2. Allylmorpholine is not an intermediate reaction product, and the formation of it and (2,3-dimethylenebutyl)morpholine occurs as a result of parallel reactions.

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SOME REACTIONS OF 4-METHYL-5,6-DIHYDROPYRAN AND ITS ISOMERS

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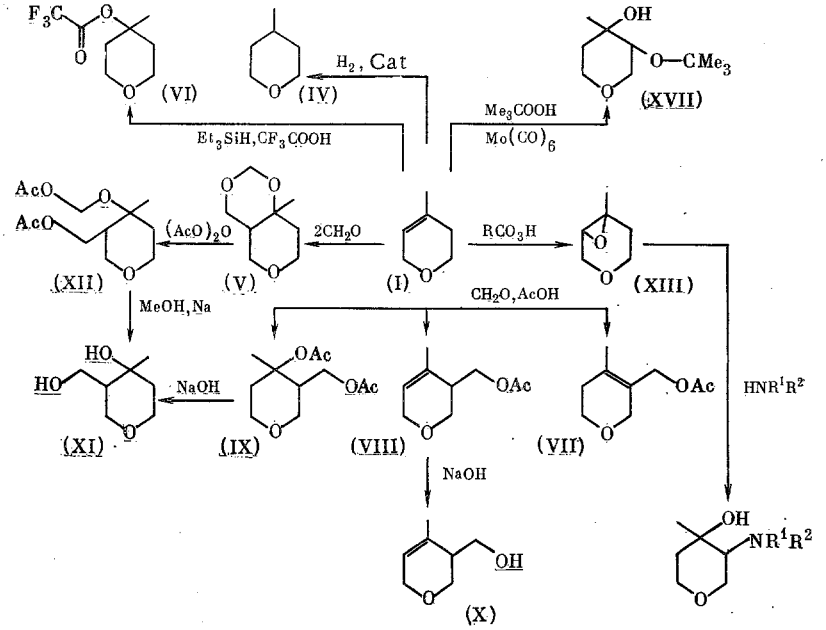
In the present work we studied some reactions of 4-methyl-5,6-dihydropyran (I) and 4-methylenetetrahydropyran (II), which are side products in the industrial synthesis of isoprene from isobutylene and formaldehyde [1], and of 2-methyl-5,6-dihydropyran (III), and also the transformations of pyrans formed in these reactions. For pyran (I), the reactions studied are indicated in the following scheme:



The behavior of (I) in an H_2 atmosphere in the presence of Pd, Pt, and Ni—Cr catalysts was studied at temperatures varying from 120-305°C, and at feedstock space velocities of 0.6-1.5 h^{-1}. The main product of hydrogenation over palladium (GIPKh-108) and nickel—chromium (Ni/Cr_2O_3) catalysts is 4-methyltetrahydropyran (IV). A quantitative yield of the product is attained, depending on the feeding rate of (I) in the range of 120-180°C. At 200°C and above, the amount of normal and isoalkanes (n-hexane, 2- and 3-methylpentanes), identified by GLC, increased. Platinum catalysts (AP-64 and AP-15) cause cleavage of the pyran

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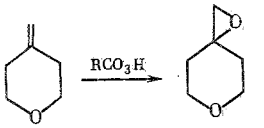
ring, and the transformation of (I) into gaseous products probably lower alkanes. Compound (I) also partially isomerizes (10-12%) into (II). Unsaturated cyclic ethers were found to be more inert to the ionic hydrogenation reached by the triethylsilane—CF_3COOH system than alkenes and cycloalkenes [2]. Thus, hydrogenation of (I) takes place only at 70°C and with a 2-5-fold excess of CF_3COOH to give (IV) in a yield at 65%. At 50°C, (I) remains practically unchanged, and at 60°C it is transformed mainly into 4-methyl-4-trifluoroacetoxytetrahydropyran (VI). At 80-90°C, strong resinification is observed, which is apparently explained by polymerization of (I), initiated by the intermediate carbonium ion. In all cases the reaction is accompanied by the formation of triethylsiloxane (12%).

During the reaction of (I) with formaldehyde in AcOH, the isomeric 3-acetoxymethyl-4-methyl-5,6 (VII) and 3,6-dihydropyrans (VIII) are formed as the main products in a ratio of 3:4, as well as 3-acetoxymethyl-4-methyl-4-acetoxytetrahydropyran (IX).

By saponification of (VIII) and (IX) with an aqueous-alcoholic solution of alkali, 3-hydroxymethyl-4-methyl-3,6-dihydropyran (X) and 3-hydroxymethyl-4-methyl-4-hydroxytetrahydropyran (XI) were obtained. The diol (XI) was also synthesized from cis-10-methyl-1,3,7-trioxadecalin, obtained from (I) by a Prins reaction via 3-acetoxymethyl-4-methyl-4-acetoxymethyloxatetrahydropyran (XII). The identical structure of the diol samples obtained from (IX) and (XII) was confirmed by their identical physicochemical properties and by GLC and PMR data; it was found that these reactions proceed with complete retention of the cis-configuration.

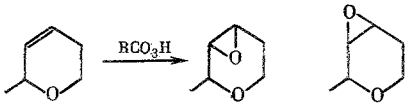
The epoxidation of the pyran compounds aroused the interest of research workers mostly because of its unique synthetic possibilities due to the high reactivity of the α-oxide ring. The known data are mainly on the cyclic vinyl ethers [3], while only separate reports are available on 5,6-dihydropyrans [4].

We studied the behavior of (I)-(III) under the conditions of the Prilezhaev reaction. As the oxidizing agents (RCO_3H), we used monoperphthalic (MPPA) and perbenzoic (PBA) acids. We found that the rate of the reaction is determined by the structure of the initial pyran and the nature of the solvent. Better results were obtained in the epoxidation of (I) and (III) in a chloroform medium. It is important to note that the reaction of MPPA and PBA with (I) and (II) proceeds exclusively as an α-attack on the double bond and leads to oxides (XIII) (see scheme) and (XIV) only:



(II) (XIV)

In the oxidation of (III) a mixture of epimeric α-oxides (XV) and (XVI) is obtained in the ratio of 87:13:



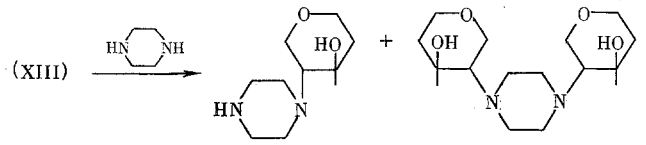
(III) (XV) (XVI)

This means that even inappreciable steric hindrances produced by the CH_3 group in (III) cause a high stereodirectivity of the reaction, i.e., an α-attack on the oxidizing agent preferentially proceeds from the side opposite the substituent.

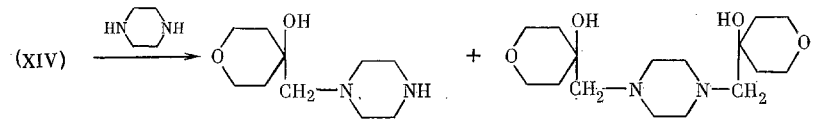
During the epoxidation of (I) in the tert-butyl hydroperoxide—$Mo(CO)_6$ system, the α-oxide ring opens and 4-methyl-3-tert-butoxytetrahydropyran-4-ol (XVII) is formed.

As has already been shown [4], by the action of aqueous solution of amines or ammonia, epoxides such as those discussed above are transformed into the corresponding aminopyranols, with the opening of the oxide ring proceeding strictly according to the Krasuski rule, i.e., at the least substituted C-atom. It was shown that this rule also holds when a series of oxides (XIII) and (XIV) is treated with aqueous solutions of secondary acyclic and cyclic amines.

In the reaction of (XIII) and (XIV) with piperazine, not only 4-methyl-3-piperazinotetrahydropyran-4-ol (XVIII) and 4-piperazinomethyltetrahydropyran-4-ol (XIX), but also the bis-adducts (XX) and (XXI) are formed.



(XVIII) (XX)

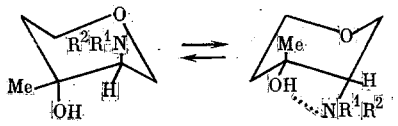


(XXI)

The presence of the individual aminopyranols obtained was confirmed by TLC and their structure was proved by IR and PMR spectra and by chemical transformations.

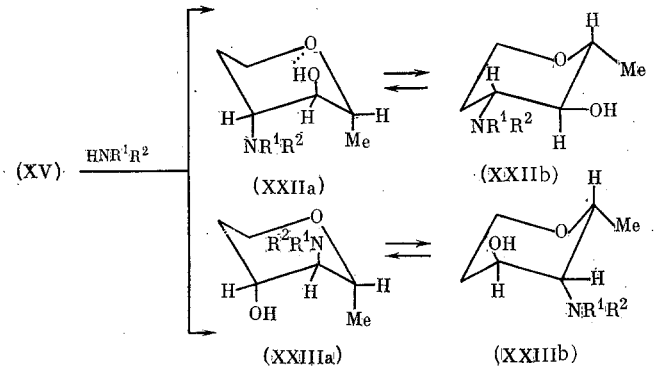
The opening of the oxide ring by nucleophilic reagents proceeds according to the Furst–Plattner rule, i.e., trans-diaxially, and the position of the hydroxyl group in the reaction product is determined by the position of the epoxide ring in the initial compound. The direction of the introduction of the amino group depends mainly on the steric structure of the epoxide.

According to the spectra, the initially formed products with a trans-diaxial configuration of the amine and hydroxyl groups undergo complete inversion in solution:



This is indicated by the presence in the IR spectra of an intense absorption band in the 3450-3500 cm^{-1} region of the stretching vibrations of the hydroxyl group, bound to nitrogen by an intramolecular bond.

In the reactions of (XV) with amines, we might expect that 2-methyl-4-aminotetrahydropyran-3-ols and 2-methyl-3-aminotetrahydropyran-4-ols, or mixtures of compounds (XXIIa,b) and (XXIIIa,b) are formed



(XXIIa) (XXIIb)

(XXIIIa) (XXIIIb)

By using TLC it was confirmed that the reaction studied is regioselective in character, and leads preferentially to one of the possible products. In the IR spectrum of a dilute solution, there are absorption bands in the 3250-3500 cm^{-1} region characteristic of the stretching vibrations of the hydroxyl group, intramolecularly bound to oxygen by a hydrogen bond. The occurrence of this bond is possible only in the case of structure (XXIIa). The results agree well with the data of [5] on the study of the regularities of oxide ring opening of trans-2-ethoxy-3,5-epoxytetrahydropyran.

2-Methyl-4-aminotetrahydropyran-3-ols, which are syrup-like liquids, were identified as hydrochlorides. For 4-methyl-3-piperidinotetrahydropyran-4-ol, p-nitrobenzoate (XXIV) was obtained. All the aminopyranols and their hydrochlorides are readily soluble in water and in organic solvents.

EXPERIMENTAL

The IR spectra were recorded on the UR-20 apparatus in a thin film or in the form of a suspension in mineral oil and in CCl_4 solutions, and the PMR spectra on the Tesla BS-487C apparatus with working frequency of 80 MHz in a CCl_4 solution.

Catalytic Reduction of 4-Methyl-5,6-dihydropyran (I). The hydrogenation was carried out in a quartz flow-type reactor (450 × 40 mm) with a stationary layer of the catalyst placed in a tubular-type electrical furnace, in a continuous H_2 current (60 ml/min). Before the experiments, the catalysts were activated at 450-500°C for 2 h in an H_2 current. The reaction products were analyzed by GLC with an internal standard (n-nonane) on an apparatus with a heat conductivity detector (2000 × 4 mm, H_2 40-45 ml/min, 130°C, 15% Carbowax-6000 on Chezasorb AW-HMDS).

Ionic Hydrogenation of (I). A 9-ml portion (0.081 mole) of (I) was added with stirring to a solution of 9.4 g (0.081 mole) of triethylsilane in 25 ml (0.0405 mole) of CF_3COOH. The temperature increased to 40°C, and the reaction mixture turned red and became homogeneous. The mixture was held for 50 h at 70°C, and then washed with water, neutralized with sodium carbonate solution, dried over $MgSO_4$, and distilled to yield 5.3 g (65%) of 4-methyltetrahydropyran (IV), bp 105-106°C, n_D^{20} 1.4220; 5.1 g (15%) of triethylsiloxane, bp 122-124°C (26 mm), n_D^{20} 1.4370; and 3.5 g (20%) of 4-methyl-4-trifluoroacetoxytetrahydropyran (VI), bp 75-77°C (13 mm), n_D^{20} 1.3895. Found: C 60.45; H 9.55%. $C_8H_{11}F_3O_3$. Calculated: C 60.37; H 9.43%. IR spectrum (ν, cm^{-1}): 1780 (C=O), 1130 (CO), 1230, 1170 (CF). PMR spectrum (δ, ppm): 1.25 s (CH_3), 3.5-3.8 t ($2H_2$ and $6H_2$), 1.5-1.65 q ($3H_2$ and $5H_2$).

Synthesis of 3-Acetoxymethyl-4-methyl-4-acetoxytetrahydropyran (IX), 3-acetoxymethyl-4-methyl-5,6- (VII), and 3,6-dihydropyrans (VIII). A 98-g portion (1.0 mole) of (I) was added rapidly, with stirring and cooling, to a mixture of 40 g (1.3 mole) of paraform, 250 ml (4.4 mole) of glacial AcOH, and 22 ml (0.4 mole) of concentrated H_2SO_4. The reaction mixture was stirred for 2 h at 20°C and for 2 h at 40°C, and then neutralized with $NaHCO_3$ solution and extracted by a mixture of ether and hexane 1:1. After removal of solvents, the residue was distilled. According to GLC data, the first fraction (20 g) contained two products in the ratio of 3:4, and the second (10 g) a pure pyran (IX), bp 125-126°C (2 mm), n_D^{20} 1.4682. PMR spectrum of (IX) (δ, ppm): 1.18 s ($4CH_3$), 1.98 s (OCH_3), 1.59 t ($5H_2$), 1.8 sextet (3H), 3.20-4.43 m ($2H_2$, $6H_2$ and CH_2O). By oft-repeated distillation of the first fraction, compound (VIII) was isolated, bp 67-71°C (21 mm), n_D^{20} 1.4660, in whose PMR spectrum the $4CH_3$ group is observed at 1.69 ppm, and 5H at 1.6 ppm. The formation of compound (VII) was confirmed by the presence in the PMR spectrum of the mixture of signals at 1.28 ppm (CH_3) and 1.5 ppm (5H) together with the signals corresponding to (VIII). The CH_3 group of the acetyl resonates at 1.81 ppm for the two isomers.

Saponification of Acetates (VII) and (VIII). The reaction was carried out by the usual method by boiling the acetates in an aqueous-alcoholic solution 1:1 of an alkali (4 h). By oft-repeated distillation of the saponification products in vacuo, compound (X), bp 71-73°C (4 mm), n_D^{20} 1.4838, was isolated. PMR spectrum (δ, ppm): 1.65 d ($4CH_3$), 2.94 (OH), 3.31-4.06 m ($2H_2$, $6H_2$ and CH_2O), 5.4 sextet (5H), 1.6 m (3H). Similarly, from (IX), compound (XI), bp 141-142°C (4 mm), n_D^{20} 1.4859, was obtained.

Synthesis of (XI) and (XII) from cis-10-methyl-1,3,7-trioxadecalin (V). A mixture of 32 ml (0.3 mole) of Ac_2O and 0.03 ml (0.6 mole) of concentrated H_2SO_4 was added with vigorous stirring to 33.6 g (0.2 mole) of decalin [6]. The reaction mixture turned dark and heated up to 32°C. The mixture was then heated for 1.5 h on a boiling-water bath, neutralized by $NaHCO_3$, filtered, and successively distilled in the vacuum of a water jet and oil pump to yield 32 g (62%) of 3-acetoxymethyl-4-methyl-4-acetoxymethyloxatetrahydropyran (XII), bp 202-204°C (10 mm), n_D^{20} 1.4626. PMR spectrum (δ, ppm): 1.33 s (CH_3), 1.98 s (CH_3 of ester group), 1.55 q (3H), 1.68 t and 1.9 t ($5H_2$), 3.53 t and 3.73 t ($6H_2$), 3.78 q and 4.2 sextet ($2H_2$), 5.25 s (CH_2O).

A 20-g portion (0.08 mole) of (XII) was added to 0.08 g (2 mmoles) of sodium dissolved in 40 ml of MeOH, and the mixture was heated on a water bath, with distillation of the methyl acetate formed as an azeotrope with MeOH by means of a full reflux distillation head. At the end of the reaction, the residue was neutralized with a calculated amount of AcOH, and distilled in vacuo to yield 6.2 g (60%) of diol (XI) with properties and PMR spectrum identical to those of (XI) obtained from (IX).

TABLE 1. Aminopyranols and Their Hydrochlorides

Compound	Yield, %	mp, °C (solvent)	Empirical formula	Found / Calculated, % C	H	N	Cl	IR spectrum (ν, cm^{-1})	PMR spectrum (δ, ppm)
4-Methyl-3-dimethylamino-tetrahydropyran-4-ol	80	165 (isoamyl alcohol)	$C_8H_{17}NO_2$	60,21 60,38	10,58 10,69	8,61 8,80		3500 (OH...N)	1,5 s ($4CH_3$), 1,75 t ($5H_2$), 2,65 s (CH_3), 3,71 d.d ($6H_2$), 4,1 d ($2H_a$), 5,6 s (OH)
Its hydrochloride	85	160–162	$C_8H_{18}ClNO_2$	49,10 49,05	9,17 9,21	7,21 7,16	18,30 18,16		
4-Methyl-3-piperidinotetra-hydropyran-4-ol	97	89 (petr. ether)	$C_{11}H_{21}NO_2$	66,22 66,33	10,45 10,55	6,98 7,03		3450 (OH...N)	1,2 s (CH_3), 1,5 t ($5H_2$), 2,1–2,95 m (4H of piperidine), 1,5–1,75 m (6H of piperidine) 3,1 s (OH), 3,87 d ($2H_a$), 3,92 d ($2H_e$), 3,62 d.d ($6H_2$)
4-Methyl-3-morpholino-tetrahydropyran-4-ol	53	104 (petr. ether)	$C_{10}H_{19}NO_3$	59,45 59,70	9,24 9,45	6,75 6,96		3500 (OH...N)	1,1 s (CH_3), 1,56 d.d ($5H_2$), 2,3–2,8 m (8H), 3,25 s (OH), 3,5 t ($6H_2$), 3,75 d ($2H_a$), 3,87 d ($2H_e$)
Its hydrochloride	89	188–189	$C_{10}H_{20}ClNO_3$	50,48 50,53	8,37 8,42	5,75 5,89	14,90 14,95		
N,N'-Bis(4-hydroxy-4-methyl-tetrahydropyranyl)piperazine	1,2	>250	$C_{16}H_{30}N_2O_4$	61,07 61,14	9,62 9,55	8,84 8,90			
4-Dimethylaminomethyl-tetrahydropyran-4-ol	10	169–170 (isoamyl alcohol)	$C_8H_{17}NO_2$	60,31 60,38	10,72 10,69	8,82 8,80		3250 (OH)	
4-Methyl-3-piperazinotetra-hydropyran-4-ol	54	123–124 (benzene)	$C_{10}H_{20}N_2O_2$	59,87 60,00	9,89 10,00	13,92 14,00		3300 (NH) 3460 (OH...N)	1,2 s ($2H_3$), 1,56 d.d ($5H_2$), 2,3 (NH), 2,5 s (OH), 2,7–2,75 m (8H), 3,69 t (3H), 3,37 t ($6H_2$), 3,93 d.d ($2H_2$)
Its hydrochloride	94	192–193	$C_{10}H_{21}ClN_2O_2$	50,71 50,74	8,82 8,88	11,76 11,84	15,10 15,01		
4-Piperidinomethyltetra-hydropyran-4-ol	55	76–77 (petr. ether)	$C_{11}H_{21}NO_2$	65,78 66,38	10,35 10,55	6,61 7,03		3250 (OH) 3400 (OH...N)	1,6–2,0 m (6H), 2,43 s ($-CH_2-$), 2,62–2,85 m (4H), 3,8 m ($2H_2$+$6H_2$), 4,15 s (OH)
4-Piperazinomethyltetra-hydropyran-4-ol	86	154–155 (ethanol)	$C_{10}H_{20}N_2O_2$	59,85 60,00	9,85 10,00	13,92 14,00		3400 (NH) 3480 (OH...N)	2,1 s ($-CH_2-$), 5,0 s (OH), 3,0 s (8H), 2,45 (NH), 1,5 t ($5H_2$+$3H_2$), 3,6 m ($2H_2$+$6H_2$)
Its hydrochloride	82	165–166	$C_{10}H_{21}ClN_2O_2$	50,67 50,74	8,31 8,88	11,87 11,84	15,10 15,01		

TABLE 1 (continued)

Compound	Yield, %	mp, °C (solvent)	Empirical formula	Found / Calculated, %				IR spectrum (ν, cm^{-1})	PMR spectrum (δ, ppm)
				C	H	N	Cl		
N,N'-Bis(4-hydroxytetrahydropyranomethyl)piperazine	12	>250	$C_{16}H_{30}N_2O_4$	60.61 61,14	9,37 9,55	8,71 8,90		3560 (OH)	2,6m ($3H_4$ and $5H_4$), 2,1d ($-CH_2-$), 4,0 d.d ($2H_4$ and $6H_4$), 3,2 s (8H of piperazine), 4,0 s (OH)
4-Methyl-3-hexamethyleneiminotetrahydropyran-4-ol hydrochloride	75	167	$C_{12}H_{24}ClNO_2$	57,32 57,72	9,25 9,62	5,29 5,61	13,81 14,23		
4-Methyl-3-diethylaminotetrahydropyran-4-ol hydrochloride	16	176–177	$C_{10}H_{22}ClNO_2$	53,21 53,24	9,25 9,84	5,82 6,26	15,21 15,88	3300 (OH)	
4-Hexamethyleneiminomethyltetrahydropyran-4-ol hydrochloride	64	148	$C_{12}H_{24}ClNO_2$	57,64 57,71	9,56 9,62	5,63 5,61	14,19 14,23		
4-Morpholinomethyltetrahydropyran-4-ol hydrochloride	76	150	$C_{10}H_{20}ClNO_3$	50,46 50,53	8,37 8,42	5,93 5,89	14,90 14,95		
2-Methyl-4-piperidinotetrahydropyran-3-ol hydrochloride	54	185–186	$C_{11}H_{22}ClNO_2$	55,89 56,05	9,18 9,34	5,35 5,94	14,73 15,07		1,6 s (CH_3), 1,87 t ($5H_2$), 2,25 m (10H), 3,6 m ($6H_2$ and 2H), 3,36 s (OH)
2-Methyl-4-hexamethyleneiminotetrahydropyran-3-ol hydrochloride	39	206	$C_{12}H_{24}ClNO_2$	57,75 57,71	9,67 9,62	5,53 5,61	14,13 14,23	3250 (OH...O)	
2-Methyl-4-piperazinotetrahydropyran-3-ol hydrochloride	11	241 (decomp.)	$C_{10}H_{21}ClN_2O_2$	50,67 50,74	8,81 8,88	11,74 11,84	14,89 15,01	3250 (OH...O)	

Epoxidation of Pyrans (I)-(III). a) An ethereal solution of 0.22 mole of MPPA was added dropwise without heating, and with stirring, to a mixture of 50 ml of dry ether and 0.2 mole of pyran. The reaction mixture was stirred for another hour in the cold, and for 5-7 days at 20°C. To decompose the excess MPPA, the mixture was heated with stirring for 2-3 h. It was then neutralized with a 5% solution of sodium carbonate, the solvent was distilled, and the residue was fractionated in vacuo. The oxidation with PBA was carried out similarly in a chloroform solution for 3-5 days. From (I), 4-methyl-3,4-epoxytetrahydropyran (XIII) was obtained, bp 60°C (40 mm), n_D^{20} 1.4453, d_4^{20} 1.0272; from (II), 2-tetrahydropyranyloxypyran (XIV), bp 60°C (145 mm), n_D^{20} 1.4514, d_4^{20} 1.044. Found: C 63.28, H 8.73%. $C_6H_{10}O_2$. Calculated: C 63.16, H 8.77%. PMR spectrum (δ, ppm): 1.6 m ($3H_2$ + $5H_2$), 2.5 s (C—CH_2), 3.71 d. d ($2H_2$ + $6H_2$); from (III), 2-methyl-3,4-epoxytetrahydropyran in the form of a mixture of epimers (XV) and (XVI), bp 74°C (60 mm), n_D^{20} 1.4566, d_4^{20} 1.0394. PMR spectrum (δ, ppm): 1.25 d (CH_3), 1.87 t. d. ($5H_2$), 2.8 d (3H), 3-3.2 m ($6H_a$), 3.22 (4H), 3-3.6 m ($6H_e$), 3.7 m (2H).

b) A 15.8-g portion of tert-butyl peroxide in 10 ml of benzene was added dropwise, with stirring, to a mixture of 14.5 g of (I), 50 ml of dry benzene, and 0.196 g of $Mo(CO)_6$. The reaction mixture was then heated with simultaneous distillation of a benzene–tert-butanol azeotrope in the course of 1-1.5 h. When cool, benzene was added to the initial volume, and the azeotrope was distilled again. The operation was repeated 2-3 times. After the removal of solvent, compound (XVII) was isolated by distillation in vacuo, bp 70°C (40 mm), n_D^{20} 1.4538. PMR spectrum (δ, ppm): 2.0 m ($5H_2$), 1.25 s ($4CH_3$), 1.15 s (t-Bu), 3.25 (3H), 3.75-4.2 m ($2H_2$ + $6H_2$), 7.25 s (OH).

Synthesis of Aminopyranols from Epoxypyrans (XIII) and (XIV). A mixture of 0.02 mole of epoxypyran, 0.08-0.1 mole of secondary amine, and 2 ml of water was held for 3-5 days at 20°C. After distillation of excess of amine and water, the residue was recrystallized from a suitable solvent. The characteristic data of the compounds obtained are listed in Table 1.

Synthesis of Aminopyranol Hydrochlorides. The hydrochlorides were obtained by passing a current of dry HCl through the solution of the aminopyranol (0.2 g) in 10 ml of dry ether or chloroform until no more precipitate was formed. The precipitate was then filtered and recrystallized (Table 1).

Synthesis of 4-Methyl-3-piperidinotetrahydropyran-4-ol p-Nitrobenzoate (XXIV). A mixture of 0.5 g of aminopyranol, 3 ml of pyridine, 7 ml of petroleum ether, and 1.2 g of p-nitrobenzoyl chloride was boiled for 30 min, and the reaction product was recrystallized from petroleum ether to yield 0.52 g (60%) of (XXIV), mp 172-173°C. Found: C 62.09; H 5.96; N 7.92%. $C_{18}H_{24}N_2O_5$. Calculated: C 62.07; H 6.90; N 8.05%.

CONCLUSIONS

1. 4-Methyl-5,6-dihydropyran is quantitatively hydrogenated in the presence of Pd and Ni–Cr catalysts. Under ionic hydrogenation conditions, the yield of 4-methyltetrahydropyran does not exceed 65%.

2. In the reaction between 4-methyl-5,6-dihydropyran and CH_2O in AcOH, the acetates of the isomeric dihydropyranols and pyrandiol diacetate are formed, which on saponification give the corresponding alcohols and 3-hydroxymethyl-4-methyl-4-hydroxytetrahydropyran. This diol can also be obtained by the action of Na in MeOH on the product of acetolysis of cis-10-methyl-1,3,7-trioxadecalin. These reactions are highly stereospecific.

3. By the action of monoperphthalic and perbenzoic acids, 4-methyl-5,6-dihydro- and 4-methylenetetrahydropyrans form the corresponding epoxides. In the case of 2-methyl-5,6-dihydropyran, a mixture of epimers is obtained with the trans-isomer predominating. The hydroperoxide oxidation in the presence of $Mo(CO)_6$ is accompanied by cleavage of the α-oxide ring.

4. The reaction of the epoxides obtained with several secondary amines proceeds with a trans-diaxial cleavage of the oxide ring at the least substituted carbon atom, and the initially formed aminopyranols undergo a complete inversion.

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RADICAL ARYLATION OF N-SUBSTITUTED CARBOXYLIC ACID THIOAMIDES AND CYCLIC THIOAMIDES

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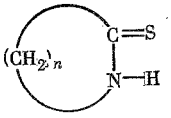
Radical arylation of the N-arylthioamides of substituted benzoic acids produces the corresponding S-phenyl-N-arylisothiobenzamides in high yields [1, 2]. With the objective of extending this reaction to other classes of thioamides, this paper reports a study of radical arylation of thioamides of the type R^1CSNHR^2 (where R^1 and R^2 are alkyl, cycloalkyl, and aralkyl groups) as well as the cyclic thioamides  ($n = 3, 4, 5$) and α-thiopyridone.

The arylation was performed according to a procedure described earlier in [1], with the use of N-nitrosoacetanilide (NAA) or phenylazotriphenylmethane (PAT) as a source of phenyl radicals. The results obtained are shown in Table 1. In the arylation of N-alkylsubstituted thiobenzamides (tests 1-6, Table 1), the corresponding S-phenylisothioamides are formed with yields of up to 70-90%. Unlike the N-arylthiobenzamides [1, 2], the reaction is accompanied in this case by the formation of diphenyl disulfide (10-15% yield). The N-substituted thioacetamides behave differently in this reaction, depending on the nature of the substituent on the N. When this is an aryl substituent, the reaction results in the corresponding S-phenylisothioanilide (test 7); when it is an alkyl or benzyl substituent, the major sulfur-bearing reaction product is diphenyl disulfide (tests 8 and 9). The formation of S-phenylisothioamides and diphenyl disulfide in these reactions indicates that the phenyl radicals add to the sulfur atom of the C=S group in all the examples studied with the formation of radical addition products according to the scheme

$$R^1-\underset{\underset{NHR^2}{|}}{C}=S + Ph^{\cdot} \rightarrow R^1-\underset{\underset{NHR^2}{|}}{\dot{C}}-SPh \qquad (1)$$

(A)

The selective or preferred formation of diphenyl disulfide in these reactions cannot be explained by the decomposition of the arylation products, the respective S-phenylisothioamides, since these substances consist of stable crystalline compounds or oils which can be distilled without decomposition (see [3]). Apparently, the formation of diphenyl disulfide is explained by fragmentation or secondary radical-addition-product (A) reactions. When R^1 and R^2 are aryl radicals, such a radical is stabilized by the α-aryl, on the one hand, and the elimination of its hydrogen in the quasibenzyl position is facilitated, on the other hand. This leads to its preferential stabilization according to Scheme (2):

$$R^1-\underset{\underset{NHR^2}{|}}{\dot{C}}-SPh \xrightarrow{X^{\cdot}} R^1-\underset{\underset{NR^2}{\|}}{C}-SPh + XH \qquad (2)$$

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