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Isopropoxyaluminum 1,1′-biphenyl-2-oxy-2′-perfluorooctanesulfonamide as a catalyst for Tishchenko reaction

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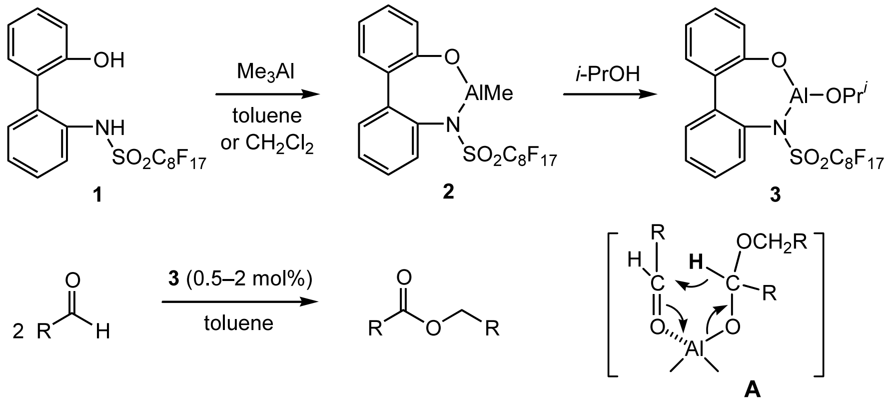
Abstract—Isopropoxyaluminum 1,1′-biphenyl-2-oxy-2′-perfluorooctanesulfonamide (**3**) has been evaluated as an aluminum-based catalyst for the Tishchenko reaction. Compound **3** was found to exert high catalytic activity in the reaction with aliphatic aldehydes and also enabled smooth dimerization of enolizable aldehydes. This advantage was highlighted by the quantitative formation of ethyl acetate from acetaldehyde by the present system. © 2003 Elsevier Science Ltd. All rights reserved.

We recently introduced modified aluminum alkoxide, isopropoxyaluminum 1,1′-biphenyl-2-oxy-2′-perfluorooctanesulfonamide (**3**), readily prepared from 2-hydroxy-2′-(perfluorooctanesulfonylamino)biphenyl (**1**), Me_3Al and 2-propanol, as a highly reactive aluminum-based catalyst for Meerwein–Ponndorf–Verley reduction of ketones with 2-propanol as a hydride donor.[1a] In addition, the effectiveness of the organoaluminum pre-catalyst **2** for Oppenauer oxidation of alcohols with pivalaldehyde or acetone as a hydride acceptor was also demonstrated.[1b] This practical reduction–oxidation method is found to be broadly useful. In our continuing effort to further expand the synthetic utility of this type of catalyst, we have been interested in the application of **3** to the Tishchenko reaction, a dimerization reaction of aldehydes that involves an oxidation–reduction sequence through a six-membered transition state **A** to give the corresponding carboxylic esters (Scheme 1).[2–4] In this letter, we wish to describe the results of this attempt, featuring the advantage of **3**.

Selected examples are listed in Table 1. Isopropoxyaluminum 1,1′-biphenyl-2-oxy-2′-perfluorooctanesulfonamide (**3**) can be prepared in situ by the sequential treatment of **1** with Me_3Al and 2-propanol (molar ratio = 1:1:1) in toluene at room temperature for 30



Scheme 1.

Keywords: aldehydes; aluminum alkoxide; carboxylic esters; Tishchenko reaction.

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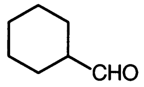
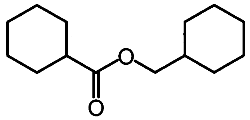
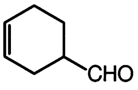
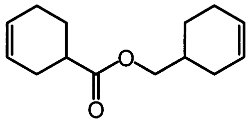
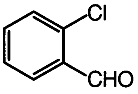
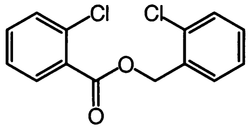
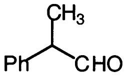
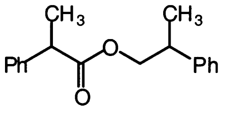
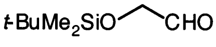
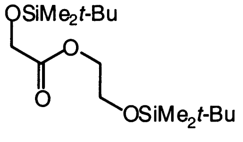
Table 1. Efficient Tishchenko reaction of aldehydes with modified aluminum alkoxide **3** as a catalyst[a]

entry	aldehyde	mol % of catalyst **3**	react. time (h)	product	% yield [b]
1	$C_5H_{11}CHO$	1	1	$C_5H_{11}CO_2C_6H_{13}$	88
2		0.5	1		86
3		0.5	0.5		93
4		0.5	0.5		95
5		2	5		88
6	PhCHO	2	5	$PhCO_2CH_2Ph$	68
7		1	0.5		89
8		2	2		81
9	CH_3CHO	1	2	$CH_3CO_2CH_2CH_3$	>99 [c]

[a] The reaction was carried out in the presence of modified aluminum catalyst **3** in toluene (substrate concentration = 7 M) at room temperature under the given reaction conditions.

[b] Isolated yield.

[c] For the experimental procedure, see note 6.

min.[1a,5] Subsequent addition of hexanal and continuous stirring at room temperature for 1 h resulted in clean formation of the Tishchenko product in 88% yield. The catalyst loading can be reduced to 0.5 mol% without decreasing the catalytic activity (entries 1 and 2). Similarly, other aliphatic aldehydes possessing α-substituent were smoothly dimerized to the corresponding carboxylic esters in excellent chemical yields (entries 3 and 4). The reaction with aromatic aldehydes also appeared to be feasible, although a certain decrease in the reactivity was observed (entries 5 and 6).

It should be noted that the aluminum alkoxide **3** is effective for the dimerization of enolizable aldehydes as demonstrated in the reactions of 2-phenylpropionaldehyde and *tert*-butyldimethylsilyloxyacetaldehyde (entries 7 and 8). Further, simple acetaldehyde, which is susceptible to undesired side reactions such as self-aldol reaction, was efficiently converted to ethyl acetate quantitatively, implying the possibility of industrial applications (entry 9).[7,8]

A typical experimental procedure is as follows (entry 7 in Table 1): 2-Hydroxy-2′-(perfluorooctanesulfonylamino)biphenyl (**1**, 66.7 mg, 0.1 mmol) was placed in a dry two-neck flask with a stirring bar under Ar, and freshly distilled toluene (200 μL) was introduced. To this suspension was added a 1 M hexane solution of Me_3Al (100 μL, 0.1 mmol) at room temperature and the resulting mixture was stirred for 15 min (**2** was generated in situ).[1a] 2-Propanol (7.7 μL, 0.1 mmol) distilled from CaH_2 was added at the same temperature and the stirring was continued for an additional 30 min (1 equiv. of methane gas toward the Al-Me of **2** was evolved). Then, freshly distilled 2-phenylpropionaldehyde (1.33 mL, 10 mmol) was added dropwise and the reaction mixture was stirred for 30 min at room temperature. The reaction was quenched by the addition of 1N HCl and the extractive workup was performed with ether. The ethereal extracts were washed with brine and dried over Na_2SO_4. Evaporation of solvents and purification of the residual oil by column chromatography on silica gel (ether/hexane = 1:30 as eluent) gave the corresponding carboxylic ester as a colorless oil (1.19 g, 4.44 mmol; 89%).

Acknowledgements

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3. For recent studies on the development of new catalysts, see for example: Simpura, I.; Nevalainen, V. *Tetrahedron* **2001**, *57*, 9867 and references cited therein.
4. For our contribution with bidentate aluminum catalysts, see: Ooi, T.; Miura, T.; Takaya, K.; Maruoka, K. *Tetrahedron Lett.* **1999**, *40*, 7695. See also, Ooi, T.; Miura, T.; Itagaki, Y.; Ichikawa, H.; Maruoka, K. *Synthesis* **2002**, 279.
5. Although the catalyst **3** can be prepared by simple mixing of $Al(OPr^i)_3$ [purchased from Aldrich Chemical Co., Ltd. (99.99% purity)] and **1** at room temperature,[1a] in this case the use of CH_2Cl_2 as solvent was a prerequisite, and led to a slight decrease of chemical yield. For instance, attempted dimerization of 3-cyclohexenecarbaldehyde with 0.5 mol% of **3** thus prepared in CH_2Cl_2 at room temperature for 30 min gave the corresponding ester in 88% yield (cf. entry 4 in Table 1).
6. Experimental procedure for the reaction of acetaldehyde (entry 9 in Table 1): To a solution of **3** prepared as described in the text was added a solution of acetaldehyde (10 vol% in toluene–heptane; 5 mL, 8.9 mmol) at 0°C and the flask was then tightly closed. The reaction mixture was stirred for 2 h at room temperature. The yield of ethyl acetate was determined to be >99% by GC analysis using Shimadzu GC-14A with a capillary column of DB-1 (J&W Scientific 123–1032, 0.32×30,000 mm); $t_R = 1.1$ min for acetaldehyde, 1.5 min for ethyl acetate and 2.3 min for heptane (internal standard) at the column temperature of 40°C (3 min) to 140°C (1 min) (100°C/9 min).
7. The dimerization of acetaldehyde with our previously developed bidentate catalyst, (2,7-dimethyl-1,8-biphenylenedioxy)bis(diisopropoxyaluminum) (0.5 mol%),[4] under otherwise similar conditions was found to be slower, giving ethyl acetate in 91% yield after 2.5 h.
8. SHOWA DENKO K. K. produces ethyl acetate from acetaldehyde on a world-wide level (150,000 ton/year) using aluminum alkoxide type catalyst.