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STEREOCHEMISTRY OF FOUR ISOMERIC TELOMERS (N=3) OF VINYLENE CARBONATE WITH CARBON TETRACHLORIDE AS NOVEL SYNTHETIC INTERMEDIATES FOR HEPTOSES

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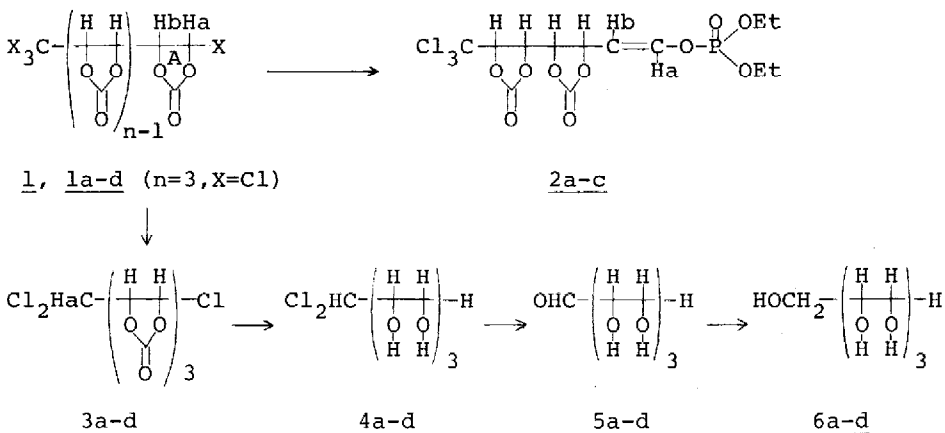
Previous papers described the free radical telomerization of vinylene carbonate in the medium of polyhalomethanes with stereoselective formation of type 1 telomers.[1)] Among the low telomers ($n \leq 4$) isolated, the n=3 products are of particular significance as the potential sources of biologically unique heptoses, octoses and related compounds. Studies on the telomers showed the need for conclusive assignment of their configurations which would permit the stereochemical elucidation of telomerization course as well as the conversion to compounds related to aldo-sugars of definite stereochemistry.

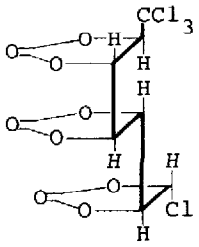


Telomerization of vinylene carbonate with carbon tetrachloride in a mole ratio of 1:5 gave four isomeric n=3 telomers, 1a (mp 244°), 1b (mp 230°),

1c (mp 290°) and 1d (mp 228°) stereoselectively, though in low yield (6%). Treatment of telomers 1b and 1c with two fold mole of trietyl phosphite in boiling toluene[2] gave the identical novel enol phosphate 2b(=2c) (mp 136°, 11%) whose structure was established on the basis of the spectral data (ir: 1830, 1680 and 1250 cm^{-1},nmr: δ6.90 (Ha,d-d,J=12.0 Hz, J'=8.0 Hz) and 5.54 (Hb,d-d,J=12.0 Hz, J'=9.2 Hz), indicative of the isomers different configurationally only at the carbonate-ring A. Isomer 1a underwent the similar conversion to the corresponding enol phosphate 2a (an oil,18% yield, nmr: δ6.92 (Ha),5.50(Hb),$J_{a,b}$=12.0 Hz), which was distinctly different from the above 2b, though scant quantity of pure isomer 1d prevented this type of transformation. Coupling constants between vinylic protons of 2a and 2b strongly support trans configuration with respect to the double bond.

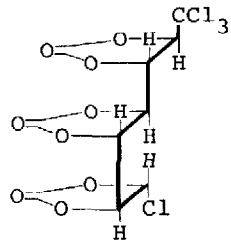
On the other hand, 1a, 1b, 1c and 1d[3] were successfully transformed into the heptoses, 5a, 5b, 5c and 5d,[3] respectively, by three-step procedures involving selective photolysis in tetrahydrofuran[4] to dichloromethyl compounds 3a (mp 233°,74%, δ6.22(Ha)), 3b (mp 234°,84%, δ6.28(Ha)), 3c (mp 295°,80%, δ6.20(Ha)) and 3d[3] followed by borohydride reduction and subsequent hydrolysis with aqueous silver nitrate.[5] The heptoses thus formed, without attempts to isolate in purified forms, were reduced to the heptitols 6a, 6b, 6c and 6d[3] which were identified as threo glycero-galacto-, erythro glycero-ido-, threo(meso)glycero-ido- and erythro glycero-galacto-heptitols[6] by the gas chromatographic (1.5%QF-1,2%XF-1105)[7] comparison with the optically active authentic specimens.[8]

On the basis of the findings described above, and the small coupling constants ($J_{a,b}$=~2.0 Hz) between the A-ring protons of the telomers, indicative of trans stereochemistry, the aldoses 5b and 5c must be erythro glycero-ido- and threo glycero-ido-heptoses[6] and hence, isomers 1b and 1c could be stereochemically assigned as trans-"anti"-trans-"syn"-trans and trans-"anti"-trans-"anti"-trans forms, respectively.



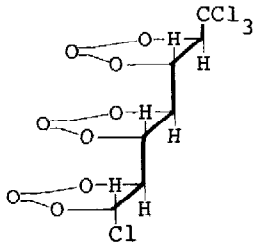
1a

trans-"syn"-trans-"anti"-trans



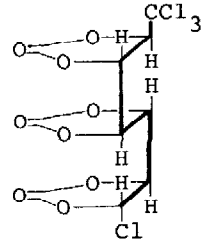
1b

trans-"anti"-trans-"syn"-trans



1c

trans-"anti"-trans-"anti"-trans



1d

trans-"syn"-trans-"syn"-trans

Assumed that such trans addition mechanism is only operative in this telomerization as substantiated in the n=1 and n=2 telomers,[5] compounds 5a and 5d may be threo glycero-galacto- and erythro glycero-galacto-heptoses,[6] respectively, and therefore trans-"syn"-trans-"anti"-trans and trans-"syn"-trans-"syn"-trans configurations could be assigned to telomers 1a and 1d, respectively.

Thus, it has now become feasible to lead to the biologically interesting poly-alcohols with definite configurations including heptoses and octoses, which will be reported elsewhere.

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Notes and References

1) T. Tamura, T. Kunieda and T. Takizawa, Tetrahedron Lett., 2219 (19
idem., J. Org. Chem., 39, 38 (1974).
T. Kunieda and T. Takizawa, J. Syn. Org. (Japan), 33, 560 (1975).

2) N. Mitsuo, T. Kunieda and T. Takizawa, submitted for publication

3) Contaminated with a trace of the corresponding c isomer

4) N. Mitsuo, T. Kunieda and T. Takizawa, J. Org. Chem., 38, 2255 (19

5) T. Takahata, T. Kunieda and T. Takizawa, Chem. Pharm. Bull. (Tokyo
3017 (1975).

6) This paper uses the prefixes "threo" and "erythro" which mean the
ship between the configurations at C_5 and C_6, since an extended ap
of the rule (Biochemistry, 10, 3983 (1971)) to racemic heptoses an
mono-saccharide seems to be somewhat confusing and inadequate.
Thus, threo glycero-galacto-heptose means a 1:1 mixture of D-glyce
galacto-heptose and L-glycero-D-galacto-heptose.

7) T. Imanari, Y. Arakawa and Z. Tamura, Chem. Pharm. Bull. (Tokyo),
(1969).

8) Kindly supplied by Dr. N. K. Richtmyer and Mr. E. Zissis of the Na
Institutes of Health (U.S.A.).