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1,3-DIOXOL-2-ONE (VINYLENE CARBONATE) TELOMERS OF SYNTHETIC POTENTIAL

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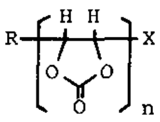
Smooth and stereoselective formation of type 1 telomers by free radical telomerization of 1,3-dioxol-2-one (vinylene carbonate) in the medium of a chain transfer agent such as polyhalomethanes was reported at the earlier meeting of this symposium.

In the continuation of our program, radical addition reaction has become apparent to proceed exclusively in trans fashion to give trans telomers (1,n=1,2,3) which have much potential as synthetic intermediates for monosaccharides of trioses to octoses including deoxyaldoses. In this symposium recent results on reactivity and utilization of radical and ionic vinylene carbonate telomers (1 and 2) are surveyed from a preparative point of view.

On the basis of the findings on reactivity of telomers (1), four general synthetic routes have been explored for aldoses and they (a,b,c and d) involve hydolysis of 1 via acetals, two-step conversion of polyhalomethyl group to formyl, introduction of C_1-unit into telomers and hydrolysis of enol-phosphates arising from reaction with phosphites, as key steps, respectively.

Ionic reaction of vinylene carbonate with methanol (or ethanethiol) in the presence of metallic compounds gives type 2 telomers (n=1,2,3), among which n=2 products consist mainly of "cis-syn" telomer leading to erythrose on hydrolysis. Attempt for asymmetric synthesis of aldoses using chiral alkoxides is discussed.



1 : R = CCl_3, $CHBr_2$, CH_2Br
X = Cl, Br, H

2 : R = OCH_3, SCH_2CH_3
X = H