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Attempted Preparation of Trisphenol-II

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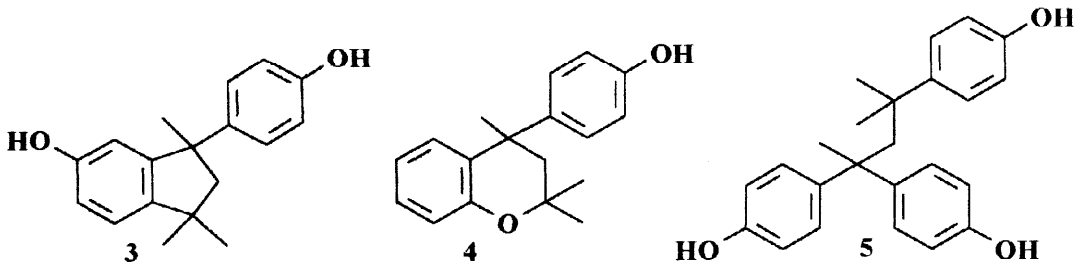
Abstract: Condensation of 4,4-bis-(4-methoxyphenyl)-2-methyl-2-pentanol with phenol, in the presence of hydrogen chloride, gives 1,3,3-trimethyl-1-(4-methoxyphenyl)-5-methoxyindan and tris-(4-methoxyphenyl)-ethane instead of expected 2,2,4-tris-(4-methoxyphenyl)-4-methylpentane (*trisphenol-II*). tris-(4-Hydroxyphenyl)-ethane was obtained, together with *bisphenol-A*, by condensation of phenol with acetylacetone.

Condensation of phenol and acetone in the presence of an acidic catalyst is the source of 2,2-bis-(4-hydroxyphenyl)-propane (**1**), commonly known as *bisphenol-A*.[1] Increasing demand for the „polycarbonate grade" product resulted in several modifications of the manufacturing process striving for decrease of the number and amount of side products. New methods of purification of crude *bisphenol-A* were developed as well as chromatographic techniques of detection, identification and determination of the impurities on the ppm level. There is also an intriguing problem of chemical nature *viz.* provenience of the by-products, especially those of more complex structure. The **1** molecule emerges as the result of electrophilic attack of 4-hydroxycumyl carbocation on phenol [2] and the same reaction path is responsible for the formation of some impurities, as the **1** isomers, *trisphenol-I* (2,4-bis-(4-hydroxycumyl)-phenol) [3] and *tetrakisphenols*.[4] There is also a group of troublesome by-products containing in their molecules the C_6 residue of mesityl oxide. This residue may form an unsaturated chain as in the dimers of 4-isopropenylphenol (**2**) or may be a part of chroman or indan systems, as shown on the scheme below.



Analogously, in the structure of 2,4,6-tris-(4-hydroxyphenyl)-2,6-dimethyl-3-heptene and 6,6'-dihydroxy-3,3,3',3'-tetramethyl-1,1'-spirobiindan,[5] the phorone residues can be easily recognised. Mesityl oxide and phorone are formed from acetone under influence of hydrogen chloride, however presumption that they are precursors of the aforementioned compounds seems to be an oversimplification.

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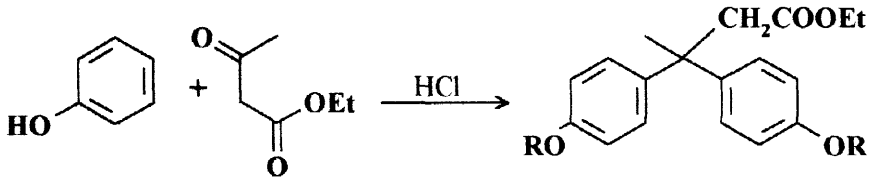
Compound **3**, known as *cyclodimer*, can be obtained from 2,4-bis-(4-hydroxyphenyl)-4-methyl-1-pentene (**2**) under influence of an acid.[6] Baker *et al.* have demonstrated that 2,2,4-trimethyl-*2H*-chromene reacts with phenol in the presence of hydrogen chloride yielding *codimer* (**4**).[7] The same reactions can accompany *bisphenol-A* synthesis, since the aforementioned intermediates have been detected in the crude product, but the way of their formation from phenol and acetone is obscure. The structures of **3** and **4** are established beyond any doubts but the third compound shown on the scheme (**5**, 2,2,4-tris-(4-hydroxyphenyl)-4-methylpentane) is a hypothetical side product, formed during condensation of phenol with acetone. Reinking and Barnabeo gave it a trivial name of *trisphenol-II* but provided no evidence of its presence in crude *bisphenol-A*.[8] Our aim was to prepare this compound and confirm its presence in commercial **1** using previously described procedure.[4]

The Pechmann reaction is the well known method of coumarins preparation but condensation of ethyl acetoacetate with phenol, in the presence of hydrogen chloride, provides ethyl 3,3-bis-(4-hydroksyphenyl)-butyrate (**6**) in moderate yield due to the partial hydrolysis of the ester group. Methylation of the phenolic function in the aqueous potassium hydroxide – dimethylsulphoxide system remains carboethoxy group intact and the products can be separated chromatographically.

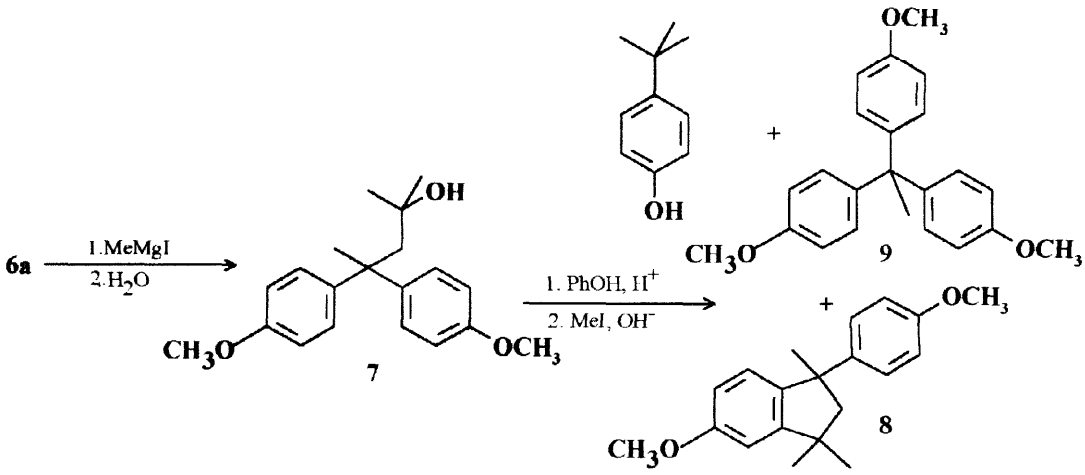


R = H (**6**) ⟶ R = Me (**6a**)

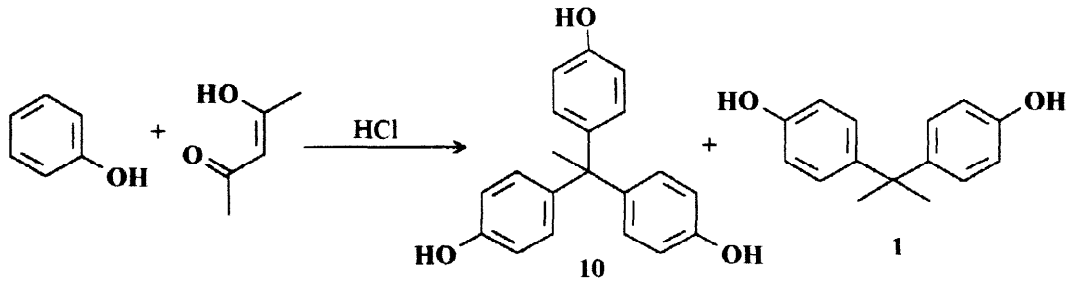
Addition of methylmagnesium iodide to the ester (**6a**), as described in,[9] gave the corresponding carbinol (**7**) which was isolated as a viscous, non-volatile liquid of 95% purity according to GC analysis. Its ^{1}H-NMR spectrum was consistent with the structure (**7**) given on the scheme below. The crude product was dissolved in an excess of phenol and saturated with gaseous hydrogen chloride. After two days at room temperature, the mixture was diluted with water, neutralised and steam – distilled. From the final fraction of the distillate, 4-t-butylphenol crystallised as long, white needles. It was identified by comparison (mixed m.p., GC, IR) with the authentic sample. The non-volatile residue was methylated with methyl iodide in the aq. KOH – DMSO system, two main products were isolated chromatographically and identified by spectroscopic methods.

The mass and NMR spectra of 6,4'-dimethoxy-1,1,3-trimethyl-3-phenylindan (**8**) and *cyclodimer* dimethyl ether (**3a**) are indistinguishable. On the other hand, **8** has higher melting point than **3a** (53 – 55°C *vs.* 43 – 44°C) and on the gas chromatogram the compounds form two separate signals so they must be isomers of closely related structures. The only peaks in the IR spectra of **3a** and **8** which do not overlap, appears in the region of planar (1089 *vs.* 1136 cm^{-1}) and out-of-plane (807, 821, 832 *vs.* 811, 828 cm^{-1}) deformations of aromatic protons hence position of MeO substituent is the only difference in their structure.

It seems self-evident that **8** is formed by the intermolecular electrophilic substitution with the intermediacy of carbocation formed from the carbinol **7**.

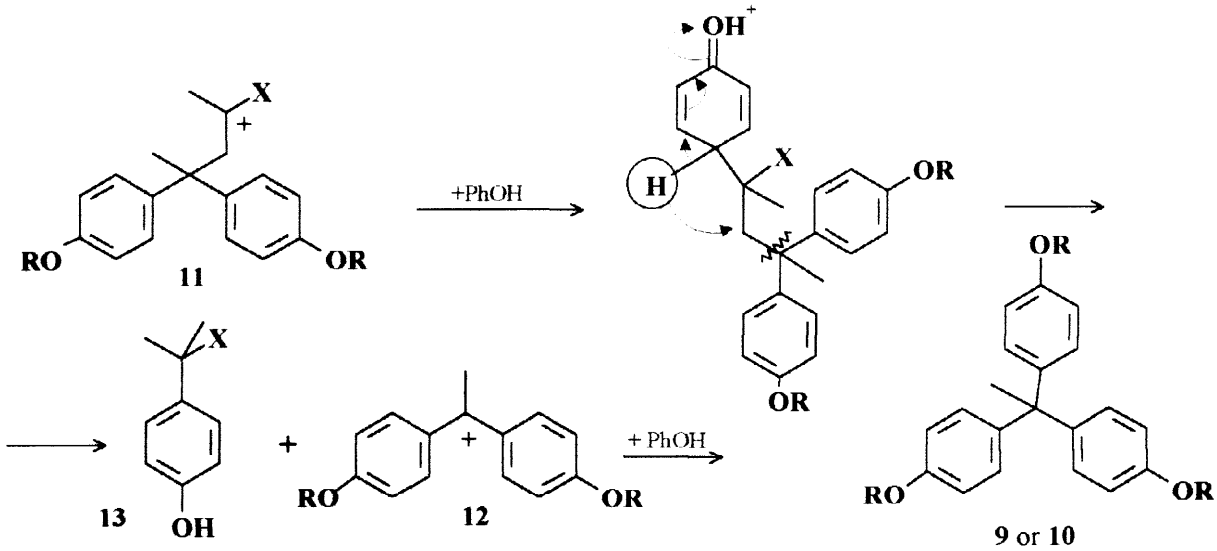


The second compound (**9**, m.p. 160 – 161°C from hexane) gives the mass spectrum (m/z 348, M^+ and m/z 333, $[M - CH_3]^+$) and elemental analysis inconsistent with the structure of **5** trimethyl ether (**5a**) or any other expected product. The NMR spectra of **9** are very simple: two doublets at 6.80 and 7.01 ppm indicate the presence of para substituted aromatic ring and two singlets at 3.78 and 2.11 ppm are characteristic of three methoxy and one methyl group. In the aliphatic region of the ^{13}C-NMR spectrum, the signals at 55.3 (O-CH_3) and 30.9 ppm (C-CH_3) are accompanied with the singlet at 50.8 ppm coming from the quaternary carbon. Consequently, the structure of 1,1,1-tris-(4-methoxyphenyl)-ethane has been assigned to this compound (**9**). Its parent phenol (**10**) we have obtained in the parallel experiment *viz.* condensation of acetylacetone with phenol in the presence of hydrogen chloride.



From the tarry, multicomponent reaction mixture two main products were isolated by the column chromatography. To our surprise, one of this compound appeared to be identical with **1** and another product was identified as 1,1,1-tris-(4-hydroxyphenyl)-ethane (m.p. 243 – 245°C from toluene). The most abundant peaks in its mass spectrum (m/z 306, 291 and 213) corresponded to the molecular ion and two daughter ions resulted from expulsion of the methyl group and one phenolic moiety. In the ^{1}H-NMR spectrum, hydroxylic protons gave the sharp singlet (in DMSO-d_6) at 9.18 ppm, two doublets (^3J = 8.5 Hz) at 6.81 and 6.63 ppm were assigned to the aromatic protons and the methyl group gave the singlet at 1.96 ppm. The signals of C-1 and C-2 appeared at 49.9 and 30.4 ppm in the ^{13}C-NMR spectrum. Methylation of **10** gave **9** in almost

quantitative yield; their identity was established using spectroscopic (IR, NMR) and chromatographic (TLC, GC) methods. Probably, the both compounds *viz.* **10** and its dimethyl ether (isolated after methylation as **9**) are formed on an analogous pathway from **11**.



This carbocation can be generated either from **7** (R = X = CH_3) or from acetylacetone by the condensation of carbonyl group with phenol as in **1** synthesis (R = H, X = OH). It attacks the phenol molecule forming a σ-complex which fragments into another carbocation **12** and phenolic molecule **13** by simple sigmatropic [1,3] shift of hydrogen atom. If X = CH_3, **13** is isolated as 4-t-butylphenol, if X = OH, 4-hydroxycumyl cation is formed and reacts with phenol yielding *bisphenol-A* as the final product. Condensation of diacetone alcohol with phenol can provide **11**, a hypothetical precursor of **5**. Since our results indicate that either ring closure or β-cleavage of **11** predominate, we suppose that **5** is not formed during *bisphenol-A* manufacturing.

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