An Efficient Method for the Synthesis of Symmetrical Disiloxanes from Alkoxysilanes Using Meerwein's Reagent

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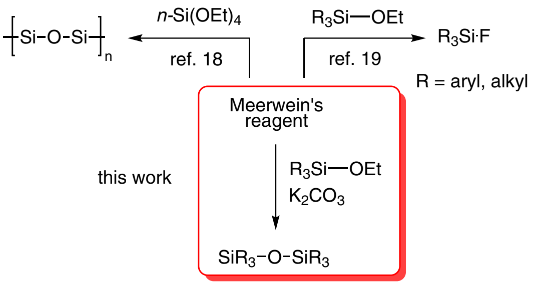
Abstract: We report here a new and efficient route to symmetrical disiloxanes from their corresponding alkoxysilanes using Meerwein's reagent as mediator and potassium carbonate as additive under mild reaction conditions in acetonitrile. Our methodology is very simple, economic, and high yielding. We have also proposed a reaction mechanism with the plausible silyloxonium intermediates.

Key words: Meerwein's reagent, disiloxane, alkoxysilane condensation, fluorine anion, silicon

Siloxanes with Si–O–Si backbone are ubiquitous in nature. They have a broad range of potential applications, including health care products, dry-cleaning process,[1a] and adhesives.[1b] Liquid crystalline siloxane oligomers were investigated for their mesogenic properties.[2] Water repellent siloxanes act as antiperspirants.[3] A polyorganosiloxane[4a] emulsion[4b] is used for the preparation of cosmetic products.[4c] Particularly, disiloxanes act as an important class of compounds with versatile applications. They are used in microelectronic device and sensor fabrication[5] and as liquid crystal display element.[6] Anion recognition phenomenon was observed by Kondo and Unno in the presence of disiloxane-1,3-diol.[7] Gunji and co-workers used 1,3-diphenyldisiloxane as a building block of silsesquioxanes.[8] Narumi and Miyano reported the use of disiloxane to prepare bridged calix[4]arenes.[9] Napier used disiloxanes as cross-coupling partner in Hiyama-type coupling reaction with aryl halides.[10] Marciniec efficiently used divinyl-substituted silanes and disiloxanes in cross-metathesis in the presence of Grubbs catalyst.[11]

The general strategy to efficiently generate disiloxanes is via hydrosilanes. Hydrolytic oxidation of hydrosilanes in the presence of cationic oxorhenium catalyst provides disiloxanes.[12] Matsuo and Kawaguchi observed the formation of disiloxane from CO_2 and hydrosilanes using zirconium–borane complexes.[13] Chojnowski et al. used tris(pentafluorophenyl)borane as Lewis acid catalyst to produce disiloxanes via coupling reaction of hydrosilanes with alkoxysilanes.[14] Lewis acids were further utilized as catalyst in the synthesis of symmetrical disiloxanes via aerobic oxidation of hydrosilanes.[15] Schubert recently reported the use of transition-metal catalyst to generate disiloxanes from hydridosilanes.[16]

In our recent report, we discovered a novel sol-gel polycondensation of tetraethoxysilane (TEOS) to silica using Meerwein's reagent (MR)[17] in acetonitrile (MeCN) solvent.[18] We extended our work on MR and successfully achieved various fluorosilanes from alkoxysilanes via nucleophilic fluorination to the silicon centre (S_N2–Si) in excellent yields (Scheme 1).[19] Here, in this work we suppressed the effect of fluoride ion by using K_2CO_3 as an additive and demonstrated the synthesis of various symmetrical disiloxanes from their corresponding monoalkoxysilanes (Scheme 1). We further propose the possible reaction mechanism of alkoxysilanes condensation. To our knowledge this is the first report of MR-assisted alkoxysilanes condensation to corresponding symmetrical disiloxanes proceeding via silyloxonium intermediate.



Scheme 1 MR-Mediated symmetrical disiloxane synthesis

In our present approach, the primary concern was to overcome the problem of unexpected nucleophilic substitution of fluoride ion to the silicon center and completely suppress the formation of fluorosilanes. Consequently, we first examined various additives that will serve as a fluoride ion inhibitor (see Table S1 in the Supporting Information). We have used (4-bromophenyl)ethoxy[di(prop-2-enyl)]silane (**1a**)[20] as a model substrate and examined various alkali metal carbonates like Li_2CO_3, Na_2CO_3, K_2CO_3, and Cs_2CO_3 as additives. However, K_2CO_3 was found to be the best additive, affording disiloxane **2a** in high yield without the formation of fluorosilane **3** as a side product.

Table 1 illustrates optimization of mediator for the synthesis of disiloxane **2a** under various reaction conditions including equivalent of mediator, temperature and solvent.[21]

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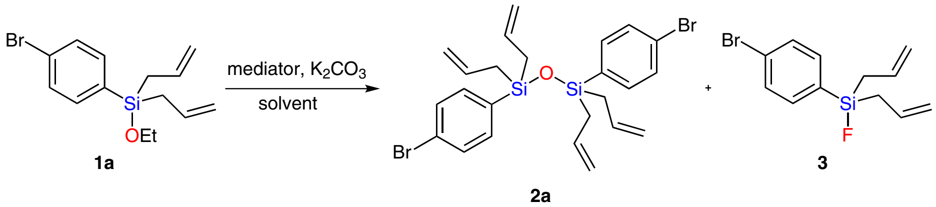
Initially, we performed a blank reaction in the absence of mediator in MeCN. This reaction did not provide any product even after 24 hours of stirring at 100 °C (entry 1). Astonishingly, the same reaction in the presence of Me_3OBF_4 under identical conditions reached to completion within 1.5 hours to give exclusively disiloxane **2a** in high yield (90%, entry 2). Although entry 3 with 0.1 equivalent of Me_3OBF_4 provided traces of disiloxane **2a**, entries 4 and 5 with 0.25 equivalent and 0.5 equivalent of mediator improved the yields of disiloxane **2a** to 29% and 54%, respectively. Comparison of entry 2 with entries 3–6 indicates that both the mediator and additive were essential to achieve excellent yields of disiloxane **2a**. Particularly, entry 6 with <1.0 equivalent of K_2CO_3 is unable to inhibit the naked fluoride ion attack to the silicon center which consequently leads to undesired fluorosilane **3** in 80% yield. Entry 7, with two-fold excess of K_2CO_3 afforded disiloxane **2a** in 91% yield. The use of Et_3OBF_4 instead of Me_3OBF_4 also showed favorable results with the formation of disiloxane **2a** (90%, entry 8). The change in counteranion from BF_4 to PF_6 did not adversely affect the reaction and provided excellent yield of disiloxane **2a** (91%, entry 9). Reaction temperature was found to be one of the important parameters to successfully achieve disiloxane in high yields. Although the reaction carried out at 25 °C failed to provide disiloxane **2a**, at 50 °C it reached

Table 1 Symmetrical Disiloxanes Synthesis under Various Reaction Conditions[a]



Entry	Mediator (equiv)	Solvent	Time (h)	Yield (%)[b] 1a	2a	3
1	no mediator	MeCN	12	91	–	–
2	Me_3OBF_4 (1.0)	MeCN	1.5	–	90	–
3	Me_3OBF_4 (0.10)	MeCN	12	90	trace	–
4	Me_3OBF_4 (0.25)	MeCN	12	66	29	–
5	Me_3OBF_4 (0.50)	MeCN	12	41	54	–
6[c]	Me_3OBF_4 (1.0)	MeCN	0.5	–	12	80
7[d]	Me_3OBF_4 (1.0)	MeCN	1.5	–	91	–
8	Et_3OBF_4 (1.0)	MeCN	1.5	–	90	–
9	Et_3OPF_6 (1.0)	MeCN	2	–	91	–
10[e]	Me_3OBF_4 (1.0)	MeCN	12	91	–	–
11[f]	Me_3OBF_4 (1.0)	MeCN	12	–	89	–
12[g]	Me_3OBF_4 (1.0)	MeCN	0.17	–	18	67
13	Me_3OBF_4 (1.0)	toluene	2	trace	6	80
14	Me_3OBF_4 (1.0)	1,4-dioxane	2	–	–	91
15	Me_3OBF_4 (1.0)	*t*-BuOH	2	–	65	8
16	$ZnCl_2$ (0.25)	MeCN	12	91	–	–
17[h]	MeOTf (1.0)	MeCN	12	–	–	–

[a] Reactions were carried out on a 1.0-mmol reaction scale of (4-bromophenyl)di(prop-2-enyl)ethoxysilane (**1a**), Me_3OBF_4 (1.0 equiv), and K_2CO_3 (1.0 equiv) in MeCN (5.0 mL) at 100 °C.
[b] Isolated yield.
[c] K_2CO_3 (0.5 equiv) was used.
[d] K_2CO_3 (2.0 equiv) was used.
[e] Reaction was carried out at 25 °C.
[f] Reaction was carried out at 50 °C.
[g] Reaction was carried out at 125 °C.
[h] ^1H NMR showed a complex mixture.

completion after 12 hours to the desired product (entries 10 and 11). The reaction at 125 °C generated fluorosilane as a major side product due to enhanced nucleophilic fluorination (entry 12). Following our optimization studies, we next screened different solvents to find that pure MeCN was the best-performing medium.[22] Entries 13–15, with toluene, 1,4-dioxane, and *tert*-butyl alcohol provided 6%, 0%, and 65% of desired disiloxane **2a**, respectively. This behavior is presumably due to poor solubility of MR in the above solvents. The use of Lewis acid like zinc chloride did not furnish the desired disiloxane (entry 16).[23] Our attempt with methyl triflate as the conventional methylating agent failed to give disiloxane (entry 17).

With these optimized conditions, we proceeded to establish the scope of our protocol with various alkoxysilanes (Table 2).

Table 2 Symmetrical Disiloxanes Synthesis in the Presence of MR[a]

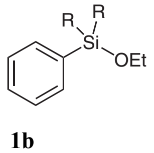
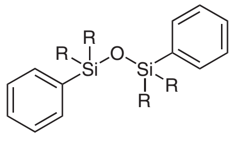
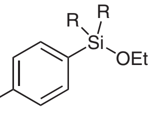
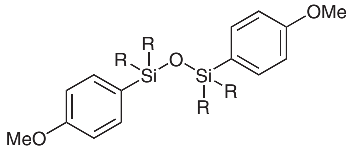
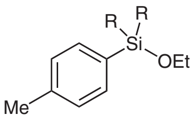
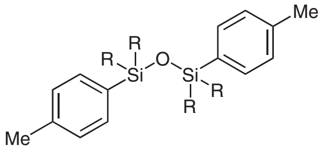
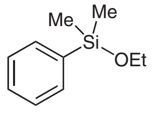
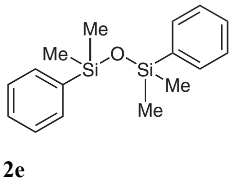
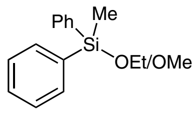
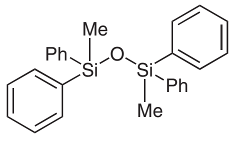
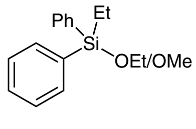
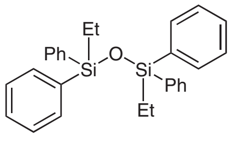
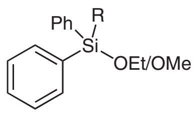
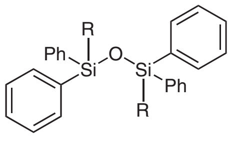
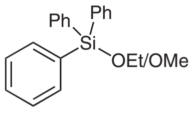
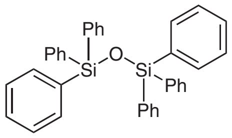
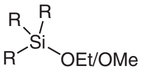
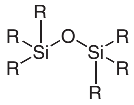
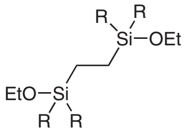
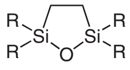
Entry	Alkoxysilane	Disiloxane	Product yield (%)[b]	
			Method A	Method B
1	 **1b**	 **2b**	85	86
2	 **1c**	 **2c**	91	88
3	 **1d**	 **2d**	88	89
4	 **1e**	 **2e**	78	82
5	 **1f/g**	 **4**	88:85	86:82
6	 **1h/i**	 **5**	89:88	88:86
7	 **1j/k**	 **6**	78:75	75:74

Table 2 Symmetrical Disiloxanes Synthesis in the Presence of MR[a] (continued)

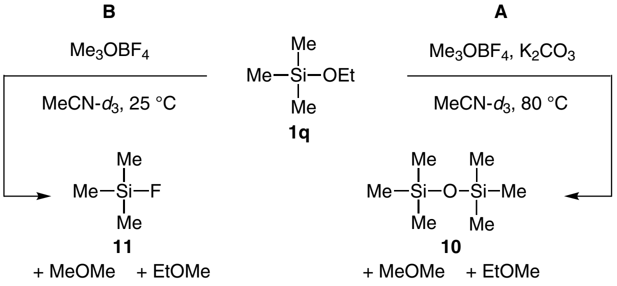
Entry	Alkoxysilane	Disiloxane	Product yield (%)[b] Method A	 Method B
8	 **1l/m**	 **7**	90:89	90:88
9	 **1n/o**	 **8**	72:75	72:74
10[c]	 **1p**	 **9**	65	67

[a] All reactions were carried out on a 1.0-mmol reaction scale of ethoxy-/methoxysilane **1** using K_2CO_3 (1.5 mmol) and Me_3OBF_4 (1.0 mmol, method A) and Et_3OBF_4 (1.0 mmol, method B) in MeCN (5.0 mL) at 100 °C and R = allyl.

[b] Isolated yield.

[c] Reaction was carried out at 80 °C for 4 h.

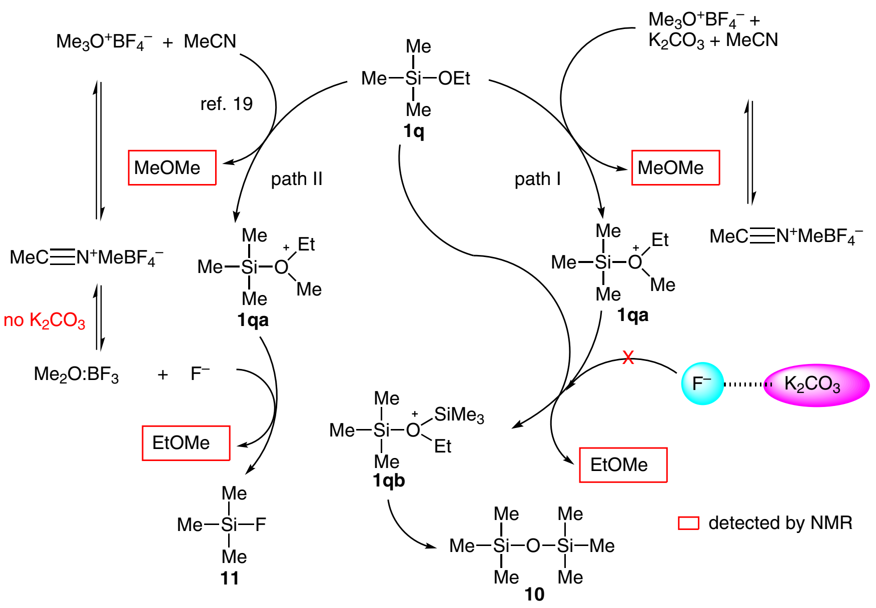
All the alkoxysilanes reacted smoothly with MR to yield the corresponding symmetrical disiloxanes with moderate to excellent yields. Diallylphenylethoxysilane subsequently reacted with Me_3OBF_4 and Et_3OBF_4 to generate disiloxane **2b** in 85% and 86% yields, respectively (entry 1). *para*-Substituted phenyl alkoxysilanes **1c** and **1d** also furnished excellent yields of novel symmetrical disiloxanes **2c** and **2d**, respectively (entries 2 and 3). Entry 4 with ethoxy(dimethylphenyl)silane (**1e**) afforded disiloxane **2e** in moderate yield. Both ethoxy- and methoxysilanes were found to react smoothly with MR giving moderate to excellent yields of disiloxanes (entries 5–9). Interestingly, 1,2-bis[ethoxydi(prop-2-enyl)silyl]ethane (**1p**) successfully furnished a new cyclic disiloxane **9** in moderate yield (entry 10). In order to propose a plausible mechanism, additionally we performed two separate reactions in MeCN-d_3 (Scheme 2).



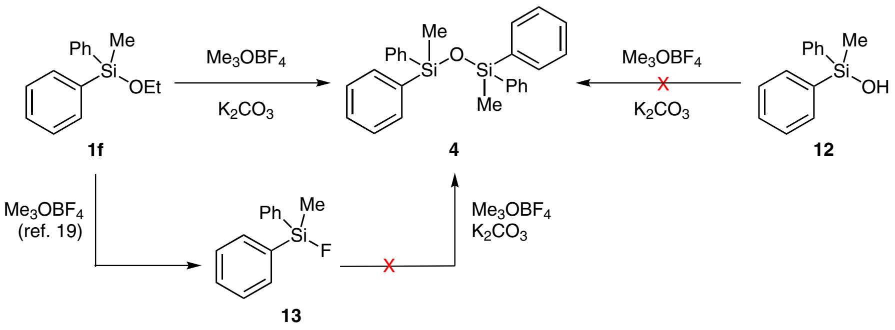
Scheme 2 Additional experiments

Reaction **A** with 1.0 equivalent each of ethoxytrimethylsilane (**1q**) and Me_3OBF_4 in the presence of K_2CO_3 (1.5 equiv) was run in MeCN-d_3 using NMR tube with J Young valve whereas, reaction **B** with 1.0 equivalent each of ethoxytrimethylsilane (**1q**) and Me_3OBF_4 in the absence of K_2CO_3 was run in MeCN-d_3 (Scheme 2). The formation of dimethyl ether and ethyl methyl ether together with hexamethyldisiloxane (**10**) in reaction **A** as well as that of dimethyl ether and ethyl methyl ether together with fluorotrimethylsilane (**11**) in reaction **B** were observed, respectively (see the Supporting Information). On the basis of these findings, a plausible reaction mechanism for MR-assisted disiloxane synthesis is outlined in the Scheme 3. In our previous reports, we proposed diethylsilyl oxonium and ethylmethylsilyl oxonium as intermediates for TEOS polycondensations with Et_3OBF_4 and Me_3OBF_4, respectively.[18] On the same ground and also from our present NMR studies, we propose silyloxonium intermediates **1qa** and **1qb**.

Me_3OBF_4 dissociates into methyl cation which presumably alkylates the ethoxy group of ethoxytrimethylsilane **1q** to form ethylmethyl silyloxonium intermediate **1qa** via path **I**. At a later stage, disilyl ethyloxonium **1qb** will be also generated by the nucleophilic attack of **1q** toward the silicon atom of **1qa**. In the absence of K_2CO_3 silyloxonium **1qa** will get attacked by naked fluoride ion to generate fluorotrimethylsilane **11** via path **II**.[19] In the presence of K_2CO_3, the nucleophilic attack by fluoride ion to the Si centre is inhibited, whereas the attack by ethoxy group with additional mole of ethoxysilane **1q** will be preferred. Independent reports by Shimada,[19] Sakurai,[24] Olah,[25] and Charpentier[26] on the detection of silyloxonium intermedi-



Scheme 3 Mechanistic proposal



Scheme 4 Additional control experiments

ates supports our claim of the proposed intermediates **1qa** and **1qb**.

Two additional control experiments were run to exclude the possibility of other reaction pathways (Scheme 4).[27] First, subjecting silanol **12** to the optimized conditions afforded no product. Second, the reaction of fluorosilane **13**[19] with Me_3OBF_4 (1.0 equiv) and K_2CO_3 (1.5 equiv) under identical conditions did not afford a disiloxane **4**, showing that a disiloxane is formed via silyloxonium intermediates as depicted in the Scheme 3.

In conclusion, a simple, convenient, efficient and economical method is developed to achieve various symmetrical disiloxanes using well-known and commercially available MR. Furthermore, we investigated our protocol with additional experiments to determine intermediates and provide insight into the reaction mechanism of condensation of alkoxysilanes to disiloxane. This protocol can be considered as an environmentally friendly process due to the absence of any toxic metal catalyst or hazardous chemicals. The current methodology is a good alternative to prepare symmetrical disiloxanes from the corresponding alkoxysilanes in excellent yields.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(21) **Typical Experimental Procedure for the Synthesis of Symmetrical Disiloxane (Table 1, entries 2, 8 and 9)**: A dry and nitrogen-flushed 10-mL screw-capped vial was charged with alkoxysilane (1.0 mmol), MeCN (5.0 mL) followed by the addition of K_2CO_3 (138.2 mg, 1.0 mmol) and Me_3OBF_4 (148 mg, 1.0 mmol) or Et_3OBF_4 (190 mg, 1.0 mmol) or Et_3OPF_6 (248 mg, 1.0 mmol). The reaction mixture was stirred at 100 °C for 90 min and quenched by dropwise addition of H_2O (1.0–2.0 mL). It was then diluted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhyd $MgSO_4$, and evaporated under reduced pressure. The crude mixture was purified by chromatography on silica gel (5% EtOAc–hexane as eluent) to give the symmetrical disiloxane.

1,3-Bis(4-bromophenyl)-1,1,3,3-tetra(prop-2-enyl)-disiloxane (2a): colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.87–1.93 (m, 8 H), 4.86–4.88 (m, 4 H), 4.90–4.94 (m, 4 H), 5.64–5.80 (m, 4 H), 7.37 (d, *J* = 8.4 Hz, 4 H), 7.49 (d, *J* = 8.4 Hz, 4 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 23.1, 115.3, 124.7, 130.9, 132.6, 134.8, 135.2. HRMS (FAB$^+$): *m*/*z* $[M - C_3H_5]^+$ calcd for $C_{21}H_{23}Br_2OSi_2$: 504.9654; found: 504.9651.

1,3-Diphenyl-1,1,3,3-tetra(prop-2-enyl)disiloxane (2b): colorless liquid. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.88–1.92 (m, 8 H), 4.86–4.94 (m, 8 H), 5.69–5.85 (m, 4 H), 7.32–7.40 (m, 6 H), 7.52–7.56 (m, 4 H). ^{13}C NMR (68 MHz, $CDCl_3$): δ = 22.3, 114.8, 127.7, 129.7, 133.2, 133.7, 136.3. HRMS (EI$^+$): *m*/*z* $[M]^+$ calcd for $C_{24}H_{30}OSi_2$: 390.1835; found: 390.1839.

1,3-Bis(4-methoxyphenyl)-1,1,3,3-tetra(prop-2-enyl)-disiloxane (2c): colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85–1.87 (m, 8 H), 3.82 (s, 6 H), 4.86–4.91 (m, 8 H), 5.73–5.80 (m, 4 H), 7.89 (d, *J* = 6.8 Hz, 4 H), 7.46 (d, *J* = 6.8 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.4, 55.0, 113.4, 114.6, 127.3, 133.4, 135.2, 160.8. HRMS (EI$^+$): *m*/*z* $[M]^+$ calcd for $C_{26}H_{34}O_3Si_2$: 450.2046; found: 450.2049.

1,3-Bis(4-methylphenyl)-1,1,3,3-tetra(prop-2-enyl)-disiloxane (2d): colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86–1.88 (m, 8 H), 2.35 (s, 6 H), 4.86–4.92 (m, 8 H), 5.73–5.80 (m, 4 H), 7.17 (d, *J* = 7.2 Hz, 4 H), 7.43 (d, *J* = 7.2 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 23.4, 114.6, 128.5, 132.7, 133.4, 133.7, 139.5. HRMS (EI$^+$): *m*/*z* $[M]^+$ calcd for $C_{26}H_{34}OSi_2$: 418.2148; found: 418.2152.

(22) The role of MeCN is currently unclear. For the reports on the formation of *N*-methyl- and *N*-ethylnitrilium ions with MeCN in the presence of MR, see: (a) Meerwein, H.; Laasch, P.; Mersch, R.; Spille, J. *Chem. Ber.* **1956**, *89*, 209. (b) Gordon, J.; Turrell, G. *J. Org. Chem.* **1959**, *24*, 269.

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(27) For detailed procedures, see the Supporting Information.