

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

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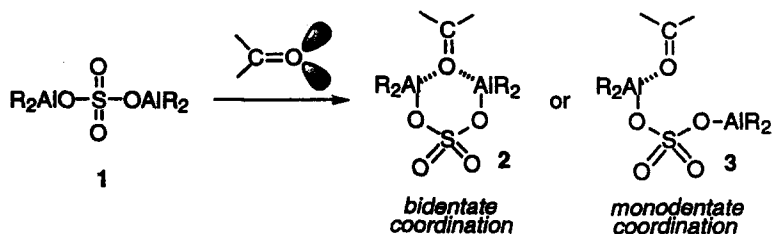
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Abstract

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 $(\text{Me}_2\text{AlO})_2\text{SO}_2$ 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.

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Bis(dialkylaluminum) sulfates, $(\text{R}_2\text{AlO})_2\text{SO}_2$ **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 $(\text{Me}_2\text{AlO})_2\text{SO}_2$ for typical carbonyl allylation in comparison with $\text{Me}_2\text{AlOSO}_2\text{Me}$ and $\text{Me}_2\text{AlOSO}_2\text{OSiMe}_3$ 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 R ¹ R ²		Al reagent	reaction condition (°C, h)	% yield ^b
1	Ph	Me	(Me ₂ AlO) ₂ SO ₂	-20, 0.5	79
2			Me ₂ AlOSO ₂ Me	-20, 0.5	4
3			Me ₂ AlOSO ₂ OSiMe ₃	-20, 0.5	13
4	Bu	Bu	(Me ₂ AlO) ₂ SO ₂	-20, 4	88
5			Me ₂ AlOSO ₂ Me	-20, 4	5
6			(Et ₂ AlO) ₂ SO ₂	0, 3.5	81
7			Et ₂ AlOSO ₂ Me	0, 3.5	8
8	-(CH ₂) ₅ -		(Me ₂ AlO) ₂ SO ₂	-45, 3	65
9			Me ₂ AlOSO ₂ Me	-45, 3	19

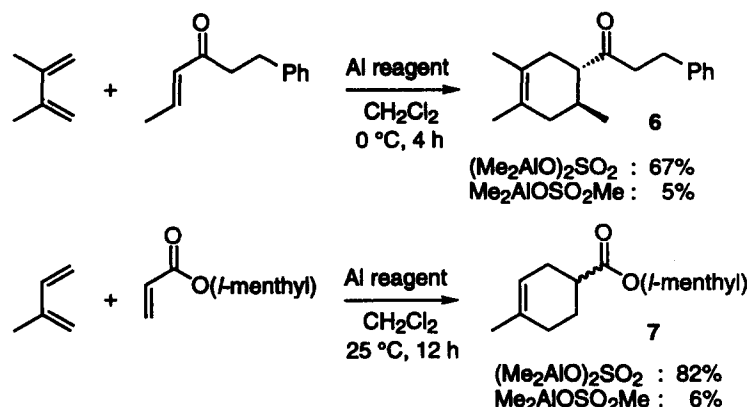
^a Carbonyl allylation was carried out with various Al reagents in CH₂Cl₂ under the given reaction conditions. ^b Isolated yield.

shown in Table 1. The requisite (Me₂AlO)₂SO₂ can be readily prepared by mixing Me₃Al (2 equiv.) with (Me₃SiO)₂SO₂ (1 equiv.) in CH₂Cl₂ at 0°C for 30 min.^{6,7} Complexation of acetophenone 4 (R¹=Ph; R²=Me) with (Me₂AlO)₂SO₂ in CH₂Cl₂ and subsequent treatment with Bu₃SnCH₂CH=CH₂ (1.1 equiv.) at -20°C for 0.5 h afforded 2-phenyl-4-penten-2-ol 5 (R¹=Ph; R²=Me) in 79% yield (entry 1). In marked contrast, however, treatment of this ketone with Me₂AlOSO₂Me or Me₂AlOSO₂OSiMe₃ (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 (Et₂AlO)₂SO₂ versus Et₂AlOSO₂Me (entry 6 versus 7). These results imply the importance of the Al-OSO₂O-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, (Me₂AlO)₂SO₂, and mono-Al analogue, Me₂AlOSO₂Me, 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 (Me₂AlO)₂SO₂ in CH₂Cl₂ at 0°C for 4 h proceeded smoothly to furnish the corresponding Diels–Alder adduct 6 in 67% yield, although its monodentate counterpart, Me₂AlOSO₂Me, 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 (Me₂AlO)₂SO₂ reagent.⁸

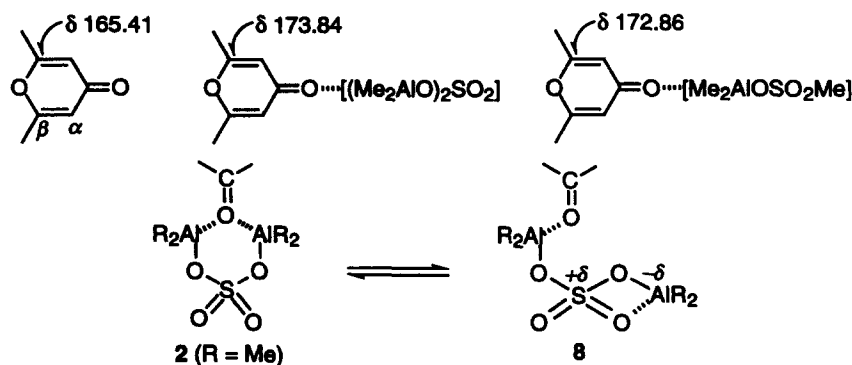
Such activation phenomenon of (Me₂AlO)₂SO₂ versus Me₂AlOSO₂Me is also observed by ¹³C NMR spectroscopy using 2,6-dimethyl-γ-pyrone as carbonyl substrate. Thus, the 75 MHz ¹³C NMR measurement of the 1:1 2,6-dimethyl-γ-pyrone/(Me₂AlO)₂SO₂ complex in CDCl₃ at -50°C showed that the original signal of pyrone 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/Me₂AlOSO₂Me 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.

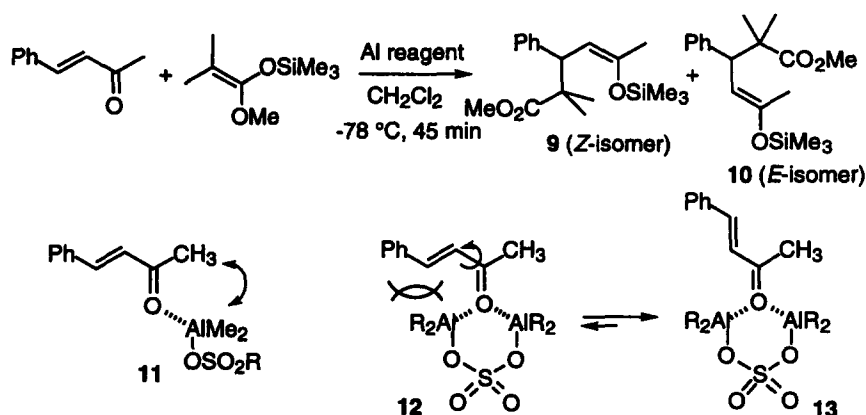
of $(\text{Me}_2\text{AlO})_2\text{SO}_2$ toward carbonyl substrates is ascribed to the double coordination **2** ($\text{R}=\text{Me}$) of bis-Al reagent to the carbonyl oxygen (Scheme 3). However, another activation mode of type **8** is also conceivable for the ketone/ $(\text{Me}_2\text{AlO})_2\text{SO}_2$ 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 $\text{Me}_2\text{AlOSO}_2\text{Me}$ gave rise to a mixture of Michael adducts **9** and **10** (83% yield; $E:Z=17:83$) with high Z -selectivity (Scheme 4). $\text{Me}_2\text{AlOSO}_2\text{OSiMe}_3$ **11** ($\text{R}=\text{OSiMe}_3$) showed similar Z -selectivity (78% yield; $E:Z=35:65$). In contrast, switching these mono-Al reagents **11** ($\text{R}=\text{Me}$, OSiMe_3) to bis-Al reagent, $(\text{Me}_2\text{AlO})_2\text{SO}_2$, 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 $\text{Me}_2\text{AlOSO}_2\text{Me}$. Using bidentate $(\text{Me}_2\text{AlO})_2\text{SO}_2$, 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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7. This preparative method provides a very convenient way for the synthesis of (R₂AlO)₂SO₂ (R=Me, Et). The facile transmetalation of (Me₃SiO)₂SO₂ with Me₃Al in CDCl₃ is readily confirmed by ¹H NMR analysis.
8. The cycloadduct **7** was obtained as a diastereomeric mixture (ratio=∼1:1).
9. We also assume that major complex **8** is in equilibrium with minor bidentate **2** (R=Me), which could behave as a reactive species for further chemical transformation.
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