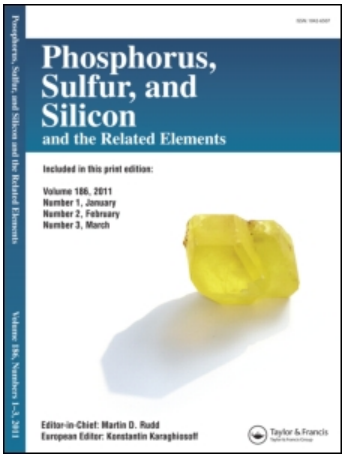

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Margarita Mladenova[a]; Françoise Gaudemar-Bardon[b]
[a] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria [b] Université P. et M. Curie, Laboratoire de Synthèse Organométallique, Btiment F, Paris Cedex 05, France

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STEREOCHEMISTRY OF THE ADDITION OF α-METALLATED *N,N*-DIMETHYLSULFONAMIDES TO 4-t-BUTYLCYCLOHEXANONE

MARGARITA MLADENOVA[a,*] and FRANÇOISE GAUDEMAR-BARDONE[b]

[a]*Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria*

[b]*Université P. et M. Curie, Laboratoire de Synthèse Organométallique, Bâtiment F, 4, Place Jussieu, F-75230 Paris Cedex 05, France*

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The effects of some reaction conditions on the aldol reaction of $RCH(M)SO_2N(CH_3)_2$ and product stereochemistries are reported. Under thermodynamic control the reaction is nonstereoselective. Under kinetic control, stereoselectivity varies with R. For R = H, axial attack is slightly favoured, while equatorial attack is dominant for $R = CH_3$. Dimethyl phenylmethanesulfonamide reacts highly stereoselectively. Equatorial attack is favoured with M = MgCl and M = Li, while M = Na gives 100% axial attack. These, and several more observations cannot be interpreted in terms of current concepts of nucleophilic additions to 4-t-butylcyclohexanone.

Key words: α-Metallated *N,N*-dimethylsulfonamides; 4-t-butylcyclohexanone; *N,N*-dimethylamides of β-hydroxysulfonic acids; aldol reaction; stereochemistry; axial (equatorial) attack.

INTRODUCTION

The steric course of nucleophilic additions to conformationally stable cyclic ketones as 4-t-butyl cyclohexanone attracts considerable interest in the last decades. Observed reaction stereochemistries are directed by the combination of two opposed factors:[1] i) steric factor (steric approach control)[2,3] favouring the equatorial attack due to steric strain between the entering nucleophile and axial hydrogens at C-3 and C-5, and ii) nonsteric factor of complex nature, favouring the axial attack. A variety of suggestions have been advanced as explanations of observed stereochemistries due to considerable extents of axial attack: product thermodynamic stabilities,[4] torsional strain (sigma bond repulsion) between the entering nucleophile and axial substituents at C-2 and C-6,[5] frontier orbital configurations,[6,7] antiperiplanarity of axial hydrogens at C-2 and C-6 (two-electron stabilizing interaction,[8–10] nucleophile hardness, resp. softness.[11]

According to the suggestion of Seyden-Penne *et al.*[11] the attack of a hard nucleophile (carbeniate) in the absence of substantial steric hindrance is charge controlled. Sterically, this attack is preferentially axial due to LUMO dissymmetry.[6,7] Soft nucleophiles (enolates), in turn, react under orbital control, and prefer equatorial attack. Gaudemar *et al.*[12–14] report systematical studies of the

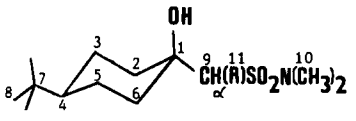
*Author to whom all correspondence should be addressed.

relationship between hardness of organometallics of the allyl,[12,14] acetate,[13] and phenylacetate[14] series and stereochemistry of their additions to 4-t-butylcyclohexanone. These studies support the explanation put forth by Seyden-Penne,[11] thereby defining a relatively wide range of reactions where the dynamical structure of reagents can be probed by reaction stereochemistry.

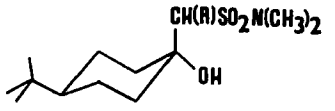
We reported recently[15] on the stereochemistry of sulfonamide carbanion additions to aldehydes. The sensitivity of these reactions with respect to steric requirements of substituents at the prochiral atoms forming the new C–C bond is very low even with bulky substituents as i-Pr, t-Bu, α-naphthyl. The stereoselectivity of these sulfonamide additions, as compared to other aldol reactions, is also lower. Sulfonamide carbanions thus behave as if their effectve volume were negligible. We therefore suggest pyramidal configurations of these reagents[15] and report here on a study of their addition to 4-t-butylcyclohexanone within the mentioned stereochemical concepts.[11–14]

RESULTS AND DISCUSSION

Additions of metal derivatives of *N,N*-dimethylamides of methanesulfonic **1a**, ethanesulfonic **1b**, and phenylmethanesulfonic **1c** acids to 4-t-butylcyclohexanone **2** yield isomer mixtures of corresponding β-hydroxysulfonamides **3-ax** and **3-eq** without side reactions.



3-ax



3-eq

3a: R = H; **3b**: R = CH_3; **3c**: R = C_6H_5.

The structures of these hydroxysulfonamides are confirmed by elemental analyses and spectral data. Stereochemically pure **3a-eq**, **3b-ax** **3c-ax**, and **3c-eq** are obtained by fractional recrystallization.

IR spectra of 1% chloroform solutions of **3a-c** show absorptions of associated O–H in the range of 3514–3532 cm^{-1}, intense bands between 1315–1331 and 1132–1146 cm^{-1}, assigned as symmetrical and asymmetrical SO_2-stretching vibrations and less intense bands within the 960–974 cm^{-1} range for the S–N-stretching vibrations, characteristic for sulfonamides.[16]

The configurations of β-hydrosulfonamides **3a-c** are assigned on the basis of their proton and ^{13}C NMR spectra. In $CDCl_3$, the α-proton (with respect to sulfonamide function) signals of **3-ax** (axial OH, result of equatorial attack) are shifted upfield relative to corresponding signals of **3-eq** (axial attack, equatorial OH):

$$\delta_{H_\alpha(3\text{-ax})} < \delta_{H_\alpha(3\text{-eq})}$$

In C_6H_6, t-Bu proton signals of **3-ax** are shifted downfield, $\delta_{t\text{-Bu}(3\text{-ax})} > \delta_{t\text{-Bu}(3\text{-eq})}$,

with respect to those of **3-eq** with the exception of **3c**, where the t-Bu proton chemical shifts are identical. These correlations are observed previously by Gaudemar *et al.*[12–14,17] for a large number of cyclohexanols of the type 4-t-Bu-C_6H_9—OH(Y), where Y = H, CH_2R, $CH_2CH{=}CH_2$, CH_2COOR, $CH_2CON(R)_2$, CH_2CN, CH_2COOH, $CH_2C{\equiv}CH$, CH(Ph)COOH, CH(Ph)$CON(CH_3)_2$, CH(Ph)$COOC(CH_3)_3$, CH(Ph)$CSN(CH_3)_2$.

The above configurations are confirmed also by the observed ^{13}C γ-effects.[18,19] The C-9 signals of **3-eq** are shifted upfield by 5.5 to 7.3 ppm relative to **3-ax**., i.e. $\delta_{C\text{-}9(ax)} > \delta_{C\text{-}9(eq)}$. Correlations of the type $\delta_{C\text{-}1,C\text{-}3,5(ax)} < \delta_{C\text{-}1,C\text{-}3,5(eq)}$ are also observed for cyclohexanols 4-t-Bu-C_6H_9—OH(Y), where Y = CH_2COOH,[3] CH_2CN[12–14] and CH(R)$CSN(CH_3)_2$.[20]

Studies of reaction mechamisms by product stereochemistry require strict maintenance of either kinetic or thermodynamic control. These results are summarized in Table I. Proof of kinetic control is given by metallation of stereochemically pure isomers, **3-ax** or **3-eq**, under the conditions of the corresponding addition (solvent, temperature, duration)[21] and subsequent hydrolysis and workup, which recover quantitatively the unchanged initial **3**.

Thermodynamically controlled stereochemistry is achieved by allowing the reaction mixture after the usual addition (kinetic control conditions) to warm up to ambient temperature and stirring until a constant ratio of **ax/eq**. As shown by the last entries for each series of experiments in Table I (entries 5, 10, 15), axial and equatorial aldolates are thermodynamically equally stable for R = H. The axial aldolates are slightly more stable for R = CH_3 and R = C_6H_5.

Under kinetic control, the role of counterions and solvents of varying basicity in reaction stereochemistry is studied with R = H, CH_3 and C_6H_5. The hardness

TABLE I

Addition of RCH(M)$SO_2N(CH_3)_2$ to 4-t-butylcyclohexanone (**2**) (conc. 0.4 mol/l; **2**/sulfonamide = 0.9; Yields based on **2**)

			Reaction conditions					
Entry	R	M	Solvent	Temperature, °C	Time (min)	**3**	Yield %	**ax:eq**
1*	H	MgCl	THF	−50	10	**3a**	62	39:61
2*	H	Li	THF	−50	10	**3a**	73	38:62
3*	H	Li	THF + 20%HMPT	−50	2	**3a**	78	38:62
4*	H	Na	THF	−55	2	**3a**	63	38:62
5**	H	Li	THF + 20%HMPT	−50→r.t.	180	**3a**	70	50:50
6*	CH_3	MgCl	THF	−50	10	**3b**	64	73:27
7*	CH_3	Li	THF	−50	10	**3b**	72	78:22
8*	CH_3	Li	THF + 20%HMPT	−55	5	**3b**	77	79:21
9*	CH_3	Na	THF	−55	3	**3b**	60	77:23
10**	CH_3	Li	THF + 20%HMPT	−50→r.t.	180	**3b**	73	57:43
11*	C_6H_5	MgCl	THF	−55	10	**3c**	65	88:12
12*	C_6H_5	Li	THF	−55	2	**3c**	74	94:06
13*	C_6H_5	Li	THF + 20%HMPT	−55	2	**3c**	81	95:05
14*	C_6H_5	Na	THF	−55	2	**3c**	44	0-, 100
15**	C_6H_5	Li	THF	−55→r.t.	60	**3c**	67	55:45

* Kinetic control.
** Thermodynamic control.

of organometallics of constant structure is known to parallel the hardness of the counterion[12,22] and increases with the improved cation solvation.[12,23] Strongly basic solvents as HMPT or DMSO, however, can also change reagent structures from enolate to carbeniate and additionally increase its hardness, favouring axial attack.[13,24,25]

Table I shows that, for R = H, the reaction is slightly stereoselective in favour of **3a-eq**. Similar stereochemistry is observed with hard reagents like allyllithium,[12] metallated acetonitrile, independently of the cation and the solvent,[13] and bromozinc reagents of acetic acid ethyl ester and dimethylamide in THF/DMSO or HMPT.[13] A weakly basic solvent as methylal, where the last two reagents are known to exist as enolates, is however sufficient to give the inverted stereochemistry.[13] For a comparison we mention here the additions of metallated acetic dimethylthioamides, enolates, i.e. soft reagents, which give 75% equatorial attack.[17] Entries 1–4 of Table I show invariant stereochemistry with respect to the counterion and the solvent. The preferred axial attack confirms our understanding of metallated *N,N*-dimethylamides of methanesulfonic acid as an effectively small, pyramidal, i.e. hard, species. Its pyramidal structure remains unchanged with solvent variation. With $R = CH_3$ and $R = C_6H_5$, however, the situation seems more complicated. As indicated by entries 6–9 of the table, for $R = CH_3$ product stereochemistry is the opposite, and the axial isomer (equatorial attack) is favoured. Addition of HMPT leaves the stereochemistry unchanged, and only the use of MgCl as the counterion increases slightly the axial attack, i.e. reduces the stereoselectivity. Similar effect of the replacement of magnesium for lithium is observed by Gaudemar *et al.*[13] with dimethylacetamide and trimethylsilylacetate reagents; this result is still unexplained, as no data on the structures of the lithium reagents are available. With $R = C_6H_5$, the addition of lithium and magnesium reagents is even more selective in favour of **3c-ax**, equatorial attack. Here, too, the stereoselectivity with magnesium is slightly lower (entries 11 and 12). Better solvating medium, addition of HMPT, leaves product stereochemistry unchanged (entry 13). Entry 14, however deserves special notice. With the sodium counterion, only the opposite isomer, **3c-eq**, is obtained. This result is interesting from the synthetical point of view, as a change of the metallating agent is sufficient to obtain one, **3c-ax** with lithium, or another isomer, **3c-eq** with sodium. This result is surprising from the theoretical point of view and remains for us a puzzle. In the absence of steric hindrance, a harder reagent should increase the preference to axial attack, but, seemingly, not significantly different from the lithium reagent in the presence of HMPT, neither higher than observed for R = H. The completely axial addition of sodium *N,N*-dimethyl phenylmethanesulfonamide to 4-t-butylcyclohexanone to give **3c-eq** is proved without doubt. No side products are found in the crude reaction mixture to indicate possible transformation of **3c-ax**. Pure **3c-ax** after metallation with naphthalene-sodium and stirred for 3 min at −55°C is recovered completely after hydrolysis. Leaving out the latter result, the rest of the studied additions still seem inconsistent with our structural concepts and former results on sulfonamide aldol additions. If we assume structures of reagents unchanged, the observed stereochemistries could be understood as the result of severely increased steric demand from R = H to $R = CH_3$ and $R = C_6H_5$ resulting in strongly favoured equatorial

attack. This assumption is, however, inconsistent with the low stereoselectivities of the additions of same reagents to aldehydes as pivalaldehyde and α-naphthaldehyde, which should have been sensitive to the change of effective bulk of the nucleophiles. A comparison with the studies of allyl, crotyl and cinnamyl reagents shows, on the other hand, that the increase of steric demand from H to CH_3 to C_6H_5 is insufficiently large. Therefore, reagent hardness should still be considered the substantial factor determining the stereochemistry of nucleophilic additions to 4-t-butylcyclohexanone.[14]

An alternative explanation of observed results could be based on the assumption of insignificant steric factors, but changes in the reagent structures, i.e. hardness. Pyramidal structure of the reagent from *N,N*-dimethyl methanesulfonamide is adopted on the basis of theoretical studies of Bors and Streitwieser,[26] and is consistent with the observed stereochemical results of additions of hard reagents. For $R = CH_3$ and $R = C_6H_5$, where equatorial attack is predominant, one should thus assume soft reagents. For $R = C_6H_5$ one could indeed assume carbanion planarisation and reagent softening, but for $R = CH_3$ there are no reasons for the same assumption. This explanation is then as unsatisfactory as the previous.

Additional examples of stereochemical results, which cannot be explained on the basis of current concepts can be found in a recent paper by Dobrev *et al.*[27]—under kinetic control, sodium cyclopentane-carbonitrile addition to 4-t-butylcyclohexanone reveals 100% equatorial attack, and sodium cyclohexane-carbonitrile 100% axial attack. One could pursue the role of more factors, customarily left out of consideration, but having substantial role in the reaction mechanism.

EXPERIMENTAL

All reactions were carried out under dry argon. THF was freshly distilled over $LiAlH_4$ prior to use. HMPT was distilled over CaH_2 and stored over molecular sieves. The ^{1}H- and ^{13}C-NMR spectra in $CDCl_3$ were recorded on a Bruker WM spectrometer at 250 MHz with TMS as internal standard. The assignment of ^{13}C signals was carried out by off-resonance technique. The ^{1}H-NMR spectra in C_6H_6 (internal standard TMS) were recorded on a Perkin-Elmer R 12 spectrometer at 60 MHz. M.p.s (uncorrected) were taken on a Boëtius hot-stage microscope.

Synthesis of β-hydroxysulfonamides **3**. *General procedure.* a) Metallation of sulfonamides **1**. M = MgCl: To 3.3 mmol titrated (by 1 N sec-BuOH in abs. xylene, indicator 1,10-phenanthroline[28]) solution of i-PrMgCl in THF was added dropwise 3 mmol of the sulfonamide **1**. The mixture was stirred 1 hr at 35–40°C for **1a** and **1b**, and at ambient temperature for **1c**.

M = Li: 3 mmol **1**, dissolved in THF was added dropwise at −20°C to 3.3 mmol n-BuLi (1.6 N in hexane, Merck–Schuchardt). The mixture was stirred at −20°C for 1 hr.

M = Na: To 3.3 mmol naphthalene–sodium in THF[29] was added dropwise at −20°C 3 mmol **1**, dissolved in THF. The mixture was stirred 1 hr at ambient temperature for **1a** and **1b**, and 30 min at −20°C for **1c**.

b) Addition of α-metallated **1** to **2**.

The total amount of solvent used for the metallation of **1** and the addition of **2** was adjusted to a reaction concentration of 0.4 mol/l. The THF solution of **2** (3 mmol) was added dropwise to the THF or THF/HMPT solution of the organometallic reagent. After stirring for predetermined time at the chosen temperature (see the Table) the reaction mixture was acidified with 1:1 HCl, saturated with NaCl and extracted by 20 ml of ether. The water phase was extracted additionally by 4 × 10 ml of ether. The combined extract was washed to neutral reaction with saturated solution of NaCl and dried over $MgSO_4$. The solvent was removed in vacuo and the crude product dissolved in $CHCl_3$ to a

calibrated volume. Aliquots of these solutions were subjected to NMR determination of **ax/eq** ratio and total yield. The yield was determined independently by preparative TLC (BDH silica gel, 13% $CaSO_4$, eluent ether/hexane 1:1). Pure isomers were obtained by recrystallization (chloroform/hexane).

c) Description of **3**.

N,N-Dimethylamides of [1-hydroxy-4-t-butyl-cyclohexyl]-methanesulfonic acid **3a**. **3a-eq**: m.p. 124–125°C, $C_{13}H_{27}NO_3S$ (277.4), Calc. %: C, 56.28; H, 9.81; N, 5.05. Found: C, 56.09; H, 9.80; N, 4.93.
^{1}H-NMR: 0.87 (s, 9H), 1.04–2.16 (m, 8H), 2.98 (s, 6H), 3.11 (s, $2H_\alpha$), 3.90 (s, 1H).
^{13}C-NMR: 24.4 and 27.5 (C-3, 5), 27.6 (C-8), 32.3 (C-7), 37.4 (C-10), 38.4 (C-2, 6), 47.3 (C-4), 52.6 (C-9), 71.9 (C-1).

3a-ax: (from a mixture with **3a-eq**) Found %: C, 56.39, H, 9.73 N, 5.10.
^{1}H-NMR: 0.87 (s, 9H), 1.04–2.08 (m, 8H), 2.87 (s, 6H), 2.96 (s, $2H_\alpha$), 3.26 (s, 1H).
^{13}C-NMR: 22.1 and 24.4 (C-3, 5), 27.6 (C-8), 32.4 (C-7), 37.8 (C-10), 38.4 (C-2, 6), 47.6 (C-4), 58.1 (C-9), 69.5 (C-1).
^{1}H-NMR(C_6H_5): $\delta_{t\text{-Bu}} = 0.88$(**3a-ax**); 0.79(**3a-eq**); 0.72(**2**).

N,N-Dimethylamides of 1-[1-hydroxy-4-t-butyl-cyclohexyl]-ethanesulfonic acid **3b**. **3b-ax**: m.p. 137–138°C, $C_{14}H_{29}NO_3S$ (291.4), Calc. %: 57.69; H, 10.03; N, 4.80; Found: C, 57.45; H, 9.89; N, 4.68.
^{1}H-NMR: 0.86 (s, 9H), 1.42–2.04 (m, 8H), 1.29 (d, 3H, $J = 7.1$ Hz), 2.92 (s, 6H), 3.16 (q, $1H_\alpha$, $J = 7.1$ Hz), 3.77 (s, 1H).
^{13}C-NMR: 11.6 (C-11), 22.0 and 22.1 (C-3, 5), 27.6 (C-8), 32.4 (C-7), 32.8 and 37.6 (C-10), 36.2 (C-2, 6), 47.5 (C-4), 66.1 (C-9), 72.3 (C-1).

3b-eq: (from a mixture with **3b-ax**): Found %: 57.41; H, 9.85 N, 4.87.
^{1}H-NMR: 0.86 (s, 9H), 1.31 (d, 3H, $J = 7.2$), 1.40–2.03 (m, 8H), 2.96 (s, 6H), 3.47 (s, 1H), 3.52 (q, $1H_\alpha$, $J = 7.2$).
^{13}C-NMR: 10.1 (C-11), 23.5 and 24.2 (C-3, 5), 27.6 (C-8), 32.3 (C-7), 32.4 and 36.2 (C-10), 36.2 (C-2, 6), 47.1 (C-4), 60.0 (C-9), 72.8 (C-1).
^{1}H-NMR (C_6H_5): $\delta_{t\text{-Bu}} = 0.90$(**3b-ax**); 0.82(**3b-eq**).

N,N-Dimethylamides of [1-hydroxy-4-t-butyl-cyclohexyl]-phenyl-methanesulfonic acid **3c**. **3c-ax**: m.p. 141–142°C, $C_{19}H_{31}NO_3S$ (353.5), Calc. %: C, 64.55, H, 8.84; N, 3.96; Found %: C, 64.31; H, 8, 67; N, 3.77.
^{1}H-NMR: 0.82 (s, 9H), 1.07–1.98 (m, 8H), 2.48 (s, 6H), 3.69 (s, 1H), 4.20 (s, $1H_\alpha$), 7.10–7.96 (m, 5H).
^{13}C-NMR: 22.2 and 22.3 (C-3, 5), 27.5 (C-8), 32.3 (C-7), 37.6 (C-2, 6), 37.7 (C-10), 47.4 (C-4), 76.8 (C-9), 73.7 (C-1), 128.5, 128.7, 128.9, 129.5, 130.0 and 132.3 (C-11).

3c-eq: m.p. 138–139°C, Found %: C, 64.70; H, 8.89; N, 3.90.
^{1}H-NMR: 0.82 (s, 9H), 1.07–1.95 (m, 8H), 2.42 (s, 6H), 3.89 (s, 1H), 4.52 (s, $1H_\alpha$), 7.11–8.12 (m, 5H).
^{13}C-NMR: 23.3 and 24.6 (C-3, 5), 27.6 (C-8), 32.3 (C-7), 37.0 and 37.6 (C-10), 38.7 (C-2, 6), 46.9 (C-4), 69.5 (C-9), 74.4 (C-1), 128.4, 128.8, 128.9, 130.5, 131.3 and 131.8 (C-11).
^{1}H-NMR (C_6H_5): $\delta_{t\text{-Bu}} = 0.83$(**3c-ax**); 0.83(**3c-eq**).

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