Aluminum Trisphenoxide Polymer as a Lewis Acidic, Solid Catalyst

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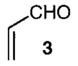
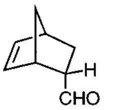
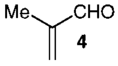
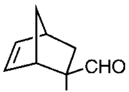
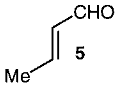
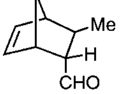
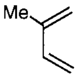
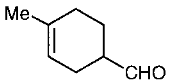
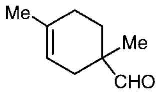
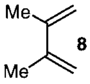
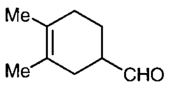
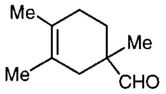
Abstract: A newly introduced, solid polymer of an aluminum trisphenoxide has been demonstrated an efficient catalyst for promoting the Diels–Alder reaction of α,β-enals.

Key words: aluminum trisphenoxide, solid catalyst, Lewis acidic polymer, Diels–Alder reaction, ATPH

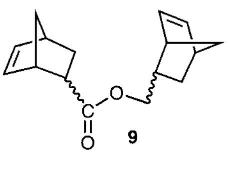
Homogeneous, Lewis acidic aluminum aryloxides have shown stereochemical advantages in important carbon-carbon bond-forming reactions; these transformations frequently require at least a stoichiometric amount of the reagents.[1] A catalytic application of these species is thus limited to several cases especially where a bidentate ligand is incorporated into the metal.[2] However, turnover frequencies observed are not always high. An entirely different strategy that enables a catalytic use of aluminum aryloxides has yet to be explored. We report here a hitherto unknown aluminum trisphenoxide solid polymer as an efficient Lewis acid catalyst, a function of which is highlighted by the catalytic Diels-Alder reaction.

Ligand **1** for the aluminum polymer was readily accessible on a large scale as described in the literature.[3] The aluminum polymer **2** was prepared as outlined in Scheme 1: treatment of biphenol **1** (0.15 mmol) in toluene with a hexane solution of Me_3Al (0.10 mmol) at room temperature while maintaining a gentle stream of argon, followed by exposure to ultrasonic irradiation[4] for 15~20 min during which time the reaction vessel was immersed in a water bath to avoid a violent reflux. Insoluble pale yellow precipitates appeared immediately following the treatment with Me_3Al, and after the prolonged irradiation time, the color changed to a pale yellow-green.[5] The mixture was filtered and the filtrate was quenched with 1M HCl to

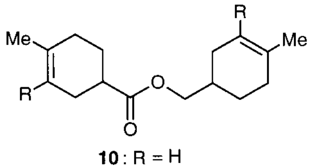
Table 1. Diels-Alder Reaction of α,β-Enals Catalyzed by **2** [a]

entry	dienophile	diene	conditions (°C, h)	(major) product	yield (%)[b] [*endo*:*exo*][c]
1	 **3**	 **6**	-78, 1		>99 [78:22]
2[d]			-78, 15 rt, 32		95 [77:23]
3			-78, 1 rt, 28		59[f] [96:4]
4	 **4**	**6**	-20, 5		92 [11:89]
5	 **5**	**6**	0, 12		94 [84:16]
6[e]	**3**	 **7**	0, 11		41[f]
7[e]	**4**	**7**	0, 16 rt, 18		90
8[e]	**3**	 **8**	0, 18		40[f]
9[e]	**4**	**8**	0, 23		73

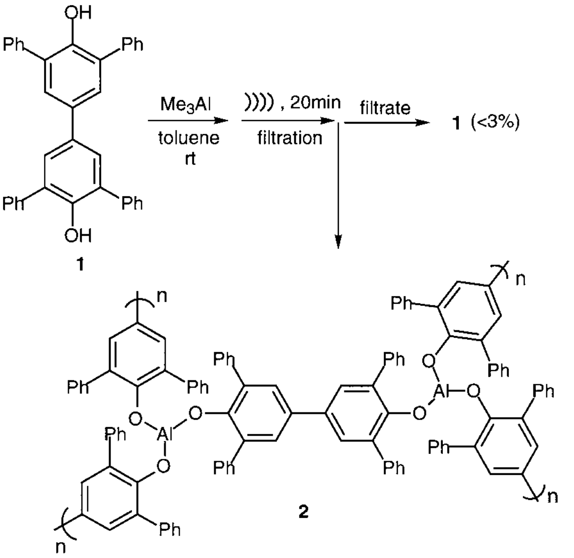
[a] Unless otherwise specified, reactions were carried out using 1 mol% of **2**, dienophile (100 mol%), and diene (300 mol%) in toluene under the indicated conditions. [b] Of isolated, purified products. [c] Determined by ^1H NMR analysis. [d] 0.1 (mol%) of **2** was used. [e] 2 mol% of **2** was used. [f] Tishchenko adducts, **9** (38%, entry 3), **10** (54%, entry 6), **11** (55%, entry 8) were obtained, respectively



9



10 : R = H
11 : = Me



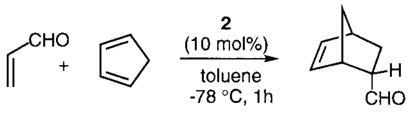
Scheme 1

check the remainder in the organic layer, giving less than 3% of **1**. Furthermore, when the obtained solid portion was exposed to methanol, we observed a negligible amount of gas evolution. An ultrasonic treatment is thus assumed to be indispensable for complete consumption of **1** on reaction with Me_3Al. Under otherwise identical reaction and technical conditions, a significant amount of starting biphenol **1** was recovered from the filtrate (20%).

We next investigated the reactivity profile of **2** in the Diels–Alder reaction of α,β-enals, following the above preparation procedure for **2** with exclusion of the filtration step. Table 1 shows several unique characteristics of this catalytic process, and there are several key issues to be discussed. (1) In general, a 1~2 mol% of the catalyst proved sufficient to affect the Diels–Alder reactions examined. The enhanced catalytic activity was also confirmed by a reasonable yield obtained with 0.1 mol% of the catalyst (entry 2). Further evidence that a rate enhancement was apparently affected by **2** was provided by the following studies: for comparison, the corresponding monomeric, aluminum tris(2,6-diphenylphenoxide) (ATPH)[6] (1 mol%) was subjected to the Diels–Alder reaction of **5** with **6** under similar conditions except a prolonged reaction time (0 °C, 22h) to give the cycloadduct with a decline in isolated yield of 78%. (2) A rather low, but nonnegligible level of *exo* (entries 1, 2, and 5) and *endo* (entry 4) preferences can be ascribed to the ligand effect of the catalyst. In fact, the Diels–Alder reaction of **3** with **6** using ATPH (-78 °C, toluene) gives an *endo/exo* ratio of 85:15.[7] These comparable selectivities are suggestive of a structural similarity between **2** and ATPH. (3) Several Diels–Alder adducts underwent Tishchenko reaction[8] affording self-dimerization to give esters **9**, **10** and **11** (entries 3, 6, and 8, respectively). These results also support an increase in the catalytic activity.

$$\text{dienophile} + \text{diene} \xrightarrow[\text{toluene} \\ \text{conditions}]{\mathbf{2} \\ (0.1\sim2\text{ mol\%})} \text{Diels-Alder adduct}$$

The polymer catalyst **2** could be recovered quantitatively (>95%) by simple filtration and reused. The activity of the recovered **2** did not decrease even after seven uses (Scheme 2).



1st use, 84%; 2nd use, 90%; 3rd use, 92%; 4th use, 93%
5th use, 99%; 6th use, 86%; 7th use, 85%

Scheme 2

In summary, we developed an aluminum trisphenoxide polymer as an efficient solid catalyst which showed pronounced Lewis acidity in the Diels–Alder reaction of α,β-enals. An alternative strategy that further enhances the catalytic activity of aluminum aryloxides is now under investigation.

References and Notes

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(4) The internal irradiation system, ultrasonic disrupter UD-201 (TOMY TECH) equipped with a converter, horn connector, and TP-040 (TOMY TECH) was used, and an output power of 150 W and 20 kHz applied for all the reactions tested. For the review of ultrasonic irradiation in organic synthesis, see: Einhorn, C.; Einhorn, J.; Luche, J.-L. *Synthesis* **1989**, 787.

(5) The color of the precipitate is crucial and should be controlled in order to retain and reproduce the catalytic activity of **2**. For example, the pale yellow color persists with insufficient irradiation (<10 min) to cause a catalyst with a relatively weak activating capability, whereas the pale yellow-green color turned red with excess irradiation (>30 min), and the catalytic activity decreased significantly, probably due to the decomposition of highly active species. It is recommended that the catalyst is prepared just before use, or stored at low temperature (<-40 °C) under argon atmosphere.

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