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Correction to "Organic Hydroxylamine Derivatives. VIII"*

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In Table 1 (p. 3254), column II, the pK_A value for compound IVc should read 8.4.

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The Oligomerization of Ethylene Oxide to Macrocyclic Ethers, Including 1,4,7-Trioxacyclononane

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Cyclic homologues of ethylene oxide, $[-CH_2-CH_2-O-]_n$, have attracted much attention due to their remarkable complexing power for alkali and other cations.¹⁻³ Laboratory methods for the preparation of the higher members ($n > 4$) have been described² which involve several steps and use di-, tri-, or tetraethylene glycol as starting materials; these methods fail to yield the medium rings ($n = 3$ and 4). Clearly, the simplest conceivable way to prepare this class of cyclic ethers is the direct oligomerization of ethylene oxide. In fact, it has been reported⁴ that the cyclic tetramer (1,4,7,10-tetraoxacyclododecane) is obtained together with mainly dioxan and polymer from ethylene oxide in the presence of trialkylaluminium. On the other hand, although BF_3 is reported⁵ to catalyse the conversion of propylene oxide to isomeric cyclic tetramers and pentamers, ethylene oxide under the same conditions gave only dioxan and polymers.

We can now report that a mixture of all the possible cyclic oligomers, including the hitherto unknown trimer 1,4,7-trioxacyclononane, m.p. 0 °C, and unaccompanied by open-chain oligomers and polymers, can be easily obtained from ethylene oxide at room temperature and atmospheric pressure in the presence of BF_3 or similar acidic fluorine compounds (PF_5 , SbF_5). The important point is to exclude any substance capable of furnishing permanent end groups to polymeric chains. Thus, the common practice of using BF_3 as its etherate leads to a mixture of the rings and open-chain compounds terminated by ethoxy groups. Another common practice, to add water as a cocatalyst to speed up the reaction,⁶ leads to hydroxyl-terminated open-chain compounds. Only dry HF gas proved acceptable as a cocatalyst, in accordance with the low nucleophilicity of fluoride ion. Likewise, any solvent must be inert (benzene, saturated hydrocarbons); even diethyl ether suppresses totally the formation of macrocyclic compounds, while dioxan, being one of the products, is a suitable solvent.

Other Lewis acids are either ineffective as catalysts ($AlCl_3$, $FeCl_3$) or give waxy polymers ($SnCl_4$, $SbCl_3$), while oxygen acids ($HClO_4$, *p*-toluene sulfonic acid) are rapidly transformed to half-esters of ethylene glycol.

Surprisingly, the product composition is little dependent on the concentration of monomer, so that similar products are obtained from

undiluted liquid ethylene oxide as from 5 % solutions. The most convenient procedure is to add cooled liquid ethylene oxide gradually to a small volume of dioxan containing initially about 1 % BF_3/HF (1:1). The catalyst is destroyed with NH_3 gas.

A typical product distribution as determined by distillation and gas chromatography is:

<i>n</i> :	2	3	4	5	6	7	8	9	10	11	higher
%:	40	1	15	5	4	3	2	2	1	1	25

With PF_5 and SbF_5 the distribution of ring sizes is similar, except that relatively more trimer and pentamer are formed.

The composition of the mixture does not change with reaction time, although for entropy reasons the smallest unstrained ring, dioxan, corresponding to the largest number of molecules, must be the thermodynamically stable end product. Since furthermore the isolated products are stable in the presence of the catalyst, one might be led to the conclusion that the reaction is kinetically controlled. In the presence of ethylene oxide and catalyst, however, the larger rings are degraded to dioxan. The product composition seems therefore to be determined by the balancing rates of oligomerization and of degradation of the products to dioxan, both dependent on ethylene oxide concentration. This is in accord with observations⁶ on the degradation of the polymer.

Ethylene oxide may in part be dehydrated by BF_3 in the gas phase, in non-basic solvents (hexane), and generally at higher temperatures. Dark-coloured tars are then formed and the resulting hydrated catalyst gives rise also to open-chain polyethers.

Only very little of cyclic acetals are observed. 2-Methyl-1,3-dioxolan is present in the dioxan fraction only when the reaction is carried out at higher temperatures. 2-Methyl-1,3,6-trioxacyclooctane occurs as impurity in the cyclic trimer fraction and must be removed by mild hydrolysis.

Experimental. Example of oligomerization procedure. A stock solution of catalyst is prepared by absorbing first gaseous BF_3 (7 g), thereafter gaseous HF (2 g), in dioxan (50 ml). This solution does not attack glass and is stable for months at room temperature. A portion of this solution (2 ml) was diluted with dioxan (40 ml) and cooled liquid ethylene oxide (250 g) added, with vigorous stirring, at a rate slow enough to prevent the temperature to rise above 30 °C. After 18 h, the solution was neutralized with gaseous NH_3 and fractionally distilled. Unreacted ethylene oxide (20–40 %) and dioxan distilled at atmospheric pressure, the trimer and most of the tetramer at 10 mmHg, and the remaining tetramer and the higher fractions including the octamer at 0.1 mmHg; in the last fractions at 200 °C rings up to the undecamer were identified.

Purification of 1,4,7-trioxacyclononane. The trimer fraction (100 mg), b.p. 110 °C/10 mmHg, was dissolved in ether (10 ml) containing water (0.1 ml) and a trace of *p*-toluenesulfonic acid, and the solution refluxed for one hour. After evaporation of the ether, the residue was taken up in pentane, stirred with basic alumina and filtered. The filtrate was concentrated and distilled to give pure 1,4,7-trioxacyclononane, b.p. 168–172 °C/760 mmHg, m.p. 0 °C. The NMR-spectrum in CDCl_3 showed a single line at δ 3.77 at room temperature, showed the molecular ion in MS, and had the following main infrared bands in the liquid: 2910, 2890, 2840, 1385, 1370, 1305, 1285, 1275, 1260, 1155, 1145, 1135, 1120, 1065, 1005, 910, 885, 835, 525 and 505 cm^{-1} .

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