

Compared reactivity of allyl ribosides in UV-initiated free radical copolymerization with acceptor monomers

*Loic Pichavant, Céline Guillermain, Stéphane Duchiron and Xavier Coqueret**

Université de Reims Champagne Ardenne, Institut de Chimie Moléculaire de Reims

CNRS UMR 6229, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2, France

Tel-Fax: 33 3 26913338 ; E-mail: xavier.coqueret@univ-reims.fr

Allyl hexylether (AHE)

n-Hexanol (10g, 0,1 mol) and tetrabutylammonium (0,33g, 0,01 eq) were added to toluene (47 mL). A 50% w/w sodium hydroxide solution (13 mL) was added and the biphasic mixture was mechanically stirred. Allylbromide (9.5 mL, 0.11 mol) was then added dropwise over period of 20 minutes. The reaction was monitored by TLC (silica gel, light petroleum-ethyl acetate, 9:1 v/v) and allowed to proceed under vigorous stirring for 24 hours. After addition of water (85 mL) and funnel separation, the organic layer was washed with water to neutrality and finally dried over anhydrous sodium sulfate. Evaporation of the solvent yielded an oil further purified by flash chromatography (light petroleum - ethyl acetate, 9:1 v/v) which gave 6,4 g of a yellow syrup (yield 45 %). The structure of allylhexylether ($R_f=0,85$) was confirmed by comparison with literature data.

$^1\text{H-NMR}$ data in CDCl_3 (internal Me_4Si) : δ (ppm) = 0.82 (t, $J=6.9\text{Hz}$, 3H, CH_3), 1.22 (m, 6H, $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2$), 1.51 (dq, $J=6.7, 7.2\text{Hz}$, 2H, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{O}$), 3.35 (t, $J=6.6\text{Hz}$, $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{O}$),

3.89 (dt, $J=5.7, 1.34\text{ Hz}$, 2H, $\text{OCH}_2\text{-CH=CH}_2$), 5.09 (dq, $J= 10.3, 1.3\text{ Hz}$, 1H, $\text{CH}_2\text{-CH=CHH}_{cis}$), 5.23 (dq, $J= 17.2, 1.6\text{ Hz}$, 1H, $\text{CH}_2\text{-CH=CH}_{trans}\text{H}$), 5.83 (ddt, $J= 17.2, 10.3, 5.5\text{ Hz}$, 1H, CH=).

^{13}C -NMR data in CDCl_3 (internal Me_4Si) : δ (ppm) = 70.6 ($-\text{CH}_2\text{O}$), 29.8 ($\text{CH}_2\text{-CH}_2\text{-O}$), 26.0 ($-\text{CH}_2\text{-CH}_2\text{-O-}$), 31.8 ($-\text{CH}_2\text{-CH}_2\text{-CH}_3$), 22.7 ($-\text{CH}_2\text{-CH}_3$), 14.1 ($-\text{CH}_3$), 71.9 ($-\text{OCH}_2\text{-CH-}$), 116.7 ($=\text{CH}_2$), 135.2 ($=\text{CH-}$).

Allyl isopropylidene glycerol (AIG)

A solution of of isopropylidene glycerol (10.6 mL – 85 mmol) and tetrabutylammonium bromide (0.28 g, 0.8 mmol) in toluene (40 mL) was mechanically stirred in a reactor equipped with a reflux condenser and a dropping funnel. The mixture became white and was very viscous. When the solution became homogeneous, allylbromide (8 mL, 0.93 mmol) was added dropwise over a period of 20 minutes. The stirring was continued for 18 hours at room temperature. The reaction was monitored by TLC (silica gel, ethyl acetate - light petroleum 1:1 v/v). After 15 h of reaction, the disappearance of the isopropylidene glycerol ($R_f=0.16$) was observed with concomitant formation of allyl isopropylidene glycerol ($R_f=0.8$). After adding 70 mL of water, two layers were separated and the organic layer was washed five times with water (15 mL) to neutrality and finally treated over anhydrous sodium sulfate. After evaporation of the solvent, 13.3g of colorless liquid was obtained (yield 90 %).

^1H -NMR data in CDCl_3 (internal Me_4Si): δ (ppm) = 1.37 and 1.4 (2s, 6H, 2 CH_3), 3.48 and 3.50 (2 dq, $J=1.34, 9.95\text{ Hz}$, 2H, $-\text{CH}_2\text{-O-CH}_2\text{-CH=}$), 3.7 (m, 1H, $\text{C}(\text{CH}_3)_2\text{-O-CH}_2\text{-}$), 4.1(m, 3H, 1H $\text{C}(\text{CH}_3)_2\text{-O-CH}_2\text{-}$ + 2H $-\text{O-CH}_2\text{-CH=CH}_2$), 4.3 (dqui, $J=1.2, 6.0\text{ Hz}$, 1H, $-\text{O-CH-}$), 5.2 (dq, $J= 10.3, 1.2\text{ Hz}$, 1H, $\text{CH}_2\text{-CH=CHH}_{cis}$), 5.3(dq, $J= 17.2, 1.5\text{ Hz}$, 1H, $\text{CH}_2\text{-CH=CH}_{trans}\text{H}$), 5.9 (m, 1H, $-\text{CH=}$).

^{13}C -NMR data in CDCl_3 (internal Me_4Si) : δ (ppm) = 25.4, 26.8 (2 $-\text{CH}_3$), 66.9 ($\text{C}(\text{CH}_3)_2\text{-O-CH}_2\text{-}$), 71.1 ($-\text{CH}_2\text{-O-CH}_2\text{-CH=CH}_2$), 72.5 ($-\text{O-CH}$), 74.7 ($-\text{O-CH}_2\text{-CH=CH}_2$), 109.4 (C), 117.3 ($=\text{CH}_2$), 134.5 ($-\text{CH=}$).

Allyl α,β -D-ribofuranoside (AR)

Concentrated sulfuric acid (0.6 mL) was added dropwise to a vigorously stirred and ice-cooled suspension of D-ribose (5.2 g, 34.7 mmol) and granulated calcium sulfate (ca 2.6 g) in allyl alcohol (1.1

mol, 72 mL) previously treated over anhydrous MgSO_4 . The mixture was stirred at room temperature under argon and allowed to proceed for 6 hours with monitoring by TLC (silica gel, ethylacetate - 1-propanol - water, 5:3:1 v/v/v). Within 6 hours, the D-ribose ($R_f=0.45$) was converted into two components, the first one with $R_f=0.8$ and a second one ($R_f=0.75$) in minor amounts which has been identified as the allyl D-ribose. The mixture was filtered and rinsed with small fractions of anhydrous allyl alcohol. The filtrate was neutralised by addition of Amberlyst A26 (hydroxide form). After filtration, the solution was concentrated in a rotating evaporator and further treated under high vacuum to yield a yellow syrup (6.3g, 96 %).

^{13}C -NMR data in $\text{DMSO}-d_6$: α anomer: δ (ppm) = 101.4 (C1), 71.5 (C2), 69.6 (C3), 85.3 (C4), 61.9 (C5), 67.9 (OCH_2), 135.3 ($=\text{CH}$), 116.4 ($=\text{CH}_2$); β anomer: δ (ppm) = 106.8 (C1), 74.7 (C2), 71.4 (C3), 84.3 (C4), 63.6 (C5), 67.3 (OCH_2), 135.2 ($=\text{CH}$), 116.3 ($=\text{CH}_2$).

Allyl 2,3-isopropylidene- β -D-ribofuranoside (AIR)

Allyl α,β -D-ribofuranoside (4.5g - 23.7 mmol) was stirred with 200 mL of dry acetone under atmosphere of argon. When the mixture was homogenized, concentrated sulphuric acid (1mL) was added. The solution was stirred at room temperature for 72 hours and monitored by TLC (eluant ethyl acetate - light petroleum, 1:1 v/v). The Allyl α,β -D-ribofuranoside ($R_f=0.1$) was then converted into two different products ($R_f=0.26$ and $R_f=0.72$), the second one corresponding to the desired product, Allyl 2,3-isopropylidene- α,β -D-ribofuranoside. The acid was then neutralised by addition of anhydrous sodium carbonate. The filtered solution was concentrated under vacuum to obtain a brown syrup which was purified by flash chromatography (ethyl acetate - light petroleum, 1:1 v/v). After drying under vacuum, the residue 2.9 g was recovered as an orange syrup.

^{13}C -NMR data in $\text{DMSO}-d_6$: δ (ppm) = 106.8 (C1), 87.2 (C2), 81.8 (C3), 85.0 (C4), 62.5 (C5), 26.6 and 24.9 (2CH_3), 67.4 (OCH_2), 111.3 (C), 133.1 ($=\text{CH}$), 117.0 ($=\text{CH}_2$).