Renewable materials as precursors of linear nitrile-acid derivatives via cross-metathesis of fatty esters and acids with acrylonitrile and fumaronitrile

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Supplementary data

Catalysts I, II and III were purchased from Sigma-Aldrich and Umicore, respectively, and were stored under Argon. Derivatives 1, 2 and 4 were obtained from Arkema (purity 90-95%). Solvents were freshly distilled and dried prior to use following classical procedures; over CaH₂ for dichloromethane and Na for toluene. Products were characterised using a Bruker 200 dpx NMR spectrometer and a Shimadzu 2014 gaz chromatograph with internal calibration.

Synthesis of the C18 diester 3 (method 1):
30 g (0.1 mol) of 4 were refluxed in 200 mL of methanol in the presence of 1 mL of concentrated H₂SO₄ (95-98%) for 3 hours. The reaction mixture was allowed to cool down to room temperature before addition of 100 mL of distilled water. Methanol was evaporated and the obtained mixture was extracted with dichloromethane. The organic phase was dried over MgSO₄ to give 29.4 g (Y= 90%) of the diester 3.

¹H NMR (200 MHz, CDCl₃): δ (ppm) 5.3 (m, 2H, CH=CH), 3.64 (s, 6H, COOC₃H₇), 2.28 (t, 4H, C₆H₄COOMe), 1.99 (m, 4H), 1.59 (m, 4H), 1.25 (m, 16H).

Synthesis of the C18 diester 3 (method 2):
100 mg of 4 were reacted with 0.2 mL of DMF-dimethylacetal and 0.5 mL of pyridine at 100°C for 1h. The product obtained was analyzed by GC and NMR. The same data as for method 1 were recorded.

Cross metathesis of C11 ester 1 with acrylonitrile (general procedure):
In a Schlenck tube under argon, 198 mg (1 mmol) of 1 and 106 mg (2 mmol) of acrylonitrile were dissolved in 20 mL of toluene before addition of 1 mol% of ruthenium catalyst. The reaction mixture was then heated at 100°C. Samples were taken at different times under argon and analysed by gas chromatography. Purification by column
chromatography using petroleum ether / diethyl ether (9/1 and 8/2 v/v) as the eluant yielded 190 mg (86 %) of 5 obtained as a colourless oil.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) = 1.2-1.8 (m, 12H, CH$_2$), 2.15-2.45 (m, 4H, CH$_2$), 3.65 (s, 3H, COOC$_2$H$_5$), 5.27-5.35 (m, 1H, CH), 6.51 (dt, 7.7 Hz, 10.8 Hz, 0.7 H, CH), 6.75 (dt, 7.3 Hz, 17.4 Hz, 0.3 H, CH).

Cross metathesis of C11 acid 2 with acrylonitrile (general procedure):
In a schlenck tube under argon, 184 mg (1 mmol) of 2 and 106 mg (2 mmol) of acrylonitrile were dissolved in 20 mL of toluene before addition of 1 mol% of ruthenium catalyst. The reaction mixture was then heated at 100°C. Samples were taken at different times under argon atmosphere and reacted with 0.05 mL of DMF-dimethylacetal and 0.1 mL of pyridine for 1h at 100°C in order to get the esterified products suitable for gas chromatography analysis.

Cross metathesis of C18 diester 3 with acrylonitrile (general procedure):
In a Schlenck tube under argon, 340 mg (1 mmol) of 3 and 212 mg (4 mmol, 4 equiv.) of acrylonitrile were dissolved in 20 mL of toluene before addition of 5 mol% of II and tetradecane (10 mol%) as the gas chromatography internal standard. The reaction mixture was then heated at 100°C. Samples of the reaction mixture were taken at different times under argon atmosphere and then analyzed by GC analysis. Purification by column chromatography using petroleum ether / diethyl ether (9/1 and 8/2 v/v) as the eluant yielded 288 mg (82 %) of 7 obtained as a colourless oil.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) = 1.20-1.85 (m, 10H, CH$_2$), 2.15-2.5 (m, 4H, CH$_2$), 3.68 (s, 3H, COOCH$_3$), 5.27-5.35 (m, 1H, CH), 6.48 (dt, 7.8 Hz, 10.8 Hz, 0.71 H, CH), 6.72 (dt, 6.8 Hz, 16.4 Hz, 0.29 H, CH).

Cross metathesis of C18 diacid 4 with acrylonitrile (general procedure):
In a Schlenck tube under argon, 310 mg (1 mmol) of 4 and 212 mg (4 mmol) of acrylonitrile were dissolved in 20 mL of toluene before addition of 5 mol% of ruthenium catalyst. The reaction mixture was then heated at 100°C. Samples of the reaction mixture were taken at different times under argon atmosphere. Each sample was reacted with 0.05 mL of DMF-dimethylacetal and 0.1 mL of pyridine for 1h at 100°C and then analyzed by gas chromatography.
**Hydrogenation tests. General method**

3 mL of a non purified reaction mixture, obtained after the cross metathesis of diester 3 with acrylonitrile were transferred into a stainless steel autoclave, degassed and pressurised to 10 bars of H₂. The reaction was then heated at 50°C for 16 hours. The reaction mixture was filtrated on a short plug of silica affording 10 as the single reaction product. 

\(^1\)H NMR (200 MHz, CDCl₃): \(\delta\) (ppm) = 1.80-1.20 (m, 14H, CH₂), 2.50-2.25 (m, 4H, CH₂), 3.64 (s, 3H, CH₃).

**Cross metathesis of C18 diester 3 with fumaronitrile (general procedure):**

In a Schlenck tube under argon, 340 mg (1mmol) of 3 and 156 mg (2 mmol) of fumaronitrile were dissolved in 20 mL of distilled toluene before addition of 5 mol% of catalyst. The reaction mixture was then heated at 100°C for 2h. Samples of the reaction mixture were taken at different times under argon atmosphere and then checked by GC analysis. Purification by column chromatography using petroleum ether / diethyl ether (8/2 v/v) as the eluant yielded 387 mg (92 %) of 7 obtained as a colourless oil.