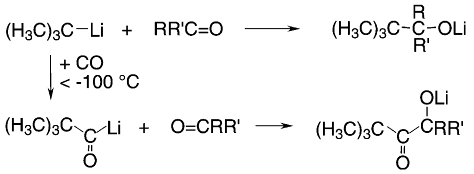
Dedicated to Professor Herbert Mayr on the occasion of his 65th birthday

Abstract: Short-lived pivaloylmetals, $(H_3C)_3C$-COM, were established as the reactive intermediates arising through thermal heterolytic expulsion of O = C*t*Bu$_2$ from the overcrowded metal alkoxides *t*BuC(=O)-C(-OM)*t*Bu$_2$ (M = MgX, Li, K). In all three cases, this fission step is counteracted by a faster return process, as shown through the trapping of *t*Bu-COM by O = C(*t*Bu)-C(CD$_3$)$_3$ with formation of the deuterated starting alkoxides. If generated in the absence of trapping agents, all three *t*Bu-COM species "dimerize" to give the enediolates MO-C-(*t*Bu) = C(*t*Bu)-OM along with O = C*t*Bu$_2$ (2 equiv). A common-component rate depression by surplus O = C*t*Bu$_2$ proves the existence of some free *t*Bu-COM (separated from O = C*t*Bu$_2$); but companion intermediates with the traits of an undissociated complex such as *t*Bu-COM & O = C*t*Bu$_2$ had to be postulated. The slow fission step generating *t*Bu-COMgX in THF levels the overall rates of dimerization, ketone addition, and deuterium incorporation. Formed by much faster fission steps, both *t*Bu-COLi and *t*Bu-COK add very rapidly to ketones and dimerize somewhat slower (but still fairly fast, as shown through trapping of the emerging O = C*t*Bu$_2$ by H$_3$CLi or PhCH$_2$K, respectively). At first sight surprisingly, the rapid fission, return, and dimerization steps combine to very slow overall decay rates of the precursor Li and K alkoxides in the absence of trapping agents: A detailed study revealed that the fast fission step, generating *t*Bu-COLi in THF, is followed by a kinetic partitioning that is heavily biased toward return and against the product-forming dimerization. Both *t*Bu-COLi and *t*Bu-COK form *t*Bu-CH = O with HN(SiMe$_3$)$_3$, but only *t*Bu-COK is basic enough for being protonated by the precursor acyloin *t*BuC(=O)-C(-OH)*t*Bu$_2$.

Keywords: acyl anions · cleavage reactions · reaction mechanisms · reactive intermediates · strained molecules

Introduction

Pivaloyllithium (*t*Bu-COLi in Scheme 1) is thought to be the unstable reagent that can be generated[1,2] by flooding *tert*-butyllithium (*t*BuLi) with gaseous carbon monoxide; it must be handled at below −100 °C. Related reagents[3] were prepared in a similar way that was shown[4] to involve electron transfer steps. While *t*Bu-COLi can efficiently be trapped by electrophiles such as ketones[1,2] (Scheme 1), the parent *t*BuLi will typically compete with *t*Bu-COLi for these electrophiles and thus may furnish unwelcome side-products as shown. Similar problems were encountered when *t*Bu-COLi was generated[5] from *t*BuC(=O)-Te-*n*Bu with *n*-butyllithium. The simplest method[6] of generating *t*Bu-COLi by deprotonation of pivalaldehyde (*t*Bu-CH = O) with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) will probably meet difficulties when striving for reactions of *t*Bu-COLi other than the addition to unreacted *t*Bu-CH = O.



Scheme 1. Traditional generation and trapping of pivaloyllithium.

We have discovered and describe here a cleaner way of creating pivaloylmagnesium, -lithium, and -potassium under conditions that permit qualitative kinetic characterizations of these transient intermediates, even though their more direct observation (using NMR spectroscopy) has still not become possible.[7]

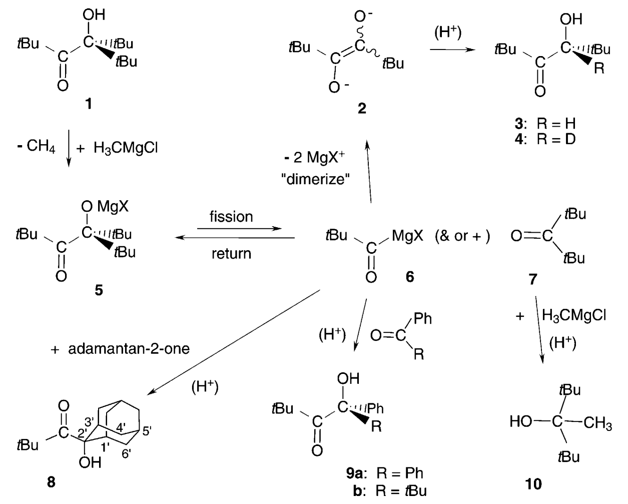
Results and Discussion

Pivaloylmagnesium: The deprotonation (Scheme 2) of tri-*tert*-butylacyloin[8–10] (**1**) by (*tert*-butyl- or) methylmagnesium chloride in tetrahydrofuran (THF) produced two structurally undefined Mg alkoxides **5** (detected through ^{1}H NMR spectroscopy in situ) which approached their equilibrium ratio (ca. 75:25) with a first half-life time ($t_{1/2}$) of roughly 8 min at room temperature.[11] Both alkoxides **5** could coex-

---

[a] Prof. R. Knorr, Dr. G. Böhrer, Dr. B. Schubert, P. Böhrer
Department Chemie der Ludwig-Maximilians-Universität
Butenandtstrasse 5–13 (Haus F), 81377 München (Germany)
E-mail: rhk@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102867.

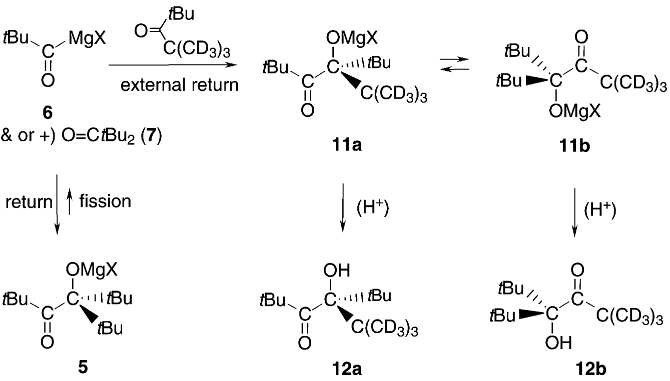


Scheme 2. Novel generation and trapping of pivaloylmagnesium: see Ref. [16] for the meaning of &. X = Cl, -C(O)-*t*Bu.

ist with **1** without showing indications of ^{1}H NMR coalescence, and they slowly released di-*tert*-butyl ketone (O = C*t*Bu$_2$, **7**) at 60 °C ("fission" in Scheme 2). An excess (3.3 equiv) of the deprotonating agent H$_3$C-MgCl did not accelerate this decay of **5** but reacted slowly with the emerging O = C*t*Bu$_2$ rather than with the keto function of **5**, affording the known[12,13] alcohol **10**; a control experiment[11] confirmed the surprisingly sluggish formation of **10** (first $t_{1/2}$ = 19 min at 60 °C) from **7** with H$_3$C-MgCl (2.9 equiv) in THF.

The remaining fragment pivaloylmagnesium (**6**) is thought to "dimerize" with formation of the enediolate **2**, which could not be detected by ^{1}H NMR in situ but was identified through protonation or deuterolysis (with H$_3$COD), producing pivaloin (**3**) or [4D]pivaloin (**4**), respectively. The approximately measurable overall decay rate (corresponding to a second[14] $t_{1/2}$ of ca. 45 min at 60 °C) of the two alkoxides **5** was hardly increased (less than doubled) in the presence of ketones (Scheme 2), affording small portions of pivaloin (**3**) upon aqueous workup and mainly the adducts **8** from adamantan-2-one (0.8 equiv), **9a** from benzophenone (1.6 equiv), or **9b**[15] from pivalophenone (2.0 equiv). The observed product mixtures indicated that the product-forming steps from **6** to **8**, **9a**, and **9b** are hardly faster than the "dimerization" step to give **3** (from **2**). Moreover, the overall reaction rates of these three ketones are hardly greater than that of the "dimerizing" decay of the Mg alkoxides **5**, which suggested that the proposed pre-equilibrium, generating **6** from **5**, provided a common upper limit for these similar overall rate values. All of these trapping modes may be envisioned as operating either on the separated species **6**+**7** or on a transient complex **6**&**7** (which is postulated here in anticipation of the evidence presented in Section B).[16] Neither of these two intermediates was detected through NMR in situ; therefore, they appeared to be present in steady-state concentrations below the NMR detection level due to their rapid consumption by "dimerization" and/or by a fast back reaction such as the "return" step in Scheme 2.[17] The existence of an "external return" process[18,19] from **6** or **6**&**7** to **5** was established through the following experiment.

The presence of O = C(*t*Bu)-C(CD$_3$)$_3$ ([D$_9$]**7**, 0.3 equiv)[20] in a THF solution of **5** decaying at 60 °C led to deuterium incorporation in the recovered portion of **5** (Scheme 3):



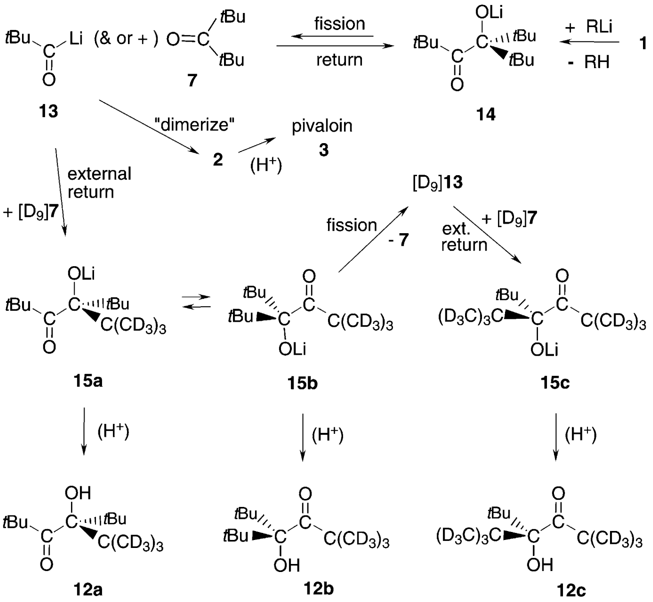
Scheme 3. Deuterium incorporation into the starting material **5** affords **11a** (= [D$_9$]**5**) through "external return" of pivaloylmagnesium (**6**): see Ref. [16] for the meaning of &.

Upon termination by acidification after 25 min (25 % conversion to pivaloin **3**), the deuterium analyses[21] both in situ (experiment 2a in Ref. [22]) and after aqueous workup (experiment 2b in Ref. [22]) revealed 10 % of **12a** and roughly 5 % of **12b**. Obviously, the intermediate(s) had been trapped by [D$_9$]**7** through external return to give first the alkoxide **11a** and then **11b** by *t*Bu migration.[23] This result shows that "external return" can compete with the "dimerization" step in Scheme 2; but it does not provide an estimate of the rate ratio of "fission" over "return". However, "external return" should surely be somewhat slower than the above additions of **6** to less bulky ketones, which were shown above to be hardly faster than the "dimerization" step. Therefore, "return" of **7** to **5**, being kinetically equivalent with the "external return" of [D$_9$]**7** (Scheme 3) except for a tiny isotope effect, can be expected to take place roughly as fast as (or slower than) the "dimerization" step. Both "return" and "dimerization" should then be faster than the "fission" step in view of the low steady-state concentrations of **6** and/or **6**&**7**.

Free O = C*t*Bu$_2$ (**7**, added or emerging as the byproduct) should accelerate the return of free pivaloylmagnesium (**6**) to **5** (or first to **6**&**7**), so that the overall decay rate of **5** to give the enediolate **2** might decrease. The detection of this common-component[24] (or "mass-law")[25] rate depression would provide unambiguous[18] evidence for **6** as a free intermediate. In fact, the overall decay rate of **5** became roughly halved (second[14] $t_{1/2}$ ca. 95 min) in the presence of excess O = C*t*Bu$_2$ (3.6 equiv), showing[18] that the proposed intermediate **6** was generated at least partially as a free species separated from **7**. (This does not exclude the presence of a second reactive[19] intermediate, such as a complex **6**&**7**, which cannot be repressed by free O = C*t*Bu$_2$.) A rather modest common-component retardation appeared to show up also in cases without O = C*t*Bu$_2$ addition, when the very first decay phase could be observed: Due to the initially tiny $O=CtBu_2$ concentrations (hence initially insignificant back reaction), the overall decay rate of **5** at 60 °C often seemed to be abnormally high (albeit not great enough for more precise measurements at room temperature) and dropped soon with the production of $O=CtBu_2$, so that the first $t_{1/2}$ values generally became ill-defined and the second or later[26] $t_{1/2}$ data[14] had to be used for semiquantitative specifications.

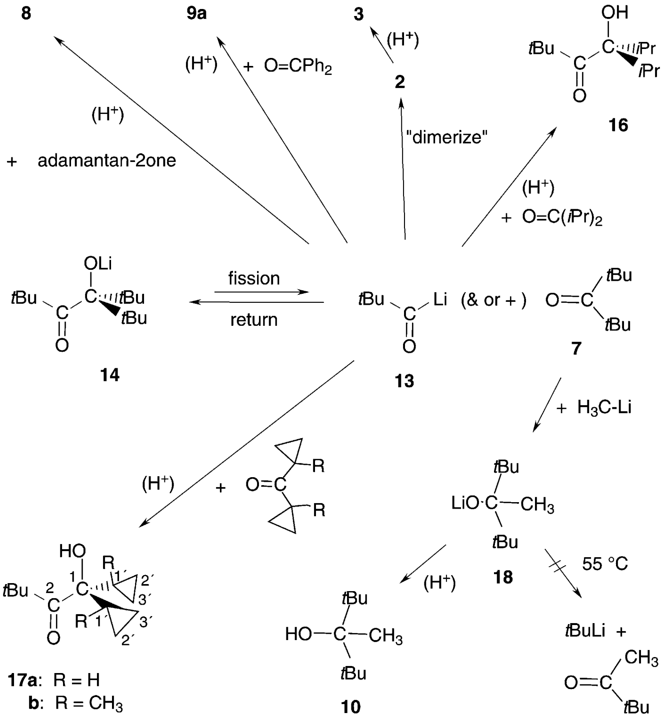
The results of this section support the mechanistic proposal of Scheme 2, with the rate sequencing of "return" ≈ "dimerization" > "fission" during a proceeding decay of the Mg alkoxides **5**.

Pivaloyllithium: Two structurally undefined Li alkoxides **14** (population ratio ca. 20:80 by ^{1}H NMR in situ) resulted from deprotonation (Scheme 4) of tri-*tert*-butyl acyloin[8,9,10] (**1**) in THF by methyllithium, whereas only one kind of Li alkoxide **14** was formed from **1** in hydrocarbon solution with *n*-butyllithium (*n*BuLi).[11] The cleavage of these alkoxides ("fission" in Scheme 4) will generate pivaloyllithium[7] (**13**) or its complex **13&7** with $O=CtBu_2$ (**7**). In analogy with Scheme 2, the entailing "dimerization" is thought to form the NMR-silent enediolate **2** and therefrom (after acidification) pivaloin (**3**, 0.5 equiv) along with $O=CtBu_2$ (**7**).



Scheme 4. Decay of **14**, and deuterium incorporation through "external return" of pivalolyllithium (**13**): see Ref. [16] for the meaning of &.

Crude estimates of the second[14,26] $t_{1/2}$ values for this overall decay process, starting with comparable initial concentrations (typically 0.2–0.3 M), were found to be 15 min in THF at 60 °C but 105 h at 21 °C, and in benzene solution 44 min at 60 °C but roughly 14 h at 21 °C. In striking contrast to this sluggish decay, the very fast incorporation of $O=C(tBu)\text{-}C(CD_3)_3$[20] ([D$_9$]**7**, 5 equiv, added to **14** in THF at −70 °C) was practically finished within 4 min at 21 °C and furnished **12a** (31 %), **12b** (7 %), and **12c** (3 %) upon acidification (experiments 3a,b in Ref. [22]). Obviously, the deuterated Li alkoxides **15a** and **15b** were generated through "external return" with subsequent *t*Bu migration,[23] followed by the fission of **15b** to give $LiOC\text{-}C(CD_3)_3$ ([D$_9$]**13**) and a subsequent second external return that converted [D$_9$]**13** into **15c**. In terms of the reaction sequence proposed in Scheme 4, these "external return" events generating **15a** and **15c** are mechanistically equivalent with return of **13** to **14** (except for a tiny isotope effect), so that all of these "return" processes must be faster (because successful already at 21 °C) than the "dimerization" step forming enediolate **2**. In addition, these return processes are also substantially faster than the "fission" step of **14**, because **13** and/or **13&7** (both undetected) do not accumulate.[17] Therefore, the fast "fission" step limits the rate of deuterium incorporation and should become a common kinetic "bottleneck" in the cases of other reagents (Scheme 5) which capture **7** or **13** with significantly higher rates than those of the "dimerization" and "return" processes, as explored in the sequel.



Scheme 5. Trapping of the fission products **7** and **13** of Li alkoxide **14**: see Ref. [16] for the meaning of &.

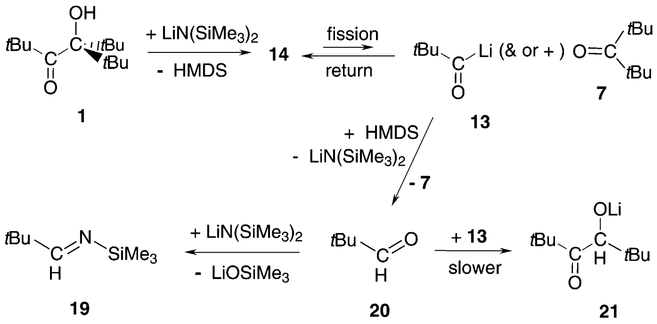
The Li alkoxide **14** vanished in the presence of benzophenone (1.9 equiv) in THF at 21 °C (**9a** isolated after aqueous workup) with a second[14,26] $t_{1/2}$ of ca. 3 min, to be compared with the above 105 h in the absence of trapping agents; a similar run with benzophenone in benzene solution also was complete in < 12 min. A mixture of **14** and its parent substance **1** (ca. 1:9), generated with only 0.1 equiv of

H_3CLi, produced very little $O=CtBu_2$ (**7**) at 21 °C within 4.4 h, showing that the acyloin **1** did not intercept **13** or **13&7** by protonation (no acceleration of the overall decay). However, the subsequent addition of adamantan-2-one (1 equiv) completed the consumption of both **14** and **1** within <16 min, affording the adduct **8** after aqueous workup; this implies fast proton transfer from **1** to the product alkoxide of **8**, so that more of **14** became available for continuing the decay process. Di-isopropyl ketone (2 equiv) consumed **14** in benzene solution at 29 °C with a second[14,26] $t_{1/2}$ of ca. 6 min; in the solvent THF, this reaction did not occur at −45 °C but proceeded as usual at 20 °C, furnishing the adduct **16** after aqueous workup. However, cyclohexanone did not capture **13** in benzene or in THF, presumably due to fast proton transfer to **14** with re-generation of **1**, although the expected ketone adduct had been obtained[1] with **13** as generated from *t*BuLi and carbon monoxide at −110 °C. This failure of our system dictated the choice of two small, non-enolizable ketones as trapping agents: dicyclopropyl ketone (1 equiv) and Li alkoxide **14** in pentane or in THF afforded $O=CtBu_2$ and the adduct **17a** after aqueous workup, providing no evidence of ring-opened products that would have been expected from a radical mechanism. The very slow decay of **14** in benzene at 20 °C was accelerated to a time-domain[14] of about 2 min through the injection of bis(α-methylcyclopropyl) ketone[27] (1.2 equiv) whose adduct **17b** to **13** was obtained as the only product along with $O=CtBu_2$ after aqueous workup. A further simple and instructive mode of suppressing the "return" reaction utilized the rapid removal of $O=CtBu_2$ (**7**): Li alkoxide **14**, prepared from **1** at −70 °C with an excess of methyllithium in THF and warmed quickly to 23 °C, vanished through trapping of **7** by residual H_3CLi (2.1 equiv) with a third[14,26] $t_{1/2}$ of ca. 4 min; the subsequent acidification revealed the formation of adduct **10** and pivaloin (**3**) in situ. Since the pivaloyllithium (**13**) left behind on consumption of **7** cannot return in the absence of **7** but nevertheless still does not accumulate, this experiment confirms that the "dimerization" step toward **2** and **3** can proceed faster (as if stimulated by the interception of **7**) than the "fission" of **14**. In practice, any excess over the stoichiometric amount of H_3CLi at ambient temperature should be avoided through careful titration of the acyloin **1** with H_3CLi (measuring CH_4 in a gas burette, for instance) at or below −40 °C, lest the rapid formation of the alkoxide **18** of adduct **10** consume **14**, frustrating a different application of **13**. Besides, the conceivable possibility (Scheme 5) of a cleavage of **18** in THF to give *t*BuLi was excluded through prolonged warming of an authentic sample of **18** which remained intact at 55 °C for more than 90 min.

All of the above crude estimates of time domains agree with an upper limit of few minutes (or a corresponding lower limit of the reaction rates) for the observed overall decay, pointing to a rate-limiting "fission" step of the Li alkoxide **14** at room temperature; but considerably higher overall decay rates could not always be excluded by such crude timing. However, the latter possibility was dismissed as follows. The Li alkoxide **14** was prepared from **1** with H_3CLi (3.0 equiv) with magnetic stirring at −40 °C (CH_4 evolution) and then warmed quickly up to 3 °C under dry argon gas. Three samples were withdrawn after reaction periods of 2, 12, and 240 min and quenched with iced HCl (1 M). Extractions with Et_2O furnished three clean product mixtures (no $O=CtBu_2$, no $tBuCH=O$) of starting material **1**, product **10**, and pivaloin (**3**) in the molar ratios of 97:3:1, 94:6:4, and 0:65:35, respectively, all in acceptable agreement with the expected **10/3** ratio of 2:1. This low reaction rate at 3 °C appears to be compatible with a time domain (and $t_{1/2}$) narrowed down to approximately 3 min at ambient temperature for the "fission" step as a kinetic "bottleneck" of the overall decay rates. Reverting to the very much slower overall decay ($t_{1/2}$ ca. 105 h) with "dimerization" (upper part of Scheme 4), this attenuation by a factor of roughly 3 min/105 h ≈ 1/2000 in the absence of efficient trapping agents (such as ketones) suggests that the rapid initial "fission" event of **14** is followed by a 1/2000 partitioning between "dimerization" and "return".[28] This information does not define absolute time domains for "dimerization" and "return", both of which were classified above as being substantially faster than the "fission" step.

If the complex **13&7** were the only "dimerizing" intermediate that produces the enediolate **2**, the overall decay rate would not depend on the concentration of free $O=CtBu_2$ (**7**). On the other hand, the free intermediate **13** (separated from **7**) alone would be recognized through an inverse linear dependence of the overall decay rate on the concentration of free **7** under the present condition of a mobile pre-equilibrium ("return" being faster than "fission" and "dimerization"). However, the common-component[24] rate depression expected for this case was again found to be rather small: In the presence of a substantial excess (3.8 equiv) of $O=CtBu_2$, the overall decay rate of **14** was only halved with a second[14,26] $t_{1/2}$ of ca. 30 min THF at 60 °C. This rate depression provides unambiguous[18] evidence for at least some free pivaloyllithium (**13**); its low magnitude points to the existence of a second pathway that consumes **14** and can generate the same products as free **13** but cannot be retarded by free $O=CtBu_2$ (**7**). This suggests that both **13** and **13&7** may indeed be present as transient intermediates (corresponding to the kinetic system[18] of a free ion and its ion pair). The surprisingly similar decay rates of **14** in both THF and hydrocarbons may have to do with a temporary stabilization of **13** in **13&7** by the interaction of the Li center with $O=CtBu_2$ in either solvent.

Pivaloyllithium (**13**) is a weaker base than LiTMP ($pK_a=37.0$ for TMP in THF[29]), as shown by the deprotonation[6] of pivalaldehyde ($tBuCH=O$) with LiTMP mentioned in the Introduction. Thus, a pK_a value in the range of 27–36 can be expected for the aldehyde proton in $tBuCH=O$, because the following experiment shows that **13** is a stronger base than $LiN(SiMe_3)_2$ (LiHMDS) in THF. The injection of $HN(SiMe_3)_2$ (HMDS, 1.4 equiv, $pK_a=25.8$[30] in THF) into a very slowly decaying THF solution of the two Li alkoxides **14** initiated a vivid consumption of **14** (95 % conversion



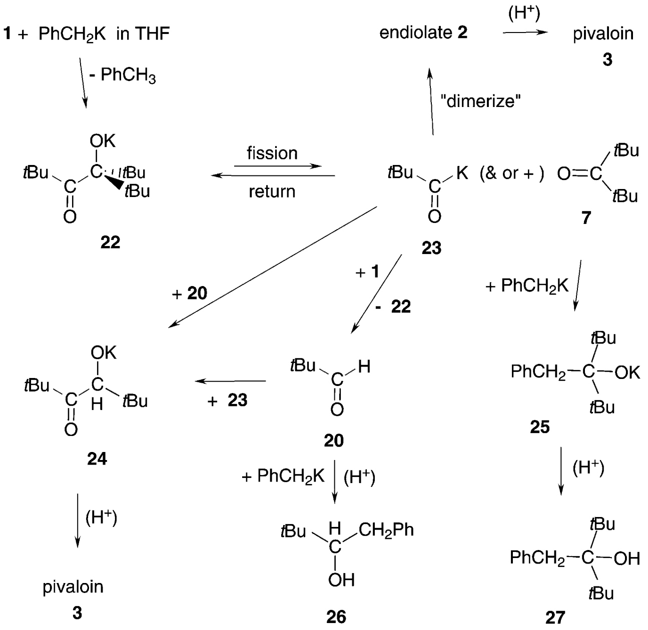
Scheme 6. Protonation of pivaloyllithium (**13**) by HN(SiMe$_3$)$_2$ (HMDS): see Ref. [16] for the meaning of &.

during 20 min at 23 °C), affording (Scheme 6) O = C*t*Bu$_2$ (**7**) and *t*BuCH = N-SiMe$_3$[11,31] (**19**) as the only derivatives of **14** observed through ^{1}H NMR in situ. Evidently, the fast protonation of **13** by HMDS generated *t*BuCH = O (**20**) and the weaker base LiHMDS; a separate experiment confirmed that these two primary products furnished the imine **19** quickly. The latter condensation reaction to give **19** is faster than the fast deprotonation of acyloin **1** (Scheme 6) by LiHMDS: A catalytic amount of LiHMDS (0.2 equiv) in THF containing HMDS (1.1 equiv) initiated a moderately accelerated consumption of **1** (67 % conversion in 90 min), producing O = C*t*Bu$_2$ (**7**) and *t*BuCH = O (**20**) along with some short-lived imine **19**, but neither the pivaloin alkoxide **21** nor pivaloin (**3**). Recalling the hesitance of acyloin **1** to protonate **13**, it is clear that **13** became protonated by the acid HMDS with regeneration of LiHMDS, so that the overall decay from **1** to **7** and *t*BuCH = O (**20**) was temporarily catalyzed by LiHMDS. However, this catalyst was soon poisoned through its faster condensation with the accumulating **20** to give **19**, such that the initially fast overall decay of **1** discontinued at 70 % conversion. Obviously, the remaining bases LiOSiMe$_3$ and HMDS were unsuited for deprotonating the last 30 % of **1**. The interception of **13** by HMDS was fast enough to prevent **13** from adding to the accumulated **20** with formation of the pivaloin alkoxide **21**, although this addition is known to occur readily[1] even at −135 °C and hence should be quite fast at 23 °C. Besides, small amounts of *t*Bu-CH$_2$OH and the Tishchenko ester *t*BuCO$_2$-CH$_2$*t*Bu[32] were observed in situ after several d at 20 °C.

With a greater portion of LiHMDS (1.2 equiv) and less HMDS (0.55 equiv), the faster consumption of acyloin **1** (85 % conversion in 5 min at 21 °C) furnished only O = C*t*Bu$_2$ (**7**) and the imine[11,31] **19** in place of **20**, but again no pivaloin alkoxide **21**; separate runs established that LiHMDS does not deprotonate **21** (to generate enediolate **2**) in THF at 21 °C. For a somewhat sharper estimate of the rapidity of trapping **13** with HMDS, the acyloin **1** was added to a THF solution of HMDS (0.34 equiv), LiHMDS (1.2 equiv), and adamantan-2-one (2.4 equiv) at −78 °C. The ^{1}H NMR spectrum in situ, recorded 4 min after a quick warm-up, showed residual Li alkoxide **14** (only the major component with $\delta_H = 1.01$ and 1.28 ppm, as always with LiHMDS as the base), O = C*t*Bu$_2$ (50 % conversion), and imine **19** (0.23 equiv), supplemented by the adduct **8** (0.51 equiv) and a little[33] pivaloin (**3**) but no *t*BuCH = O (**20**) after acidification. Thus, the **19**/**8** ratio of 0.45 indicates that both HMDS and adamantan-2-one intercepted pivaloyllithium (**13**) with similar efficiency and that LiHMDS is, therefore, not always recommendable for generating **13**.

The rate sequencing as deduced in this section for the kinetic setup in Scheme 4 and Scheme 5 is "return" ≫ "dimerization" > "fission" during a proceeding decay of the Li alkoxides **14**.

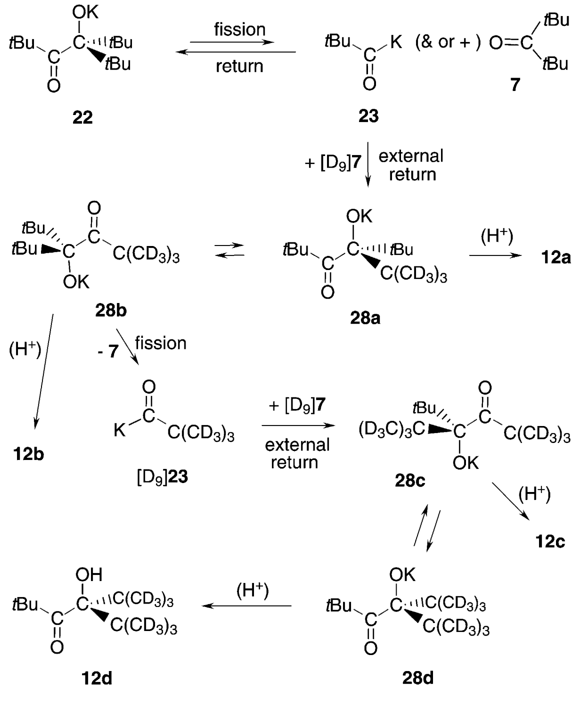
Pivaloylpotassium: Benzylpotassium (PhCH$_2$K, Scheme 7) is a suitable base for generating pivaloylpotassium (**23**) from the acyloin **1**: Its preparation[34] from KO*t*Bu, toluene, and *n*BuLi in saturated hydrocarbons at room temperature is easy and safe; the brick-red PhCH$_2$K precipitates from the hydrocarbon solution, can be purified through washing with pentane or cyclopentane, and is stable as a powder in an inert atmosphere. Its dark red solution in anhydrous THF is relatively unstable above −20 °C but will partially survive a rapidly performed ^{1}H NMR[35] analysis at ambient temperature under argon cover gas. Its titration at −70 °C by adding small batches of the acyloin **1** up to decolorization afforded toluene and the K alkoxide[11] **22** which may be a rapidly (on the NMR time scale) interconverting pair of alkoxides (in contrast to the slow interconversion of the Li alkoxides **14** as described in Section B). Observed in a tightly closed NMR tube under argon gas, **22** decayed very slowly (second[14,26] $t_{1/2}$ ca. 8 h) at 20 °C with formation of O = C*t*Bu$_2$ (**7**); no other product became visible until an acidification disclosed pivaloin (**3**, 0.51 equiv relative to **7** as required), which in this case can derive only from the NMR-silent ene-



Scheme 7. Formation and decay of the potassium alkoxide **22**: see Ref. [16] for the meaning of &.

diolate **2** as formed through “dimerization” of pivaloylpotassium (**23**) in analogy with the behavior of pivaloyllithium (**13**), except for the new side-product[11,36] **26** (0.07 equiv) as generated from pivalaldehyde (**20**) with $PhCH_2K$. At 60 °C, **22** decayed again much faster (within 1 h) than the Li alkoxide **14**, but all further runs with **22** were conducted at or below ambient temperature.

Most of the properties of the system **22**/**23** can be understood on the basis of lessons learned in Section B: In the presence of surplus (1.0 equiv) benzylpotassium, the decay of K alkoxide **22** ran down with a dramatically shortened second[14,26] $t_{1/2}$ of 4 min (instead of 8 h) at 20 °C. NMR spectra in situ revealed that the K alkoxide[11] **25** was present in place of O = C*t*Bu$_2$ (**7**) whereas pivaloin (**3**) and its K alkoxide[11] **24** were absent; clearly, the rapid conversion of **7** to **25** had overcome the “return” process of pivaloylpotassium (**23**) with **7** toward **22** and thus brought the fast “fission” step of **22** to **23** into focus. After aqueous workup, the main product[11,37] **27** was accompanied by pivaloin (**3**, 0.38 equiv)[33] and by the adduct **26** (0.32 equiv)[11] of $PhCH_2K$ to **20**. These products indicate that pivaloylpotassium (**23**), being restrained from returning to **22**, had rapidly “dimerized” to generate the NMR-silent enediolate **2** (→later **3**) and was also protonated with a comparable efficiency to furnish **20** that formed the K alkoxide of **26** with surplus $PhCH_2K$. In this strongly basic milieu,[38] a portion of the initially present acyloin **1** must have served as the only available acid for proton transfer to the rapidly emerging pivaloylpotassium (**23**) in preference to protonating the enediolate **2** or the more basic $PhCH_2K$. This fast proton transfer from **1** to **23** constitutes a prominent difference of pivaloylpotassium (**23**) from pivaloyllithium (**13**) and was confirmed as follows. Employing a substoichiometric amount of $PhCH_2K$ (0.27 equiv only), the overall decay of K alkoxide **22** was again accelerated rather than slowed down: After the initial consumption of $PhCH_2K$ by **1** had furnished **22** and plenty of O = C*t*Bu$_2$ (but no **25**) in the first 4 min (immediate decolorization), the decay of surplus **1** was fast (96 % conversion in 25 min) at 21 °C due to the partial suppression of the “return” reaction through trapping of **23** by proton transfer from **1** with formation of pivaldehyde (**20**). However, **20** could not be detected by ^1H NMR in situ because of its interception by **23** (instead of $PhCH_2K$) to give the K alkoxide **24** and because of the concomitant transformation of **20** into the Tishchenko ester[32] *t*BuCO$_2$-CH$_2$*t*Bu which began to emerge already after 12 min. In this absence of detectable amounts of **20**, **24** is a diagnostic in-situ indicator of the partial protonation of **23** to give **20**, as opposed to the “dimerization” of **23** affording the NMR-silent enediolate **2** (which was shown above not to be protonated by **1**); on aqueous workup, however, both **2** and **24** (Scheme 7) are converted to pivaloin (**3**), of course. The unpleasant high decay rate of the K alkoxide **22** caused by surplus amounts of either acyloin **1** (protonating **23**) or $PhCH_2K$ (trapping **7**) is limited by the initial “fission step” of **22** which could be frozen by cooling to −27 °C. Therefore, preparations of **22** should be performed at a lower temperature by fast deprotonation of **1**, so to avoid the side-reactions described above. The suitable base $PhCH_2K$ may not be replaced by KH.[11] Similar accelerations up to the limiting rate of the common “fission” step (the “kinetic bottle-neck”) were found with two ketones as trapping agents for **23** or **23**&**7**: The addition of benzophenone ($Ph_2C{=}O$, 0.4 equiv) accelerated a slowly decaying solution of **22** in THF and consumed an equivalent amount of **22** in less than 6 min at 22 °C,[11] yielding the adduct **9a** after aqueous workup. Similarly, pivalophenone (*t*BuCO-Ph, 1.0 equiv) consumed **22** in THF at 20 °C within <9 min, affording O = C*t*Bu$_2$ (**7**) together with the K alkoxide[11] of **9b** and therefrom after aqueous workup the pure adduct **9b** (85 % yield). These time domains[14] agree with the above 4 min estimate for the “fission” step, whereas the actual addition rates of **23** to the ketones were certainly much higher: Namely, these rates should be higher than that of the corresponding addition of **23** to the more shielded (hence less reactive) O = C*t*Bu$_2$ (**7**) which is the “return” reaction to **22** and must already be much faster than the “fission” step, since **23** did not accumulate.[17] A direct visualization of this “return” step and the limiting “bottle-neck” rate was again achieved with the isotopologue[20] [D$_9$]**7** of O = C*t*Bu$_2$ as follows. A slowly decaying THF solution of **22** containing just only 3 % of **7** was mixed with [D$_9$]**7** (0.6 equiv) at −70 °C, then warmed up quickly to 23 °C and quenched after 6 min with $F_3C\text{-}CO_2H$. Upon aqueous workup, ^1H and ^{13}C analyses[21] revealed the production of additional O = C*t*Bu$_2$ (total 0.37 equiv) along with the deuterated starting material as formed through the following reaction sequence (Scheme 8):



Scheme 8. Trapping of pivaloylpotassium (**23**), and deuterium incorporation into the starting material (**28a** = [D$_9$]**22**) through “external return” of **23**: see Ref. [16] for the meaning of &.

Capture of **23** by [D$_9$]**7** to give the labeled K alkoxide **28a** (converted into 36% of **12a** through acidification), *t*Bu migration[23] in **28a** to produce **28b** (→10% of **12b**), fission of **28b** to generate [D$_9$]**23** whose capture by [D$_9$]**7** afforded **28c** (→6% of **12c**), and (D$_3$C)$_3$C migration in **28c** to produce **28d** (→3% of **12d**), as analyzed in experiments no. 4–6 in Ref. [22] Clearly, this deuterium incorporation occurred again in a time domain[14] of some minutes as imposed by the "fission bottle-neck" from **22** to **23**. Considering that both free *t*Bu-COK (**23** separated from **7**) and its complex **23**&**7** might take part in the D incorporation, we sought unambiguous[18] evidence for at least some free **23** through an assessment of the common-component[24] rate depression of **22**: The overall decay rate of **22** became strongly reduced in the presence of free O=C*t*Bu$_2$ (**7**, 2.0 equiv) and was reanimated through subsequent heating at 60°C, which led to completion of the run within 55 min. Unfortunately, the qualitatively obvious rate depression could not be quantified due to the poor numerical reproducibility as caused by the above-mentioned strong acceleration effects of varying **1**/PhCH$_2$K ratios. It appeared probable that free *t*Bu-COK (**23**) contributes with a substantial portion, while a contribution of the undissociated complex **23**&**7** could not be excluded.

Summing up, the kinetic assessments of **23**(& or +)**7** were aggravated by the adverse kinetic properties of this system which tends to disturbances through trapping reactions by both surplus PhCH$_2$K and the parent acyloin **1** at room temperature. The "return" and "dimerization" steps are substantially faster than the "fission" step (generating **23**), so that "fission" is a common kinetic "bottle-neck" that levels the overall rates of deuterium incorporation and of the other perturbations of the pre-equilibrium to a common time domain of a few minutes. The rate sequencing of electrophiles for trapping **23** appears to be *t*BuCH=O (**20**) > protonation by acyloin **1** > adamantan-2-one > O=C*t*Bu$_2$ (**7**). The results of this section support the mechanistic proposal of Scheme 7, with the rate sequencing of "return" > "dimerization" > "fission" during a proceeding decay of the K alkoxides **22**.

Conclusion

The acyloin **1** was considered[39] for some time as an antiknock additive to Diesel fuels, which may suggest a propensity toward radical reactions. However, the presently investigated metal alkoxides of **1** do not decay by a radical pathway (not even in a perceptible side-reaction) which would generate the thermodynamically stable ketyl radical-anion of O=C*t*Bu$_2$ along with the kinetically unstable pivaloyl radical (*t*Bu-CO•): The evolution of carbon monoxide expected from the fast[40,41] decay of *t*Bu-CO• was never observed here. Instead, our pivaloylmetals are the first acylmetals that were generated through the heterolytic thermal cleavage of metal alkoxides. These short-lived acylmetals are formed not only as the free particles *t*Bu-COM (separated from O=C*t*Bu$_2$) but apparently also as activated species exhibiting the traits expected for undissociated complexes such as *t*Bu-COM & O=C*t*Bu$_2$.[16] The latter formulation disregards the possibility of molecular aggregation that is quite usual for polar organometallics (and perhaps also favorable in the unknown course of the "dimerization" step producing the enediolate **2**).

The precursor alkoxide **5** of *t*Bu-COMgX (**6**) is most easily prepared because it is stable at room temperature in THF, presumably owing to its slow initial fission step. However, the subsequent "dimerization" of **6** can successfully compete with the addition to ketones, so that product mixtures may be obtained. The precursor alkoxide **14** of pivaloyllithium (**13**) is fairly stable at 23°C in the absence of surplus organolithium compounds that can capture O=C*t*Bu$_2$ from the mobile pre-equilibrium. The fast "fission" step of **14** is slower than the "dimerization" and "return" steps of **13**, although its high rate is not immediately evident from the very sluggish overall decay of **14**. In fact, "fission" was recognized as the common fast "bottle-neck" step: All overall rates which involve ensuing faster reactions of **13** are leveled to a common time domain of several minutes. The K alkoxide **22** decays most readily, compared with **5** and **14**, but still with a very low overall rate that appears to hide a similar kinetic system as above with fast "fission" and faster "return" and "dimerization" steps. The equilibrium component *t*Bu-COK (**23**) is more reactive than *t*Bu-COLi (**13**) in deprotonating the acyloin **1**; this property and the somewhat complicate PhCH$_2$K technique as required for preparing the precursor **22** impair the practicability of **23**. Considering the various kinetic effects and reaction conditions reported in this work, a rate sequencing as controlled by the metal cations during the proceeding decay reactions appears to be $K > Li \gg Mg$ for the "fission" step. For all three cations, a step rate gradation of "return" > "dimerization" > "fission" was inferred.

Although the present method of generating polar acylmetals through alkoxide fission is restricted to the salts of acyloin **1**,[23] this singular system provided novel knowledge about reactivity patterns of this type of short-lived[42] intermediates. This may have become possible because *t*Bu-COLi and *t*Bu-COK are "domesticated" through frequently repeated return events, as mediated by the maintained contact to O=C*t*Bu$_2$ in *t*Bu-COK & O=C*t*Bu$_2$ or by the fast recapturing the free pivaloyl species with free O=C*t*Bu$_2$, so that the overall "dimerizing" decay reactions were strongly impeded. As a simpler alternative mechanism, the direct (S$_E$2-type) attack of the electrophilic reagents on the labile alkoxides *t*BuC(=O)-C(-OM)*t*Bu$_2$ causing a concerted *t*Bu-COM transfer (no intermediates?) would not only be hard to believe but must also be dismissed: The sterically quite dissimilar ketone reagents [from dicyclopropyl ketone to O=C(*t*Bu)-C(CD$_3$)$_3$] should then react with widely differing rates, whereas their rates were found to be leveled to the rate of the common initial "bottle-neck" fission that does not involve the ketones.

Experimental Section

Typical procedures: Using *t*Bu-COMgX, see compound **9b**; using *t*Bu-COLi, see compounds **8**, **16**, **17a**, or **17b**; using *t*Bu-COK, see compound **9a**. All ^1H and ^{13}C NMR chemical shifts are referenced to internal Me_4Si.

1-(2′-Hydroxyadamant-2’-yl)-2,2-dimethylpropan-1-one (8) from 1, catalyzed by methyllithium: A catalytic amount of methyllithium (0.01 mL, 0.02 mmol) in Et_2O was added to an NMR tube containing the acyloin **1** (39 mg, 0.17 mmol) in THF (0.70 mL) and [D_{12}]cyclohexane (0.03 mL) at −70 °C. Adamantan-2-one (31 mg, 0.20 mmol) was added at ambient temperature and consumed the acyloin **1** and its Li alkoxides[11] **14** within 16 min, at which time the product started to crystallize from the THF solution. After vigorous shaking with Et_2O and water, the Et_2O layer was washed until neutral, dried over Na_2SO_4, filtered, and concentrated under 60 Torr to leave a solid mixture (75 mg) containing adamantan-2-one, the product **8**, and O=C*t*Bu$_2$ (**7**) in a 19:81:75 ratio together with some THF and a trace of Et_2O. The crude material from different runs was recrystallized first from methanol, then from hexane: Colorless needles, m.p. 134–135 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.29$ (sharp s, 9H; C*Me$_3$*), 1.60 (d, $^2J = 12.5$ Hz, 2H; two equiv protons of 2 CH_2 groups), 1.69 (unresolved, $^3J \approx 2.5$ Hz, 2H; 1′-/3′-H), 1.75 (partially hidden d, $^2J \approx 13$ Hz, ca. 2H; two equiv protons of 2 CH_2 groups), 1.77 (s, 1H; OH), 1.79 (m, $^3J \approx 2.5$ Hz, 2H; enantiotopic CH_2), 1.95 (d, $^2J = 12.5$ Hz, 2H; 2 equiv protons of 2 CH_2 groups), 2.20 (d, $^2J = 13$ Hz, 2H; 2 equiv protons of 2 CH_2 groups), 2.25 ppm (unresolved, 2H; 2 *tert*-CH); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 26.7$ and 26.8 (2 *tert*-CH), 29.3 (C*Me$_3$*), 32.8 (2 CH_2), 34.9 (2 CH_2+2 CH), 37.7 (1 CH_2), 45.2 (*C*Me$_3$), 83.0 ppm (C-2′); IR (KBr): $\tilde{\nu} = 3474$ (sharp O-H), 2916, 1683 (sharp C=O) cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{24}O_2$ (236.35): C 76.23, H 10.23; found: C 76.15, H 10.02.

1-Hydroxy-3,3-dimethyl-1,1-diphenylbutan-2-one (9a) from 1 with benzylpotassium: A dry NMR tube (5 mm) was kept under a blanket of streaming dry argon gas while being loaded with potassium *tert*-butoxide (45 mg, 0.40 mmol) and anhydrous toluene (0.12 mL, 1.1 mmol) and during the following operations. The tube was cooled to −70 °C, cyclopentane (0.30 mL) and then *n*-butyllithium (0.41 mmol) in hexanes (0.20 mL) were introduced without shaking, and the sealed tube was violently shaken at ambient temperature for 2.5 min. The red precipitate[34] was left settling at room temperature for one hour, whereafter the supernatant was withdrawn by syringe and discarded. Cyclopentane (0.5 mL) was injected into the tube, which was resealed and shaken briefly to whirl up the precipitate. Upon deposition for 10–20 min, the same washing procedure with cyclopentane was repeated three times. The red precipitate remaining after the last withdrawal was covered with anhydrous THF (0.50 mL) at −70 °C with subsequent extensive shaking of the sealed tube for complete dissolution at room temperature. This dark red solution of benzylpotassium[35] was titrated at −70 °C to decolorization by adding small batches of the acyloin **1** (total 71 mg, 0.31 mmol, 78 % yield of $PhCH_2K$), then diluted with further anhydrous THF (0.20 mL), [D_{12}]cyclohexane (0.030 mL), and a trace of TMS. A ^1H NMR spectrum taken after 40 min at 20 °C revealed the K alkoxide[11] **22** (0.23 mmol) with $\delta_H = 1.01$ and 1.32 ppm (18:9) and already some O=C*t*Bu$_2$ (0.081 mmol); the potassium salt of the enediolate **2** remained invisible. Benzophenone (23 mg, 0.13 mmol, 0.4 equiv) was added at −70 °C to give a green solution at 23 °C containing residual alkoxide **22** (0.11 mmol after 6 min, 0.10 mmol after 26 min). The golden colored, clear solution was treated with a second portion of benzophenone (33 mg, 0.18 mmol, 1.8 equiv) and remained dark green during the ^1H NMR measurement that confirmed the complete consumption of residual alkoxide **22** within 4 min at 23 °C. The product alkoxide showed strongly broadened ^1H NMR signals (and those of residual benzophenone were extremely broad) which sharpened on acidification with F_3C-CO_2H. After workup with Et_2O and NaOH (1 M) and drying the non-acidic fraction at 4 mbar for 19 h,[33] the crude product (82 mg) contained the adduct **9a** (0.24 mmol, 77 %), Ph_2C=O (0.07 mmol), and $PhCH_2$-CH(OH)-*t*Bu[11] (**26**, 0.03 mmol). The collected crude material from several runs was crystallized from boiling petroleum ether: Colorless needles, m.p. 108–109 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.23$ (s, 9H; C*Me$_3$*), 3.16 (s, OH), 7.27–7.34 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 27.6$ (q, C*Me$_3$*), 45.9 (s, *C*Me$_3$), 88.2 (s, COH), 127.6 and 128.2 (2 d, 4 *o*-C and 4 *m*-C), 127.8 (d, 2 *p*-C), 143.2 (s, 2 *i*-C), 215.0 ppm (s, C=O), assigned through HSQC and off-resonance {^1H} decoupling; IR (KBr): $\tilde{\nu} = 3491$ (sharp O-H), 1687 (C=O), 1447, 1061, 696 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{20}O_2$ (268.4): C 80.56, H 7.51; found: C 80.89, H 7.63.

4-Hydroxy-2,2,5,5-tetramethyl-4-phenylhexan-3-one (9b) from 1 with methylmagnesium chloride: Pivalophenone (0.040 mL, 0.24 mmol, prepared from benzonitrile with *t*BuLi in Et_2O, $\delta_H = 1.35$ ppm in $CDCl_3$, 1.307 ppm in THF) was added to an NMR tube containing the two Mg alkoxides[11] **5** (85:15, 0.12 mmol, prepared from **1** with H_3C-MgCl) in THF (0.6 mL) and [D_{12}]cyclohexane (0.030 mL). The sealed tube was heated at 60 °C for 2 h, but ^1H NMR signals of the product could be detected only after methanol (0.020 mL) had been added. The acidified mixture was dissolved in Et_2O and the Et_2O layer was extracted with NaOH (1 M), washed until neutral, dried over Na_2SO_4, concentrated in vacuo, and evacuated in a desiccator for 3 min to give the non-acidic product fraction containing **9b** and pivaloin[33] (**3**) in a 91:9 ratio. Pivaloin and residual pivalophenone vanished within 5 d in an evacuated desiccator, leaving crude **9b** which was crystallized twice from hexane: Transparent blocks (28 mg, 93 %), m.p. 104–105 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 1.02$ (s, 9H; 3×CH_3-6), 1.06 (s, 9H; 3×CH_3-1),[15] 2.54 (OH), 7.26 (tt, $^3J \approx 7$ Hz, $^4J = 1.5$ Hz, 1H; *p*-H), 7.31 (tm, $^3J \approx 7.5$ Hz, 2H; 2 *m*-H), 7.39 ppm (dm, $^3J \approx 7.5$ Hz, 2H; 2 *o*-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 26.23$ (qsept, $^1J = 125.8$ Hz, $^3J = 4.8$ Hz, 3×C-6), 27.80 (qsept, $^1J = 127.0$ Hz, $^3J = 4.9$ Hz, 3×C-1), 40.16 (oct, broad, $^2J \approx 3.4$ Hz, C-5), 46.13 (>oct, sharp, $^2J = 3.8$ Hz, C-2), 88.64 (unresolved, COH), 126.60 (dt, $^1J = 159.0$ Hz, $^3J = 6.7$ Hz, 2 *o*-C), 127.19 (dt, $^1J = 160.5$ Hz, $^3J = 7.4$ Hz, *p*-C), 127.43 (dd, $^1J = 159.5$ Hz, $^3J = 7.2$ Hz, 2 *m*-C), 138.23 (td, $^3J = 7$ Hz, $^3J = 3.6$ Hz to O*H*, *i*-C), 214.93 ppm (>oct, $^3J = 3.5$ Hz, C=O), assigned through HSQC and through HMBC with the ^3J interactions C=O↔1-C*H$_3$*↔C-1 and *C*-OH↔6-C*H$_3$*↔C-6 in addition to the ^2J correlations 1-C*H$_3$*↔C-2 and 6-C*H$_3$*↔C-5; IR (ATR on diamond): $\tilde{\nu} = 3537$ (sharp O-H), 2956, 2925, 2870, 1685 (C=O),[15] 1483, 1363, 1077, 729, 698 cm^{-1}; elemental analysis calcd (%) for $C_{16}H_{24}O_2$ (248.4): C 77.38, H 9.74; found: C 77.32, H 9.69.

4-Hydroxy-2,2,5-trimethyl-4-isopropylhexan-3-one (16) from 1 with *n*-butyllithium: A suspension of the acyloin **1** (228 mg, 1.00 mmol) in pentane (5 mL) was stirred at −40 °C during the addition of *n*BuLi (1.00 mmol) in hexane (0.41 mL). After 10 min, dry di-isopropyl ketone (0.151 mL, 1.10 mmol) was injected and the mixture was warmed up to room temperature, then diluted with water and shaken with pentane (50 mL). The pentane phase was washed with brine until neutral, dried over Na_2SO_4, and concentrated, affording **16** as the only product together with O=C*t*Bu$_2$ (**7**) and a rest of di-isopropyl ketone. M.p. 79–80 °C (twice from pentane); ^1H NMR (CCl_4, 80 MHz): $\delta = 0.87$ and 0.91 (2 d, $^3J = 6.8$ Hz, 12H; 4×5-CH_3), 1.21 (s, 9H; C*Me$_3$*), 1.63 (broad s, OH), 2.07 ppm (sept, $^3J = 6.8$ Hz, 2H; 2×5-H); ^{13}C NMR ($CDCl_3$, 20 MHz): $\delta = 17.6$ and 18.6 (4×5-CH_3), 28.1 (C*Me$_3$*), 35.5 (2×C-5), 45.5 (*C*Me$_3$), 89.4 (C-4), 219.2 ppm (C-3), assigned through off-resonance {^1H} decoupling; IR (KBr): $\tilde{\nu} = 3496$ (sharp O-H), 2968, 1676 (s, C=O), 1468, 1150, 1009 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{24}O_2$ (200.32): C 71.95, H 12.08; found: C 72.21, H 11.94.

1,1-Dicyclopropyl-1-hydroxy-3,3-dimethylbutan-2-one (17a) from 1 with methyllithium: A solution of the acyloin **1** (500 mg, 2.19 mmol) in anhydrous THF (3 mL) was stirred at −40 °C under dry argon gas and titrated with methyllithium (2.19 mmol) in Et_2O (1.46 mL). After 10 min, the generated Li alkoxides[11] **14** were treated with dicyclopropyl ketone (0.260 mL, 2.18 mmol) in THF (1 mL) and warmed up to room temperature. The mixture was diluted with water and shaken with Et_2O (3×10 mL). The combined Et_2O extracts were washed with water (3×5 mL), dried over Na_2SO_4, and concentrated to give a 1:1 mixture (680 mg) of **17a** and O=C*t*Bu$_2$ (**7**). Distillation at 40–60 °C (bath temp.)/0.022 Torr removed **7** at the expense of a diminishing yield (128 mg, 30 %) of **17a** as a colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 0.17$ and 0.68 (m, 4H; 2×2′-H and 2×3′-H, all trans to 1′-H), 0.25 and 0.42 (m, 4H; 2×cis-2’-H and 2×cis-3′-H), 1.27 (tt, 2H; 2×1′-H), 1.38 (s, 9H; C*Me$_3$*), 3.65 ppm (s, OH), δ values assigned through comparison with **17b** and in proportion to the following ^{1}H,^{1}H coupling constants as extracted by a crude computational simulation of the observed ^{1}H NMR multiplets (error limits ±0.5 Hz): ^{3}J(1′/cis-2′) ≈ ^{3}J(1′/cis-3′) = 8.3 Hz, ^{3}J(1′/trans-2′) ≈ ^{3}J(1′/trans-3′) = 5.3 Hz, ^{2}J(cis-2′/trans-2′) ≈ ^{2}J(cis-3′/trans-3′) = −4.3 Hz, ^{3}J(cis-2′/cis-3′) ≈ ^{3}J(trans-2’/trans-3′) = 9.4 Hz, ^{3}J(cis-2’/trans-3′) ≈ ^{3}J(cis-3′/trans-2′) = 6.4 Hz; ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = -0.30$ and 1.59 (2+2 × CH_2), 16.97 (2 × CH), 28.67 (C*Me*$_3$), 43.34 (*C*Me_3), 82.67 (COH), 217.48 ppm (C=O), assigned through comparison with **17b**; IR (film): $\tilde{\nu} = 3424$ (O-H), 3092 (w), 3009, 2973, 2873, 1678 (C=O), 1482, 1367, 1008 cm^{-1}; elemental analysis calcd (%) for $C_{12}H_{20}O_2$ (196.29): C 73.43, H 10.27; found: C 73.09, H 10.28.

1,1-Bis(1’-methylcyclopropyl)-1-hydroxy-3,3-dimethylbutan-2-one (17b) from 1 with methyllithium: The acyloin **1** (100 mg, 0.44 mmol) in anhydrous THF (2.2 mL) was stirred at −40 °C under dry argon gas during the dropwise addition of methyllithium in Et_2O till the sharp endpoint of CH_4 evolution (collected in a gas burette). After 10 min, bis(α-methylcyclopropyl) ketone[27] (73 mg, 0.53 mmol) was added by pipette and stirred for 5 min. The mixture was warmed up to room temperature, diluted with water and extracted with pentane (50 mL). The extract was washed with brine (3 × 15 mL), dried over Na_2SO_4, and concentrated to yield a mixture of O=C*t*Bu$_2$ (**7**), product **17b**, and pivaloin (**3**), but no acyloin **1**. Repeated crystallizations from petroleum ether furnished pure **17b**: M.p. 87–88 °C; ^{1}H NMR[43] ($CDCl_3$, 400 MHz): $\delta = 0.239$ and 0.245 (dm, 4H; BC spectral system with additional ^{2}J and ^{4}J, 2 × cis-2′-H and 2 × cis-3′-H relative to 1′-CH_3), 0.617 (dm, 2H; 2 × trans-2’-H), 0.904 (dm, 2H; 2 × trans-3′-H), 1.17 (m, 6H; 2 × 1′-CH_3), 1.22 (s, 9H; C*Me*$_3$), 1.63 (s, OH) ppm, with the ^{1}H,^{1}H coupling constants ^{4}J(1′-CH_3/trans-2′) = 0.719 Hz, ^{4}J(1′-CH_3/trans-3′) = 0.768 Hz, ^{2}J(cis-2’/trans-2’) = −4.463 Hz, ^{2}J(cis-3′/trans-3′) = −4.475 Hz, ^{3}J(cis-2’/cis-3′) = 9.350 Hz, ^{3}J(trans-2’/trans-3′) = 9.780 Hz, ^{3}J(cis-2’/trans-3′) = 5.853 Hz, ^{3}J(cis-3′/trans-2’) = 5.859 Hz; ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 10.79$ and 11.44 (2+2 × CH_2), 22.17 (2 × C-1′), 22.75 (2 × 1′-CH_3), 27.73 (C*Me*$_3$), 45.33 (*C*Me_3), 85.00 (COH), 216.02 ppm (C=O); IR (KBr): $\tilde{\nu} = 3555$ (sharp O-H), 3006, 1681 (C=O), 1485, 1381, 1101, 1083, 1022, 761 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{24}O_2$ (224.34): C 74.95, H 10.78; found: C 75.25, H 10.64.

Sterically Congested Molecules, Part 25. Part 24: Ref. [22].

Acknowledgements

Financial support of this project by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank the Chemistry Department of the LMU München for supporting the final stage of this work.

---

[1] D. Seyferth, R. M. Weinstein, R. C. Hui, W.-L. Wang, C. M. Archer, *J. Org. Chem.* **1992**, *57*, 5620–5629.

[2] For a survey of the literature for the years 1973–1990, see Ref. [1].

[3] For the earlier literature beginning in 1919, see: a) M. Schlosser, *Angew. Chem.* **1964**, *76*, 124–143, on p.138; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 287–306; b) C. Hilf, F. Bosold, K. Harms, J. C. W. Lohrenz, M. Marsch, M. Schiemeczek, G. Boche, *Chem. Ber./Recueil* **1997**, *130*, 1201–1212.

[4] N. S. Nudelman, F. Doctorovich, *Tetrahedron* **1994**, *50*, 4651–4666, and refs. cited therein.

[5] T. Hiiro, Y. Morita, T. Inoue, N. Kambe, A. Ogawa, I. Ryu, N. Sonoda, *J. Am. Chem. Soc.* **1990**, *112*, 455–457.

[6] C. S. Shiner, A. H. Berks, A. M. Fisher, *J. Am. Chem. Soc.* **1988**, *110*, 957–958.

[7] Detailed experimental evidence of the structures of these largely ionic intermediates is not known, but impressions of the structural possibilities may be gathered from the following refs: a) E. Kaufmann, P. von R. Schleyer, S. Gronert, A. Streitwieser, M. Halpern, *J. Am. Chem. Soc.* **1987**, *109*, 2553–2559; b) M. Tacke, *Chem. Ber.* **1995**, *128*, 1051–1053; c) K. Ohno, S. Maeda, *J. Phys. Chem. A* **2006**, *110*, 8933–8941.

[8] G. F. Hennion, C. F. Raley, *J. Am. Chem. Soc.* **1948**, *70*, 865–866.

[9] G. J. Abruscato, T. T. Tidwell, *J. Org. Chem.* **1972**, *37*, 4151–4156, compound **19** therein.

[10] G. Böhrer, R. Knorr, P. Böhrer, B. Schubert, *Liebigs Ann.* **1997**, 193–202, compound **19** therein.

[11] See the Supporting Information.

[12] M. S. Newman, A. Arkell, T. Fukunaga, *J. Am. Chem. Soc.* **1960**, *82*, 2498–2501.

[13] a) ^{1}H NMR: A. Furuhata, M. Hirano, I. Fujimoto, M. Matsui, *Agricultural Biol. Chem.* **1987**, *51*, 1633–1640, compound **28** therein; b) ^{13}C NMR: A. Ejchart, *Org. Magn. Reson.* **1977**, *9*, 351–354.

[14] The $t_{1/2}$ values were based on initial 0.2–0.5 M NMR concentrations of the reacting compounds. More precise rate measurements could not be achieved because of the intricate kinetic properties of the present systems.

[15] ^{1}H NMR and IR data of the chiral component **9b** are equal to those reported for a “recrystallized” substance to which the achiral constitution Ph-C(=O)-C(-OH)*t*Bu$_2$ had been assigned by D. Seyferth, R. C. Hui, W.-L. Wang, *J. Org. Chem.* **1993**, *58*, 5843–5845, on p.5845.

[16] “&” symbolizes a not yet established type of bonding between *t*BuCOM and O=C*t*Bu$_2$ (**7**), perhaps a coordinative bond or an electrostatic attraction between the oxygen atom of **7** and the metal cation.

[17] The possibility of an accumulation of NMR-silent intermediates (in analogy with the NMR-inactive enediolate **2**) was dismissed through the in situ observation of an always constant sum of the concentrations of starting alkoxides and the product O=C*t*Bu$_2$.

[18] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, G. C. Robinson, *J. Am. Chem. Soc.* **1956**, *78*, 328–335.

[19] The kinetic system **5**→**6**&**7**→**6**<**M**+ >**7**→**2** as implied in Scheme 2 is similar to the S_N1 ionization sequence analyzed in Ref. [18]: “External return” of a foreign component may occur by unification of the free components or by a ligand exchange reaction at the complex **6**&**7**.

[20] See Ref. [22] for the preparation and deuterium analysis of [D_9]**7**.

[21] See Ref. [22] for the deuterium analyses by ^{1}H and ^{13}C NMR of the products presented here.

[22] R. Knorr, D. S. Stephenson, *Chem. Eur. J.* **2012**, DOI:10.1002/chem.201102865, accompanying paper.

[23] Similar fairly fast *t*Bu migrations preclude extensions of the present cleavage method to the generation of other acylmetals.

[24] Named in analogy with the common-ion rate depression shown in Ref. [18].

[25] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, N. A. Taher, *J. Chem. Soc.* **1940**, 979–1011.

[26] See Tables IV and V of Ref. [18] for the observation that steady rate constants were obtained only after ca. 40 % conversion.

[27] G. Böhrer, R. Knorr, P. Böhrer, *Chem. Ber.* **1990**, *123*, 2161–2166.

[28] This partitioning factor derives from the quotient of (overall decay rate) = (fission × dimerization/return) rates, divided by the rate of the fission step.

[29] H. Ahlbrecht, G. Schneider, *Tetrahedron* **1986**, *42*, 4729–4741.

[30] R. R. Fraser, T. S. Mansour, S. Savard, *J. Org. Chem.* **1985**, *50*, 3232–3254.

[31] H. Hoberg, V. Götz, A. Milchereit, *J. Organomet. Chem.* **1976**, *118*, C6-C7.

[32] For NMR data, see the Supporting Information of: M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. A. Procopiou, *Org. Lett.* **2007**, *9*, 331–333.

[33] Yields of isolated pivaloin (**3**) are sometimes low (< $^{1}/_{2}$ of **7**) because of losses through volatility in vacuo and/or perceptible solubility in water.

[34] a) L. Lochmann, J. Pospišil, D. Lím, *Tetrahedron Lett.* **1966**, *7*, 257–262; b) M. Schlosser, *J. Organomet. Chem.* **1967**, *8*, 9–16; c) compare: M. Schlosser, *Organometallics in Synthesis* 2nd ed., Wiley, Chichester, **2002**, p. 273.

[35] ^{1}H NMR in THF at −30 °C: G. Vanermen, S. Toppet, M. van Beylen, P. Geerlings, *J. Chem. Soc. Perkin Trans. 2* **1986**, 699–705, Table 4 therein.

[36] a) ^{1}H NMR and conformation: O. Takahashi, K. Saito, Y. Kohno, H. Suezawa, S. Ishihara, M. Nishio, *Eur. J. Org. Chem.* **2004**, 2398–2403; b) ^{13}C and ^{1}H NMR: S. Zushi, Y. Kodama, Y. Fukuda, K. Nishihata, M. Nishio, M. Hirota, J. Uzawa, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2113–2119.

[37] a) J. S. Lomas, S. Briand, D. Fain, *J. Org. Chem.* **1991**, *56*, 166–175, compound **3e** therein; b) Deviating data: M. Sasaki, J. Collin, H. B. Kagan, *New J. Chem.* **1992**, *16*, 89–94, compound **5** therein.

[38] pK_a = 40.7 for $PhCH_2K$ in equilibrium with toluene in THF at −78 °C according to p. 4739 of Ref. [29]

[39] G. Mendenhall, H. T. Chen, US Patent 4595784, Chem. Abstr., **1986**, *105*, P82043q.

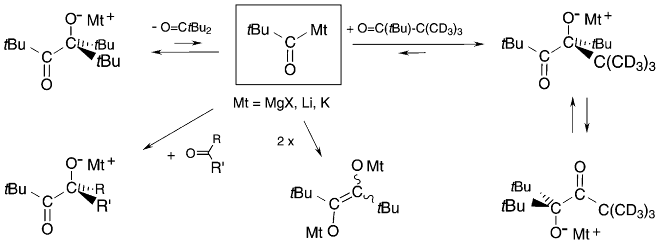
[40] H. Schuh, E. J. Hamilton, H. Paul, H. Fischer, *Helv. Chim. Acta* **1974**, *57*, 2011–2024.

[41] Y. P. Tsentalovich, H. Fischer, *J. Chem. Soc. Perkin Trans. 2* **1994**, 729–733, Table 2 therein.

[42] For comparison, benzoyllithium (Ph-COLi) was reported[5] as being short-lived even at −105 °C.

[43] We thank Dr. David S. Stephenson for the computational ^{1}H NMR simulation for **17b** with his program DAVINX.

Received: September 13, 2011
Revised: December 1, 2011



NMR-invisible intermediates pivaloylmagnesium, -lithium, or -potassium, have been generated through the novel, reversible heterolytic C–C bond cleavage of the overcrowded alkoxides of the parent tri-*tert*-butyl acyloin. Their interception by protonation or by ketones reveals that a common initial fission step limits the overall rate (see scheme).

Reactive Intermediates

R. Knorr, G. Böhrer, B. Schubert, P. Böhrer* .... ▮▮▮▮–▮▮▮▮

Pivaloylmetals (*t*Bu-COM: M = Li, MgX, K) as Equilibrium Components