Remote Anisotropic Effects in Diastereomeric Esters of Fluorinated *O*-Aryllactic Acids

Jean-Louis Gras,*[a] Thierry Soto,[a] and Andreas Heumann[a]

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The enantiomeric purity of a chiral compound is determined by NMR spectroscopic analysis of the diastereomers formed with a chiral derivatizing agent. Fluorinated *O*-aryllactic acids (FAC) **1** are efficient chiral reporters, whose spectacular remote anisotropic effects allow an easy identification and measurement of diastereomers. The remote effects are attributed to the particular design of FAC esters relative to other CDAs.

Introduction

Many methods exist for determining the enantiomeric purity of a chiral compound, particularly GC and HPLC analysis, which are widely used in industry for quality control,[1] and NMR based methods. Chiral lanthanide shift-reagents or chiral solvating agents form in situ diastereomeric complexes with chiral compounds, and the formation of diastereomers with chiral derivatizing agents (CDA) prior to NMR analysis has been established as a powerful and reliable method for determining the enantiomeric excess of hydroxyl or amino substrates.[2] α-Methoxy-α-trifluoromethylphenylacetic acid (MTPA, Mosher's acid)[3] is the cornerstone for the invention of many CDAs.

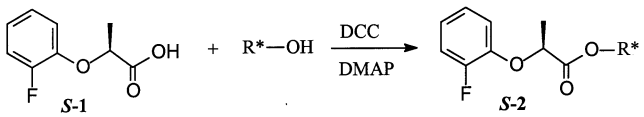
Chiral recognition due to an optically active auxiliary is generally limited to proximal centers; enantioseparation of distant groups is much less common. Nevertheless, NMR shift differentiation is possible such as with the oxazolidin-2-selone NMR reagents that recognize chiral CHD carbons five atoms away from a chiral center.[4] ^{19}F-NMR analysis with diastereomeric α-cyano-α-fluorophenylacetic esters allows the visualization of remote centers up to seven bonds away.[5]

We have developed easily accessible fluorinated *O*-aryllactic acids (FAC) that turned out to be efficient in distinguishing diastereomeric esters by ^{19}F-NMR spectroscopy, with the spectator fluorine being up to nine bonds away from the chiral center.[6] It was also possible to distinguish diastereotopic protons with this kind of propionic acid.[7] Careful ^{1}H-NMR spectroscopic analysis of the diastereomeric esters allowed us to assign the absolute configuration of chiral menthols and to propose a new model with Hα in the acid plane and a hitherto unprecedented conformation. These observations were strengthened by an X-ray structure analysis[8] and by Nuclear Overhauser effects.[9]

We report here on the general use of FAC **1** as a chiral reporter, whose spectacular remote anisotropic effects allow an easy identification and measurement of diastereomers.

Results and Discussion

Fluorinated *O*-aryllactic acid **1** (FAC) reacted with primary and secondary alcohols to give the corresponding fluorinated-*O*-aryl lactates **2** (Scheme 1).



Scheme 1. Synthesis of FAC-esters

We applied the chiral aryllactic acid reagents FAC to the control of the enantiomeric purity of various primary and secondary alcohols which are intermediates in the synthesis of chiral conformationally restricted arachidonic acid analogues derived from tartaric acid.[10,11] We found that these acids were the reagent of choice for this purpose, and that many remote diastereomeric protons in the alcohols became separated.

The series of alcohols **3–10** includes primary and secondary alcohols, a primary diol, and *cis*- and *trans*-substituted 5- and 6-membered heterocycles (Figure 1).[12]

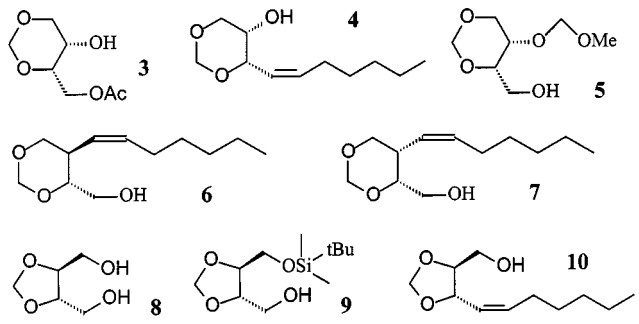


Figure 1. Analyzed primary and secondary alcohols

The esters were formed with dicyclohexylcarbodiimide (DCC) as a coupling agent in the presence of the acyl-trans-

[a] Université d'Aix-Marseille III, Laboratoire ReSo,
UMR-CNRS 6516,
Faculté des Sciences St. Jérôme D12,
F-13397 Marseille Cedex 20, France
E-mail: jean-louis.gras@reso.u-3mrs.fr

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fer catalyst dimethylaminopyridine (DMAP).[13] No racemization was observed during esterification. The NMR spectra were recorded in $CDCl_3$ at 200 MHz for ^1H and 50.6 MHz for ^{13}C. The unexpectedly good results of this study indicated that there was no need to record ^{19}F-NMR spectra as almost all the diastereomeric H and C atoms were perfectly resolved. Table 1 lists selected clearly resolved signals. Analyses were made on the esters formed with the chiral acid (***S*-1**) and, first, the racemic alcohol, then with a pure enantiomer (**11 15, 18**). The esters (*S,S*)-**16** and (*S,S*)-**17** were made from the pure alcohols (*S,S*)-**8** and (*S,S*)-**9**, respectively, and each of the (*S*)-, (*R*)-**1** acids.

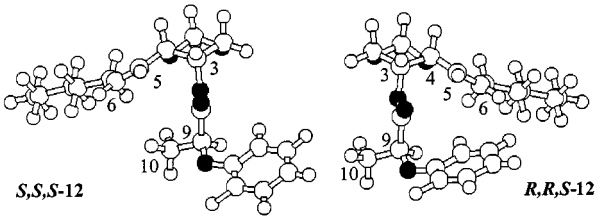

Figure 2. MM2-minimized diastereomeric esters (***S,S,S*)-12** and (***R,R,S*)-12**; most affected protons: 3-H, 4-H, 6-H; most affected carbon atoms: C-3, C-5, C-6, C-9, C-10

Table 1. Selected ^1H Δδ (200 MHz) and ^{13}C Δδ (50.3 MHz) in diastereomers **11–18**; $\Delta\delta = \delta_{S,S\text{-}S} - \delta_{R,R\text{-}S} \times 10^{-1}$ pm; *eq* = equatorial, *ax* = axial; *A, B*: non-equivalent geminated protons; [a]: $\Delta\delta = \delta_{S,R\text{-}S} - \delta_{R,S\text{-}S}$; [b]: $\Delta\delta = \delta_{S,S\text{-}S} - \delta_{S,S\text{-}R}$

Δδ	1-H	2-H	3-H	4-H	5-H	6-H	7-H	9-H	10-H	C-1	C-2	C-3	C-4	C-5	C-6	C-8	C-9	C-10
11	eq:0.3	eq:0.2	-0.1				0.2		-0.1		1	2		-1	-1	1	2	
12	eq:0.3		-0.4		-0.5	0.5							-3	2	-2		2	2
13	eq:-0.1 ax:-0.4	 ax:0.3	0.7	-0.4		-0.3						1	0.7	2	0.3		2	
14[a]	ax:0.2	eq:-0.2	0.2		A:0.3 B:-0.4					3				2			-2	2
15	eq:0.2 ax:0.3			0.2	0.1			0.1	0.1				-3	2	-2		2	-2
16[b]	A:0.1 B:-0.6	0.2								-4	-3	-3				-4	-3	-4
17[b]	A:-0.2 B:-0.5	-0.4		A:0.5 B:0.1	-0.4			-0.2	-0.2	1	1	3	2	2				
18	A:-0.6 B:-0.7		0.01	A:0.2 B:-0.2		0.2		0.2	0.2	1				-1	1		1	

The discrimination of the diastereomers was effective regardless of the class of the alcohol involved in esters **2**: secondary (**11**, **12**), primary (**13** to **18**) or tertiary.[15] Compounds **11–18** are built on a dioxane or dioxolane core but the discriminative anisotropic effects were found to be independent of the *cis*/*trans* substitution pattern and the resulting axial/equatorial relationship of the rings. MM2 calculations did not show any electronic interaction between the heterocycle and the aryl group. Therefore the discrimination should not be related to the presence of heteroatoms (Figure 2). Moreover the flexibility of the pendant groups indicates that this method is not limited to conformationally restricted structures. We did not measure any NOE between the aryl group and the heterocycle or the pendant groups.

The discrimination could be measured in the CDA-part by analyzing the Me signal (**11**, **15, 17**, **18**) and/or the first proton of the alcohol moiety (3-H in **11**, **12**, 5-H or 4-H in case of the esters of primary alcohols). The discriminations were up to 0.05 ppm but more striking differences, and easier to observe signals, were found at much longer distances. In fact, recognition was much higher on signals far from the alcohol molecule such as the acetate Me in **11**.

We attributed these remote discriminating (shielding/deshielding) effects to the aryl group rather than to the interactions between the cumulated stereogenic centers. For instance, all the methylene acetal protons 1-H, which are easy to localize, were highly affected even when located nine bonds away from the first aromatic sp^2 carbon. This shift between diastereomers rises to 0.07 ppm in **18**. The MOM protons 6-H in **13**, 5-H in **17**, and vinylic 6-H in **18** showed shift differences of up to 0.04 ppm even though they are separated from the aryl group by 10 bonds, i.e. a most surprising 1–11 interaction. In acetate **11** the methyl protons

were well resolved (0.02 ppm) with *a record 1–12 interaction* with the aryl group.

The discrimination observed in the proton NMR spectra was confirmed by the ^{13}C values (Table 1). Again, the lactic carbons C-9 and C-10 were shifted, in most cases up to 0.4 ppm. Many other carbon atoms were also affected, including the alcohol functional group *C*–O (C-3 or C-5).

Spectacular 1–9 and 1–10 interactions between the linker aromatic sp^2-C and C-6 were measured in **11**, **12**, **13**, **15**, and **18**. Finally a 1–11 remote effect occurred between the carbonyl and the aromatic group in the highly flexible diester **16**, that induced a 0.4 ppm shift in one of the diastereomers.

The significant effects induced by the chiral reporter FAC can be rationalized in the following manner to explain the unusual remote shift differences observed. Several aromatic acids have been used as chiral reporters to induce chemical shift differences within an alcohol substrate: α-phenylbutyric acid (MTPA) (Helmchen, ref.[16]) MTPA (Mosher),[3] *O*-methylmandelic acid (MMA) (Mosher, Trost).[17] The phenyl group α to the ester shields a portion of the molecule in each relevant conformation of the respective esters (Figure 3).

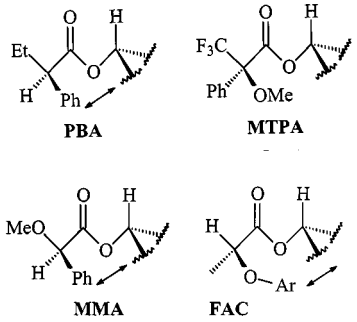

Figure 3. Comparative conformations of aryl CDAs

It has been shown by NMR analysis of all eight enantiomeric FAC-menthol esters that the chemical shift variations in the alcohol part were the consequence of the conformational arrangement of the acid-part. X-ray structure analysis[8] and nuclear Overhauser effect (NOE) measurements[9] have recently confirmed this spatial conformation of *O*-aryllactic esters. When possible, these chiral reagents adopt a preferential conformation in which the acid substituent, the ester –CO–O– linkage and the ether methine are in a common plane (acid plane). The preferred *syn*-periplanar conformation of the ester linkage also helps to place the aromatic π-system close to one of the alcohol substituents (or H). This through-space interaction naturally produces an anisotropic effect on these groups (Figure 4).

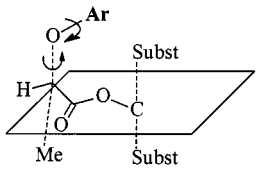

Figure 4. Enhanced through-space interaction in FAC-esters (*S*)-**2**

The FAC reporter has two specific features that enhance the anisotropic effect when compared to other phenyl acetic acids:

A quantitative effect: the phenyl group is one bond further away from the ester function and free rotation around the C–OAr bond allows the phenyl to act as a propeller. Consequently, interactions (and shift differences) at specific sites can be significant at very long distances.

A qualitative effect: another free rotation around the O–Ar bond allows the aryl group to freely orientate itself, and thus to induce either shielding or deshielding effects simultaneously at various sites in the molecule. In any case FAC affords a very high probability to get a clear-cut shift effect onto several remote parts of the esters. The varying direction of the effects increases the opportunity to differentiate each diastereomer and to quantify their ratio.

The relevant perturbations observed for the methylene ketal protons 1-H in compounds **11**–**18**, which are independent of the nature of the analyzed parent alcohol, obviously illustrate the twisting structure of esters ***S*-2**. This causes the aromatic system to interact with significantly remote protons or carbons, as expected.

Conclusion

The combination of both quantitative and qualitative effects makes FAC a general candidate for the efficient discrimination and quantification of diastereomers. The dramatic remote anisotropic effects occur regardless of the class of the alcohol and are not associated to a particular conformational bias.

Experimental Section

General Remarks: ^1H- and ^{13}C-NMR spectra were recorded with an AC 200 Bruker instrument with $CDCl_3$ as internal reference for chemical shifts, respectively 7.24 and 77.1, expressed as δ values in ppm and coupling constants in Hz. – Chromatography was carried out on columns packed with Merck silica gel 60 (70–230 mesh).

Typical Procedure for the Synthesis of Esters 11–18: Dicyclohexylcarbodiimide (103 mg, 0.5 mmol) and (*S*)-(−)-(2-fluorophenyl)-2-phenoxypropionic acid (92 mg, 0.5 mmol), were dissolved in 5 mL of dry, ethanol-free CH_2Cl_2 or THF. The clear solution became rapidly cloudy. The alcohol (0.5 mmol) was then added together with some crystals of dimethylaminopyridine and the reaction mixture stirred for ca. 12 h. The solution was filtered and the solvent evaporated without heating. The solid or semisolid residue was transferred to a small silica gel (2 g) column and the product(s) eluted with 10 mL portions of hexane, and 1,2,5,10 and 20% diethyl ether/hexane mixtures. All fractions containing the ester(s), usually fractions 3 and 4 (2 and 5% diethyl ether, respectively) were combined and the solvent evaporated. Yields 70–85%.

(*S*,*S*-*S*)-11: ^1H NMR: δ = 7.11–6.91 (m, 4 H), 5.13 (br. d, *J* = 6.3 Hz, 1 H), 4.90 (q, *J* = 6.8 Hz, 1 H), 4.80 (br. s, *J* = 7.2 Hz, 1 H), 4.75 (d, *J* = 6.3 Hz, 1 H), 4.12 (d, *J* = 13.1 Hz, 1 H), 4.07–3.98 (m, 3 H), 3.84 (dd, *J* = 13.2, 1.6 Hz, 1 H), 2.02 (s, 3 H), 1.68 (d, *J* = 6.9 Hz, 1 H). – ^{13}C NMR: δ = 171.4, 170.4, 153.1 (d, *J* = 246

Hz), 145.4 (d, J = 14.5 Hz), 124.4 (d, J = 3.2 Hz), 122.7 (d, J = 6.4 Hz), 117.3, 116.8 (d, J = 18.3 Hz), 93.5, 74.5, 74.2, 68.6, 66.8, 62.5, 20.6, 18.6.

(*S,S-S*)-12: ^{1}H NMR: δ = 7.10–6.89 (m, 4 H), 5.50 (dtd, J = 11.1, 7.4, 1.0 Hz, 1 H), 5.27 (ddt, J = 11.1, 7.5, 1.4 Hz, 1 H), 5.14 (br. d, J = 6.4 Hz, 1 H), 4.90 (q, J = 6.8 Hz, 1 H), 4.81 (d, J = 6.4 Hz, 1 H), 4.72 (br. d, J = 1.4 Hz, 1 H), 4.57 (dt, J = 7.5, 1.1 Hz, 1 H), 4.09 (d, J = 13.0 Hz, 1 H), 3.75 (dd, J = 13.0, 1.6 Hz, 1 H), 2.02 (m, 2 H), 1.68 (d, J = 6.8 Hz, 3 H), 1.36–1.20 (m, 6 H), 0.86 (t, J = 6.7 Hz, 3 H). – ^{13}C NMR: δ = 171.5, 152.5 (d, J = 246 Hz), 145.6 (d, J = 10.3 Hz), 135.1, 124.3, 124.3 (d, J = 3.3 Hz), 122.6 (d, J = 7.0 Hz), 117.1, 116.7 (d, J = 18.6 Hz), 93.5, 74.0, 73.7, 69.4, 68.7, 31.4, 29.0, 28.1, 22.5, 18.8, 14.0.

(*S,S-S*)-13: ^{1}H NMR: δ = 7.10–6.85 (m, 4 H), 5.07 (br. d, J = 6.3 Hz, 1 H), 4.79 (q, J = 6.8 Hz, 1 H), 4.72 (d, J = 7.2 Hz, 1 H), 4.68 (d, J = 7.2 Hz, 1 H), 4.56 (d, J = 6.1 Hz, 1 H), 4.34 (dd, J = 11.4, 7.1 Hz, 1 H), 4.26 (dd, J = 11.4, 5.1 Hz, 1 H), 4.17 (dt, J = 12.6, 1.3 Hz, 1 H), 3.85 (ddd, J = 5.3, 1.7 Hz, 1 H), 3.67 (dd, J = 12.6, 1.4 Hz, 1 H), 3.41 (br. s, 1 H), 3.36 (s, 3 H), 1.62 (d, J = 6.8 Hz, 3 H). – ^{13}C NMR: δ = 171.5, 153.2 (d, J = 246 Hz), 145.5 (d, J = 10.3 Hz), 124.3 (d, J = 4.0 Hz), 122.7 (d, J = 7.1 Hz), 117.4, 116.7 (d, J = 18.7 Hz), 95.77, 93.5, 75.9, 74.4, 69.3, 68.7, 64.3, 55.9, 18.5.

(*S,R-S*)-14: ^{1}H NMR: δ = 7.11–6.88 (m, 4 H), 5.54 (dt, J = 10.9, 7.4 Hz, 1 H), 5.03 (d, J = 6.2 Hz, 1 H), 4.89 (dd, J = 10.8, 9.8 Hz, 1 H), 4.78 (q, J = 6.8 Hz, 1 H), 4.61 (d, J = 6.3 Hz, 1 H), 4.36 (dd, J = 11.8, 2.3 Hz, 1 H), 4.05 (dd, J = 11.8, 6.8 Hz, 1 H), 3.86 (dd, J = 11.3, 4.7 Hz, 1 H), 3.55 (ddd, J = 9.7, 6.8, 2.3 Hz, 1 H), 3.32 (t, J = 11.3 Hz, 1 H), 2.78 (dtd, J = 10.7, 10.0, 5.0 Hz, 1 H), 1.97 (m, 2 H), 1.85 (t, J = 6.6 Hz, 3 H), 1.28 (m, 6 H). – ^{13}C NMR: δ = 171.6, 153.2 (d, J = 246 Hz), 145.6 (d, J = 10.6 Hz), 135.9, 124.3 (d, J = 3.9 Hz), 123.2, 122.6 (d, J = 7.1 Hz), 117.5, 116.6 (d, J = 18.5 Hz), 93.4, 78.4, 74.4, 69.9, 65.4, 35.9, 31.4, 29.2, 27.9, 22.5, 18.6, 14.0.

(*S,S-S*)-15: ^{1}H NMR: δ = 7.11–6.88 (m, 4 H), 5.82 (dd, J = 11.0, 10.4 Hz, 1 H), 5.55 (dt, J = 11.2, 7.0 Hz, 1 H), 5.07 (d, J = 6.1 Hz, 1 H), 4.79 (q, J = 6.8 Hz, 1 H), 4.68 (d, J = 6.0 Hz, 1 H), 3.84 (m, 3 H), 3.62 (ddd, J = 11.7, 8.4, 3.4 Hz, 1 H), 3.40 (ddd, J = 11.7, 8.6, 3.6 Hz, 1 H), 2.41 (dd, J = 10.2, 1.8 Hz, 1 H), 1.95 (dd, J = 14.0, 6.8 Hz, 2 H), 1.64 (d, J = 6.8 Hz, 3 H), 1.27 (m, 6 H), 0.85 (t, J = 6.6 Hz, 3 H). – ^{13}C NMR: δ = 171.4, 153.2 (d, J = 246 Hz), 145.5 (d, J = 10.6 Hz), 132.5, 125.5, 124.1 (d, J = 3.8 Hz), 122.5 (d, J = 6.0 Hz), 117.5, 116.7 (d, J = 18.5 Hz), 94.0, 79.6, 72.1, 65.0, 34.8, 31.4, 29.2, 27.5, 22.4, 18.5, 13.9.

(*S,S-S*)-16: ^{1}H NMR: δ = 7.10–6.86 (m, 8 H), 4.95 (s, 1 H), 4.88 (s, 1 H), 4.80 (q, J = 6.8 Hz, 2 H), 4.21 (m, 4 H), 3.91 (m, 2 H). – ^{13}C NMR: δ = 171.2, 153.1 (d, J = 246 Hz), 145.4 (d, J = 10.6 Hz), 124.3 (d, J = 3.2 Hz), 122.8 (d, J = 6.6 Hz), 117.4, 116.6 (d, J = 18.6 Hz), 95.4, 75.3, 74.3, 63.8, 18.4.

(*S,S-S*)-17: ^{1}H NMR: δ = 7.10–6.87 (m, 4 H), 4.96 (s, 1 H), 4.93 (s, 1 H), 4.80 (q, J = 6.8 Hz, 1 H), 4.33 (dd, J = 11.6, 3.9 Hz, 1 H), 4.22 (dd, J = 11.7, 5.8 Hz, 1 H), 4.07 (ddd J = 5.5, 4.0 Hz, 1 H), 3.68 (m, 3 H), 1.65 (d, J = 6.8 Hz, 3 H), 0.86 (s, 9 H), 0.04 (s, 6 H). – ^{13}C NMR: δ = 171.4, 153.3 (d, J = 248 Hz), 145.5 (d, J = 10.3 Hz), 124.3 (d, J = 3.9 Hz), 122.7 (d, J = 7.2 Hz), 117.5, 116.7 (d, J = 18.9 Hz), 95.6, 77.7, 76.2, 64.7, 63.2, 25.9, 18.6, 18.3, –5.4.

(*S,S-S*)-18: ^{1}H NMR: δ = 7.12–6.88 (m, 4 H), 5.70 (dt, J = 10.9, 7.9 Hz, 1 H), 5.38 (dtd, J = 10.7, 9.0, 1.4 Hz, 1 H), 5.02 (s, 1 H), 4.89 (s, 1 H), 4.81 (q, J = 6.8 Hz, 1 H), 4.45 (dd, J = 8.7, 8.2 Hz, 1 H), 4.36 (dd, J = 12.0, 3.4 Hz, 1 H), 4.17 (dd, J = 12.0, 5.5 Hz, 1 H), 3.76 (ddd, J = 8.8, 5.5, 3.5 Hz, 1 H), 2.06 (m, 2 H), 1.65 (d, J = 6.8 Hz, 3 H), 1.34 (m, 6 H), 0.86 (t, J = 6.3 Hz, 3 H). – ^{13}C NMR: δ = 171.4, 153.3 (d, J = 247 Hz), 145.6 (d, J = 10.6), 137.3, 124.9, 124.3 (d, J = 3.1 Hz), 122.8 (d, J = 7.1 Hz), 117.6, 116.7 (d, J = 18.0 Hz), 95.3, 78.8, 74.5, 73.8, 63.4, 31.4, 29.3, 27.8, 22.5, 18.6, 14.0.

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