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# NEW STEREOSPECIFIC SYNTHESIS OF CHIRAL α-SULFINYLESTERS OF KNOWN ABSOLUTE CONFIGURATION.

*Charles Mioskowski and Guy Solladié**

*Laboratoire de Chimie Organique de l'Ecole Nationale Supérieure de Chimie, Université L.Pasteur, B.P.296/R8 - 67008 Strasbourg, France.*

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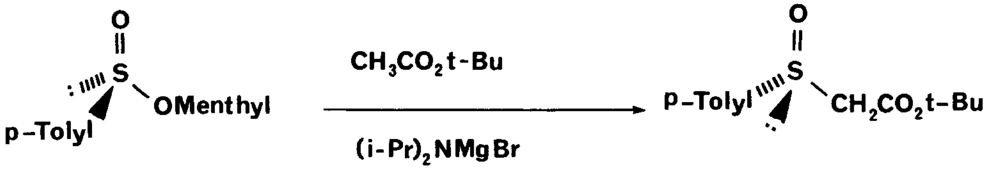
Optically active α-sulfinylesters such as 2 are generally obtained by optical resolution (the main route to these molecules being the oxidation of corresponding sulfides[1]).Recent papers[2,3]on the reactivity of these functionalised sulfoxides prompted us to report a stereospecific synthesis of chiral α-sulfinylesters.

We have found that the O-menthyl group of an optically active sulfinate ester,(-)S 1,can be displaced by the magnesium enolate of t-butylacetate leading to (+) R t-butyl α-(p-tolylsulfinyl) acetate 2 with complete inversion of configuration at sulfur atom.



(-) S, 1 (+)R, 2

To a solution of 0.051 M of diisopropylaminomagnesium bromide in 50 ml of ether at - 20° were added 0.017 M of t-butylacetate in 10 ml of ether and then 5 g. of (-)S menthyl p-toluenesulfinate 1[4]($|\alpha|_D^{20}$=-200°,acetone,c 2.0)dissolved in 50 ml of ether.Stirring was continued overnight allowing temperature to raise very slowly room temperature.Usual work-up and purification by chromatography lead to 2.6 g. (60% yield) of liquid 2:

I.R. ($CCl_4$):$\nu_{C=O}$ 1725,$\nu_{S=O}$ 1055 $cm^{-1}$.

NMR ($CDCl_3$):δ=1.4 (9H,s,t-Bu),2.32 (3H,s,Me),AB system (2H,$|J_{AB}|$=13 Hz, $\nu_A$3.78,$\nu_B$3.57),7.2-7.7 (m,3 Arom.H).

$|\alpha|_D$= +149° (EtOH,c 2.25,20°C).

Optical purity:100%,calculated on $^1$H NMR spectra in presence of Tris-|3-

-(trifluoromethylhydroxymethylene)-d-camphorato|Europium III as chiral shift reagent.The conditions were determined on a partially racemised sample of 2, $|\alpha|^{20}_{D}$= +99°.In $CDCl_3$ with a ratio:|Complexe| /|2|=0.36,separated signals are observed from initially enantiotopic (external comparison)t-butyl groups (2 singlets,$\Delta\delta$=0.06 ppm) and $CH_2$ groups (2 AB systems,$\Delta\delta$=0.05 ppm) leading to an optical purity of 65 ± 2% and a specific rotation $|\alpha|^{20}_{D}$=+152 ± 4° for the α-sulfinylester 2 optically pure.

One must point out that this last result is consistent with the fact that only one signal could be detected by $^1H$ NMR of the sample $|\alpha|^{20}_{D}$= +149° for the t-butyl protons (and only one AB system for the $CH_2$) with the chiral shift reagent.

The absolute configuration of (+) 2 has been determined by ORD.Results listed in table I show that (+) 2 lead to a strong positive Cotton effect between 270 and 250 nm which is characteristic of the absolute R configuration at Sulfur atom in alkyl aryl sulfoxides[5].

TABLE I

ORD of (+) 2 in EtOH (c 2.25 to 340 nm,0.74 to 290 nm,then 0.35)

| λ | 400 | 390 | 380 | 370 | 360 | 350 | 340 | 330 | 320 | 310 | 300 | 290 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\vert\alpha\vert^{20}$ | +533 | +610 | +685 | +775 | +890 | +1035 | +1225 | +1490 | +1860 | +2430 | +3380 | +6330 |

| 275 | 270 | 268 | 260 | 255 | 254 | 252 | 250 |
|---|---|---|---|---|---|---|---|
| +9500 | +10650 | +10350 | +8050 | +1435 | 0 | -4030 | -9200 |

UV Absorption of 2 in EtOH (c 0.0348 g/l)

| $\lambda_{max}$ | 274 (Sh.) | 243 | 223 |
|---|---|---|---|
| ε | 876 | 3470 | 6060 |

References.

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Note.

For R and S nomenclature of sulfinate esters see ref.5,note 10.

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