

## II. Radical Formation

### A. Reaction Mechanism

Radical formation begins when  $\text{SmI}_2$  coordinates with a substituent in a carbohydrate derivative (see Scheme 1), that is, when a carbohydrate derivative replaces a solvent molecule within the coordination sphere of samarium(II) iodide. Within this new complex an electron is transferred from  $\text{SmI}_2$  to the carbohydrate derivative to produce a radical anion. This radical anion dissociates rapidly to give a carbohydrate radical and an anion complexed with  $\text{SmI}_2$ . It is possible in some instances that the radical anion never actually forms; instead, the bond between the carbohydrate and the functional group breaks during electron transfer.<sup>3</sup> [Section II.C.3 of Chapter 3 in Volume I contains additional information about samarium(II) iodide and the complexes it forms.]

### B. Effect of HMPA

Reaction with  $\text{SmI}_2$  typically is conducted in tetrahydrofuran (THF). Adding the cosolvent hexamethylphosphoramide (HMPA) to the reaction mixture dramatically increases the rate constant for samarium(II) iodide reaction.<sup>10,11</sup> Since the redox potential ( $E^\circ$ ) of  $\text{Sm}^{2+}/\text{Sm}^{3+}$  increases from -1.33 V to -2.05 V with the addition of four equiv of HMPA to a THF solution of  $\text{SmI}_2$ ,<sup>12</sup> the rate enhancement brought about by added HMPA can be attributed to the substantially increased ability of  $\text{SmI}_2$  to donate an electron. (Addition of HMPA beyond four equivalents does not further increase reaction rates.<sup>10</sup>)

One explanation for the effect of HMPA on the reactivity of  $\text{SmI}_2$  is based on the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals pictured in Figure 1.<sup>13</sup> (In the reaction represented in this diagram it is assumed that the substrate is a phenyl sulfone.) When HMPA complexes with  $\text{SmI}_2$ , it raises the HOMO energy of the resulting complex and, in so doing, reduces the energy required for electron transfer to the  $\sigma^*$  orbital (LUMO) of the sulfone (Figure 1). This energy reduction translates into a larger rate constant for reaction. HMPA also increases the rate of reaction of  $\text{SmI}_2$  with halogenated compounds by elongating the carbon-halogen bond.<sup>11b</sup>

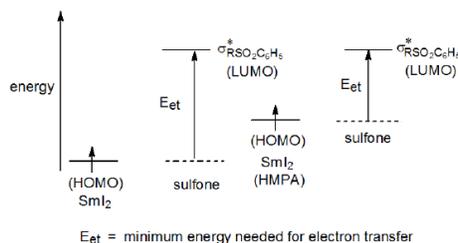
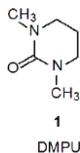


Figure1. Effect of HMPA on the HOMO energy of  $\text{SmI}_2$

Radical formation by reaction of samarium(II) iodide with carbohydrate derivatives has been conducted under a variety of conditions.<sup>14–18</sup> In addition to HMPA, other additives used are DMPU (**1**),<sup>14</sup> ethylene glycol,<sup>19</sup> and visible light.<sup>17</sup> Alternative conditions also include reaction with HMPA in the presence of a proton donor<sup>14–18</sup> or a catalytic amount of nickel(II) halide.<sup>9,17</sup> Motivation for trying new reaction conditions comes from the possibilities of gaining greater understanding of the reaction mechanism, improving product yields, developing greater stereoselectivity, and finding a promoter for  $\text{SmI}_2$  reaction that is safer than HMPA.



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