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Toward the continuous-flow synthesis of chiral tertiary alcohols by enantioselective addition of organozinc reagents to ketones using nanosize isoborneol ligands

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Dedicated to Professor Yoshinori Yamamoto on the ocassion of his 65th birthday

Abstract—The catalytic enantioselective addition of different organozinc reagents, such as alkyl or in situ generated phenylzinc derivatives to simple aryl ketones, was accomplished using titanium tetraisopropoxide and chiral ligands derived from *trans*-1-arenesulfonylamino-2-isoborneolsulfonylamidocyclohexane and Fréchet-type dendrons with up to 2.5 nm of diameter, giving the corresponding tertiary alcohols with enantioselectivities up to >99%. A simple and efficient procedure for the synthesis of the ligands used is also described, involving the radical addition of the corresponding thiol dendron to the chiral styryl-isoborneol derivative.

1. Introduction

The high economical and environmental cost of a single use chiral ligand has forced the development of new alternatives, such as the anchoring of a chiral ligand onto inert polymers.[1] However, this strategy usually renders lower results, in comparison to the homogeneous version. Another alternative is the anchoring of a chiral ligand to a dendrimeric skeleton (dendron).[2] In this way, the reaction is performed under homogeneous conditions and the dendrimer can be usually recovered by precipitation. More interesting is the use of nanosize ligands,[3] since they allow the reaction to be carried out under continuous-flow conditions,[4] by the use of membranes thus avoiding the leaching of the nanosize catalyst from the reaction vessel.[5] One of the most used dendrons is a polyether having a repeated 3,5-dioxybenzyl structure (Fréchet-type dendron), which has been attached to different chiral sub-units. Among them, dendrimers containing hydroxymethylpyridine,[6] TADDOL,[7] BINOL,[8] and 2-aminoalcohols[9,10] have been used in the enantioselective addition of dialkylzinc reagents to aldehydes[11] in the presence of titanium tetraisopropoxide,[12] with very broad ranging results.

As an integrated part of our program on the design and synthesis of chiral sulfonamides,[13] as well as their use as chiral promoters[14] in the addition of organozinc reagents to ketones,[15] obtaining molecules with a challenging quaternary stereocenter,[16] we envisaged that the incorporation of the chiral isoborneolsulfonamide sub-unit into a Fréchet dendron will not only lead to a new dendrimeric ligand for application in catalysis, but will also provide a unique opportunity to study the influence of the shape and architecture of the dendrimer on the enantioselectivity.

Herein, we report the first synthesis of nanosize ligands derived from isoborneolsulfonamide and Fréchet dendritic wedges, which were joined using a new radical strategy, as well as their use in the enantioselective alkylation and arylation[17] of ketones.

2. Results and discussion

Among the three general strategies to place a chiral subunit into a dendrimer, (a) peripheral, (b) building blocks or (c) core, we choose the last one, with the hope that the

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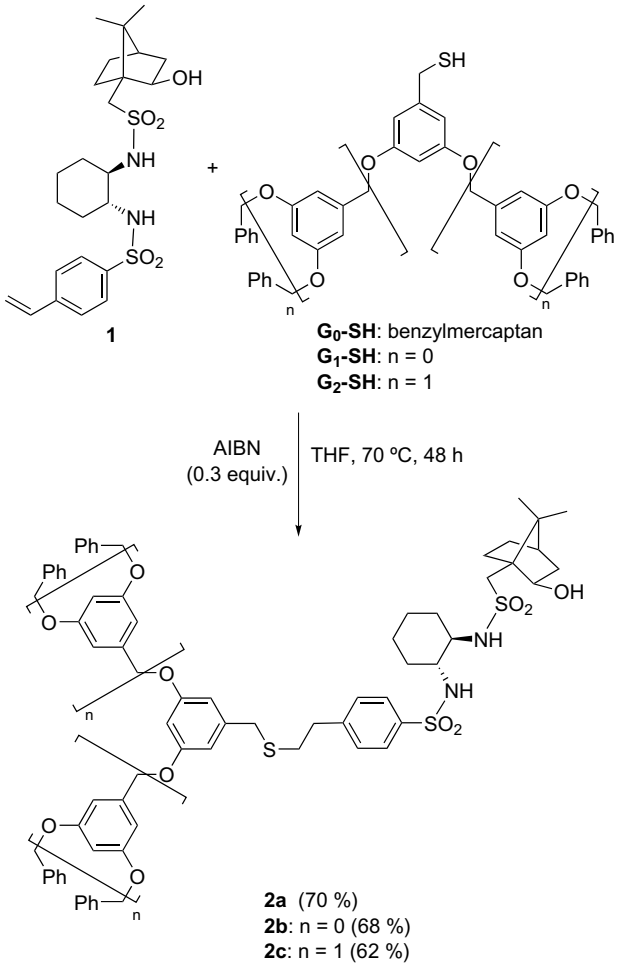
asymmetric core could force the achiral branch into a specific arrangement, thus enhancing the anisotropy around of isoborneol–titanium center, as enzymes do, and therefore increasing the enantioselectivity of the reaction.

While $\mathbf{G_0}$-**SH** (benzylmercaptan) is comercially available, the dendritic wedges $\mathbf{G_1}$-**SH**[18] and $\mathbf{G_2}$-**SH**[19] were prepared in 50% and 34% yields, respectively, following a convergent approach starting for both from 3,5-dihydroxybenzyl alcohol.[20] The benzylation of the above catechol under standard conditions followed by the mesylation of the bencylic alcohol,[21] substitution with potassium thioacetate, and the reduction of the thioester[22] gave the expected $\mathbf{G_1}$-**SH**. However, for the preparation of related $\mathbf{G_2}$-**SH**, after mesylation, the obtained benzylic sulfonate derivative was reacted again with another equivalent of 3,5-dihydroxybenzyl alcohol, rendering the corresponding benzylic alcohol of the second generation,[23] which was transformed into the corresponding sulfanyl derivative as above. The final radical addition of sulfanyl derivatives $\mathbf{G}_n$-**SH** to the chiral styryl-isoborneol compound **1**[17f] initiated by AIBN[24] gave the expected chiral dendrimers **2** in good yields (Scheme 1), practically independent of the generation prepared, with this approach being used for the first time in the preparation of Fréchet dendrimers.



Scheme 1. Radical preparation of Fréchet dendrimeric isoborneolsulfonamide ligands **2**.

Measurements of the specific rotations of dendrimers **2** showed that the $[\alpha]_D$ values decreased when increasing the generation number. This is in agreement with earlier findings[7,25] which showed that an attachment of achiral branches to a chiral core leads to a kind of dilution effect of the specific rotation. The molar rotation $[\Phi]_D$ values showed a higher value for the first generation in comparison to zero and second generations (Fig. 1).

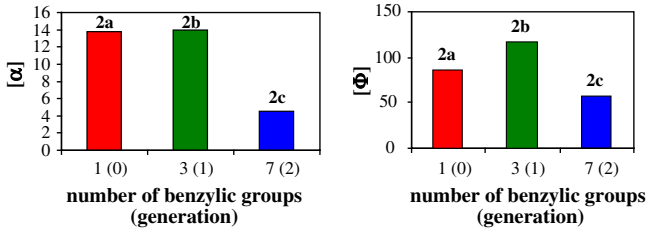


Figure 1. Comparison between the specific and molar rotation for dendrimers **2**.

The CD spectra of 10^{-4} M solutions of compound **1** and dendrimers **2** in acetonitrile were recorded in order to study the influence of dendritic wedges on the spectroscopic properties. To avoid distortion of the dichotic absorption caused by the presence of an increasing number of benzene chromophores in the dendrimer, the obtained $\Delta\varepsilon$ values were divided by the number of phenyl rings present in each compound. All compounds showed a small positive Cotton effect. While dendrimers **2** present a maximum value at 230 nm, decreasing the intensity with increasing generation, the initial core sub-unit **1** showed the maximum at higher values, ca. 260 (Fig. 2).

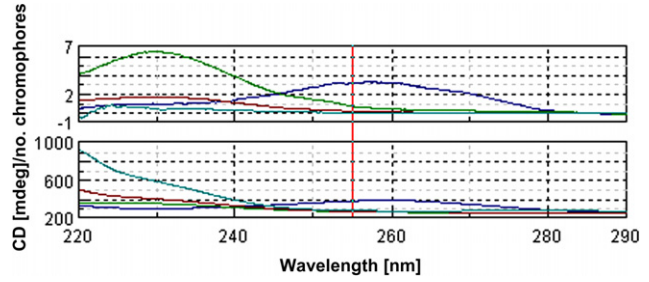
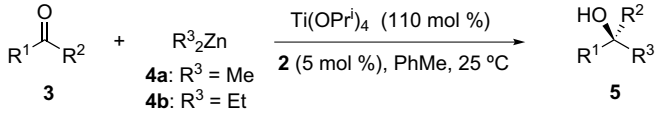


Figure 2. CD spectra of compounds **1** (dark blue), **2a** (green), **2b** (red), and **2c** (pale blue).

Unfortunately, all the aforementioned chiroptical properties seem to show that the anisotropy does not increase around the core due to the specific spatial arrangement of the Fréchet dendron. Although under some reaction conditions, this fact could be changed.

Next, we performed calculations to visualize the molecular shape of second generation dendrimer **2c**. First, in order to search for a set of low-energy conformers, the conformational analysis was carried out by molecular mechanics. Then, the resulting structures were further optimized by a PM3 method showing that the maximum differences between the heats of formation of conformers were lower than 5 kcal/mol, and the globular structures have an

Table 1. Enantioselective alkylation of ketones using dendrimeric ligands **2**



Entry	Ligand	R^1	R^2	R^3	Time (d)	Alcohol	Yield[a] (%)	ee[b] (%)
1	**2a**	Ph	Me	Et	4	**5a**	66	95 (*S*)
2	**2a**	4-MeC_6H_4	Me	Et	4	**5b**	30	86 (−)
3	**2a**	4-FC_6H_4	Me	Et	3	**5c**	92	81 (−)
4	**2a**	4-BrC_6H_4	Me	Et	2	**5d**	97	93 (−)
5	**2a**	2-Naphthyl	Me	Et	4	**5e**	52	75 (−)
6	**2a**	PhC≡C	Me	Et	2	**5f**	98	88 (+)
7	**2a**	Ph	Et	Me	8	*ent*-**5a**	25	>99[c] (*R*)
8	**2b**	Ph	Me	Et	4	**5a**	53	97 (*S*)
9	**2b**	4-MeC_6H_4	Me	Et	4	**5b**	29	96 (−)
10	**2b**	4-FC_6H_4	Me	Et	2	**5c**	92	85 (−)
11	**2b**	4-BrC_6H_4	Me	Et	2	**5d**	98	90 (−)
12	**2b**	2-Naphthyl	Me	Et	3	**5e**	98	57 (−)
13	**2b**	PhC≡C	Me	Et	2	**5f**	97	88 (+)
14	**2b**	Ph	Et	Me	7	*ent*-**5a**	21	>99[c] (*R*)
15	**2c**	Ph	Me	Et	4	**5a**	59	99 (*S*)
16	**2c**	4-MeC_6H_4	Me	Et	5	**5b**	34	98 (−)
17	**2c**	PhC≡C	Me	Et	3	**5f**	96	86 (+)

[a] Isolated yield after column chromatography.
[b] Determinated by HPLC using Chiracel columns; the absolute configuration or the sign of the predominant enantiomer is indicated in parentheses.
[c] Only one enantiomer detected.

approximate diameter of 2.5 nm (Fig. 3), with these numbers being similar when a titanium atom was added to form the expected complex.

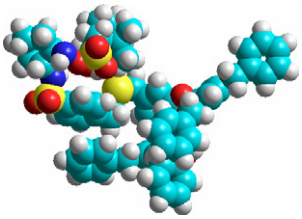
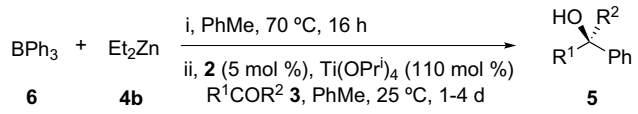


Figure 3. Calculated globular structure of ligand **2c**.

Finally, the activity of chiral dendrimers **2** was tested through the enantioselective alkylation of ketones **3** to give the expected tertiary alcohols in good results (Table 1). The nature of the ketone has any important effect on the enantioselectivity, with α,β-unsaturated compounds giving lower ee (compare entries 1, 8, and 15 with 6, 13, and 17, respectively). Also, the chemical yield was clearly influenced by the ketone nature, with alkyl aryl ketones possessing an electron-donating group at the *para*-position giving worse chemical yields than those possessing electron-withdrawing groups (compare entries 2 and 3, 4 in Table 1). The bulkiness of the aryl substituent also has a detrimental effect, not only on the chemical yield but on the enantioselectivity (compare entries 1 and 5 in Table 1). The nature of the dialkylzinc reagent, methyl or ethyl, has an important effect on the reaction rate, as well as on the chemical yield (compare entry 1 with 7). Finally, comparing all ligands, it is worthy of note that the results obtained were homogeneous independent of the dendrimeric wedge used; benzylsulfanyl derivative **2a**, first generation **2b** ($n = 0$) or second generation **2c** ($n = 1$), practically rendered the same

Table 2. Enantioselective phenylation of ketones using dendrimeric ligands **2**



Entry	L	R^1	R^2	No	Yield[a] (%)	ee[b] (%)
1	**2a**	Bu^n	Me	**5g**	97	34 (*R*)
2	**2a**	4-MeC_6H_4	Me	**5h**	51	80 (−)
3	**2a**	3-MeC_6H_4	Me	**5i**	83	80 (−)
4	**2a**	4-$CF_3C_6H_4$	Me	**5j**	98	85 (+)
5	**2a**	4-FC_6H_4	Me	**5k**	98	86 (+)
6	**2a**	4-ClC_6H_4	Me	**5l**	97	83 (+)
7	**2a**	4-BrC_6H_4	Me	**5m**	91	>99[c] (+)
8	**2a**	4-BrC_6H_4	Et	**5n**	55	72 (+)
9	**2b**	Bu^n	Me	**5g**	76	35 (*R*)
10	**2b**	4-MeC_6H_4	Me	**5h**	65	80 (−)
11	**2b**	3-MeC_6H_4	Me	**5i**	67	84 (−)
12	**2b**	4-$CF_3C_6H_4$	Me	**5j**	88	83 (+)
13	**2b**	4-FC_6H_4	Me	**5k**	90	84 (+)
14	**2b**	4-ClC_6H_4	Me	**5l**	91	64 (+)
15	**2b**	4-BrC_6H_4	Me	**5m**	89	78 (+)
16	**2b**	4-BrC_6H_4	Et	**5n**	51	78 (+)
17	**2c**	3-MeC_6H_4	Me	**5i**	95	84 (−)
18	**2c**	4-$CF_3C_6H_4$	Me	**5j**	97	81 (+)
19	**2c**	4-BrC_6H_4	Me	**5m**	84	75 (+)

[a] Isolated yield after column chromatography.
[b] Determinated by HPLC using Chiracel columns; the absolute configuration or the sign of the predominant enantiomer is indicated in parentheses.
[c] Only one enantiomer detected.

chemical yield, enantioselectivity and reaction times (compare for instance, entries 1, 8, and 15).

After the success obtained with the alkylation process, we focused our efforts on the arylation process. Due to the instability of pure diphenylzinc, we chose to prepare the corresponding phenylzinc reagent by the transmetallation of triphenylborane **6** with diethylzinc **4b** at 70 °C, and the in situ obtained reagent was submitted to further reaction with ketones **3** in the presence of nearly stoichiometric amounts of titanium tetraisopropoxide and substoichiometric amounts of chiral dendrimeric ligands,[17d–f] as depicted in Table 2.

First, it should be pointed out that the results using 2-hexanone are quite different with regard to the enantioselectivities from those obtained with alkyl aryl ketones, since the differentiation between the two acyclic alkyl groups is far more difficult than between aryl and alkyl groups (compare entries 1 and 2 in Table 2). As in the previous alkylation process, the results are quite homogeneous, independent of the generation ligand used (compare entries 2–6 and 10–14 in Table 2). The electronic character of the substituent on the aryl group has a minimal effect on the chemical yield (Table 2, entries 2 and 4). However, in the phenylation process, the bulkiness of the alkyl group of the ketone has a dramatic effect on the chemical yield and enantioselectivity (entries 7 and 8 in Table 2).

3. Conclusion

In conclusion, we have developed a new strategy to attach chiral styryl derivatives to an achiral Fréchet dendron by a radical approach. The dendrimers obtained have been successfully used in the catalytic enantioselective nucleophilic alkylation and arylation of simple ketones. These complexes have diameters in the range of nanosize, that would permit their use in a continuous-flow membrane reactor, although so far the reaction rates make this probability very difficult. Work is currently in progress in order to fulfill all these requirements.

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