A new Procedure for the Synthesis of (E)-1-iodo-1-alkenes.

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Dedicated to Professor Michael Hanack on the occasion of his 60th birthday

Abstract:

(E)-1-iodo-1-alkenes 4 can be prepared stereoselectively from aldehydes 1 via IH-elimination of 1, 1-Di-iodoalkanes 3 with DBU.

Vinyl iodides are an important class of compounds extensively used in organic synthesis mainly for the formation of C-C bonds via coupling reactions¹. The stereocontrolled synthesis of 1-iodoalkenes from acetylenic precursors is now available, but involves several steps, unstable intermediates and moderate yields². The stereoselective one-carbon homologation of carbonyl compounds to alkenyl iodides is also reported in the literature³. However there are not any synthetic method for the conversion of aldehydes in vinylic iodides having the same number of carbon atoms. It is thus clear that a method which combines stereoselectivity, good yields and easy isolation procedure is needed. The reaction of aldehydes 1 with triflic anhydride (Tf₂O) affords gem-bistriflates 2⁴, which can be converted into 1,1-diiodoalkanes 3 by reaction with magnesium iodide⁵. The synthesis of 3 provides to find simple conditions to prepare 1-iodo-1-alkenes 4 via IH-elimination. We have now found that, the reaction of 1,1-diiodoalkanes 3 with DBU⁶, affords in good yields and high stereoselectivity the corresponding (E)-1-iodo-1-alkenes 4 (Scheme). The results are shown in the table.

In a typical procedure, aldehyde 1, Tf₂O (1.1 molar amount) and N,N-Diisobutyl-2,4-dimethyl-3pentylamine⁷ (1.2 molecular amount) were reacted in methylene chloride for 12 h at O°C yielding (47-73%) the corresponding gem-bistriflate 2. Treatment of crude 2 with magnesium iodide (2.5 molecular amount) in carbon disulphide at O°C for 2 h gave rise to 80% of 1,1-diiodoalkane 3 which did not need further purification. DBU and 3 (equimolecular amount) were mixed together and heated at 100°C until appereance of a brown solid (ca. 15-20 min.). The elimination can be easily monitored by tlc. Vinyl iodides were isolated by direct distillation from reaction mixture. For higher vinyl iodides the reaction was carried out using DMSO as solvent and the reaction mixture was extracted with pentane. No changes in yield and stereoselectivity were observed.

R ¹	R ²	Yield(%)	E/Z ratio	
C ₂ H ₅ -	Н	80	96/4	
n-C ₄ H ₉ -	н	97	95/5	
n-C ₆ H ₁₃ -	Н	98	98/2	
C ₆ H ₅ -	н	83	99/1	
C ₆ H ₅ -CH ₂ -	H	77	97/3	
C ₆ H ₅ -	CH ₃	86	98/2	
-(C ₅ H ₁₀)-		80		
C ₂ H ₅ -	C ₂ H ₅ -	85		

Table . (E)-1-iodo-1-alkenes Prepared.

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- 8. Selected data.(E)-1-iodo-3-phenylpropene. Bp(Kugelrohr):150°C/10 torr. IR(neat): ν 1615(C=C), 950(trans CH=CH) cm⁻¹. ¹H-NMR(300 MHz, CDCl₃) δ = 3.45(dd, J₁ = 7 Hz, J₂ = 1 Hz, 2H, CH₂), 6.15(dt, J₁ = 14 Hz, J₂ = 1 Hz, 1H, =CHI), 6.80(dt, J₁ = 14 Hz, J₂ = 7 Hz, 1H, -CH=), 7.20-7.50(m, 5H, aromatic) ppm. ¹³C-NMR(CDCl₃) δ = 42.05(CH₂), 76.35(=CHI), 126.43, 128.43, 128.52, 137.80(aromatic ring), 144.61 (-CH=CHI) ppm.
- Yields in distilled vinyl iodide. All compounds were characterized fully based on IR, ¹H-NMR, ¹³C-NMR and mass spectral analysis. The assignment of stereochemistry was easily made from coupling constants of the olefinic protons.

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