

Organic Chemistry

Some features of an SmI_2 – $(\text{Me}_2\text{N})_3\text{P}$ –THF system. Transformation of esters into dimethylamides

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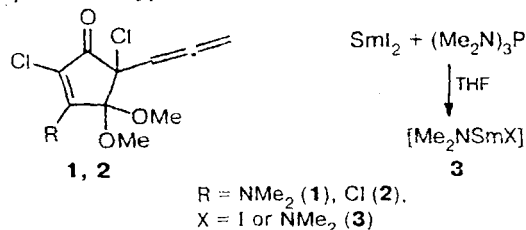
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Sm^{II} -intermediates generated upon addition of $(\text{Me}_2\text{N})_3\text{P}$ to a solution of SmI_2 in THF exhibit the properties of a single-electron reducing agent and an N-nucleophile. In particular, *N,N*-dimethylamides are formed from esters.

Key words: esters, samarium diiodide, tris(dimethylamino)phosphine, nucleophilic addition, *N,N*-dimethylamides.

An ether-soluble single-electron reducing agent SmI_2 ¹ is widely used for synthetic purposes.^{2,3} In THF, SmI_2 readily generates radicals from halogen derivatives, aldehydes, and ketones, which can be captured by olefinic or other appropriate groups. Organosamarium intermediates formed from SmI_2 can be involved in the Barbier, Reformatskii, and similar reactions. SmI_2 is an attractive reagent because, first of all, its reactions can be carried out under mild conditions and are highly chemo- and stereoselective. In some cases, multi-step "one-pot" transformations of substrates can be performed, which is extremely important in design of effective strategies for the synthesis of complex natural compounds. The instability (>-50 °C) of organosamarium intermediates derived from SmI_2 and organic iodides and bromides limits the use of the reagent. This drawback is eliminated if SmCp_2 (Ref. 4) and $\text{Sm}(\text{OTf})_2/\text{LiOTf}$ (Ref. 5) in THF are employed or if THF is replaced by tetrahydropyran (THP). In particular, allyl and benzyl organosamarium derivatives of SmI_2 are stable in THF at 0 to -15 °C.⁶ It should also be noted that the reducing ability of SmI_2 in THF is not always sufficient for efficient generation of carbon-centered radicals.^{2,3} The reducing ability of SmI_2 –THF is enhanced in the presence of $(\text{Me}_2\text{N})_3\text{P}$ ⁶ and other strong electron-donating N-ligands (DBU, TMG, or $\text{N}(\text{Et}_3)$).⁷

While studying reactions of allenylcyclopentenones (**1**) and (**2**) with SmI_2 in THF in the presence of $(\text{Me}_2\text{N})_3\text{PO}$, we faced the problem of the reactivity of SmI_2 . Mollander *et al.* widely used this system for intramolecular cyclizations of various functionalized ω -enones.^{8,9} In our case, however, cyclopentenones **1** and **2** were recovered unchanged when treated with an SmI_2 – $(\text{Me}_2\text{N})_3\text{PO}$ –THF system. The situation changes radically when the amide component ($(\text{Me}_2\text{N})_3\text{PO}$) of the above system is replaced by $(\text{Me}_2\text{N})_3\text{P}$. The starting compound **1** is rapidly consumed to produce the expected cyclization product, *viz.*, functionalized derivatives of cycloocta-2,6-dienone.¹⁰ These results provide unambiguous evidence for the formation of a stronger reducing system than the known ones. Taking into account a probable exchange reaction between SmI_2 and $(\text{Me}_2\text{N})_3\text{P}$, its active intermediates are organosamarium(II) compounds of type **3**.



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References

1. P. Girard, I. L. Namy, and H. B. Kogan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.
2. G. A. Mollander, *Chem. Rev.*, 1992, **92**, 29.
3. G. A. Mollander and C. R. Harris, *Chem. Rev.*, 1996, **96**, 307.
4. C. Bied, J. Collin, and H. B. Kogan, *Tetrahedron*, 1992, **48**, 3877.
5. S. I. Fukuzawa, R. Mutho, T. Tsuchimoto, and T. Hiyama, *J. Org. Chem.*, 1996, **61**, 5400.
6. V. Harda, J. Iranaga, and M. Vamaguchi, *J. Chem. Soc., Chem. Commun.*, 1989, 289.
7. W. Cabri, I. Candani, M. Colombo, L. Krantoi, and A. Bedesch, *Tetrahedron Lett.*, 1995, **36**, 949.
8. G. A. Mollander and J. A. Mckie, *J. Org. Chem.*, 1995, **60**, 872.
9. G. A. Mollander and C. Kenny, *J. Am. Chem. Soc.*, 1989, **111**, 8236.
10. N. A. Ivanova, A. M. Shainurova, L. V. Spirikhin, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2552 [*Russ. Chem. Bull.*, 1998, **47**, 2469 (Engl. Transl.)].
11. Hon and V. Wakatsuki, *J. Chem. Soc., Chem. Commun.*, 1994, 1205.
12. *Comprehensive Organic Chemistry*, Eds. D. Barton and W. D. Ollis, Vol. 2, Pergamon Press, Oxford—New York—Toronto—Sydney—Paris—Frankfurt, 1979.
13. L. Basset and C. R. Tomas, *J. Chem. Soc.*, 1954, 1188.

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