Pergamon

Tetrahedron Letters, Vol. 35, No. 16, pp. 2545-2548, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0360-A

Diiodosamarium, a Catalyst Precursor for Diels-Alder and Hetero Diels-Alder Reactions.

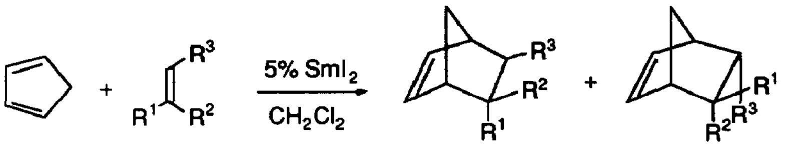
Pierre Van de Weghe, Jacqueline Collin*.

Laboratoire de Synthèse Asymétrique associé au CNRS, Institut de Chimie Moléculaire d'Orsay. Université Paris-Sud, 91405 Orsay, France.

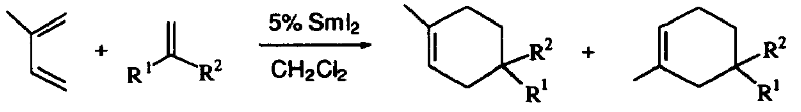
Abstract : SmI_2 presents catalytic activity for Diels-Alder reactions between cyclopentadiene or isoprene and various dienophiles, and for hetero Diels-Alder reactions.

Diiodosamarium is generally employed stoechiometrically as a reducing agent or to promote carbon-carbon bonds formation[1-4]. However, SmI_2 has been used as an *in situ* catalyst precursor for oxydo-reduction reactions, such as the Meerwein Ponndorf Verley Oppenauer or Tishchenko reactions[5-7], and for epoxide rearrangements[8]. We have previously shown that SmI_2 is the precursor of an effective catalyst for Michael and for aldolisation reactions involving enols silanes[9]. We now report the catalytic activity of diiodosamarium in Diels-Alder and hetero Diels-Alder reactions[10].

We have found that the Diels-Alder reactions between cyclopentadiene or isoprene and various dienophiles are performed in good yields by the use of 5 % mol eq. $SmI_2(THF)_2$ in suspension in CH_2Cl_2 (eq. (1), (2), Table). In a typical experiment, cyclopentadiene (10 mmol, 0.82 ml) and acrolein (5 mmol, 0.33 ml) were successively added to a blue suspension of $SmI_2(THF)_2$ (0.25 mmol) in 10 ml CH_2Cl_2 maintained at -30°C. The reaction mixture turned immediately yellow, and was hydrolyzed after 2h ; the product was extracted with ether and purified by column chromatography on silica gel with hexane/ethyl acetate : 80/20 as eluent (0.487 g, 80% yield, *endo* /*exo*, 80/20).

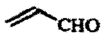
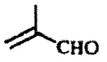
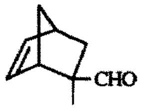
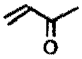
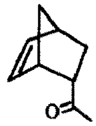
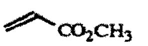
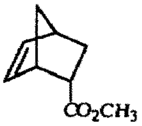
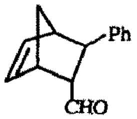
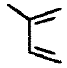
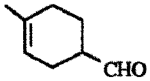
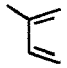
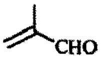
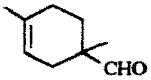
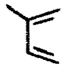
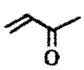
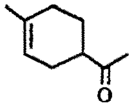


(1)



(2)

Table : Diels-Alder reactions catalyzed by SmI$_2$

Entry	Diene	Dienophile	T°C	t	Major product	*endo*/*exo*[a]	1,4/1,3[a]	Yield[b]
1			-30	2 h		80/20		80
2			-30	2 h		10/90[c]		80
3			-30	18 h		90/10		62
4			25	24 h		90/10		92
5			25	24h		80/20[d]		70
6			25	24 h			95/5	72
7			25	24 h			90/10	65
8			25	48 h			85/15	30

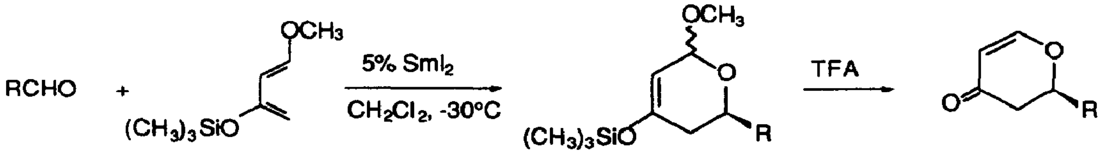
[a] Determined by GLC analysis and ^{1}H NMR. [b] Isolated yield %, (see text for experimental details). All compounds have been fully characterized spectroscopically by ^{1}H NMR, GC/MS, IR. [c] Aldehyde is in exo position in the major product. [d] Phenyl group is mainly in exo position.

Various dienophiles, such as α,β-unsaturated aldehydes, methyl vinyl ketone or methyl acrylate undergo cycloaddition reactions catalyzed by SmI$_2$. With cyclopentadiene the *endo* product is always the major isomer (entries 1, 3-5), except for methacrolein (entry 2) where the *exo* isomer is the major product, as usually observed when Lewis acid catalyses are used[15]. With isoprene the major adducts are 1,4-substituted cyclohexene (entries 6-8).

Compared to other lanthanides derivatives, SmI_2 displays a broad activity : lanthanide (III) chlorides do not catalyze the reaction of cyclopentadiene with acrolein or methyl acrylate, and Yb(fod)3 does not induce any reaction between cyclopentadiene and α,β-unsaturated ketones[11,16]. Although the adduct of methyl vinyl ketone with isoprene was isolated with a low yield (entry 8), samarium diiodide is more effective than ytterbium triflate, but less effective than scandium triflate[17]. Moreover the reactions of methacrolein and methyl vinyl ketone were run at -30°C with SmI_2 (entries 1,3) and they require a smaller amount of catalyst than with $Yb(OTf)_3$.

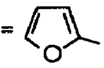
We also examined the reactions of aromatic aldehydes with Danishevsky's diene **1** in the presence of 5 mol % eq. $SmI_2(THF)_2$ in CH_2Cl_2 at -30°C. The condensation products obtained after 24 h were transformed into pyrones by treatment with trifluoroacetic acid (eq 3). In a typical experiment, 1-methoxy-3-(trimethylsilyloxy)-1,3-butadiene **1** (7.5 mmol, 1.46 ml) and benzaldehyde (5 mmol, 0.51 ml) were successively added to a blue suspension of 0.25 mmol of $SmI_2(THF)_2$ in 10 ml CH_2Cl_2 maintained at -30°C. The reaction mixture turned immediately yellow and was hydrolyzed after 24 h. After extraction with ether the crude product was added to a solution of trifluoroacetic acid (5.05 mmol, 0.39 ml) in THF (10 ml). After 2 h, the resulting pyrone was extracted with ether, washed with Na_2CO_3, purified by column chromatography on silica gel and eluted with hexane /ethyl acetate : 95/5 (0.56 g, 64% yield).

The yields observed for products **3** are similar to those reported for the reactions catalyzed by $Eu(fod)_3$ which require higher temperatures than those using SmI_2[18]. With cinnamaldehyde, the formation of product **3b** shows that the regioselectivity is similar to the one observed in the reactions catalyzed by $Eu(fod)_3$ or $Yb(fod)_3$[18,19].



(3)

1 2 3

	¹H NMR, GC, yield		Isolated yield
a R=Ph	**2a** 80%		**3a** 64%
b R=Ph−CH=CH	**2b** 98%	*cis/trans* 86/14	**3b** 66%
c R= 	**2c** 80%	*cis/trans* 70/30	**3c** 49%

The reactivity of SmI_2 in CH_2Cl_2 as a Lewis acid catalyst, previously examplified in Mukaiyama aldolisation and Michael reactions[9] has been extended to Diels-Alder and hetero Diels-Alder reactions. The change of colour from blue to yellow observed in all cases after the addition of the reactants suggests that the actual catalyst is trivalent[20]. Considering the mild reactions conditions and the small amounts required (5% mol eq), SmI_2 compares well with other lanthanide used as cycloaddition reaction catalysts. It can therefore be employed with success alternatively to $Eu(fod)_3$ or $Yb(fod)_3$. Further developments of these reactions and studies of asymmetric catalysts are currently under investigation .

Acknowledgements : We are indebted to Pr Kagan for constant support and fruitful discussions. One of us (P. W.) acknowledges the help of the Ministry of Research and Space (MRS) for a fellowship.

References

1 Namy J.L., Girard P., Kagan H.B., *New J. Chem.*, **1977**, *1*, 5-7.

2 Kagan H. B., Namy J. L., *Tetrahedron*, **1986**, *42*, 6573-6614.

3 Soderquist J.A., *Aldrichimica Acta*, **1991**, *24*, 15.

4 Molander, G.A., *Chem. Rev.*, **1992**, 29-68.

5 (a) Namy J.L., Souppe J., Collin J., Kagan H.B., *J. Org. Chem.*, **1984**, *49*, 2045-2049 ; b) Collin J., Namy J.L., Kagan H.B., *New. J. Chem.*, **1986**, *10*, 229-232.

6 Evans D.A., Rieger D.L., Jones T.K., Kaldor S.W., *J. Org. Chem.*, **1990**, *55*, 6260-6268.

7 Evans D.A., Kaldor S.W., Jones T.K., Clardy J., Stout T.J., *J. Am. Chem. Soc.*, **1990**, *110*, 7001-7031.

8 Prandi J., Namy J. L., Menoret G., Kagan H. B., *J. Organometal. Chem.*, **1985**, *285*, 449-460.

9 Van de Weghe P., Collin J., *Tetrahedron Lett.*, **1993**, *34*, 3881-3884.

10 Trivalent lanthanides catalyze hetero Diels-Alder reactions ($Ln(fod)_3$) and Diels-Alder reactions ($Ln(fod)_3$, $LnCl_3$, $Yb(OTf)_3$) and asymmetric inductions have been obtained in catalysis of hetero Diels-Alder ($Eu(hfc)_3$) and of Diels-Alder reactions (asymmetric ytterbium compound prepared from ytterbium triflate)[4,11-14].

11 Liao S., Yu S., Chen, Z., Yu D., Shi L., Yang R., Shen Q., *J. Mol. Cat.*, **1992**, *72*, 209-219 .

12 Kobayashi S., Hachiya I., Takahori H., Araki M., *Tetrahedron Lett.*, **1992**, *33*, 6815-6818.

13 Kagan H.B., Riant O., *Chem.Rev.*, **1992**, *92*, 1007-1019.

14 Kobayashi S., Hachiya I., Ishitani H., Araki M., *Tetrahedron Lett.*, **1993**, *34*, 4535-4538.

15 Pindur U., Lutz G., Otto C., *Chem.Rev.*, **1993**, *93*, 741-761.

16 Danishevsky S., Bednarski M., *Tetrahedron Lett.*, **1985**, *26*, 2507-2508.

17 Kobayashi S., Hachiya I., Araki M., Ishitani H., *Tetrahedron Lett.*, **1993**, *34*, 3755-3758.

18 Bednarski M., Danishevsky, *J. Am. Chem. Soc.*, **1983**, *105*, 3716-3717.

19 Castellino S., Sims J.J., *Tetrahedron Lett.*, **1984**, *25*, 2307-2310 and 4059-4062.

20 SmI_3 and $ROSmI_2$ have been recently reported to catalyze hydroboration of olefins and Meerwein-Ponndorf reactions[21,22].

21 Evans D.A., Muci A. R., Stürmer R., *J. Org. Chem.*, **1993**, *58*, 5307-5309.

22 Evans D.A., Nelson S.C., Gagné M.R., Muci A. R., *J. Am. Chem. Soc.*, **1993**, *115*, 9800-9801.

(Received in France 17 *December* 1993; *accepted* 15 *February* 1994)