Chemistry

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Abstract

Full Text

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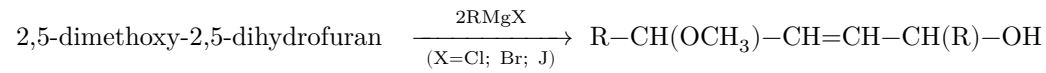
THE REACTION OF ORGANOMAGNESIUM COMPOUNDS WITH 2,5-DIMETHOXY-2,5-DIHYDROFURANS

Organomagnesium compounds react under fairly severe conditions with acetals and ketals, forming ethers of secondary and, respectively, tertiary alcohols ([1]).

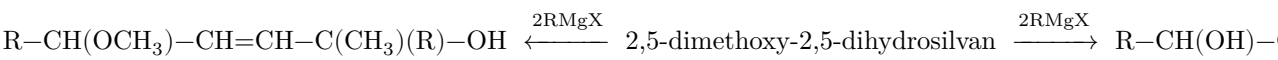
We have for the first time studied the reaction of organomagnesium compounds with heterocyclic acetals—2,5-dimethoxy-2,5-dihydrofuran and 2,5-dimethoxy-2,5-dihydrosilvan. As was to be expected, it proceeds with opening of the dihydrofuran ring* and is accompanied by replacement of one of the methoxyl groups by an alkyl radical according to the scheme:



(A)

The products of cleavage of 2,5-dimethoxy-2,5-dihydrofuran by Grignard reagents are 1,4-dialkyl-substituted 4-methoxybuten-2-ol-1s (A), formed in yields of up to 60%. Their physical constants, analytical data, and yields are given in Table 1 (I–VI). The structure of the substances obtained is confirmed by infrared spectroscopy data (Fig. 1a). In addition, functional analysis showed that they have no carbonyl group and contain one double bond. Determination of active hydrogen by the Chugaev–Tserevitinov method showed the presence of one hydroxyl group in the molecule.

In the reaction of organomagnesium compounds with 2,5-dimethoxy-2,5-dihydrosilvan, depending on the site of cleavage of the C—O bond in the ring, one might expect the formation of two final reaction products (B and C):



(B) (C)

It turned out that 2,5-dimethoxy-2,5-dihydrosilvan reacts with organomagnesium compounds less vigorously than the corresponding dihydrofuran, and the yields of the final products (VII) and (VIII) do not exceed 15-20% (Table 1). The structure of the compounds obtained corresponds to structure C.

This conclusion was drawn on the basis of IR-spectroscopic data. Comparison of the infrared absorption spectra of compounds I and VII (Fig. 1a and b) shows their considerable similarity (in the spectrum of VII there appears only one extra intense band at 1168 cm^{-1}, corresponding to skeletal vibrations of the group $> C(CH_3)_2$).

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* Until now it had been known that the dihydrofuran ring is opened only upon hydrolysis ([2]) and oxidation ([3]).

Table 1

Products of the interaction of 2,5-dimethoxy-2,5-dihydrofuran and silvan with magnesium haloalkyls

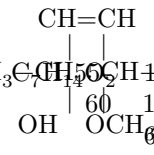
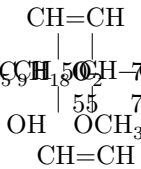
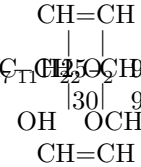
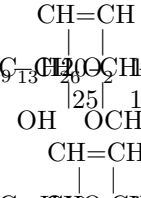
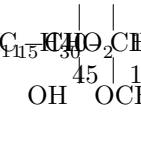
Compound	Starting halide	Compound obtained	Gross formula	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Calculated, % C	Calculated, % H
I	CH_3I		$C_7H_{14}O_2$	79	60 180/75559-60/3	1,4405	0,9237	37,18	37,23	64,28	11,01	64,58	10,84
II	C_2H_5Br		$C_9H_{18}O_2$	74	55 76/3	1,4480	0,9080	46,62	46,46	68,03	11,72	68,31	11,47
III	C_3H_7Br		$C_{11}H_{22}O_2$	93	30 95/3	1,4495	0,8965	55,79	55,70	70,77	12,06	70,92	11,90
IV	C_4H_9Br		$C_{13}H_{26}O_2$	118	25 115/3	1,4510	0,8873	65,31	64,93	72,56	12,65	72,84	12,23
V	iso-$C_5H_{11}I$		$C_{15}H_{30}O_2$	113	45 115/1,5	1,4525	0,8773	74,61	74,17	73,91	13,88	74,32	12,48

Fig. 1. IR spectra. a –1,4-dimethyl-4-methoxybut-2-en-1-ol (I), b – 1,4,4-trimethyl-4-methoxybut-2-en-1-ol (II)

Figure 1: Fig. 1. IR spectra. a –1,4-dimethyl-4-methoxybut-2-en-1-ol (I), b – 1,4,4-trimethyl-4-methoxybut-2-en-1-ol (II)

Compound	Starting halide	Gross formula	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calculated	Found, % C	Found, % H	Calculated, % C	Calculated, % H
VI	C_6H_5Br	$C_{17}H_{16}O_2$	55	166/1	1,5810	1,094	77,48	76,20	80,79	7,10	80,28	7,13
VII	C_3H_7I	$C_8H_{16}O_2$	20	55/3	1,4470	0,9203	41,88	41,84	66,40	11,39	66,63	11,18
VIII	C_2H_5Br	$C_{10}H_{20}O_2$	10	76/3	1,4520	0,9132	50,89	51,08	69,65	11,63	69,72	11,70

In the region of C–O bond vibrations, both substances have two intense peaks at 1070–1080 cm^{-1} (75%) and 1100–1105 cm^{-1} (75%). This indicates that both compounds contain a secondary hydroxyl group, to which the characteristic frequency ~ 1100 cm^{-1} corresponds.

In the case of structure B, containing a tertiary hydroxyl, the absorption maximum of the C–OH group would be shifted into a shorter-wavelength region of the spectrum (~ 1150 cm^{-1}). The presence of a secondary hydroxyl group was also confirmed by the drop reaction with sulfur, which is specific for secondary alcohols ([4]).

Fig. 1. IR spectra. *a* –1,4-dimethyl-4-methoxybut-2-en-1-ol (I), *b* –1,4,4-trimethyl-4-methoxybut-2-en-1-ol (II)

The formation of a secondary alcohol upon cleavage of 2,5-dimethoxy-2,5-dihydrosilvan is of considerable theoretical interest, since it represents a case of cleavage of the oxide ring at the bond between oxygen and the more highly substituted carbon atom. Until now it had been known that α- and β-oxides are cleaved by organomagnesium compounds predominantly at the bond between oxygen and the less substituted carbon atom ([1,5,6]). Assuming

that the observed direction of opening of the oxide ring is generally characteristic of γ-oxides,* we studied the reaction of methylmagnesium iodide with tetrahydrosilvan at 200°. As a result, hexan-2-ol was obtained in 13% yield.

Thus, in the present case cleavage occurred at the bond between oxygen and the least substituted carbon atom:

$$\text{2-methyltetrahydrofuran} \xrightarrow[(\text{HOH})]{\text{CH}_3\text{MgI}} \text{CH}_3\text{CH(OH)CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

i.e., analogously to α- and β-oxides.

* Cleavage of γ-oxides by organomagnesium compounds has been described only in two isolated examples ([7],[8]).

Experimental Part

Preparation of Derivatives of 4-Methoxybut-2-en-1-ol

Into a three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel are placed 12.2 g (0.5 g-atom) of magnesium turnings, 100 ml of dry ether, and, gradually, 0.5 g-mole of the corresponding alkyl or phenyl halide mixed with 50 ml of dry ether is added. The reaction mixture is heated until the magnesium has completely dissolved. To the still uncooled solution of the Grignard reagent, 0.2 g-mole of 2,5-dimethoxy-2,5-dihydrofuran or silvane is added dropwise. If, after approximately half of the second component has been introduced, no reaction has begun, the flask is carefully warmed. After the addition of 2,5-dimethoxy-2,5-dihydrofuran (silvane) is complete, the reaction mixture is heated for a further 1 hr, cooled, and 200 ml of water and 70 ml of acetic acid solution (1 : 1) are added to it. The ether layer is separated from the aqueous layer, and the latter is extracted twice with 50-ml portions of ether.

The ether extracts are washed with solutions of sodium carbonate and sodium thiosulfate and dried over magnesium sulfate. The ether is distilled off, and the residue is fractionated in vacuum. The yields and properties of the reaction products obtained in this manner are given in Table 1.

Interaction of Tetrahydrosilvane with Methylmagnesium Iodide

To a mixture of 21 g (0.25 g-mole) of tetrahydrosilvane and 6.1 g (0.25 g-atom) of magnesium turnings, 42.6 g (0.3 g-mole) of methyl iodide is gradually added with water cooling. After the magnesium has dissolved, the reaction mixture is heated in an oil bath to 200° for 1 hour, cooled, and decomposed with dilute acetic acid. After the usual work-up, 3.3 g (13%) of hexan-2-ol is isolated, b.p. 135–140°; n_D^{20} 1.4250. After repeated distillation it had b.p. 130–139°; n_D^{20} 1.4200

(literature data [9]: b.p. 136–139°; n_D^{18} 1.4190), and gave a 3,5-dinitrobenzoate with m.p. 37–38° (literature data [9]: 38.5°).

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Note: Figure translations are in progress. See original paper for figures.