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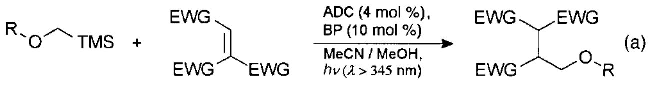
[8] a) J. S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, Cambridge, **1961**, p. 271. b) If the Fe^{II} was in a tetrahedral geometry, the deviations from Curie–Weiss behavior are consistent with strong antiferromagnetic interactions between high-spin $S = 2$ Fe^{II} and $S = 1/2$ $[TCNE]^{\bullet -}$ above 240 K ($\theta = -120$ K) and strong ferromagnetic coupling between 115 and 185 K ($\theta \sim +100$ K).
[9] As observed for the preparation of $[V(tcne)_x] \cdot y$ solvent,[3, 4] reactions of $[M^{II}I_2] \cdot x$MeCN (M = Mn, Fe, Co, Ni) in MeCN led to magnetic materials with reduced T_c values.
[10] Powder diffraction data: corrected d spacing [Å] (normalized intensity): M = Fe: 7.393 (38), 5.123 (25), 4.425 (100), 3.266 (25), 2.862 (21), 2.462 (21); M = Mn: 7.455 (15), 5.210 (17), 4.470 (100), 3.314 (33), 2.912 (25), 2.494 (23).

α-Silyl Ethers as Hydroxymethyl Anion Equivalents in Photoinduced Radical Electron Transfer Additions**

Guido Gutenberger, Eberhard Steckhan,* and Siegfried Blechert

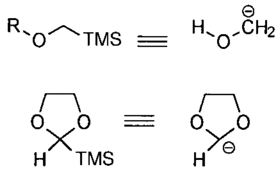
Hydroxymethyl anion equivalents (d^1-synthons) are desirable umpoled synthetic building blocks in organic chemistry.[1] In one of the very rare descriptions of its successful generation Hoppe et al. lithiated carbamates in the presence of (−)-sparteine.[2] Addition of nucleophilic hydroxy- or alkoxymethyl radicals to electron-poor alkenes can be considered as a general alternative. The oxidation of ethers, for example electrochemically,[3] provides the desired radical after one-electron oxidation and deprotonation; however, due to their high oxidation potentials ethers are difficult to oxidize. Besides, the generated alkoxy radical would be further oxidized immediately to the corresponding carbenium ion. The oxidation potential can be decreased significantly by introducing a silyl group to the position α to oxygen.[4] Nevertheless, also in this case further oxidation of the radical to the corresponding cation after desilylation cannot be avoided. Following our recent investigations of aminomethyl radicals[5] we are now presenting a new method for the generation of hydroxymethyl anion equivalents by photoinduced electron transfer catalysis (PET catalysis) starting from α-silyl ethers. This approach provides protected α-hydroxymethyl radicals under mild,[6] nonoxidizing conditions. A multiple-step alternative for the generation of α-silyloxyalkyl radicals is the radical Brook rearrangement of β-silylalkoxy radicals, which are accessible by radical cyclization of ω-bromoacylsilanes.[7]

In our method one-electron oxidation generates an intermediate α-silyl ether radical cation, which fragments with cleavage of the silyl group as an electrofuge. In the presence of catalytic amounts of 9,10-anthracenedicarbonitrile (ADC; 4 mol %) and biphenyl (BP; 10 mol %), irradiation with UV/Vis light leads to the addition of α-silyl ethers to acceptor-substituted alkenes. In this way, γ-acceptor-substituted ethers and alcohols can be prepared (Scheme 1).



Scheme 1. PET-catalyzed addition of α-silyl ethers to acceptor-substituted alkenes. EWG = electron-withdrawing group, TMS = trimethylsilyl, R = benzyl, TBDMS, methyl.

The α-silyl ethers **1**–**4** employed react as hydroxymethyl anion equivalents or, in the case of 2-trimethylsilyl-1,3-dioxolane (**5**), as formyl anion equivalents (Scheme 2). Consequently, this reaction can be considered to be a new route, analogous to the Michael addition, for the direct addition of hydroxymethyl groups to electron-poor alkenes.



Scheme 2. α-Silyl ethers and acetals as d^1-synthons.

We studied this transformation with the starting materials listed in Table 1. Methoxymethyltrimethylsilane (**1**) was successfully tested in addition reactions with methyl 2-cyanocrotonate (**6**) to give **11**. Because of the difficult cleavage of the methyl ether to generate the free OH function, trimethylsilylmethanol and other α-silyl ethers carrying readily cleavable protecting groups were examined. Reaction of the unprotected trimethysilylmethanol leads, according to GCMS analysis, to a product formed by addition of a trimethylsilyloxymethyl radical to the electron-poor double bond. Isolation of the product was impossible due to its instability. An explanation for the formation of this product would be deprotonation at the carbon or oxygen atom of the intermediate radical cation generated under electron transfer conditions. Subsequent Brook rearrangement[7, 8] would give the trimethylsilyloxymethyl radical.

Next we investigated the behavior of α-silyl ethers carrying protecting groups on oxygen that can be cleaved easily like trimethylsilyl, *tert*-butyldimethylsilyl (TBDMS; **4**), benzyl (**2**), and triisopropylsilyl (TIPS; **3**). The addition product obtained from a trimethylsilyl-protected α-silyl ether is identical, according to GCMS analysis, to that formed from trimethyl-

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[*] Prof. Dr. E. Steckhan, Dipl.-Chem. G. Gutenberger
Kekulé Institut für Organische Chemie und
Biochemie der Universität
Gerhard-Domagk-Strasse 1, D-53121 Bonn (Germany)
Fax: (+49) 228-735683
E-mail: steckhan@uni-bonn.de

Prof. Dr. S. Blechert
Institut für Organische Chemie der Technischen Universität Berlin

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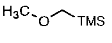
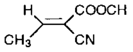
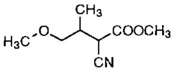
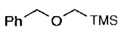
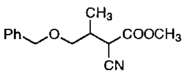
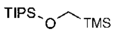
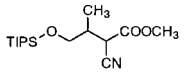
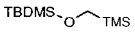
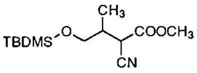
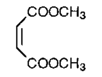
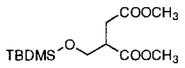
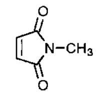
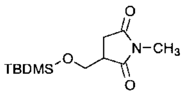
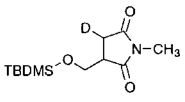
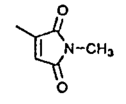
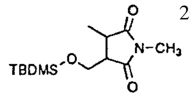
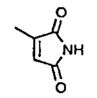
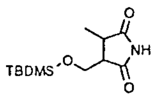
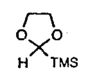
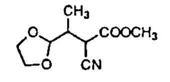
Table 1. Photoinduced radical additions of α-silyl ethers to electron-poor alkenes.

α-Silyl ether	Alkene	Product [a]	Yield [%]	d.r.
 **1**	 **6**	 **11**	46[b]	
 **2**	**6**	 **12**	64[c]	2:1
 **3**	**6**	 **13**	25[b]	
 **4**	**6**	 **14**	42[c]	1.8:1
4	 **7**	 **15**	38[b]	2.5:1
4	 **8**	 **16**	42[b]	
4	**8**	 **17**	55[c] 20[b] 21[b, d]	2.5:1 – –
4	 **9**	 **18**	20[b, e, f]	–
4	 **10**	 **19**	18[b, d]	86:14
 **5**	**6**	 **20**	15[b, d] 50[b]	86:14 1.9:1

[a] All addition products were characterized by ^{13}C and ^{1}H NMR spectroscopy, and MS, HRMS, and CHN elemental analysis. [b] Yields of isolated products. [c] Yield determined by gas chromatography using a calibration curve. [d] Lower yields were obtained due to the easy polymerization of cyclic alkenes. [e] In presence of CH_3OD. [f] Overlapping NMR signals prevented determination of d.r.

silylmethanol. Also in this case, the product could not be isolated due to its instability. However, all other α-silyl ethers form the expected products. Of the α-silyl ethers, the TBDMS-protected derivative **4** proved to react most effectively with the acceptor-substituted alkenes **6**–**10**.

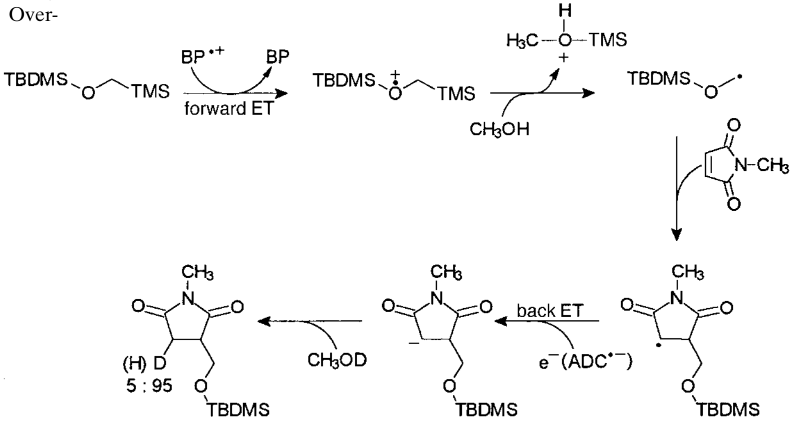
Compound **5** served as a model of an acyl anion equivalent. Cyclic α-silyl ethers and acetals are known to adopt a conformation in which the free π-electrons of the oxygen and the Si–C σ bond[4] are "in plane". This leads to faster, nucleophile-assisted desilylation. The higher yield is presumably due to the increased reactivity of the radical (Table 1). The reactivity is influenced not only by the different O-protecting groups but also by the radical acceptors. When aliphatic, electron-poor alkenes such as methyl 2-cyanocrotonate (**6**) are used, only poor diastereoselectivity (d.r. = 1.8:1 to 2.5:1) is observed (Table 1). A possible explanation might be the free rotation around the C–C single bond. Application of cyclic, electron-poor alkenes like 1,3-dimethyl-1*H*-pyrrole-2,5-dione (**9**) and 3-methyl-1*H*-pyrrole-2,5-dione (**10**), however, results in considerably higher diastereoselectivity with a *cis:trans* ratio of 86:14 (Table 1). The *cis* product is formed preferentially under kinetic control. This behavior can be explained on the basis of the mechanism. ET quenching between the primary electron donor BP (E_{ox} = 1.98 V vs. SCE) and photochemically excited ADC* (E_{red}(S1) = 2.0 V vs. SCE)[9] generates the biphenyl radical cation (Scheme 3), which subsequently oxidizes the α-silyl ether (E_{ox} = 1.41–1.66 V vs. Ag/AgNO$_3$)[10] to give its radical cation through a one-electron transfer reaction (redox photosensitization)[11] (Scheme 4). After cleavage of the silyl group,[12] the resulting nucleophilic radical is trapped by an electron-poor alkene. Back electron transfer from the ADC radical anion to the radical addition product and protonation complete the electron transfer catalytic cycle.

$$\mathrm{BP + ADC} \underset{}{\overset{h\nu}{\rightleftharpoons}} \underset{\mathrm{CIP}}{\left(\mathrm{BP^{\bullet+}/ADC^{\bullet-}}\right)} \longrightarrow \underset{\mathrm{FRI}}{\mathrm{BP^{\bullet+} + ADC^{\bullet-}}}$$

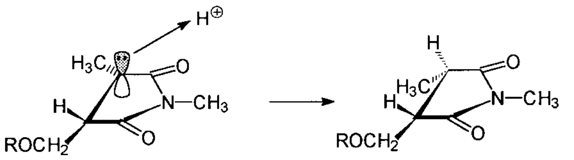
Scheme 3. Redox photosenzitation with ADC und BP. CIP = contact radical ion pair, FRI = free radical ions.

We wondered whether the α-carbonyl radical abstracts hydrogen from the solvent, or whether the carbanion intermediate is protonated. By using CH_3OD instead of CH_3OH as the solvent, we proved that the carbanion intermediate is protonated preferentially. GCMS analysis indicated the ratio of deuterated to nondeuterated product to be 95:5. The product itself shows no H/D exchange under the same reaction conditions.

The diastereoselectivity results from preferred protonation of the carbanion intermediate from the sterically less hindered side under kinetic control (Scheme 5). By treatment of the *cis* product with methoxide in methanol, the thermodynamically more stable *trans* product can be formed.



Scheme 4. Proof of protonation of the anionic intermediate.



Scheme 5. Model for stereochemical control of the protonation step.

In addition to the intermolecular additions to electron-poor alkenes described here, intramolecular cyclization of α-silyl ethers having electron-poor double bonds also seems promising.

Experimental Section

General conditions for PET reactions: A jacketed Schlenk tube was charged with a solution of the α-silyl ethers **1**–**5** in acetonitrile/methanol (2/1) containing ADC (4 mol%) and BP (10 mol%). The electron-poor alkenes **6** and **7**, each dissolved in 3 mL of CH_3CN, were added before irradiation, solutions of **8**–**10** were added dropwise during irradiation. A 450 W xenon-arc lamp with a wavelength filter ($\lambda > 345$ nm) was used as a light source. The solutions were degassed with argon prior to and during irradiation and thermostated by water-cooling.

11: (analogous for **12**–**15** and **20**): A mixture of **1** (350 mg, 2.9 mmol), **6** (543 mg, 4.3 mmol), BP (45 mg), and ADC (7 mg) was dissolved in 20 mL of acetonitrile and 10 mL of methanol. During subsequent irradiation for 11 h two 10-mg portions of ADC were added every 3–4 h (27 mg total). Evaporation of the solvent followed by flash chromatography on silica gel (first separation: ethyl acetate/*n*-heptane 1/5; $R_f = 0.31$), (second separation: petroleum ether/dichloromethane 2/1; $R_f = 0.1$)) provided 228.5 mg (46%) of a light yellow oil. The signal doubling observed in the ^1H and ^{13}C NMR spectra indicates the formation of diastereomers. The data for the diastereomers are separated by slashes. ^1H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.98/1.05 (d, $J = 6.8$ Hz, 3H), 2.45–2.6 (m, 1H), 3.18–3.22 (1H), 3.25/3.3 (s, 3H), 3.31–3.4 (m, 1H), 3.51/3.9 (d, $J = 4.2$ Hz, 1H), 3.73/3.75 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 12.9/14.9$, 34.6/35.1, 40.2/41.3, 53.1/53.3, 58.9/59.0, 74.0, 114.8/115.4, 166.2/166.6; MS (EI, 70 eV): m/z (%): 171 (1) [M^+], 140 (7), 109 (7), 72 (58), 45 (100); HRMS (EI, 70 eV): calcd for $C_8H_{13}NO_3$: 171.0895; found 171.0890; CHN analysis calcd for $C_8H_{13}NO_3$: C 56.13, H 7.65, N 8.18; found C 56.40, H 7.83, N 7.64.

18: (analogous for **16**, **17**, and **19**): A mixture of **4** (348 mg, 1.6 mmol), ADC (21.8 mg, 0.09 mmol), and BP (24.6 mg, 0.16 mmol) were dissolved in 20 mL of acetonitrile and 10 mL of methanol. A solution of **9** (300 mg, 2.4 mmol) in 3 mL of CH_3CN was added dropwise to the reaction mixture, which was irradiated for 18 h. Evaporation of the solvent and subsequent flash chromatography on silica gel (cyclohexane/ethyl acetate 10/1; $R_f =$ 0.05) provided 115 mg (18%) of a light yellow oil. The data refer to the *cis* product. The relative configuration was determined by NOE experiments. ^1H NMR (500 MHz, C_6D_6): $\delta = -0.11$ (s, 3H), -0.09 (s, 3H), 0.70 (s, 9H), 1.26 (d, $J = 6.9$ Hz, 3H), 2.76–2.85 (m, 2H), 2.88 (s, 3H), 3.42–3.45 (dd, $J = 10.0$ Hz, $J = 2.0$ Hz, 1H), 3.86–3.89 (dd, $J = 10.0$ Hz, $J = 3.2$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 181.1$, 179.0, 60.4, 47.1, 37.6, 26.0, 25.1, 18.3, 9.7, -5.2, -5.3; MS (EI, 70 eV): m/z (%): 270 (1) [$M^+ - H$], 256 (41), 214 (100), 156 (4), 129 (4), 75 (14); HRMS (EI, 70 eV): calcd. for $C_{13}H_{25}NO_3Si$: 271.1603; found: 256.1371 [$M^+ - 15$]; CHN analysis calcd for $C_{13}H_{25}NO_3Si \cdot 1/6\,H_2O$: C 57.53, H 9.28, N 5.16; found: C 56.99, H 9.26, N 5.27.

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Heck Reactions without Salt Formation: Aromatic Carboxylic Anhydrides as Arylating Agents[**]

Massoud S. Stephan,[*] Antonius J. J. M. Teunissen, Gerard K. M. Verzijl, and Johannes G. de Vries[*]

The Friedel-Crafts reaction is still the most commonly used method for the attachment of a carbon fragment to an aromatic ring. From an industrial point of view the reaction is less desirable because of the highly corrosive conditions and the concomitant formation of a large amount of waste. Recently the Heck reaction has come into the spotlight as a means of arylating double bonds.[1] Though the reaction has a wide scope, the arylating agent is limited to aryl bromides, iodides, or triflates, aroyl halides, arylsulfonyl halides, and aryldiazonium salts. In all cases a stoichiometric amount of base is required to neutralize the acid that is formed during the reaction. In addition, an equivalent amount of halide salt is formed as waste.

The development of a stable palladium catalyst, based upon a palladacycle, has allowed the conversion of activated aryl chlorides with high turnover numbers and has brought the Heck reaction into the industrial realm.[2] But also in this reaction a stoichiometric amount of chloride salt is formed as waste product. There clearly is a need for a cheap aryl source that does not lead to the formation of halide salts in the Heck reaction.

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[*] Dr. M. Stephan, Dr. J. G. de Vries, A. J. J. M. Teunissen,
G. K. M. Verzijl
DSM Research, Dept. Fine Chemicals
PO Box 18, NL-6160 MD Geleen (The Netherlands)
Fax: (+31) 46-476-7604
E-mail: j.g.vries-de@research.dsm.nl

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