Tetrahydrofuran Ring Opening Initiated by a Catalytic Action of a Diazoalkanes/Boron Trifluoride Etherate Combination

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Research carried out in different conditions on the reactivity of THF towards various reagents, resulting in ring opening, was the subject of a number of reports. The cleavage of the etheral bond in a THF molecule was achieved by the action of strong bases in the gas phase [1], but the use of some electrophiles proved to be more effective and useful for synthetic purposes. Thus, THF was transformed into the following products: 4-chlorobutyl acetate, in a thermal or photochemical reaction with acetyl chloride in the presence of $Mo(CO)_6$ [2]; 1-iodo-4-trimethylsiloxybutane, when heated with Et_2NSiMe_3/MeI [3]; 1,4-diiodobutane, by heating in a mixture of P_2O_5/H_3PO_4/KI [4]; 4-lithiobutoxide intermediate, in a reductive ether bond cleavage by a lithium 4,4′-di-tert-butyldiphenylide/BF_3·Et_2O mixture [5]; dichloro and chlorohydroxy dimeric species, when a complex with $TiCl_4$ was thermally decomposed [6]; 4,4′-dichlorodibutyl ether, in a thermal reaction with $POCl_3$/H_2SO_4 [7]. In addition, some earlier experiments on the ether-linkage reactivity towards inorganic acid chlorides are discussed in [6].

Besides these methods, there are a few others in which carbenes, formed from diazocompounds, generate an oxonium ylide with a THF molecule either by Rh(II)-catalyzed [8] or by a photochemical stimulation [9,10,11]. In all of these cases [8–11], the components of the reacting mixture are incorporated into the product molecule at the end of the reaction. In contrast to that, the observations described in this report show that the combination of N_2CHR/BF_3·Et_2O, without any additional reagent or photochemical initiation, behaves as a catalyst of electrophilic properties causing, at room temperature, a ring opening of a lot of the THF molecules followed by a simultaneous polymerization of the cationic intermediates.

Separately, both these reagents are inactive towards THF under the applied conditions, as evidenced, on the one hand, by common practice that reactions of various compounds with diazomethane or its derivatives are often carried out in ethyl ether/THF solutions and, on the other hand, by the fact that the BF_3·THF complex is a commercially available reagent. Though it has been well established [12] that the acid catalyzed decomposition of α-diazo ketones involves the formation of a highly electrophilic diazonium ion undergoing a facile nucleophilic substitution with a loss

of nitrogen, the composition described here shows specific properties, since any attempt to use another acid than BF_3, such as oxalic acid or acetic acid, did not cause any THF cleavage.

In the case described in this report, when a solution of 284 mg (2 mmole) of ethyl diazopyruvate [13] and of 0.25 ml (2 mmole) of commercial boron trifluoride diethyl etherate in 16 ml of THF covered with argon in a flask wrapped with aluminium foil to protect the contents from light was left overnight at room temperature, it changed into a thick oil. This was then diluted with a second portion of THF (20 ml) and stirring was continued for the next 12 h, which again resulted in a thickening of the reaction mixture up to an immobilization of the magnetic bar. As the crude reaction mixture dissolved in $CHCl_3$ (or Et_2O or AcOEt), when washed with water, gave a hard to separate jelly emulsion, the isolation of the product was achieved either by washing the neat product with water by decantation followed by drying its etheral solution over anhydrous Na_2SO_4, or by dilution of the reaction mixture with benzene and filtering the resulting solution through neutral Al_2O_3 II grade (7.5 g), followed by concentration, that yielded 17.93 g of almost colourless oil, which solidified after staying at room temperature. This result shows that one molecule of the ethyl diazopyruvate/$BF_3 \cdot Et_2O$ complex is responsible for the reaction of ring opening and the polymerization of about 125 THF molecules. The paraffin wax-like material melted sharply at 42–43.5°C and could not be distilled over when heated up to 255° under pressure reduced to about 1 mm Hg.

The product contained neither nitrogen, fluorine, nor boron, which was confirmed by a combustion analysis in addition to the ^{19}F NMR and ^{11}B NMR determination. The combustion analysis (%C 63.08, %H 10.76) fitted best to the molecular formula $C_{16}H_{34}O_5$, the elemental composition of which suggests its origin to be derived from four THF molecules supplied with one water molecule, $C_{16}H_{32}O_4 \cdot H_2O$. The additional water molecule in the formula could be the result of the presence of the terminal OH groups in an open chain oligomer molecule, but it can also exist as a separate molecule attached by hydrogen bonds, either to a chain terminated by both vinyl and OH groups or to a cyclic ether structure. The last suggestion is consistent with the lack of both the OH and the vinyl absorption in IR ($CDCl_3$, 1104 cm^{-1}, C–O absorption as the only diagnostic band) and the presence of only two signals in ^{1}H NMR ($CDCl_3$, 1.62 ppm and 3.42 ppm, the protons are shielded by about 0.2–0.3 ppm if compared with the corresponding THF resonance signals) as well as in ^{13}C NMR ($CDCl_3$, 26.42 ppm and 70.61 ppm) and a negative result in attempts to prepare an acetoxy or tosyloxy derivative by treating a pyridine solution of the THF oligomeric product with acetic anhydride or *p*-toluenesulfonyl chloride, respectively. Besides, the oligomerization product was recovered unchanged in an almost quantitative yield, after being treated with $KMnO_4$ in acetone for one hour at room temperature.

It appeared that a benzene solution of the THF–oligomer, when kept for 3 days over molecular sieves (A4, freshly heated at 500°C for 6 h) and, then, concentrated under diminished pressure, lost a water molecule yielding a solid material, the combustion analysis of which (%C 65.91, %H 11.00) gave results close to those calcu-

lated for the formula $(C_4H_8O)_n$. These observations strongly support the suggestion of the cyclic molecular structure of the product. According to MIKES and B^2/E Linked Scan experiments, it has to be mentioned, however, that the product is not homogeneous, but a mixture consisting mainly of a cyclic THF trimer and a tetramer contaminated by some higher oligomers. The presence of a dimeric structure [14] was not found.
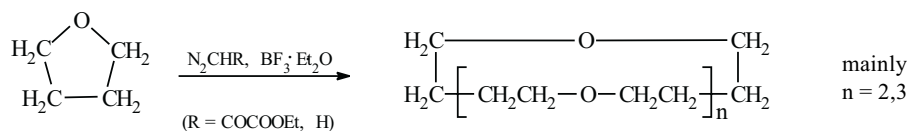

Though the EIMS showed a trace of the signal at 289 ($4 \times C_4H_8O + 1$) as the highest m/z value, the LSIMS, using NBA as a matrix, recorded the peak at m/z 215 to be M-1 of elemental composition $C_{12}H_{23}O_3$ according to the HRMS. This ion easily separates the fragment of m/z 72, yielding an ion at 143 as shown by the MIKES experiment. According to B^2/E Linked Scan technique estimations, the ion of m/z 215 is also derived (besides the parent ion of m/z 216) from m/z 287 (tetramer, M-1) and even from m/z 233, 359 and 430, but with less participation.

When, instead of the solid ethyl diazopyruvate, an etheral solution of diazomethane (prepared from 2 g of nitrosomethylurea) was used, its reaction with THF (15 ml) in the presence of $BF_3 \cdot Et_2O$ (0.13 ml, 1 mmole) occurred similarly giving the THF−oligomer of the same properties, but with a lower yield [1.73 g, which corresponded to 24 THF molecules/1 BF_3] than when it was carried out in a neat THF solvent medium.

When exposed to atmospheric air at daylight for a few days, the THF−oligomer spontaneously undergoes a transformation into a much less soluble in the most commonly used solvents, colourless, rubber-like material melting at 86–100°C. The results of a combustion analysis of this product (%C 62.06, %H 10.44) fitted excellently to those calculated for a hydroperoxide of a formula $C_{24}H_{48}O_8$ (or the hydroxy derivative $C_{12}H_{24}O_4$) though, however, the ion of m/z 464 (contrary to that at 232) could not be found in MS. Both the ^{13}C NMR (26.962 ppm and 72.985 ppm) as well as the ^1H NMR pattern with signals of almost equal intensity at 1.823 ppm and 3.803 ppm for the CF_3COOD solutions did not show any significant change compared to the spectrum of the starting THF−oligomer. The strong and broad IR absorption in the O–H stretching vibration region (3750–2500 cm^{-1}) with a maximum at 3549 cm^{-1} supports the assumption that the product has a structure of a hydroperoxide derivative of the parent THF−oligomer. This absorption was replaced by a very weak band with a maximum at 3434 cm^{-1} on behalf of a very strong absorption owing to the C–O stretching vibration at 1113 cm^{-1}, when the supposed hydroperoxide was kept in the CF_3COOH solution for a few days at room temperature.

When 75 mmole of THF (6.1 ml) was subjected to the action of one mmole of the $N_2CHCOCOOEt/BF_3 \cdot Et_2O$ (142 mg/0.13 ml, respectively) combination in the presence of acetic anhydride (7.1 ml) in an equimolar to the THF amount, the cleavage of

the THF etheral linkage also occurred. After stirring for two days at room temperature, the excess of the solvent was removed, first, under diminished pressure at room temperature, then, by treating it with ice-water and, finally, the product was taken into AcOEt. Removing the solvent gave 1.700 g of a light pink, mobile liquid showing in MS the M + 1 signals at m/z 247, 319 and 391, which correspond to the diacetate of a dimeric, trimeric and tetrameric ether structure, respectively. Heating this material up to 190°C under pressure diminished to 1 mm Hg made it possible to collect in the range 90–190°C about 50% of the material submitted to distillation, consisting of diacetates of THF dimer and trimer in the ratio of 1.8 to 1, respectively, as indicated by a comparison of the signal integrations values in the ^{1}H NMR spectrum (IR: 1740, 1242, 1116 and 1048 cm^{-1}).
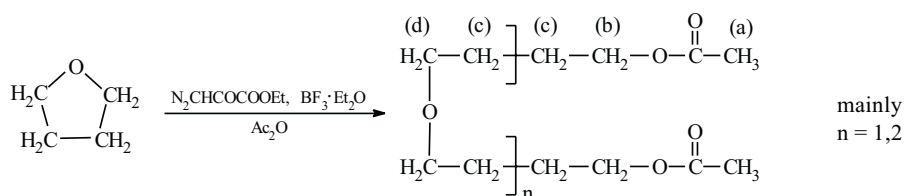
The redistillation gave an almost pure dimer diacetate [7] and trimer diacetate at about 115°C /1 mm Hg and 150°C/1 mm Hg, respectively, of identical (except for the proton signals' relative intensities) ^{1}H and ^{13}C NMR spectra for the CDCl$_3$ solutions in the case of both homologues with n = 1 or 2 [^{1}H NMR: 1.58–1.76 ppm, m, H(c); 2.05 ppm, s, H(a); 3.43 ppm, t, line separation 6.04 and 6.32 Hz, H(d); 4.09 ppm, t, l. s. 6.32 and 6.04 Hz, H(b). ^{13}C NMR: 20.912 ppm, C(a); 25.402 and 26.126 ppm, C(c); 64.251 ppm, C(b); 70.197 ppm, C(d); 171.177 ppm, C=O].

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