## **Gold(III)** Chloride-Catalyzed Diastereoselective Alkylation Reactions with Chiral Benzylic Acetates

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Dedicated to Professor Andreas Pfaltz on the occasion of his 60th birthday.

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**Abstract:** Gold(III) chloride was shown to be an efficient catalyst for the diastereoselective C–C bond formation of various chiral *para*-methoxybenzylic acetates and different nucleophiles. All electrophilic acetates carried next to the reacting center a stereogenic carbon center bound to a functional group (FG), a methyl substituent and a proton. Selectivities were good (dr > 80/20) in favor of the *anti*-product for FG = COOMe, NO<sub>2</sub>, CN and in favor of the *syn*-product for FG = SO<sub>2</sub>Et, PO(OEt)<sub>2</sub>. The reactions proceed most likely *via* a free carbocation, in which a face differentiation is facilitated by a preferred con-

## Introduction

The typical choice of electrophilic substrates in Friedel-Crafts alkylation reactions<sup>[1]</sup> includes alkyl chlorides, alkenes or alkanols and their derivatives. The reactions are promoted by a Lewis or Brønsted acid and involve in many instances the formation of free carbenium ions. While alkylation reactions with alkyl chlorides and alkenes require only very small quantities of the catalyst, reactions with alcohols and related alkylating agents (esters, ethers, etc.) have classically been conducted with stoichiometric quantities of the catalyst.<sup>[2]</sup> In recent times there have been extensive efforts to find catalytic reaction conditions for the Friedel-Crafts alkylation with alcohols and their derivatives. Highly effective Lewis acids have been found which catalyze cleanly the reaction of various arenes with alcohols<sup>[3]</sup> and acetates.<sup>[4]</sup> The use of gold-(III) chloride<sup>[5]</sup> for the catalytic Friedel–Crafts alkylation with benzylic acetates as described by Beller et al.<sup>[6]</sup> and with benzylic alcohols as described by Dyker et al.<sup>[7]</sup> is of particular relevance to the present work.<sup>[8]</sup> Hashmi et al.<sup>[9]</sup> compared the reactivity of AuCl<sub>3</sub> with other catalysts for use in the condensation

formation. Several arene nucleophiles were shown to be compatible with the catalysis conditions providing the corresponding substitution products in high yields (13 examples, 62–98%). Moreover, other nucleophiles (allyltrimethylsilane, trimethylsilyl cyanide, 2,2-dimethyl-3-(trimethylsilyloxy)butane, p-toluenesulfonamide, and acetylacetone) reacted with a representative chiral electrophile in a high yielding and diastereoselective fashion.

**Keywords:** alkylation; carbocations; diastereoselectivity; Friedel–Crafts reactions; gold; Lewis acids

of carbonyl compounds with electron-rich arenes. They established the suitability of  $AuCl_3$  to catalyze this sequential transformation, which also involves an  $S_N1$ -type arylation.

Recently, we have launched a research program which aims to systematically elucidate the diastereoselectivity of reactions occurring at trigonal carbenium ions.<sup>[10]</sup> One of the first reactions we have studied is the Friedel–Crafts alkylation of arenes Ar'H using chiral benzylic alcohols **I** as cation precursors (Scheme 1). It was shown that, depending on the functional group (FG) and on the alkyl substituent R, a significant preference for either the *anti*-product *anti*-**II** or for the *syn*-product *syn*-**II** can be expected.



Scheme 1. Diastereoselective reaction of chiral benzylic alcohols I and arenes Ar'H promoted by stoichiometric amounts of  $HBF_4 \cdot OEt_2$ .



With R = Me, the functional groups methoxycarbonyl (COOMe), nitro (NO<sub>2</sub>), cyano (CN), trimethylsilylalkynyl (CCTMS) and chloro (Cl) favor the formation of product *anti*-**II** in a decreasing order of selectivity along this collection. For COOMe, NO<sub>2</sub> and CN the observed diastereomeric ratios (*dr*) often exceed 90/10. Contrary to that, the functional groups ethylsulfonyl (SO<sub>2</sub>Et), ethoxysulfonyl (SO<sub>2</sub>OEt), *tert*-butyl (*t*-Bu), and diethoxyphosphonyl [PO(OEt)<sub>2</sub>] exhibit a preference for *syn*-**II** in an increasing order of selectivity along this enumeration.

Standard reaction conditions employed in all previous experiments included the stoichiometric use of HBF<sub>4</sub>·OEt<sub>2</sub> as a Brønsted acid and a gradual warming from -78 °C to ambient temperature in CH<sub>2</sub>Cl<sub>2</sub> as the solvent. While the reason for the observed diastereoselectivities awaits further studies, it was desirable from a synthetic point of view to conduct the reactions at ambient temperature possibly employing an appropriate Lewis acid in catalytic amounts. We now disclose that benzylic acetates derived from alcohols of type I can be successfully converted into Friedel-Crafts alkylation products **II** using AuCl<sub>3</sub><sup>[11]</sup> as the catalyst. Despite the fact that the reactions were conducted at room temperature the observed diastereoselectivities were similar to the previously recorded values. Moreover, it could be shown that nucleophiles other than arenes can be employed in these transformations. Full details of our experimental study are given below.

## **Results and Discussion**

#### **Catalyst Screening**

For an initial catalyst screening the well-established reaction of benzylic alcohol **1** with 2-methylthiophene was chosen.<sup>[10b]</sup> As expected, the *syn*-product *syn*-**3** was predominantly formed (Scheme 2). Several catalysts including  $\text{FeCl}_3^{[12]}$  (in  $\text{CH}_2\text{Cl}_2$ ) and  $\text{Bi}(\text{OTf})_3^{[13]}$  (in MeNO<sub>2</sub>) performed well providing a rapid, clean and diastereoselective conversion to product *syn*-**3**. From this first set of screening results AuCl<sub>3</sub> did not show an outstanding profile. Yields for *syn*-**3** were similar compared to FeCl<sub>3</sub> (79%) and Bi(OTf)<sub>3</sub> (83%) with FeCl<sub>3</sub> even providing a slightly improved diastereoselectivity (dr = 95/5).

The choice for AuCl<sub>3</sub> as preferred catalyst for the current study eventually rested on its superior functional group compatibility. The reaction of phosphonate **4** and 2-methylthiophene to product **6** was not promoted by either one of the catalysts, which had performed well in the reaction  $1 \rightarrow syn$ -**3**. Only AuCl<sub>3</sub> gave a significant yield, which could be further improved by choosing the acetate **5** as the precursor in this reaction. A similar observation was made in the



Scheme 2. Comparison between alcohols 1 and 4 and the corresponding acetates 2 and 5 in the AuCl<sub>3</sub>-catalyzed arylation of 2-methylthiophene.

reaction to product *syn-3*, the rate of which was accelerated significantly by changing the electrophile precursor from alcohol 1 to acetate 2. In the first example the reaction required 18 h for full conversion, in the latter example the reaction was over in less than 2 h with the increased diastereoselectivity being an additional benefit.

#### Variation of the Electrophile

With resorcine dimethyl ether as a reference electrophile we screened various chiral acetates 5, 7-11 in the Au-catalyzed conversion to products 12-17 (Table 1). The acetates were prepared from the known alcohols<sup>[10d]</sup> by simple acetylation (AcCl, pyridine, N,N-dimethylaminopyridine in CH<sub>2</sub>Cl<sub>2</sub>). This set of alkylation experiments undermined the high functional group compatibility of the catalyst. All reactions proceeded cleanly and in good to excellent yields. What is more, the high diastereoselectivities of Friedel-Crafts alkylation reactions earlier observed in the HBF<sub>4</sub>-promoted reactions could be fully reproduced (entries 1, 2, 4–6) or even improved (entry 3). Preparatively useful levels of diastereoselectivity were achieved with almost all electrophiles except for the chloro-substituted substrate (9, entry 4, FG = Cl). Reactions were conducted by adding the catalyst AuCl<sub>3</sub> at ambient temperature to a solution of resorcine dimethyl ether and the respective acetate in nitromethane. The products 12-17 have been earlier studied and the configuration assignment was discussed elsewhere.<sup>[10d]</sup> It was proven for the Au-catalyzed experiments that the reactions proceed stereoconvergently,

OMe OMe OMe 10 mol% AuCl<sub>3</sub> r.t. (CH<sub>3</sub>NO<sub>2</sub>) FG vs OMe OMe FG FG MeO MeO 5, 7 - 11 syn-12 - 17 anti-12 - 17  $dr^{[a]}$ Yield<sup>[b]</sup> [%] Entry Substrate FG Major product Time [h] 2 1 5 PO(OEt)<sub>2</sub> syn-12 5/95 86 7 5 2 CO<sub>2</sub>Me anti-13 93/7 86 8 3 87 3 CN anti-14 93/7 9 97 4 Cl anti-15 1 65/35 79 5 10 SO<sub>2</sub>Et syn-16 2.5 13/87 62 6 11  $NO_2$ anti-17 0.5 94/6

 Table 1. AuCl<sub>3</sub>-catalyzed diastereoselective alkylation of resorcine dimethyl ether with chiral acetates 5, 7–11.

 OMe

<sup>[a]</sup> The diastereomeric ratio (*anti/syn*) of the crude product was determined by <sup>1</sup>H NMR spectroscopy.

<sup>[b]</sup> Yield of isolated product.

that is, the relative configuration of the substrate did not influence the product configuration. Many of the Au-catalyzed reactions display an intense blue or red color, which turns at the end of the reactions frequently into brown.

#### Variation of the Arene Nucleophile

The  $\beta$ -acetoxycarboxylate 7 was employed to assess the reactivity pattern of various arenes in the Au-catalyzed Friedel-Crafts alkylation. This electrophile 7 appears to be one of the synthetically most useful building blocks tested in the earlier series (5, 7-11), exhibiting a high diastereoselectivity for an otherwise difficult selective  $\beta$ -arylation of a carboxylate. We were delighted to note that the functional group tolerance of the catalyst was perfectly corroborated by these studies as was the previously observed diastereoselectivity.<sup>[10d]</sup> The method allows access to diastereomerically (and if required also enantiomerically) pure  $\beta$ -branched 3,3-diarylpropionates via the easily accessible aldol products. Products anti-18-24 were obtained in yields of 63-99% in a diastereomeric ratio ranging from 95/15 to 97/3. The difference in diastereoselectivity seems to parallel the steric requirements of the incoming nucleophile. Arenes which do not carry a bulky ortho-substituent (entries 1, 3, 5, 7) react with lower diastereoselectivity than arenes with an ortho-substituent (entries 2, 6). The reaction of hydroquinone dimethyl ether (entry 4) was somewhat sluggish possibly because of competing demethylation and oxidation reactions. In

general, a lower catalyst loading in the alkylation reactions is possible but it led expectedly to a decreased reaction rate. The reaction of acetate **7** with 2-methylthiophene (*cf.* entry 1) was catalyzed by 1 mol% of AuCl<sub>3</sub>. It was complete after 23 h and yielded 92% of product **18**. The ratio of the two product diastereomers *anti*-**18** and *syn*-**18** (dr = 90/10) was unchanged as compared to the reaction catalyzed by 10 mol% of AuCl<sub>3</sub>. Due to the relatively small scale on which the reactions were conducted, we consistently used 10 mol% of catalyst. The latter result and a more extended study (*vide infra*) clearly demonstrate, however, that a catalyst loading of 1 mol% is fully sufficient to achieve high yields and reasonable turnovers.

To account for the observed diastereoselectivity we have suggested a model according to which the free carbenium ion intermediate adopts a preferred conformation which, in turn, is dictated by 1,3-allylic strain.<sup>[10b,d]</sup> The  $\alpha$ -proton at the stereogenic center is positioned syn periplanar to the aryl group with the methoxycarbonyl group pointing into one diastereotopic face and the methyl group into the other. With the latter group being bigger than the former, the incoming nucleophile prefers the less congested approach. Expectedly, the Au-catalyzed reaction with  $\beta$ acetoxycarboxylates, which do not carry a methyl but a larger alkyl (ethyl, isopropyl) group in the  $\alpha$ -position, proceeded with even increased diastereoselectivity. With methylthiophene (entry 1) the selectivity for substrate 7 with a methyl group at the stereogenic center was 90/10 (99% yield) but increased with ethyl to 95/5 (98%) and with isopropyl even to 98/2 (92%).

#### **Other Nucleophiles**

An extension of the Friedel-Crafts methodology presented above and in previous papers<sup>[10a-d]</sup> was conceived using other nucleophiles either with a proton (NuH) or a TMS group (NuTMS) as electrophilic leaving group. It was shown that the C-C bond forming reactions with allyltrimethylsilane, trimethylsilyl cyanide and acetylacetone (Table 2, entries 1, 2, 4) occur in high yields (88-94%) and with good diastereoselectivity (dr = 91/9 - 97/3). The reaction with the heteroatom nucleophile TsNH<sub>2</sub> (entry 3) proceeded

Table 2. AuCl<sub>3</sub>-catalyzed diastereoselective alkylation of various arenes Ar'H with chiral acetate 7.



with disappointing selectivity, which may be due to the low steric demand of the nucleophile. The generation of stereogenic centers is reversed as compared to classical Michael-type addition reactions, in which the stereogenic center in  $\beta$ -position is generated prior to formation of the stereogenic center in  $\alpha$ -position, the latter determining the configuration of the former. In the bond set presented herein the easily generated  $\alpha$ stereogenic center dictates the stereoselectivity of the β-stereogenic center. The reaction may therefore serve in some cases as an alternative useful bond set for the construction of  $\alpha,\beta$ -substituted propionates.

Weaker nucleophiles such as trimethylvinylsilane did not react with substrate 7 under AuCl<sub>3</sub> catalysis. A slow decomposition was notable with the methoxyphenyl group of 7 acting as a nucleophile and leading to dimeric and oligomeric material. AuCl<sub>3</sub> could also been used to catalyze the reaction of silvl enol ethers (e.g. Table 3, entry 5) but is slightly inferior to Bi- $(OTf)_3^{[10e]}$  for this specific reaction. The screening of different catalyst loadings for the reaction of 7 with acetylacetone (entry 4) showed that these reactions can be performed with a much lower catalyst loading than 10 mol% AuCl<sub>3</sub>. Indeed, the catalyst loading of 10 mol% AuCl<sub>3</sub> was – as already stated previously – chosen for synthetic convenience. The reaction with 5 mol%, 2.5 mol% and 1 mol% AuCl<sub>3</sub> varied only slightly in the reaction times from 2 h to 3.5 h and in terms of yield (91% to 81%). The diastereomeric ratio of product 28 was unchanged as compared to the reaction catalyzed by 10 mol% of AuCl<sub>3</sub>. Individual results based on a 0.25-mmol scale, employing

Table 3. AuCl<sub>3</sub>-catalyzed diastereoselective alkylation of various nucleophiles NuH or NuTMS with chiral acetate 7.



Entry	Nucleophile	Major product	Time [h]	$dr^{[a]}$	Yield <sup>[b]</sup>
1	ТМЯ	anti- <b>25</b>	0.1	92/8	90
2	NC-TMS	anti- <b>26</b>	0.5	91/9	77
3	TsNH− <b>H</b>	anti- <b>27</b>	1	71/29	94
4	O O H	anti- <b>28</b>	1.5	97/3	88
5	OTMS	anti- <b>29</b>	1	95/5	73

[a] The diastereomeric ratio (anti/syn) of the crude product was determined by <sup>1</sup>H NMR spectroscopy. [b]

[a] The diastereomeric ratio (anti/syn) of the crude product was determined by <sup>1</sup>H NMR spectroscopy.

[b] Yield of isolated product.

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Yield of isolated product.

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four equivalents of acetylacetone and a substrate concentration of 0.12M were (yield and reaction time) with 5 mol% AuCl<sub>3</sub> 91% and 2 h, with 2.5 mol% AuCl<sub>3</sub> 84% and 3 h, with 1 mol% AuCl<sub>3</sub> 81% and 3.5 h. On larger scale (1 mmol of **7**) at a concentration of 0.25 M, using 1 mol% AuCl<sub>3</sub> it was not only possible to decrease the amount of acetylacetone to 2 equiv. but also to match the 94% yield achieved with 10 mol% on a smaller scale (0.25 mmol). The ratio of the two product diastereomers *anti*-**28** and *syn*-**28** (dr = 97/3) remained unchanged.

## Conclusions

In summary, AuCl<sub>3</sub> was shown to be a generally applicable catalyst for the diastereoselective conversion of various benzylic acetates to the corresponding  $S_N1$ type substitution products. Arenes reacted in a Friedel–Crafts alkylation to provide the corresponding products **12–24** in good to very good yields (62–99%) and with varying selectivities depending on the substitution pattern at the stereogenic center. The  $\beta$ -acetoxycarboxylate **7**, which evolved from this study as a representative  $\beta$ -electrophilic acrylate equivalent, underwent selective reactions with several other nucleophiles such as allyltrimethylsilane, trimethylsilyl cyanide, acetylacetone, and 2,2-dimethyl-3-(trimethylsilyloxy)butane (73–90% yield, dr = 91/9-97/3).

## **Experimental Section**

# General Procedure for the Acetylation of Benzylic Alcohols

The alcohol (1 equiv., 3 mmol), pyridine (6–10 equiv.), the acetylating agent (Ac<sub>2</sub>O or AcCl, 2 equiv.) and a catalytic amount of DMAP were stirred in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) for the specified time (see Supporting Information). The reaction was quenched by addition of saturated aqueous NH<sub>4</sub>Cl (20 mL) and the aqueous layer was extracted with ethyl acetate ( $3 \times 20$  mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography.

# General Procedure for the AuCl<sub>3</sub>-Catalyzed Alkylation with Benzylic Acetates

The acetate (1 equiv., 0.25 mmol) and the nucleophile (4 equiv., 1.0 mmol) were dissolved in nitromethane (2 mL), AuCl<sub>3</sub> (7.6 mg, 25  $\mu$ mol) was added in one portion and the solution was stirred until the reaction was complete. The reaction was quenched by addition of water (10 mL), diluted with ethyl acetate (10 mL) and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with water (20 mL) and brine (20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed under re-

duced pressure. The crude product was purified by flash chromatography. The products were obtained as diastereomeric mixtures.

#### **Supporting Information**

General information, detailed reaction conditions, spectroscopic and analytical data of compounds 5, 8–11, *anti-*21, 25, 26, *anti-*28 and 29.

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