Experimental Section

CoAPO-5 was prepared according to a standard recipe procedure[13] starting from the following gel composition: $0.75\,R[Co_{0.02}Al_{0.98}P_1]O_4 \cdot 20\,H_2O$ with R, the template molecule triethylamine (Janssen Chimica, 99 %), and with $Co(CH_3CO_2)_2 \cdot 4\,H_2O$ (Acros, p.a.). Pseudo-boehmite from Vista (Capatal Alumina 70 % Al_2O_3) was used as the Al source, and H_3PO_4 (Janssen Chimica, 85 % in H_2O) as the P source. Diffuse reflectance spectra in the UV/Vis–NIR region were measured by using a Varian Cary 5 spectrometer equipped with a diffuse reflectance attachment with integration sphere. The spectra were recorded against a halon white reflectance standard in the range 2500–200 nm. ESR measurements were recorded on a Bruker ESP300E spectrometer with an Oxford Instruments liquid helium cryostat at −263 °C. Simulations of the ESR spectra were performed by simulation programs developed by Mabbs and Collison.[18] Powder X-ray diffraction patterns of the obtained solids were recorded on a Siemens D5000 diffractometer by using $Cu_{K\alpha}$ radiation.

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First Catalytic Aldol-Transfer Reaction via Aluminum Enolates: A New Way To Generate Aldol Adducts of Aldehydes from Aldol Adducts of Ketones**

Ilkka Simpura and Vesa Nevalainen*

The addition of nucleophiles to carbonyl compounds has been under investigation for decades.[1] Examples include the addition of enolates to aldehydes and the Meerwein–Ponndorf–Verley (MPV) reduction of ketones[2] (hydride as the nucleophile, Figure 1, (**a**)). Amongst recent achievements in this area are: alkynyl transfer reactions reported by Maruoka and co-workers[3] (Figure 1 (**b**)), allyl-transfer reactions reported by Nokami et al.[4] (Figure 1, (**c**)), which as the reaction is proposed to occur by a stepwise ionic mechanism[4] is only formally analogous to the MPV reaction, and cyanide-transfer reactions reported by Inoue and co-workers[5] (Figure 1, (**d**)). The major advantage of these nucleophile-transfer reactions

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[*] Dr. V. Nevalainen, I. Simpura
Department of Chemistry
University of Helsinki
P.O. Box 55 (A.I. Virtasen aukio 1), 00014 Helsinki (Finland)
Fax: (+358) 9-191-40466
E-mail: vesa.nevalainen@helsinki.fi

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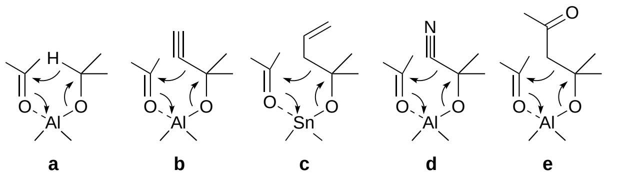
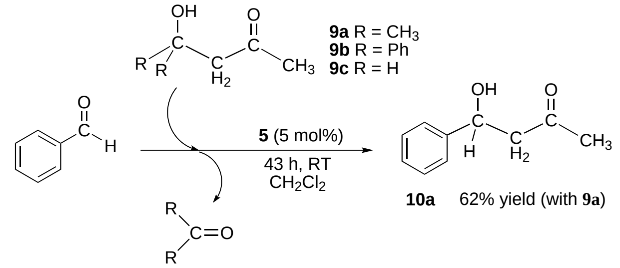


Figure 1. Formal flow of electrons in the six-membered cyclic transition states (**a**–**d**) of the MPV-type nucleophile-transfer reactions described in the literature. The related hypothetical mechanism of the aluminum-catalyzed aldol-transfer reaction is illustrated by **e**. Despite of formal analogy of **a**–**e**, the reactions depicted by **c** (ref. [4]) and **e** (Scheme 2) are proposed to take place by a stepwise ionic mechanism.

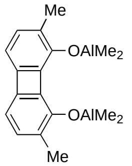


Scheme 1. The catalytic aldol-transfer reaction of benzaldehyde utilizing β-hydroxy ketones (**9a**–**c**) as starting material.

is the utilization of cheap and simple propargyl alcohols (e.g. 2-methyl-3-propyn-2-ol)[3] or allyl alcohols (e.g. 2-methyl-3-propen-2-ol)[4] as starting materials for the construction of more complicated alcohols under mild reaction conditions.

Herein we report the first catalytic aldol-transfer reaction (Figure 1, (**e**)) for various aldehydes in which diacetone alcohol (**9a**)was used as an aldol source (see Scheme 1). Other methods for the synthesis of aldols have been reported by the groups of Lerner[6] (enzymatic and biomimetic), Yamamoto[7] (using hindered aluminum bisphenoxides), and Morken[8] (using the reduction of α,β-unsaturates esters).

The present work was inspired by the pioneering studies of Maruoka et al.[9] who reported that the bis(dialkylaluminum) reagent **1** accelerated the addition of nucleophiles to carbonyl compounds. Thus, for the aldol-transfer reaction we considered using the aluminum chelates **2** and **3**, their bisaluminum analogues **4**–**6**, and simple alkoxides **7** and **8**.[10]



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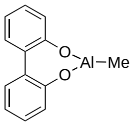

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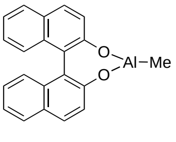

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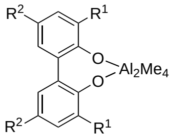
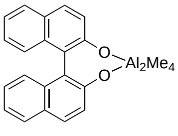


4a R^1, R^2 = H;
4b R^1 = OMe, R^2 = *n*Bu



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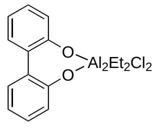

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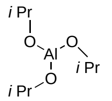

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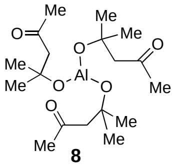

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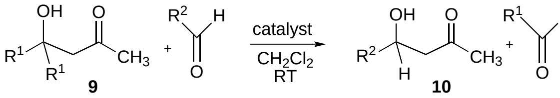
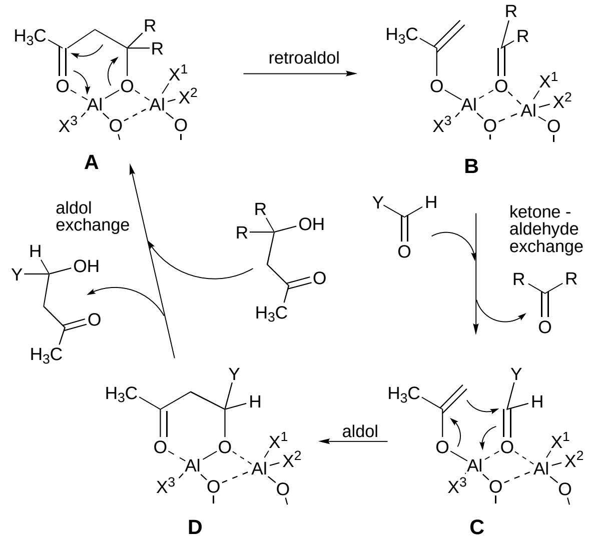
A typical procedure is shown in Scheme 1: the aldol-transfer reaction of the alcohol **9a** with benzaldehyde catalyzed by **5**, gave the aldol adduct **10a** in 62 % yield (after flash chromatography). The generality of this aldol-transfer method was confirmed by the synthesis of aldol adducts **10a**–**j** (Table 1). A possible mechanism to rationalize the aldol-transfer reaction is illustrated in Scheme 2.

Table 1. The catalytic aldol-transfer reaction of aldehydes



Entry	R^2	Catalyst	Aldol source	Run time [h]	mol % of catalyst	*trans*-aldol	Yield [%]
1	C_6H_5	**5**	**9a**	43	5	**10a**	62
2	C_6H_5	**5**	**9a**	22	5	**10a**	43
3	C_6H_5	**4a**	**9a**	22	5	**10a**	39
4	C_6H_5	**4a**	**9a**	22	10	**10a**	53
5	C_6H_5	**4a**	**9b**	21	5	**10a**	49
6	C_6H_5	**7**	**9a**	22	10	**10a**	28
7	C_6H_5	**8**	**9a**	22	10	**10a**	43
8	C_6H_5	**4b**	**9a**	22	5	**10a**	36
9	4-O_2N-C_6H_4	**4a**	**9a**	22	10	**10b**	58
10	4-Cl-C_6H_4	**4a**	**9a**	22	10	**10c**	56
11	4-H_3CO-C_6H_4	**4a**	**9a**	22	10	**10d**	47
12	hept-3-yl	**5**	**9a**	26	5	**10e**	73
13	$(CH_3)_3C$	**5**	**9a**	40	5	**10f**	72
14	1-phenylethyl	**4a**	**9a**	22	10	**10g**	63
15	$H_3C(CH_2)_2$	**5**	**9a**	40	5	**10h**	26
16	$H_3C(CH_2)_2$[a]	**4a**	**9a**	48	5	**10h**	47
17	prop-2-yl	**5**	**9a**	22	5	**10i**	24
18	C_6H_5-CH=CH	**5**	**9a**	22	5	**10j**	11

[a] Two equivalents of **9a** were used.



Scheme 2. The proposed mechanism of the aldol-transfer reaction described in Scheme 1. X^1, X^2, and X^3 = alkyl, alkoxy, and aryloxy, respectively. R = alkyl. Y = aryl.

The results indicate that the aldol-transfer reaction of **9a** with benzaldehyde can be induced by any of the compounds **4**–**8**[10] (entries 1–8, Table 1; data for compound **6** is not listed in the Table because it gave only trace amounts of **10a**). With compound **3** as the catalyst the yield of **10a** was only 7%. If **3** is allowed to react[10] with one more equivalent of Me_3Al then complex **5** is generated. With **5** as the catalyst the yield of **10a** increased substantially (43%, entry 2). The related reaction with **4a** gave a slightly lower yield of **10a** (39%, entry 3). The yield of **10a**, however, increased to 53% (entry 4) when 10 mol% of **4a** was used (instead 5 mol%) indicating the importance of the amount of the catalyst added. The reaction of benzaldehyde with **9a** catalyzed by **8**[10] gave **10a** in 43% yield (entry 7). Surprisingly, the yield of **10a** decreased to a trace amount when **8**[10] was used as a reagent and not as the catalyst. The reaction with **7** as the catalyst gave **10a** in only 28% yield (entry 6). These results indicate that the aryloxy groups of **4a** improve the yield of **10a** obtained only by about 10% over that obtained from comparable reactions with **8** which contains β-alkyloxy groups. The performance of **7** containing simple alkoxy groups is clearly inferior to that of **4a** and **8**.

Enhancing the electron richness of the aromatic ligand in the catalyst did not provide any advantages: Aldol **10a** was obtained in 36% yield (entry 8, Table 1) with catalyst **4b**, whereas with **4a** the yield was 39% (entry 3). Altering the electron richness of the aluminum center of the catalyst was not beneficial. When Et_2AlCl was used to prepare the catalyst (in situ formation of **6**[10]), product **10a** was detected only in trace amounts.

A comparison of the reactivity of the precursor aldols **9a**–**c** (Scheme 1) reveals factors that support the retro-aldol–aldol mechanism (Scheme 2) of the aldol-transfer reaction (Scheme 1). The aluminum chelate **A** (Scheme 2) undergoes a retro-aldol reaction to give **B**, the stability of which is dependent on the electron-donating effects of the R groups. Because the intermediate **B** (R = Ph) generated from **9b** should be more stable than **B** ($R = CH_3$) generated from **9a**, the retro-aldol step (**A** → **B**) should be easier for **9b** than for **9a**. Indeed, aldol **10a** was produced from **9b** in a higher yield than from **9a** (entries 5 and 3, respectively, Table 1). On the other hand, as the stability of **B** should decrease with the decreasing electron-donating effects of the R group, the aldol-transfer reaction of **9c** should give much lower yields than that of **9a**. This trend was confirmed experimentally; the aldol-transfer reactions of **9c** (both with butanal and *o*-phthalic aldehyde, catalyzed by **4a** (5 mol%)) failed.

Although the aldol-transfer reactions utilizing **9a** and **9b** (Scheme 1) as starting materials gave aldols in modest yields, the related reactions of β-hydroxy esters (benzaldehyde with ethyl 3-hydroxy-butanoate or ethyl 3-methyl-3-hydroxybutanoate catalyzed by **4a** (10 mol%)) and β-hydroxyaldehydes (benzaldehyde with 2-ethyl-3-ethoxycarbonyl-3-hydroxy butanal catalyzed by **4a** (10 mol%)) failed. Further limitations of the aldol-transfer reaction were found with ketones as reactants instead of aldehydes. Because the aldol-transfer reaction of **9a**, **b** produces a sacrificial ketone (that is $R_2C{=}O$, Scheme 1) the ketone that reacts in place of the aldehyde should have properties that differ from those of the sacrificial one. However, an aldol-transfer reaction of **9a** with acetophenone catalyzed by **5** (5 mol%) gave the product aldol in only 6% yield.

Aldol-transfer reactions of **9a** with benzaldehyde catalyzed by **4a** or **5** give yields in the range of 50 ± 14% (entries 1–5 and 8, Table 1). Slightly better yields are obtained with electron-poor benzaldehydes than with benzaldehyde(cf. entries 4 with 9 and 10). This suggests that electron-donating substituents on the aldehyde moiety decrease the yield and electron -withdrawing substituents on the aldehyde moiety increase the yield. For instance with respect to that obtained for benzaldehyde the aldol-transfer reaction of 4-methoxy benzaldehyde with **9a** gave aldol **10d** in 47% yield (entry 11) which is lower than the yields of reactions of related more electron -poor aldehydes (cf. entries 4, 9, and 10).

The best yields (Table 1) were achieved with α-substituted alkanals. When compared with the yield of **10a** derived from benzaldehyde, yields of **10e**, **10f**, and **10g** derived from 2-ethylhexanal (compare entries 2 and 12), 2,2-dimethylpropanal (cf. entries 1 and 13) and 2-phenylpropanal (cf. entries 4 and 14), respectively, were clearly higher. These results indicate that the aldol-transfer reaction favors sterically crowded or electron-poor aldehydes. This conclusion is supported by results obtained with *n*-butanal and 2-methylpropanal. In the former the case aldol **10h** was obtained in 26% yield and in the latter case **10i** in 24% yield (entries 15 and 17, respectively, Table 1). This is substantially less than the yield obtained for the aldol **10e** from 2-ethylhexanal (73%, entry 12). However, when two equivalents of **9a** were used (instead of one equivalent) with *n*-butanal the yield of **10h** was 47% (entry 16). A comparison of the yields (entries 15 and 16, Table 1) indicates that excess of **9a** could enhance the yield of **10a** (although the catalytic performance of **4a** and **5** is very similar only a rough comparision is possible).

The aldol-transfer reaction is favored by a bulky aldehyde moiety, this was confirmed by the reaction of **9a** with the sterically undemanding aldehyde 3-phenylpropenal. This reaction was catalyzed by **5** (5 mol%, entry 18) and gave the aldol **10j** in only 11% yield. Although the low yield obtained with *n*-butanal and 2-methylpropanal (entries 16 and 17) can be explained by the lower stability of aldehyde complex **C** (relative to ketone complex **B**, Scheme 2) it does not explain the poor yield of 11% obtained from 3-phenylpropenal. This result could be attributable to the higher stabilization of **D** (R = CH=CH-Ph; Scheme 2) by conjugation. If **D** is significantly more stable than **A** the aldol-transfer reaction cannot be catalytic (that is the regeneration step **D** → **A** hardly occurs).

In conclusion, we have shown that it is possible to utilize simple and cheap aldol adducts of ketones (such as **9a**) as starting materials for the construction of aldol adducts of aldehydes. Further studies on the synthetic utility, choice of metals (related $[Ti(OiPr)_4]^-$ (3 equivalents) promoted reactions of rapamycin and one related compound with two aldehydes have been recently reported [12]) and the mechanism of this aldol-transfer reaction are in progress.

Experimental Section

Typical procedure for the MPV transfer of the CH_3-CO-CH_3 unit of diacetone alcohol to aldehydes: A suspension of bi-2-naphthol (23.2 mg, 80 µmol) in dry CH_2Cl_2 (1 mL) was degassed, and a 2 M solution of Me_3Al (80 µL, 0.16 mmol in toluene/heptane, Aldrich) was added at room temperature under argon and the mixture was then stirred for 60 min. Immediately after evolution of gas had stopped the solution obtained (containing **5**) was cooled to 0 °C, equal amounts of benzaldehyde (0.16 mL, 1.6 mmol) and diacetone alcohol (0.20 mL, 1.6 mmol) were added simultaneously to the solution. After evolution of gas ceased the clear light yellow solution obtained was allowed to warm up to room temperature. The mixture was stirred for 43 h then poured into a 0.5 M HCl solution (5 mL) and extracted with diethyl ether. The combined extracts were dried over $MgSO_4$. Evaporation of solvents and purification of the residual oil by flash chromatography (silica gel, hexane/ethyl acetate, 1/5) gave 3-oxo-1-phenyl-butan-1-ol (**10a**, 164 mg, 1.0 mmol) as a colorless oil (62 % yield). ^1H NMR (200 MHz, $CDCl_3$, 20 °C, $CHCl_3$ ref.$\delta = 7.27$): $\delta =$ 7.4–7.2 (m, 5H, Ph), 5.1 (m $J = 3.3$ Hz, $J' = 3.7$ Hz, $J'' = 8.1$ Hz, 1H; CH), 3.3 (d, $J = 3.3$ Hz, 1H; OH), 2.83 (dd, $J = 8.1$ Hz, $J' = 17.6$ Hz, 1H; CH_2), 2.79 (dd, $J = 3.7$ Hz, $J' = 17.6$ Hz, 1H; CH_2), 2.1 (s, 3H; CH_3).

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[10] Aluminum complexes used as catalysts: a) complex **3** was generated by treatment of binaphthol with one equivalent of Me_3Al (in toluene/heptane, Aldrich); b) complexes **4a**, **4b**, and **5** were generated by the treatment of the corresponding biphenols of binaphthol with two equivalents of Me_3Al; c) complex **6** was generated by treatment of biphenol with two equivalents of Et_2AlCl (in hexane, Aldrich); d) isopropoxide **7** was from Fluka and was used as supplied; e) alkoxide **8** was formed in situ by treatment of Me_3Al by 20 equivalents of diacetone alcohol; f) for use as a reagent the alkoxide **8** was formed by treatment of Me_3Al with three equivalents of diacetone alcohol.
[11] The reaction of **9b** (entry 5, Table 1) produced benzophenone as a side product, which was detected while monitoring the reaction by thin-layer chromatography.
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Applications of a Nonlinear Organic Reaction of Carbamates To Proliferate Aliphatic Amines

Koji Arimitsu, Mana Miyamoto, and
Kunihiro Ichimura*

We recently proposed the concept of acid proliferations in which acid-sensitive compounds (referred to as acid amplifiers) generate strong acids in a nonlinear manner.[1] The compounds developed so far undergo fragmentations to form sulfonic acids which are acidic enough to lead to autocatalytic decomposition. The addition of the acid amplifiers to chemically amplified photoresists (composed of photoacid generators and acid-sensitive polymers[2]) enhances the photosensitivity and improves resist performance.[3] This happens because the number of photogenerated acid molecules increases markedly as a result of the acid proliferation of the doped acid amplifiers. On the other hand, despite the widespread use of base catalysis in organic chemistry, analogous chemically amplified resist systems relying on the photochemical liberation of a basic species[4] has received far less attention. This may be because of relatively low quantum yields for photobase photogeneration, which leads to low photosensitivity. If base molecules could be produced, for example, by the base-catalyzed transformation of a precursor, to increase the amount of basic species in a geometric progression, the rates of subsequent base-catalyzed reactions should be enhanced considerably, in a manner similar to that of systems involving acid proliferation. This idea led us to the molecular design and synthesis of base precursors which can be termed "base amplifiers"; this name is appropriate because the compounds generate more base molecules than they react with. Base proliferation processes can be coupled with versatile base-catalyzed reactions to develop various types of nonlinear chemical transformation. We were particularly interested in combinating a base amplifier with a photobase generator because a tiny amount of a photogenerated base may enhance rates of subsequent base-catalyzed reactions owing to the autocatalytic decomposition of the base amplifier. This process leads to the improvement of photosensitivity of base-sensitive photopolymer systems. Herein we describe novel base-sensitive compounds as base amplifiers that improve the efficiency of the photoinduced insolubilization of poly(glycidyl methacrylate) (PGMA) as a base-sensitive polymer.[5]

Our efforts have focused on the development of base amplifiers which should fulfill the following requirements: first, a base amplifier should undergo a base-catalyzed decomposition to liberate a base, thus leading to autocatalytic decomposition; second, a base amplifier should be thermally stable in the absence of a base under reaction conditions that advance both the autocatalytic decomposition and the subsequent base-catalyzed reaction; third, the liberated base

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[*] Prof. Dr. K. Ichimura, K. Arimitsu, M. Miyamoto
Chemical Resources Laboratory
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 226-8503 (Japan)
Fax: (+81) 45-924-5276
E-mail: kichimur@res.titech.ac.jp

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