J. Am. Chem. Soc. **1996,** *118,* 261−262

Reactions of SmI_2 with Olefins: Mechanism and Complexation Effect on Chemoselectivity

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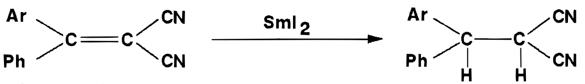
Received March 21, 1995
Revised Manuscript Received July 17, 1995

Radical anions of activated olefins may serve as good models for the transition state of Michael addition reactions.[1,2] In our search for a suitable reducing agent to effect the generation of these radical anions[3] our attention was drawn to SmI_2, which is well-known to have exceptional qualities as a single electron transfer reductant.[4,5] Our initial studies revealed, however, that SmI_2 displays an extremely interesting and multifaceted mechanistic chemistry of which very little is well understood.[6] We believe therefore that an exploration of the mechanistic chemistry of SmI_2 is justified on its own merits. Equation 1 outlines the reactions studied.



(1)

DP; Ar = Ph
MA; Ar = Anisyl

In a competition experiment, a mixture of MA and DP in THF was reacted with SmI_2 in the presence of a proton donor.[7,8] The product ratio was found to depend on the concentration of the latter. At low proton donor concentration, the selectivity is relatively high and approaches the thermodynamic stability ratio of the two radical anions.[9] As the proton donor concentration increases, the selectivity decreases, finally reaching a constant value. For MeOH and trifluoroacetic acid (TFA), at high concentration, the product ratio approaches unity (Figure 1). These results are consistent with a mechanism where the protonation competes with the equilibration of the radical anions. At the lower proton donor concentration range, the lifetime of the radical anions is long enough to permit equilibration resulting in a relatively high selectivity. As the proton donor concentration increases, the equilibration is suppressed, thus leading to a lower selectivity. Consistent with the suggested mechanism, the plateau for the much stronger acid TFA is achieved at a concentration (0.25 M) much lower than that of MeOH (2.5 M).

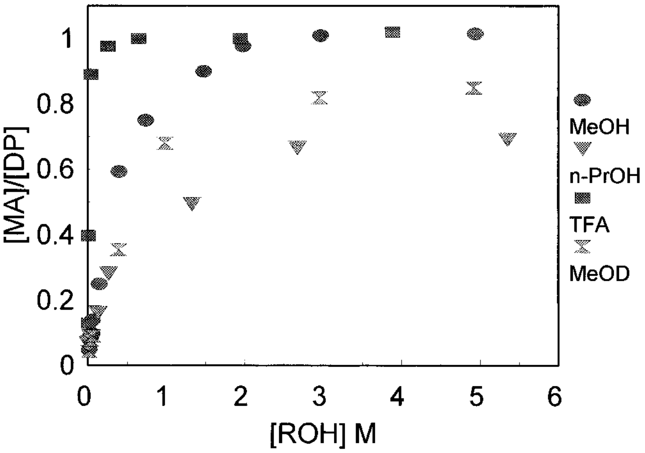


Figure 1. Ratio of the products derived from MA and DP as a function of the identity and concentration of the proton donor.

Surprisingly, for PrOH and MeOD, proton donors having kinetic acidity lower than MeOH, the plateau level is achieved at a product ratio below unity (0.7 and 0.8, respectively). The absence of selectivity at the plateau region for TFA and MeOH indicates a fast and unselective reaction of SmI_2 with the two substrates.[10] The lack of dependence of the selectivity on the "external" concentration of the various proton donors at the plateau regions, combined with the fact that for MeOD and PrOH plateau is achieved below unity, suggests that protonation occurs internally, probably within a triple complex such as $ROH{\cdot}SmI_2{\cdot}MA^{\bullet-}$ (or $ROH{\cdot}SmI_2{\cdot}DP^{\bullet-}$).[11] The triple complexes can either undergo equilibration (and gravitate to their thermodynamic distribution ratio) or undergo an internal protonation which will "lock" the product distribution. *The height of the plateau is determined by a competition between two processes: internal protonation within the triple complex and equilibration of the radical anions of the two substrates*. In the case of MeOH this protonation is fast enough to prohibit any appreciable equilibration. Slowing down the protonation rate by using acids with lower kinetic acidity (MeOD and PrOH) permits a certain extent of equilibration. The level of the plateau is, hence, determined by the relative rates of the two processes, internal protonation and equilibration. The lower the kinetic acidity, the lower will be the plateau level.

As shown in Scheme 1, the triple complex may be formed in a reaction between the alcohol and the $SmI_2{\cdot}$substrate ion

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(1) Hoz, S. *Acc. Chem. Res.* **1993**, *26*, 69.

(2) Gross, Z.; Hoz, S. *J. Am. Chem. Soc.* **1994**, *116*, 7489.

(3) The scope included Na in liquid ammonia, Na/naphthalenide, $Na_2S_2O_4$, electrochemistry (see also: Avaca, L. A.; Utely, J. H. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 971; *J. Chem. Soc., Perkin Trans. 2* **1975**, 161); all gave reduction of the double bond but were less amenable for detailed studies.

(4) Namy, J. L.; Girard, P.; Kagan, H. B. *New J. Chem.* **1977**, *1*, 5.

(5) (a) Molander, G. A. *Chem. Rev.* **1992**, *92*, 26. (b) Molander, G. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, pp 251. (c) Soderquist, J. A. *Aldrichimica Acta* **1991**, *24*, 15. (d) Kagan, H. B. *New J. Chem.* **1990**, *14*, 453. (e) Molander, G. A. In *Chemistry of the Carbon-Metal Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1989; Vol. 5, p 319. (f) Kagan, H. B.; Sasaki, M.; Collin, J. *Pure Appl. Chem.* **1988**, *60*, 1725. (g) Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. (h) Hasegawa, E.; Curran, D. P. *J. Org. Chem.* **1993**, *58*, 5008 and references cited therein.

(6) In spite of the wealth of literature in the rapidly developing field of SmI_2, it has been studied primarily from a synthetic perspective. To the best of our knowledge, the leading reference for mechanisms in SmI_2 chemistry is ref 14 below.

(7) Unless otherwise indicated, the total concentration of the substrate(s) was in the range of 0.012 M (depending on the concentration of the SmI_2 as determined by titration) and that of SmI_2 was 0.006 M. Two equivalents of SmI_2 is needed to fully reduce 1 equiv of the olefin.

(8) The reactions are very colorful. Immediately upon mixing of the reactants, the blue color of SmI_2 vanishes and a red color appears. This color gives way to a yellow one (probably Sm^{3+}) at a rate which depends on the concentration and acidity of the proton donor. In the experiments with TFA and DP the intermediate red color is not seen at all; in the presence of 2.5 M MeOH it persists for less than 1 s. After the completion of the reaction, the solutions were taken out of the glovebox, treated with CH_2Cl_2−water, and analyzed (reactants and products) by NMR and/or by HPLC. The agreement between the two methods was better than 5%. Products were stable with time.

(9) $E_{1/2}$ −1.08 and −1.16 V *vs* SCE for DP and MA respectively, unpublished results.

(10) The $E_{1/2}$ of SmI_2 in acetonitrile is −1.62 V *vs* SCE (Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852). According to this value there is a thermodynamic driving force of *ca.* 13 kcal/mol for the electron transfer reaction. This value is sufficient for a diffusion-controlled reaction. However, the intrinsic barrier due to the internal reorganization of the ligation sphere may be too high to enable such a fast process (Eberson, L. *Electron Transfer in Organic Chemistry*; Springer-Verlag: Berlin, 1987; Chapter 4).

(11) (a) Throughout this paper we use the term radical anion although other intermediates such as charge transfer complex or Grignard samarium may be the actual chemical species involved. (b) On the basis of other results it seems to us that, unlike the alcohols, TFA does not form complexes with samarium.

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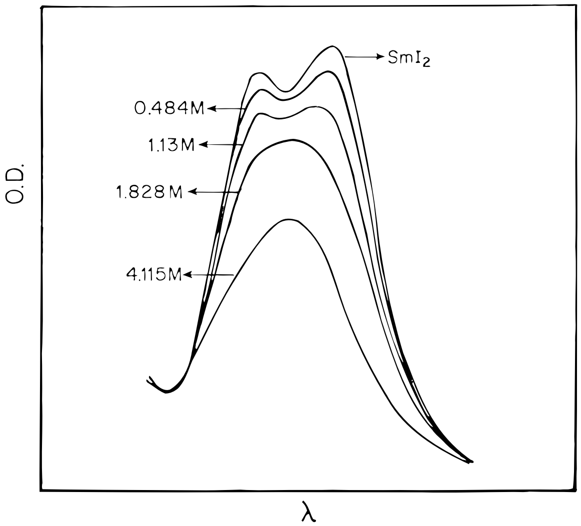
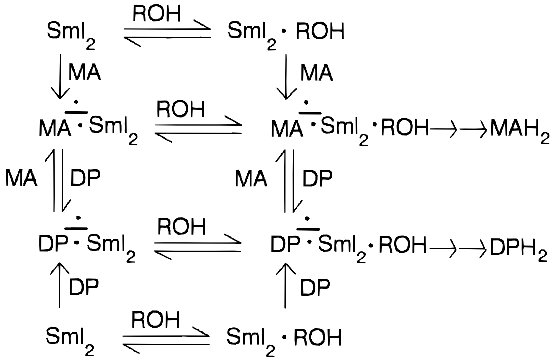


Figure 2. Variations of the UV spectrum of SmI_2 as a function of the concentration of the added MeOH. λ_{max}: for SmI_2, 616 and 552 nm; for the MeOH complex, 584 nm.

Scheme 1



pair (e.g., $SmI_2 \cdot MA^{\bullet -}$) as well as in the reaction of a $SmI_2 \cdot ROH$ complex with the substrate. The ability of SmI_2 to form a complex with ROH was spectroscopically demonstrated. Figure 2 shows the effect of added MeOH on the UV absorption spectra of SmI_2. Regression analysis of the data for MeOH and PrOH gave the complex formation equilibrium constants[12] of 0.56 and 0.22 M^{-1}, respectively. The kinetic implication of this complexation was demonstrated by using a variation of the experimental procedure. In the "normal" addition mode, the THF solution of SmI_2 was mixed with a THF solution containing the substrate and the proton donor. In the "inverse" addition mode, the substrate solution was added to a mixture of SmI_2 and the proton donor in THF.[13] Since formation of the triple complex $MeOH \cdot SmI_2 \cdot MA^{\bullet -}$ (or $DP^{\bullet -}$) retards the equilibration at the radical anion level, in an inverse addition experiment, the plateau is expected to be reached at a lower concentration of the alcohol. This was indeed observed, and the plateau was achieved at ca. 0.8 M rather than at 2.5 M MeOH.

Thus, the overall reaction mechanism involves two paths: one in which the free SmI_2 reacts with the substrate prior to the reaction with the alcohol; and a second in which the complex $SmI_2 \cdot ROH$ reacts with the substrate. *The relative contribution of each of these reaction paths is governed by the addition mode as well as by the reactants' concentration.*

Much to our surprise it was found that, in the inverse addition mode, *not only is the alcohol molecule bound firmly to SmI_2, but the isotopic identity of the labile proton is also largely retained*. This was demonstrated in the following experiments. When SmI_2 was added to a substrate solution containing equal amounts of MeOH and MeOD (1.25 M each), the H/D incorporation ratio into the benzylic position of DP was 1.2. Under the same conditions but having the MeOH in the SmI_2 solution and MeOD in the substrate solution, *the incorporation ratio increased to 7.15.*

In his 1981 review Kagan stated[14] that Sm in THF is bound to several molecules of THF. It would seem that the bond of Sm (especially the trivalent samarium) to alcohols (and their labile proton) is stronger than one would expect.[15] As we have shown, this feature of Sm can be used to affect chemoselectivity in reduction as well as in isotopic labeling reactions.

Acknowledgment. This study was supported by the Research Authority of Bar-Ilan University.

JA950937D

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[12] Calculations were based on a 1:1 complex composition. Correlation coefficients are higher than 0.994.

[13] The alcohol was preincubated with the SmI_2 usually for about a minute, the time necessary to complete the operations in the glovebox.

[14] Kagan, H. B. *Tetrahedron* **1981**, *37*, Suppl. 1, 175.

[15] A referee had sugggested that the samarium may insert into the O−H bond to give a hydride which does not easily exchange the proton. We have tried to computationally explore this avenue. However, although pseudopotentials are available for Sm, we found that, with programs such as Gaussian and Gamess, polyatomic gradient optimization is not possible with f-functions.