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SYNTHESIS AND REARRANGEMENT OF PHENYL ETHERS OF 5,6-DIHYDROPYRANS

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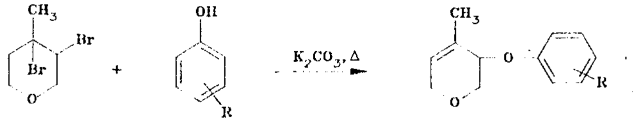
4-Methyl-5-phenoxy-5,6-dihydropyrans were synthesized by the reaction of 3,4-dibromo-4-methyltetrahydropyran with a number of substituted phenols. The products are converted to the corresponding phenols under the conditions of the Claisen rearrangement.

3,4-Dibromo-4-methyltetrahydropyran (I), which is readily formed in the bromination of a side product in the synthesis of isoprene, viz., 4-methyl-5,6-dihydropyran, is a potentially valuable intermediate for organic synthesis. The first research devoted to this topic was published by Gevorkyan and co-workers [1]. They synthesized a number of amines starting from the dibromide.

We have studied the reaction of I with phenol and its alkyl, nitro, and halo derivatives.

We found that dehydrobromination of the tertiary bromine atom and substitution of the secondary bromine atom to give the corresponding phenyl ethers (II) occur when the dibromide is heated with phenols in methyl ethyl ketone in the presence of potassium carbonate (Table 1):



I

II a-e

II a R=H, b R=p-NO_2, c R=o-Cl, d R=p-I, e R=2.6-CH_3

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	bp [mp], °C (mm)	n_D^{20}	IR spectrum, ν_{OH}, cm^{-1}	PMR spectrum, δ, ppm	Found, %		Empirical formula	Calc., %		Yield, %
					C	H		C	H	
IIa	113—114 (1—3)	1,5380		1,75 (3H, s, CH_3); 3,75—4,25 (5H, m, CH, CH_2—O—CH_2); 5,6 (1H, m CH=C); 6,62—7,0 (5H, m, Ar)	75,3	7,7	$C_{12}H_{14}O_2$	75,7	7,4	67
IIb	153—154 (1—3)	1,5652		1,70 (3H, s, CH_3); 3,88—4,75 (5H, m, CH, CH_2—O—CH_2); 5,62 (1H, m, CH=C); 6,5—8,0 (4H, m, Ar)	61,6	6,0	$C_{12}H_{13}NO_4$	61,3	5,6	63
IIc	123—125 (3)	1,5574		1,72 (3H, s, CH_3); 3,80— 4,5 (5H, m, CH, CH_2—O—CH_2); 5,5 (1H, m, CH=C); 6,6—7,25 (4H, m, Ar)	64,6	5,4	$C_{12}H_{13}ClO_2$	64,1	5,8	74
IId	178 [65] (1)	—		1,75 (3H, s, CH_3); 3,62—4,37 (5H, m, CH, CH_2—O—CH_2); 5,62 (1H, m, CH=C); 6,65—7,5 (4H, m, Ar)	41,8	3,7	$C_{12}H_{13}IO_2$	41,4	3,8	50
IIe	120—123 (1—3)	1,5415		1,78 (3H, s, CH_3); 2,25 (6H, s, CH_3—Ar); 3,01—4,15 (5H, m, CH, CH_2—O—CH_2); 5,5 (1H, m, CH=C); 6,75 (3H, m, Ar)	77,3	7,9	$C_{14}H_{18}O_2$	77,0	8,3	35
IIIa	109 (1—3)	1,5539	3330	1,73 (3H, s, CH_3); 3,80—4,50 (6H, m, OH, CH, CH_2—O—CH_2); 5,6 (1H, m, CH=C); 6,62—7,0 (4H, m, Ar)	76,2	7,0	$C_{12}H_{14}O_2$	75,8	7,4	65
IIIb	160 (1—3)	1,5860	3220	1,72 (3H, s, CH_3); 3,60—4,75 (6H, m, OH, CH, CH_2—O—CH_2); 5,6 (1H, m, CH=C); 6,62—7,0 (4H, m, Ar)	61,8	5,9	$C_{12}H_{13}NO_4$	61,3	5,6	80
IIIc	137 [73] (1—3)	—	3510	1,68 (3H, s, 3H); 3,55—4,60 (6H, m, OH, CH, CH_2—O—CH_2); 5,65 (1H, m, CH=C); 6,75 (3H, m, Ar)	63,8	5,4	$C_{12}H_{13}ClO_2$	64,1	5,8	75
IIId	150 (1—3)	1,5712	3560	1,68 (3H, s, CH_3); 3,58—4,65 (6H, m, OH, CH, CH_2—O—CH_2); 5,72 (1H, m, CH=C); 6,49—7,30 (3H, m, Ar)	41,6	3,5	$C_{12}H_{13}IO_2$	41,4	3,8	60
IIIe	145 [134] (1—3)	—	3520	1,47 (3H, s, CH_3); 2,13 (6H, s, CH_3—Ar); 2,47 (1H, m, CH); 3,5—4,1 (4H, m, CH_2—O—CH_2); 5,58 (1H, m, CH=C); 6,73 (2H, m, Ar); 8,0 (1H, s, OH)	77,5	7,9	$C_{14}H_{18}O_2$	77,0	8,3	60

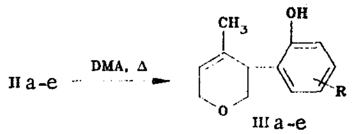
trans-Diaxial elimination of HBr evidentally precedes substitution for a phenoxy group; this is confirmed by the absence of other isomeric olefins in the reaction mixture [according to gas–liquid chromatography (GLC)].

It is apparent from the data presented in Table 1 that an ether of the dihydropyran series is formed in lowest yield when 2,6-dimethylphenol is used. In all likelihood, this is the result of steric hindrance created by the two methyl groups adjacent to the hydroxy group.

The structures of the synthesized ethers were proved by spectral methods. Signals of protons of CH_3 groups (1.70-1.75 ppm, 3H), the CH_2–O–CH_2 grouping, the pyran ring CH proton (3.75-4.7 ppm, 5H), the CH=C proton (5.5-5.7 ppm, 1H), and the aromatic ring (6.62-7.0 ppm, 5H) are present in the PMR spectra. The IR spectra contained two absorption bands at 1060-1080 and 1220 cm^{-1}, which are due to participation in the vibration of two polar C–O–C bonds, and a band at 1680 cm^{-1}, which is characteristic for the vibration of a trisubstituted double bond [2].

It is well known that allyl aryl ethers are capable of undergoing the Claisen rearrangement to the corresponding phenols [2]. The phenyl ethers that we synthesized have an allylic structure; however, there is no information whatsoever in the literature regarding the possibility of the rearrangement of such compounds.

We have established that the corresponding phenols of the dihydropyran series (Table 1) are formed in good yields (65-80%) when IIa-e are refluxed in N,N-dimethyl(butyl)aniline for 4-5 h:



The introduction of a catalyst ($ZnCl_2$) into the rearrangment process and the use of different solvents (o-xylene, nitrobenzene) do not lead to an increase in the yields of the phenols. Moreover, the presence of a Lewis acid gives rise to pronounced resinification. According to the results of GLC, two other compounds are present in the reaction mixture, in addition to the principal product; however, in view of the small amounts, we were unable to isolate and identify them.

According to the data in [4], the thermal rearrangement of allyl aryl ethers proceeds primarily in the ortho position, and the presence of an alkyl substituent attached to the β carbon atom of the allyl group does not cause any complications. Ethers IIa-b undergo rearrangement to phenols with the formation of the ortho isomers (GLC), whereas ether II gives the para isomer because of the absence of unsubstituted ortho positions.

The structures of the compounds obtained were proved by physicochemical methods. An intense absorption band of an OH group is present at 3000-3600 cm^{-1} in the IR spectra of IIIa-e. Four groups of signals are observed in the PMR spectrum of IIIa: for the methyl protons (1.73 ppm, CH_3, s), the hydroxy, methylidyne, and methylene protons of the pyran ring (3.80-4.30 ppm, 6H, m), the proton attached to the CH=C double bond (5.6 ppm, m), and the aromatic ring (6.62-7.0 ppm, 4H).

The signal of the proton of the OH group in the PMR spectrum was identified by deuterium exchange. The presence of a hydroxy group was also proved by qualitative reactions: IIIa-e are quite soluble in 20% alkali solution and give a qualitative reaction with $FeCl_3$.

EXPERIMENTAL

The IR spectra of thin layers or solutions of the compounds in CCl_4 were obtained with a UR-20 spectrometer. The PMR spectra of solutions in CCl_4 and $CDCl_3$ were obtained with a Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard.

Analysis by GLC was carried out with an LKhMD chromatograph with a 300 by 0.3 cm column packed with 10% SE-30 on Chromosorb W with helium as the carrier gas.

3,4-Dibromo-4-methyltetrahydropyran (I) was synthesized by the method in [1].

4-Methyl-5-phenoxy-5,6-dihydropyran (IIa). A mixture of 12.9 g (50 mmoles) of I, 4.7 g (50 mmoles) of phenol, and 13.8 g (100 mmoles) of potassium carbonate in 50 ml of methyl

ethyl ketone was refluxed for 20 h. It was then cooled, and the resulting precipitate was removed by filtration and washed with ether. The combined filtrate was treated with 10% alkali solution, and the organic layer was separated and dried over K_2CO_3. The ether and methyl ethyl ketone were removed by distillation, and the product was isolated by fractionation in vacuo (Table 1).

Compounds IIb-e were similarly obtained.

4-Methyl-5-(o-hydroxyphenyl)-5,6-dihydropyran (IIIa). A 4.75-g (25 mmoles) sample of IIa was heated in 30 ml of N,N-dimethylaniline to 170°C and maintained at this temperature for 4 h. The mixture was then cooled and subjected to fractional distillation *in vacuo*, as a result of which, dimethylaniline and product IIIa were isolated.

Compounds IIIb-e were similarly obtained (Table 1).

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REACTIONS INVOLVING SHIFTING OF THE DOUBLE BOND IN CYCLIC ETHERS

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4-Methylenetetrahydropyran undergoes isomerization to 4-methyl-5,6-dihydropyran in the presence of sodium on aluminum oxide. Both pyrans are converted to a vinyl ether, viz., 4-methyl-2,3-dihydropyran, under the influence of iron pentacarbonyl.

The isomerization of olefins with shifting of the double bond is a rather widespread reaction that is often used in synthetic organic chemistry. However, there are not many examples of this sort in the six-membered cyclic ether series. In the present research we examined the known reactions involving shifting of the double bond as applied to some dihydro- and 4-methylenetetrahydropyrans.

The conversion of 4-methyl-5,6-dihydropyran (I), when it is passed over CaO at 250-350°C, is very slight, and the expected vinyl ether, viz., 4-methyl-2,3-dihydropyran (II), is formed in trace amounts. The conversion of dihydropyran I increases when the temperature is raised (450-500°C), but this is due mainly to thermal cracking to give isoprene and formaldehyde.

Examples of the successful use of potassium tert-butoxide as a catalyst for the isomerization of dihydrofurans [1] and 2-alkyl-5,6-dihydropyrans [2] are known. However, the reaction of this alkoxide with dihydropyran I and 4-methylenetetrahydropryan (III) under conditions close to those described in [2] was accompanied by pronounced resinification, and the yield of II in both cases did not exceed 3%, although a high degree of conversion of the ethers (72-100%) was achieved. The introduction of dimethyl sulfoxide (DMSO), which usually promotes shifting of the double bond as a consequence of an increase in the basicity of the catalyst, also did not give the desired results. Judging from the data in [2], the presence of 2R-substituents, upon the whole, promotes isomerization; the formation of both 3,6- and

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