Single-Electron-Transfer Oxidation of Trifluoroborates and Silicates with Organic Reagents: A Comparative Study

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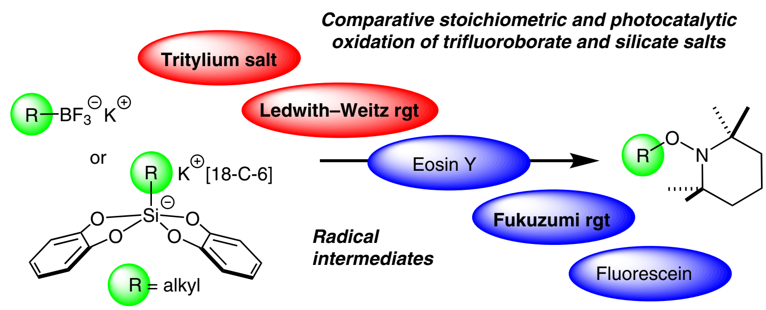

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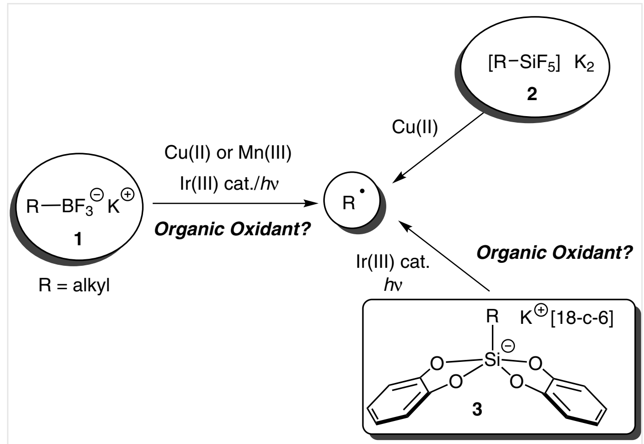
Abstract In this report, the single-electron-transfer oxidation of alkyl trifluoroborates and silicates has been studied. Different types of oxidation reagents have been examined, focusing on organic oxidants and particularly the use of dyes in photocatalytic oxidations. Both trifluoroborates and silicates could provide C-centered radicals when using a tritylium salt or the Ledwith–Weitz aminium salt. Photocatalysis with the Fukuzumi reagent suggested that trifluoroborates are more easily oxidized than biscatecholato silicates under these conditions.

Key words radicals, dyes, photocatalysis, trifluoroborates, silicates, single-electron transfer, oxidation

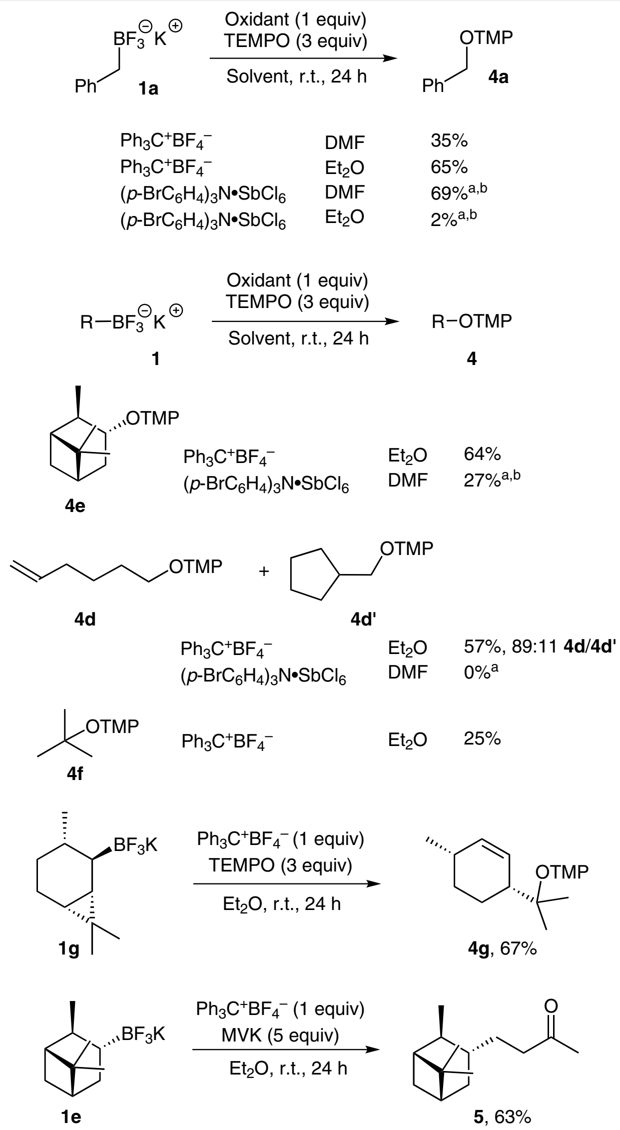
The single-electron-transfer (SET) oxidation of soft carbanions is a very versatile method to access to C-centered radicals.[1] Among possible candidates, ate complexes based for instance on boron, trifluoroborates being the most popular reagents, have already shown versatile reactivities for the generation of radicals.[2] To a lesser extent, hypervalent biscatecholato silicon species have recently emerged as very promising alternatives to the boron derivatives, avoiding any release of noxious fluorinated byproducts.[3] Their synthesis is known[4] yielding bench-stable compounds,[3] and their high electron density make them suitable candidates for oxidation. In this letter, we provide new elements on the SET oxidation of alkyl trifluoroborates **1** and silicates **3**, notably focusing on the use of organic oxidants (Scheme 1).



Scheme 1 Generation of alkyl radicals by SET oxidation of alkyl trifluoroborates and silicates

Our own endeavors in this domain started with the copper(II)-mediated oxidation of alkyl trifluoroborates **1** (Scheme 1),[5] a previously known reaction[6] but not exploited in radical chemistry. In conditions inspired from the related copper(II) oxidation of alkyl pentafluorosilicates **2** by Kumada and coworkers,[7] a series of alkyl (from primary to tertiary ones) trifluoroborates were engaged in oxidative processes. Postfunctionalization of the resulting radical intermediate was achieved by TEMPO spin trapping, allylation, and conjugate addition.[5]

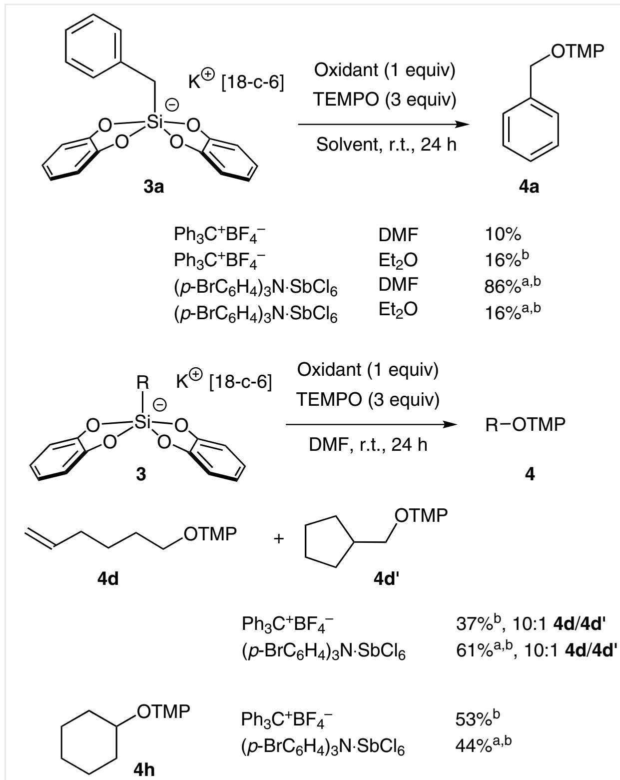
Following these preliminary reports, we wanted to investigate the use of nonmetallic oxidants. We initially showed that the Dess–Martin periodinane (DMP) could be efficiently used for the oxidation of trifluoroborates.[5] Tritylium tetrafluoroborate, an underexplored oxidant,[8] was also tested with a series of trifluoroborates (Scheme 2). For reasons which need to be elucidated, DMF did not appear as the best solvent for these oxidations. Gratifyingly, good yields of TEMPO adducts **4** were obtained in Et_2O as solvent with benzyl precursor (**4a** obtained), but also in secondary (**4e** and **4g**) and primary series (**4d**,**d′**).[9] Only *tert*-butyl precursor **1f** failed to give a good yield of product (**4f**, 25%), presumably for steric reasons. Interestingly, these conditions proved to be compatible with conjugate addition since methyl vinyl ketone (MVK) adduct **5** was isolated in satisfactory yield (63%).



Scheme 2 Stoichiometric oxidation of trifluoroborates by organic reagents. [a] Calculated yield from a mixture with $(p\text{-BrC}_6H_4)_3N$. [b] NMR yield.

We also examined the possibility of using Ledwith–Weitz aminium salt (oxidation potential: 1.06 V vs. SCE)[10] as SET oxidative agent of soft carbanions which, to the best of our knowledge, has never been accomplished. A strong solvent effect (Et_2O vs. DMF) was observed in the oxidation of **1a**, respectively 2% vs. 69% of **4a**. This led us to pursue our study in DMF with this oxidant. However, even in this solvent, the results proved to be much less satisfying compared to the ones obtained with the tritylium oxidant. Only 27% yield (**4e**) with the secondary substrate **1e**, and no TEMPO adduct in the primary alkyl series.

Next, we investigated the reactivity of biscatecholato pentavalent silicates **3**. These substrates are amenable to large-scale synthesis and can be rendered rock stable by complexing the potassium counteranion by the 18-c-6 crown ether.[3a] Benzyl silicate **3a** served as a preliminary probe (Scheme 3). It was submitted in Et_2O and DMF to one equivalent of tritylium and aminium. In both solvents, tritylium gave poor yields of **4a** (< 20%). However, the use of the aminium salt was more rewarding (86% of **4a** in DMF, 16% in Et_2O).[11] This oxidant proved to be competent in DMF for secondary and primary alkyl substrates giving, respectively, 44% of **4h** and 61% of **4d**,**d′**. Tritylium can also be used as a reliable alternative oxidant for the silicates **3**.

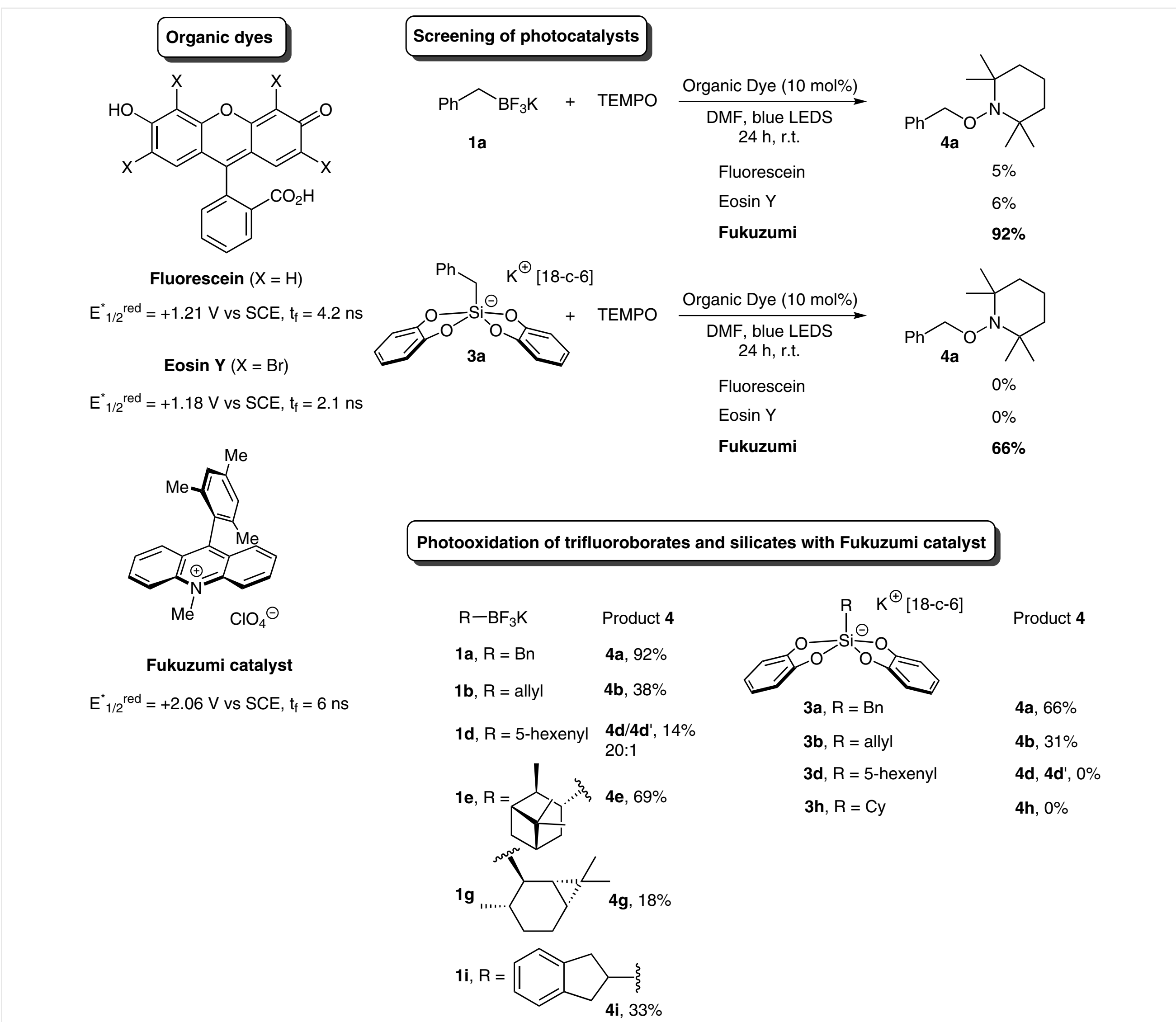


Scheme 3 Stoichiometric oxidation of biscatecholato silicates by organic reagents. [a] Calculated yield from a mixture with $(p\text{-BrC}_6H_4)_3N$. [b] NMR yield.

Because of its mild conditions and high substrate tolerance, visible-light photocatalytic oxidation was the obvious next step.[12] In the case of trifluoroborates, several groups have established the feasibility of this transformation using ruthenium(II)- or iridium(III)-based photocatalysts.[13] Of note, the resulting radicals can be engaged in photoredox/nickel dual catalysis.[13g–k] While pentafluorosilicates **2** failed in our hands to undergo any oxidation,[14] we recently showed that biscatecholato silicates constitute advantageous alternatives to the trifluoroborates since they allow upon iridium(III) {Ir[(dF(CF$_3$)ppy)$_2$(bpy)](PF$_6$)} photocatalysis the generation of very unstabilized primary radicals, also successfully engaged in photoredox/nickel dual catalysis.[3]

Herein, we wanted to examine the possibility to use organic dyes[12,15] as possible catalysts for the oxidation of these soft carbanions. Based on their frequent use, the following dyes were considered: eosin Y, fluorescein,[16] and Fukuzumi acridinium as catalysts.[17] A preliminary screening with benzyltrifluoroborate **1a** showed that the Fukuzumi catalyst was by far the best one (Scheme 4).

Similar behavior was observed for **3a**. Therefore we kept this catalyst for further testing. Both substrate families showed the same trend, that is, the less stabilized is the generated radical, the lower is the yield. Thus, for trifluoroborates, a gradual decrease of yield was observed from benzyl product **4a** to least stabilized primary radical adducts **4d**,**4d′**. One could argue that **1g**, a secondary substrate, should have given a better yield. But in that case, the final radical is a tertiary one which may undergo competitive pathways and lead to only 18% of **4g**. In the case of silicates **3**, only stabilized benzyl and allyl radicals could be generated (66% for **4a**, 31% for **4b**). Interestingly, allyltrifluoroborate **1b** and allylsilicate **3b** provided **4b** in close yields (38% vs. 31%). In sharp contrast, however, secondary trifluoroborates could give TEMPO adducts **4e** and **4i** contrary to secondary silicate **3h** (no **4h** formed).[18]



Scheme 4 Photocatalytic oxidation of trifluoroborates and biscatecholato silicates by organic dyes.

A direct correlation of these findings with redox potentials is not obvious. Oxidation potentials for trifluoroborates span from 1.1 V (benzyl et alkoxymethyl) to 1.83 V vs. SCE (primary and aryl)[13a,b,12s] while they have been determined to range from 0.61 V for benzylsilicate **3a** to 0.75 V vs. SCE for **3d**.[3] Some other key factors are at play in these reactions that we will try to uncover. In all the successful oxidations, TEMPO would act as a sacrificial oxidant to regenerate the photocatalyst and sustain the photocatalytic cycle in agreement with the literature data.[3a,13a,19]

In conclusion, this study shows the unprecedented oxidation of trifluoroborates and silicates with a tritylium or an aminium salt as stoichiometric oxidant to generate C-centered radicals. Photocatalytic oxidation could also be achieved with the Fukuzumi acridinium showing a higher reactivity of trifluoroborates than silicates in these conditions. Studies are ongoing to improve silicates photooxidation with organic dyes. The effect of the silyl substituents will notably be studied.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561337.

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(9) To a Schlenk flask was added potassium 5-hexenyl-1-trifluoroborate (**1d**) or potassium [18-crown-6] bis(catecholato)-5-hexenyl-1-silicate (**3d**, 0.3 mmol, 1 equiv), the oxidizing agent (0.3 mmol, 1 equiv), and TEMPO (0.9 mmol, 141 mg, 3 equiv). The Schlenk flask was sealed with a rubber septum, and evacuated–purged with vacuum–argon three times. Degassed Et_2O or DMF (3 mL) was introduced followed by two freeze–pump–thaw cycles. The reaction mixture was stirred at room temperature for 24 h under an argon atmosphere. The reaction mixture was diluted with Et_2O (50 mL), washed with H_2O or $NaHCO_3$ (2×), brine (2×), dried over $MgSO_4$, and evaporated under reduced pressure. The reaction residue was purified by flash column chromatography on silica gel to afford an inseparable mixture of **4d** and **4d′** in a 9:1 to 10:1 ratio and an overall yield (37–61%) depending on the oxidizing agent.
Compound **4d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.82 (m, 1 H), 5.01 (m, 1 H), 4.94 (m, 1 H), 3.73 (t, *J* = 6.1 Hz, 2 H), 2.07 (q, *J* = 7.2 Hz, 2 H), 1.55–1.20 (m, 10 H), 1.14 (s, 6 H), 1.09 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1, 114.5, 80.8, 59.9, 59.8, 39.7, 34.0, 33.2, 28.4, 25.9, 20.3, 17.3 ppm.
Compound **4d′**: ^{1}H NMR (400 MHz, $CDCl_3$): characteristic signal at δ = 3.64 ppm (CH_2O). ^{13}C NMR (100 MHz, $CDCl_3$): characteristic signal at δ = 76.7 ppm (CH_2O).

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(11) In comparison, oxidation with 1 equiv of $Cu(OAc)_2$ gave 45% yield of **4a** and with 1 equiv of DMP, 26% of **4a**.

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(18) To a Schlenk flask were added the organotrifluoroborate **1** or organosilicate **3** (0.3 mmol, 1 equiv), 9-mesityl-10-methylacridinium perchlorate as photocatalyst (0.03 mmol, 10 mol%), and TEMPO (0.66 mmol, 2.2 equiv.). The Schlenk flask was sealed with a rubber septum and evacuated–purged with vacuum–argon three times. Degassed DMF (3 mL) was introduced followed by two freeze–pump–thaw cycles. The reaction mixture was stirred under blue LEDs irradiation at room temperature for 24 h under an argon atmosphere. The reaction mixture was diluted with Et_2O (50 mL), washed with sat. $NaHCO_3$ (2×), brine (2×), dried over $MgSO_4$, and evaporated under reduced pressure. The reaction residue was purified by flash column chromatography on silica gel.

(19) The generated TEMPO *N*-oxide anion could be silylated or borylated. The resulting anionic products would be eliminated during the aqueous workup. We thank one of the referees for this suggestion.