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The Reaction of Samarium(III) Iodide with Samarium Metal in Tetrahydrofuran. A New Method for the Preparation of Samarium(II) Iodide

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Samarium(III) iodide reacts with samarium metal in tetrahydrofuran under mild conditions to afford samarium(II) iodide in almost quantitative yield. A solution of samarium(II) iodide in tetrahydrofuran is prepared from samarium metal and iodine.

Divalent samarium possesses large reducing potential and is capable of reducing various functional groups. Kagan and his co-workers initially prepared a solution of samarium(II) iodide (SmI_2) in tetrahydrofuran (THF) and demonstrated that SmI_2 is extremely useful as a reducing agent in organic syntheses.[1] Moreover, other research groups have also found interesting reactions of SmI_2 with organic functional groups.[2,3]

The solution of SmI_2 used for practical organic syntheses is prepared almost exclusively by the Kagan's method using samarium metal and 1,2-diiodoethane (Scheme 1).[1,4] The reaction is generally considered to proceed through the

$$\mathrm{Sm} + \mathrm{ICH_2CH_2I} \longrightarrow \mathrm{SmI_2} + \mathrm{CH_2{=}CH_2} \qquad (1)$$

initial oxidative addition of samarium to 1,2-diiodoethane and subsequent β-elimination of the intermediate divalent organosamarium species. We anticipated that another route to SmI_2 might exist in addition to the generally accepted pathway. Thus, as shown in Schemes 2 and 3, SmI_2 generated through the pathway mentioned above may react with 1,2-diiodoethane to give samarium(III) iodide (SmI_3), which in turn may react with samarium metal to provide SmI_2.

$$2\ \mathrm{SmI_2} + \mathrm{ICH_2CH_2I} \longrightarrow 2\ \mathrm{SmI_3} + \mathrm{CH_2{=}CH_2} \qquad (2)$$

$$2\ \mathrm{SmI_3} + \mathrm{Sm} \xrightarrow{\mathrm{THF}} 3\ \mathrm{SmI_2} \qquad (3)$$

In order to demonstrate our hypothesis, particularly to ascertain that the latter reaction (Scheme 3) occurs under mild conditions, SmI_3 was allowed to react with samarium metal in THF. The characteristic green color of divalent samarium appeared even at room temperature, and the reaction proceeded smoothly at refluxing temperature. Generation of divalent samarium species was observed also in the reaction of samarium(III) chloride ($SmCl_3$) with samarium metal in the presence of a stoichiometric amount of NaI or KI. On the contrary, no trace of divalent samarium was generated on treatment of $SmCl_3$ with samarium metal in the absence of NaI or KI under similar conditions.

On the basis of these findings, we have exploited a new method for the preparation of SmI_2 using samarium metal and iodine. Thus, iodine (5.1 g, 20 mmol) was added with stirring to a mixture of samarium powder (ca. 40 mesh) (3.3 g, 22 mmol) and dry THF (200 ml). The initial mild exothermic reaction subsided within several min to form a yellow suspension of SmI_3. The mixture was then refluxed with stirring under nitrogen. The color of the suspension turned gradually from yellow to green and finally to intense blue-green. Refluxing overnight provided a solution (0.1 M/l) of SmI_2.5,6)

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2) For representative examples, see: N. R. Natale, Tetrahedron Lett., 23, 5009 (1982); T. P. Ananthanarayan, T. Gallagher, and P. Magnus, J. Chem. Soc., Chem. Commun., 1982, 709; G. A. Molander and J. B. Etter, Tetrahedron Lett., 25, 3281 (1984); G. A. Molander and G. Hahn, J. Org. Chem., 51, 1135, 2596 (1986); S. Fukuzawa, A. Nakanishi, T. Fujinami, and S. Sakai, J. Chem. Soc., Chem. Commun., 1986, 624; T. Tabuchi, J. Inanaga, and M. Yamaguchi, Tetrahedron Lett., 27, 601, 1195, 3891, 5237 (1986); T. Tabuchi, K. Kawamura, J. Inanaga, and M. Yamaguchi, ibid., 27, 3889 (1986); T. Imamoto, T. Takeyama, and M. Yokoyama, ibid., 25, 795 (1984); T. Imamoto, T. Takeyama, and H. Koto, ibid., 27, 3243 (1986).
3) Evans et al. reported novel carbon-carbon bond-forming reactions using a divalent organosamarium complex, $(C_5Me_5)_2Sm(THF)_2$. W. J. Evans, J. W. Grate, L. A. Hughes, H. Zhang, and J. L. Atwood, J. Am. Chem. Soc., 107, 3728 (1985); W. J. Evans, L. A. Hughes, D. K. Drummond, H. Zhang, and J. L. Atwood, ibid., 108, 1722 (1986).
4) Divalent samarium can be generated also by the other methods, although they require drastic conditions and/or unusual techniques for organic chemists. D. A. Johnson, Adv. Inorg. Chem. Radiochem., 20, 1 (1977); W. J. Evans, I. Bloom, W. E. Hunter, and J. L. Atwood, J. Am. Chem. Soc., 103, 6507 (1981); W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. J. Hunter, and J. L. Atwood, ibid., 107, 941 (1985).
5) The concentration of SmI_2 was determined by titration under nitrogen. The SmI_2 solution (ca. 5 ml) was transferred by the use of a syringe to a 30 ml two-necked flask. A solution (0.1 M/l) of iodine in dry toluene was added dropwise from a syringe until the color of the mixture turned from green to yellow.
6) A concentrated solution of SmI_2 was not obtained because of the low solubility of SmI_2 in THF. Instead, a slurry of SmI_2 was prepared in a similar procedure using a diminished amount of THF.

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