

SHORT
COMMUNICATIONS

Unexpected Transformation of Butyl Vinyl Ether Treated with HF

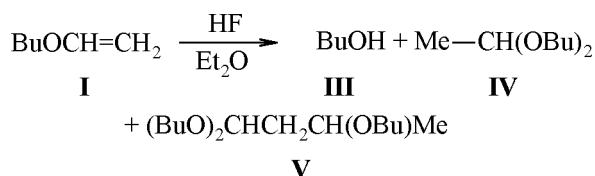
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Hydrogen halides HX (X = Cl, Br) are known to add to vinyl ethers readily and nearly quantitatively in the cold affording α -haloethyl ethers ROCHXCH₃ [1]. No published data appeared concerning the reaction between the vinyl ethers and HF. We found that anhydrous hydrogen fluoride does not add to the double bond of butyl vinyl ether (**I**). Passing HF through ether **I** at 0°C in the absence of a solvent resulted in formation of poly(butyl vinyl ether) [–CH(OBu)–CH₂–]_n (**II**) as proved by ¹H and ¹³C NMR data. Yet the treating of butyl vinyl ether with an ether solution of hydrogen fluoride gave rise to 1-butanol (**III**), acetaldehyde dibutyl acetal (**IV**), and 1,1,4-tributoxybutane (**V**). The reaction products were separated by preparative GLC. Apparently the 1-butanol arose due to ether **I** hydrolysis by traces of water. Acetals **IV** and **V** originate from reaction of ether **I** with 1-butanol and acetal **IV** respectively [2].

Thus in contrast to HCl and HBr HF does not add to vinyl ethers but in the cold depending on the conditions either initiates a cationic polymerization or generates hydrolysis and formation of acetals and their telomers.



Reaction of vinyl butyl ether (I) with HF. (a) On cooling 1.1 g of pure vinyl butyl ether **I** to 0°C a flow of anhydrous HF was passed through it for 10 min. The resinous polymer **II** obtained was dissolved in deuterobenzene and analyzed by means of ¹H and ¹³C NMR spectroscopy. ¹H NMR spectrum, δ , ppm: 1.02 (3H), 1.4–1.6 (2H), 1.6–2.3 (4H), 3.4–4.0 (3H). ¹³C NMR spectrum, δ_C , ppm: 14.91 (CH₃), 20.67

(CH₃CH₂), 33.58 (OCH₂CH₂), 40.50 (OCHCH₂), 69.40 (OCH₂), 75.05 (OCH).

(b) Anhydrous ethyl ether (30 ml) was saturated with HF at cooling to –5°C by passing HF for 20 min while stirring. At the same temperature to the solution obtained was added dropwise at stirring 7.5 ml of ether **I** dissolved in 20 ml of anhydrous ethyl ether. The mixture was stirred for 1 h at room temperature. The excess HF was removed by NaF addition till pH 7.0, then the solution was filtered, the ethyl ether was distilled off, and the residue was analyzed by GLC and separated by fractional distillation in three fractions of bp 92–116°C, 79–110°C (16 mm Hg), 110°C (15 mm Hg). Individual products **III–V** were isolated by preparative GLC and identified by ¹H and ¹³C NMR spectra and by comparison of refractive indices with the published data.

Acetaldehyde dibutyl acetal (IV). n_D^{20} 1.4090 (n_D^{20} 1.4090 [3]). ¹H NMR spectrum (C¹H₃C²H₂C³H₂C⁴H₂O)₂C⁵HC⁶H₃, δ , ppm: 0.92 t (6H, CH₃CH₂, J 7.3 Hz), 1.25 d (3H, CH₃CH, J 5.3 Hz), 1.38 m (4H, CH₃CH₂), 1.52 m (4H, CH₂CH₂CH₂), 3.37 d.t (2H, OCH^A, J 6.5, 9.3 Hz), 3.54 d.t (2H, OCH^B, J 6.6, 9.3 Hz), 4.62 q (1H, CH, J 5.4 Hz). ¹³C NMR spectrum (C¹H₃C²H₂C³H₂C⁴H₂O)₂C⁵HC⁶H₃, δ_C , ppm: 14.09 (C¹), 19.69 (C²), 19.84 (C⁶), 32.27 (C³), 64.76 (C⁴), 99.60 (C⁵).

1,1,3-Tributoxybutane (V). n_D^{20} 1.4300 (n_D^{20} 1.4255 [3]). ¹H NMR spectrum (C¹H₃C²H₂C³H₂C⁴H₂O)₂–C⁵HC⁶H₂C⁷H–(C⁸H₃)OC⁹H₂C¹⁰H₂C¹¹H₂C¹²H₃, δ , ppm: 0.916 t, 0.921 t, 0.927 t (9H, CH₂CH₃, J 7.3 Hz), 1.12 d (3H, CHCH₃, J 6.1 Hz), 1.38 m (6H, CH₂CH₃), 1.52 m (6H, CH₂CH₂CH₂), 1.63 d.d.d (1H, CHCH^ACH, J 4.4, 7.5, 14.0 Hz), 1.76 d.d.d (1H, CHCH^BCH, J 4.1, 8.5, 13.9 Hz), 3.20–3.65 m

(7H, OCH), 4.60 d.d (1H, OCHO, J 4.0, 7.5 Hz).
 ^{13}C NMR spectrum ($\text{C}^1\text{H}_3\text{C}^2\text{H}_2\text{C}^3\text{H}_2\text{C}^4\text{H}_2\text{O}$) $_2\text{C}^5\text{H}-$
 $\text{C}^6\text{H}_2\text{C}^7\text{H}(\text{C}^8\text{H}_3)\text{OC}^9\text{H}_2\text{C}^{10}\text{H}_2\text{C}^{11}\text{H}_2\text{C}^{12}\text{H}_3$, δ_{C} , ppm:
 14.05 (C^1 , C^{12}), 19.58 (C^{11}), 19.61, 19.63 (C^2 , $\text{C}^{2'}$),
 20.03 (C^8), 32.19, 32.22 (C^3 , $\text{C}^{3'}$), 32.43 (C^{10}),
 41.32 (C^6), 65.14 (C^4), 65.75 (C^4), 68.19 (C^9),
 72.05 (C^7), 100.81 (C^5).

NMR spectra were recorded on spectrometer Bruker DPX-400 at operating frequencies 400 MHz for protons and 100 MHz for ^{13}C , internal reference HMDS. GLC analyses were carried out on LKhM-80 device, detector katharometer, carrier gas helium, column 2000×3 mm, stationary phase 5% SE-30 on

Chromaton N-AW-DMCS. Preparative separation was performed on chromatograph PAKhV-07, column 2000×3 mm, stationary phase 5% SE-30 on Chromaton N-AW-DMCS.

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