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Double coordination ability of bis(dimethylaluminum) sulfate toward carbonyl substrates

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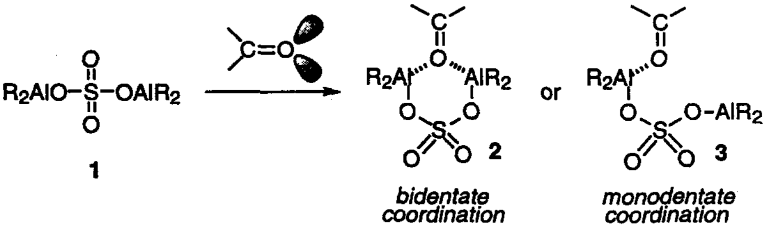
Abstract

New insight into the crucial role of bis(dimethylaluminum) sulfate as bidentate Lewis acid has been demonstrated using typical carbonyl allylation and Diels–Alder reaction in comparison with monodentate counterparts. The double coordination phenomenon of bidentate $(Me_2AlO)_2SO_2$ is characterized with 2,6-dimethyl-γ-pyrone by ^{13}C NMR spectroscopy and Mukaiyama-type Michael addition. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: aluminum; aluminum compounds; allylation; Diels–Alder reactions; Michael reactions.

Bis(dialkylaluminum) sulfates, $(R_2AlO)_2SO_2$ **1** are known as highly oxygenophilic Lewis acid reagents.[1,2] Their Lewis acidity stems from the strong electron-withdrawing sulfate moiety on aluminum. This property has been successfully utilized for the polymerization catalysts and allylation of various carbon electrophiles.[3,4] In the course of our continuing research on recently developed bidentate Lewis acid chemistry,[5] we have been interested in the nature of the Lewis acidity of bis(dialkylaluminum) sulfates **1**, i.e., the possibility of forming a double coordination complex of type **2** toward carbonyl substrates rather than a single coordination complex **3** (Scheme 1).



Scheme 1.

First, we examined the reactivity of $(Me_2AlO)_2SO_2$ for typical carbonyl allylation in comparison with Me_2AlOSO_2Me and $Me_2AlOSO_2OSiMe_3$ as monodentate analogues, and the selected results are

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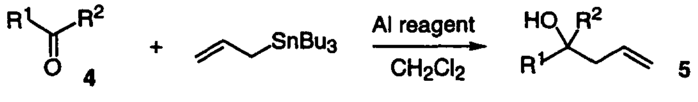
Table 1
Allylation of ketones with various organoaluminum sulfates[a]



entry	ketone 4		Al reagent	reaction condition	% yield[b]
	R^1	R^2		(°C, h)	
1	Ph	Me	$(Me_2AlO)_2SO_2$	-20, 0.5	79
2			Me_2AlOSO_2Me	-20, 0.5	4
3			$Me_2AlOSO_2OSiMe_3$	-20, 0.5	13
4	Bu	Bu	$(Me_2AlO)_2SO_2$	-20, 4	88
5			Me_2AlOSO_2Me	-20, 4	5
6			$(Et_2AlO)_2SO_2$	0, 3.5	81
7			Et_2AlOSO_2Me	0, 3.5	8
8	$-(CH_2)_5-$		$(Me_2AlO)_2SO_2$	-45, 3	65
9			Me_2AlOSO_2Me	-45, 3	19

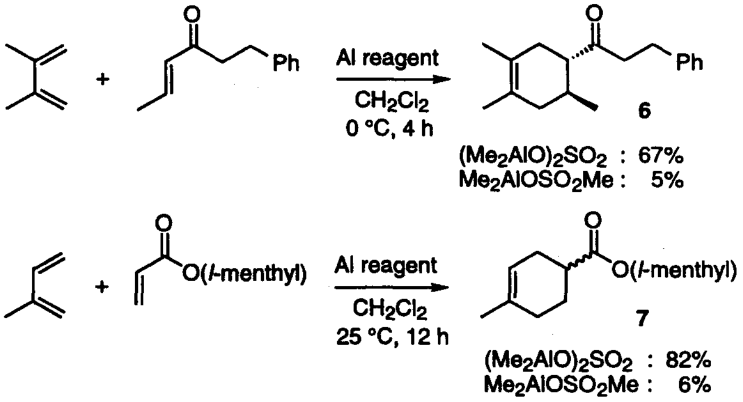
[a] Carbonyl allylation was carried out with various Al reagents in CH_2Cl_2 under the given reaction conditions. [b] Isolated yield.

shown in Table 1. The requisite $(Me_2AlO)_2SO_2$ can be readily prepared by mixing Me_3Al (2 equiv.) with $(Me_3SiO)_2SO_2$ (1 equiv.) in CH_2Cl_2 at 0°C for 30 min.[6,7] Complexation of acetophenone **4** (R^1=Ph; R^2=Me) with $(Me_2AlO)_2SO_2$ in CH_2Cl_2 and subsequent treatment with $Bu_3SnCH_2CH{=}CH_2$ (1.1 equiv.) at −20°C for 0.5 h afforded 2-phenyl-4-penten-2-ol **5** (R^1=Ph; R^2=Me) in 79% yield (entry 1). In marked contrast, however, treatment of this ketone with Me_2AlOSO_2Me or $Me_2AlOSO_2OSiMe_3$ (1 equiv.) under otherwise similar allylation conditions gave the corresponding allylation product in low yields (4–13%) (entries 2 and 3). A similar tendency was observed with 5-nonanone using $(Et_2AlO)_2SO_2$ versus Et_2AlOSO_2Me (entry 6 versus 7). These results imply the importance of the Al-OSO_2O-Al unit for activation of the ketone carbonyl. Other examples are also included in Table 1.

A similar difference of reactivity between bis-Al sulfate, $(Me_2AlO)_2SO_2$, and mono-Al analogue, Me_2AlOSO_2Me, is observed in the Diels–Alder reaction of dienes and α,β-unsaturated carbonyl substrates. Thus, reaction of (*E*)-6-phenyl-2-hexen-4-one and 2,3-dimethyl-1,3-butadiene (1.1 equiv.) with $(Me_2AlO)_2SO_2$ in CH_2Cl_2 at 0°C for 4 h proceeded smoothly to furnish the corresponding Diels–Alder adduct **6** in 67% yield, although its monodentate counterpart, Me_2AlOSO_2Me, yielded only 5% of cycloadduct **6** under similar conditions (Scheme 2). Diels–Alder reaction of isoprene and *l*-menthyl acrylate giving a cycloadduct **7** works equally well with the $(Me_2AlO)_2SO_2$ reagent.[8]

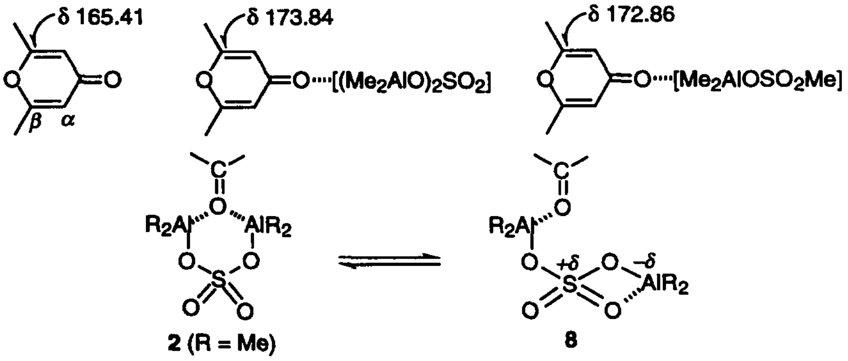
Such activation phenomenon of $(Me_2AlO)_2SO_2$ versus Me_2AlOSO_2Me is also observed by ^{13}C NMR spectroscopy using 2,6-dimethyl-γ-pyrone as carbonyl substrate. Thus, the 75 MHz ^{13}C NMR measurement of the 1:1 2,6-dimethyl-γ-pyrone/$(Me_2AlO)_2SO_2$ complex in $CDCl_3$ at −50°C showed that the original signal of pyrone β-carbons at δ 165.41 shifted strongly to δ 173.84. Further addition of one more equivalent of 2,6-dimethyl-γ-pyrone to this complex showed pyrone β-carbons at δ 172.14. In contrast, the 1:1 2,6-dimethyl-γ-pyrone/Me_2AlOSO_2Me complex under similar conditions undergoes a downfield shift for the pyrone β-carbons (δ 172.86), implying the weaker electrophilic activation of the pyrone carbonyl.

Based on the experimental and spectroscopic data described above, the activation phenomenon



Scheme 2.

of $(Me_2AlO)_2SO_2$ toward carbonyl substrates is ascribed to the double coordination **2** (R=Me) of bis-Al reagent to the carbonyl oxygen (Scheme 3). However, another activation mode of type **8** is also conceivable for the ketone/$(Me_2AlO)_2SO_2$ complex.[9] Accordingly, we carried out the regio- and stereocontrolled Michael addition of silyl ketene acetals to α,β-unsaturated ketones as acceptors.[10] Reaction of benzalacetone and silyl ketene acetal with Me_2AlOSO_2Me gave rise to a mixture of Michael adducts **9** and **10** (83% yield; *E*:*Z*=17:83) with high *Z*-selectivity (Scheme 4). $Me_2AlOSO_2OSiMe_3$ **11** (R=$OSiMe_3$) showed similar *Z*-selectivity (78% yield; *E*:*Z*=35:65). In contrast, switching these mono-Al reagents **11** (R=Me, $OSiMe_3$) to bis-Al reagent, $(Me_2AlO)_2SO_2$, afforded high *E*-selectivity (76% yield; *E*:*Z*=67:23). Based on the experimental findings, the stereochemical outcome of the *Z*-isomeric Michael adduct **9** is interpreted by the preferable formation of complex **11** with sterically less hindered Me_2AlOSO_2Me. Using bidentate $(Me_2AlO)_2SO_2$, the coordination complex **13** with *s-trans* conformation is then favored rather than the sterically congested complex **12** with *s-cis* conformation, thereby increasing the formation of *E*-isomeric Michael adduct **10**.[5a]



Scheme 3.

Acknowledgements

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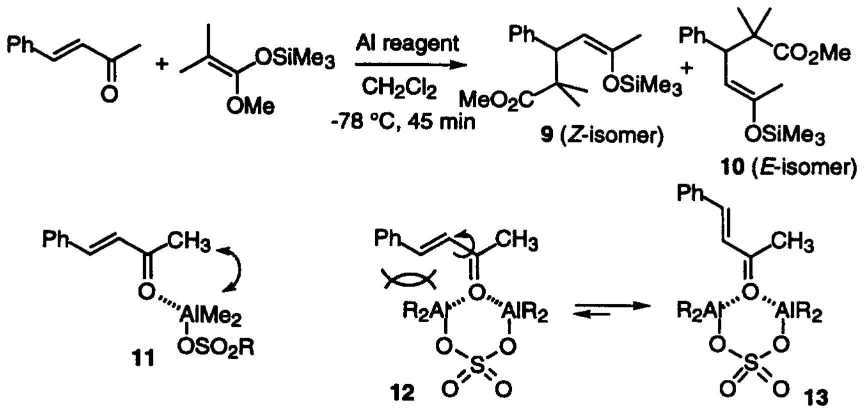

Scheme 4.

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8. The cycloadduct **7** was obtained as a diastereomeric mixture (ratio=~1:1).
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