# Samarium(II) iodide promoted carbon–carbon bond fragmentation: a facile route to bridged eight membered rings and 1,3-disubstituted cyclopentanes

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**Samarium(II) iodide has been found to induce carbon–carbon bond cleavage in a number of bicyclo[2.2.1]heptane derivatives having a 1,4-dicarbonyl moiety under conditions at which the 1,4-dicarbonyl moiety undergoes intramolecular pinacol coupling.**

The development of reactions promoted by samarium(II) iodide is of continued interest in organic synthesis. After its introduction as a powerful single electron transfer agent, it has been extensively used in C–C bond formation reactions.[1] Reactions involving fragmentation of carbon–heteroatom bonds[2] like dehalogenation, deoxygenation and deamination utilising samarium(II) iodide have also been widely investigated. However, little attention has been focused on fragmentation of C–C bonds. In 1982, Magnus and co-workers[3] reported a SmI$_2$-promoted reductive cleavage of a C–C bond of a six membered ring in a steroidal system. Subsequently C–C bond cleavage induced by SmI$_2$ has been observed in cyclopropanes[4] and cyclopentanes.[5] However, in the latter case, reduction was found to compete favourably with ring cleavage. To date these are the only rings reported to undergo cleavage promoted by SmI$_2$.

Hoffmann and co-workers[6] have recently demonstrated that 1,4-diketones undergo smooth pinacol coupling with SmI$_2$ to produce cyclobutane-1,2-diols. Even pinacol formation was found to be facile to produce cyclobutane-1,2-diols incorporated in highly strained ring systems. In connection with our interest in the synthesis of propellanes[7] of various ring sizes from the diketone **1**, we anticipated that its intramolecular pinacol coupling, according to Hoffmann *et al.,* would proceed smoothly to provide an easy access to [3.3.2]propellanes. Herein, we report our findings on attempted pinacol coupling of the 1,4-diketone embodied in norbornane derivatives leading to facile C–C bond cleavage.

Treatment of a solution of the diketone **1** (Scheme 1) in THF–HMPA (8:1) containing a catalytic amount of Bu$^t$OH at room temperature with 2.5 equiv. of SmI$_2$ (0.1 M in THF) afforded a liquid in quantitative yield. Surprisingly the product was found to contain carbonyl groups as evidenced by an IR absorption at 1700 cm$^{-1}$, and a COMe singlet at $\delta$ 2.15 integrating for six protons and a carbonyl carbon at $\delta$ 210.5 by $^1$H and $^{13}$C NMR spectra,† respectively. All these data indicated that the reaction did not follow the usual course of intramolecular pinacol coupling. Careful analysis of the $^1$H and $^{13}$C NMR spectra of the product revealed its structure to be that of **2**. The presence of two sets of methine carbons at $\delta$ 43.8 and 55.1 in the $^{13}$C NMR spectrum of the product instead of only one set of methine carbons at $\delta$ 52.7 in the starting diketone **1** was a clear indication of the cleavage of the 2,6-bond. Conclusive evidence of the ring cleavage was obtained when the product epimerised on refluxing with NaOMe–MeOH to produce a mixture of the epimeric diketones **2** and **3** with the latter predominating. The stereochemical assignment of the ring cleaved product **2** was made by comparing the chemical shift of its bridgehead protons with that of the epimerised product. The bridgehead protons *syn* to the COMe group as in **2** must experience a deshielding effect of the carbonyl group. Thus, the diketone with the bridgehead protons appearing at $\delta$ 3.36 was assigned the structure **2** and the

major component of the epimerised product with bridgehead protons at $\delta$ 3.06 was assigned the structure **3**.

The cleavage of the C–C bond in **1** having a 1,4-dicarbonyl functionality suitably oriented for intramolecular pinacol type coupling is remarkable. Pinacol reaction of the diketone **1** would probably involve an enormous increase in strain energy of the strained norbornene system. Hence the initially formed diketyl radical, instead of coupling, undergoes homolysis of the C–C bond to produce a relatively less strained system.

However, reduction of the strain of the parent system by structural modification left the reaction course unaltered. For example, the saturated diketone **4** underwent smooth ring cleavage under the same conditions. Similarly, a mixture of the *endo* and *exo* diketones **6** produced a single ring cleaved product **7** in excellent yield. Even the simple norbornene diketone **8** produced exclusively the ring cleaved product **9**. Finally, the diketone **10** in which the carbonyl groups are oriented *anti* to each other also underwent ring cleavage to produce the highly functionalised cyclopentane derivative **11**.
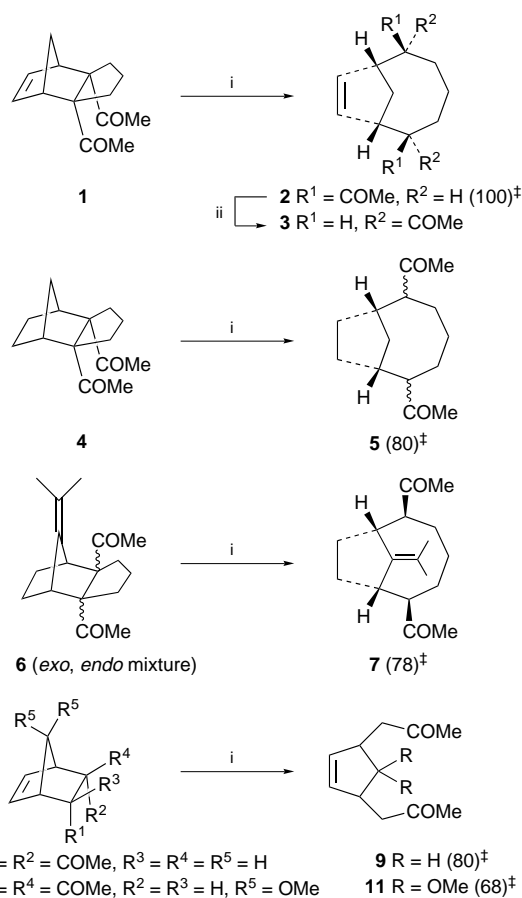


Scheme 1 *Reagents and conditions*: i, SmI$_2$, THF, HMPA, Bu$^t$OH, room temp., 2–3 min, then 0.1 M HCl; ii, 2% NaOMe, MeOH, reflux, 7 h

The samarium(II) iodide promoted cleavage of C–C bonds in norbornene derivatives may be useful for application in organic synthesis. For example, the cleavage of the diketones **1**, **4** and **6** to provide the bridged eight membered ring derivatives **2**, **5** and **7**, respectively, may provide a convenient route for entry into taxanes.[8] The 1,3-disubstituted cyclopentenes have previously served as precursors[9] to cyclopentanoid natural products.

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## Footnotes and References

1 G. A. Molander and C. R. Haris, *Chem. Rev.,* 1996, **96**, 307.
2 For a comprehensive account of carbon–heteroatom bond cleavage see: G. A. Molander, *Chem. Rev.,* 1992, **92**, 29; For some recent work see: G. A. Molander and P. J. Stengel, *J. Org. Chem.,* 1995, **60**, 6660; E. J. Enholm and J. A. Schreier, *J. Org. Chem.,* 1995, **60**, 1110.
3 T. P. Ananthanarayan, T. Gallagher and P. Magnus, *J. Chem. Soc., Chem. Commun.,* 1982, 709.
4 G. A. Molander and J. A. Mckie, *J. Org. Chem.,* 1991, **56**, 4112; R. A. Batey and W. B. Motherwell, *Tetrahedron Lett.,* 1991, **32**, 6649; R. Beerli, E. J. Bruner and H. J. Broschberg, *Tetrahedron Lett.,* 1992, **33**, 6449.
5 T. Honda, K. Naito, S. Yamane and Y. Suzuki, *J. Chem. Soc., Chem. Commun.,* 1992, 1218.
6 H. M. R. Hoffmann, I. Munnich, O. Nowitzki, H. Stucke and D. J. Williams, *Tetrahedron,* 1996, **52**, 11783; O. Nowitzki, I. Munnich, H. Stucke and H. M. R. Hoffmann, *Tetrahedron,* 1996, **52**, 11 799.
7 S. Ghosh, S. Saha Roy and A. Bhattacharya, *Synth. Commun.,* 1989, **19**, 3191.
8 K. C. Nicolaou, W. Dai and R. K. Guy, *Angew. Chem., Int. Ed. Engl.,* 1994, **33**, 15; A. N. Boa, P. R. Jenkins and N. J. Lawrence, *Contemp. Org. Synth.,* 1994, 47.
9 D. P. Curran and M. Chen, *Tetrahedron Lett.,* 1985, **26**, 4991.