Tetrahedron Letters,Vol.28,No.12,pp 1307-1308,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

DIVALENT SAMARIUM-INDUCED CYCLOPROPANATION OF LITHIUM ENOLATES. A ONE-POT SYNTHESIS OF CYCLOPROPANOLS FROM KETONES

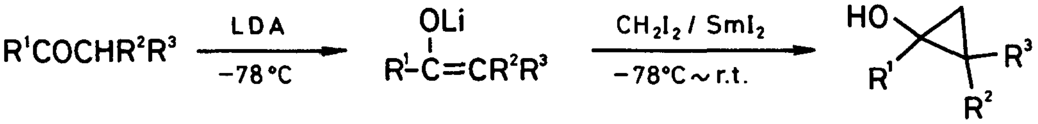
Tsuneo Imamoto* and Nobuyuki Takiyama
Department of Chemistry, Faculty of Science, Chiba University,
Yayoi-cho, Chiba 260, Japan

Summary: Lithium enolates, generated by deprotonation of ketones with lithium diisopropylamide, react with diiodomethane in the presence of SmI_2 to give cyclopropanols.

Despite its anticipated utility in organic synthesis, the cyclopropanation of metal enolates to cyclopropanols by the Simmons-Smith reaction has not yet been reported.1-3) We report herein the first example of the Simmons-Smith type cyclopropanation of metal enolates, and in addition wish to describe a one-pot synthesis of cyclopropanols from ketones.

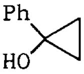
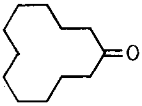
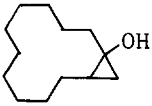
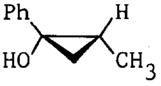
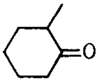
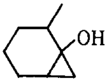
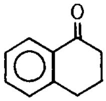
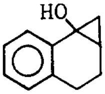
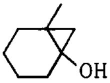
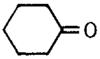
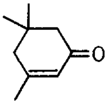
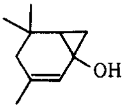
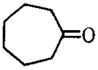
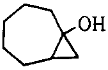
Previously, we reported that α-haloketones and 1,2-dibenzoylethane reacted with diiodomethane in the presence of samarium metal to give cyclopropanols.4) The reaction was considered to proceed through the Simmons-Smith type cyclopropanation of metal enolates (samarium enolates) which were generated by the reaction of α-haloketones or 1,2-dibenzoylethane with divalent samarium or samarium metal. In order to prove the pathway of the reaction, we tried the reaction of the lithium enolate derived from acetophenone5) with diiodomethane and samarium(II) iodide. The reaction proceeded rapidly at 0 °C to give 1-phenylcyclopropanol in 81% yield.

On the basis of this finding, a one-pot synthesis of cyclopropanols from ketones was tried. Thus, ketones were deprotonated with lithium diisopropylamide (LDA) at -78 °C, and the generated lithium enolates were treated with CH_2I_2/SmI_2 at -78 °C through to room temperature. As shown in Table 1, several cyclopropanols were synthesized in one-pot from ketones in moderate to good yields. This method may be applicable to the synthesis of other synthetically useful cyclopropanols by the employment of the established procedures for the regio- and stereoselective generation of lithium enolates.



General Procedure: A carbonyl compound (1 mmol) was added at -78 °C to a solution of LDA (1.2 mmol) in THF-hexane (3:1) (4 ml). After stirring for 1.5 h at the same temperature, a suspension of SmI_2, prepared from Sm (6 mg atom) and

Table 1. Synthesis of Cyclopropanols from Ketones

Entry	Ketone	Product	Yield a)	Entry	Ketone	Product	Yield a)
1	$PhCOCH_3$		58%	6			46%
2	$PhCOC_2H_5$		56%	7		 b)	59%
3			57%	8c)	"		62%
4			56%	9			62%
5			58%				

a) Isolated yield. b) A mixture (ca. 2:3) of stereoisomers. c) Lithiation was carried out under equilibrium conditions according to the procedure described in Ref. 8.

1,2-diiodoethane (5 mmol) in THF (10 ml),6,7) was added by the use of a pipet. Diiodomethane (2.5 mmol) was then added and the mixture was warmed with stirring to room temperature during 1 h. The reaction mixture was treated with aqueous HCl and extracted with ether. The combined extracts were dried over $MgSO_4$ and concentrated. The residual oil was subjected to preparative thin layer chromatography on silica gel to give the corresponding cyclopropanol.

References

1) For a representative review on the Simmons-Smith reaction: H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, Org. Reac., 20, 1 (1973).

2) Whitlock and Overman reported that the reaction of lithium enolates with the Simmons-Smith reagent prepared from diiodomethane and zinc-copper couple afforded α-methylated ketones. H. W. Whitlock, Jr. and L. E. Overman, J. Org. Chem., 34, 1962 (1969).

3) The Simmons-Smith reaction of silyl enol ethers has been reported by several research groups. S. Murai, T. Aya, and N. Sonoda, J. Org. Chem., 38, 4354 (1973); R. LeGoaller and J.-L. Pierre, Bull. Soc. Chim. Fr., 1973, 1531; G. H. Rubottom and M. I. Lopez, J. Org. Chem., 38, 2097 (1973); C. Girad and J. M. Conia, Tetrahedron Lett., 1974, 3327.

4) T. Imamoto, T. Takeyama, and H. Koto, Tetrahedron Lett., 27, 3243 (1986).

5) This lithium enolate was generated by the reaction of 1-phenyl-1-trimethylsiloxyethylene with butyllithium. G. Stork and P. F. Hudrlick, J. Am. Chem. Soc., 90, 4462 (1968).

6) P. Girard, J. L. Namy, and H. B. Kagan, J. Am. Chem. Soc., 102, 2693 (1980).

7) G. A. Molander and G. Hahn, J. Org. Chem., 51, 1135 (1986).

8) S. C. Welch and S. Chayabunjonglerd, J. Am. Chem. Soc., 101, 6768 (1979).

(Received in Japan 16 December 1986)