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SYNTHESIS OF SOME 3-CHROMANONE DERIVATIVES

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As shown in [1], in reaction with phenol in the presence of sulfuric acid 3,3-dimethyl-2-acetyloxirane (I) forms a mixture of products containing small amounts of 2,2,4-trimethyl-3-chromanone, the formation of which was explained by cyclization of the unisolated 4-methyl-3-hydroxy-4-phenoxy-2-pentanone.

In the present work it was possible to obtain the phenoxy ketols (II-V) required for cyclization to chromanones with satisfactory yields by the reaction of oxirane (I) with phenol and o-, m-, and p-cresols in dichloroethane solution in the presence of boron trifluoride etherate at 0-5°C. In the reaction of the above-mentioned oxirane with phenol in ether in the presence of perchloric acid the yield of the phenoxy ketol (II) amounted to only 8%. The low yields of the phenoxy ketols (II-V) were due to isomerization [2] of the oxirane (I), occurring in parallel with the main reaction and leading to the ketoaldehyde (VI), which undergoes ketone cleavage into methyl isopropyl ketone (VII) and formic acid when the reaction mixture is treated with sodium hydroxide solution to remove the excess of phenol. The ketone (VII) was identified by its 2,4-dinitrophenylhydrazone [3] by treatment of the dichloroethane, distilled from the reaction mixture, with a hydrochloric acid solution of 2,4-dinitrophenylhydrazine.

The yield of the phenoxy ketol (III) was considerably lower than that of its analogs (II, IV, V), and this was evidently due to steric hindrances created by the methyl group of o-cresol during attack by the unshared electron pair of the phenolic oxygen at the β-carbon atom of the oxirane (I).

The structures of the phenoxy ketols (II-V) were established on the basis of data from quantitative periodate oxidation of the acyloin group [4] (the content of the α-ketol amounted to 98-100%) and the IR spectra, in which there were absorption bands for the hydroxyl group combined by a hydrogen bond (3470-3480 cm^{-1}), a band for the stretching vibrations of the carbonyl group (1715-1725 cm^{-1}), bands for the vibrations of the phenyl fragment in the regions of 1600, 1500, 700, and 3050 cm^{-1}, and strong absorption bands in the region of 1230-1240 cm^{-1}, due to the asymmetric stretching vibrations of the C—O bond of the phenyl ether, and a band for the stretching vibrations of the C—OH bond of a secondary hydroxyl (1100 cm^{-1}) [5].

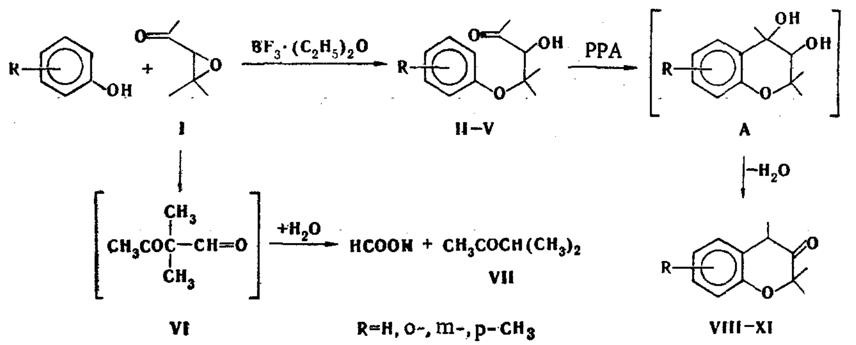

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TABLE 1. Characteristics of the Obtained Compounds

№	Compound	bp, °C (pressure, mm Hg)	n_D^{20}	d_4^{20}	Found, %		Molecular formula	Calculated		Yield, %
					C	H		C	H	
II	4-Methyl-3-hydroxy-4-phenoxy-2-pentanone	117—119 (2)	1,5080	1,0777	69,4	7,82	$C_{12}H_{16}O_3$	69,2	7,8	38
III	4-Methyl-3-hydroxy-4-o-cresyloxy-2-pentanone	120—122 (2)	1,5089	1,0652	70,2	8,1	$C_{13}H_{18}O_3$	70,3	8,1	29
IV	4-Methyl-3-hydroxy-m-cresyloxy-2-pentanone	121—123 (2)	1,5070	1,0671	70,3	8,0	$C_{13}H_{18}O_3$	70,3	8,1	42
V	4-Methyl-3-hydroxy-4-p-cresyloxy-2-pentanone	118—120 (2)	1,5075	1,0602	70,2	8,1	$C_{13}H_{18}O_3$	70,3	8,1	39
VIII	2,2,4-Trimethyl-3-chromanone	125—127 (17)	1,5195	1,0771	75,7	7,3	$C_{12}H_{14}O_2$	75,8	7,4	58
IX	2,2,4,8-Tetramethyl-3-chromanone	134—136 (17)	1,5165	1,0572	76,3	7,9	$C_{13}H_{16}O_2$	76,4	7,9	51
X	2,2,4,7-Tetramethyl-3-chromanone	135—137 (17)	1,5170	1,0567	76,5	8,0	$C_{13}H_{16}O_2$	76,4	7,8	56
XI	2,2,4,6-Tetramethyl-3-chromanone	135—137 (17)	1,5175	1,0582	76,4	7,8	$C_{13}H_{16}O_2$	76,4	7,8	63

When treated with polyphosphoric acid (PPA), the phenoxy ketols (II-V) undergo cyclization to the corresponding 3-chromanones (VIII-XI) with good yields. They are probably formed through the intermediate chromandiols (A), which readily rearrange [6] under the experimental conditions with the loss of a molecule of water to the corresponding 3-chromanones. The IR spectra of the chromanones (VIII-XI) have a strong absorption band in the region of 1733 cm^{-1}, characteristic of the stretching vibrations of the carbonyl group in 3-chromanones [7], and also a series of absorption bands for the benzene ring and a frequency in the region of 1255 cm^{-1}, due to the asymmetric vibrations of the C—O bond [5].

In the PMR spectra of the chromanones (VIII-XI) there are signals for two methyl groups at $C_{(3)}$ (δ, 1.22-1.24 and 1.34-1.36), a doublet for the methyl group at $C_{(4)}$ (1.39, J = 7.0-6.8 Hz), a quartet for the methine proton (3.43-3.46, J = 7.0-6.8 Hz), and multiplets for the aromatic protons (6.5-7.3 ppm). In the spectra of compounds (IX-XI) there is a singlet for the methyl group (1.96-2.03 ppm).

EXPERIMENTAL

The IR spectra of thin films of the samples were recorded on a UR-20 spectrophotometer. The PMR spectra were recorded on a Varian HA-100 spectrometer with carbon tetrachloride as solvent and TMS as internal standard.

The oxirane (I) was obtained by the method described in the literature [8].

4-Methyl-3-hydroxy-4-phenoxy-2-pentanones (II-V). To a solution of 0.21 mole of phenol and 2 ml of boron trifluoride etherate in 20 ml of dichloroethane, while cooling and stirring (0-5°C), we added a solution of 0.38 mole of the oxirane (I) in 0.22 mole of phenol over 25 min. The mixture was stirred for a further 15 min, and a 10% solution of sodium hydroxide was then added with cooling. The organic layer was separated, the aqueous layer was extracted with dichloroethane, and the combined extracts were washed with water and dried with sodium sulfate. After removal of the solvent the residue was distilled on a Vigreux column at reduced pressure (Table 1). By treatment of 20 ml of the distilled dichloroethane with a saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid with subsequent distillation of the dichloroethane and crystallization of the residue from alcohol we obtained methyl isopropyl ketone 2,4-dinitrophenylhydrazone; mp 118-119°C [3].

3-Chromanones (VIII-XI). To 125 g of polyphosphoric acid at 30-40°C over 30 min we added 0.1 mole of the phenoxy ketol (II-V). The reaction mixture was then diluted with 160 ml of water with cooling, and extracted with hexane. The extract was washed with water and dried with sodium sulfate. After distillation of the solvent the residue was submitted to fractional distillation on a Vigreux column at reduced pressure.

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MACROCYCLIC FORMAZANS — DERIVATIVES OF [1,11,4,5,7,8]-DIOXATETRAAZACYCLOTETRADECYNE

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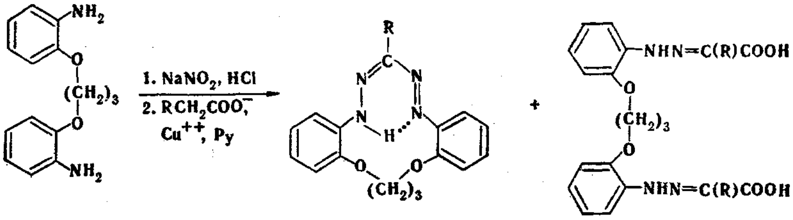
Quadridentate 14-membered macrocycles attract attention, as shown by research into the metal chelates of macrocyclic ligands of the $[N_4]$ [1-3] and $[N_2S_2]$ [4] types. In some cases these metal chelates were obtained by a condensation reaction [1, 4], and in others they were obtained by nucleophilic substitution of halogen in ortho-halogenoazoarenes [2, 3]. The free ligands were not synthesized. We have synthesized metal-free [1, 11, 4, 5, 7, 8]-dioxatetraazacyclotetradecynes of the $[N_2O_2]$ type containing the formazan group in the inner coordination contour, i.e., the so-called crown formazans. This synthesis was realized by the double azo coupling of bisdiazotized bis(2-aminophenoxy)-1,3-propane [5] with cyanoacetic, acetoacetic, or malonic acids in pyridine in the presence of copper (II) ions:



I–II a R=H; b R=$COCH_3$; c R=CN   Ia–c   IIa–c

The obtained crown formazans (Ia–c) have a chelate structure, as shown by the absence of the NH band in the IR spectra and by the presence of the NH signal in the downfield region of the PMR spectra. In the absence of copper the main products are the dihydrazones (IIa–c).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in the region of 400-800 cm^{-1} in hexachlorobutadiene and in the region of 1900-400 cm^{-1} in Vaseline oil. The PMR spectra were recorded on an XL-100-12 instrument with TMS as internal standard. The reaction products were separated by column chromatography on silica gel.

16,17-Dihydro-5H,7H,15H-dibenzo[b,i][1,11,4,5,7,8]-dioxatetraazacyclotetradecyne (Ia). A 2.58-g sample (0.01 mole) of 1,3-bis(2-aminophenoxy)propane in solution in 20 ml of water and 5 ml of concentrated hydrochloric acid at –5°C was diazotized with a solution of 1.38 g (0.02 mole) of sodium nitrite in 8 ml of water for 1 h 30 min. The filtered mixture was added dropwise with stirring to a solution of 1.04 g (0.01 mole) of malonic acid in 20 ml of water, 20 g of sodium acetate trihydrate, 200 ml of pyridine, and 1 g of copper(II) sulfate pentahydrate. The mixture was stirred at –5°C for 1 h 30 min. The reaction mass

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