Chromium-Mediated Stereoselective Synthesis of Carbohydrate Derived \((E)\)-\(\alpha,\beta\)-Unsaturated Esters or Amides

Humberto Rodríguez-Solla,*† Carmen Concellón,† Elena G. Blanco,† Juan Ignacio Sarmiento,† Pamela Díaz,† and Raquel G. Soengas‡

† Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Julián Clavería 7, 33006 Oviedo, Spain
‡ Departamento de Química Orgánica, Facultad de Química, Universidad de Santiago de Compostela, Avda. das Ciencias s/n, 15782, Santiago de Compostela, Spain

hrsolla@uniovi.es

General

Ethyl \((E)\)-2,3-dideoxy-4,5-\(O\)-isopropylidene-D-glycero-pent-2-enonate (3a) S2

Ethyl \((E)\)-2,3-dideoxy-4,5:6,7-di-\(O\)-isopropylidene-L-xylo-hept-2-enonate (3b) S3

Ethyl \((E)\)-3-O-benzyl-5,6-dideoxy-1,2-\(O\)-isopropylidene-\(\alpha\)-D-xylo-hept-5-enofuranonate (3c) S4

Ethyl \((E)\)-2,3-dideoxy-4,5:6,7-di-\(O\)-isopropylidene-2-C-phenylmethyl-L-xylo-hept-2-enonate (3d) S5

Ethyl \((E)\)-3-O-benzyl-5,6-dideoxy-1,2-\(O\)-isopropylidene-6-C-phenylmethyl-\(\alpha\)-D-xylo-hept-5-enofuranonate (3e) S6

Isopropyl \((E)\)-3-O-benzyl-5,6-dideoxy-1,2-\(O\)-isopropylidene-6-C-methyl-\(\alpha\)-D-xylo-hept-5-enofuranonate (3f) S7

Isopropyl \((E)\)-6,7-dideoxy-1,2:3,4-di-\(O\)-isopropylidene-7-C-phenylmethyl-\(\beta\)-D-galacto-oct-6-enopyranonate (3g) S8

Isopropyl \((E)\)-6-O-benzyl-2,3-dideoxy-4,5-\(O\)-isopropylidene-2-C-phenylmethyl-D-erythro-hex-2-enonate (3h) S9

Ethyl \((E)\)-3-O-methyl-5,6-dideoxy-1,2-\(O\)-isopropylidene-6-C-phenylmethyl-\(\alpha\)-D-xylo-hept-5-enofuranonate (3i) S10

\((E)\)-\(N,N\)-Diethyl-6,7-dideoxy-1,2:3,4-di-\(O\)-isopropylidene-\(\beta\)-D-galacto-oct-6-enopyranosiduronamide (5a) S11

\((E)\)-\(N,N\)-Diethyl-1-O-\(t\)-butyldimethylsilyl-5,6-dideoxy-2,3-\(O\)-isopropylidene-\(\alpha\)-D-\(\delta\)xyo-hept-5-enofuranosiduronamide (5b) S12

\((E)\)-\(N,N\)-Diethyl-3-O-methyl-5,6-dideoxy-1,2-\(O\)-isopropylidene-\(\alpha\)-D-xylo-hept-5-enofuranosiduronamide (5c) S13

\((E)\)-\(N,N\)-Diethyl-3-O-benzyl-5,6-dideoxy-1,2-\(O\)-isopropylidene-\(\alpha\)-D-xylo-hept-5-enofuranosiduronamide (5d) S14
GENERAL
Reactions requiring an inert atmosphere were conducted under dry nitrogen, and the glassware was oven dried (120 °C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased in the higher quality available and were used without further purification. Flash column chromatography was carried out on silica gel 230-400 mesh. Compounds were visualized on analytical thin layer chromatograms (TLC) by UV light (254 nm). $^1$H NMR spectra were recorded at 300 or 400 MHz. $^{13}$C NMR spectra and DEPT experiments were determined at 75 or 100 MHz. Chemical shifts are given in ppm relative to tetramethylsilane (TMS), which is used as an internal standard, and coupling constants ($J$) are reported in Hz. The diastereoisomeric ratios were obtained using $^1$H-NMR analysis and GC-MS of crude products. GC-MS and HRMS were measured at 70 eV or using FAB conditions. When HRMS could not be measured on molecular ion the HRMS of a significant fragment is given. Only the most important IR absorptions ($\text{cm}^{-1}$) and the molecular ions and/or base peaks in MS are given.