

FLASH VACUUM THERMOLYSIS OF 2-BROMOETHANOL.
FORMATION OF α -BROMOETHYLETERS VIA 1-BROMOETHANOL.

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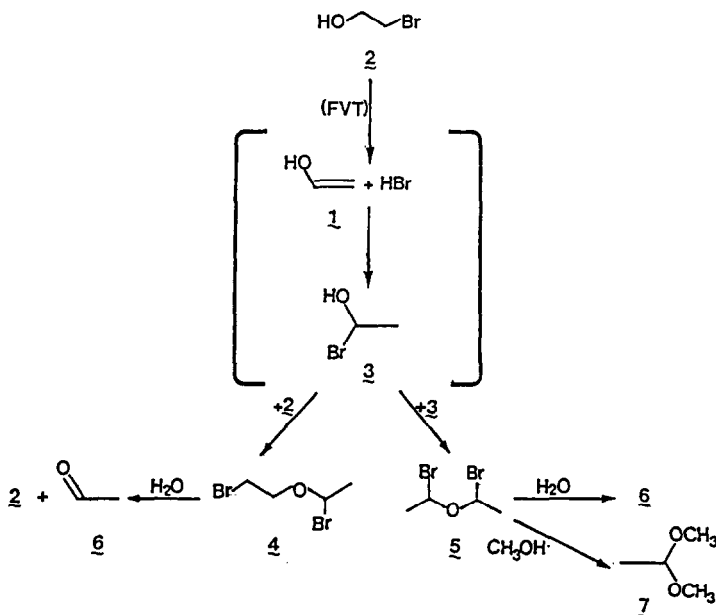
Abstract: Flash Vacuum Thermolysis of 2-bromoethanol (2) leads to the quantitative formation of 1-bromo-1-(1-bromoethoxy)ethane (5, di- α -bromoethylether). Low temperature IR spectroscopy shows that 5 arises from the dimerization of 1-bromoethanol (3), which is observed below -100°C as the primary product.

Flash Vacuum Thermolysis is often the best method for the isolation of highly reactive species. For example ethenol (1, vinylalcohol) was prepared by one of us via the retro-Diels-Alder reaction of its formal anthracene adduct.¹ The equilibration kinetics of simple enols to the keto-tautomers were only recently studied.² There are no reports on the addition of hydrogen halides to pure enol-tautomers, despite the fact that 1-haloalcohols (α -halohydrins) are commonly mentioned as transient intermediates in the reversible equilibration between hydrogen halides and carbonyl compounds.³ Since this equilibrium is mostly on the carbonyl side⁴, 1-haloalcohols cannot be isolated by addition of hydrogen halides to carbonyl compounds, except in some cases with polyfluoroketones.⁵ Besides the transient α -halohydrins do react extremely fast with themselves or with alcohols to form α -haloethers.⁶ Nevertheless in the addition of hydrogen halides to a pure enol-tautomer the equilibrium may be shifted to the side of the 1-haloalcohol so that it can be observed spectroscopically at low temperature, before it disappears via condensation and/or elimination reactions.

Since gasphase hydrogen halide eliminations of alkyl halides to olefins are well documented⁷, we reasoned that 2-bromoethanol (2) could be a potential FVT precursor for ethenol (1) and subsequently might form 1-bro-

methanol (3) with the simultaneously trapped hydrogen bromide. Runs were made in the usual apparatus⁸ by evaporating 2 g. quantities of pre-cooled 2 at a pressure below 0.1 mm Hg into the quartz tube in ca. 1 hour. At 650°C 2 was recovered unchanged. In the pyrolysate obtained at 750°C only 10% starting material 2 had remained and two new products, identified as 1-bromo-1-(2-bromoethoxy)ethane (4) and 1-bromo-1-(1-bromoethoxy)ethane (5), respectively, were obtained in 80% and 10% yield (SCHEME). At 900°C-950°C the pyrolysate was exclusively 5.^{9,10} The low field ¹H-NMR signals at δ 6.03 (q, ³J=5.6 Hz) and δ 6.13 (q, ³J=5.6 Hz) of 4 and 5, respectively are to be expected for α -bromoethers.¹¹ Compound 4 was unknown and 5 has only been anticipated.^{4,6} Their structures are also corroborated by their chemical behaviour. Treatment of 5 with either water or methanol gave quantitatively ethanal (6, acetaldehyde) and 1,1-dimethoxyethane (7), respectively. The 750°C pyrolysate and water yielded in a similar way a ca. 1:1 mixture of 2 and 6 (SCHEME).

SCHEME



The formation of 4 and 5 is at best rationalized when 1-bromoethanol (3) is the intermediate precursor. In the reaction at 750°C part of the starting material 2 has not been converted and will be trapped by 3 to give 4. Pure 3, likely to be formed by internal quenching of the primary pyrolysis products ethenol (1) and hydrogen bromide, is expected to dimerize exclusively to 5.^{3,6} We must disagree with an earlier report¹² on the preparation of 1-bromoethanol (3) by treatment of 6 with HBr-CBr₂F₂. The ¹H-NMR spectrum, lacking an OH signal, and corresponding with ours for 5, was interpreted as tentative evidence for 3. To obtain more information about the occurrence of these intermediates, the pyrolysate from FVT at 900°C was directly trapped on a -196°C cooled NaCl window of an IR cell.¹ Spectra were taken at -196°C, -150°C, -100°C, -75°C and -50°C, respectively. The spectrum at -196°C did neither reveal absorptions of the starting material 2 (3250, 1420, 1280, 1218, 1150, 1075, 1050, 1025, 1005, 930, 860 and 665 cm⁻¹, respectively) nor those of ethenol (1, 3240, 1710 and 815 cm⁻¹, respectively)¹ and ethanal (6, 1750 cm⁻¹). Instead a broad OH absorption at 3180 cm⁻¹ and absorptions at 1440, 1380, 1230, 1115, 1080, 1000, 895, 730 and 665 cm⁻¹, respectively were observed. This spectrum shows major changes on warming between -100°C and -50°C. First of all the broad OH absorption disappears and, secondly, the other bands are replaced by new ones at 1440, 1410, 1375, 1340, 1280, 1240, 1140, 1110, 1055, 1010, 950 and 665 cm⁻¹, respectively. They are consistent with the IR data available for 5.⁶ Therefore we assign the initial IR spectrum obtained at -196°C of the 900°C pyrolysate to the elusive 1-bromoethanol (3), which apparently is so reactive that it rapidly dimerizes to 5 above -100°C.

References and Notes

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9. Analyzed by $^1\text{H-NMR}$ (270 MHz) by dissolving the pyrolysate, after warming up the trap, into CDCl_3 .
 $\underline{4}$: $\delta(\text{H})$ 6.03 (q, $^3\text{J}=5.6$ Hz, 1H), 4.19 (ddd, $^2\text{J}=-11.3$ Hz, $^3\text{J}=5.6$ Hz, $^4\text{J}=5.6$ Hz, 1H), 3.79 (ddd, $^2\text{J}=-11.3$ Hz, $^3\text{J}=7.0$ Hz, $^4\text{J}=5.6$ Hz, 1H), 3.53-3.49 (m, 2H) and 2.04 (d, $^3\text{J}=5.6$ Hz, 3H), ppm;
 $\underline{5}$: $\delta(\text{H})$ 6.13 (q, $^3\text{J}=5.6$ Hz, 2H) and 2.01 (d, $^3\text{J}=5.6$ Hz, 6H) ppm.
 Both compounds were too unstable for MS analysis.
10. CAUTION: α -haloethers like $\underline{4}$ and $\underline{5}$ are suspected to be carcinogens!
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