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Fast Aldol-Tishchenko Reaction Utilizing 1,3-Diol Monoalcoholates as the Catalysts

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Abstract:
The aldol-Tishchenko reaction of enolizable aldehydes is a simple and effective way to prepare 1,3-diol monoesters, which are widely used as coalescing agents in the paint industry. The use of monoalcoholates of 1,3-diols as catalysts gives fast and clean reactions compared with the previous use of several inorganic catalysts. The use of the proper 1,3-diol moiety in the catalyst also reduces the amount of side products which are due to ester interchange between product esters and the catalyst. The rapid water-free method developed herein allows fast preparation of monoesters with excellent yield and minimized formation of side products.

Introduction
In many cases traditional Tishchenko1 and aldol-Tishchenko2 reactions are competitive with each other.3 However, these reactions can sometimes proceed selectively with the proper choice of catalyst. The aldol-Tishchenko reaction usually requires a basic metal hydroxide catalyst which can activate both aldol reaction and Tishchenko esterification.4 Some other catalysts have also been used such as metal alkoxides of monofunctional alcohols,5,6 LiWO4,7 Cp*2Sm(thf)8, polynuclear carbonyl ferrates,9 and simple metal hydroxides.10 Traditional Tishchenko esterification is usually activated in the presence of Lewis acidic catalysts such as aluminum alcoholates.11 In a typical aldol-Tishchenko reaction (Scheme 1), an aldol reaction of the easily enolizable aldehyde first takes place, and the product forms a hemiacetal-like 1,3-dioxan-4-ol 4 (also called aldoxan at this case) with the free aldehyde.12 Dioxanol 4 reacts to give the diol monoester 5 via a Tishchenko reaction in which an intramolecular hydride shift takes place.13 In the presence of the catalyst, for example, Ca(OH)2, and with heating, the balance between monoesters 5 and 6 is slowly converted to the more stable monoester 6 having a secondary alcohol group instead of a primary one as in 5.2 This aldol-Tishchenko reaction is very closely related to the Evans—Tishchenko reaction in which β-hydroxyketones react with a free aldehyde to give a glycol monoester with excellent anti-selectivity.14

In our previous work we have studied the chemistry of 1,3-dioxan-4-ols and their behaviour in the Tishchenko reaction. It is well-known that several metal hydroxides destroy esters by hydrolysis and thereby reduce the yield. We started to search for substitute catalysts and found that diol monoalcoholates solve this problem.15 Herein we wish to report the results of our studies on the homogeneous aldol-Tishchenko reaction, wherein we have achieved fast reactions from enolizable aldehyde 1 to monoesters 5 and 6 with

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excellent yields. This work was focused on converting isobutyraldehyde 7 to diol monoesters 9 and 10 which are the most common coalescing agents, for example, for latex paints. Consumption of 7 to condensation and esterification products was 260 million pounds in 1997 exclusively in the U.S.\(^\text{16}\)

Results and Discussion

To our knowledge, this is the first time that monoalcoholates of 1,3-diols have been studied as catalysts for aldol-Tishchenko reactions. The use of sodium alcoholates of monofunctional alcohols has been reported, but in this case the yield of monoesters of the diol was reduced due to ester interchange between the catalyst and the product ester.\(^\text{17}\) The effect of the catalyst on the reaction rate was found to be crucial in our experiments, giving a reaction several times faster than that obtained with the metal hydroxides traditionally used. This is partly due to the completely homogeneous reaction system. In some industrial processes the use of metal hydroxides can require the presence of some water which can create quantities of wastewater and thus extra costs.\(^\text{18}\)

Another considerable disadvantage with metal hydroxide catalysts is the fast and irreversible hydrolysis of the product esters. In our procedure, water-free reaction conditions are used, and after the reaction and short workup, the solvent and products can be easily separated by means of fractional distillation. However, rather fast ester interchange between the catalyst and the product ester can still cause slight loss in the yield. This can be avoided by choosing a suitable 1,3-diol as the catalyst. We have here studied the role of different alkali metals in the catalyst and optimized the reaction conditions for this process. In our previous experiments we used the monolithium alcoholate of 2,2-dimethylpropan-1,3-diol (neopentyl glycol; later NPG) 8 as the catalyst in the Tishchenko esterification of 1,3-dioxan-4-ol derivatives.\(^\text{15}\)

In the first experiment of this paper, it was figured out how unavoidable the ester interchange between the catalyst and the product is. The same Li–NPG catalyst 8 (30 mol %) was used here in the case of the aldol-Tishchenko reaction. Isobutyraldehyde 7 (R=CH\(_3\) in Scheme 1) was used as the starting material and added directly into the catalyst solution (0.5 M in THF, 30 mol %). At room temperature, the reaction was found to be suprisingly fast.

The desired products were the glycol monoesters (2,2-dimethyl-3-hydroxy-1-isopropyl-propyl)-2-methylpropionate 9 and (3-hydroxy-2,2,4-trimethylpentyl)-2-methylpropionate 10. Formation of NPG-monoisobutyrate 11 and 2,2,4-trimethylpentan-1,3-diol 12 were observed after only 15 min, proving that there was fast ester interchange between products (9 and 10) and the catalyst 8 (Scheme 2). In later experiments, we decided to use monoalcoholates prepared from diol 12 as the catalysts to avoid the formation of side products related to monoester 11. The catalysts used in the experiments are shown in Scheme 3. Catalysts 13, 14, and 15 were prepared in a straightforward fashion by adding a solution of 12 in THF (or hexanes) into the hydride slurry at 0 °C under argon. When BuLi (13) or Et\(_2\)Zn (16) were used, these were added directly into the precooled THF or hexane solution of diol 12. The catalyst solution was stirred for 60 min at 0 °C before use.

In the experiment series, freshly distilled isobutyraldehyde 7 (4.50 g, 50 mmol) was fed over 2 min into the reaction containing the catalyst solution, giving an exothermic reaction (Scheme 4). The amount of catalyst used was always 1 mol % except entry 5 (30 mol %) in which case ester interchange with a bulky catalyst was studied. In all entries of Table 1 the temperature was kept stable at +55 °C (±3 °C) with external cooling and heating at the very end of the reaction. After a reaction time of 30 min the reaction was


Table 1. Effect of solvent, catalyst and reaction times on yields in the aldol-Tishchenko reaction of 2-methylpropanal at (+55 °C)

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (M)</th>
<th>solvent</th>
<th>time (add) (min)</th>
<th>time (react) (min)</th>
<th>12 (%)</th>
<th>9 (%)</th>
<th>10 (%)</th>
<th>18 (%)</th>
<th>7 (%)</th>
<th>yield (%) (9 and 10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>THF</td>
<td>6.5</td>
<td>20</td>
<td>9.1</td>
<td>27.5</td>
<td>39.6</td>
<td>7.7</td>
<td>16.0</td>
<td>77</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>Hex</td>
<td>2.5</td>
<td>40</td>
<td>14.9</td>
<td>22.2</td>
<td>36.5</td>
<td>8.7</td>
<td>17.7</td>
<td>73</td>
</tr>
<tr>
<td>3</td>
<td>13</td>
<td>0.1</td>
<td>2</td>
<td>60</td>
<td>15.0</td>
<td>23.8</td>
<td>36.1</td>
<td>14.8</td>
<td>10.3</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>14</td>
<td>THF</td>
<td>3.5</td>
<td>20</td>
<td>5.1</td>
<td>22.8</td>
<td>34.0</td>
<td>1.3</td>
<td>36.7</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>t-BuOLi</td>
<td>0.5</td>
<td>THF</td>
<td>3</td>
<td>11.3</td>
<td>25.7</td>
<td>39.3</td>
<td>13.2</td>
<td>13.2</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>0.1</td>
<td>Hex</td>
<td>2</td>
<td>30</td>
<td>6.6</td>
<td>32.4</td>
<td>40.8</td>
<td>1.3</td>
<td>19.0</td>
</tr>
<tr>
<td>7</td>
<td>13</td>
<td>0.1</td>
<td>THF</td>
<td>2</td>
<td>30</td>
<td>10.6</td>
<td>23.7</td>
<td>45.9</td>
<td>9.4</td>
<td>10.5</td>
</tr>
<tr>
<td>8</td>
<td>14</td>
<td>0.1</td>
<td>THF</td>
<td>2</td>
<td>30</td>
<td>8.3</td>
<td>27.2</td>
<td>50.8</td>
<td>3.1</td>
<td>10.6</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>0.1</td>
<td>THF</td>
<td>2</td>
<td>30</td>
<td>4.3</td>
<td>17.1</td>
<td>29.1</td>
<td>0.0</td>
<td>49.5</td>
</tr>
</tbody>
</table>

1. 10. mol% of catalyst was used in every experiment.
2. mol% of the product mixture.
3. Contains both unreacted free aldehyde and aldoxan.
4. (wt)% of 9 & 10 (compared to theoretical yield if all 7 would have reacted to 9 and 10).
5. Prepared from diol 12 and KHMDS (method b).

To avoid diester formation, coordination has to be prevented. The effect of the solvent was studied by changing THF to hexanes, and significant differences were observed (entries 6–7). Reduced formation of the diester was observed in hexanes but also worse conversion of 7, due to a slower aldol reaction.

Steric effects might also have an effect on the course of the reaction. Bulky t-BuOLi was expected to give weaker coordination of the catalyst to the carbonyl group of the product ester. We expected that this might slow the ester interchange. However, noticeable effects were not observed (entry 5). The use of TMEDA to chelate lithium had no effect either. To study further the effect of the countercation a series of experiments was performed (entries 7–9). The effect of the countercation was studied by using sodium instead of lithium. Ester interchange was slower, but longer reaction times were needed to reach the same conversion. Obviously, bulkier metals (weaker coordination to carbonyl oxygen) give slower ester interchange but also a slightly slower aldol reaction. Again, the reduced rate of the aldol reaction can be observed as a worse conversion of 7 to the products (entry 4). Results from the potassium alcoholate were expected to be the best of the alkali metal alcoholates. Measurement of an exact amount of 30% KH—oil dispersion was difficult, and this was the reason for the distortion of results. The amount of KH was too large which was observed as a loss in the yield of esters 9 and 10 via efficient ester interchange to 12 and 18. An alternative way to prepare the catalyst was to treat diol 12 with KHMDS and remove the silylamide residues before use. The effect of the potassium alcoholate can be observed in entry 9, and the results are in line with the theory. It should be noticed that the formation of diester 18 was not observed at all (NMR, TLC). On the other hand, the conversion of 7 was poor due to sluggish aldol reaction with potassium countercation. The catalyst 14 was also studied on a larger scale (3 mol of 7) but the cooling capacity was found to be the limiting factor of the system and, the experiment failed. This can be avoided with slower addition of 7, but then conversion of product monoesters to diester 18 is increased as a function of time. On the basis of the results of Table 1, the use of hexane as the solvent and an alcoholate catalyst bearing a bulky cation such as potassium

could partly solve this problem of limited cooling capacity to give a sluggish aldol reaction but also slow formation of diester 18. The effect of the water and acid content in aldehyde 7 towards the reaction rate was also studied. If the amount of isobutyric acid in aldehyde was close to the amount of the catalyst, the reaction terminated halfway. In experiments with 10 mol % of the catalyst and aldehyde containing 1–2 mol % of water, a copious LiOH precipitate formed during the reaction which made stirring impossible and the system totally heterogeneous. In larger scales such precipitation can obstruct stirring and cause serious safety risks due to exothermicity. Further, in such a heterogeneous system the heat transfer is limited, and local overheating can occur. Additionally, the water content of aldehyde forms lithium hydroxide which hydrolyses some of the product esters. We attempted to reduce the formation of diester 18 by changing the metal of the catalyst to an alkali earth metal (Mg) or a transition metal (Zn) both of which are known to catalyze at least aldol reactions and could coordinate weakly enough to the carbonyl oxygen of the monoesters. Attempts to prepare 17 from magnesium turnings and diol 12 in hexanes with iodine catalysis and reflux failed. After several hours refluxing, aldehyde 7 was added, but no reaction was obtained. Preparation of catalyst 16 was examined by treatment of diol 12 with 200 mol % of n-BuLi in hexane and then exchanging lithium with zinc using ZnCl₂. The solution was separated from the LiCl precipitate into the reaction vessel, and aldehyde 7 was added. After 40 min monoesters 9 and 10 were obtained in a moderate 65% yield together with 11% of diester 18 in the product mixture. In the next reaction diol 12 was treated again with 200 mol % n-BuLi, but Et₂Zn was used instead of ZnCl₂. The yield of 9 and 10 was 87%. However, it is difficult to conclude if the metal interchange was complete before addition of 7 and whether lithium or zinc catalyzed the formation of 18. In the final experiment diol 12 was directly treated with Et₂Zn to obtain 16. Isobutyraldehyde 7 was added to a 0.1 M catalyst solution of 16 (1.0 mol-%). After 35 min, the conversion of 7 was only 57%. However, monoesters 9 and 10 were the main products, and only traces of 18 were observed. Also, the presence of a small amount of 2-methyl-3-pentanol was observed in the 1H NMR which was due to the reaction between unreacted Et₂Zn and 7.

On the basis of the fact that transesterification is a reversible reaction, we decided to use diester 18 as the solvent. NaOMe (30% in MeOH) was added into 18, and MeOH was removed under reduced pressure at +40 °C to prepare the catalyst 14 via ester interchange. If the reaction mixture was quenched and analysed at this point, all of the products, 12, 9, 10, and 18 were present. This was a clear indication of ester interchange and formation of 14 (and methyl isobutyrate) from 18. The aldehyde was added over 2 min, and after 30 min the yield of monoesters was 93%. On a larger scale the advantages are that after the workup the products can be fractionally distilled and the least volatile component in the reactor, side product 18, can be recycled as the solvent in the next batch.

Conclusions
Monoalcoholates of 1,3-diols give very fast aldol-Tishchenko reactions with an excellent yield of monoesters of 1,3-diols. To our knowledge, only sodium monoesters of monofunctional alcohols have been used as catalysts for this particular reaction. On the basis of our results, 1,3-diol-based alcoholates give slightly better yields, the reaction temperature is lower, and the reaction itself is faster. The results are in accordance with literature, and different solvents and metals have clear effects on the reaction rates. Furthermore, these catalysts provide water-free reaction conditions, and no hydrolysis has been observed. Even if the formation of diester cannot be totally avoided here, it is a minor problem compared to the hydrolysis caused by metal hydroxide catalysts. The products can be easily separated by means of distillation, and the diester can be recycled as a solvent in the next batch if needed. Because of rather fast transesterification (9 → 18) it is important that the diol used in the catalyst is the same as the diol moiety in the product ester. Finally, the reaction can be run with 1.0 mol % of the catalyst (or even less), but use of an acid-free and dry aldehyde is required in this procedure. We avoided hydrolysis of the monoesters, but formation of diester 18 was found to be a new problem.

Experimental Section
Materials and Instrumentation. All chemicals were purchased from commercial sources (purity >98%) and used directly except isobutyraldehyde which was dried over Na₂SO₄ and fractionally distilled under argon before use. All solvents used were dry and distilled immediately before use. Merck silica gel 60F (230–400 mesh) plates were used for TLC analyses. The TLC plates were stained with anisaldehyde in acidic ethanol. The 1H- and 13C NMR spectra were recorded in CDCl₃ with 0.25% of TMS or DMSO on a Bruker AM-200 instrument. Gas chromatography was performed on a Perkin-Elmer model PE8420 with OV-1701 column. Mass spectra were recorded on a Kratos MS80 RF Autoconsole instrument.

Lithioxy-2,2-dimethyl-3-hydroxypropane (13). Catalyst 13 was prepared by two alternative methods. Method A. To a cooled (−78 °C) solution of diol 12 (0.073 g, 0.5 mmol) in THF (4.78 mL) under argon n-BuLi (2.30 M in hexane, 0.22 mL, 0.5 mmol) was added dropwise to give 0.1 M catalyst solution. The solution was stirred for 60 min at 0 °C and used instantly. Method B. Diol 12 (0.74 g, 0.5 mmol) in 4 mL of THF was added dropwise to a cooled (0 °C) suspension of 95% LiH (0.004 g, 0.5 mmol) in 1 mL of THF under argon. The resulting solution was stirred for 60 min at 0 °C before use.

Sodium Oxy-2,2-dimethyl-3-hydroxypropane (14). Catalyst 14 was also prepared using two alternative methods. Method A. A 50% NaH suspension in mineral oil (0.024 g, 0.5 mmol) was first washed with 2 × 2 mL of dry hexanes under argon. THF (5 mL) (or hexanes) was added, and diol 12 (0.073 g, 0.5 mmol) was added into this suspension giving a 0.1 M solution of 14. The catalyst solution was stirred for 60 min at 0 °C before use. Method B. Diol 12 (0.073 g, 0.5 mmol) and 30% NaOMe (in MeOH, 0.090 g, 0.05 mmol)
were mixed under argon, the solution was warmed to +40 °C, and MeOH was evaporated under reduced pressure (0.1–10 mmHg). After evaporation, THF or 18 (5 mL) was added. The solution was ready for use.

**Potassium Oxy-2,2-dimethyl-3-hydroxypropane (15).**  
**Method A.** Preparation was as for method A of catalyst 14. Exact measurement of the fluid 30% KI/mineral oil suspension (0.0681 g, 0.51 mmol) was difficult which caused some distortions of the results. **Method B.** Dil of 12 (0.074 g, 0.5 mmol) was dissolved in 1 mL of dry THF under argon and cooled to 0 °C. n-BuLi (1.33 M, 1.3 mL, 2.0 mmol) was added dropwise and stirred for 60 min. The solution was cooled to 0 °C before use. Solvents and formed bis(trimethylsilyl)amide residue were evaporated before use under reduced pressure (0.08 mmHg). Right before use 5 mL of dry THF was added to prepare 0.1 M solution of bis(trimethylsilyl)amide residue were evaporated before use.

**2,2-Trimethyl-1,3-pentanediol diisobutyrate (18):**  

**Monoester (10):** TLC (EtOAc:Hex/1:9) Rf = 0.21. 1H NMR (CDCl3; 200 MHz) δ 3.91 (dd, 2 H, OCH2CH₂, J = 10.9 Hz), 3.21 (d, 1 H, CHCHOH, J = 2.6 Hz), 2.54 (sep, 1 H, CHCOO, J = 7.0 Hz), 1.88 (sep-d, 1 H, Me₂CHCHOH, J = 6.8 Hz, J = 2.3 Hz), 1.15 (d, 6 H, Me₂CHCOO, J = 7.0 Hz), 0.97 (dd, 3 H, CH₃CHCHOH, J = 6.9 Hz), 0.93 (s, 3 H, CH₂(C₂H₅), 0.92 (s, 3 H, CH₂(C₂H₅), 0.89 (d, 3 H, CH₂CH₂CH₂O, J = 6.8 Hz). 13C NMR (CDCl3; 50 MHz) δ 177.2, 79.4, 71.3, 39.3, 34.1, 28.6, 23.5, 22.0, 20.4, 19.0, 16.0. MS (CI, NH₃): (M + 1) = 217, ((M + 1 + NH₃) = 234).

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