396 J. Org. Chem. 1998, 63, 396−400

Diastereoselective Enolate Coupling through Redox Umpolung in Silicon and Titanium Bisenolates: A Novel Concept Based on Intramolecularization of Carbon−Carbon Bond Formation[†]

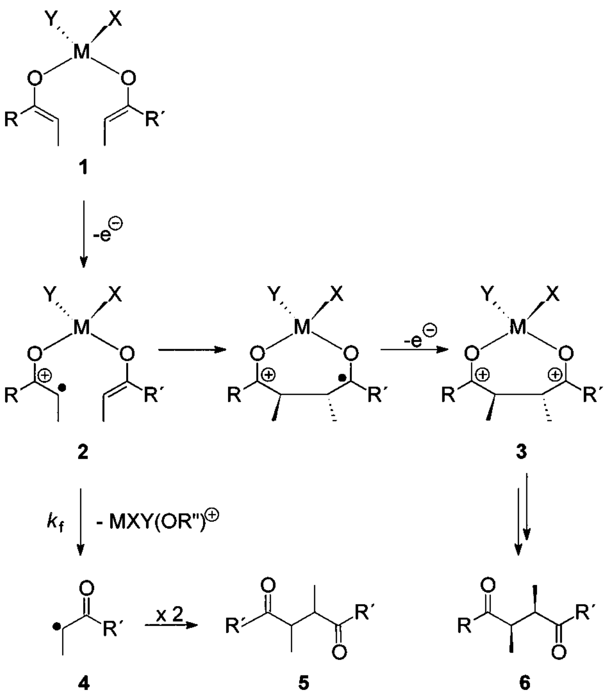
Michael Schmittel,[*,‡] Armin Burghart,[‡]
Wolfgang Malisch,[§] Joachim Reising,[§] and Rolf Söllner[‡]

Institut für Organische Chemie and Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

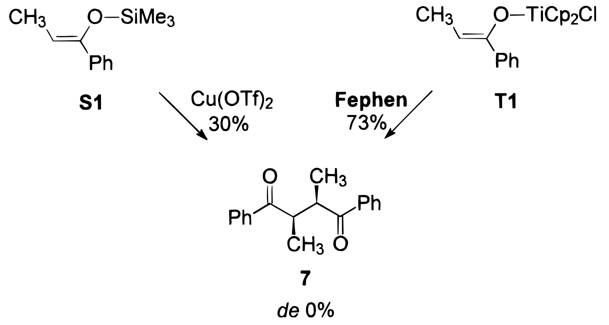
Received September 4, 1997

Although the oxidative coupling of enolates and other enol derivatives has been exploited over many years[1] as a valuable route to 1,4-dicarbonyl compounds,[2,3] three severe limitations have prevented its wider use in organic synthesis up to now: (i) diastereoselectivity is low, (ii) enantioselective procedures have not been developed yet,[4] and (iii) cross coupling between two different enol derivatives cannot be achieved in high yield. While these aspects have been partly solved in singular cases,[5−7] we now wish to report on the elaboration of a novel *useful concept* that may prove to be applicable for a wider variety of substrates since diastereoselectivity arises from intramolecularizing the oxidative carbon−carbon bond formation: The two enolate units are covalently linked to the same tether M,[8] and after umpolung of one of them through single electron-transfer oxidation (SET) the following reaction sequence to 1,4-diketones takes place (Scheme 1).

Scheme 1. The Concept



Scheme 2



It is important to stress that without intramolecularization the oxidative SET dimerization of enol derivatives proceeds without any diastereoselectivity, as demonstrated with **S1** and **T1** (Scheme 2).[2f] For silyl enol ether **S1**, Ag_2O in DMSO is a better oxidation system, furnishing **7** in 70% yield, but also as a 1:1 mixture of diastereomers.[2d]

From the concept (Scheme 1) it is obvious that two prerequisites ought to be satisfied for a stereoselective reaction with regard to tether M in the bisenolate **1**: M−O bond cleavage should be (i) sufficiently slow at the stage of the radical cation **2** to set up intramolecular cyclization yielding **6** (thus avoiding formation of α-carbonyl radicals **4** which would lead to formation of **5**), but

---

[‡] Institut für Organische Chemie der Universität Würzburg.

[§] Institut für Anorganische Chemie der Universität Würzburg.

[*] To whom correspondence should be addressed: Tel. Int. + 49 931 888 5318; FAX Int. + 49 931 888 4606; e-mail: mjls@chemie.uni-wuerzburg.de.

[†] Electroactive Protecting Groups and Reaction Units, part 7; for part 6 see ref 2f.

(1) (a) Ivanoff, D.; Spassoff, A. *Bull. Soc. Chem. Fr.* **1935**, *2*, 76. (b) Schäfer, H.; Alazrak, A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 474. (c) Brettle, R.; Parkin, J. G.; Seddon, D. *J. Chem. Soc. (C)* **1970**, 1317. (d) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 4605. (e) VandenBorn, H. W.; Evans, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 4296. (f) Kobayashi, Y.; Taguchi, T.; Tokuno, E. *Tetrahedron Lett.* **1977**, *18*, 3741.

(2) Diketones: (a) Baciocchi, E.; Casu, A.; Ruzziconi, R. *Tetrahedron Lett.* **1989**, *30*, 3707. (b) Fujii, T.; Hirao, T.; Ohshiro, Y. *Tetrahedron Lett.* **1992**, *33*, 5823. (c) Paolobelli, A. B.; Latini, D.; Ruzziconi, R. *Tetrahedron Lett.* **1993**, *34*, 721. (d) Drewes, S. E.; Hogan, C. J.; Kaye, P. T.; Roos, G. H. P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1585. (e) Moeller, K. D.; Tinao, L. V. *J. Am. Chem. Soc.* **1992**, *114*, 1033. (f) Schmittel, M.; Söllner, R. *Chem. Ber.* **1997**, *130*, 771.

(3) Dicarboxylic acids and derivatives: (a) Babler, J. H.; Sarussi, S. J. *J. Org. Chem.* **1987**, *52*, 3462. (b) Renaud, P.; Fox, M. A. *J. Org. Chem.* **1988**, *53*, 3745. (c) Peek, R.; Streukens, M.; Thomas, H. G.; Vanderfuhr, A.; Wellen, U. *Chem. Ber.* **1994**, *127*, 1257.

(4) While a pure enantioselective variant is not known, yet (cf. Kise, N.; Tokioka, K.; Aoyama, Y.; Matsumura, Y. *J. Org. Chem.* **1995**, *60*, 1100), induced diastereoselectivity in auxiliary controlled reactions has been realized, see ref 4 and ref 6a−c.

(5) For some special cases, cross-coupling of two different silyl enol ethers has been accomplished via intermediate radical cations using chemical one-electron oxidants. This approach, however, requires a very subtle control over the oxidation potentials of both reactants as well as their steric requirements, cf. ref 2c.

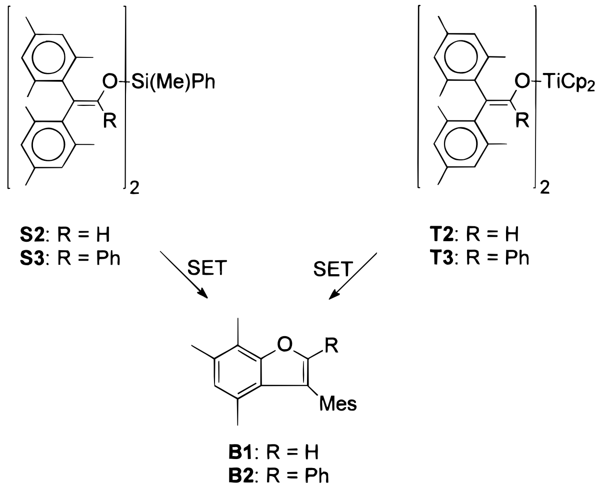
(6) Highly diastereoselective oxidative couplings have been realized starting from chiral ester enolates in auxiliary controlled variants: (a) Porter, N. A.; Su, Q.; Harp, J. J.; Rosenstein, I. J.; McPhail, A. T. *Tetrahedron Lett.* **1993**, *34*, 4457. (b) Langer, T.; Illich, M.; Helmchen, G. *Tetrahedron Lett.* **1995**, *36*, 4409. (c) Langer, T.; Illich, M.; Helmchen, G. *Synlett* **1996**, 1137, or with enolates derived from *N*-(diphenylmethylene)glycine esters: (d) Alvarez-Ibarra, C.; Csákÿ, A. G.; Colmenero, B.; Quiroga, M. L. *J. Org. Chem.* **1997**, *62*, 2478. See also ref 3a.

(7) High simple diastereoselectivity has been observed in phenylacetic acid couplings: (a) Belletire, J. L.; Spletzer, E. G.; Pinhas, A. R. *Tetrahedron Lett.* **1984**, *25*, 5969. (b) Matsumura, Y.; Nishimura, M.; Hiu, H.; Watanabe, M.; Kise, N. *J. Org. Chem.* **1996**, *61*, 2809.

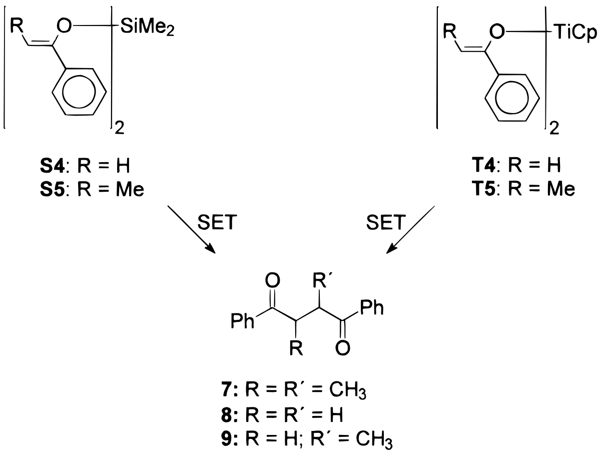
(8) An interesting review about silicon-tethers in organic synthesis: Fensterbank, L.; Malacria, M.; Sieburth, S. McN. *Synthesis* **1997**, 813.

S0022-3263(97)01650-2 CCC: $15.00

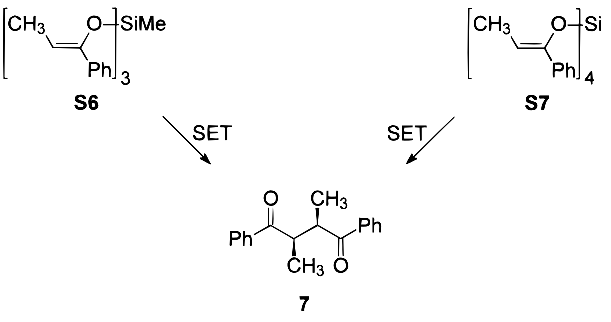
Scheme 3



Scheme 4



Scheme 5



(ii) fast enough in the dication **3** to release the product **6**. We have decided to probe this conception with M = Si, Ti and hence have synthesized a series of various silicon and titanium bisenolates (Schemes 3−5) using standard procedures.[9]

To test whether both M−O bonds can be cleaved in the oxidation process of bisenolates, the sterically shielded representatives **S2,3** and **T2,3**[10] (Scheme 3) were treated with various amounts of $[\mathrm{Fe(phen)_3}]^{3+}$ (**Fephen**, phen: 1,10-phenanthroline) as well-defined one-electron transfer oxidant ($E_{1/2} = 0.69$ V vs Fc[11]). Oxidation of **T2** (or **T3**) with 200 and 400 mol % of **Fephen** furnished benzofuran **B1** (or **B2**) in 51% (44%) and 94% (88%) yield based on enolate equivalents, respectively.[12] Similarly, upon oxidation of **S2** and **S3** with 400 mol % of **Fephen** 69% of **B1** and 77% of **B2** were obtained. Clearly, the high yield of benzofurans is indicative of the fact that at some stage of the reaction both O−M bonds are cleaved. In line with earlier mechanistic investigations,[13] 2 equiv of oxidant are needed per 1 equiv of benzofuran formed. In addition, cyclic voltammetry (CV) experiments indicated that the follow-up reaction of the bisenolate radical cations $\mathbf{S2,3}^{\bullet+}$ and $\mathbf{T2,3}^{\bullet+}$ is slow (M−O bond cleavage with k_f between 0.1 and 30 s^{-1}) and that both M−O bonds are cleaved sequentially.[10]

Table 1. Oxidation of Silicon and Titanium Bisenolates with Various Oxidants in Acetonitrile ($\mathbf{Cu(OTf)_2}$: $E_{1/2} = 0.67$ V *vs* Fc, CAN = $\mathbf{Ce(NH_4)_2(NO_3)_6}$: $E_{1/2} = 0.66$ V *vs* Fc)[11]

bisenolate (μmol)	E_{pa} [V *vs* Fc] of bisenolate	oxidant (μmol)	product (% yield)	de, %
S4 (74)	1.29	$Cu(OTf)_2$[b] (148)	**8** (48)	−
S5 (110)	1.11	**Fephen** (220)	**7** (57)	82
S5 (64)	1.11	CAN (127)	**7** (59)	80
S4/S5 (2 × 39)	1.29/1.11	$Cu(OTf)_2$[b] (80)	**7** + **8**[c]	−
T4 (83)	nd[a]	**Fephen** (166)	**8** (17)	−
T5 (45)	0.35	**Fephen** (90)	**7** (39)	0
T5 (123)	0.35	$Cu(OTf)_2$[b] (247)	**7** (23)	0
T4/T5 (2 × 58)	nd[a]/0.35	**Fephen** (230)	**7** + **8** + **9**[d]	−
S6 (34)	1.13	**Fephen**[b] (200)	**7** (63)	84
S6 (34)	1.13	$Cu(OTf)_2$[b] (68)	**7** (40)[e]	95
S6 (27)	1.13	CAN[b] (156)	**7** (60)	97
S7 (36)	1.16	$Cu(OTf)_2$[b] (71)	**7** (44)	95
S7 (36)	1.16	$Cu(OTf)_2$[b] (280)	**7** (58)	96

[a] Not determined. [b] In presence of di-*tert*-butylpyridine. [c] About 30% for **S4** → **8** and 50% for **S5** → **7**; **9** was not detected. [d] Product ratio **7**:**8**:**9** = 2.8:0.1:1. [e] 34% of **S6** unreacted.

With O−Si/O−Ti bond scission being that slow, we expected that in less sterically encumbered bisenolates intramolecular carbon−carbon bond formation (**2** ⟶ **3**) should prevail after oxidation. We have thus prepared bisenolates **S4,5** and **T4,5** (Scheme 4) along standard routes. Both propiophenone-derived products, **S5** and **T5**, were obtained as stereochemically pure compounds exhibiting *Z*-configuration at both enolate units. CV investigations indicated that titanium enolate **T5** is much more readily oxidized than the silyl enol ethers (see Table 1) which could be of advantage in cases when other oxidizable groups were present.

In line with the above expectation the sterically unshielded bisenolates exhibited no reversible wave in CV experiments even at scan rates as high as 15000 V s^{-1}. This points to a very fast follow-up reaction ($k > 10^4$ s^{-1}), much faster than one would expect from the O−M bond cleavage rate constants as determined for compounds **S2,3** and **T2**. In addition, chemical oxidation proceeded smoothly at room temperature within 1 min in case of the titanium bisenolates **T4,5** and over 12 h for the silicon bisenolates **S4,5** to afford the diketones **7,8** in acceptable to good yields (Table 1). The slower reaction with **S4,5** is readily understandable in light of their much higher

---

[9] (a) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075. (b) For **S4** and **S5**: Walkup, R. D. *Tetrahedron Lett.* **1987**, *28*, 511.

[10] M. Schmittel, R. Söllner, A. Burghart, unpublished results.

[11] All potentials are referenced to the ferrocene/ferrocenium (Fc) redox couple unless otherwise noted. To obtain values *vs* SCE simply add +0.39 V.

[12] In case of **S2**, **S3**, **T2**, and **T3** the yields are based on enolate equivalents in order to avoid yields >100% which would result if the yields were based on the molar amount of the substrates.

[13] (a) Schmittel, M.; Keller, M.; Burghart, A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2327. (b) Schmittel, M.; Söllner, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2107. See also ref 2f.

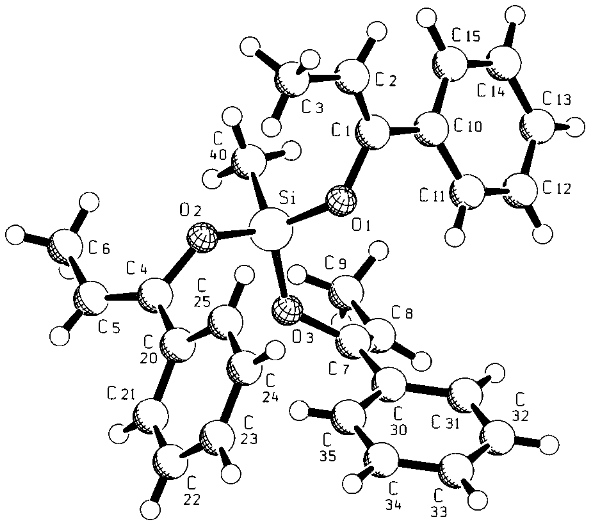


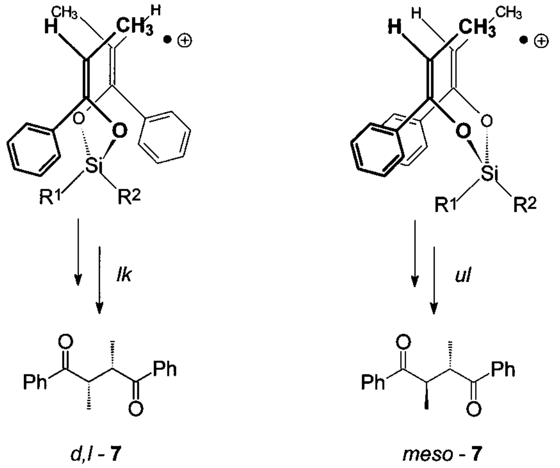
Figure 1. SCHAKAL-plot of crystal structure of tris(enoxy)-silane **S6**. Selected bond lengths [Å]: Si–O1 1.630(2), O1–C1 1.390(3), C1–C2 1.324(3), C2–C3 1.483(3), Si–O2 1.618(2), O2–C4 1.389(3), C4–C5 1.321(3), C4–C20 1.468(3), Si–O3 1.625(2), O3–C7 1.392(3), C7–C8 1.317(3). Selected bond angles [deg]: O2–Si–O1 107.67(9), O2–Si–O3 106.58(9), O3–Si–O1 109.91(9), O3–Si–C40 114.15(12), C1–O1–Si 124.09(13), C4–O2–Si 131.13(14), C7–O3–Si 129.92(14), C7–C8–C9 127.4(3).

oxidation potentials. Rewardingly, diketone *d,l*-**7** was formed in high diastereomeric excess (de = 82%) from **S5**, supporting the utility of our strategy. In contrast, however, the analogous oxidation of **T5** furnished diketone **7** in a *meso*:*d,l* ratio = 1:1.[14] This divergent reaction outcome is unexpected at first but can be rationalized from a mechanistic crossover experiment: while oxidation of a 1:1 mixture of **S4,5** only afforded **7** and **8**, the oxidation of a mixture of **T4,5** furnished the unsymmetrical diketone **9** as one of the main products (Table 1). Accordingly, carbon–carbon bond formation proceeds via an intramolecular route in **S5**$^{\bullet+}$ but intermolecularly with **T5**$^{\bullet+}$.

These results suggested the extension of this chemistry to other silicon bisenolates and to increase the steric bulk about the silicon tether as was realized in **S6** and **S7** (Scheme 5). As with **S5,T5** all the enolate units in **S6,S7** exhibited a *Z*-configuration as derived from their ^{1}H NMR spectra. To further support this assignment, a X-ray structure analysis was obtained from **S6** (Figure 1). Indeed, all the silyl enol ether units in **S6** have *Z*-configuration which is in agreement with the preferred kinetic formation of *Z*-enolates from propiophenones as described by Heathcock.[15]

Interestingly, with the sterically bulkier substrates **S6,S7** the simple diastereoselectivity in the oxidative diketone formation could be improved up to de = 97% (Table 1). The mediocre yield of **7** from **S7** (given on a molar basis) indicates, however, that not all four enolate groups in **S7** can be used for the diketone formation. Hence, it will be of importance to further probe the concept of steric bulk to increase diastereoselectivity in bisenolate cyclizations using two unoxidizable groups R at the silicon.

Scheme 6. Different Approaches in the Cyclization of the Bisenolate Radical Cation



From the above investigations a rather clear picture of the mechanism has emerged. Accordingly, carbon–carbon bond formation takes place at the stage of the bisenolate radical cation either in an inter- (with M = Ti) or intramolecular (with M = Si) way. From the arrangement of the enolate groups in **S6** it seems reasonable to propose that the diastereoselectivity in the oxidative coupling of the silicon bisenolates **S5**–**S7** is not controlled by ground-state conformational preferences but by transition state energy differences of the two diafacial differentiating approaches. Indeed, simple transition state model considerations favor the *lk*[16] approach of two enolate moieties in the bisenolate radical cation over the *ul* approach (Scheme 6) since steric repulsion of the eclipsed methyl and phenyl substituents can be avoided in the former. Obviously, a similar situation should be expected in the cyclization of **T5**, but apparently the small O–Ti–O bond angle of about 95–99°[17] prevents an intramolecular cyclization via a seven-membered transition state.

The present results establish that with silicon as tether in the oxidative intramolecular cyclization of bisenolates high diastereoselectivities can be obtained in formal enolate dimerization reactions. Moreover, because of its generality this approach holds great promise for realizing stereoselective cross-coupling of two different enolates[18] and maybe even of phenolates.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry argon by using standard Schlenk tube techniques. Solvents were purified by standard literature methods and distilled directly from their drying agents under nitrogen: THF/potassium, diethyl ether/sodium, *n*-hexane/potassium, *n*-pentane/sodium, acetonitrile/CaH$_2$. Solvents for CV measurements and one-electron oxidation experiments: aceto-

---

[14] Control experiments in the presence of base indicate that the diastereoselectivity in the coupling reactions under standard conditions (see General Procedure for One-Electron Oxidations) was not changed through epimerization induced by traces of acid.

[15] Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066.

[16] Helmchen, G. Vocabulary and Nomenclature of Organic Stereochemistry. In Houben-Weyl E21a: *Stereoselective Synthesis*; Helmchen, G., Hoffmann, R. W., Mulzer, J., Schaumann, E., Eds.; 1995, Vol. 1.

[17] (a) Curtis, M. D.; Thanedar, S.; Butler, W. M. *Organometallics* **1984**, *3*, 1855. (b) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4892.

[18] Synthesis of unsymmetrically substituted silicon bisenolates R^{1}O–SiX$_2$–OR:^{2} Rathke, M. W.; Weipert, P. D. *Synth. Commun.* **1991**, *21*, 1337.

nitrile was purchased in HPLC quality from Riedel-de-Haën, distilled from calcium hydride, and filtered through basic alumina (ICN); dichloromethane was purchased in HPLC quality from Riedel-de-Haën, distilled from P_4O_{10} and filtered through basic alumina (ICN). Supporting electrolyte tetra-*n*-butylammonium hexafluorophosphate (Fluka) was of electrochemical grade and used without further purification. Dichlorotitanocene was prepared according to ref 19, and silyl enol ether **S1** according to ref 9a, respectively. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 and AM 250 instruments and calibrated with tetramethylsilane as an internal reference (TMS, $\delta = 0.0$ ppm). IR spectra were recorded on a Perkin-Elmer 1605 series FT-IR-spectrometer. Melting points were recorded on a Büchi melting point apparatus and are uncorrected. Elemental analyses were carried out on a Carlo Erba Elemental Analyzer 1106. Mass spectra were recorded on a Finnigan MAT-90 mass spectrometer under electron-impact ionization (EI; 70 eV) conditions.

Dimethylbis(1-phenylethenoxy)silane (S4).[20] To a cooled (ice, NaCl) solution of diisopropylamine (0.76 g, 7.5 mmol) in THF (25 mL) was added *n*-butyllithium (4.7 mL, 1.6 M solution in hexane, 7.5 mmol). After stirring the solution for 0.5 h, acetophenone (0.90 g, 7.5 mmol) was added, and the reaction mixture was allowed to stir for another 1.5 h while cooling. Then dichlorodimethylsilane (0.48 g, 3.7 mmol) was added, and the solution was stirred overnight at room temperature. After filtering off the precipitate, the solvent was removed at reduced pressure, and the residue was filtered through basic Al_2O_3 using *n*-hexane/diethyl ether 4:1. The product was purified by MPLC (basic Al_2O_3, *n*-hexane/diethyl ether 4:1) affording 0.47 g (21%) of a colorless oil (**S4**): ^1H NMR (200 MHz, $CDCl_3$) δ 0.42 (s, 6 H, $SiCH_3$), 4.68 (d, $J = 2.0$ Hz, 2 H, C2-H), 5.00 (d, $J = 2.0$ Hz, 2 H, C2-H), 7.30−7.38 (m, 6 H, PhH), 7.52−7.66 (m, 4 H, PhH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.7 ($SiCH_3$), 92.3 (C2), 125.2 (Ar), 128.2 (Ar), 128.4 (Ar), 136.9 (Ar), 154.6 (C1); IR (neat) 2960.6, 1622.2, 1574.4, 1316.7, 1283.6, 1260.0, 1112.0, 1014.4 cm^{-1}.

(*Z*,*Z*)-Dimethylbis(1-phenyl-1-propenoxy)silane (S5). The synthesis was accomplished analogously to the preparation of **S4** using the following reagents: diisopropylamine (2.0 g, 20 mmol) in THF (50 mL), *n*-butyllithium (13 mL, 1.6 M in hexane, 21 mmol), propiophenone (2.7 g, 20 mmol), dichlorodimethylsilane (1.3 g, 10 mmol). The product was purified by flash chromatography on basic Al_2O_3 with *n*-hexane/diethyl ether 6:1 furnishing 0.68 g (20%) of a colorless oil (**S5**): ^1H NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 6 H, $SiCH_3$), 1.80 (d, $J = 7.0$ Hz, 6 H, CH_3), 5.42 (q, $J = 7.0$ Hz, C2-H, 2 H), 7.17−7.29 (m, 6 H, PhH), 7.40−7.51 (m, 4 H, PhH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −1.4 ($SiCH_3$), 11.6 (C3), 105.6 (C2), 125.2 (Ph), 127.4 (Ph), 128.1 (Ph), 138.6 (Ph), 149.1 (C1); IR (neat) 2962.0, 1653.2, 1493.8, 1445.6, 1320.2, 1260.6, 1060.9 cm^{-1}; MS, *m/z* (rel intensity) 324 (M^+, 4), 309 ($M^+ - CH_3$, 1), 190 (100), 175 (12), 117 (17), 115 (19), 91 (12), 75 (45); HRMS (M^+) calcd for $C_{20}H_{24}O_2Si$ 324.1546, found 324.1541.

(*Z*,*Z*,*Z*)-Methyltris(1-phenyl-1-propenoxy)silane (S6). A solution of propiophenone (2.0 g, 15 mmol) in acetonitrile (50 mL) was reacted with triethylamine (1.5 g, 15 mmol). After stirring the solution for 10 min, trichloromethylsilane (0.74 g, 5.0 mmol) and then NaI (2.4 g, 15 mmol) were added. The heterogeneous mixture was stirred at room temperature for 4 h and then filtered, and the solvent was removed at reduced pressure. The product was isolated as colorless crystals after flash chromatography on basic Al_2O_3 with *n*-hexane/diethyl ether 4:1. Recrystallization from *n*-hexane furnished 1.3 g (59%) of colorless crystals (**S6**): mp 52 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 0.01 (s, 3 H, $SiCH_3$), 1.73 (d, $J = 7.0$ Hz, 9 H, CH_3), 5.35 (q, $J = 7.0$ Hz, 3 H, C2H), 7.20−7.27 (m, 9 H, PhH), 7.34−7.45 (m, 6 H, PhH); ^{13}C NMR (50 MHz, $CDCl_3$) δ −4.8 ($SiCH_3$), 11.4 (C3), 106.1 (C2), 125.2 (Ar), 127.4 (Ar), 128.0 (Ar), 138.1 (Ar), 148.3 (C1); IR (KBr) 2912.0, 1656.4, 1492.7, 1317.2, 1267.6, 1056.4, 1028.5, 893.4 cm^{-1}. Anal. Calcd for $C_{28}H_{30}O_3Si$: C, 75.98; H, 6.83. Found: C, 75.66; H, 7.18.

(*Z*,*Z*,*Z*,*Z*)-Tetrakis(1-phenyl-1-propenoxy)silane (S7). Preparation was analogous to that for **S6** using the following reagents: propiophenone (2.0 g, 15 mmol), triethylamine (1.5 g, 15 mmol), tetrachlorosilane (0.64 g, 3.8 mmol), NaI (2.4 g, 15 mmol). After recrystallization from *n*-hexane, colorless crystals of **S7** (0.9 g, 43%) were obtained: mp 58 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.57 (d, $J = 7.0$ Hz, 12 H, CH_3), 5.22 (q, $J = 7.0$ Hz, 4 H, C=CH), 7.15−7.20 (m, 12 H, PhH), 7.31−7.37 (m, 8 H, PhH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.2 (C3), 106.3 (C2), 125.2 (Ar), 127.3 (Ar), 127.9 (Ar), 137.7 (Ar), 147.9 (C1); IR (KBr) 2913.3, 1655.1, 1492.1, 1316.6, 1282.0, 1268.8, 1119.8, 1083.8, 1029.8 cm^{-1}. Anal. Calcd for $C_{36}H_{36}O_4Si$: C, 77.11; H, 6.47. Found: C, 76.92; H, 6.67.

Bis(1-phenylethenoxy)titanocene (T4). To a solution of diisopropylamine (2.29 g, 22.6 mmol) in THF (80 mL) a solution of *n*-butyllithium (14 mL, 1.5 M in hexane, 21 mmol) was added at −78 °C and stirred for 30 min. Then acetophenone (2.66 g, 22.1 mmol) was added at this temperature, and the mixture was stirred for 1 h. After addition of dichlorotitanocene (2.49 g, 10.0 mmol), the reaction mixture was allowed to warm overnight. The solvent was evaporated in vacuo, and the remaining dark residue was extracted with diethyl ether (100 mL). The resultant mixture was filtered through Celite and concentrated to about 10 mL. After addition of *n*-hexane (60 mL) and storage at −40 °C for 3 days, a precipitate formed which was filtered off and dried in vacuo affording **T4** as a yellow-brown powder (2.59 g, 6.22 mmol). Due to the paramount sensitivity toward hydrolysis, the crude product was used for one-electron oxidation experiments without further purification: ^1H NMR (200 MHz, $CDCl_3$) δ 3.87 (s, 2 H, C2-H), 4.52 (s, 2 H, C2-H), 6.25 (s, 10 H, C_5H_5), 7.10−7.22 (m, 6 H, PhH), 7.40−7.50 (m, 4 H, PhH).

(*Z*,*Z*)-Bis(1-phenyl-1-propenoxy)titanocene (T5). To a suspension of potassium hydride (1.22 g, 30.4 mmol) in THF (200 mL) was added propiophenone (4.89 g, 36.4 mmol) at 0 °C. The mixture was stirred at this temperature for about 3 h until gas evolution was finished. Thereafter, dichlorotitanocene (3.13 g, 12.6 mmol) was added, and the mixture was stirred for additional 72 h while it was allowed to slowly warm to room temperature. Then the solvent was evaporated in vacuo and the residue extracted with benzene (200 mL). The dark red mixture was filtered and the filtrate concentrated to about 30 mL. After addition of *n*-pentane (200 mL) and storage at −40 °C for 3 days a precipitate formed which was filtered off and dried in vacuo affording **T5** as a orange powder (3.90 g, 8.78 mmol): ^1H NMR (200 MHz, $CDCl_3$) δ 1.82 (d, $J = 7.0$ Hz, 6 H, CH_3), 5.11 (q, $J = 7.0$ Hz, 2 H, C2-H), 6.25 (s, 10 H, C_5H_5), 7.16−7.30 (m, 6 H, PhH), 7.50−7.62 (m, 4 H, PhH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.4 (C3), 97.4 (C2), 116.3 (C_5H_5), 125.5 (Ph), 126.7 (Ph), 127.8 (Ph), 141.0 (Ph), 166.1 (C1). Anal. Calcd for $C_{28}H_{28}O_2Ti$: C, 75.58; H, 6.35. Found: C, 75.47; H, 6.61.

General Procedure for One-Electron Oxidations. In an argon-filled glovebox the desired amounts (see Table 1) of the one-electron oxidants (**Fephen**, $Cu(OTf)_2$ or $Ce(NH_4)_2(NO_3)_6$) and the silicon or titanium enolate were placed into two separate test tubes equipped with stirring rods. Under a high purity argon line, 3 mL of the appropriate solvent (acetonitrile or dichloromethane) was added in each test tube to dissolve the reactants. The solution of the silicon or titanium enolate was added through a syringe to the solution of the one-electron oxidant. The resulting mixture was stirred at room temperature for 1 min (in the case of the titanium bisenolates) or 14 h (in the case of the silicon enolates), quenched with saturated aqueous $NaHCO_3$ (10 mL), and diluted with dichloromethane (10 mL). The aqueous layer was extracted three times with dichloromethane, and the combined organic layers were washed with water and dried with Na_2SO_4. If **Fephen** was used as oxidant the solution was filtered through silica gel in order to remove the red $[Fe(phen)_3](PF_6)_2$. Removal of the solvent afforded the crude product. Product analysis was performed by ^1H NMR spectroscopy. All products were identified by comparison with data of authentic samples. Yields were determined by

---

(19) Wilkinson, G.; Birmingham, J. B. *J. Am. Chem. Soc.* **1954**, *76*, 4281.

(20) Fataftah, Z. A.; Ibrahim, M. R.; Abu-Agil, M. S. *Tetrahedron Lett.* **1986**, *27*, 4067.

adding *m*-nitroacetophenone as an internal ^1H NMR standard.

Data of 3-mesityl-4,6,7-trimethylbenzo[*b*]furan (B1):[21a] ^1H NMR (250 MHz, $CDCl_3$) δ 1.92 (s, 3 H, *p*-Mes-CH_3), 2.06 (s, 6 H, *o*-Mes-CH_3), 2.33 (s, 3 H, C4-CH_3), 2.38 (s, 3 H, C6-CH_3), 2.43 (s, 3 H, C7-CH_3), 6.75 (s, 1 H, C5-H), 6.94 (s, 2 H, Mes-H), 7.33 (s, 1 H, C2-H).

Data of 3-mesityl-2-phenyl-4,6,7-trimethylbenzo[*b*]furan (B2):[21b] ^1H NMR (250 MHz, $CDCl_3$) δ 1.89 (s, 3 H, *p*-Mes-CH_3), 2.02 (s, 6 H, *o*-Mes-CH_3), 2.39 and 2.40 (two s, each 3 H, C4- and C6-CH_3), 2.54 (s, 3 H, C7-CH_3), 6.76 (s, 1 H, C5-H), 6.98 (s, 2 H, Mes-H), 7.17−7.30 (m, 3 H, PhH), 7.48−7.55 (m, 2 H, PhH).

Data of *d,l*-2,3-dimethyl-1,4-diphenylbutane-1,4-dione (*d,l*-7):[2d] ^1H NMR (200 MHz, $CDCl_3$) δ 1.26−1.29 (m, 6 H, CH_3), 3.91−3.99 (m, 2 H, CH), 7.4−7.6 (m, 6 H, PhH), 7.95−8.00 (m, 4 H, PhH).

Data of *meso*-2,3-dimethyl-1,4-diphenylbutane-1,4-dione (*meso*-7):[2d] ^1H NMR (200 MHz, $CDCl_3$,) δ 1.10−1.13 (m, 6 H, CH_3), 3.99−4.07 (m, 2 H, CH), 7.4−7.6 (m, 6 H, PhH), 8.02−8.07 (m, 4 H, PhH).

Data of 1,4-diphenylbutane-1,4-dione (8):[22] ^1H NMR (200 MHz, $CDCl_3$) δ 3.46 (s, 4 H, CH_2), 7.47 (t, $J = 7.0$ Hz, 4 H, PhH), 7.57 (t, $J = 7.0$ Hz, 2 H, PhH) 8.04 (d, $J = 7.0$ Hz, 4 H, PhH).

Data of 2-methyl-1,4-diphenylbutane-1,4-dione (9):[22] ^1H NMR (200 MHz, $CDCl_3$,) δ 1.25−1.27 (m, 3 H, CH_3), 3.12 (dd, 1 H, $J = 18$ and 5 Hz), 3.74 (dd, 1 H, $J = 18$ and 8 Hz), 4.15−4.25 (m, 1 H), 7.3−8.3 (m, 10 H, PhH).

Acknowledgment. This research was generously supported by the Deutsche Forschungsgemeinschaft (SFB 347, Selective reactions of metal activated molecules) and the Fonds der Chemischen Industrie. For a gift of electrode materials we are indebted to the Degussa.

Supporting Information Available: A discussion of some structural features of **S6**, as well as experimental data of the X-ray structural analysis of **S6** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO971650X

---

(21) (a) Schmittel, M.; Baumann, U. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 541. (b) Röck, M.; Schmittel, M. *J. Prakt. Chem.* **1994**, *336*, 325.

(22) Russell, G. A.; Kulkarni, S. V.; Khanna, R. K. *J. Org. Chem.* **1990**, *55*, 1080.