

Selective Preparation of Cation-complexing Cyclic Oligoethers from Ethylene Oxide by a Template Effect

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Summary Ethylene oxide gives the cyclic tetra-, penta-, and hexa-mer with BF_3 in the presence of fluoroborates, fluorophosphates, or fluoroantimonates of alkali metals, alkaline earths or transition metals.

We have shown earlier¹ how ethylene oxide can be exclusively converted into cyclic oligomers $[-\text{CH}_2-\text{CH}_2-\text{O}]_n$ with BF_3 and similar catalysts. The product distribution could not, however, be markedly influenced, and the most interesting cation complexers ($n=4-8$) were formed in only modest yields. We have now found that the presence of

certain salts directs the oligomerization by a template effect to those rings which complex most strongly the cation used.[†] Salts of alkali metals are preferred, but also salts of the alkaline earths and transition metals can be used. Common salts, like halides and sulphates, cannot be used since their basic anions will immediately neutralise the Lewis acid catalyst ($\text{BF}_3, \text{BF}_5, \text{SbF}_5$). Only anions of the type BF_4^- , PF_6^- and SbF_6^- are therefore acceptable.

Ethylene oxide was added slowly to an ice-cooled suspension of the insoluble salt (e.g. NaBF_4) in dioxan (or benzene, CH_2Cl_2 , etc.) containing the catalyst. The salt

[†] Patent applications have been filed and the method is being exploited commercially by Borregaard Industries Limited, 1701 Sarpsborg, Norway.

immediately starts to dissolve and may dissolve partially or completely before the complexes which are formed gradually either precipitate or form a separate liquid phase. The complex may be separated without prior neutralization and the mother liquor used for further reaction. The cyclic ethers are most simply liberated by pyrolysis under reduced pressure, leaving a dry free-flowing salt, which can be used again without purification. Pure compounds can be obtained by fractional distillation or by fractional crystallization of the complexes before pyrolysis.

TABLE. Typical distribution of cyclic oligoethers in separated complex when ethylene oxide is oligomerized in dioxan with suspended anhydrous salts.

Salt	% Tetramer ^a	% Pentamer ^b	% Hexamer ^c
LiBF ₄	30	70	—
NaBF ₄	25	50	25
KBF ₄	—	50	50
KPF ₆	20	40	40
KSbF ₆	40	20	40
RbBF ₄	—	—	100
CsBF ₄	—	—	100
Ca(BF ₄) ₂	50	50	—
Sr(BF ₄) ₂	10	45	45
Ba(BF ₄) ₂	10	30	60
AgBF ₄	35	30	35
Hg(BF ₄) ₂	20	70	10
Ni(BF ₄) ₂	20	80	—
Cu(BF ₄) ₂	5	90	5
Zn(BF ₄) ₂	5	90	5

^a 1,4,7,10-Tetraoxacyclododecane. ^b 1,4,7,10,13-Pentaoxacyclopentadecane. ^c 1,4,7,10,13,16-Hexaoxacyclo-octadecane.

The use of fluoroborates, fluorophosphates, or fluoroantimonates thus satisfies the following conditions. (i) Only these salts are compatible with the catalyst system. (ii) The anions do not furnish end groups which may prevent cyclization and favour polymer formation.¹ (iii) The complexes which are formed, unlike complexes of most other salts, are insoluble enough to separate from the medium. (iv) These anions are sufficiently unreactive to allow pyrolysis, whereas other anions become so activated that the cyclic ether is destroyed on heating, and cumbersome chromatographic procedures are needed.²

Only the cyclic tetramer, pentamer, and hexamer ($n=4, 5$, and 6) are formed by this template effect, although stable 1:1 complexes can be prepared with independently synthesized heptamer and octamer.² Cations of high coordination number form instead 2:1 sandwich-type complexes which retain their identity in the solid and solution. Thus, whereas lithium produces 1:1 complexes with both tetramer³ and pentamer, sodium produces a 2:1 complex with the tetramer³⁻⁵ and 1:1 complexes with penta- and hexamer, and potassium produces a 2:1 complex with the pentamer and a 1:1 complex with the hexamer.

The yields depend on the conditions, as there is a limit to the quantity of unchanged salt and precipitated complex which can be stirred effectively, and to the rate at which the salt can dissolve compared with the rate of oligomerization. At least twice the quantity of ethylene oxide required for full complexing must be used for complete utilization of the salt. Dioxan ($n=2$) is also formed, and in some cases cocrystallizes with the complex even though dioxan alone does not complex these cations. For these reasons the Table gives only typical results for the distribution of the ring sizes ($n=4-6$) within the precipitated complex from experiments run in dioxan. The mother liquor will usually have the normal 'steady state' ring distribution as obtained without added salt.¹

The template effect of the cation seems to act both by promoting the appropriate folding of the growing chain before cyclization and by protecting the rings which are formed from subsequent degradation to dioxan, the positive charge preventing formation of the oxonium salt needed to start degradation. Experiments with deuteriated dioxan show that it is incorporated in the growing chain so that the product equilibrium is thereby effectively displaced from degradable large rings to complexed rings.

Template effects in the synthesis of cyclic oligoethers have been reported earlier,^{2,6} but only in irreversible Williamson reactions.

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