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Intramolecular Diels-Alder Reaction of Chiral Silatrienes. Synthesis of 4-Sila-3,4,4a,5-tetrahydro-2*H*-isoquinolin-1-one.

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Abstract : The intramolecular Diels-Alder reaction of a pyran-2-one-6-carboxamide linked to a vinyl dienophile by a chiral silicon atom, followed by CO₂ elimination through a retro Diels-Alder reaction, afforded diastereoselectively a 4-silatetrahydroisoquinolin-2-one. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Chiral silicon compounds are rarely used in asymmetric synthesis and the reactions in which they are involved are, in general, poorly diastereoselective.¹ However excellent diastereoselectivities were reported for some reactions carried out at very low temperatures.² All these reports concern intermolecular reactions. Since intramolecular reactions could be more selective than intermolecular ones we studied intramolecular Diels-Alder reactions of silatrienes 1 and 2 in which an alkenyl substituent and a pyranone group ³ are linked by a chiral silicon atom.



The silatrienes **1a,b** and **2a,b** were prepared starting from the commercially available chlorobis(chloromethyl)methylsilane **3** as shown as follows.

$Me = R^{2} = R^{3} = CI \qquad R^{1} = R^{3}$	4 R ¹ = R, R ² = R ³ = Cl 7 R ¹ = R, R ² = OH, R ³ = O ₂ C-CH(CH ₃) ₂ 5 R ¹ = R, R ² = R ³ = OAc 8 R ¹ = R, R ² = Br, R ³ = O ₂ C-CH(CH ₃) ₂ 6 R ¹ = R, R ² = R ³ = OH 9 R ¹ = R, R ² = NH-CH ₂ Ph, R ³ = O ₂ C-CH(CH ₃) ₂
	$\mathbf{a} \mathbf{R} = \mathbf{CH} = \mathbf{CH}_2$ $\mathbf{b} \mathbf{R} = \mathbf{CH}_2 - \mathbf{CH} = \mathbf{CH}_2$
$3 \xrightarrow{a} 4a 75\% \xrightarrow{b} 5a 98\% \xrightarrow{c} 6a 93\% \xrightarrow{d} 57a 60\% \xrightarrow{g} 2a 89\% 7a \underbrace{c} 8a 98\% \xrightarrow{f} 9a 67\% \xrightarrow{g} 1a 93\% 4b 75\% 5b 88\% 6b 83\% 7b 65\% 2b 90\% 7b 8b 92\% 9b 72\% 1b 85\%$	
a) RMgCl, CuCN (5%), Et ₂ O, rt b) KOAc, NBu ₄ Br, TiO ₂ , 80°C c) LiAlH ₄ , Et ₂ O, -20°C to rt d) Lizzer from Condition many (CUL) CUCO CUL 2000 1 1^{4} CD DD CUL CUL	
b) Lipase from Canalaa rugosa, $(CH_3)_2CHCO_2CH_3$, 20°C, 1 d e) CBr ₄ PPh ₃ , CH ₂ Cl ₂ , rt f) PhCH ₂ NH ₂ , 100°C g) Pyran-2-one-6-carbonyl chloride ⁶ , NEt ₃ , CH ₂ Cl ₂ , 0°C	

Heating 2.5 hours at 140°C a dilute solution of carboxamide 1a in xylene afforded 4-silatetrahydro-2*H*isoquinolin-1-one 10⁷ in 78% yield as a mixture of two diastereomers (de 8 = 36%) which were not

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0040-4039/98/\$19.00 © 1998 Published by Elsevier Science Ltd. All rights reserved. PII: S0040-4039(98)00698-4 separated by silica gel chromatography and no trace of the tricyclic intermediate was observed. When the reaction was performed at 110°C for 1 day, the yield of the silaisoquinolinone 10 decreased to 42% and 4-siladihydro-2*H*-isoquinolin-1-one 11, probably formed by aromatisation of compound 10, was isolated (8% yield). The diastereometric excess of the compound 10 (de 8 = 36%) was similar to that of the compound obtained at 140°C.

Recently it has been reported that commercially available chromatography silica gel (EM Science # 60) promotes cycloaddition reactions of 2-pyrones with dienophiles at room temperature and prevents loss of CO_2 from the initial cycloadducts.⁹ Stirring, at room temperature during 7 days, a solution of carboxamide 1a in CH₂Cl₂ in the presence of chromatography silica gel 60 (SDS, 70-250 mesh) afforded the same silaisoquinolinone 10, resulting from the retro Diels-Alder reaction, in a 50% yield with a 40% diastereomeric excess.⁸



On the other hand the longer carboxamide homolog **1b** and pyran-2-one-6-carboxylates **2a** and **2b** were less reactive. After heating at 180°C during 1 day (toluene solutions, sealed tube) most part of these compounds remained untransformed. Further heating at 200°C (1 day) leads to complete transformation of these compounds and cycloaddition products were never detected.

In conclusion, the inverse electron demand Diels-Alder reactions of N-(vinylsilylmethyl)pyran-2-one-6carboxamide followed by CO_2 extrusion through a retro Diels-Alder reaction allows the preparation of still unknown 4-silatetrahydro-2*H*-isoquinolin-1-one. Further studies to maximize stereocontrol are pursued and the results will be reported in due course.

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