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Chiral Sulfinic Acids: Synthesis of Sodium *(1S,2S,5R)*-2-Isopropyl-5-methylcyclohexanesulfinate by a Novel Route.

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Abstract: *We describe a convenient stereocontrolled synthesis of the title compound from (-)-menthol; this approach should also be suitable for the synthesis of other sulfo-derivatives with menthyl or neomenthyl moieties, such as chiral sulfides, sulfoxides and sulfones -some of which were isolated and characterized in this work- or of their 8-aryl derivatives.*

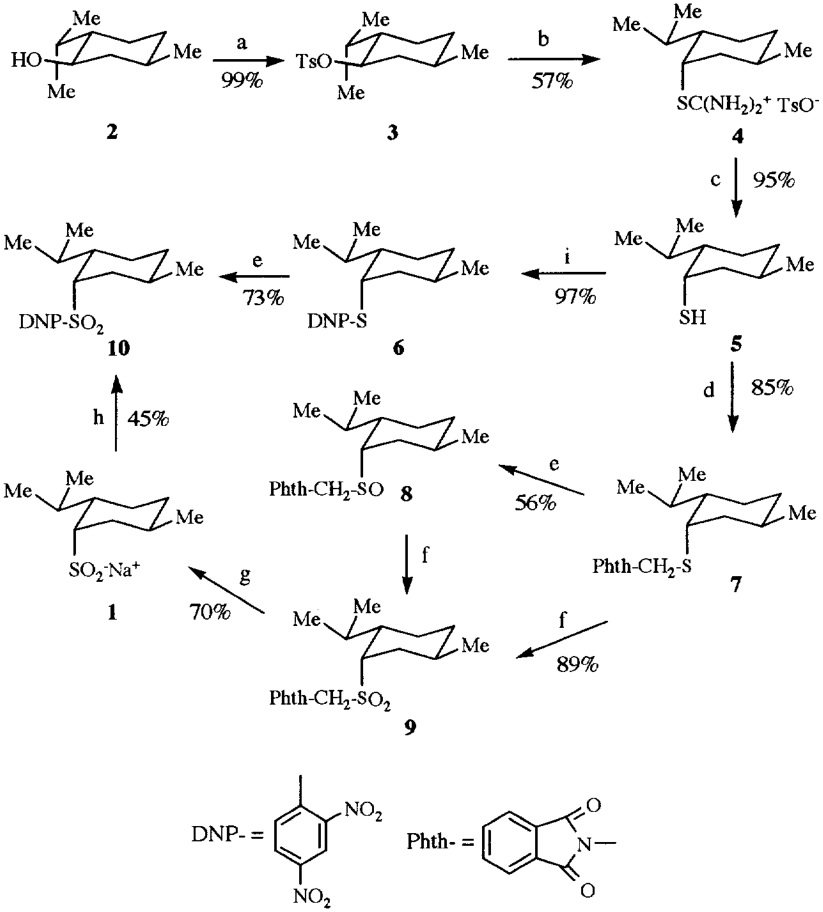
Interest in chiral sulfinic acids stems from their use as precursors of chiral sulfonyl cyanides,[1] which can be used in the stereoselective synthesis of saturated heterocycles[2,3] or α-cyanoketones.[4] We previously reported[5] difficulties with the preparation of sodium (1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanesulfinate (**1**) from (−)-menthol (**2**) *via* an approach to chiral sulfinic acids[6] that until then had always proved successful. Re-examination of the reaction conditions and products of key steps in this approach has now led us to adjust the former, and so enabled synthesis of **1** by the route shown in Scheme 1. This approach should be generalizable to the stereocontrolled synthesis of other chiral sulfur derivatives with a neomenthyl or a menthyl moiety, and of their 8-aryl derivatives.

The starting material **2** [(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanol] was converted to (−)-menthyl tosylate (**3**) in almost quantitative yield. Reaction of **3** with thiourea in isopropyl alcohol afforded the salt **4** in a fair yield.[7] Although no reference to compound **4** was found in the literature, the stereochemistry and high diastereomeric purity of the product suggest that thiurea displaces the tosylate group by an S_N2 mechanism. The ^{1}H NMR spectrum of **4** indicated that it was highly pure and that inversion of configuration had occurred at C1 of the cyclohexane ring: the signal for *axial* H1 in **3** was a triplet of doublets at δ 4.40 ppm ($J_{ax,ax}$ = 10.3 Hz and $J_{ax,eq}$ = 4.4 Hz, respectively)[5] while that of *equatorial* H in **4** was an unresolved multiplet with a narrow triangular envelope and $w_{1/2}$ = 8.1 Hz, centered at δ 4.05 ppm; this signal was the only one in the range δ 2.50 - 7.00 ppm.

Cleavage of **4** in dilute sodium hydroxide gave (+)-neomenthanethiol (**5**) in 95% yield (53% overall yield from (−)-menthol; *cf.* 42%, the highest reported yield[8]). The $[\alpha]_D$ of distilled **5** was 3% higher than that reported[8] for the same compound with optical purity ≥ 95%.[9] Compound **5** was further characterized *via* its 2,4-dinitrophenyl and phthalimidomethyl derivatives (**6** and **7**, respectively), both prepared in high yield from crude **5**. The *axial* configuration of the thiol group was confirmed by ^{1}H NMR spectroscopic studies of **5**, **6** and **7**, as was the high diastereomeric purity of these neomenthyl sulfur derivatives.

Oxidation of the phthalimidomethyl sulfide **7** under standard conditions[5] afforded a product which, on the basis of previous results, was thought initially to be the sulfone **9**. However, the ^1H NMR spectrum of this crude material indicated a complex mixture of oxidation products, and the attempted cleavage of it[10] gave sulfinate **1** in only 13% yield. Two compounds were successfully isolated from the reaction mixture by column chromatography; their mass, IR and ^1H NMR spectra identified them as a sulfoxide **8** and the sulfone **9**, which were estimated to have formed in an overall yield of 80% and in the ratio 70:30 (**8**:**9**). Oxidizing **7**, **8** or mixtures of both under the same reaction conditions as before but for prolonged reaction times afforded the sulfone **9** as the sole recognizable product in a good yield.

SCHEME 1



^{a}key: a) TsCl, pyr, rt, 21 h; b) $SC(NH_2)_2$, *i*-PrOH, Δ, 15 h; c) 0.4 M NaOH, Δ; d) $PhthCH_2Br$, 100°C, 36 h; e) $KMnO_4$, AcOH, rt, 23 h; f) $KMnO_4$, AcOH, rt, 78 h; g) EtONa, EtOH, Δ, 20 h; h) DNPCl, EtOH, Δ, 20 h; i) NaOH, EtOH, DNPCl, 60°C, 10 min.

In EIMS, the unfragmented molecular ion is detected as a low intensity peak for the sulfoxide **8**, but is virtually negligible for the sulfone **9**. Most characteristic fragmentations of the molecular ions of these oxidation products are the losses of neomenthanesulfinyl and phthalimidomethanesulfinyl radicals for **8** (or those of neomenthanesulfonyl and phthalimidomethanesulfonyl radicals for **9**) which give rise to the peaks at m/z = 160 (base peak) and m/z = 139, while the losses of neutral molecules origin the molecular ions of methylphthalimide (m/z = 161) and menthene (m/z = 138). Fragmentations due to the loss of a neutral molecule of menthene (m/z = 209 or 225 for **8** or **9**, respectively) or to that of the phthalimidomethyl radical (m/z = 187 or 203 for **8** or **9**, respectively), specifically characterize each of these compounds. The ^{1}H NMR spectra of **8** and **9** showed a signal for H1 which confirmed its *equatorial* configuration (a narrow unresolved multiplet with $w_{1/2}$ = 11.7 Hz for **8** and $w_{1/2}$ = 10.5 Hz for **9**), and thus the *axial* configuration of the sulfur atom. No attempt was made to determine the absolute configuration at the sulfur atom of **8**.

Cleavage of sulfone **9** was effected using sodium ethoxide as nucleophile instead of the usual[6] sodium salt of **5**, since the former gave sulfinate **1** in better yield; titration of a solution of **1** with potassium permanganate indicated that it was 96 ± 2% pure. The reaction did not proceed with epimerization at the neomenthyl C1, since no epimerized starting material was recovered from reactions which were not allowed to reach completion, and reaction of **1** with 2,4-dinitrochlorobenzene gave a sulfone which was identical (mp, $[\alpha]_D^{25}$, IR, NMR) with (1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2,4-dinitrophenyl sulfone (**10**) obtained by direct oxidation of the sulfide **6** with $KMnO_4$/AcOH.

EXPERIMENTAL PART

Commercial grade (−)-menthol, 2,4-dinitrochlorobenzene, *N*-(bromomethyl)phthalimide, thiourea and potassium permanganate were from Aldrich; and silica gel (230 mesh) for CC and pre-coated chromatoplates for TLC were from Merck. Melting points are uncorrected and were determined on a Reichert Kofler Thermopan; microanalyses were performed by a Perkin-Elmer 240B Elemental Analyser (Microanalysis Service, University of Santiago); sodium D line polarimetry was performed in a Perkin-Elmer 241 polarimeter at 25 °C; IR spectra of samples in KBr discs were recorded in a Perkin-Elmer 1600 FT spectrometer; ^{1}H NMR spectra were recorded in Bruker WN 250 or AMX300 spectrometers; and EIMS were performed in a VARIAN MAT-711 spectrometer, at 70 eV. GC was carried out on a Hewlett Packard 5710A instrument equipped with a FID detector and an HP-3380S integrator. Column: 10 % OV-210 on Chromosorb W-HP (2 m x 1/8"); carrier gas: N_2, 20 mL/min; oven temperature: 120 °C. (−)-Menthyl tosylate (**3**) was prepared from (−)-menthol as previously described.[5]

2-[(1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl]thiouronium *p*-toluenesulfonate (**4**). A mixture of **3** (130.0 g, 418.7 mmol) and thiourea (64.58 g, 848.4 mmol) in *i*-PrOH (500 mL) was refluxed until **3** is no longer detected by TLC (*ca.* 15 h). The solvent was removed *in vacuo* and the solid residue was ground, suspended in cold water (200 mL), quickly collected by suction filtration and then vacuum dried over P_2O_5 to give **4** (83.2 g, 57 %) as a white solid; a small amount was recrystallized twice from *i*-PrOH to afford an analytical sample: mp 224-225 °C; $[\alpha]_D^{25}$ +28.0 (*c* 3.5, $CHCl_3$); IR 3293 and 3123 ($C^+(NH_2)_2$), 1654 (C=N), 1123, 1034 and 1009 (SO_3^-), 679 (C-S) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.55 (br s, 2H, exchangeable with D_2O), 7.75 (d, 2H, J = 8.1), 7.41 (br s, 2H, exchangeable with D_2O), 7.18 (d, 2H, J = 8.1), 1.01-0.81 (m, 2H), 4.05 (m, 1H, $w_{1/2}$ = 8.1), 2.38 (s, 3H), 1.95-1.63 (m, 4H), 1.48-1.14 (m, 3H), 0.88 (d, 3H, J = 6.7), 0.86 (d, 3H, J = 6.7), 0.83 (d, 3H, J = 6.2). Anal. Calcd for $C_{18}H_{30}N_2O_3S_2$: C, 55.93;

H, 7.82; N, 7.25. Found: C, 56.21; H, 7.97; N, 7.19.

(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexanethiol (5). A mixture of crude **4** (29.93 g, 77.4 mmol) and 0.40 N NaOH (200 mL) was heated and water and the product were allowed to distill out while more water was dripped in to maintain the volume of the reacting mixture aprox. constant. When 500 ml of distillate had collected, it was extracted with CH_2Cl_2 (4 × 75 mL), the combined organic extracts were washed with H_2O (2 × 100 mL) and dried (Na_2SO_4), and the solvent was removed *in vacuo* to leave virtually pure (99 % by GC) **4** (12.61 g, 95 %), as a colourless oil; this crude material was used in the next synthetic steps; an analytical sample was obtained by bulb to bulb vacuum distillation: bp 96-98 °C/14 torr (lit.[11] 91-94 °C/11-12 torr); $[\alpha]_D^{25}$ +55.6 (*c* 9.10, $CHCl_3$) (lit.[8] $[\alpha]_D^{20}$ +53.9 (*c* 1.85, $CHCl_3$)); ^1H NMR ($CDCl_3$) δ 3.48 (m, 1H, $w_{1/2}$ = 13.3), 1.91-1.63 (m, 4H), 1.56-1.24 (m, 3H), 1.20 (d, 1H, J = 7.0, slowly exchangeable with D_2O), 1.08-0.98 (m, 1H), 0.95-0.82 (m, 1H), 0.89 (d, 6H, J = 6.7), 0.85 (d, 3H, J = 6.2). Anal. Calcd for $C_{10}H_{20}S$: C, 69.70; H, 11.70. Found: C, 69.92; H, 11.93.

(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2,4-dinitrophenyl sulfide (6). Crude **5** (4.50 g, 26.1 mmol) in EtOH (55 mL) was mixed with 5 N NaOH (5.2 mL) and a solution of 2,4-dinitrochlorobenzene (5.27 g, 26.0 mmol) in EtOH (50 mL). The mixture was stirred at 60 °C for 10 min and then allowed to stand at 0 °C overnight. The product which separated was isolated by suction filtration and recrystallized twice from hexane to give virtually pure **6** (8.53 g, 97%) as yellow crystals: mp 156-157 °C; $[\alpha]_D^{25}$ +26.8 (*c* 9.7, $CHCl_3$); IR 1582 and 1526 (arom), 1512 and 1336 (NO_2), 680 (C-S) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.01 (d, 1H, J = 2.5), 8.34 (dd, 1H, J = 9.1, 2.5), 7.63 (d, 1H, J = 9.1), 3.91 (m, 1H, $w_{1/2}$ = 8.1), 2.05-1.71 (m, 5H), 1.46-1.26 (m, 3H), 1.03-0.93 (m, 1H), 0.97 (d, 3H, J = 6.6), 0.88 (d, 3H, J = 6.6), 0.87 (d, 3H, J = 6.1). Anal. Calcd for $C_{16}H_{22}N_2O_4S$: C, 56.79; H, 6.55; N, 8.28. Found: C, 57.11; H, 6.45; N, 8.17.

(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl phthalimidomethyl sulfide (7). Crude **5** (2.64 g, 15.32 mmol) and *N*-(bromomethyl)phthalimide (3.69 g, 15.37 mmol) were stirred together at 100 °C under nitrogen and when all the **5** had reacted (*ca.* 36 h, GLC monitoring) the reaction mixture was dissolved in benzene (100 mL) and washed with 1.5 M $NaHCO_3$ (150 mL). The aqueous phase was re-extracted with more benzene (2 × 50 mL), and the combined organic extracts were dried (Na_2SO_4), then filtered through a bed of silica gel and concentrated *in vacuo*. The residue was recrystallized from *i*-PrOH to afford virtually pure **7** (4.33 g, 85 %) as a white solid; an analytical sample was obtained by a further recrystallization from *i*-PrOH: mp 94-95 °C; $[\alpha]_D^{25}$ +162 (*c* 0.75, $CHCl_3$); IR 1775 and 1713 (C=O), 1605 and 1470 (arom), 529 (C-S) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.88-7.84 (m, 2H)0.75 (d, 3H, J = 6.5), 7.75-7.71 (m, 2H), 4.81 and 4.68 (AB system, 2H, J = 14.1), 3.42 (m, 1H, $w_{1/2}$ = 8.5), 2.03 (dm, 1H, J(d) = 13.7), 1.96-1.83 (m, 1H), 1.74-1.64 (m, 2H), 1.60-1.52 (m, 1H), 1.26 (ddd, 1H, J = 13.7, 11.7, 3.1), 1.09-1.00 (m, 2H), 0.97-0.84 (m, 1H), 0.85 (d, 3H, J = 6.2), 0.82 (d, 3H, J = 6.5). Anal. Calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23. Found: C, 69.03; H, 7.58; N, 4.17.

(1*S*,2*S*,5*R*,Sξ)-2-Isopropyl-5-methylcyclohexyl phthalimidomethyl sulfoxide (8). Finely powdered $KMnO_4$ (1.38 g, 8.73 mmol) was added in a single portion to a solution of **7** (2.42 g, 7.30 mmol) in AcOH (73 mL), and the mixture was stirred at room temperature until all of **7** had disappeared (23 h, TLC monitoring). The solvent was evaporated at reduced pressure (the final traces of AcOH were removed by co-distillation with toluene) and the solid residue was stirred in 1.5 N aqueous $NaHSO_3$ (140 mL). Insoluble solids were filtered out, the filtrate and the cake were each extracted with CH_2Cl_2 (3 × 50 mL), and the combined extracts were washed with water (2 × 50 mL), and dried (Na_2SO_4). The solvent was then evaporated *in vacuo* to afford a white solid residue (2.56 g), which was chromatographed on silica gel (65 g) with 1:1:1 hexane/toluene/EtOAc as eluant (14 × 25 mL), and TLC and/or NMR monitoring: fractions 5-7 left an almost pure compound (TLC), later identified as **9** (yield 0.63 g, 24%), and fractions 8-11 contained **8** (yield 1.42 g, 56%; TLC indicated a single spot); an analytical sample of the sulfoxide was obtained by recrystallizing the chromatographed material from *i*-PrOH: mp 122-123 °C; $[\alpha]_D^{25}$ −29.7 (*c* 0.76, $CHCl_3$); IR 1776 and 1726 (C=O), 1608 and 1466 (arom), 1032 (SO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.92-7.88 (m, 2H), 7.80-7.75 (m, 2H), 4.83 (s, 2H), 3.16 (m, 1H, $w_{1/2}$ = 11.7), 2.54 (dm, 1H, *J*(d) = 14.4) 2.17-2.01 (m, 1H), 1.94-1.65 (m, 3H), 1.55-1.25 (m, 3H), 0.97 (d, 3H, *J* = 6.5), 0.98-0.84 (m, 1H), 0.88 (d, 3H, *J* = 6.5), 0.85 (d, 3H, *J* = 6.5), ; EIMS *m/z* (%) 347 (M, 1.4), 209 (2.6), 187 (0.4), 161 (14.3), 160 (100), 139 (4.9), 138 (2.3). Anal. Calcd for $C_{19}H_{25}NO_3S$: C, 65.68; H, 7.25; N, 4.03. Found: C, 65.83; H, 7.10; N, 3.93.

(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl phthalimidomethyl sulfone (9). Finely powdered $KMnO_4$ (1.61 g, 10.20 mmol) was added in a single portion to a solution of **7** (2.51 g, 7.57 mmol) in 75 ml of AcOH, and stirred at room temperature until neither **7** nor **8** were detected by TLC (78 h). Following work-up as described above for the sulfoxide, a solid residue was isolated (2.62 g), which was chromatographed on silica gel (150 g), with 4:1 toluene/EtOAc as eluant (10 × 75 mL): fractions 5-7 left virtually pure (TLC) **9** (yield 2.45 g, 89%) as a white solid; an analytical sample was obtained by recrystallizing the chromatographed material from *i*-PrOH: mp 138-139 °C; $[\alpha]_D^{25}$ + 13.2 (*c* 0.83, $CHCl_3$); IR 1784 and 1721 (C=O), 1610 and 1470 (arom), 1302 and 1121 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94-7.90 (m, 2H), 7.82-7.78 (m, 2H), 5.05 and 4.84 (AB system, 2H, *J* = 14.2), 3.75 (m, 1H, $w_{1/2}$ = 10.5), 2.41 (dm, 1H, *J*(d) = 14.8, $w_{1/2}$(m) = 8.8), 2.19-2.10 (m, 2H), 1.88 (dm, 1H, *J*(d) = 11.5, $w_{1/2}$(m) = 10.5), 1.83-1.75 (m, 2H), 1.39-1.30 (m, 2H), 1.00-0.88 (m, 1H), 0.99 (d, 3H, *J* = 6.4), 0.93 (d, 3H, *J* = 6.5), 0.90 (d, 3H, *J* = 6.5); EIMS *m/z* (%) 225 (4.0), 203 (1.5), 161 (39.7), 160 (100), 139 (33.5), 138 (10.0). Anal. Calcd for $C_{19}H_{25}NO_4S$: C, 62.79; H, 6.93; N, 3.85. Found: C, 62.85; H, 6.82; N, 3.79.

Sodium (1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanesulfinate (1). The sulfone **9** (1.50 g, 4.13 mmol) was added to a stirred solution of sodium ethoxide prepared from freshly cut sodium metal (95 mg, 4.13 mmol) and anhydrous EtOH (30 mL). The mixture was refluxed under argon until TLC showed all of **9** to have disappeared (*ca.* 20 h, TLC monitoring), passed while hot through a sintered glass filter, and the filtrate was evaporated to dryness. Extraction of residue left with hot benzene (2 × 30 mL), and drying of the insoluble portion under vacuum, afforded the sulfinate **1** (655 mg, 70 %): ^1H NMR (DMSO-d_6) δ 4.68 (m, 1H, $w_{1/2}$ = 8.0), 2.35 (dm, 1H, *J*(d) = 12.7, $w_{1/2}$(m) = 10.5), 2.13-2.00 (m, 1H), 1.94-1.83 (m, 2H), 1.68-1.51 (m, 3H), 0.95 (d, 3H, *J* = 6.4), 0.83 (d, 3H, *J* = 6.6), 0.92-0.77 (m, 1H), 0.72 (d, 3H, *J* = 6.5), 0.65 (dd, 1H, *J* = 12.5, 4.1).

(1*S*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2,4-dinitrophenyl sulfone (10). Method A. A mixture of the sulfinate **9** (433 mg, 1.91 mmol) in anhydrous EtOH (10 mL) and 2,4-dinitrochlorobenzene (430 mg, 2.12 mmol) in anhydrous EtOH (8 mL) is refluxed under an argon atmosphere for 20 h and then left to stand at 5 °C overnight. Compound **10** precipitated from the mixture and was isolated by suction filtration (318 mg, 45 %); an analytical sample was obtained by recrystallization from ethanol: mp 198-199 °C; $[\alpha]_D^{25}$ −170 (*c* 0.70, $CHCl_3$); IR 1605 and 1555 (arom), 1538 and 1355 (NO_2), 1300 and 1135 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.64 (s, 1H), 8.57 (dd, 1H, *J* = 8.2, *J* = 2.1), 8.36 (d, 1H, *J* = 8.6 Hz), 4.41 (m, 1H, $w_{1/2}$

= 10.4), 2.19-1.81 (m, 6H), 1.56-1.25 (m, 2H), 1.11-0.89 (m, 1H), 0.99 (d, 6H, *J* = 6.5), 0.81 (d, 3H, *J* = 6.2). Anal. Calcd for $C_{16}H_{22}N_2O_6S$: C, 51.88; H, 5.99; N, 7.56. Found: C, 52.03; H, 5.92; N, 7.66. **Method B.** Finely powdered $KMnO_4$ (4.79 g, 30.30 mmol) was added in a single portion to a cold solution of sulfide **6** (8.55 g, 25.30 mmol) in AcOH (250 mL), and stirred at room temperature for 24 h. The solvent was evaporated at reduced pressure and the dark solid residue was stirred in cold aqueous 1.5 M $NaHSO_3$ (300 mL). The insoluble material was filtered out and the cake was extracted with CH_2Cl_2 (3 × 100 mL). The pooled organic extracts were washed with water (3 × 40 mL), dried (Na_2SO_4), and the solvent was taken off *in vacuo* to leave **10** (6.82 g, 73 %) as bright yellow scales. One recrystallization from *i*-PrOH afforded a material of mp 199-200 °C; $[\alpha]_D^{25}$ −170 (*c* 0.68, $CHCl_3$), and IR and ^1H NMR spectra superimposible with those of the product from the **method A.**

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