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REGIOSELECTIVITY OF THE ADDITION OF α-METALLATED *N,N*-DIMETHYL SULFONAMIDES TO α,β-UNSATURATED CARBONYL COMPOUNDS

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The regioselectivity of the addition of lithiated sulfonamides covers all the possible variations, from pure 1,2- or pure 1,4-additions to mixtures of the two. The 1,2- *vs* 1,4-addition competition is directed by the "hardness" of sulfonamide "carbanions" in terms of stronger preferance of the aldol type addition, on one hand, and by factors such as the steric bulk of the attacking "carbanions" and metal salt dissociation or aggregation in the solvent which retard the 1,2- more than the 1,4-addition, on the other hand.

Key words: α-Metallated *N,N*-dimethylsulfonamides, β-hydroxysulfonamides, δ-ketosulfonamides, α,β-unsaturated carbonyl compounds, regioselectivity, 1,2- *vs* 1,4-addition.

INTRODUCTION

Additions of nucleophiles to α,β-unsaturated carbonyl compounds may occur in either a 1,2- (aldol type carbonyl addition[1]), or in a 1,4- (Michael type conjugate addition[2]) fashion. Results of the addition of a broad variety of organometallic reagents to α-enones and, less frequently, to α-enals range from pure 1,2- or pure 1,4-addition to complete loss of regioselectivity. The significant number of accumulated experimental data,[3–30] as well as some early theoretical work[8b,23,31–33] now allow for both monitoring and, to a certain extent, prediction of regioselectivity.

The nature of the organometallic reagent is one of the most important factors determining regioselectivity. Publications concerning the addition of functional organometallics generated from ketones,[3–5] carboxylic acids,[6,7] esters[4b,7–11] including esters of unsaturated acids,[12] dithioesters,[13] amides,[14,15] thioamides,[14b,16] nitriles,[17,18] cyanoacetates,[19] α-heterosubstituted (N, O, Cl, P, S, Se-containing) active methylene compounds,[20–25] imines,[26] etc. to α-enones and α-enals appear regularly. Silylketene acetals,[27] silylthioketene acetals,[28] *bis*-(trimethylsilyl) ketene acetals,[29] as well as titanium "ate"-complexes of ketone or ester enolates[30] also have been recently employed as nucleophiles in these types of addition reactions.

Recent high level theoretical studies of regio- and stereoselectivity of model alkyl copper addition to conjugated enones[33] indicate clearly the preference of "soft," solvated, organometallics for larger six-membered ring transition structures. "Hard," less solvated, nucleophiles prefer four rather than six-membered transition structures in a process involving initial association of metal "ions" with carbonyl oxygen.

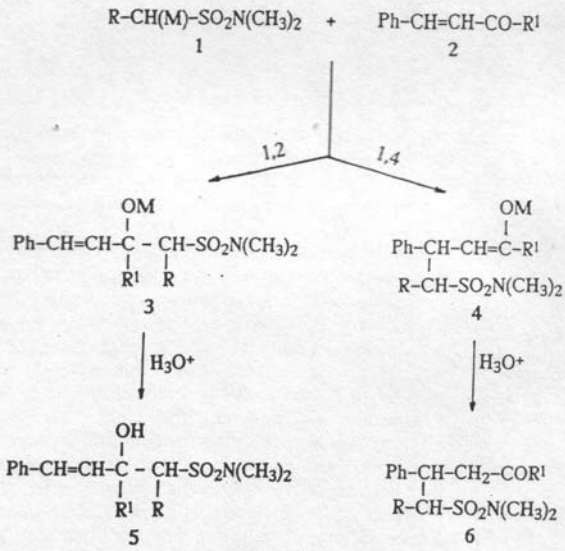
Six-membered ring transition structures are involved in the path to 1,4-Michael type addition products. Experiments and calculations show their energetic and geometric parameters have the same sensitivity to steric effects, as in cases of nucleophilic additions to carbonyl groups.

Earlier interpretations of regioselectivity have been suggested on the basis of the HSAB principle[34] and the generalized perturbation theory of chemical reactivity.[35] According to these theories,[8b,31a,32] in the absence of electrophilic assistance by Lewis acids,[31b] charge control favours the carbonyl attack, as given also by the coulombic term in Klopman's perturbation energy equation. Conjugate 1,4-addition, in contrast, is favoured by orbital control. More recently, the importance of repulsive steric and exchange interactions has also been pointed out.[23]

We report here the results of our study of addition of organometallics generated from sulfonamides to α,β-unsaturated aldehydes and ketones.

RESULTS AND DISCUSSION

We have studied the interaction of metal (mostly lithium) derivatives of *N,N*-dimethylamides of methane-, ethane- and phenylmethanesulfonic acids with cinnamaldehyde, benzylideneacetone and chalcone, according to Scheme 1.



SCHEME 1

The reactions proceed smoothly and after hydrolysis of the salts **3** and **4** give in good yields either β-hydroxysulfonamides **5** (1,2-addition), or δ-ketosulfonamides **6** (1,4-addition), or a mixture of the two.

The choice of reagents covers all the possible variations of regioselectivity, depending on either the organometallic reagent, or the unsaturated carbonyl compound. Under kinetic control cinnamaldehyde shows 1,2-regioselectivity regardless of R, that is, aldol addition (Table I, entries 1, 6, 12). On the other hand, the lithium derivative of methanesulfonamide (R = H) also shows exclusively 1,2-

TABLE I

Addition of $RCH(M)SO_2N(CH_3)_2$ to $C_6H_5CH{=}CH{-}COR^1$

Entry	Compound			M	Reaction conditions	Yield %	5 %	6 %
	R	R^1	5, 6			(5 + 6)	(M/m)	(M/m)
1*	H	H	a	Li	A	75	100	0
2*	H	CH_3	b	Li	A	71	100	0
3*	H	C_6H_5	c	Li	A	78	100	0
4*	H	C_6H_5	c	Li	B	80	95	5
5**	H	C_6H_5	c	Li	C	60	0	100
6*	CH_3	H	d	Li	A	72	100 (55/45)	0
7*	CH_3	CH_3	e	Li	A	64	70 (67/33)	30 (>95/5)
8**	CH_3	CH_3	e	Li	D	62	56 (78/22)	44 (>95/5)
9*	CH_3	C_6H_5	f	Li	A	80	26 (>95/5)	74 (75/25)
10**	CH_3	C_6H_5	f	Li	D	70	0	100 (90/10)
11*	CH_3	C_6H_5	f	MgCl	A	32	33 (>95/5)	67 (70/30)
12*	C_6H_5	H	g	Li	A	83	100 (67/33)	0
13*	C_6H_5	CH_3	h	Li	A	70	42 (55/45)	58 (>95/5)
14*	C_6H_5	CH_3	h	MgCl	A	56	79 (67/33)	21 (70/30)
15*	C_6H_5	C_6H_5	i	Li	E	80	0	100 (95/5)

* kinetic control; ** thermodynamic control;

A: THF, -50°C, 10 min; B: THF -50° → -20°C, 60 min; C: THF + 20% HMPT, -50° → r.t., 3 h; D: THF -50° → -20°C, 3 h; E: THF, -50°C, 2 min.

regioselectivity even with chalcone, which is well known for its intrinsic propensity to undergo 1,4-addition; that is, Michael conjugate addition (entries 1–3).

With R = CH_3 under kinetic control, the reaction gives mixtures of 1,2- and 1,4-addition products (entries 7 and 9). The aldol reaction is predominant with benzylidene acetone, while with chalcone the dominant product is that of conjugate addition. The additional phenyl substituent extending the conjugated system in chalcone evidently increases the propensity for Michael addition. 1,4-addition is predominant also for the reactions of metallated phenylmethanesulfonamide (R = Ph), the δ-ketosulfonamide being the sole product with chalcone (entry 15).

Thermodynamic factors favour, as observed in numerous cases,[3h,4b,10,11,17a,17d,21] 1,4-type Michael additions. However, an unusual equilibrium of the kinetically controlled 1,4-adduct and the 1,2-adduct has been reported as well.[32a] Thermodynamically more stable in our cases are the 1,4-adducts. For example, the kinetically controlled 1,2-adduct **3c** obtained in THF at −50°C for 10 min, was converted into the 1,4-adduct **4c** by adding 20% HMPT, allowing the reaction mixture to warm up to room temperature and then stirring the mixture for an extended time (entry 5).

As outlined, the observed regioselectivity is not surprising having in mind the results of our previous studies on the same sulfonamide reagents and their somewhat contradictory behaviour towards aldehydes,[36] on one hand, and 4-*t*-butylcyclohexanone,[37] on the other. It is well known that a parallelism exists between the orientation, axial or equatorial, of the attack of a nucleophile and the regioselectivity of its addition to α-enones.

Stereochemical studies have shown that sulfonamide carbonions have a very low sensitivity to the steric requirements of substituents (even as bulky as *i*-Pr, *t*-Bu, α-naphthyl) around the incipient C—C bond,[36] compared to aldehyde additions of other organometallics. Sulfonamide carbanions thus behave as if their effective volume were negligible.

On the other hand, the addition to 4-*t*-butylcyclohexanone showed a slightly favoured axial attack only in the case of methanesulfonamide, whereas equatorial attack was moderately preferred with ethanesulfonamide (R = CH_3) and highly preferred when R = Ph.[37]

AM1 calculations of reaction transition structure[38] provide a sufficiently sound basis to interpret the experimental results of C-metallated sulfonamide additions to α,β-unsaturated carbonyl compounds, showing that metal "salts" of sulfonamide carbanions are "harder" nucleophiles than the corresponding carboxamide or thiocarboxamide derivatives (see Table II) in terms of a stronger preference of sulfonamide derivatives for 1,2-; i.e., aldol type addition. There is, however, little obvious relation of the calculated atomic charges and orbital energies of the carbonyl compounds to the observed regioselectivity. The competition between 1,2- and 1,4-addition is directed by factors such as the steric bulk of the attacking "carbanions" and metal salt dissociation and, possibly, aggregation in the corresponding solvent to an extent commensurate to orbital control of 1,4-addition, or charge control of 1,2-addition.

To discuss the role of counterions in regioselectivity of metallated sulfonamide additions to α-enones and enals, we go back to the results listed in Table I and compare entry 9 to 11, and 13 to 14. Replacement of Li by Mg increases the 1,2-

TABLE II

AM1 anion charges (in *e*) and ionization potentials (HOMO energies, *eV*) for carboxamide (XX = CO), thioamide (XX = CS), and sulfonamide (XX = SO_2) carbanions, R—CH—XX—NH_2

XX / R	CO	CS	SO_2
H	-0.6542 2.01	-0.4482 2.63	-1.5506 3.82
CH_3	-0.6157 2.03	-0.4132 2.63	-1.4600 3.65
C_6H_5	-0.5089 2.69	-0.4216 3.13	-1.3208 3.81

to 1,4-product ratio, usually explained by the assumption of the stronger complexation capacity of magnesium compared to lithium. A similar trend has already been observed; see for example the cases of the lithium and magnesium enolates of ethyl *t*-butyl ketone,[3h] and of *N,N*-dimethylphenylacetamide.[15b] While Dorigo and Morokuma[33] suggest an interpretation for the increase of the 1,2- *vs* 1,4-product ratio by domination of the coulombic part of the interaction between reactants, this does not seem the case with our reagents. Organo-magnesium derivatives are more covalent than lithium derivatives, and the nucleophilic "carbanion" centre bears less negative charge than do the corresponding lithium derivatives. A probable explanation of this behaviour of Mg-derivatives of sulfonamides can be derived from the observations of preferred 1,2-addition of organolithiums to α-enones for less dissociating contact ion pairs, as would be the case of Mg- *vs* Li-derivatives, with rapid dissociation equilibrium between contact and solvent separated ion pairs in the latter case.[39] This interpretation stresses once again the importance of broad varieties of factors to reaction selectivity, pertaining to isolated reactant molecules as well as to reaction conditions such as solvent, temperature, etc.

Although no special attention has been paid to the stereochemical course of the 1,2- and 1,4-interactions, and the stereochemistry of products has not been elucidated (products, therefore, are designated as M, for major, and m, for minor), it is worth noticing that the 1,2-addition stereoselectivity ranges from 55/45 to higher than 95/5. The observed high diastereoselectivity (see Table I, entries 9 and 11) is surprising, having in mind the low diastereoselectivity observed for aldol reactions of sulfonamides.[36,40] Similar highly diastereoselective 1,2-additions to α-enones compared to low selectivity of addition to aldehydes of carboxamide and ester organometallics also has been reported.[14b]

EXPERIMENTAL

All reactions were carried out under dry argon. THF was distilled over $LiAlH_4$ prior to use. HMPT was distilled over CaH_2 and stored over molecular sieves. The metal reagents **1a–c** were prepared according to Reference 36.

TABLE III

Constants and ^{1}H-NMR data of compounds **5** and **6**

Compound	m.p. (°C)[a]	Molecular formula[b]	^{1}H-NMR ($CDCl_3$, TMS), δ (ppm), *J* (Hz)[c]
5a	85-86	$C_{12}H_{17}NO_3S$ (255.3)	2.91 (s, 6H); 3.14 (d, 2H, *J* = 5.9); 3.33 (br.s, 1H); 4.91 (m, 1H); 6.18 (dd, 1H, *J* = 15.8 and 5.7); 6.73 (d, 1H, *J* = 15.8); 7.28 - 7.40 (m, 5H).
5b	95-97	$C_{13}H_{19}NO_3S$ (269.4)	1.57 (s, 3H); 2.86 (s, 6H); 3.18 (d, 2H, *J* = 1.25); 4.78 (br.s, 1H); 6.31 (d, 1H, *J* = 15.8); 6.74 (d, 1H, *J* = 15.8); 7.25 - 7.41 (m, 5H).
5c	136-138	$C_{18}H_{21}NO_3S$ (331.4)	2.73 (s, 6H); 3.55 (s, 2H); 4.70 (s, 1H); 6.60 (d, 1H, *J* = 15.8); 6.79 (d, 1H, *J* = 15.8); 7.26 - 7.58 (m, 10H).
5d M	105-107	$C_{13}H_{19}NO_3S$ (269.4)	1.28 (d, 3H, *J* = 7.2); 2.96 (s, 6H); 3.26 (m, 1H); 3.75 (br.s, 1H); 4.60 (t, 1H, *J* = 7.4); 6.15 (dd, 1H, *J* = 15.7 and 7.3); 6.69 (dd, 1H, *J* = 15.7 and 1.4); 7.28 - 7.42 (m, 5H).
m	58-60		1.36 (d, 3H, *J* = 7.2); 2.98 (s, 6H); 3.18 (br.s, 1H); 3.27 (dq, 1H, *J* = 7.2 and 1.8); 4.95 (br.d, 1H, *J* = 4.9); 6.14 (dd, 1H, *J* = 15.8 and 5.5); 6.74 (d, 1H, *J* = 15.8); 7.25 - 7.42 (m, 5H).
5e M	[d]		[e]1.36 (d, 3H, *J* = 7.1); 1.57 (s, 3H); 2.92 (s,6H); 3.25 (q, 1H, *J* = 7.1); 4.37 (s, 1H); 6.24 (d, 1H, *J* = 15.9); 6.72 (d, 1H, *J* = 15.9); 7.25 - 7.42 (m, 5H).
m			[f]1.39 (d, 3H, *J* = 7.0); 1.49 (s, 3H); 2.92 (s, 6H); 3.34 (q, 1H, *J* = 7.0); 4.37 (s, 1H); 6.39 (d, 1H, *J* = 15.8); 6.75 (d, 1H, *J* = 15.8); 7.20 - 7.43 (m, 5H).
5f M	125-127	$C_{19}H_{23}NO_3S$ (345.5)	1.29 (d, 3H, *J* = 7.1); 2.76 (s, 6H); 3.65 (q, 1H, *J* = 7.1); 4.96 (s, 1H); 6.72 (d, 1H, *J* = 15.7); 6.95 (d, 1H, *J* = 15.7); 7.20 - 7.53 (m, 10H).
5g M	116-117	$C_{18}H_{21}NO_3S$ (331.4)	2.59 (s, 6H); 3.80 (br.s, 1H); 4.28 (d, 1H, *J* = 8.8); 5.18 (ddd, 1H, *J* = 6.1, 6.0 and 1.3); 5.88 (dd, 1H, *J* = 15.8 and 6.1); 6.59 (dd, 1H, *J* = 15.8 and 1.2); 7.14 - 7.59 (m, 10H).
m	137-138		2.57 (s, 6H); 4.27 (d, 1H, *J* = 1.1); 3.25 (br.s, 1H); 5.23 (br.d, 1H, *J* = 6.1); 6.03 (dd, 1H, *J* = 15.7 and 7.0); 6.64 (dd, 1H, *J* = 15.7 and 1.0); 7.19 - 7.60 (m, 10H).

	M	159-160	$C_{19}H_{23}NO_3S$	1.54 (s, 3H); 2.50 (s, 6H); 4.21 (br.s, 1H); 4.32 (s, 1H); 6.16 (d, 1H, *J* = 15.7); 6.73 (d, 1H, *J* = 15.7); 7.25 - 7.47 (m, 10H).
5h			(345.5)	
	m	-		1.31 (s, 3H); 2.52 (s, 6H); 4.39 (s, 1H); 4.60 (br.s, 1H); 6.56 (d, 1H, *J* = 16.0); 6.69 (d, 1H, *J* = 16.0); 7.34 - 7.45 (m, 10H).
6c		88-90	$C_{18}H_{21}NO_3S$	2.79 (s, 6H); 3.29 (dd, 1H, *J* = 14.0 and 6.2); 3.41 (dd, 1H, *J* = 17.4 and 5.6); 3.47 (dd, 1H, *J* = 14.0 and 7.7); 3.48 (dd, 1H, *J* = 17.4 and 8.1); 3.99 (m, 1H); 7.23 - 7.92 (m, 10H).
			(331.4)	
6e		[e]		[e]1.26 (d, 3H, *J* = 7.0); 2.10 (s, 3H); 2.91 (s, 6H); 3.06 (dd, 1H, *J* = 10.9 and 17.8); 3.21 - 3.25 (m, 2H).
	M	104-106	$C_{19}H_{23}NO_3S$	1.37 (d, 3H, *J* = 7.0); 2.95 (s, 6H); 3.35 (dq, 1H, *J* = 7.0 and 2.5); 3.62 (dd, 1H, *J* = 17.6 and 11.1); 3.85 (dd, 1H, *J* = 17.6 and 3.5); 4.18 (m, 1H); 7.18 - 7.96 (m, 10H).
6f			(345.5)	
	m	-		[g]1.11 (d, 3H, *J* = 6.9); 2.92 (s, 6H).
	M	159-160	$C_{19}H_{23}NO_3S$	1.90 (s, 3H); 2.43 (s, 6H); 2.81 (dd, 1H, *J* = 16.6 and 10.5); 3.02 (dd, 1H, *J* = 16.6 and 3.8); 4.23 (m, 1H); 4.40 (d, 1H, *J* = 7.1); 7.20 - 7.39 (m, 10H).
6h			(345.5)	
	m	-		[g]2.03 (s, 3H); 2.39 (s, 6H); 3. 16 (dd, 1H, *J* = 16.5 and 9.3); 3.50 (dd, 1H, *J* = 16.5 and 3.3) 4.08 (d, 1H, *J* = 10.5); 7.20 - 7.39 (m, 10H).
6l	M	191-193	$C_{24}H_{25}NO_3S$	2.46 (s, 6H); 3.40 (dd, 1H, *J* = 16.8 and 9.9); 3.62 (dd, 1H, *J* = 16.8 and 3.3); 4.45 (m, 1H); 4.48 (s, 1H); 7.14 - 7.78 (m, 15H).
			(407.5)	

[a] m.p.s. (uncorrected), taken on a Kofler hot-stage microscope; the products were recrystallized from $CHCl_3$/n-hexane. [b] Elemental analyses in good agreement with the theoretical values. [c]Recorded on a Bruker WM 250 MHz spectrometer. [d]Not isolated in isomerically pure state; [e]Values from the spectrum of a mixture (5e-M/5e-m = 87/13 + 6e);[f]Values from the spectrum of a mixture (5e-m/6e-M = 60/40);[g]Values from the spectrum of a mixture with the major diastereoisomer.

Addition of **1** *to* **2**. *General procedure*.

The total amount of solvent used for the preparation of **1** and the addition of **2** was adjusted to a reaction concentration of 0.4 mol/l.

A THF solution of **2** (0.9 equivalents) was added to the cooled solution of **1** maintaining the reaction temperature at −50°C. After being stirred for a predetermined time at the chosen temperature (see Table I) the reaction mixture was hydrolysed with 1:1 HCl, saturated with NaCl and the product was extracted with ether or ethyl acetate. The organic layer was washed with brine, dried ($MgSO_4$), and the solvent was evaporated in vacuo. Aliquots of the crude product were subjected to NMR determination of the 1,2/1,4, ratio, the M/m ratio and the total yield. Recrystallization, preparative TLC or column chromatography was used for the isolation of the pure isomers (Table III).

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