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ASYMMETRIC ADDITION OF PERFLUOROALKYL GROUPS ON CARBONYLS WITH ZINC AND ULTRASOUND

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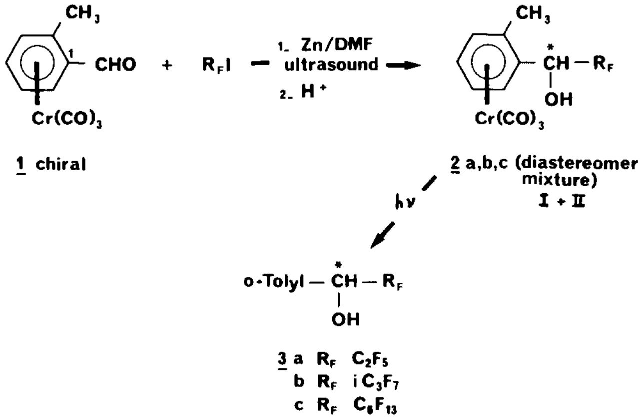
Abstract : 30 to 66% of asymmetric induction is obtained during addition of perfluoroalkyl iodide on chiral arene-chromiumtricarbonyl complexes using ultrasonically dispersed zinc at room temperature. A 3 step synthesis of both enantiomers of perfluoroalkyl arylcarbinols is presented.

During our work on asymmetric introduction of perfluoroalkyl groups on carbonyls |*1,2*| we were confronted to the difficulty of addition of C_6F_{13} group. On the other hand we were interested in using perfluoroalkylzinc compounds which are usually more stable than the corresponding magnesium or lithium compounds. Ultrasound has been shown to improve significantly the formation and the reactivity of organometallic reagents |*3,4*| but has never been used with complexes such as arene-chromium-tricarbonyl complexes.

We thus wish to report our results concerning asymmetric inductions obtained during perfluoroalkylation of the chiral complex 1 using perfluoroalkyl iodides and ultrasonically dispersed zinc.

Scheme 1



The chiral complexed aldehyde 1 is converted, *without decomplexation* in about 1 hour, into the complexed perfluoroalkylcarbinols 2a-2c scheme 1.

Good to high yields are obtained, even with $C_6F_{13}I$, using only small excess (10 to 20%) of the perfluoroalkyl iodide with respect to the complexed aldehyde 1 (Table 1), instead of the four to sixfold equivalents necessary with the lithium compounds. This method provides until now the only way to synthesise perfluoroalkyl arylcarbinols 3 with long and unbranched perfluoroalkyl groups. The diastereomer ratios and the chemical yields are first determined on the crude products then checked on the isolated compounds using 200 MHz ^1H NMR; three examples are given in schemes 2 and 3.

It appears that unbranched perfluoroalkyl iodides (C_2F_5I and $C_6F_{13}I$) lead to about 45% of asymmetric induction (runs 1 to 5) and that temperature (in the limits tested) has but negligible effect. On the other hand iso-C_3F_7I leads to up to 65% of asymmetric induction, and temperature and dilution have some effect on the asymmetric induction (runs 6 to 8). The percentage of asymmetric induction thus obtained with Zn compounds and ultrasound in the case of C_2F_5 : 44% (72/28) and iC_3F_7 : 46% (73/27) is much lower than that obtained with lithium derivatives |*1*| which is respectively 88% (94/6) and 76% (88/12). These differences could be ascribed to the temperature used and mostly to the local temperature,as ultrasounds is known to induce increases of temperature through cavitation . It must be noted however that the prefered diastereomer is the same in the two cases (from Zn compounds or from lithium compounds) as shown by 200 MHz ^1H.NMR spectra. The diastereomers of the complexed perfluoroalkylcarbinols 2a-2c are easily separated by column chromatography |*5*| and recovered in almost quantitative yields ; decomplexation is then quantitative |*6*|.

Hence, starting from optically pure aldehyde 1 |*7*|, this method provides a short (3 steps) and efficient synthesis of optically pure perfluoroalkylarylcarbinols of type 3a-3c.

Typical procedure : A flask containing complexed aldehyde 1 (200 mg, 7.8×10^{-4} mol.), zinc powder (3 equi.) , perfluoroalkyl iodide (1.1 equi.) in 5 ml N,N-dimethylformamide is irradiated in the water bath of an ultrasound laboratory cleaner (30W, 50 KHz). The solution is then poured into cold 2% HCl. The organic materials are extracted with diethylether; dried over sodium sulfate and the solvent is removed.

TABLE 1

	R_FI	t°C	Time (h)	Solv.	Product[a]	Yield %	Diastereomer ratio	Asymmetric ind. %
1	C_2F_5I	4[b]	1	DMF	2a	85	72/28	44
2	$C_6F_{13}I$	4[b]	0.5	DMF	2c	73	73/27	46
3		23-30	0.5	DMF	2c	76	70/30	40
4		23-30	2.5	DMF	2c	70	73/27	46
5		23-30	1[c]	DMF	2c	80	65/35	30
6	iC_3F_7I	4[b]	1	DMF	2b	85	75/25	50
7		23-30	1	DMF	2b	100	83/17	66
8		23-30	2.5[d]	DMF	2b	50	75/25	50
9		23-30	1	THF	2b	0	-	-

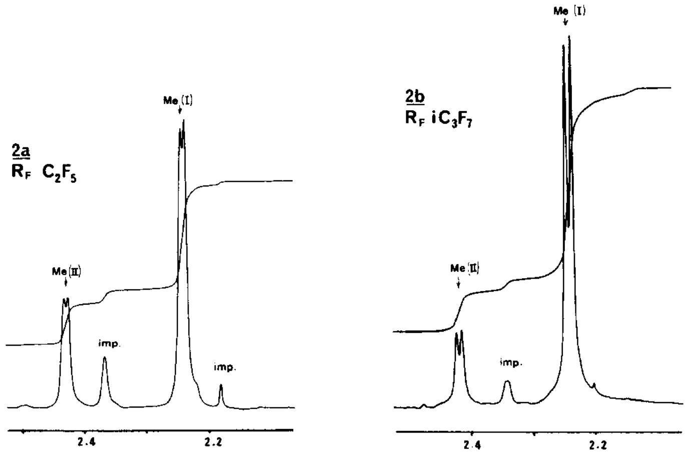
a) Structures are confirmed by means of IR, ^1H NMR, ^{19}F NMR and microanalysis.

b) The temperature of the water bath is controled and maintained at the desired value by addition of crushed ice.

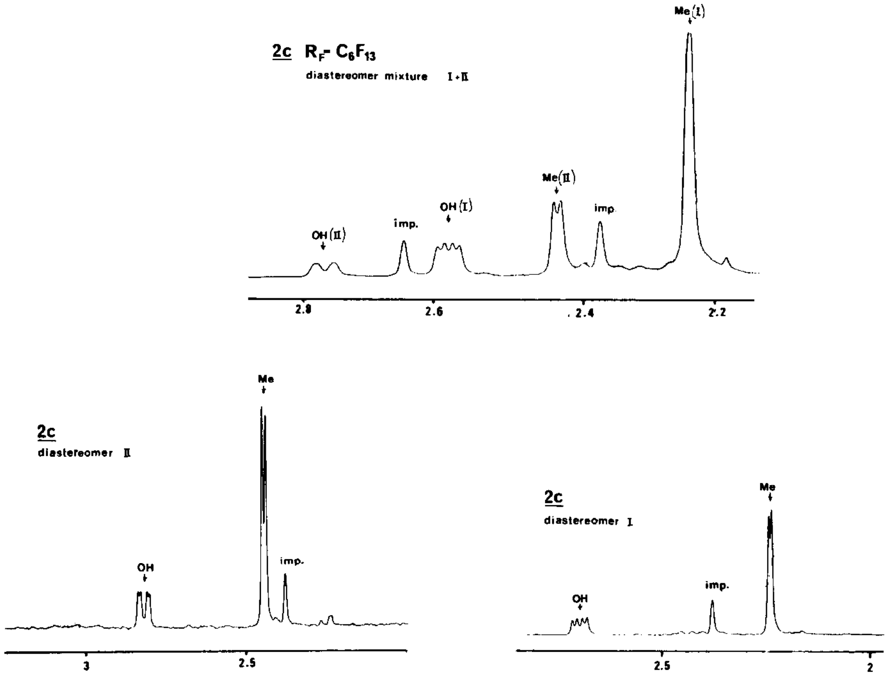
c) Another 0.5 equiv. of perfluoroalkyl iodide is added after 30 mn. reaction, in an attempt to increase the chemical yield.

d) Diluted twice.

Scheme 2



Scheme 3



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|*4*| T. KITAZUME and N. ISHIKAWA, Chem. Letters, 137 (1982); idem 1553 (1982); idem 1679 (1981)

|*5*| Silica gel 60 (230-400 mesh ASTM), diethyl ether/hexane 50/50, Flash chromatography : W.C. STILL, M. KAHN and A. MITRA, J. Org. Chem. 43, 2923 (1978)

|*6*| hν , 24 hours, stirring at room temperature

|*7*| for the resolution of this chiral complexed aldehyde see : A. SOLLADIE-CAVALLO, G. SOLLADIE and E. TSAMO, J. Org. Chem. 44, 4189 (1979)

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