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Intramolecular Nucleophilic Catalysis. Stereoselective Hydrosilylation of Diketones and α-Hydroxyketones.

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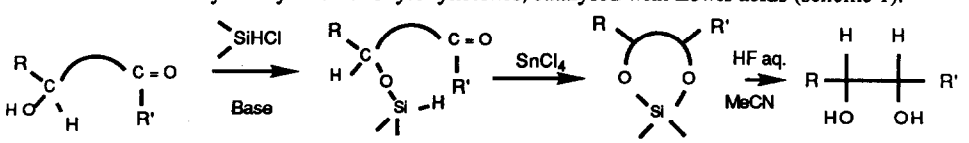
Abstract : Erythro diol skeletons are easily obtained in mild and neutral conditions, through the intra-molecular nucleophilic catalyzed hydrosilylation of diketones and hydroxy-ketones with an aminoaryltrihydrosilane.

INTRODUCTION

Over the past years, considerable effort has been devoted to the stereo-controlled synthesis of erythro and threo[2] diol systems, which are potent starting materials in the synthesis of natural products. The homogeneous asymmetric hydrogenation of 1,3- diketones with the BINAP-Ru(II) complex gives predominantly the threo 1,3-diols as (R)(R) in 100% e.e[1,3]. In contrast, substrate control in the reaction of 1,2-diketones favors the meso-diol formation, with the minor threo (S)(S) derivative. Treatment of β-hydroxyketones with tributyl borane and successively with sodium borohydride affords meso 1,3-diols in highly stereoselective manner[4]. Aluminium hydrides reduce α-hydroxyketones to a mixture of threo and erythro diols[5]. The stereoselectivity is minor with tributytin hydride[6], except in the case of benzoin.

Hydrosilanes have been extensively used[7-9] in our laboratory to selectively reduce carbonyl compounds, in the presence of nucleophilic catalysts (F^-, $RCOO^-$ or MeO^-). The stereochemistry of the reaction has been studied with prochiral aromatic ketones[10]. Hiyama described the highly diastereocontrolled reduction of α-functionalized ketones by means of activated hydrosilanes[11]. In contrast to the F^- catalyzed threo directed reduction, the ionic hydrogenation with the system R_3SiH / CF_3COOH produces mainly the erythro diols, with almost complete stereochemical control. The same reagents have been used to obtain aldols of both threo and erythro configurations[12]. Pentacoordinate hydridosilicates with optically active ligands have been used for the asymmetric reduction of carbonyl compounds[13].

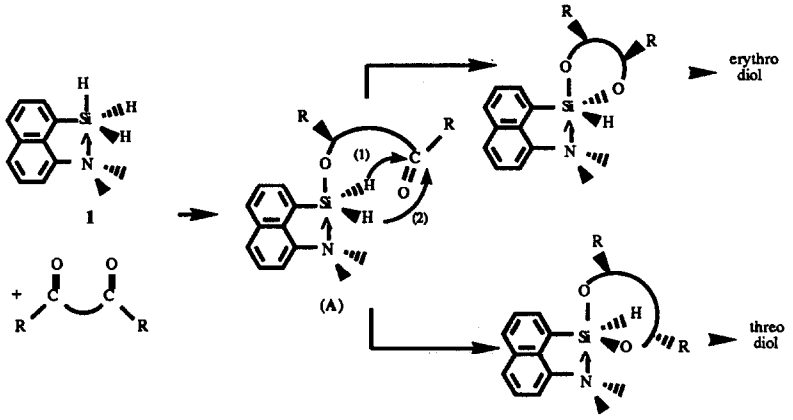
Davis has developed a new methodology[14] to selectively reduce β-hydroxyketones to threo 1,3-diols, based on the intramolecular hydrosilylation of silyloxyketones, catalysed with Lewis acids (scheme 1).



Scheme 1

Our recent interest in the use of pentacoordinated hydrosilanes as reducing agents[15,18] prompted us to develop such an approach to selectively reduce diketones and hydroxyketones to diols. In the present paper, we describe the hydrosilylation of bifunctional organic substances with **1**.

Our strategy is based on the enhanced reactivity in the second hydrosilylation step, since the three species involved, the Si-H group, the C=O function and the nucleophilic catalyst N→Si are in the same molecule. Furthermore, since the two remaining hydrogens attached to silicon in (A) are prochiral (scheme 2), we could expect some asymmetric induction in the second step.



Scheme 2

The coupling reactions with hydrosilanes occur easily, in mild and neutral conditions, with excellent yields. The different isomers of alkoxysilanes are easily identified by ^{29}Si NMR-DEPTC technique[19] (*vide infra*). After deprotection[20] with $LiAlH_4$, the major compounds are erythro diols. The results are explained in agreement with the usual models for asymmetric induction.

RESULTS

Reactions of pentacoordinated 1 with monofunctional carbonyl compounds.

We initially studied the reaction of **1** with monocarbonyl derivatives (Table 1). The products were analyzed by ^{29}Si NMR. The high values of coupling constants, $J(^1H\text{-}^{29}Si)$ 240-280 Hz, are characteristic of pentacoordinated species. With benzaldehyde, the two compounds of monohydrosilylation **2** and dihydrosilylation **3** are observed.

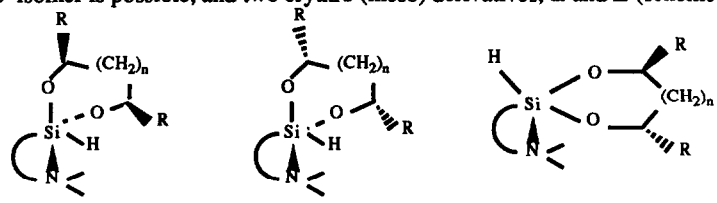
Table 1 : Hydrosilylation of monocarbonyl compounds with **1**.

Reactant	Solvent	Temp. (°C)	Time (h)	Product	^{29}Si NMR δ : ppm ($J(^1H\text{-}^{29}Si)$: Hz)	
2 PhC(O)H	CCl_4	77	24	**2**	-47.20	(t, 244)
				3	-44.62	(d, 272)
2 $CD_3C(O)CD_3$	CCl_4	77	48	**4**	-48.36	(t, 242)
$PhC(O)CH_2Ph$	CCl_4	60	40	**5**	-48.89	(t, 244)
				6	-66.51	(t, 266)
	CCl_4	40	24	**7**	-46.74 -47.48	(t, 240) (t, 239)
$CH_3C(O)COOEt$	CCl_4	25	6	**8**	-48.88	(t, 247)
$CH_3C(O)CH_2Cl$	CCl_4	77	24	**9**	-49.28	(t, 244)

With acetone, only the monoalkoxysilane is formed, even if an excess of organic compound is added. The reaction with deoxybenzoin gives a mixture of alkoxysilane **5** (60%) and enoxysilane **6** (40%). 2-methylcyclohexanone is reduced to **7** as a mixture of cis-trans silylethers in a 52/48 ratio. The chemioselectivity of the reaction has been checked with functional carbonyl compounds, ethyl pyruvate and chloro-2-propanone. The electroattractive group increases the reactivity of the unsaturated compound.

Hydrosilylation of difunctional carbonyl compounds

The pentacoordinated dioxasila-heterocycles, which are afforded in the reduction of α-hydroxyketones, 1,2-diketones and 1,3-diketones can exist, formally, in three isomeric forms: the threo- derived compound, **T**, , for which only one isomer is possible, and two erythro (meso) derivatives, **E** and **E'**(scheme 3).

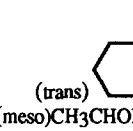


E (cis-erythro) **E'** (trans-erythro) **T** (threo)

Scheme 3

The cis-trans nomenclature of erythro compounds refers to the relative geometry of the R substituents with the remaining functional group at silicon. ^{29}Si NMR-DEPTC technique[19] is particularly useful, in the case of such compounds, to differentiate the various isomers. Authentic samples have been obtained via the exchange reaction with appropriate diols[18] (Table 2).

Table 2 : Reaction of diols with **1.**

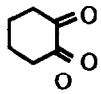
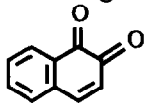
Diols	Conditions			**Product**	$\delta\ ^{29}Si$ (ppm)	
	Solvent	Temp. (°C)	Time(h)	Yield (%)	($J(^1H\text{-}^{29}Si)$, Hz)	
(meso)PhCHOH-CHOHPh	CCl_4	77	48	**10 E** (91)	-48.93	(284)
				E'	-54.33	(266)
 (trans)	CCl_4	77	48	**11 T** (87)	-50.91	(280)
(meso)$CH_3CHOH\text{-}CHOHCH_3$	CCl_4	70	24	**12 E** (68)	-49.53	(broad)
D(-)(-)$CH_3CHOH\text{-}CHOHCH_3$	CCl_4	70	40	**12 T** (79)	-49.86	(282)
$CH_3CHOHCH_2CHOHCH_3$ (meso)	CCl_4	77	48	**13 E** (94)	-53.34	(274)
				E'	-54.93	(295)
DL-$CH_3CHOHCH_2CHOHCH_3$	CCl_4	77	48	**13 T** (92)	-56.57	(279)

Starting from threo diols, the pentacoordinated dioxasila-heterocycles **T** present only one doublet in their ^{29}Si NMR-DEPTC spectra (large coupling constants with the remaining hydrogen, $J(^1H\text{-}^{29}Si)$ 260-295 Hz). With erythro (meso) diols, two ^{29}Si NMR doublets are observed. From the NMR data, we can conclude that both isomeric cis-erythro and/or trans-erythro derivatives are formed, but that method of identification does not allow to specify which is which. Therefore, these isomers will be equally quoted, in the paper, as **E** and/or **E'**.

Hydrosilylation of hydroxyketones and diketones with **1** gave the corresponding dioxasila-heterocycles

which have been analyzed as such by ^{29}Si NMR-DEPTC technique or by comparison with authentic samples after reduction with $LiAlH_4$, converting them to diols (see the experimental section). The results are presented in Table 3. The reactants were mixed at room temperature in stoichiometric amounts. The advancement of the reaction was checked by ^{1}H NMR. After complete disappearance of starting silane, the crude material was analyzed by ^{29}Si NMR. Deprotection of the siloxy derivatives with standard methods failed.[20]

Table 3 : Hydrosilylation of α-hydroxyketones and diketones with **1**.

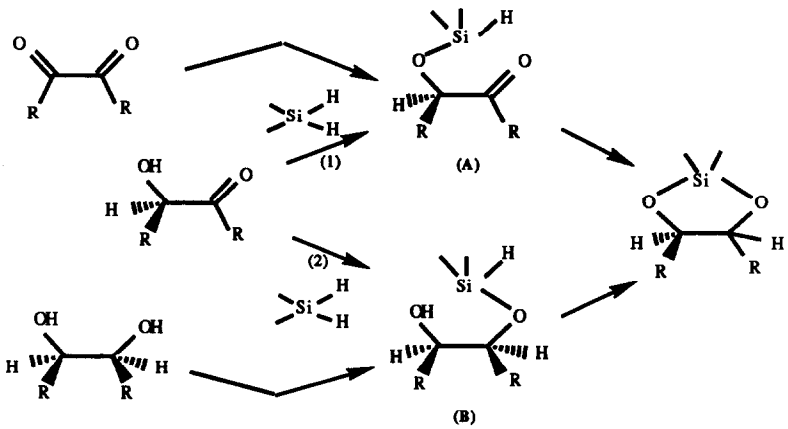
Reactant	Conditions			**Product**	$\delta\,^{29}Si$ (ppm)	E / T (%)
	Solvent	Temp. (°C)	Time (h)	Yield(%)	($J(^{1}H-^{29}Si)$, Hz)	
PhCH(OH)C(O)Ph	CH_2Cl_2	25	48	**10** (93)	-48.75 (283) E -54.20 (267) E'	<95/5>
$CH_3CH(OH)C(O)CH_3$	CH_2Cl_2	25	40	**12** (81)	-49.66 (284) E -49.86 (282) T -50.36 (278) E'	78/22
Ph-C(O)-C(O)-Ph	CH_2Cl_2	25	30	**10** (82)	-48.94 (284) E -54.40 (266) E'	<95/5>
Ph-C(O)-C(O)-CH_3	CH_2Cl_2	25	15	**14** (91)	-49.60 (280) E -49.87 (275) T -53.12 (282) E'	70/30
	CH_2Cl_2	77	24	**11** (71)	-49.10 (284) E -50.90 (294) E'	<95/5>
	CCl_4	77	24	**15** (95)	-51.65 (315) E -51.98 (315) E'	<95/5>
CH_3-C(O)-C(O)-CH_3	CH_2Cl_2	25	24	**12** (86)	-49.85 (286) E -50.14 (281) E' -50.65 (280) T	67/33
CH_3-CO-CH_2-CO-CH_3	CH_2Cl_2	60	24	**13** (88)	-53.49 (274) E -55.02 (294) E' -56.62 (280) T	85/15
t-Bu-CO-CH_2-CO-t-Bu	CH_2Cl_2	67	24	**16** (92)	-52.93 (298) T -60.19 (298) E -62.83 (282) E'	84/16

The coupling reactions of **1** with diketones and α-hydroxyketones have been performed in milder conditions than with simple ketones. The second withdrawing carbonyl group or the polar hydroxy group increases the reactivity of the C=O functionality. The most striking feature of the results in Table 3 is the preference for erythro diol derivatives as the major compounds. This selectively is observed in both cases, with α-diketones and β-diketones. The cyclic systems are highly selective with the only formation of meso diol skeletons (compounds **11E, 15E**). The results with 1,3-diketones offer a complementary method to that proposed by Davis, who obtained mainly the threo diols. The pentacoordinated hydrosilane **1** reduces 1,3-

diketones also preferentially to meso diols (after deprotection of the silicon compounds **13E, 16E**) with good yields. To check the incidence of steric effects on the course of the reaction, camphorquinone has been reduced with **1**. Only the monohydrosilylated compound, **17**, is obtained. The intramolecular hydrosilylation of the second carbonyl group is not possible in the experimental conditions .

DISCUSSION

The stereospecificity for asymmetric synthesis with carbonyl compounds having an asymmetric C atom directly bonded to a carbonyl has been ascribed to a change in the transition states[21-23]. Cram's cyclic model for steric control predicts the formation of major erythro (meso) diastereoisomers. A priori, the diketones or α-hydroxyketones we have studied fall in the predictive domain of this model. However, before to discuss the stereochemistry of the reactions, it would be crucial to know the chemioselectivity, at least for α-hydroxyketones. Which functional group reacts at first, the carbonyl or the hydroxyl group ?



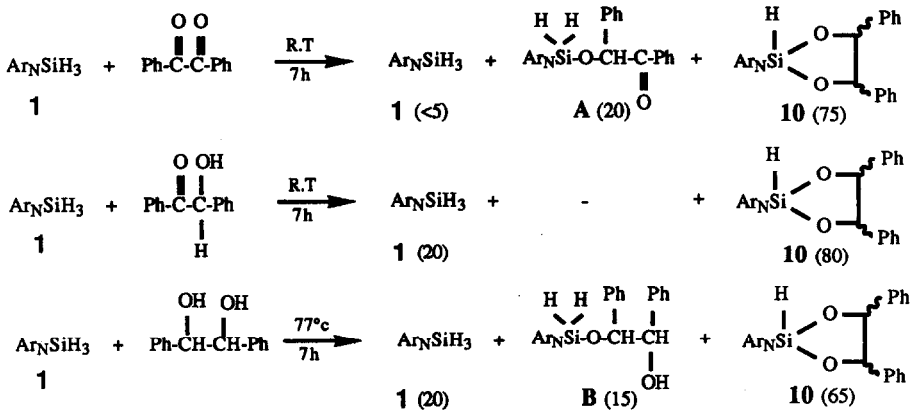
Scheme 4

The different possibilities are presented on scheme 4. If the first step is the initial exchange of the OH group, the overall stereochemistry depends on the geometry of the intermediate in the intramolecular reduction of the carbonyl. On the other hand, in the case of initial addition to the carbonyl, the stereochemistry is defined in the initial approach of the reducing agent relative to the bifunctional organic moiety, giving **B**. A possible answer to that question would come from the direct synthesis of species **A** or **B**, which are accessible in a separate way, starting from diketone or diol.

The course of the reactions with benzoin, benzil and hydrobenzoin has been checked by ^{29}Si NMR, DEPTC (scheme 5). Unfortunately, the experiments are not really very informative, since neither **A** nor **B** has been detected in the reaction of **1** with benzoin. Moreover, and this has been pointed out by one of the referees, kinetics are complex.

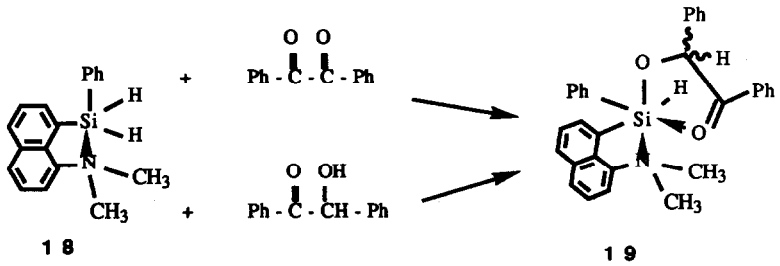
With benzil, the reaction has been checked after 7 hrs at room temperature. The mixture contains < 5% starting silane, 20% dihydrosilane and 75% **10E**, meso dioxasilacyclopentane (cis + trans). With benzoin, the reaction is not so advanced after 7 hrs at 25°C. We observe 20% of starting silane, 80% of meso dioxasilacyclopentane **10E** (cis + trans). There is no signal corresponding to dihydrosilane. With hydrobenzoin, the reaction does not proceed at room temperature. At 75°C, the reaction is completed in 48 hrs. After 7 hrs, the

mixture contains 20% of starting silane, 15% of dihydrosilane (**B**) and 60% of meso dioxasilacyclopentane, **10E**.



Scheme 5

If **A** was an intermediate in the reaction of **1** with benzoin, it would have a very short half-life in order to evade detection. In the reaction with benzil , **A** would presumably react with the same half-life, and as it would be formed more quickly the bulk of it would have more time to decay. Such a reasoning comes to the conclusion that neither **A** nor **B** is an intermediate in the reaction of **1** with benzoin, which is unlikely. Therefore,a better explanation may be that one or more of the reactions has complex and unusual kinetics.

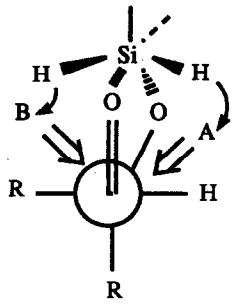


Scheme 6

The selectivity for initial dehydrocondensation of hydroxyl group in the α-hydroxyketone has been demonstrated with the more bulky dihydrosilane **18** (scheme 6). The hydrosilane which is formed in the coupling reaction with benzoin and benzil cannot cyclise, even under reflux for 48 hrs. The two reactions stop to the same monohydrosilane, **19** (^{29}Si NMR : δ - 43.3 ppm).

Numerous hexacoordinated silicon species are now well characterized[24]. A possible explanation of the enhanced reactivity of the pentacoordinated hydrosilanes would be to suppose the initial coordination of the carbonyl group[25] to silicon, to form an hexacoordinated species, as was demonstrated with silicates[7-9]. This species rearranges through hydrogen migration from silicon to carbon. The geometry of the hexacoordinate intermediate controls the stereoselectivity of the second step. As expected from molecular models meso (cis and/or trans) dioxasilacycloalkanes are formed. The hypothesis of stereochemistry directed by the formation of a chelated system ressembling the rigid Cram system leads to the same result (scheme 7).

" Cram rigid model "
A is favored → erythro (meso)



Scheme 7

CONCLUSION

The erythro selective reduction of difunctional carbonyl groups to diols via hydrosilylation with pentacoordinated aminoarylsilanes represents an alternative to previously reported methods. The reactions are performed in neutral conditions, without salt or external catalyst.

The selectivity observed in the intramolecular hydrosilylation catalyzed by nucleophiles is exactly opposite to that one observed by Davis[14], in which case intramolecular hydrosilylation, activated with Lewis acids gave preferentially anti-selectivity. Such a reversal behaviour depending on the catalyst has been already noted by Hiyama in the stereoselective reduction of keto groups with hydrosilanes[11,12].

The reduction of α-hydroxyketones has been interpreted by initial dehydrocondensation of the hydroxyl group followed by intramolecular hydrosilylation of the carbonyl moiety. The erythro selectivity is in accord with the formation of hexacoordinated intermediates.

EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of dry nitrogen, with use of dry and degassed solvents. ^{1}H NMR spectra were recorded on a BRUKER AW 60 or a Varian HA 100 spectrometer, using TMS as an internal reference. ^{29}Si NMR and ^{13}C NMR spectra were obtained with a BRUKER SP 250 AC or a BRUKER WP 200 SY. Mass spectra were recorded on a JEOL-DX 300 spectrometer (electronic impact at 70 ev). Elemental analyses were performed by the Centre de Microanalyse du CNRS at Montpellier.

Reaction of 8-dimethylamino-1-naphthylsilane 1 with the monofunctional carbonyl compounds

Benzaldehyde. A solution of **1** (1.2g, 6 mmol) and benzaldehyde (1.22 ml, 12 mmol) in 6 ml of CCl_4 was refluxed for 48 h with stirring. Evaporation of the solvent in vacuo, gave a mixture of two compounds $Ar_NSi(OCH_2Ph)H_2$, **2**, and $Ar_NSi(OCH_2Ph)_2H$, **3**, (Ar_N is 8-(dimethylamino)-1-naphthyl, which were characterized by ^{1}H NMR and ^{29}Si NMR (without further purification). ^{1}H NMR ($CDCl_3$) : δ 2.48(s, NMe_2), 4.88-5.94 (3s, SiH, OCH_2Ph, SiH_2); 7.50-8.30 (m, Ar-H); 9.75 (s, PhCHO). ^{29}Si NMR ($CDCl_3$) : δ -44.6 (**3**) $^1J(^1H\text{-}^{29}Si)$: 272 Hz (d); δ -47.20 (**2**), $^1J(^1H\text{-}^{29}Si)$: 244 Hz(t).

Acetone-d_6. A solution of **1** (1.2g, 6 mmol) and acetone-d_6 (0.86 ml, 12 mmol) in 6 ml of CCl_4 was stirred for 48h at 55°C. Evaporation of the solvent in vacuo gave $Ar_NSi[OCH(CD_3)]H_2$, **4**, as an oil, characterized by ^{1}H NMR, ^{13}C and ^{29}Si without further purification. ^{1}H NMR ($CDCl_3$) : δ 2.60(s, 6H, NMe_2), 4.08-4.40 [m, ^{1}H, $(CD_3)_2CHO$], 5.36(s, 2H, SiH_2), 7.23-8.50(m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 25.27(m, CD_3), 48.12(q, NMe_2), 65.31 [m, $(CD_3)_2\underline{C}HO$], 116.01-140.27 (m, Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -48.36 $J(^1H\text{-}^{29}Si)$: 242 Hz(t). The reaction was repeated with acetone in large excess at 25°C for 5 days

affording **4** in 82% yield. The product was characterized by ^{29}Si NMR ($CDCl_3$) : δ -48.42 J(^1H-^{29}Si) : 239 Hz(t).Analysis $C_{15}H_{21}NOSi$ requires C, 69.45; H, 8.16; N, 5.40; found C, 69,14; H, 8.21; N, 5.27.

Deoxybenzoin. The reaction was carried out as described above, giving a mixture of two monosubstituted products : $Ar_NSi(OCHPhCH_2Ph)H_2$, **5** ; ^1H NMR ($CDCl_3$) : δ 2.60(s, NMe_2, 2.94-3.10(m, $OCHPhCH_2Ph$), 5.10(s, SiH_2), 6.90-8.10(m, Ar-H), ^{13}C NMR ($CDCl_3$) : δ 45.62(q, NMe_2), 45.96(t, $PhCH_2CHO$), 77.14(d, $PhCH_2CHO$), 113.61-166.66(m, Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -48.89,J(^1H-^{29}Si): 244Hz(t). $Ar_NSi(OPhC{=}CHPh)H_2$, **6** ; ^1H NMR ($CDCl_3$): δ 2.60(s, NMe_2), 4.70(s, SiH_2), 4.95-5.30(m, OPhC=CHPh), 6.90-8.10(m, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 46.64 (q, NMe_2), 106.3 (d, OPhC=CHPh), 113.6-166.6(m, OPhC=CHPh; Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -66.5, J(^1H-^{29}Si) : 266Hz(t).

2-Methylcyclohexanone. A solution of **1** (1.2g, 6 mmol) and 2-methylcyclohexanone (0.72 ml, 6 mmol) in 6 ml of CH_2Cl_2 was refluxed for 24 h with stirring. The solvent was concentrated in vacuo, the residue was precipitated in pentane to give a mixture of cis- and trans-(2-methyl)cyclohexanoxysilane, **7**. ^1H NMR ($CDCl_3$) : δ 0.89-1.02(2d, 3H, $OCHC_5H_9C\underline{H}_3$), 1.38-2.20 (m, 9H, $OCHC_5\underline{H}_9CH_3$), 2.68(s, 6H, NMe_2), 3.00-3.98(2m, 1H, OCH), 4.92-4.96 (2s, 2H, SiH_2), 7.18-8.40 (m, 6H, Ar-H). ^{13}C NMR($CDCl_3$) : δ 15.21-45.72(m, $OCHC_5H_9C\underline{H}_3$), 48.28-48.42 (2q, NMe_2), 73.34-79.34 (2d, $O\underline{C}H$), 118.1-151.2 (m, Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -46.74, J(^1H-^{29}Si) : 240 Hz(t), -47.48, J(^1H-^{29}Si) : 239 Hz(t). Mass spectrum : m/e 313(M^+, 45), 216(M^+ -$C_6H_{10}CH_3$, 25), 200($Ar_NSiH_2^+$, 100), 185($Ar_NSiH_2^+$ -15, 3). Analysis $C_{19}H_{27}NOSi$ requires C, 72.79; H, 8.68; N, 4.47; found C, 73.04; H, 8.79; N, 4.36.

Reaction of 1 with chloro-2-propanone. A solution of **1** (1.0g, 5 mmol) and chloro-2-propanone (0.40 ml, 5 mmol) in 5 ml of CCl_4 was refluxed for 24 h with stirring; 3 ml of pentane were added, and the solvents were concentrated in vacuo. The product separated as an oil to give **9**, $Ar_NSi(OCHCH_3CH_2Cl)H_2$. Yield, 87%, ^1H NMR ($CDCl_3$) : δ 1.32-1.40(d, 3H, CH_3), 2.70(s, 6H, NMe_2), 3.50-3.65(m, 2H, CH_2Cl), 3.95-4.32(m, 1H, $OC\underline{H}CH_3$), 4.95(s, 2H, SiH), 7.22-8.33(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) δ -49.28 J(^1H-^{29}Si) : 244Hz(t). Mass spectrum m/e 292(M-H)$^+$, 100), 277[(M-H)$^+$ -15, 37], 200($Ar_NSiH_2^+$, 98), 185($Ar_NSiH_2^+$ -15, 62), 170($C_{12}H_7^+$, 47). Analysis $C_{15}H_{20}NOSiCl$ requires C, 61.31; H, 6.86; N, 4.77; found C, 62.14; H, 6.81; N, 4.42.

Reaction of 1 with ethylpyruvate. Ethylpyruvate (0.55 ml, 5 mmol) was added to a solution of **1** (1g, 5 mmol) in 5 ml of CCl_4. The mixture was stirred for 6 h at room temperature. Evaporation of the solvent gave **8**, $Ar_NSi[OCH(CH_3)COOEt]H_2$. ^1H NMR ($CDCl_3$) : δ 1.10-1.58(m, 6H, $OC\underline{H}CH_3$), $OCH_2C\underline{H}_3$). 2.60(s, 6H, NMe_2), 3.90-4.52(m, 3H, $OC\underline{H}CH_3$, $OC\underline{H}_2CH_3$), 4.80(s, 2H, SiH), 7.20-8.32(m, 6H, NMe_2), 3.90-4.52(m, 3H, $OCHCH_3$, OCH_2CH_3), 4.80(s, 2H, SiH), 7.20-8.32(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -48.88 J(^1H-^{29}Si) : 247Hz(t). Analysis $C_{17}H_{23}NO_3Si$ requires C, 64.32; H, 7.30; found C, 62.34; H, 7.19.

Reaction of 1 with α-hydroxyketones. *Benzoin.* A solution of **1** (1.2g, 6 mmol) and benzoin (1.1g, 6 mmol) in 5 ml of CH_2Cl_2 was stirred for 48 h at room temperature. 3 ml of pentane were added, the solvents were concentrated in vacuo. The product **10** separated as an oil; yield, 93%. ^1H NMR ($CDCl_3$) : δ 2.82(s, 6H, NMe_2), 5.12-5.50 (m, 2H, OCHPh), 5.62(s, 1H, SiH), 6.68-8.52(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -48.75 J(^1H-^{29}Si) : 283Hz(d), -54.20 J(^1H-^{29}Si) : 267Hz(d). Mass spectrum : m/e 411(M^+), 305(M^+ -PhCHO, 100), 199(Ar_NSiH^+). The diastereoisomers were identified by comparison of their ^{29}Si NMR spectra with those authentic samples.

3-Hydroxy-2-butanone. A solution of **1** (1.2g, 6 mmol) and 3-hydroxy-2-butanone (0.53g, 6 mmol) in 5 ml CH_2Cl_2 was stirred for 40 h at room temperature; 3 ml of pentane were added. The solvents were concentrated in

vacuo. The product **12** separated as an oil; yield, 81%. ^{1}H NMR ($CDCl_3$) : δ 1.08-1.40(2d, 6H, $OCHCH_3$), 2.25-2.88(4s, 6H, NMe_2), 3.64-4.60(m, 2H, CH_3CHO), 5.00-5.22(2s, 1H, SiH), 7.28-8.68(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -49.66 J(^{1}H-^{29}Si) : 284Hz(d), -49.86 J(^{1}H-^{29}Si) : 282Hz(d), -50.36 J(^{1}H-^{29}Si) : 278Hz(d). Analysis $C_{16}H_{21}NO_2Si$ requires C, 66.86; H, 7.36; N, 4.87; found C, 65.94; H, 7.19; N, 4.59.

Reactions of 1 with diketones.

Benzil. A mixture of **1** (1.2g, 6 mmol) and benzil (1.3g, 6 mmol) in 6 ml of CH_2Cl_2 was stirred for 30 h at room temperature, 3 ml of pentane were added, the layer of pentane was separated. Concentration of the solvent gave a mixture (50 : 50) of diastereoisomers of meso-4,5-diphenyl-1,3,2-dioxasilacyclopentane. Yield, 82%. ^{1}H NMR ($CDCl_3$) : δ 2.72(s, 6H, NMe_2), 5.08-5.38(m, 2H, PhCHO), 5.60(s, 1H, SiH), 6.86-8.54(m, 16H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 47.60-51.49(NMe_2), 79.85(CO), 116.62-150.13(Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -48.94 J(^{1}H-^{29}Si) : 284Hz(d), -54.40 J(^{1}H-^{29}Si) : 266Hz(d). Mass spectrum : m/e 411(M^+, 5), 305(M^+ -PhCHO, 100), 199(Ar_NSiH^+, 61), 184(Ar_NSiH^+ -15, 45). The diastereoisomers were identified by comparison of their ^{29}Si spectra with those of authentic samples, obtained in the reaction of **1** with meso-hydrobenzoin.

Cleavage of 2-(8-dimethylamino-1-naphthyl)-4,5-diphenyl-1,3,2-dioxasilacyclopentane. A solution of 2-(8-dimethylamino-1-naphthyl)-4,5-diphenyl-1,3,2-dioxasilacyclopentane, (1.3g, 3 mmol), in 2 ml of ether was added dropwise to $LiAlH_4$ (0.13g, 3 mmol) in 3 ml of ether at 0°C. The mixture was stirred for 24 h at room temperature. 8 ml of HCl (2N) were added at 0°C. After extraction with $CHCl_3$, the organic layers were dried and concentrated. Recrystallization in $CHCl_3$ gave 0.56g of meso-hydrobenzoin, yield 87%. m.p. 138-139°C. ^{1}H NMR ($CDCl_3$ + a drop of CF_3COOH) : δ 4.83(s, 2H, OCHPh), 5.37(s, 2H, OH), 7.20(s, 10H, Ar-H). The same reaction was repeated with $NaBH_4$ (3 mmol) as the reducing agent, in Et_2O. After work-up, only 280 mg of meso-hydrobenzoin were isolated[20], yield 44%.

The similar process was carried out as described above for the hydrosilylation of other diketones with trihydrosilane **1**. The conditions and yields are summarized in Table 3. In the case of characterization of the diastereoisomers obtained after deprotection with $LiAlH_4$, the same method as described above was used.

2-(8-Dimethylamino-1-naphthyl)-4-methyl-5-phenyl-1,3,2-dioxasilacyclopentane, **14** : (mixture of diastereoisomers), ^{1}H NMR ($CDCl_3$) : δ 1.20-1.40(2d, 3H, CH_3), 2.80(s, 6H, NMe_2), 3.60-4.06(m, 1H, CH_3CHO), 4.37-4.68(2d, 1H, PhCHO), 5.06-5.32(m, 1H, SiH), 7.25-8.30(m, 11H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 20.31-26.77 (2q, CH_3), 49.02-49.54(2q, NMe_2), 73.14-77.08(2d, CH_3CHO). 83.01-83.59(2d, PhCHO). 116.94-150.20(m, Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -49.60 J(^{1}H-^{29}Si) : 280Hz(d), -49.87 J(^{1}H-^{29}Si) : 275Hz(d), -53.12 J(^{1}H-^{29}Si) : 282Hz(d). Mass spectrum : m/e 349(M^+, 12), 305(M^+ -CH_3CHO, 100), 243(M^+ -PhCHO, 57). 199(Ar_NSiH^+, 67), 184(Ar_NSiH^+ -15, 46). Analysis $C_{21}H_{23}NO_2Si$ requires C, 72.17; H, 6.63; N, 4.01; found C, 71.34; H, 6.59; N, 3.86.

Identification of 1-phenyl-1,2-propanediol after deprotection (mixture of erythro and threo isomers)[27], yield 51%. ^{1}H NMR ($CDCl_3$) 26,27 : δ 0.80-0.87(d, CH_3) (threo), 0.85-0.94(d, CH_3) (erythro), 2.78(br, CH_3CHOH), 3.69-3.98(m, PhCHOH, CH_3CHOH), 4.20-4.29 (d, J=8 Hz, PhCHOH) (threo), 4.60-4.70(d, J=4Hz, PhCHOH) (erythro), 7.40(s, Ph-H). ^{13}C NMR ($CDCl_3$) : δ 17.02(q, CH_3) (erythro), 19.23(q, CH_3) (threo), 71.80-77.54(2d, PhCHOH, CH_3CHOH) (erythro), 72.60-79.90(2d, PhCHOH, CH_3CHOH) (threo), 126.54-141.72(2m, Ar-C).

4,5-Tetramethyleno-2-(8-dimethylamino-1-naphthyl)-1,3,2-dioxasilacyclopentane , **11**: ^{1}H NMR $CDCl_3$: δ 1.06-2.10(m, 8H, $OCHC_4\underline{H}_8CHO$), 2.48-2.66(2s, 6H, NMe_2), 3.12-3.46(m, 2H, $OC\underline{H}C_4H_8C\underline{H}O$), 4.95-5.12(1H, 2s, SiH), 7.20-8.40(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -49.10 J(^{1}H-^{29}Si) ; 284Hz(d), -50.90

$J(^1H\text{-}^{29}Si)$: 294Hz(d). Mass spectrum : m/e 312(M^+ -1), 100. Analysis $C_{18}H_{23}NO_2Si$ requires C, 68.97; H, 7.40; N, 4.47; found C, 68.34; H, 7.29; N, 4.26.

After reduction with $LiAlH_4$ and work-up[4] , recovered 1,2-cyclohexanediol , yield 49%, m.p. 94-96°C. ^1H NMR ($CDCl_3$) : δ 1.16-2.14(m, 8H, $OCHC_4\underline{H}_8CHO$), 3.28-3.48(br, 2H, OH), 4.22(s, 2H, $OC\underline{H}C_4H_8C\underline{H}O$).

4,5-(1',2'-Dihydronaphthaleno)-2-(8-dimethylamino-1-naphthyl)-1,3,2-dioxasilacyclopentane.,**15.**

1.2-naphthoquinone (0.79g, 5 mmol) in 2 ml of CCl_4, was added dropwise to a solution of **1** (1.g, 5 mmol) at 0°C. The mixture was stirred for 24 h at 65°C and concentrated. The product was characterized without further purification. ^1H NMR ($CDCl_3$) : δ 2.08-3.02(br, 6H, NMe_2), 5.20(br, 1H, CHO), 5.62(br, 1H, SiH), 6.75-8.10(m, 13H, CHO, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -51.66 $J(^1H\text{-}^{29}Si)$: 315Hz(d), -51.98 $J(^1H\text{-}^{29}Si)$: 315Hz(d). Analysis $C_{22}H_{21}NO_2Si$ requires C, 73.50; H, 5.89; N, 3.90; found C, 73.34; H, 5.79; N, 3.86.

4,5-Dimethyl-2-(8-dimethylamino-1-naphthyl)-1,3,2-dioxasilacyclopentane. **12.** ^1H NMR ($CDCl_3$) : δ 1.02-1.52(3d, 6H, CH_3CHO), 2.50 -2.72(s, 6H, NMe_2), 3.40-4.20(2m, 2H, $CH_3C\underline{H}O$), 4.80-5.00(3s, 1H, SiH), 7.25-8.20(m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 17.68-20.64(3q, CH_3), 48.86-49.15(2q, NMe_2), 72.14-76.59(3d, $CH_3\underline{C}HO$), 115.77-150.24(m, Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -49.8 $J(^1H\text{-}^{29}Si)$: 286Hz(d), -50.14 $J(^1H\text{-}^{29}Si)$: 281Hz(d), -50.65 $J(^1H\text{-}^{29}Si)$: 278Hz(d). Mass spectrum : m/e 287(M^+, 56), 243(M^+ -CH_3CHO, 100), 199(Ar_NSiH^+, 80).

4,6-Dimethyl-2-(8-dimethylamino-1-naphthyl)-1,3,2-dioxasilacyclohexane. **13.** ^1H NMR ($CDCl_3$) : δ 1.08-1.20(d, 6H, $OCHC\underline{H}_3CH_2C\underline{H}_3CHO$), 1.30-1.52(2d, 2H, $OCHCH_3C\underline{H}_2CH_3CHO$), 2.59(s, 6H, NMe_2), 3.80-4.40(br, 2H, CHO), 5.10(s, 1H, SiH), 7.32-8.40(m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 24.20-24.47($OCHCH_3\underline{C}H_2CH_3CHO$), 25.22($CH_3$), 48.05-48.21($NMe_2$), 66.43(CHO), 117.70 -152.92(Ar-C. ^{29}Si NMR ($CDCl_3$) : δ -53.49 $J(^1H\text{-}^{29}Si)$: 274Hz(d), -55.02 $J(^1H\text{-}^{29}Si)$: 294Hz(d), -56.62 $J(^1H\text{-}^{29}Si)$: 280Hz(d). Mass spectrum : m/e 301(M^+, 65), 256(M^+ -CH_3CHO), 12), 199(Ar_NSiH^+, 32), 170($C_{12}H_{13}N^+$, 100).

4,6-di(tert-Butyl)-2-(8-dimethylamino-1-naphthyl)-1,3,2-dioxasilacyclohexane., **16** ^1H NMR ($CDCl_3$) : δ 0.60-0.80(d, 2H, CH_2), 1.15(s, 18H, t-Bu). 2.60-2.72(2s, 6H, NMe_2), 3.80-4.15(m, 1H, CHO), 4.56-4.70(m, 1H, CHO), 5.70(s, 1H, SiH), 7.35-8.40(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -52.93 $J(^1H\text{-}^{29}Si)$: 298Hz(d), -60.19 $J(^1H\text{-}^{29}Si)$: 298Hz(d), -62.83 $J(^1H\text{-}^{29}Si)$: 282Hz(d). Mass spectrum : m/e 385(M^+). Analysis $C_{23}H_{35}NO_2Si$ requires C, 71.64; H, 9.15; N, 3.63; found C, 71.34; H, 9.29; N, 3.66.

Reaction of trihydrosilane 1 with camphorquinone. A solution of **1** (1.2g, 6 mmol) and camphorquinone (1g, 6 mmol) in 5 ml of CCl_4 was refluxed 48 h with stirring. After 3 ml of pentane were added, an oil deposited and the layer pentane was separated. Concentration of the oily residue gave **17**, yield 84%, with ^1H NMR ($CDCl_3$) : 1.08-1.65(m, 14H, CH_3, CH_2), 2.66 (s, 6H, NMe_2), 3.62-3.82(2s, 1H, $C\underline{H}O$), 4.92(s, 2H, SiH_2), 7.21-8.32(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -46.10 $J(^1H\text{-}^{29}Si)$: 246Hz(t), -48.26, $J(^1H\text{-}^{29}Si)$: 247Hz(t). Analysis $C_{20}H_{25}NO_2Si$ requires C, 70.76; H, 7.42; N, 4.13; found C, 70.34; H, 7.29; N, 4.26.

The reactions of **1** with benzoin and benzil were performed in a simultaneous fashion by the method described above. After 7 h, the mixtures were separately identified by comparison of their ^{29}Si NMR spectra : with benzoin, ^{29}Si NMR ($CDCl_3$) : δ -48.93 $J(^1H\text{-}^{29}Si)$: 282Hz(d), -54.36 $J(^1H\text{-}^{29}Si)$: 265Hz(d), -67.10 $J(^1H\text{-}^{29}Si)$) : 199Hz(q); with benzil, ^{29}Si NMR ($CDCl_3$) : δ -48.89 $J(^1H\text{-}^{29}Si)$: 280Hz(d), -50.47 $J(^1H\text{-}^{29}Si)$: 247Hz(t), -54.47 $J(^1H\text{-}^{29}Si)$: 266Hz(d), -67.09 $J(^1H\text{-}^{29}Si)$: 199Hz(q).

Reaction of 1 with diols. *Meso-hydrobenzoin.* A solution of **1** (1.2g, 6 mmol) and meso-hydrobenzoin (1.28 g, 6 mmol) was refluxed in 5 ml of CCl_4 for 7 h with stirring. Concentration of the solvent gave a mixture

of **10E** and **10E'**, cis-meso and trans-meso $Ar_NSi(OCHPhCHPhO)H$, plus some $Ar_NSi(OCHPhCHPhO)H_2$ and residual trihydrosilane **1**, identified by ^{29}Si NMR and mass spectrometry without further purification. ^{29}Si NMR ($CDCl_3$) : δ -48.21 J(^1H-^{29}Si) : 245Hz(t), -48.93 J(^1H-^{29}Si) : 284Hz(d), -54.33 J(^1H-^{29}Si) : 266Hz(d), -67.24 J(^1H-^{29}Si) : 199Hz(q). Mass spectrum : m/e 411(M^+, 5), 305(M^+ -PhCHO, 100), 199(Ar_NSiH^+, 40), 184($ArNSiH^+$ -15, 80). If the reflux was maintained for 48 h, the reaction went to completion, giving only meso $Ar_NSi(OCHPhCHPhO)H$, **10**. Analysis $C_{26}H_{25}NO_2Si$ requires C, 75.88; H, 6.12; N, 3.40; found C, 72.34; H, 6.19; N, 3.47.

The similar process was carried out as described above for the reaction of other diols with trihydrosilane **1**. The conditions and yields are summarized in Table 2. Characteristics of the dioxasilacycloalkanes :

Trans-1,2-cyclohexanediol.: **11T** .^1H NMR ($CDCl_3$) : δ 1.10-2.20(m, 8H, $OCHC_4\underline{H}_8CHO$), 2.60-2.72(2s, 6H, NMe_2), 3.20-3.56(m, 2H, CHO), 5.10(s, 1H, SiH), 7.12-8.30(m, 6H, Ar-H). ^{29}Si NMR ($CDCl_3$) : δ -50.91 J(^1H-^{29}Si) : 280Hz(d).

Meso-2,3-Butanediol.: **12E** . ^1H NMR ($CDCl_3$) : δ 0.98-1.20(2d, 6H, $OCHC\underline{H}_3CHC\underline{H}_3O$), 2.48-2.68(2s, 6H, NMe_2), 3.91-4.40(m, $OC\underline{H}CH_3C\underline{H}CH_3O$), 4.80-5.20(2s, 2H, SiH), 7.10-8.10(m, 6H, Ar-H. ^{29}Si NMR ($CDCl_3$) : δ -49.53 J(^1H-^{29}Si) : 248Hz, -50.26 J(^1H-^{29}Si) : 278Hz).

D(-)(-)-2,3-Butanediol.: **12T** . ^1H NMR ($CDCl_3$) : δ 1.08-1.35(2d, 6H, $OCHC\underline{H}_3CHC\underline{H}_3O$), 2.50-2.72(2s, 6H, NMe_2), 3.40-3.80(m, 2H, $OC\underline{H}CH_3C\underline{H}CH_3O$), 5.08(s, 1H, SiH), 7.20-8.20(m, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 20.96 ($\underline{C}H_3CHO$), 49.3(NMe_2), 78.07(CHO),116.1-151.32(Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -49.86 J(^1H-^{29}Si) : 282Hz(d). Mass spectrum : m/e 287(M^+, 100).

Meso-2,4-pentanediol.: **13E,E'** . A mixture of diastereoisomers was obtained ^1H NMR ($CDCl_3$) : δ 1.12-1.20(d, 6H, CH_3), 1.40-1.59(2d, 2H, CH_2), 2.60(s, NMe_2, 6H), 3.81-4.35(m, 2H, CHO), 4.95(s, 1H, SiH), 7.15-8.32(m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 25.32(q, CH_3), 46.03(t, CH_2), 48.41 -49.26(2q, NMe_2), 69.86-70.3(2d, CHO), 117.27-151.67(m, Ar-C), ^{29}Si NMR ($CDCl_3$) : δ -53.34 J(^1H-^{29}Si) : 247Hz(d), -54.93 J(^1H-^{29}Si) : 295Hz(d). Mass spectrum : m/e 301(M^+, 59), 199(Ar_NSiH^+, 55), 184(26), 42($C_3H_6^+$, 100).

DL-pentanediol.: **13T** . ^1H NMR ($CDCl_3$) : δ 1.12-1.41(2d, 6H, $OCHCH_3CH_2CH_3CHO$), 1.59-1.79(2d, 2H, $OCHCH_3CH_2CH_3CHO$), 2.60(s, 6H, NMe_2), 4.18-4.52(m, 2H, CHO), 5.12(s, 1H, SiH), 7.19-8.12(m, 6H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 15.77-24.15(2q, CH_3), 43.12(t, CH_2), 48.47(q, NMe_2), 66.7(d, CHO), 117.67-151.40(m, Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -56.67 J(^1H-^{29}Si) : 279Hz(d).

Reactions of (8-dimethylamino-1-naphthyl)phenylsilane 18 with benzoin.and benzil.

A solution of **1** (8-dimethylamino-1-naphthyl)phenylsilane (1g, 3.6 mmol), and benzoin (0.77g 3.6 mmol) in 5 ml of CCl_4 was refluxed for 24 h with stirring. Evaporation of the solvent gave a mixture of diastereoisomers of $Ar_NPhSi(OCHPhCOPh)H$, **19**. ^1H NMR ($CDCl_3$) : δ 2.08-252(2s, 6H, NMe_2), 4.80-490(br, 0.5H, PhCHO), 5.32-5.40(br, 0.5H, PhCHO), 5.45(s, 1H, SiH), 6.75-8.98(m, 21H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 45.51-53.78(2q, NMe_2), 78.54-80.84(2d, PhCHO), 116,38-150.52(Ar-C). ^{29}Si NMR ($CDCl_3$) : δ -43.36(br.). Analysis $C_{32}H_{29}NO_2Si$ requires C, 78.81; H, 5.99; N, 2.87; found C, 77.34; H, 5.19; N, 2.89.

A mixture of **18** (1.2g, 4.3 mmol) and benzil (0.91g, 4.3 mmol) in 5 ml of CCl_4 was refluxed 48 h with stirring. After 3 ml of pentane were added, an oil deposited and the layer pentane was separated. Concentration of the oily residue gave 1.87g (3.8 mmol) of **19** as a mixture of diastereoisomers of $Ar_NPhSi(OCHPh\text{-}COPh)H$ with ^1H NMR ($CDCl_3$) : 2.08-2.52(2s, 6H, NMe_2), 4.80-4.92 (br, 0.5H, PhCHO), 5.42-5.52(br, 0.5H, PhCHO), 5.50(s, 1H, SiH), 6.60-8.80(m, 21H, Ar-H). ^{13}C NMR ($CDCl_3$) : δ 45.53-53.79(2q, NMe_2), 78.55-80.86(2d, CHO), 116.04-150.51(m, Ar-C), 195.12(s, CO). ^{29}Si NMR ($CDCl_3$) : δ -43.41(br.).

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