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Oxidative radical cyclizations of malonate enolates induced by the ferrocenium ion – a remarkable influence of enolate counterion and additives

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To generalize oxidative radical cyclizations of malonate enolates induced by recyclable single electron transfer (SET) oxidant ferrocenium hexafluorophosphate **1**, the reactivity of a series of enolates **3** that differ only in their counterions was studied. Only lithium enolates were oxidized by **1**, irrespective of their generation method. The presence of amines in stoichiometric or substoichiometric amounts is necessary for SET oxidation–bicyclization of Na, K, Mg, Zn, Si, or Ti enolates **3**. The nucleophilicity of **3**, the amine, and the presence of halide ions determine the bicyclization yield of lactone **7**.

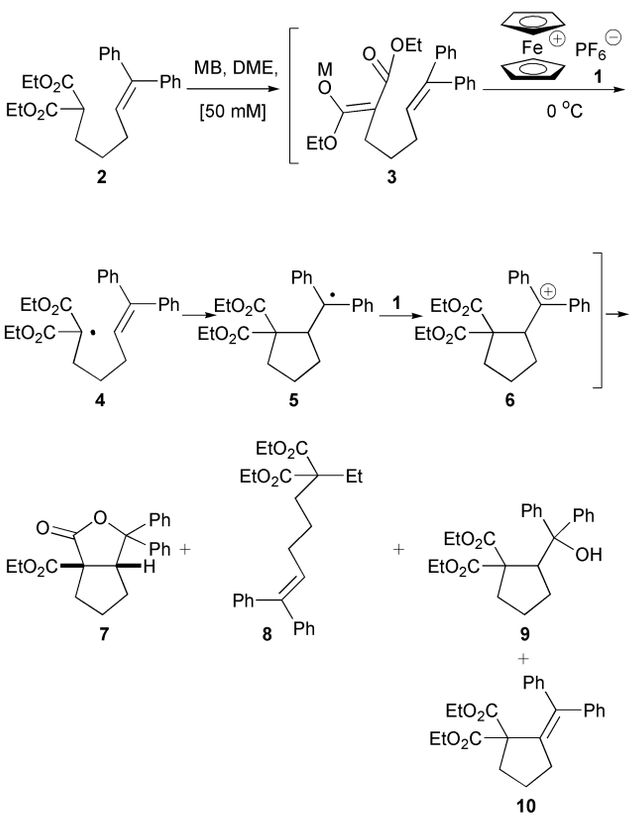
Introduction

The reactivity of carbanionic intermediates is critically dependent on the metal ion used. In particular, the reactivity of enolates is modulated by the counterion as manifested in aldol additions,[1] conjugate additions[2] or enolate alkylations.[3] Another well-known synthetic application of enolates is their SET oxidation–dimerization to 1,4-dicarbonyl compounds. Most commonly, lithium enolates were applied with different oxidants such as $FeCl_3$, Cu(II) salts or I_2;[4] other metal ions, such as Na,[5] K,[4a,d,j,k] Si,[6] Ti,[7] or Sn[8] were less frequently used. Apart from dimerization reactions, the potential of enolates as precursors for radical or radical cation reactions has been explored much less. Schmittel *et al*. studied the reactivity of dimesitylmethyl ketone enolates in cyclizations to benzofurans.[9] Kende[10] and Whiting[11] reported radical cyclizations of equilibrium-generated enolates onto phenolates induced by $K_3[Fe(CN)_6]$; however, these cyclizations are limited to the most acidic carbonyl precursors such as 1,3-diketones or nitro compounds. Deprotonated nitro compounds can be oxidatively cyclized by CAN.[6d,12] Some cyclizations of silyl enol ethers as covalent enolate equivalents, occurring in the radical cation or radical cyclization mode,[13] have been reported; these were induced by photoelectron transfer (PET) oxidation with dicyanoanthracene (DCA) or dicyanonaphthalene (DCN) that give only moderate yields of cyclized products,[14] by anodic oxidation[15] or by oxidants.[6b,c,16]

Our interest in enolate oxidation was fueled by the idea of combining the often complementary reactivities of intermediates of different oxidation states such as enolates, radicals and carbocations in reaction sequences [eqn. (1)].

$$M \longrightarrow [R^{1-} \longrightarrow R^{2-} \longrightarrow R^{3\bullet} \longrightarrow R^{4\bullet} \longrightarrow R^{5+} \longrightarrow R^{6+}] \longrightarrow P \quad (1)$$

In these reaction sequences, intermediates are umpoled (nucleophilic enolates R^{2-} to electrophilic α-carbonyl radicals $R^{3\bullet}$ or nucleophilic alkyl radicals $R^{4\bullet}$ to electrophilic carbenium ions R^{5+}) thus offering a solution to reactivity limitations of these constitutionally identical but electronically different intermediates. Recently, we discovered that ferrocenium hexafluorophosphate **1** is a very convenient reagent for the predictable SET oxidation of lithium enolates and certain radicals. From these studies, it became clear that enolates are very useful precursors for radical cyclizations[17] and radical combinations[18] (Scheme 1). Based on these results, we were then able to develop oxidative tandem processes that combine anionic and radical reactions.[19] Thus, the inherent limitations of oxidative radical reactions of neutral carbonyl compounds, mediated by $Mn(OAc)_3$[20] and CAN[21] which are most efficient for 1,3-dicarbonyl compounds, can now be overcome since our method allows oxidative reactions of all acidic carbonyl substrates such as esters, nitriles, ketones, *etc*.[22] However, to develop this field further it is of critical importance to test the general applicability of metal enolates or their covalent equivalents in SET oxidations by **1** since the efficiency of many anionic processes is determined by the metal counter ion. In this report, results of a first systematic study on the overall oxidative bicyclization efficiency of malonate enolates **3** by **1** are presented (Scheme 1). We address the remarkable influence of the metal counterion



Scheme 1

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Table 1 Oxidative cyclizations of metal 2-(5,5-diphenylpent-4-enyl)malonate enolates **3**

Entry	MB (equiv.)	**1** (equiv.)	**2** (%)	**7** (%)	**8** (%)	**9** (%)	**10** (%)
1	LDA (1.3)[a]	2.5	—	64	12	—	—
2	LiHMDS (1.1)[a]	2.4	—	57	6	—	—
3	BuLi (1.0)	3.0	13	54	—	—	—
4	NaH (2.8)	2.5	60	Trace	—	—	—
5	*t*-BuMgCl (1.3)[b]	2.2	24	52	—	—	10
6	BuLi–$ZnCl_2$ (1.3, 2)	1.5	63	26	—	3	—
7	NaH–TMSCl (1.4, 1.5)	2.9	92	—	—	—	—
8	NaH–ClTi(O*i*-Pr)$_3$ (1.4, 1.5)	2.6	90	—	—	—	—

[a] Compare ref. 17. [b] In the presence of 1.7 equivalents of HMPA to solubilize *t*-BuMgCl.

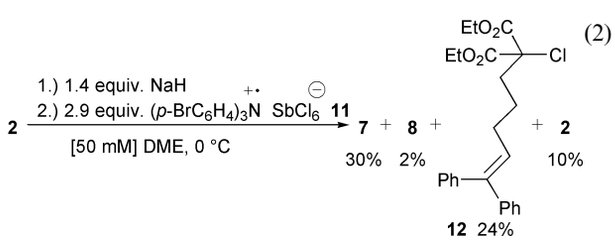
and amines on the oxidizability of the enolates **3** to α-carbonyl radical **4**. While radical 5-*exo* cyclization **4** ⟶ **5** and radical oxidation **5** ⟶ **6** are apparently not influenced by the reaction conditions, we show that stabilization of **6** to the final products **7**–**10** is again dependent on the properties of **3** and the presence of amines and halides.

Results and discussion

In our initial report on the oxidative cyclizations of **3**,[17] we employed LDA or LiHMDS as bases for deprotonation of malonate **2**[23] in DME and isolated 64% or 57%, respectively, of bicyclic lactone **7** accompanied by minor amounts of 2-ethylmalonate **8** (Table 1, entries 1,2). To gain more insight into this oxidative cyclization, we applied other common bases for malonate deprotonation followed by oxidative cyclization induced by **1**. While oxidative cyclization after deprotonation with *n*-BuLi provided an almost identical result as that obtained with amide bases (Table 1 entry 3), application of **3Na**, generated by standard treatment of **2** with NaH under otherwise identical reaction conditions, surprisingly failed completely (Table 1 entry 4). Only 60% of starting material **2** was recovered. *t*-BuMgCl as base precipitated in DME and deprotonation of **2** did not occur. To solubilize the Grignard reagent, 1.7 equivalents of HMPA had to be added prior to addition of **2**. Oxidative cyclization of **3Mg** thus generated induced by **1** provided 52% yield of **7** and a considerable 10% of **10** (Table 1 entry 5). Oxidative cyclization of the zinc enolate **3Zn**, generated by BuLi deprotonation–Li–Zn transmetalation, was not very effective, affording besides 63% recovered **2** only 26% of **7** and traces of alcohol **9** (entry 6). Oxidative cyclizations of covalent enolate equivalents, such as the silyl ketene acetal **3Si** or the titanium enolate **3Ti**, generated by deprotonation with NaH–Na–Si or Na–Ti transmetalation, were investigated for comparison, but both enolates did not cyclize after treatment with **1** (>90% recovery of **2**, entries 7, 8).

These rather surprising failures of all enolates other than **3Li** or **3Mg** to undergo oxidative cyclization induced by **1** necessitated a closer inspection of the influence of additives on the overall transformation **2** ⟶ **7**. The most promising candidates to influence the oxidative cyclizations were the amines generated during deprotonation of **2**.

This proved to be the case. In the presence of amines, all compounds **3** undergo oxidative cyclizations induced by **1** (Table 2). After deprotonation of **2** with NaHMDS instead of NaH, a smooth cyclization of **3Na** occurred to give 52% of **7** and 22% of **8** (Table 2 entry 1). More convincingly, oxidative cyclizations of **3Na**, generated by deprotonation with NaH under identical conditions as described above (compare Table 1, entry 4), proved to be effective when an amine was added immediately prior to oxidative cyclization by **1** (Table 2 entries 2–5). Diisopropylamine served well as an additive when applied in stoichiometric amounts (Table 2 entry 2) or even in a sub-stoichiometric amount of 0.5 equivalents (entry 3) providing identical yields of **7** but increasing amounts of **8**. When the amount of *i*-Pr_2NH was further reduced to 0.25 equivalents, the yield of **7** dropped to 45% while 13% of **8** and 29% of **2** were isolated. Even tertiary amines such as Hünig's base or the essentially non-basic tris(*p*-bromophenyl)amine proved to be equally useful for the induction of oxidative cyclizations of **3Na** (Table 2 entries 4,5). Similar yields and product distributions of **7**–**10** were also observed when **3K** was cyclized with **1** (Table 2 entry 6). Better yields of **7** were achieved when *i*-Pr_2NMgCl was used instead of *t*-BuMgCl although 10% of **9** was formed in addition to a 13% yield of alkene **10** (Table 2 entry 7, compare Table 1, entry 5). The amine effect is also clearly seen in the cyclization of the zinc enolate **3Zn** when *i*-Pr_2NH was present, giving **7** in the highest yield of 83% of all systems studied (Table 2 entry 8). Finally, in the presence of *i*-Pr_2NH even **3Si** and **3Ti** underwent a slow cyclization to yield **7** in moderate yield after 18 hours (Table 2 entries 9, 10). We were, however, not able to drive the reaction to completion even by increasing the amounts of amine to 2 equiv., that of **1** to 4 equiv. and extending the reaction times. Application of LDA as the base and quenching the lithium enolate **3Li** with TMSCl prior to SET oxidation facilitated the cyclization somewhat compared to NaH, but the product distribution remained very similar. To gain further insight into the role of amines in the oxidative cyclizations of **3**, we performed an experiment in which the not directly oxidizable enolate **3Na** obtained from deprotonation of **2** with NaH was treated with the stable SET oxidant tris(*p*-bromophenyl)aminium hexachloroantimonate **11**[24] [eqn. (2)]. Lactone **7** was formed as the major product in 30% yield.



(2)

In addition, an inseparable mixture of 24% of chloromalonate **12**, 2% of **8** and 10% of **2** was isolated, showing clearly that **3Na** was oxidized by stable aminium salt **11**.

To investigate the issue of conversion for **3Si**, the sodium enolate and silyl ketene acetal generation was followed by NMR spectroscopy in THF-D_8. While the sodium enolate **3Na** was formed quantitatively from **2** and NaH, addition of carefully dried TMSCl to the sodium enolate solution under inert conditions led reproducibly (triple run) to a 57 : 43 mixture of starting **2** and **3Si** as a 1 : 1 *E*/*Z*-mixture after 90 min according to ^1H and ^{13}C NMR spectroscopy. **3Si** then remained stable for at least 12 hours as indicated by the ^1H NMR spectra. To simulate the oxidative cyclization conditions more closely, we added 1.0 equivalents of dried *i*-$Pr_2NH{\cdot}HCl$ to the THF-D_8 solution of **3Si**, since we speculated that amine hydrochloride might contribute to the recovery of **2**. Indeed, a slow conversion of **3Si** back to **2** was observed. The ratio of **2**/**3Si** amounted to 70 : 30 after 12 h and the conversion to **2** was complete after 48 h. On the other hand, the reverse reaction – the conversion

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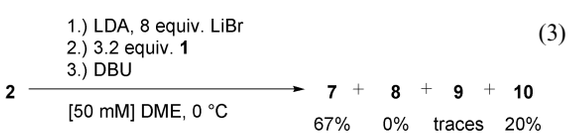
Table 2 Oxidative cyclizations of enolates **3** in the presence of amines

Entry	MB (equiv.)	Additive (equiv.)	**1** (equiv.)	**2** (%)	**7** (%)	**8** (%)	**9** (%)	**10** (%)
1	NaHMDS (1.4)	—	2.5	Trace	52	22	—	—
2	NaH (1.4)	*i*-Pr_2NH (1.4)	2.4	—	54	19	—	—
3	NaH (1.4)	*i*-Pr_2NH (0.5)	2.5	13	54	28	—	—
4	NaH (1.4)	*i*-Pr_2NEt (1.4)	4.0	6	54	36	—	—
5	NaH (1.4)	$(p\text{-BrPh})_3N$ (1.4)	2.5	5	50	28	—	—
6	KHMDS (1.4)	—	2.5	2	52	11	5	2
7	*i*-Pr_2NMgCl (1.3)	HMPA (1.7)	2.7	7	65	—	10	13
8	LDA–$ZnCl_2$ (1.3, 2)	—	2.9	3	83	2	—	—
9	NaH–TMSCl (1.4, 1.5)	*i*-Pr_2NH (1.0)	2.9	32	48	—	—	16
10	NaH–ClTi(O*i*-Pr)$_3$ (1.4, 1.5)	*i*-Pr_2NH (1.0)	2.6	56	37	—	trace	—

of **2** to **3Si** – with TMSCl–Hünig's base or diisopropylamine with or without added DMAP did not proceed at all in 24 hours.

Moreover, the formation of compound **10** was puzzling, since it was not observed in cyclizations of alkali enolates (Table 1, entries 1–3, Table 2, entries 1–5), but forms in almost all cyclization experiments where chloride ions were involved during generation of **3** (Table 1, entry 5, Table 2, entries 7, 9). To test the influence of halide ions, the oxidative cyclization of **3Li** generated by deprotonation with LDA was performed in the presence of 8 equivalents of anhydrous LiBr, † followed by addition of DBU prior to workup [eqn. (3)]. Lactone **7** was isolated



(3)

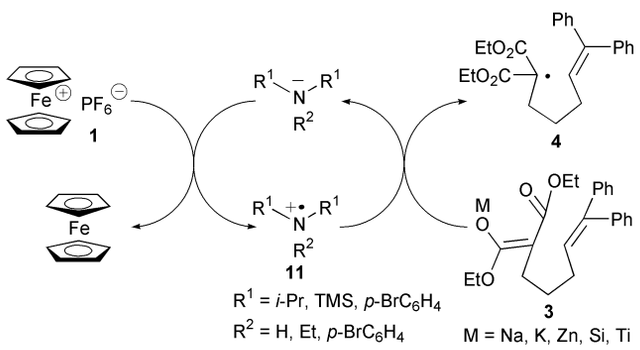
in 67% yield, comparable to the experiment in the absence of LiBr (entry 1), but significantly, no **8** was isolated and **10** was formed instead in 20% yield!

The structures of **7**–**9** and **12** were assigned on the basis of their NMR spectra. The structure of minor product **10** could be confirmed by a X-ray crystal structure analysis, which could unfortunately not be completely refined because of disorder.

Significant trends for the application of enolates as radical reaction precursors emerge from these results.

Enolate oxidation

Enolate **3Li** is the only anion oxidized smoothly by **1** irrespective of the presence or absence of an amine (Table 1, entries 1–3). ‡ All other compounds **3** are oxidized slowly (M = Zn) or not at all in the absence of amine (M = Na, Si, Ti). For **3Mg**, the situation can currently not be decided with certainty since the presence of HMPA might influence the oxidation course even in the absence of amine. The results are a clear demonstration that the SET oxidation rate is strongly dependent on the enolate counterion under identical experimental conditions. However, in the presence of the secondary amines *i*-Pr_2NH, HMDS or tertiary amines, such as Hünig's base or $(p\text{-BrPh})_3N$ the SET oxidation of **3** is strongly accelerated, although it remains rather slow for covalent **3Si** or **3Ti**. This amine effect is unprecedented in enolate oxidation and must probably be ascribed to the action of the amine as the actual SET oxidant (Scheme 2). Thus, initial SET oxidation of the amine by **1** gives an aminium radical cation **11**, which abstracts the electron from enolate **3** to give malonyl radical **4** and re-forms the amine. This pathway is supported by the following facts: 1) stable aminium salt **11** promoted SET oxidation of **3Na** [eqn. (2)] followed by cyclization. However, ligand transfer from the hexachloroantimonate anion of **11** to **4** competes effectively with radical



Scheme 2

cyclization giving **12**, thus limiting the applicability of this oxidant. 2) Substoichiometric amounts of the amine suffice to promote the oxidative cyclization in comparable yield (Table 2, entry 3 *vs.* entry 2).

A similar aminium radical cation-catalyzed process was proposed very recently for the epoxidation of alkenes.[25] Although rate constants for the SET oxidation of amines by **1** are unknown to the best of our knowledge, § they should be reasonably fast, since Nelsen *et al*. showed that hydrazines are oxidized by **1** with rate constants ranging from 1.4×10^4–8.1×10^5 M^{-1} s^{-1}.[26] An alternative amine coordination to the metal, leading to a modification of **3** easier to oxidize, seems to be less likely, since at least $(p\text{-BrPh})_3N$ exhibits only low basicity/nucleophilicity. Moreover, Collum and coworkers showed recently that diisopropylamine coordination can not compete with diethyl ether solvent coordination to the lithium ion of enolates.[27]

The reactivity of covalent **3Si** is different from that of the ionic enolates. In oxidative cyclizations to **7**, considerable amounts of starting **2** were always recovered (Table 2, entry 9). This may be due to an unidentified proton transfer reaction, as seen in the NMR experiments (*vide supra*), prior to SET oxidation of **3Si** by **1**, but we do not believe this to be the major reason,[28] since the cyclization yields of **3Si** to **7** and **10** in the preparative experiments in DME were consistently higher than the amount of **3Si** formed in the NMR experiments (64% *vs.* 43%). More significantly, because of the higher oxidation potential of the silyl ketene acetal compared to the ionic enolates, oxidation of **3Si** is much slower. ¶ In the last step of the sequence, **6** will most probably be fragmented to **7** and *i*-$Pr_2NH_2PF_6$ (Scheme 3), which should irreversibly desilylate **3Si** to **2** in competition to SET oxidation in analogy to *i*-Pr_2NH·HCl in the NMR experiments. The same arguments should hold for the cyclization of the titanium enolate.

† Lithium chloride as chloride source was not useful due to its very poor solubility in DME.

‡ The lithium methylmalonate enolate has an oxidation potential of +0.03 V *vs.* the Fc/Fc^+ redox couple as determined by cyclic voltammetry (ref. 29).

§ In one study, it was established that **1** undergoes fast reduction to ferrocene in the presence of amines (ref. 30).

¶ Oxidation potentials of simple silyl ketene acetals vary between +0.83 and +1.3 V *vs.* SCE. Although not known exactly, the oxidation potential of **3Si** is expected to be found at the upper limit of this range. Known electron transfer rate constants between simple silyl ketene acetals and **1** support the very slow oxidation of **3Si** by **1** (ref. 31).

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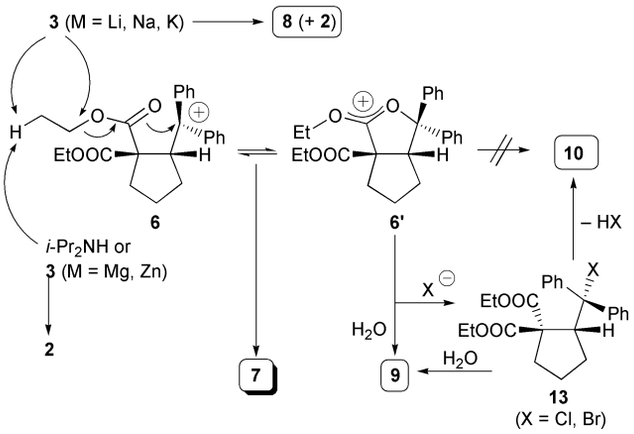

Scheme 3

Stabilization of 6 to 7–10

The product distribution in the oxidative cyclizations is also dependent on the enolate properties (Scheme 3). Apparently, SET oxidation of **3** to **4** is slower than radical cyclization **4** ⟶ **5**–SET oxidation **5** ⟶ **6**, thus **3** is still present when **6** is formed. Two opportunities for the deethylation of **6** to **7** can be envisaged. The more nucleophilic alkali enolates of **3** (M = Li, Na, K) in part deethylate **6** or its bicyclic congener **6′** forming 2-ethylmalonate **8** in addition to **7**, and are bases leading to some starting malonate **2** and ethylene. The less nucleophilic magnesium or zinc enolates **3** cannot undergo alkylation by **6** and consequently do not form **8**. Therefore, stabilization of **6** must occur by β-deprotonation at the ethyl group. The actual base for deprotonation of **6** to **7** can be either **3** (Table 1, entries 5, 6) or if present *i*-Pr_2NH, since almost no **2** was recovered in these cyclization reactions and the yields were the highest of the series (Table 2, entries 7, 8). Thus, enolates of intermediate nucleophilicities/basicities should be best suited to promote reaction sequences involving carbenium ions.

It must be emphasized that product distribution is also governed by halide ions. In the absence of halides, stabilization of **6** occurs by lactonization to **7** and not by deprotonation of **6** to **10**. For the formation of **10**, halide ions should trap **6**, forming activated diphenylmethyl halides **13** from which alkene **10** can be formed easily *via* dehydrohalogenation under the basic reaction conditions while the small amounts of alcohol **9** may result from solvolysis of **13** during workup.

In conclusion, we have shown that most ionic malonate enolates **3** are oxidized easily by the ferrocenium ion **1**, provided a secondary or tertiary amine is present as the actual SET oxidant. Covalent enolate equivalents represented by the silyl ketene acetal or a titanium enolate are only slowly oxidized by **1** even in the presence of amines. The final product distribution is determined by the nucleophilicity/basicity of the enolate and the presence of amines or halide ions in the reaction mixtures. Enolates of moderate nucleophilicity/basicity provide the best yields of bicyclic lactone **7** while halides compete for carbenium ion **6** leading to alkene **10**.

Experimental

General

All reactions were conducted in flame dried glassware under a nitrogen atmosphere. DME, HMPA, diisopropylamine and hexamethyldisilazane were dried with standard methods. LiBr and $ZnCl_2$ were dried in vacuum (160 °C, 0.8 mbar) for 8 h. TLC plates POLYGRAM SIL G/UV_{254} (Macherey-Nagel) were used for monitoring reactions. Chromatographic separations were performed on silica gel 60 (Fluka, 230–400 mesh) with *n*-hexane–ethyl acetate as eluent in the given ratio. Melting points are uncorrected. IR spectra were taken on a Nicolet DX-320 FT-IR spectrometer. UV–VIS spectra were taken in CH_3CN, on a Hewlett Packard 8452 diode array spectrometer. NMR spectra were, unless otherwise noted, recorded in $CDCl_3$ with reference to Me_4Si for ^1H spectra and $CDCl_3$ for ^{13}C spectra on Bruker DRX 400 or AC 200 spectrometers. The coupling constants are given in Hz. EI-mass spectra were recorded on Finnigan MAT 8430 or MAT 8400 spectrometers at 70 eV. Combustion analyses were performed at the Microanalytical Laboratories of the Technical University of Braunschweig.

Deprotonation of 2 with amide bases or BuLi–oxidative cyclization (general procedure)

At −78 °C, 250 mg (0.657 mmol) of **2** was added to a solution of the lithium, sodium or potassium amide or BuLi (1.6 M in *n*-hexane) in 13 ml dry DME (for the amount of base, see Table 1, entries 1–3; Table 2, entries 1,6). The solution was stirred for 30 min between −78 and −60 °C. Solid **1** was added in portions at 0 °C until a blue–green color of the reaction mixture persisted for 30 min. The mixture was stirred at 0 °C for 2 h. The mixture was quenched with four drops of a saturated NH_4Cl solution and warmed to room temperature. The reaction mixture was diluted with 20 ml diethyl ether and filtered through a pad of silica gel. The solvent was evaporated and the inhomogeneous residue was preadsorbed on silica gel. Crude flash chromatography (50 : 1 gradient to 10 : 1) gave >90% ferrocene followed by **8**, **9**, **10**, **2** and **7**, respectively. The individual compounds were further purified by flash chromatography as indicated in the characterization section.

Deprotonation of 2 with NaH

At 0 °C, 250 mg (0.657 mmol) of **2** was added to a suspension of NaH (80% in mineral oil) in 13 ml dry DME. After stirring the solution for 30 min at 0 °C, *i*-Pr_2NH, *i*-Pr_2NEt or $(p\text{-}BrPh)_3N$ was added (for the amount of NaH, and amine, see Table 2, entries 2–5). After stirring for another 60 min at 0 °C, **1** was added and workup was conducted according to the general procedure.

Deprotonation of 2 with magnesium bases

At 0 °C, 250 mg (0.657 mmol) of **2** was added to a solution of 0.427 ml (0.854 mmol) *t*-BuMgCl (2 M in diethyl ether) or *i*-Pr_2NMgCl (prepared by addition of 0.120 ml (0.854 mmol) *i*-Pr_2NH to a solution of 0.427 ml (0.854 mmol) *t*-BuMgCl) in 0.2 ml HMPA and 13 ml DME at 0 °C. The solution was stirred for 60 min at 0 °C. Addition of **1** and workup were conducted according to the general procedure.

Transmetalation of 3Li with $ZnCl_2$

At −78 °C, 250 mg (0.657 mmol) of **2** was added to a solution of 0.854 mmol LDA or BuLi in 4 ml dry DME and the resulting solution was stirred for 30 min between −78 and 0 °C. This solution was transferred *via* syringe to a suspension of 180 mg (1.321 mmol) anhydrous $ZnCl_2$ in 9 ml dry DME and stirred for 40 min at room temperature. Addition of **1** and workup were conducted at 0 °C according to the general procedure.

Oxidative cyclization of 3Si

At 0 °C, 250 mg (0.657 mmol) of **2** was added to 28 mg (0.920 mmol) NaH (80% in mineral oil) in 13 ml dry DME. After stirring for 45 min at 0 °C, 0.125 ml (0.986 mmol) TMSCl was added (colorless precipitate of NaCl) and the mixture was stirred at room temperature for 60 min. *i*-Pr_2NH (0.092 ml, 0.657 mmol) was added and the solution was stirred for 5 min before addition of 631 mg (1.9 mmol) **1** in one portion at room temperature. The blue–green inhomogeneous reaction mixture was stirred at room temperature for 18 h and worked up according to the general procedure.

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Reaction of 3Si with *i*-Pr_2NH·HCl (procedure A)

In a NMR tube, 50 mg (0.131 mmol) of **2** was added to 6 mg (0.2 mmol) NaH (80% in mineral oil) in 1.3 ml dry THF-D_8 at room temperature. After shaking for 120 min at room temperature, ^1H and ^{13}C NMR spectra showed complete formation of **3Na**. On addition of 0.025 ml (0.197 mmol) TMSCl a colorless precipitate of NaCl was formed. The mixture was shaken at room temperature for 90 min, and the reaction mixture was analyzed by NMR spectroscopy. The reaction mixture consisted of a mixture of **3Si** (M = TMS, $E/Z \approx 1:1$) and **2** in a ratio of 43 : 57, which did not significantly change during 12 h at room temperature. Addition of 18 mg (0.131 mmol) *i*-Pr_2NH·HCl changed the **3Si**–**2** ratio to 30 : 70 during 12 h. After 48 h, conversion to **2** was complete.

Attempted generation of 3Si (procedure B)

In a NMR tube, 50 mg (0.131 mmol) of **2** in 1.3 ml dry $CDCl_3$ was mixed with 0.039 ml (0.223 mmol) *i*-Pr_2NEt and 0.025 ml (0.197 mmol) TMSCl at room temperature. NMR spectroscopic analysis of the reaction mixture after 90 min, 14 h and 24 h showed no conversion. Similarly, no conversion was observed in the presence of DMAP or Et_3N as the base.

3Na. δ_H(400 MHz, THF-D_8) 1.12 (6 H, t, *J* 7.0, OCH_2CH_3), 1.50 (2 H, quint, *J* 7.4, $CH_2CH_2CH_2$), 2.08 (2 H, q, *J* 7.4, $=CHCH_2$), 2.24 (2 H, t, *J* 7.3, $=CCH_2$), 3.90 (4 H, q, *J* 7.1, OCH_2), 6.17 (1 H, t, *J* 7.4, =CH) and 7.09–7.32 (10 H, m, *Ph*); δ_C(100 MHz, THF-D_8) 15.7 (q, OCH_2CH_3), 26.7 (t), 30.8 (t), 33.0 (t), 57.0 (t, OCH_2), 74.5 (s, $C=CO_2$), 127.1 (d, *Ph*), 127.3 (d, *Ph*), 128.1 (d, *Ph*), 128.6 (d, *Ph*), 128.7 (d, *Ph*), 130.9 (d, *Ph*), 132.9 (s, $=CO_2$), 141.4 (s, *Ph*), 141.7 (s, *Ph*), 144.5 (s, C=CH) and 172.2 (s, $-CO_2$).

(*E*/*Z*)-3Si. δ_H(400 MHz, THF-D_8) 0.23 (9 H, s, $SiCH_3$), 0.27 (9 H, s, $SiCH_3$), 1.13–1.26 (12 H, m, OCH_2CH_3), 1.54 (4 H, quint, *J* 7.6, $CH_2CH_2CH_2$), 2.05–2.28 (8 H, m, $CH_2CH_2CH_2$), 3.94–4.19 (8 H, m, OCH_2), 6.09 (2 H, t, *J* 7.4, =CH) and 7.13–7.37 (20 H, m, *Ph*); δ_C(100 MHz, THF-D_8) 0.22 (q, $SiCH_3$), 0.86 (q, $SiCH_3$), 14.7 (q, OCH_2CH_3), 15.0 (q, OCH_2CH_3), 15.1 (q, OCH_2CH_3), 26.2 (t), 27.8 (t), 30.37 (t), 30.41 (t), 30.5 (t), 31.1 (t), 59.5 (t, OCH_2), 61.0 (t, OCH_2), 90.2 (s, $C=CO_2$), 95.4 (s, $C=CO_2$), 127.28 (d, *Ph*), 127.30 (d, *Ph*), 127.5 (d, *Ph*), 127.6 (d, *Ph*), 127.88 (d, *Ph*), 127.91 (d, *Ph*), 128.6 (d, *Ph*), 128.78 (d, *Ph*), 128.81 (d, *Ph*), 129.6 (d, *Ph*), 130.7 (d, *Ph*), 141.29 (s), 141.34 (s), 142.4 (s), 142.6 (s), 143.0 (s), 143.9 (s), 162.7 (s, $-CO_2$) and 167.6 (s, $-CO_2$) (The two expected $C=CO_2$ resonances could not be observed with certainty.)

Oxidative cyclization of 3Ti

At 0 °C, 250 mg (0.657 mmol) of **2** was added to 28 mg (0.920 mmol) NaH (80% in mineral oil) in 13 ml dry DME. After stirring for 45 min at 0 °C, 0.986 ml (0.986 mmol) $(i\text{-PrO})_3TiCl$ (1 M in *n*-hexane) was added and the solution was stirred for an additional 60 min. *i*-Pr_2NH 0.092 ml (0.657 mmol) was added and the solution was stirred for 5 min before addition of 560 mg (1.692 mmol) **1** in one portion at room temperature. The blue–green inhomogeneous reaction mixture was stirred at room temperature for 18 h and worked up according to the general procedure.

Deprotonation of 2 with NaH and oxidative cyclization induced by $(p\text{-BrPh})_3NSbCl_6$ (11)

At 0 °C, 250 mg (0.657 mmol) of **2** was added to a suspension of 28 mg (0.933 mmol) NaH (80% in mineral oil) in 13 ml dry DME. After stirring the solution for 40 min at 0 °C, 1.56 g (1.911 mmol) **11** was added in two portions. The green reaction mixture was stirred at 0 °C for 90 min. The mixture was quenched with four drops of a saturated NH_4Cl solution and warmed to room temperature. The reaction mixture was diluted with 20 ml diethyl ether and filtered through a pad of silica gel. The solvent was evaporated and the residue was preadsorbed on silica gel. Crude flash chromatography (50 : 1 gradient to 1 : 1) gave **8**, **2**, **12** and **7** contaminated with considerable amounts of Sb residues. The individual components were dissolved in 2 ml *n*-hexane and filtered through a pad of silica gel before they were subjected to another flash chromatography.

Oxidative cyclization of 2 in the presence of LiBr

At −78 °C, 250 mg (0.657 mmol) of **2** was added to a mixture of 456 mg (5.256 mmol) anhydrous LiBr and 0.854 mmol LDA in 13 ml dry DME. The mixture was stirred for 30 min between −78 and −60 °C. Solid **1** 696 mg (2.1 mmol) was added in three portions at 0 °C before a persistent blue–green color of the reaction mixture was observed. After 10 min, the color of the mixture changed slowly to brown. After stirring at 0 °C for 15 min, 5 drops of DBU were added. The mixture was stirred at 0 °C for an additional 10 min, quenched with six drops of a 2 M HCl solution, stirred for 10 min and warmed to room temperature. Workup was conducted according to the general procedure.

Ethyl 3-oxo-1,1-diphenyltetrahydrocyclopenta[*c*]furan-3a-carboxylate (7)

[R_f (2 : 1) 0.71], mp 88 °C (colorless blocks from pentane) (Found C, 75.1; H, 6.4. $C_{22}H_{22}O_4$ requires C, 75.4; H, 6.3%); λ_{max}/nm 194 (ε/dm^3 mol^{-1} cm^{-1} 46700), 204 (44300), 222 (39400) and 260 (21200); ν_{max}(KBr)/cm^{-1} 1764, 1725, 762 and 702; δ_H(400 MHz) 0.78 (3 H, t, *J* 7.2, OCH_2CH_3), 1.30 (1 H, m, $CHCH_2$), 1.73 (3 H, m, $CHCH_2CH_2$), 2.34 (2 H, m, CH_2CCO_2), 3.47 (1 H, dq, *J* 10.7 and 7.2, OCH_2), 3.76 (1 H, dq, *J* 10.7 and 7.2, OCH_2), 4.03 (1 H, t, *J* 8.4, CH_2CH), 7.17–7.32 (6 H, m, *Ph*), 7.40 (2 H, m, *Ph*) and 7.55 (2 H, m, *Ph*); δ_C(100 MHz) 13.3 (q, OCH_2CH_3), 26.2 (t), 31.1 (t), 36.5 (t), 55.9 (d, $CHCH_2$), 61.8 (t, OCH_2), 63.2 (s, CCO_2), 89.7 (s, CPh_2), 124.7 (d, *Ph*), 125.5 (d, *Ph*), 127.3 (d, *Ph*), 127.7 (d, *Ph*), 128.3 (d, *Ph*), 128.4 (d, *Ph*), 141.4 (s, *Ph*), 143.4 (s, *Ph*), 170.9 (s, CO_2CH_2) and 175.2 (s, CO_2CPh_2); *m*/*z* (EI): 350 (M^+, 46%), 183 (100), 140 (42) and 105 (41).

Diethyl 2-(5,5-diphenylpent-4-enyl)-2-ethylmalonate (8)

Flash chromatography (50 : 1) gave **8** [R_f (5 : 1) = 0.56] as a colorless oil (Found C, 76.3; H, 7.9. $C_{26}H_{32}O_4$ requires C, 76.4; H, 7.9%); λ_{max}/nm 194 (ε/dm^3 mol^{-1} cm^{-1} 46 400), 212 (42300), 218 (40800), 226 (39500), 252 (38500), 264 (36900), 274 (33400) and 282 (30400); ν_{max}(film)/cm^{-1} 2977, 1731, 1445, 1028 and 702; δ_H(200 MHz) 0.72 (3 H, t, *J* 7.5, CCH_2CH_3), 1.13 (6 H, t, *J* 7.1, OCH_2CH_3), 1.22 (2 H, m, $=CHCH_2CH_2$), 1.78 (2 H, m, CCH_2CH_2), 1.84 (2 H, q, *J* 7.5, CCH_2CH_3), 2.04 (2 H, q, *J* 7.4, $=CHCH_2$), 4.08 (4 H, q, *J* 7.1, OCH_2), 5.97 (1 H, t, *J* 7.4, =CH) and 7.06–7.33 (10 H, m, *Ph*); δ_C(50 MHz) 8.4 (q, CCH_2CH_3), 14.1 (q, OCH_2CH_3), 24.4 (t, CH_2CH_3), 25.2 (t, CH_2CH_2C), 29.9 (t), 31.3 (t), 57.9 (s, CCH_2), 60.9 (t, OCH_2), 126.8 (d, *Ph*), 126.9 (d, *Ph*), 127.2 (d, *Ph*), 128.0 (d, *Ph*), 128.1 (d, *Ph*), 129.1 (d, =CH), 129.8 (d, *Ph*), 140.1 (s), 142.1 (s), 142.6 (s) and 171.7 (s, CO_2); *m*/*z* (EI): 408.2292 (M^+, $C_{26}H_{32}O_4$ requires 408.2301, 58%), 362 (42), 289 (30), 288 (80), 206 (100), 205 (23), 191 (24), 188 (24), 178 (20), 115 (27) and 91 (27).

Diethyl 2-(diphenylhydroxymethyl)cyclopentane-1,1-dicarboxylate (9)

Flash chromatography (50 : 1) gave **9** as a colorless oil [R_f (5 : 1) = 0.52]. λ_{max}/nm 198 (ε/dm^3 mol^{-1} cm^{-1} 45800), 218 (41400), 224 (40600), 230 (39500), 252 (38700) and 276 (32300); ν_{max}(film)/cm^{-1} 3459, 2978, 1730, 1242, 1177, 1086 and 702; δ_H(200 MHz) 0.89 (3 H, t, *J* 7.2, OCH_2CH_3), 1.18 (1 H, m), 1.24 (3 H, t, *J* 7.1, OCH_2CH_3), 1.44 (1 H, m), 1.82 (2 H, m),

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2.24 (1 H, dt, *J* 12.7 and 5.7), 2.45 (1 H, dd, *J* 12.2 and 5.2), 2.69 (1 H, dq, *J* 10.8 and 7.1, OCH_2), 3.54 (1 H, dq, *J* 10.8 and 7.1, OCH_2), 4.15 (2 H, q, *J* 7.1, OCH_2), 4.47 (1 H, t, *J* 8.0, CHCH$_2$), 4.72 (1 H, s, OH) and 7.00–7.72 (10 H, m, *Ph*); δ_C(50 MHz) 13.3 (q, OCH$_2$CH_3), 14.0 (q, OCH$_2$CH_3), 24.4 (t), 27.8 (t), 39.0 (t), 51.8 (d, CH$_2$$C$H), 61.7 (t, O$CH_2$), 62.0 (t, O$CH_2$), 64.3 (s, CCH$_2$), 79.4 (s, COH), 125.2 (d, *Ph*), 125.8 (d, *Ph*), 126.0 (d, *Ph*), 126.4 (d, *Ph*), 127.85 (d, *Ph*), 127.93 (d, *Ph*), 147.0 (s, *Ph*), 147.1 (s, *Ph*), 172.3 (s, CO$_2$) and 174.9 (s, CO$_2$); *m*/*z* (EI): 396 (M$^+$, 1%), 379 (8), 260 (10), 232 (9), 214 (21), 183 (52), 182 (51), 168 (22), 105 (100) and 77 (46).

Diethyl 2-(diphenylmethylene)cyclopentane-1,1-dicarboxylate (10)

[R_f (5 : 1) = 0.47]; mp 61–62 °C (colorless blocks from CHCl$_3$) (Found C, 76.1; H, 7.0. $C_{22}H_{26}O_4$ requires C, 76.2; H, 6.9%); λ_{max}/nm 196 (ε/dm^3 mol^{-1} cm^{-1} 45400), 202 (45100), 206 (44600), 220 (41000), 238 (40100), 258 (38200) and 272 (33600); ν_{max}(film)/cm^{-1} 2981, 1732, 1264, 1175 and 703; δ_H(200 MHz) 1.09 (6 H, t, *J* 7.1, OCH$_2$CH_3), 1.60 (2 H, tt, *J* 7.4 and 7.0, CCH$_2$CH_2), 2.41 (2 H, t, *J* 7.4, CCH_2), 2.43 (2 H, t, *J* 6.9, CCH_2), 3.69 (2 H, dq, *J* 10.7 and 7.1, OCH_2), 3.88 (2 H, dq, *J* 10.7 and 7.1, OCH_2) and 7.09–7.36 (10 H, m, *Ph*); δ_C(50 MHz) 13.8 (q, OCH$_2$$CH_3$), 23.1 (t), 32.7 (t), 40.0 (t), 61.3 (t, OCH$_2$), 65.0 (s, CCO$_2$), 126.4 (d, *Ph*), 126.6 (d, *Ph*), 127.5 (d, *Ph*), 128.1 (d, *Ph*), 128.3 (d, *Ph*), 129.2 (d, *Ph*), 138.96 (s), 139.02 (s), 141.0 (s), 144.1 (s), 169.4 (s, CO$_2$) and 171.0 (s, CO$_2$); *m*/*z* (EI): 378.1823 (M$^+$, $C_{24}H_{26}O_4$ requires 378.1831, 32%), 260 (33), 259 (42), 232 (33), 231 (100), 216 (33), 215 (40), 203 (31), 202 (42), 184 (20) and 165 (26).

Diethyl 2-(5,5-diphenylpent-4-enyl)-2-chloromalonate (12)

Flash chromatography (50 : 1) gave an inseparable 5 : 1 : 12 mixture of **2**, **8** and **12** as a colorless oil [R_f (5 : 1) = 0.52]. δ_H(400 MHz) 1.24 (6 H, t, *J* 7.1, OCH$_2$CH_3), 1.52 (2 H, m), 2.04–2.23 (4 H, m), 4.22 (4 H, q, *J* 7.1, OCH_2), 6.05 (1 H, t, *J* 7.4, =CHCH$_2$) and 7.10–7.35 (10 H, m, *Ph*); δ_C(100 MHz) 13.9 (q, OCH$_2$$CH_3$), 24.4 (t), 29.2 (t), 37.0 (t), 62.9 (t, OCH$_2$), 70.9 (s, CCl), 126.9 (d, *Ph*), 127.0 (d, *Ph*), 127.2 (d, *Ph*), 128.1 (d, *Ph*), 128.2 (d, *Ph*), 128.5 (d, =CH), 129.8 (d, *Ph*), 140.0 (s), 142.46 (s), 142.55 (s) and 166.7 (s, CO$_2$); *m*/*z* (EI): 414/416 (M$^+$, 0.9/0.3%) and 379 (1.7).

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