



Communication

The promoted Tishchenko reaction and catalytic intermediate by 2-aminopyrrolyl dilithium compounds

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ABSTRACT

The dimerization of aldehydes to the analogous carboxylic esters (Tishchenko reaction) has been achieved in impressive yields using the dilithium compounds containing bidentate di-anionic pyrrolyl ligands as initiators. The initiated intermediate $\{[2-(^t\text{BuNCH})\text{C}_4\text{H}_3\text{N}]\text{Li}[\text{PhCH}_2\text{OLi}(\text{TMEDA})]\}_2$ was isolated and characterized by satisfactory C, H and N microanalysis, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^7Li NMR spectra in pyridine- d_5 at ambient temperature, and single crystal X-ray structural data. The processes involve a redox reaction of 2-aminopyrrolyl dilithium compound with aldehyde.

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With the increasing global environmental awareness, atom–economic reactions, which emphasize all or most of the atoms of starting materials in the process are converted into molecules of the desired product rather than into wasted by-products, have attracted high interest in recent years [1]. Among these, the Tishchenko reaction, a good typical atom–economic reaction, has been known for more than a century [2]. During this period, the Tishchenko reaction has been studied thoroughly and many types of catalysts have been developed to obtain the object esters in high yields. For example, traditional aluminum alkoxides [3], metal catalysts including alkaline metals [4], alkaline metal oxides or alkaline earth metal oxides [5], transition metals [6], lanthanides [7], actinides [8] and various other catalysts [9] have been developed towards the improvement of Tishchenko chemistry. Furthermore, some new methods were also found to be very effective for Tishchenko reactions, such as supercritical carbon dioxide [5g], microwave irradiation [9g] and high speed ball milling (HSBM) [4e].

Recently, we have reported the dilithium compounds containing bidentate dianionic pyrrolyl ligands and their application in amidation of aldehydes with amines [10]. Inspired by these unique

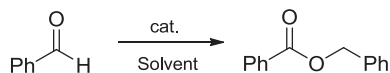
structural features with η^1 , η^5 or both bonding modes and good activity for the amidation reactions, we now assess their reactivity about the Tishchenko reaction with a range of aromatic substrates and heterocyclic aldehydes, and present a new synthetically useful protocol to the Tishchenko reaction under mild reaction conditions.

The initially studied of the reaction was carried out using benzaldehyde as a model substrate with dilithium compound of $\{[2-(\text{CH}_3\text{NCH}_2)\text{C}_4\text{H}_3\text{N}]\text{Li}_2(\text{TMEDA})_3\}$ (**1**) [10]. And we were pleased to find that in the presence of 5% mol **1**, the dimerization of benzaldehyde can proceed smoothly at room temperature in hexane to afford ester with 93.7% isolated yield after 48 h. When the temperature increased to 70 °C, the reaction went to completion in 3 h with 83.3% isolated yield. Different amounts of catalysts (1, 2, 5 mol%) afforded almost the same yield of product (82.6%, 84.4%, 83.3%), respectively. Among the different solvents used for optimization (Table 1, entries 3, 5–8), benzene yielded best results, but this was still inferior to solvent-free condition (Table 1, entry 8). With a view to the electronic effect and steric hindrance of ligands, we evaluated the catalytic behavior of other four aminopyrrolyl dilithium compounds $\{[\mu-\eta^5-2-[(\text{CH}_3\text{CH}_2\text{NCH}_2)\text{C}_4\text{H}_3\text{N}]\text{Li}_2(\text{TMEDA})_2\}$ (**2**), $\{[\mu-\eta^5:\eta^1-2-[(\text{CH}_3)_3\text{CNCH}_2]\text{C}_4\text{H}_3\text{N}]\text{Li}_2(\text{TMEDA})_2\}$ (**3**), $\{[\eta^5-2-[(\text{CH}_3)_2\text{CHNCH}_2]\text{C}_4\text{H}_3\text{N}]\text{Li}_2(\text{TMEDA})_2\}$ (**4**) and $\{[\eta^5-2-[(\text{CH}_2)_5\text{CHNCH}_2]\text{C}_4\text{H}_3\text{N}]\text{Li}_2(\text{TMEDA})_2\}$ (**5**) [10], the results show that compound **1** still gave the highest yield (Table 1, entries 8–12).

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Table 1
Optimization of Tishchenko reaction catalyzed by dilithium compounds^a.



Entry	Cat.	Temp. (°C)	Solvent	Time (h)	Yield(%) ^d
1 ^b	1	Rt	Hex	48	93.7
2 ^b	1	70	Hex	3	83.3
3	1	70	Hex	3	84.4
4 ^c	1	70	Hex	3	82.6
5	1	70	Benzene	3	85.3
6	1	70	Toluene	3	82.9
7	1	70	THF	3	81.4
8	1	70	None	3	88.6
9	2	70	None	3	80.2
10	3	70	None	3	84.1
11	4	70	None	3	85.0
12	5	70	None	3	78.9

^a The catalyst amount is 2 mol%.

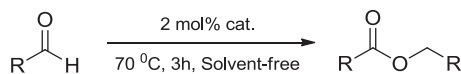
^b The catalyst amount is 5 mol%.

^c The catalyst amount was 1 mol%.

^d Isolated yield.

Having realized the appropriate conditions for benzaldehyde dimerization, we continued our quest with a variety of aromatic substrates (Table 2). The scope of our catalytic system was applicable for the range of aromatic substrates. These aldehydes containing electron donating substituents and electron withdrawing group in the para substituted aromatic ring were converted to the corresponding esters in good isolated yields in reasonable time

Table 2
Tishchenko reactions of aromatic aldehydes under 1.



Entry	Aldehyde	Product	Yield (%)
1			88.6
2			90.8
3			86.5
4			94.7
5			91.3
6			70.5

Table 2 (continued)

Entry	Aldehyde	Product	Yield (%)
7			63.3
8			34.9
9			83.7
10			62.7
11			54.8
12			75.3

The catalyst amount is 2 mol%, the yield is isolated yield, Solvent-free, 70 °C, 3 h.

(Table 2, entries 1–6). If 2-chloro- or 2-nitro-benzaldehyde was used instead of the 4-isomer, the esters were obtained in 63.3% and 34.9% yield, respectively (Table 2, entries 7 and 8). And 2-aminopyrrolyl dilithium compound catalyzed intramolecular Tishchenko reaction of o-phthalaldehyde also gave a moderate yield of the corresponding ester (Table 2, entries 10). Furthermore, the Tishchenko reaction of 3-fluoro-benzaldehyde gave esters in 83.7% yield (Table 2, entries 9). These results indicated that the steric “obstacle” created by substituent groups in the ortho position

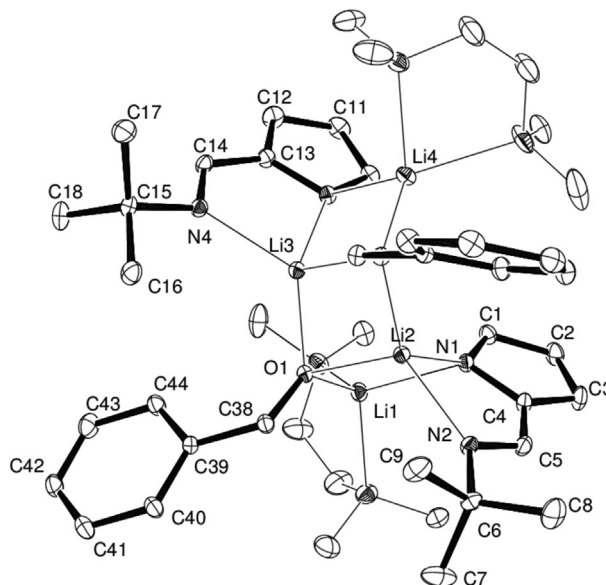


Fig. 1. ORTEP diagram of compound 6. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): N2–C5 1.279(5), N2–C6 1.485(5), N1–Li2 2.078(7), N2–Li2 2.154(7), O1–C38 1.395(4), C38–C39 1.518(5); N1–Li2–N2 85.8(3), N2–C5–C4 124.4(4), N1–C4–C5 122.0(3), O1–C38–C39 115.9(3).

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