SUMMARY

1. In the initial stages of the oxidation of lignin, intermediate products having spectra close to those of phenoxyl radicals with a half-transformation time $\tau_{1/2} = 0.013$ sec are formed.

2. Lignin contains groupings that are more readily oxidized than α-guaiacylpropanol.

3. The high reactivity of the intermediate products leads to a branching of the oxidation process.

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NEW DERIVATIVES OF 18-CROWN-6 CONTAINING A METHYLINDANONE FRAGMENT IN THE RING

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New derivatives of 18-crown-6 containing a methylindanone fragment in the ring have been obtained by the acylation of dibenzo-18-crown-6 with unsaturated acids in the presence of polyphosphoric acid.

We have previously developed a new method of obtaining derivatives of benzocrowns with attached side chains with the aid of acylation and alkylation reactions in the presence of polyphosphoric acid (PPA). Mono- and dicarboxylic acids were used as acylating agents, and alcohols as alkylating agents [1, 2].

In the present paper we consider the preparation of derivatives of 18-crown-6 containing a methylindanone fragment in the ring as a structural subunit. The synthesis of such compounds proved to be possible by using unsaturated acids in the acylation of dibenzo-18-crown-6.

The acylation of phenol and of anisole with methacrylic acid in the presence of $AlCl_3$ is accompanied by alkylation, i.e., ring-closure of the unsaturated ketone in the meta position, as a result of which 2-methyl-5-hydroxyindanone or the corresponding 5-methoxy compound is formed [3]. (Scheme, top, following page.)

We have performed the acylation of dibenzo-18-crown-6 with α-crotonic and methacrylic acids in the presence of PPA. In each case, the reaction took place quantitatively at 70°C in 4 h with the formation of almost identical amounts of the mono- and disubstituted derivatives. The reaction with methacrylic acid was carried out in the presence of a polymerization inhibitor – hydroquinone. The reaction products were separated by repeated column chromatography on alumina. The structures of the products isolated were shown with the aid of spectral methods (PMR, IR, and mass spectra). The disubstituted derivatives consisted of mixtures of structural isomers differing in melting points and solubility and in the form of the multiplet of the methylene protons of the macrocycle in their PMR spectra. For simplicity of discussion, we shall arbitrarily call the low-melting isomer the "trans" and the high-melting isomer the "cis" isomer, by analogy with the structures demonstrated previously for the isomers of 4',4"- and 4',5"-diacetyldibenzo-18-crown-6's [1].

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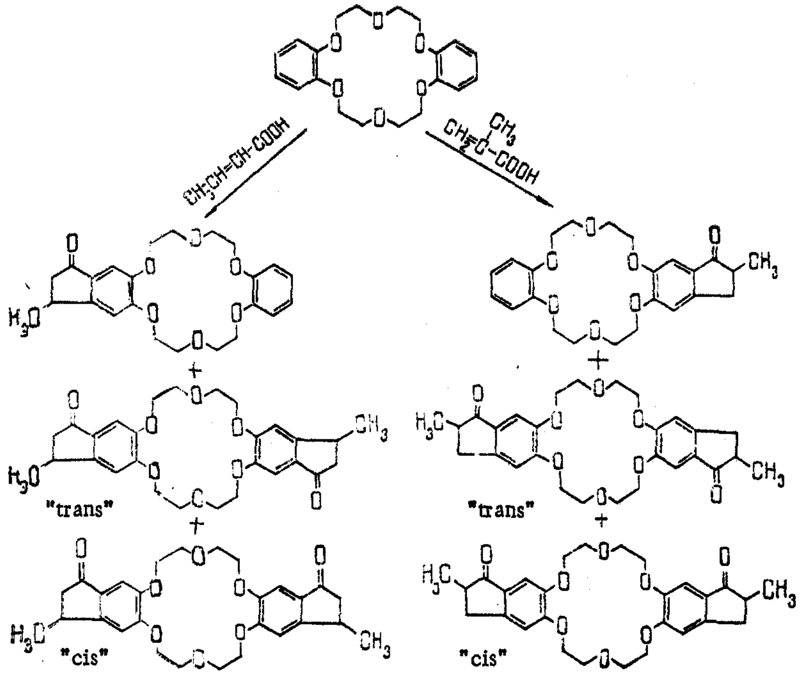

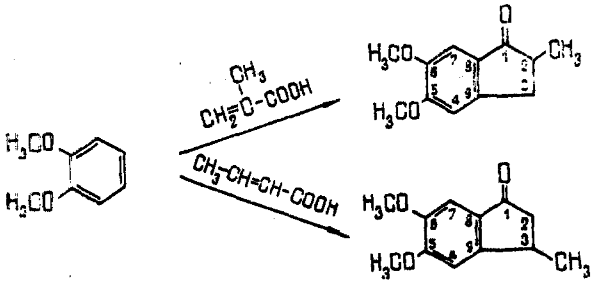

To confirm the structures of the substances obtained we synthesized model compounds: 2- and 3-methyl-5,6-dimethoxyindanones. They were obtained by acylating veratrole with methacrylic and α crotonic acids, respectively, likewise in the presence of PPA. The acylation of veratole takes place at 70-80°C but takes a longer time (12 h), and the yields of products in this process were only 70%. The performance of the reaction at 100°C shortened the reaction time (5 h) but somewhat lowered the yield of final product to ~60%.

We studied the PMR spectra of 2- and 3-methyl-5,6-dimethoxyindanones and di(2'- and 3'-methylindanono)-18-crown-6's (Fig. 1). The chemical shifts and spin-spin coupling constants are given in Table 1. For the indanone derivatives in the free state and those included in

TABLE 1. Chemical Shifts and Spin-Spin Coupling Constants of the PMR Spectra

Compound	Position of the protons						
	2	3	4	7	CH_3	OCH_3	OCH_2
2-Methyl-5,6-dimethoxyindanone	2,66	2,60; 3,27	6,77	7,08	1,23	3,83; 3,89	
Di(2'-methylindanono)-18-crown-6	2,66	2,54; 3,23	6,75	7,08	1,22		3,90—4,20
3-Methyl-5,6-dimethyoxyindanone	2,86; 2,18	3,30	6,82	7,07	1,32	3,84; 3,91	
Di(3'-methylindanono)-18-crown-6	2,84; 2,15	3,26	6,77	7,02	1,29		3,90 - 4,20

3-Methyl-5,6-dimethoxyindanone

$J_{Me-H} = 7.5\,Hz$; $J_{2-3} = 7.5\,Hz$; $J'_{2-3} = 2.5\,Hz$; $J_{gem} = -18.0\,Hz$

2-Methyl-5,6-dimethoxyindanone

$J_{Me-H} = 7.5\,Hz$; $J_{2-3} = 7.5\,Hz$ $J'_{2-3} = 4.0\,Hz$; $J_{gem} = -16.0\,Hz$

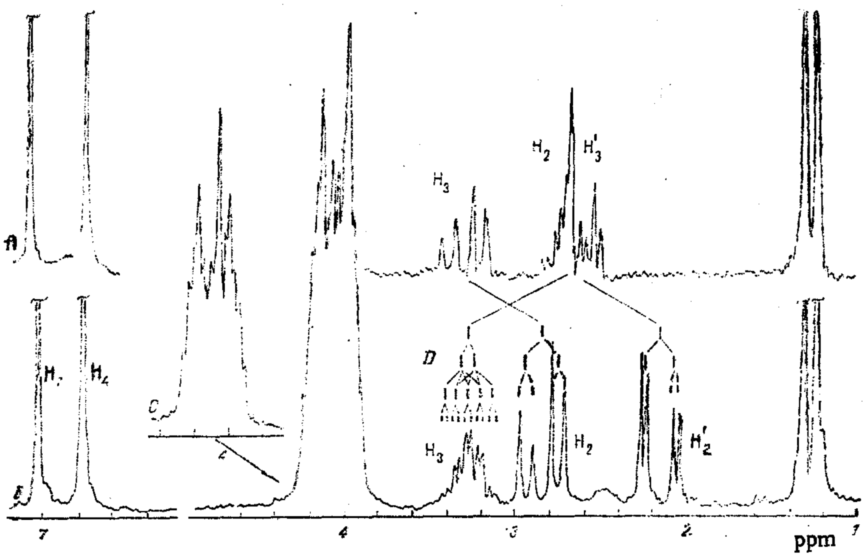

Fig. 1. PMR spectra: A) "cis"-di(2'-methylindanono)-18-crown-6; B) "cis"-di(3'-methylindanono)-18-crown-6; C) methylene protons of the macrocycle of "trans"-di(3'-methylindanono)-18-crown-6; D) scheme of splitting of the signals in spectra A and B.

the macrocycle of the crown compound, the mutual orientation of the protons, and, consequently, the conformation of the indanone rings do not change appreciably when they are included in the macrocycle. The changes in the magnitudes of the chemical shifts as the result of the fixation of the indanone fragments in the crown ether do not exceed 0.05 ppm, and the spin–spin coupling constants do not change.

A methyl group in position 2 of the indanone ring resonates at 1.23 ppm, and one in position 3 resonates at 1.32 ppm. The signal in each case appears in the form of a doublet with a spin–spin coupling constant of 7.5 Hz through interaction with the proton attached to the same carbon. The signal of the latter proton gives a multiplet of 10 lines at 2.66 and 3.30 ppm for position 2 and 3 of the methyl substituent, respectively. Two supplementary spin–spin coupling constants (7.5 and ~3 Hz) are due to interaction with the protons on the neighboring methylene group, the signals of which resonate at 3.27 and 2.60 ppm in the case of position 2 of the methyl substituent and at 2.86 and 2.18 ppm in the case of position 3. The signals of the methylene group are split by another geminal spin–spin coupling constant at 16.0 Hz for substitution in position 2 and 18.0 Hz for substitution in position 3.

The aromatic protons of the indanone ring in positions 4 and 7 resonate at 6.8 and 7.1 ppm, respectively. The downfield shift of the proton in position 7 relative to the resonance of the aromatic protons of dibenzo-18-crown-6 (6.81 ppm) [4] is due to the influence of the carbonyl group in position 1.

The methylene protons of the macrocycle form a complex multiplet in the 3.90–4.20 ppm region the structure of which cannot be deciphered. However, the form of the multiplet differs for the "cis" and "trans" isomers (the spectra of the methylene protons of the macrocycle for the isomeric di(3'-methylindanono)-18-crown-6's are shown in Fig. 1, B and C. This change in the PMR spectrum caused by the "cis/trans" isomerization of the macromolecule shows, as in the case of the 2'-methyl- and 3'-methylindanone derivatives of 18-crown-6 a spatial change in the macromolecule accompanying different types of substitution.

For the monosubstituted derivatives the spectrum of the methylindanone fragment does not change. The signals of the substituted benzene retain their chemical shifts. The protons of the unsubstituted benzene form a singlet signal at 6.81 ppm.

The structures of the compounds proposed on the basis of the results of the PMR study have been confirmed by IR and mass spectra.

EXPERIMENTAL

For general experimental information, see [1]. The PMR spectra were recorded on a Varian XL-100-15 NMR spectrometer with a working frequency for protons of 100 MHz The samples were prepared in the form of 5% solutions in deuterochloroform. To measure the chemical shifts we used an internal standard — hexamethyldisiloxane. The chemical shifts of the signals in the spin—spin coupling constants were calculated by means of the LAME program using iteration optimization.

Acylation of Dibenzo-18-crown-6 with α-Crotonic Acid. At 70°C, 3.6 g of the cyclopolyether was dissolved in 18 g of PPA, and then 3.4 g of α-crotonic acid was added, and the mixture was kept at the same temperature for 4 h. Then it was diluted with water and extracted with chloroform, and the extract was washed with saturated caustic soda solution and with water to neutrality. The solvent was driven off and the residue was separated by column chromatography in the chloroform—methylene chloride—acetone (40:1.5:1) system. In this way, 1.7 g of a fraction enriched with the monosubstituted derivative (mp 176-180°C, M^+ 428) and 2.7 g of the combined disubstituted derivatives were obtained; the disubstituted derivatives were separated after rechromatography into the "trans" isomer (mp 182-184°C, M^+ 496) and the "cis" isomer (mp 218-220°C, M^+ 496). IR (ν, cm^{-1}) 3085, 1590, 1520 (=CH) ; 2950-2885, 1270, 1130-1070 (—C—O—C—); 1690 (C=O); 880-830 (hexasubstituted benzene). The IR spectra of the following compounds was similar to those given.

Acylation of Dibenzo-18-crown-6 with Methacrylic Acid. The reaction was carried out by the method described above but in the presence of hydroquinone (10% of the weight of the acid). The chloroform—ethylene chloride (40:1.5) system was used for column chromatography. A fraction enriched with the monosubstituted derivatives (mp 198-202°C, M^+ 428) and the structural isomers of the disubstituted derivatives with mp 243-245°C (M^+ 496) and mp 263-265°C (M^+ 496) were isolated.

The acylation of veratrole with α-crotonic and methacrylic acids was carried out by the procedure described above (reaction temperatre 70-80°C, time 12 h). The reaction products were purified by column chromatography in the chloroform-hexane (35:10) system and by crystallization from hexane. Yield 74%. In the reaction with α-crotonic acid, crystals with mp 87-89°C (M^+ 206) were obtained, and in that with methacrylic acid crystals with mp 128-130°C (M^+ 206).

SUMMARY

1. The acylation of dibenzo-18-crown-6 with unsaturated acids in the presence of polyphosphoric acid has yielded new 18-crown-6 derivatives containing methylindanone fragments in the macrocycle.

2. 2- and 3-Methyl-5,6-dimethoxyindanones have been obtained by the acylation of veratrole with methacrylic and α-crotonic acids, respectively, in the presence of PPA.

3. The conformations of the indanone rings in the 2'- and 3'-methyl-5,6-dimethoxyindanones and in the di(2'- and 3'-methylindanono)-18-crown-6's do not appreciably change.

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