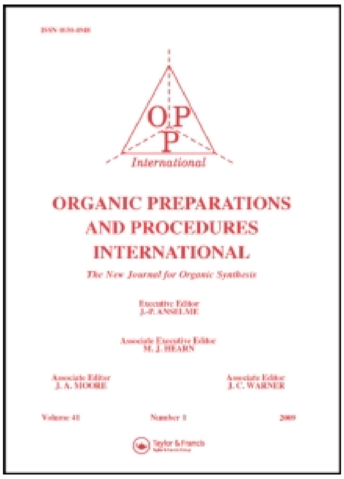

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SYNTHESIS OF (2R,3R) 0,0-DIPIVALOYLTARTARIC ACID (*DPTA*) AND OF (2R,3R) 0,0-DI(ADAMANTANE-1 CARBONYL) TARTARIC ACID (*DATA*), USEFUL CHIRAL REAGENTS FOR ASYMMETRIC PROTONATIONS

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OPPI BRIEFS

SYNTHESIS OF (2R,3R) O,O-DIPIVALOYLTARTARIC ACID (DPTA) AND OF (2R,3R) O,O-DI(ADAMANTANE-1 CARBONYL) TARTARIC ACID (DATA), USEFUL CHIRAL REAGENTS FOR ASYMMETRIC PROTONATIONS

Submitted by L. Duhamel* and J. C. Plaquevent
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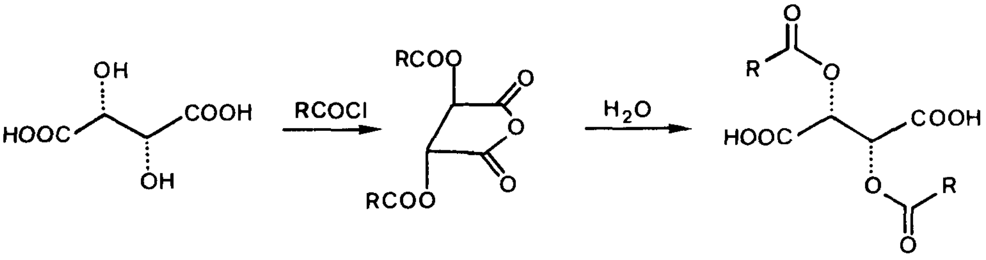
Our investigation of the deracemization of carbonyl compounds[1] and of α-aminoacids derivatives,[2] required a number of chiral acids for enantioselective protonations of prochiral enamines or lithium enolates.[3] The most promising results were observed with the title compounds, DPTA and DATA, which have not been described to date. They were obtained from a sequence based essentially on that of Zetzsche and Hubacher.[4]



DPTA, R = t-Bu DATA, R = 1-adamantyl

EXPERIMENTAL

Melting points were taken on a Köfler block and are uncorrected. ^1H NMR spectra were determined at 60 MHz with a Perkin Elmer R 12 NMR spectrometer and ^{13}C NMR spectra at 20 MHz with a Varian CFT 20 NMR spectrometer, with TMS as an internal reference. IR spectra were recorded on a Perkin Elmer model 377 spectrophotometer and optical rotations were determined on a Perkin Elmer model 241 polarimeter.

(2R,3R) O,O-Dipivaloyltartaric Acid (DPTA).- A magnetically stirred mixture of (2R,3R) tartaric acid (30 g, 0.2 mol) and pivaloyl chloride (76 ml, 0.63 mol) was warmed to 120-130° for 3 hrs, then to 140° for 1 hr. At this point, the evolution of HCl had subsided. After cooling, the reaction mixture was dissolved in hot benzene (150 ml). The anhydride was precipitated by addition of petroleum ether (bp. 60-80°; 300 ml), collected, washed with petroleum ether and dried over P_2O_5 in vacuo to afford 41 g (79 %) of a colourless crystalline powder, mp. 165°, $(\alpha)_D^{25}$ + 73.2° (c = 2, benzene); a small sample was recrystallized from benzene-petroleum ether to constant mp. 167°, $(\alpha)_D^{25}$ + 76.0° (c = 2, benzene); ^1H NMR (C_6D_6): δ 1.05 (s, 9 H), 5.2 (s, 1 H); IR (nujol mull): 1890, 1815, 1740 cm^{-1}.

To a solution of anhydride (40 g, 0.154 mol) in acetone (100 ml) was added water (5 ml).[5] The reaction mixture was stirred for 12 hrs at room temperature, then evaporated in vacuo. The residue was triturated in hexane to afford crystalline DPTA which was collected, washed with hexane and dried over P_2O_5 in vacuo to yield 43 g (98 %) of white crystals, mp. 135°, $(\alpha)_D^{25}$ - 24.2° (c = 1.7, dioxane); ^1H NMR ($CDCl_3$): δ 1.2 (s, 9 H), 5.75 (s, 1 H), 10.5 (s, broad, 1 H, exchangeable with D_2O); ^{13}C NMR ($CDCl_3$): δ 26.8 (q, J = 128 Hz), 38.8 (s), 70.2 (d, J = 152 Hz), 171.9 (s), 177 (s); IR (nujol mull): 1780, 1750, 1730, 1700 cm^{-1}; ($CHCl_3$): 1740 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97.

Found: C, 52.74; H, 7.04.

(2R,3R) O,O-Di(adamantane-1 carbonyl) Tartaric Acid (DATA).- A mixture of (2R,3R) tartaric acid (23.8 g, 0.159 mol) and adamantyl-1 carboxylic chloride (97 g, 0.487 mol) was magnetically stirred and heated to 140° for 2 hrs then to 170° for 0.5 hr. After cooling, hot benzene (500 ml) was added. After removal of a small amount of an insoluble material by

filtration, a total of three crops of anhydride were obtained (50.25 g; 70 %), mp. 218°, $(\alpha)_D^{28}$ + 33.2° (c = 1.7, dioxane). A small sample was recrystallized to constant mp. 220°, $(\alpha)_D^{25}$ + 34.8° (c = 1.7, dioxane); ^{1}H NMR ($CDCl_3$): δ1.5 to 2.2 (m, 15 H), 5.55 (s, 1 H); IR (nujol mull): 1885, 1810, 1740 cm^{-1}.

A mixture of anhydride (21.1 g, 0.046 mol), acetone (150 ml) and water (2 g, 0.11 mol) was refluxed 18 hrs (the disappearance of IR absorbance at 1810 cm^{-1} of an aliquot was used as evidence of complete reaction). The solvent was evaporated and the residue was dissolved in ether and dried over $MgSO_4$. After evaporation of the solvent, the residue was triturated with hexane to afford 21 g (96 %) of DATA, mp. 273° (dec.); $(\alpha)_D^{25}$ - 26.1° (c = 2, dioxane); ^{1}H NMR (acetone d^6): δ 1.7 to 2.2 (m, 15 H), 5.65 (s, 1 H), 9.5 (s broad, 1 H, exchangeable with D_2O); ^{13}C NMR (acetone d^6): δ 28.8 (d, J = 134 Hz), 37.1 (t, J = 128 Hz), 39,4 (t, J = 127 Hz), 41.4 (s), 71.1 (d, J = 150 Hz), 167.5 (s), 176.3 (s); IR (nujol mull): 1780, 1750, 1730, 1690 cm^{-1}; (THF): 1765, 1740 cm^{-1}.

Anal. Calcd for $C_{26}H_{34}O_8$: C, 65.80; H, 7.22.
Found : C, 65.94; H, 7.32.

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