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Transformation of organic compounds in the presence of metal complexes

VII *. Selective reduction of diketones by hydrosilylation in the presence of rhodium(I) complexes

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Abstract

An investigation was made of the hydrosilylation of 2,2,4,4-tetramethyl-1,3-cyclobutanedione with alkyl- and arylsilanes, catalyzed by a variety of rhodium(I) complexes. The selectivity of the reduction depends strongly on the steric requirements of the silane molecules. An appropriate selection of hydrosilanes (di- and certain trialkylsilanes) provides a new selective method for the preparation of 3-hydroxy-2,2,4,4-tetramethylcyclobutanone. Diphenylsilane and amylsilane are selective in the formation of isomeric diols, diphenylsilane favouring formation of the *cis*-diol, and amylsilane yielding mainly the *trans*-diol.

1. Introduction

Hydroxyketones and diols can be prepared through the hydrogenation of diketones [2], and a knowledge of the selectivity and stereoselectivity of these processes is important. Several results are available on the hydrogenation of open-chain and cyclic diketones in the presence of different metals [2–8] and metal complexes [9–12]. These investigations relate to 1,2- [5,9,12], 1,3- [3,6–8,10,11] and 1,4- [4,5] diketones. At large hydrogen excess, the hydrogenation results in diols. However, when the diketone/hydrogen molar ratio is 1:1, a 90% selectivity of hydroxyketone formation can be obtained, depending on the experimental conditions and the starting compound (especially if one of the carbonyl groups is hindered). Very few data have been reported on the selective reduction of 2,2,4,4-tetramethyl-1,3-cyclobutanedione (**1**). Catalytic hydrogenation leads to the corresponding diol in good yield, but without any selectivity (98% diol with 1:1 *cis*/*trans* ratio on 5% Ru/C) [3]. Transformation of **1** to the hydroxyketone **2** (yield 70%) has been achieved under mild experimental conditions (R–Ni, MeOH, 313 K, 3 atm) [3] (Scheme 1).

Whereas many authors have studied the hydrosilylation of open-chain ketones and α-keto-esters [13–18], relatively few data are available on the hydrosilylation of cyclic ketones. The selectivity of the reduction of alkyl-substituted cyclohexanones has been studied as a function of silane size, type of alkyl substituent [19–21] and type of ligand [22]. There are no experimental data on the hydrosilylation of open-chain and cyclic diketones. A probable reason for this is the extreme stability of the enol form of 1,3-dicarbonyl compounds and 1,2-cyclic diketones. Without such a drawback, **1** seems a perfect molecule for investigation of the reactivity and selectivity of a 1,3-diketone in hydrosilylation. Its rigid structure provides an additional opportunity to study the effects of the structure of the hydrosilane molecule and different ligands on the stereoselectivity in the formation of the isomeric diols.

In view of the above, we decided to use hydrosilylation as a viable alternative to catalytic hydrogenation. 2,2,4,4-Tetramethyl-1,3-cyclobutanedione (**1**), i.e. the dimethylketene dimer, is a unique molecule for testing

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TABLE 1. Transformation of **1** with the silanes catalyzed by $Rh(PPh_3)_3Cl$ [a]

Silane	Conversion (%)	Selectivity (%)		Ratio of 3c/3t
		2	3c+3t	
$^nC_5H_{11}SiH_3$	100	0	100	52/48
^{n}BuMeSiH$_2$	35	100	0	–
Pr_2SiH_2 (1 h)	60	100	0	–
Pr_2SiH_2 (5 h)	100	100	0	–
Ph_2SiH_2	100	5	95	65/35
Ph_2SiH_2 [b]	51	100	0	–
Et_3SiH (24 h)	0	–	–	–
Et_3SiH (60°C, 24 h)	0	–	–	–
Et_2MeSiH (24 h)	100	100	0	–
Et_2MeSiH (24 h) + Ph_2SiH_2 (3 h) [c]	100	35	65	46/54

[a] Except otherwise indicated reactions were carried out at room temperature for 2 h, and the ratio of silane/**1** was 2:1. [b] Ratio of silane/**1** was 1:1. [c] See text.

different reagents and methods in selective reductions. Both the partial hydrogenation to hydroxyketone **2**, and the stereoselectivity in the formation of isomeric diols, **3c** and **3t**, can be investigated. Important additional structural features make this molecule of interest for studies on reactivity and selectivity.

2. Results and discussion

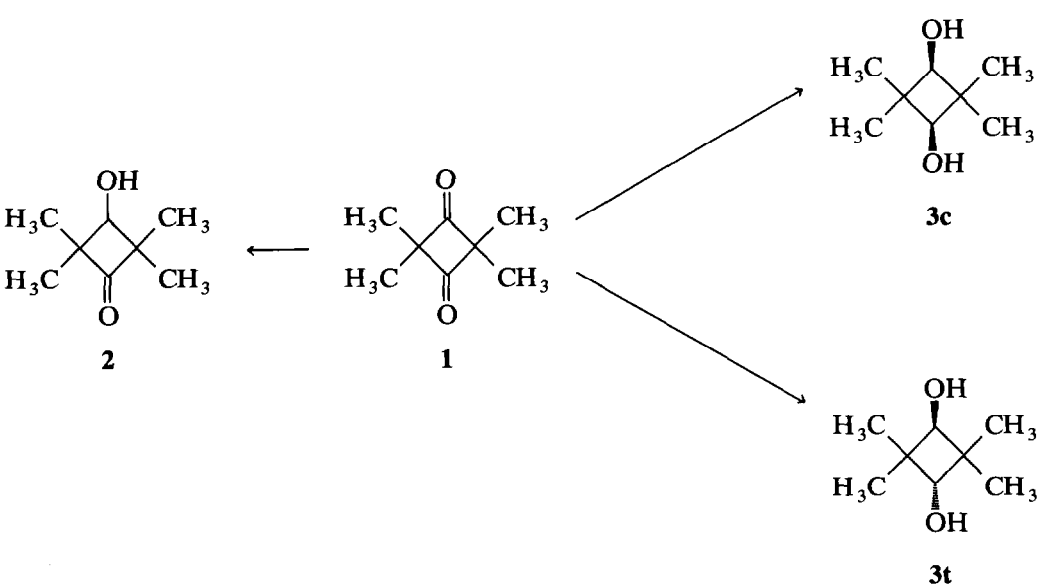
2.1. Tris(triphenylphosphine)rhodium(I) chloride as catalyst

The results of hydrosilylation of **1** with different hydrosilanes, catalyzed by commercially available Wilkinson catalyst, are presented in Table 1.

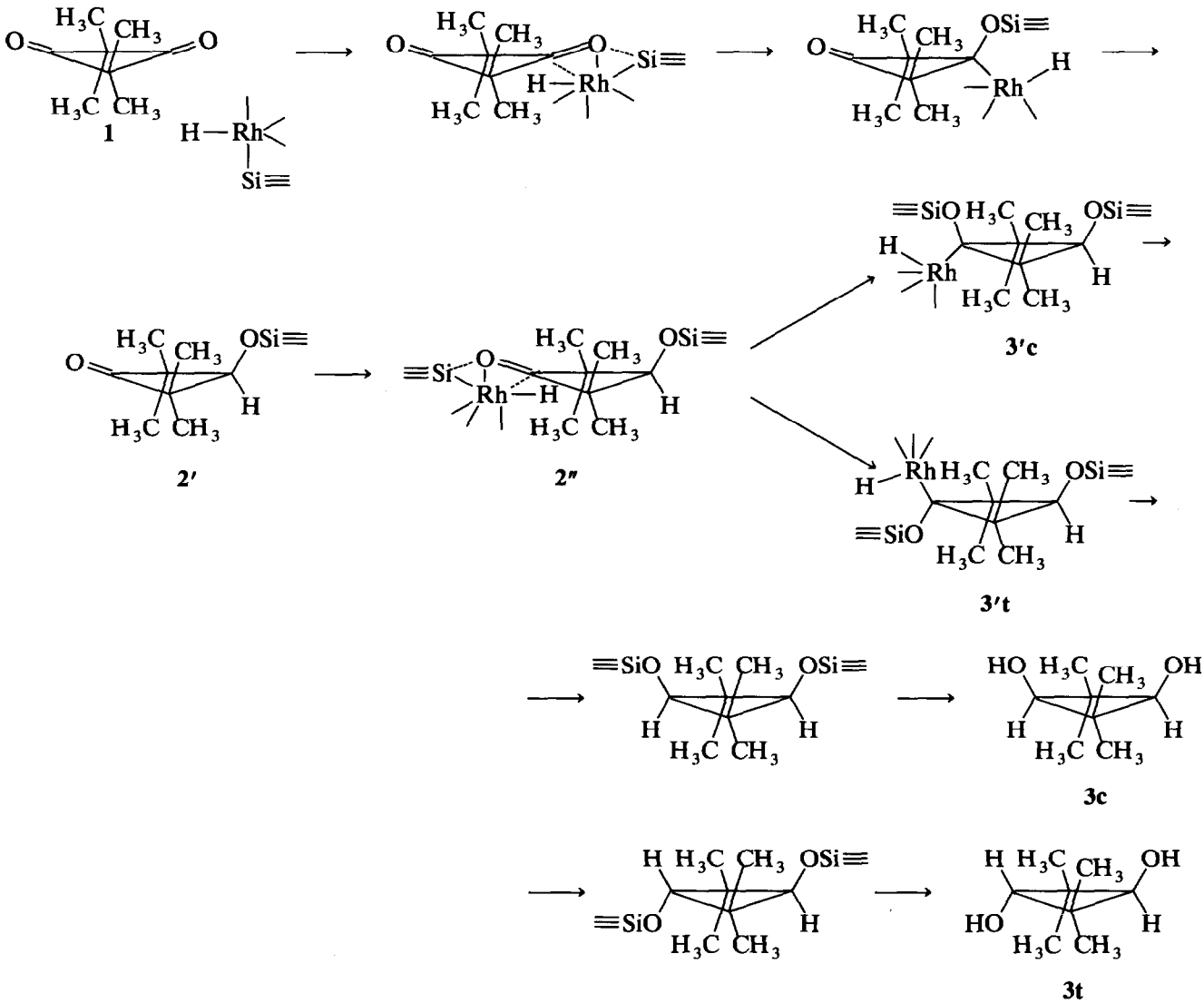
The important observations are as follows:

- Amylsilane ($AmSiH_3$) is the most highly reactive monosubstituted silane in isomeric diol production, but the transformation is not stereoselective.
- Of the disubstituted silanes, dialkylsilanes yield the hydroxyketone with excellent selectivity. Diphenylsilane can favour the formation of either **2** or **3**, depending on the reactant.
- As for the trialkylsilanes, no reaction takes place with triethylsilane, while diethylmethylsilane gives **2** in excellent yield and selectivity.

To account for these data, we can use the generally accepted mechanism suggested by Ojima *et al.* [23] for the interpretation of the hydrosilylation of alkyl-substituted cyclohexanones (Scheme 2). The orbital-distortion theory of Klein [24], used to interpret the stereochemistry of hydrosilylation of the C=O group in cyclohexanones, cannot be applied in our case. Instead, the structure of **1** must be taken into account. Although the numerical data determined by different methods for the ring puckering angle in cyclobutanone vary considerably ($10.4 \pm 2.7°$ from a combination of electron diffraction and spectroscopic data [25], and 0.5° from *ab initio* MO calculations [26]), the cyclobutane ring in **1** can be presumed to be planar, the four methyl groups exerting identical steric hindrance on both sides of the ring. These considerations lead to the conclusion that, in general, the steric requirements of the different silanes and ligands are the key factors determining the reactivity and selectivity during the transformation of **1**. These steric factors are manifested in the second reduction step, in the transformation of intermediate **2'**.



Scheme 1.



Scheme 2.

All the selectivity data in Table 1 can be interpreted by taking the above considerations into account. A monosilane ($AmSiH_3$) not exerting any appreciable steric interaction with its only alkyl group is highly reactive in both consecutive reaction steps. Dialkylsilanes exhibit a much lower reactivity and different selectivity. The selective formation of the hydroxyketone indicates that the transformation of **2'** via the insertion step from **2''** to the two possible α-silyloxyrhodium complexes (**3'c** and **3't**) is greatly hindered. It seems that considerable steric interactions can arise between the dialkylsilyloxy group and either the attacking second silane molecule (formation of **3'c**) or the bulky rhodium moiety (formation of **3't**). In contrast, the diarylsilane (Ph_2SiH_2), behaves very similarly to $AmSiH_3$. It is also clear from this result that the steric requirement of the two flat phenyl rings is small. As a result, the insertion step (the transformation of **2''** to **3'c** or **3't**) is not affected in the presence of the diphenylsilyloxy group. Since a benzylic cation-like intermediate, with the positive charge on the silicon stabilized by two phenyl groups, is certainly involved in its transformation, the high reactivity of Ph_2SiH_2 is not surprising.

A silane with three substituents (Et_3SiH) is not reactive at all. Surprisingly, however, the substitution of one methyl group for one of the ethyl groups in the unreactive Et_3SiH results in a favourable change, permitting selective monoreduction.

The results from the use of two different silanes in the same run are particularly instructive (Table 1, last entry). If the highly reactive Ph_2SiH_2 is added to the

reaction mixture containing intermediate **2'** formed in the reaction of **1** with Et_2MeSiH, the second reduction step can be achieved. This observation again testifies to the crucial role of steric factors in the reactivity and selectivity of **1**.

Overall, therefore the determining factor in the mono- *versus* direduction of **1** is the degree of substitution of the reacting silane molecule. A second important factor is the state of hybridization and substitution of the carbon atoms directly attached to the silicon.

The isomeric distribution of the diols formed can supply further information on the mechanism of hydrosilylation. The very low selectivity of reduction with $AmSiH_3$ *versus* the more selective transformation with Ph_2SiH_2 is again a clear indication of the involvement of steric factors in the latter case. The reactions of Ph_2SiH_2 in different molar ratios (Table 1, entries 5 and 6) show that the second hydrogen in intermediate **2'** is not involved in a further transformation. As a result, the intramolecular hydrosilylation described by Anwar *et al.* [27], which should lead to exclusive formation of the *cis*-diol, can be excluded.

2.2. *Catalysts prepared in situ from [Rh(COD)Cl]$_2$ and various ligands*

Catalyst systems prepared *in situ* from mono- and bidentate phosphines and $[Rh(COD)Cl]_2$ (COD = cyclooctadienyl) were studied in the hydrosilylations with $AmSiH_3$ and Ph_2SiH_2, the two silanes which proved most reactive with the Wilkinson catalyst. In all cases, the reactions proceeded with 100% conversion in 2 h. The results are listed in Table 2.

TABLE 2. Transformation of **1** with silanes in the presence of catalysts *in situ* prepared from $[Rh(COD)Cl]_2$ and various ligands [a]

Ligand	Silane	Selectivity (%)		Ratio of 3c/3t
		2	3c+3t	
PPh_3	Ph_2SiH_2	–	100	63/37
	$^nC_5H_{11}SiH_3$	–	100	53/47
Diphenylenephenyl-	Ph_2SiH_2	–	100	57/43
phosphine	$^nC_5H_{11}SiH_3$	–	100	55/45
Bisdiphenylphosphino-	Ph_2SiH_2	80	20	69/31
ethane	$^nC_5H_{11}SiH_3$	–	100	43/57
Bisdiphenylphosphino-	Ph_2SiH_2	–	100	70/30
propane	$^nC_5H_{11}SiH_3$	–	100	35/65
Bisdiphenylphosphino-	Ph_2SiH_2	85	15	61/39
butane	$^nC_5H_{11}SiH_3$	–	100	25/75
Bisdiphenylphosphino-	Ph_2SiH_2	85	15	64/36
pentane	$^nC_5H_{11}SiH_3$	–	100	50/50
Diphenylphosphino-	Ph_2SiH_2	–	100	65/35
ferrocene	$^nC_5H_{11}SiH_3$	–	100	36/64

[a] All reactions were carried out at room temperature for 2 h.

The tabulated data allow two important conclusions:
- Monodentate phosphines (PPh_3, diphenylenephenyl phosphine) do not result in significant stereoselectivity.
- Bidentate phosphines exhibit high stereoselectivity but diphenylsilane and amylsilane favour formation of the *cis* or the *trans* isomer, respectively.

It can be seen from the above data that the ligand type does not significantly affect the selectivity in the reduction with Ph_2SiH_2, which yields mainly the *cis*-diol. The selectivity is very similar to that of the reaction in the presence of the Wilkinson catalyst. This shows that the different types of rhodium complexes exert similar steric interactions. In contrast, the use of bidentate phosphines with $AmSiH_3$ results in a marked increase in selectivity and a change in the stereochemical outcome of the reduction, yielding the *trans*-diol as the main product. The less pronounced steric hindrance between the small amylsilyloxy group and the bidentate phosphine ligands compared to the monodentate phosphines allows the formation of the thermodynamically more stable isomer in a fast reaction. One may also assume a favourable electronic interaction between the oxygen of the silyloxy group and the rhodium in intermediate **3't**.

To summarize, steric factors predominate in the hydrosilylation of 2,2,4,4-tetramethyl-1,3-cyclobutanedione with different alkyl- and aryl-substituted silanes, catalyzed by a variety of rhodium(I) complexes. The correlation between the increasing degree of substitution of the alkylhydrosilanes and their decreasing reactivity was reaffirmed. Diphenylsilane exhibits a higher reactivity than the corresponding dialkylsilanes. New convenient synthetic methods are given for the synthesis of 3-hydroxy-2,2,4,4-tetramethylcyclobutanone in excellent yield and selectivity, and either *cis*- or *trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol in good selectivity.

3. Experimental details

The dimethylketene dimer and $RhCl(PPh_3)_3$ were obtained from Aldrich, while $[Rh(COD)Cl]_2$ and the ligands were purchased from Strem Chemicals (USA). Benzene was distilled from $LiAlH_4$ under argon. An authentic sample of a mixture of isomers (isomeric ratio about 1) was a product of City Chem. Corp. (New York, USA). *cis*-Diol for GC comparison was prepared by treatment of the diol mixture with dilute sulphuric acid [28]. Diphenylsilane was a Fluka product and the further alkylsilanes were prepared on the basis of the literature procedure [29].

Gas chromatographic analyses were performed with an HP 5890 GC coupled with an HP 5970 MSD system

on a 50 m HP-1 capillary column, with helium as carrier gas. The calculations were carried out with an HP 59970 Chemstation.

The products were identified *via* their ^1H NMR (400 MHz Bruker AM 400 instruments), MS (Hewlett Packard 5970 MSD) and IR (Unicam SP 2000 spectrophotometer) spectra. All compounds gave satisfactory spectral data according to previous data [3].

3.1. General reaction of 1 with hydrosilanes, catalyzed by Rh(I) complexes

Reactions were conducted under argon in a 10-ml two-necked flask fitted with a rubber septum. Liquids were transferred *via* argon-flushed syringes. The flask was charged with 9.25 mg (0.01 mmol) of $RhCl(PPh_3)_3$ catalyst and purged with argon for 15 min, and 1 ml of oxygen-free benzene was then added. To this homogeneous orange solution, 1.15 mmol of alkylsilane (in 1 ml of benzene) was added, followed by 0.5 mmol of **1** in 1 ml of benzene after stirring for 15 min. The reaction mixture was then stirred for 2 h at room temperature (exceptions are indicated in Tables 1 and 2). Work-up included the evaporation of benzene and hydrolysis of the residue with 1 ml of a *p*-TsOH/H_2O/MeOH mixture for 30 min. After removal of the solvents, the product was dissolved from the oily residue with 2 ml of diethyl ether.

For catalysts prepared *in situ*, 24.65 mg (0.01 mmol) of $[Rh(COD)Cl]_2$ and the calculated amount of ligand were first stirred for 15 min in 3 ml of benzene, and the silane and the solution of **1** were then added.

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