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SYNTHESIS OF 2-SUBSTITUTED 3-FORMYL-5-METHOXYTETRAHYDROFURANS FROM 2,5-DIMETHOXYTETRAHYDROFURYL-3-CARBINOLS

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UDC 547.724:542.952.1

The acid-catalyzed rearrangement of 2,5-dimethoxytetrahydrofuryl-3-carbinol, obtained from 2,5-dimethoxy-3-formyltetrahydrofuran, gave the 2-substituted 3-formyl-5-methoxytetrahydrofuran.

The purpose of our work was to study the properties of 2,5-dimethoxytetrahydrofuryl-3-carbinols (Ia-e), obtained from 3-formyl-2,5-dimethoxytetrahydrofuran (II) by hydrogenation with Raney nickel (Ia) [1], or by the Grignard reaction (Ib-e) (here and below all compounds were isolated as mixtures of syn- and anti-isomers, shown by the positions of the methoxy-group signals in the PMR spectra).

Alcohols Ia-e are 3-substituted cyclic diacetals and are sensitive to acid reagents. We have used this property to carry out the acid-catalyzed rearrangement of the alcohols.

Earlier, it was shown that 2-hydroxymethyl-2,5-dimethoxytetrahydrofuran was converted to 4-methoxy-2,7-dioxabicyclo[2.2.1]pentane [2] by an acid ion-exchange resin. We found that when the alcohols Ia-e were refluxed in acetic acid they underwent rearrangement to 2-substituted 3-formyl-5-methoxytetrahydrofurans (IIIa-e, Table 1).

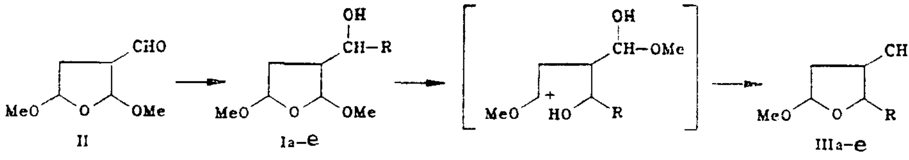
We propose that the mechanism of the reaction is that of intramolecular acetalization.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 164-166, February, 1991. Original article submitted June 27, 1989.

TABLE 1. Data for the Compounds Synthesized

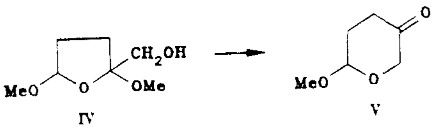
Compound	Empirical formula	Bp, °C (mm Hg)	n_D^{20}	ν, cm^{-1}	PMR spectrum, δ, ppm (J, Hz)	Yield, %
Ia	$C_7H_{14}O_4$	115 (10)	1,4451	3300...3500 (OH)	1,5...2,3 (w., m, 2H, 4-CH$_2$); 2,40 (m, 1H, 3-CH); 3,05 (br., s, 1H, OH); 3,2...3,4 (s*, 6H, OCH$_3$); 3,4...3,8 (m, 2H, OCH$_2$); 4,85...5,10 (m, 2H, 2-CH, 5-CH)	93
Ib	$C_8H_{16}O_4$	80...85 (3)	1,4470	3300...3500 (OH)	0,9 (m, 3H, CH$_3$); 1,2...2,6 (w. m, 4H, 3-CH, 4-CH$_2$, OH); 3,0...3,1 (s*, 6H, OCH$_3$); 3,50 (m, 1H, OCH); 4,75 (m, 2H, 2-CH, 5-CH)	74
Ic	$C_9H_{18}O_4$	89...94 (3)	1,4508	3300...3500 (OH)	0,95 (m, 3H, CH$_3$); 1,3...1,6 (m, 2H, CH$_2$); 1,6...2,3 (w. m, 3H, 4-CH$_2$, OH); 2,3...2,5 (m, 1H, 3-CH); 3,3...3,5 (s*, 6H, OCH$_3$); 3,55 (m, 1H, OCH); 4,9...5,2 (m, 2H, 2-CH, 5-CH)	77
Id	$C_{13}H_{18}O_4$	164...166 (3)	1,5150	3300...3500 (OH)	1,6...2,8 (w. m, 4H, 3-H, 4-CH$_2$, OH); 3,3...3,5 (s*, 6H, OCH$_3$); 4,6 (m, 1H, OCH); 4,8...5,2 (m, 2H, 2-CH, 5-CH); 7,35 (m, 5H, C$_6$H$_5$)	67
Ie	$C_{15}H_{18}O_4$	200 (3)	—	2200 (C≡C) 3300...3500 (OH)	1,8...2,8 (w. m, 4H, 3-CH, 4-CH$_2$, OH); 3,3...3,5 (s*, 6H, OCH$_3$); 4,5...4,8 (m, 1H, OCH); 5,1...5,3 (m, 2H, 2-CH, 5-CH); 7,35 (m, 5H, C$_6$H$_5$)	60
IIIa	$C_6H_{10}O_3$	70 (10)	1,4410	1730 (C=O)	2,1...2,3 (w. m, 2H, 4-CH$_2$); 2,90...3,15 (m, 1H, 3-CH); 3,22, 3,28 (s, 3H, OCH$_3$); 3,98...4,12 (m, 2H, 2-CH$_2$); 5,02 (m, 1H, 5-CH); 9,60 (d, 0,6H, CHO-trans $J=2,2$); 9,62 (d, 0,4H, CHO cis, $J=2,2$)	75
IIIb	$C_7H_{12}O_3$	75 (10)	1,4425	1730 (C=O)	1,1 (m, 3H, CH$_3$); 1,7...2,2 (w. m, 2H, 4-CH$_2$); 2,2...2,7 (m, 1H, 3-CH); 3,0...3,2 (s*, 3H, OCH$_3$); 4,0...4,3 (m, 1H, 2-CH); 4,7...4,9 (m, 1H, 5-CH); 9,1...9,7 (s*, 1H, CHO)	80
IIIc	$C_8H_{14}O_3$	80 (10)	1,4440	1730 (C=O)	1,0 (m, 3H, CH$_3$); 1,6 (m, 2H, CH$_2$); 2,0...2,6 (w. m, 3H, 3-CH, 4-CH$_2$); 3,2...3,4 (s*, 3H, OCH$_3$), 4,0...4,3 (m, 1H, 2-CH); 4,9...5,1 (m, 1H, 5-CH); 9,4...9,8 (s*, 1H, CHO)	72
IIId	$C_{12}H_{14}O_3$	130 (3)	1,5260	1730 (C=O)	1,5...3,0 (w. m, 3H, 3-CH, 4-CH$_2$); 3,0...3,2 (s*, 3H, OCH$_3$); 4,8...5,2 (m, 2H, 2-CH, 5-CH); 7,0 (m, 5H, C$_6$H$_5$); 8,7...9,5 (s*, 1H, CHO)	90
IIIe	$C_{14}H_{14}O_3$	167 (3)	—	1730 (C=O), 2200 (C≡C)	2,0...3,0 (w. m, 3H, 3-CH, 4-CH$_2$); 3,2...3,6 (s*, 3H, OCH$_3$); 5,0...5,3 (m, 2H, 2-CH, 5-CH); 7,3 (m, 5H, C$_6$H$_5$); 9,5...10,0 (s*, 1H, CHO)	70
V	$C_6H_{10}O_3$	109 (8)	1,4468	1730 (C=O)	1,95 (m, 1H, 5-CH^a); 2,22 (m, 1H, 4-CH^a); 2,47 (m, 2H, 4-CH^e, 5-CH^e); 3,40 (s, 3H, OCH$_3$); 3,87 (d, 1H, 2-CH^a, $J=16,9$); 4,12 (d, 1H, 2-CH^e, $J=16,9$); 4,84 (t, 1H, 6-CH, $J=4,25$)	78

*Series of singlets.



I, III a R=H; b R=Me; c R=Et; d R=Ph; e R=C≡CPh

Under analogous conditions, 2,5-dimethoxy-2-hydroxymethyltetrahydrofuran (IV) is recyclized to give 6-methoxydihydropyran-3-one (V), showing that this method can be extended to other systems



A study of the transformation of the alcohols Ia-e and IV in the gas phase showed that when passed through a column filled with silica gel at 200°C, products of the rearrangement of IIIa-e and V were formed in high yields (IIIa, 82%; IIIb, 78; IIIc, 80; IIId, 74; IIIe, 73; V, 79).

EXPERIMENTAL

PMR spectra were obtained on a Bruker WM-250 or a Jeol FX90Q using $CDCl_3$ as solvent; IR spectra of the compounds as thin layers were recorded on an IR-20. Analysis of the reaction mixtures was carried out by GLC on a Chrom-4 chromatograph with DPI (column 1 m × 3 mm with 5% silicone SE-30 on N-AW chromaton); the carrier-gas was helium.

General Method for the Preparation of α-Substituted 3-Hydroxymethyl-2,5-dimethoxytetrahydrofurans (Ib-d). To metallic magnesium (2.4 g, 0.1 mmole) in absolute ether (80 ml) was added slowly with stirring alkyl bromide (or methyl iodide) (0.1 mole) in ether (60 ml) in an atmosphere of argon, at such a rate that the mixture boiled gently. After the addition of the alkyl halide, the mixture was heated for 1 h, cooled, and 3-formyl-2,5-dimethoxytetrahydrofuran (16 g, 0.1 mole) in ether (50 ml) added dropwise at 0°C. The mixture was stirred for a further hour at room temperature. Ether (50 ml) was then added, followed by a solution of NH_4Cl (5.3 g, 0.1 mole) in water (30 ml) at 0°C, and the mixture extracted with ether (3 × 250 ml). The ether extracts were dried over Na_2SO_4. After evaporation of the solvent the residue was distilled.

Compound IV was obtained by the method described in [3].

2-Substituted 3-Formyl-5-methoxytetrahydrofurans (IIIa-e) and 6-Methoxydihydropyran-3-one (V). A. A solution of compound Ia-e or V (0.1 mole) in acetic acid (100 ml) was refluxed for 1 h. Then 100 ml of CH_3COOH was distilled off at reduced pressure, and the residue distilled.

B. A solution of compound Ia-e or IV in benzene (volume ratio 1:3) was passed at 20 ml/h through a quartz flowthrough reactor (diameter 10 mm), filled with silica KSK-2 gel (fraction 2 mm, height of layer 10 cm) at a nitrogen rate of 15 ml/min.

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