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Preliminary communication / Communication

Heterogeneous hydrogenation of 1-naphtol and 2-naphtol over Ru/Al$_2$O$_3$: a simple ^{1}H NMR method for determination of the diastereoselectivity

Arlette Solladié-Cavallo [a,*], Baram Ahmed [a], Michel Schmitt [a], François Garin [b]

[a] *Laboratoire de stéréochimie organométallique, ECPM/université Louis-Pasteur, 25, rue Becquerel, 67087 Strasbourg, France*
[b] *LMSPC, ECPM/université Louis-Pasteur, 25, rue Becquerel, 67087 Strasbourg cedex 2, France*

Abstract

Heterogeneous hydrogenations of 1-naphthol and 2-naphthol over Ru/Al$_2$O$_3$-9001 (from Engelhard) are presented. It was found that 1-naphthol provides almost exclusively (98–100%) the *cis*-decalols (OH equatorial and axial) while the 2-naphthol lead to mixtures of a *cis*-decalol (OH equatorial) and a *trans*-decalol (OH equatorial) in 1/1–1/2 ratio where the *trans*-decalol is major. A rapid and simple ^{1}H NMR method (based on analysis of the patterns and of the ^3J values obtained from the C<u>H</u>(OH) proton) is described, which allows unambiguous assignment of the diastereomers of 1-decalols and 2-decalols. ***To cite this article: A. Solladié-Cavallo et al., C. R. Chimie (2005)***.
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Résumé

L'hydrogénation hétérogène du 1-naphthol et du 2-naphthol sur Ru/Al$_2$O$_3$-9001 (Engelhard) est étudiée. Il a été montré que le 1-naphthol donne exclusivement les deux *cis*-décalols (OH équatorial et axial), alors que le 2-naphthol conduit à un mélange d'un *cis*-décalol (OH équatorial) et d'un *trans* décalol (OH équatorial) dans le rapport 1/1–1/2. Une méthode simple et rapide utilisant la RMN ^{1}H de base est décrite, qui permet de déterminer sans ambiguïté et simultanément la structure des diastéréomères ainsi que leur rapport. ***Pour citer cet article : A. Solladié-Cavallo et al., C. R. Chimie (2005)***.
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* Corresponding author.

E-mail address: cavallo@chimie.u-strasbg.fr (A. Solladié-Cavallo).

1. Introduction

Preparation of *cis* and/or *trans* decalols by heterogeneous hydrogenation of the corresponding naphthols over supported metals as catalysts could be a short and challenging synthetic route if highly stereoselective. Hydrogenation of 1-naphthol and 2-naphthol have been studied at the beginning of the century over nickel [1–3], reduced copper [4], platinum [6,7] or rhodium [8] and regained but few attention in recent years [9] but ruthenium has not yet been used. Moreover, ^{1}H NMR has never been used to determine the isomers' structure.

We present here a preliminary study of Ru/Al$_2$O$_3$ heterogeneous hydrogenation of 1-naphthol and

2-naphthol (**1**, **2**) to obtain decalols **3** and **4**, Fig. 1, as well as a simple, rapid and basic ^{1}H NMR method which allows simultaneous determination of isomers' ratio and three-dimension structure of the four possible diastereomers formed.

2. Results and discussion

2.1. Hydrogenation of 1-naphthol

The results of hydrogenation of 1-naphthol are gathered in Table 1. Partially hydrogenated naphthol (**5**) was the major product obtained in THF, moreover, large amount of **5** was obtained in EtOH after 1 h but none
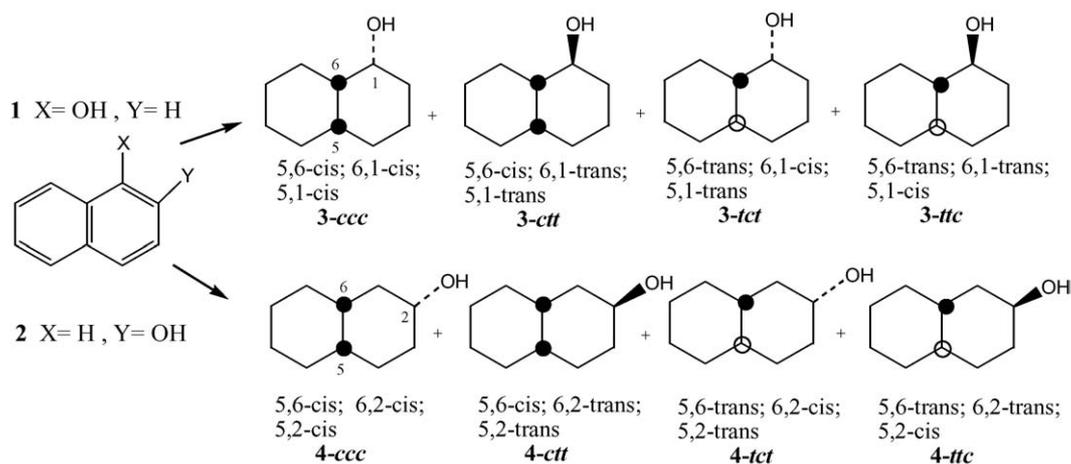
Fig. 1.

Table 1
Hydrogenation of 1-naphtol **1**

Starting material	Solvent	Temperature (°C)	React times (h)	3-ccc/3-ctt/3-tct/3-ttc	5%	*cis/trans*-decalin syst	Yield % in 3
1-Naphthol	EtOH	40	1	37/14/0/1	48	98/2	52
1-Naphthol	EtOH	40	2	238/14/2/1	45	95/5	55
1-Naphthol	EtOH	40	4	74/26/0/0	0	100/0	100
1-Naphthol	THF	40	4	0/0/0/5	75	–	5*

* 20% of starting 1-naphthol, are recovered.

Table 2
Hydrogenation of 2-naphtol **2**

Starting material	Solvent	Temperature (°C)	React times (h)	4-ccc/4-ctt/4-ttc/4-tct	*cis/trans*-decalin syst.	Yield %
2-Naphthol	EtOH	40	4.5	38/0/0/62	38/62	100
2-Naphthol	THF	40	5	48/0/5/47	48/52	100
2-Naphthol	Hexane	40	o.n.*	34/0/0/66	34/66	100

* o.n. = over night.

after 4 h, suggesting that **5** is an intermediate in these hydrogenations. Compound **5** has also been observed and proposed as intermediate by Musser et al. [5] as well as Meyers et al. [8] with nickel, copper and rhodium catalysts.
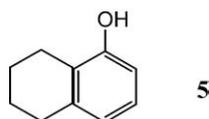
It is interesting to note that the *cis*-decalin system is obtained exclusively (Table 1, lines 1 and 2) although mixtures of *cis* and *trans*-decalin systems are usually observed in the literature upon hydrogenation of 1-naphthol over other metals [5,8] or upon hydrogenation of naphthalene over Adams platinum oxide catalyst [7].

2.2. Hydrogenation of 2-naphthol

The results of hydrogenation of 2-naphtol are gathered in Table 2.

Partially hydrogenated napthol is not observed in this case even in THF but mixtures of *cis* and *trans*-decalin systems are always obtained.

2.3. Structure assignment of 1- and 2-decalols

Assignment of the various isomers is a key step, therefore, a simple method based on very basic NMR is presented bellow. This method allows simultaneous determination of the three-dimensional structures and of the ratios between the isomers. It is worth noting that, although in this work most of the isomers have been isolated (chorotography over silica gel, using Et$_2$O/hexane as eluent) for microanalysis and checking of their structure, the method allows the use of crude product of reactions.

Determination of the structure of the diastereomers of compounds **3** and **4** was done using the patterns of the methine proton on the carbon bearing the OH group and relative values of the ^3J coupling constants observed. ^{1}H NMR spectra of diastereomers mixtures and of isolated diastereomers have been used/compared and, of course, ring inversion equilibrium have been taken into account in the case of the non-rigid *cis*-decalols

(**3-c** and **4-c**), Schemes 1 and 2, as the values observed for the ^3J coupling constants are the weighted average of the values of each conformers.

2.3.1. 1-Decalols: predictions

In isomer **3-ccc**, conformation **K1**-(OH equatorial) will be largely preferred over **K2**-(OH axial) because of syn-repulsion OH/CH$_2$ in **K2** [10] and one can thus expect for H1 a double triplet with one large coupling constant ($^3J_{trans}$) and two small ($^3J_{gauche}$).

Conformation **K1**-(OH equatorial) will also be preferred in isomer **3-ctt** but conformation **K2**-(OH axial) will not be so disfavored in this case because of no OH/CH$_2$ syn-repulsion and one can expect for H1 a triplet of doublet with two averaged coupling constants ($^3J_{trans}$ in **K2** and $^3J_{gauche}$ in **K1**) and one small ($^3J_{gauche}$ in both conformers), Scheme 1.

In the rigid *trans*-decalin system (**3-t**) the OH occupies a well-defined axial (**3-tct**) or equatorial (**3-ttc**) position providing for H1 a quadruplet (three small $^3J_{gauche}$) in **3-tct** and/or a triplet of doublet (with two large $^3J_{trans}$ and one small $^3J_{gauche}$) in **3-ttc**.

2.3.2. 1-Decalols: observed

Four signals are observed and comparison of the predicted patterns with the observed ones then provides assignment of the four isomers of 1-decalols:

H1: 3.2 ppm; ^3J = 10.5, 9.5, 4.5 Hz (two large and one small = DDd) ≡ **3-ttc**.

3.68 ppm; ^3J = 11, 4.5, 4.5 Hz (one large and two small = Dt) ≡ **3-ccc**.

3.76 ppm; ^3J = 3, 3, 3 Hz (three small = q) ≡ **3-tct**.

3.83 ppm; ^3J = 7.5, 7.5, 4 Hz (two averaged and one small = td) ≡ **3-ctt**.

The results are also gathered in Table 3.

2.3.3. 2-Decalols: predictions

The same analysis holds although H2 is now coupled with four vicinal protons instead of three, Scheme 2.

In isomer **4-ccc**, conformation **K1**-(OH equatorial) will be largely preferred over **K2**-(OH axial) because of syn-repulsion OH/CH$_2$ in **K2** [10] and one can thus expect for H2 a triplet of triplet with two large coupling constant ($^3J_{trans}$) and two small ($^3J_{gauche}$).

Conformation **K1**-(OH equatorial) will also be preferred in isomer **4-ctt** but conformation **K2**-(OH axial) will not be so disfavored in this case because of no OH/CH$_2$ syn-repulsion and one can expect for H2 a
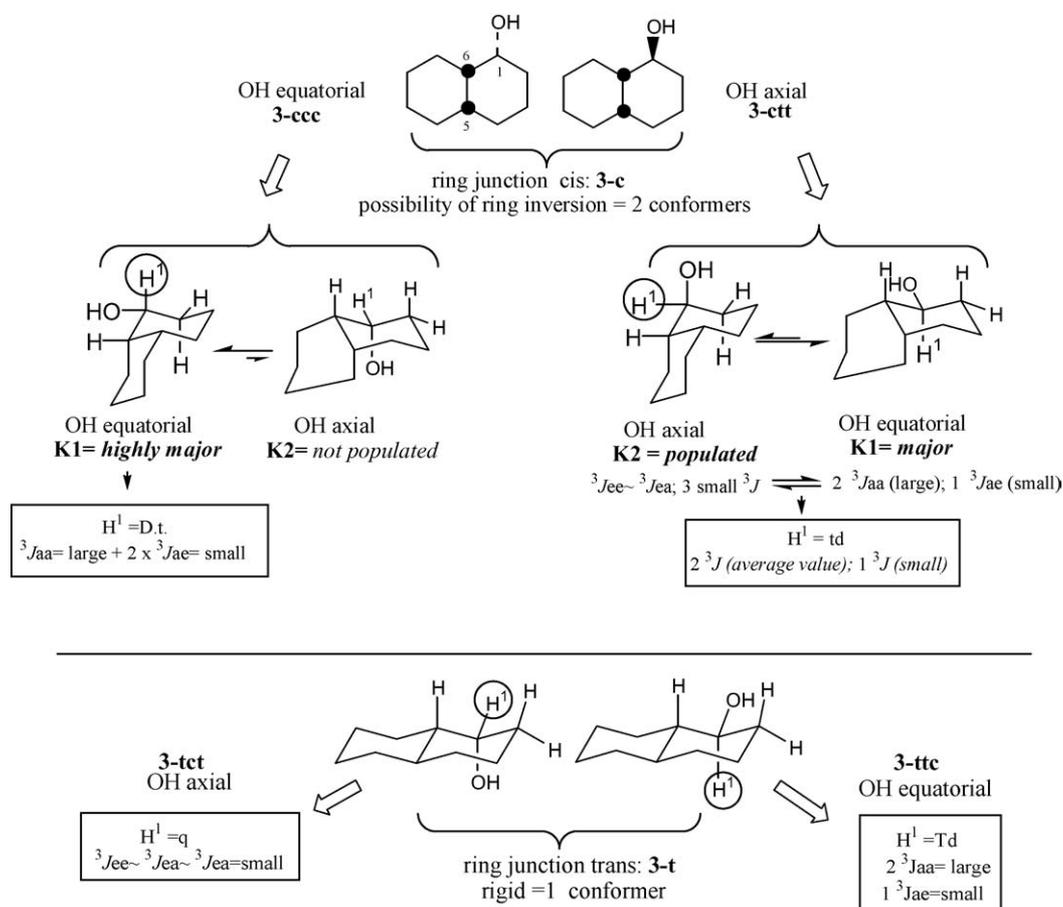
Scheme 1.

triplet of triplet with two averaged coupling constants ($^3J_{trans}$ in **K1** and $^3J_{gauche}$ in **K2**) and two small ($^3J_{gauche}$ in both conformers), Scheme 2.

In the rigid *trans*-decalin system (**4-t**) the OH occupies a well-defined equatorial (**4-tct**) or axial (**4-ttc**) position providing for H2 a pentuplet (4 small $^3J_{gauche}$) in **4-ttc** and a triplet of triplet (with two large $^3J_{trans}$ and two small $^3J_{gauche}$) in **4-tct**.

2.3.4. 2-Decalols: observed

In this case one isomer is not observed and two of them should exhibit similar patterns (both Tt), therefore, the only unambiguous assignment is the pentuplet (4.1 ppm) to isomer **4-ttc** (H2 equatorial and not inverting *trans*-decalin system). Because the values of the large coupling constants are 10 and 9.5 Hz, it is reasonable to postulate that the two other signals are not due to **4-ctt** for which one would expect an aver-

aged value of about 7.5 Hz for the large ^3J (see above). Then, both signals being Tt, the assignment was based on the width of the lines, and therefore, the Tt with narrow lines was assigned to the *trans*-decalin system (no inversion, no dynamic process) that is to **4-tct**.

H2: 3.58 ppm; ^3J = 10, 10, 5, 5 Hz narrow lines (two large and two small = Tt) ≡ **4-tct**.

3.82 ppm; ^3J = 9.5, 9.5, 4.5, 4.5 Hz broad lines (two large and two small = Tt) ≡ **4-ccc**.

4.1 ppm; ^3J = 3, 3, 3, 3 Hz (four small = pentuplet) ≡ **4-ttc**.

The results are also gathered in Table 3.

3. Conclusion

Catalytic heterogeneous hydrogenation of 1-naphthol and 2-naphthol over Ru/Al$_2$O$_3$ has shown to work in
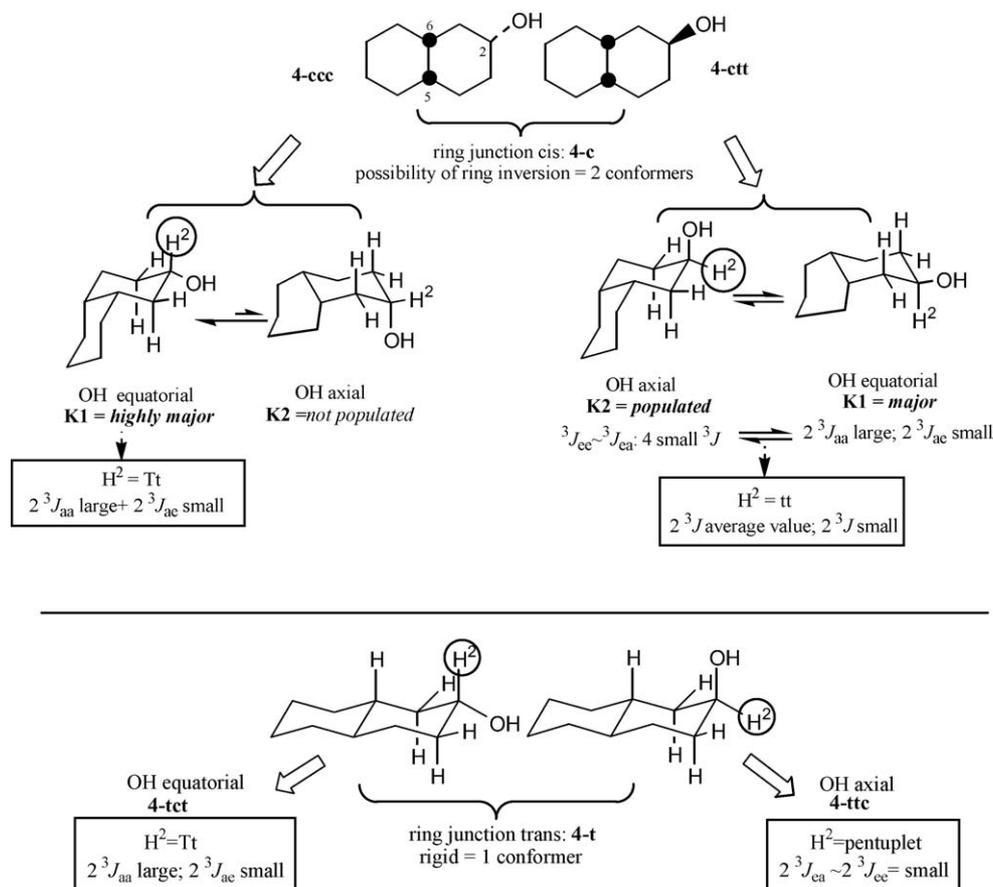
Scheme 2.

quantitative yields under 20 bar of H$_2$ and at 40 °C. It was shown that hydrogenation of 1-naphtol provides almost exclusively (100% and 98%, Table 1, lines 1, 2) the *cis*-decalols having the OH group either equatorial or axial while hydrogenation of 2-naphtol provides mixtures of *cis* and *trans* decalols having both the OH group equatorial in the ratio 1/1–1/2 (Table 2).

A rapid method based on simple ^{1}H NMR (direct determination of values and numbers of the ^3J involved in the pattern of the most deshielded proton-signal), which allows to identify and assign the diastereomers of 1-decalols and 2-decalols is described.

4. Experimental

^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded on a Bruker AC 300 spectrometer with CDCl$_3$ as solvent. Chemical shifts (δ) are given in ppm downfield from TMS as an internal standard. TLC, were performed on Merck's glass plates with silica gel 60 F$_{254}$. Silica gel Si 60 (40–60 μm) from Merck was used for the chromatographic purifications. Naphthols were purchased from Aldrich and used without further purification.

4.1. General procedure for hydrogenation

A solution of the desired naphthol (0.5 mmol, 1 equiv.) in 5 ml of solvent with 0.03 equiv. of the catalyst (Ru/Al$_2$O$_3$-9001 from Engelhard) was stirred for the desired time in an autoclave under 20 bar of H$_2$ (at 40 °C). The autoclave was equipped with a glass-socket and remaining air has been rapidly eliminated through two successive manipulations: vacuum-H$_2$ admission. The mixture was then filtrated to eliminate the catalyst, which was rinsed with solvent and recovered. The joined organic phases were then evaporated

Table 3
^{1}H NMR de H1 et H2 (δ, coupling constant, pattern) predicted and observed for all possible diastereomers of 1-decalols (**3**) and 2-decalols (**4**)

Start		3-ccc	3-ctt	3-tct	3-ttc
1	Predicted				
	Pattern[a]	Dt	td	q	Td
	δ (ppm)[b]	3.68	3.83	3.76	3.2
	Pattern[a]	Dt	td	q	DDd
	^3J (Hz)	11; 4.5; 4.5	7.5; 7.5; 4	3; 3; 3	10.5; 9.5; 4.5
		4-ccc	4-ctt	4-tct	4-ttc
2	Predicted Pattern[a]	Tt	tt	Tt	pentuplet
	δ (ppm)[b]	3.82	[c]	3.58	4.1
	Pattern[a]	Tt broad		Tt	pent
	^3J (Hz)	9.5; 9.5; 4.5; 4.5		10; 10; 5; 5	3; 3; 3; 3

[a] Capitals correspond to large values of coupling constant (~10 Hz); small letters correspond to small values of coupling constant (1–8 Hz).
[b] ^{1}H NMR in CDCl$_3$/TMS.
[c] Not observed.

under vacuum and the crude products, were analyzed by NMR, prior to purification. All the compounds were known compounds, which had correct ^{13}C NMR and analysis within accepted errors.

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