Tetrahedron Letters Vol. 21, pp 4523 - 4524 0040-4039/80/1115-4523$02.00/0
© Pergamon Press Ltd. 1980. Printed in Great Britain

THE REACTION OF 1,3-DICHLORO-1,1,3,3-TETRAISOPROPYLDISILOXANE WITH SOME OPEN CHAIN POLYHYDROXY COMPOUNDS

Wojciech T. Markiewicz+

Department of Stereochemistry of Natural Products, Institute of Organic Chemistry, Polish Academy of Sciences, 61-704 Poznań, Noskowskiego 12/14, Poland

Zdeněk Samek and Jiří Smrt

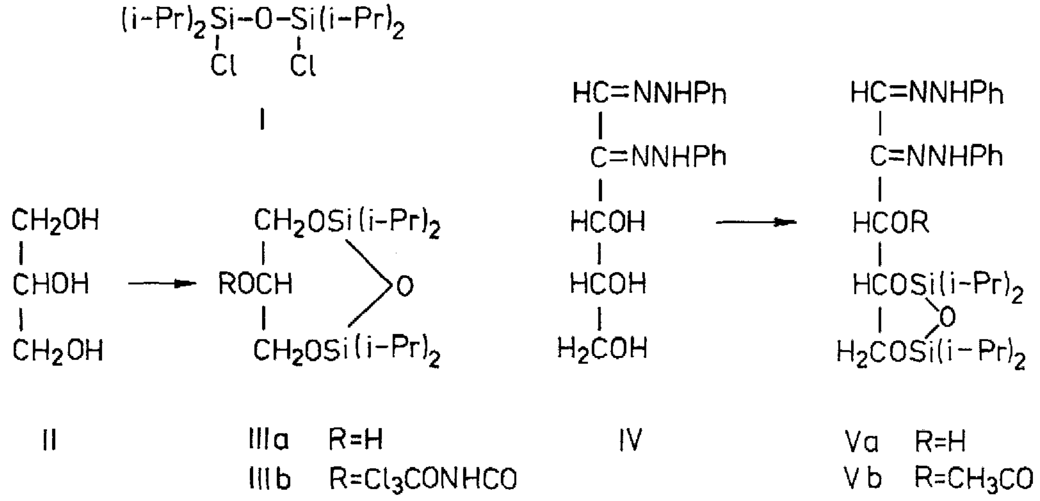
Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Praha 6, Flemingovo nám. 2, Czechoslovakia

Abstract: 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (I) forms an 8-membered ring (IIIa) with glycerol, a 7-membered ring (Va) with D-erythropentose phenylosazone (IV) and linear polymers with 1,4-butanediol resp.

1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (I) gives 3',5'-O-protected derivatives of ribonucleosides[1,2] and arabinonucleosides[3] by fast reaction with the primary 5'-OH function followed by intramolecular ring closure with the secondary 3'-OH group. The reaction of I with a nucleoside bearing the secondary hydroxyls only [1-(6-deoxy-α-L-talofuranosyl)uracil] led to a 7-member ring closure i.e. the 2',3'-O-silyl derivative was obtained[3].

In order to establish the scope and limitations of the reaction of I, its reactions with some open chain polyhydroxy compounds were performed. The reaction of glycerol (II) could possibly lead to either 7- or 8-membered ring formation when the reaction would employ two primary OH groups or a primary and a secondary hydroxyls respectively. The reaction[4] gave one product only (IIIa). The position of free hydroxyl function was established by comparison of ^{1}H-NMR spectra of the product and its acylated derivatives[1,3,5]. In the spectrum of IIIa the protons H_6,H_7 and H_8 formed a complex multiplet in the region δ 3.6-4.0. After in situ acylation[3,5] with trichloroacetyl isocyanate the signals of H_7 appeared at o 4.96 (J=5Hz) and H_6 and H_8 at δ 4.00 (J=5Hz) (in IIIb). Therefore I reacts exclusively with both primary OH groups of II under the formation of 2,2,4,4-tetraisopropyl-1,3,5-trioxa-2,4-disilacyclooctane-7-ol (IIIa).

The question arose whether a 9-membered ring could be formed. To study this problem the reaction of I and 1,4-butanediol was examined. In this case a mixture of polymeric compounds was obtained[4].



Another problem was to check whether the intramolecular cyclization with the secondary OH group would lead more easily to a 7- or an 8-membered ring formation. To check this a substrate containing 1,2,3-triol system was required. D-Erythropentose phenylosazone[6] (IV) was chosen for this purpose. The reaction of I and IV resulted in a single product (Va). The signal of the proton H_3 overlapped with the signals of H_4 and H_5 at δ 3.6-4.4 in the spectrum of Va was shifted downfield after acetylation (Vb) to δ 5.17 forming a doublet (J=6.5Hz). These data indicated the structure of Va as 4,5-O-(tetraisopropyl)-disiloxane-1,3-diyl)-D-erythropentose phenylosazone.

REFERENCES AND NOTE

1. W.T. Markiewicz, J.Chem.Res.(S), 1979, 24, J.Chem.Res.(M), 1979, 0181-0197
2. W.T. Markiewicz, and M. Wiewiórowski, Nucleic Acids Res., Spec.publ. No. 4, s185 (1978)
3. W.T. Markiewicz, N.Sh. Padyukova, Z. Samek, and J. Smrt, Collect.Czech. Chem.Commun. 45, 1860 (1980)
4. 1 equivalent of substrate and 1.1 equivalent of I were reacted (ca 2 hr.) in anhyd. pyridine (2ml/1 mmol), product purified by silica gel column chromatography in $CHCl_3$ and submitted to ^1H-NMR analysis in $CDCl_3$ or in $CHCl_3$
5. Z. Samek and M. Buděšínský, Collect.Czech.Chem.Commun., 44, 558 (1979)
6. W.T. Haskins, R.M. Hann, and C.S. Hudson, J.Amer.Chem.Soc., 68, 1766 (1946)

(Received in UK 9 September 1980)