

## SYNTHESIS AND PROPERTIES OF 2-ALKYL- AND 2,6-DIALKYL-4-ISOPROPENYLPHENOLS

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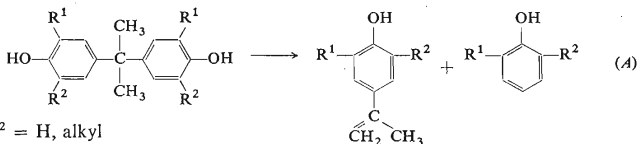
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2-Alkyl- and 2,6-dialkyl-4-isopropenylphenols were prepared by cleavage of the corresponding 4,4'-isopropylidenebisphenols, catalyzed with sodium hydroxide, sodium, or butyllithium. Reaction of hydrogen chloride with 2-methyl- and 2,6-dimethyl-4-isopropenylphenol yielded derivatives of 1,1,3-trimethyl-3-(4-hydroxyphenyl)-5-indanol. The products were characterized by the NMR, UV and IR spectra.

Condensation of alkylphenols with acetone is commonly used to prepare symmetrically alkylated 4,4'-isopropylidenebisphenols. This method, however, is not suited for the preparation of unsymmetrically alkylated 4,4'-isopropylidenebisphenols, the synthesis of which is best carried out by alkylation of phenols with 4-isopropenylphenols<sup>1,2</sup>. 4-Isopropenylphenols are formed by dehydrogenation of 4-isopropylphenols<sup>3</sup>, thermal<sup>4</sup>, acidic<sup>5,6</sup> or alkaline<sup>7</sup> cleavage of 4,4'-isopropylidenebisphenols and by the Grignard reaction from the corresponding esters. Up to now, only the parent 4-isopropenylphenol<sup>3-7</sup> and its 2-methyl\* and 3-methyl derivatives<sup>10</sup> have been described.

To prepare 2-alkyl- and 2,6-dialkyl-4-isopropenylphenols (Table I), we have used in the present work the alkaline cleavage of symmetrical 4,4'-isopropylidenebis(2-alkylphenols) and 4,4'-isopropylidenebis(2,6-dialkylphenols), performed at temperatures 100–200°C and a pressure from 2 to 50 Torr, while at the same time distilling off the product from the reaction mixture:



$\text{R}^1, \text{R}^2 = \text{H}, \text{alkyl}$

\* In the literature<sup>4</sup>, the compound is called incorrectly "4-isopropenyl-*m*-cresol" with a reference to Baker's papers<sup>8,9</sup>. In these papers, however, the heading "4-isopropenyl-*m*-cresol" is used for a description of the preparation of 3-methyl-6-isopropenylphenol *via* reaction of *m*-cresol with acetone.

With the increasing steric hindrance of hydroxyl groups of 4,4'-isopropylidenebisphenol due to alkyls the cleavage ability of sodium hydroxide decreases and sodium must be applied. A fully sterically hindered 4,4'-isopropylidenebis(2,6-ditert-butylphenol) can be cleft with butyllithium only. This parallel between cleavability and the formation of phenoxide confirms the correctness of the mechanism suggested by Schnell and Krimm<sup>11</sup>, according to which it is the formation of phenoxide that initiates the cleavage.

Owing to the difficulties presented by the preparation of 2,6-ditert-butyl-4-isopropenylphenol *via* alkaline cleavage of 4,4'-isopropylidenebis(2,6-ditert-butylphenol), other ways of preparation have been sought. Acidic cleavage of the same bisphenol with *p*-toluenesulphonic acid yielded only a mixture of tert-butylphenols and phenol. The Grignard reaction of 3,5-ditert-butyl-4-hydroxyacetophenone with methylmagnesium iodide was successful, whereas an attempt at the preparation of the 4-isopropenylphenol by the same reaction of methyl 3,5-ditert-butyl-4-hydroxybenzoate failed<sup>12</sup>.

For the identification of 4-isopropenylphenols thus prepared, catalytic hydrogenation and spectral methods were used. Similarly to 4-vinylphenol<sup>13</sup>, the benzene nucleus, too, is hydrogenated in these phenols at room temperature on platinum in glacial acetic acid, with the exception of 2,6-ditert-butyl derivative. Hydrogenation of the nucleus can be suppressed by using ethanol as solvent; even in this solvent, however, the hydrogen absorption values of alkyl-4-isopropenylphenols with small alkyls are slightly higher than it would correspond to the theoretical value for the isopropenyl group. The structures of the above compounds were confirmed by spectral methods. The infrared spectra of all 4-isopropenylphenols exhibit absorptions at 885–895 and 3075–3085  $\text{cm}^{-1}$ , characteristic of the  $\text{C}=\text{CH}_2$  group. 2,6-Ditert-butyl-4-isopropenylphenol has a sharp maximum at 3628  $\text{cm}^{-1}$  (KBr), corresponding to a free hydroxyl group<sup>14</sup>.

In the ultraviolet absorption spectra of 4-isopropenylphenols (Table I), the K-band lies within the limits 259.5–263.5 nm; its intensity, expressed by the logarithm of the molar extinction coefficient, varies within the range 4.05–4.25. The band intensity and position are similarly to other 4-(1-alkenyl)phenols<sup>15</sup>. The introduction of alkyls into a molecule of 4-isopropenylphenol has neither bathochromic nor hyperchromic effect. The molar extinction coefficients are obviously affected by the polymerization occurring in the solution under investigation, and their values cannot therefore be regarded as reliable. The fact that the K-band of 2,6-ditert-butyl-4-isopropenylphenol has the same position as the other 4-isopropenylphenols represents a further evidence for the coplanarity of a strongly sterically hindered hydroxyl group with the benzene nucleus, since a substantial disturbance of the  $n-\pi$  conjugation of the hydroxy group would necessarily lead to a hypsochromic shift of the band<sup>16</sup>.

The NMR spectral parameters, *i.e.* chemical shifts, coupling constants and relative

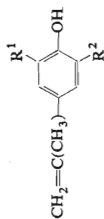


TABLE I

## Preparation and Properties of 4-Isopropenylphenols

Phenol	R <sup>1</sup>	R <sup>2</sup>	Procedure Yield, %	M.p. <sup>a</sup> °C	B.p. °C/Torr	Formula (mol. weight)	Calculated Found % C % H	Number of double bonds <sup>b</sup>	$\lambda_{\max}$ , nm (log $\epsilon$ )
<i>I</i>	H	H	<i>A</i> 90–95	85–86 <sup>c</sup>	116.5–118/15	C <sub>9</sub> H <sub>10</sub> O (134.2)	80.56 80.46	7.51 7.43	210 (inflex) 260 (4.05)
<i>II</i>	CH <sub>3</sub>	H	<i>A</i> 70–75	43–44.5 <sup>d</sup>	126–127/12	C <sub>10</sub> H <sub>12</sub> O (148.2)	81.04 80.81	8.16 8.05	210 259 (4.11)
<i>III</i>	C <sub>2</sub> H <sub>5</sub>	H	<i>B</i> 95	40–41.5	135–138/12	C <sub>11</sub> H <sub>14</sub> O (162.2)	81.44 81.00	8.70 8.82	212.5 259.5 (4.18)
<i>IV</i>	iso-C <sub>3</sub> H <sub>7</sub>	H	<i>B</i> 95	65–66	140–143/16	C <sub>12</sub> H <sub>16</sub> O (176.3)	81.77 82.06	9.15 9.20	212.5 261 (4.25)
<i>V</i>	tert-C <sub>4</sub> H <sub>9</sub>	H	<i>B</i> 80–90	20–23	130–135/9	C <sub>13</sub> H <sub>18</sub> O (190.3)	82.06 82.03	9.53 9.59	212 262 (4.20)
<i>VI</i>	tert-C <sub>8</sub> H <sub>17</sub> <sup>e</sup>	H	<i>B</i> 60	68–69	159–163/6	C <sub>17</sub> H <sub>26</sub> O (246.4)	82.87 82.86	10.64 10.67	213 263 (4.22)
<i>VII</i>	CH <sub>3</sub>	CH <sub>3</sub>	<i>B</i> 80	49–51	138–139/20	C <sub>11</sub> H <sub>14</sub> O (162.2)	81.44 81.40	8.70 8.76	213.5 261.5 (4.11)
<i>VIII</i>	CH <sub>3</sub>	tert-C <sub>4</sub> H <sub>9</sub>	<i>B</i> 82	34–35.5	142–145/15	C <sub>14</sub> H <sub>20</sub> O (204.3)	82.30 82.44	9.87 9.95	213 263.5 (4.08)
<i>IX</i>	tert-C <sub>4</sub> H <sub>9</sub>	tert-C <sub>4</sub> H <sub>9</sub>	<i>C</i> 75	77–79.5	120–125/3	C <sub>17</sub> H <sub>26</sub> O (246.4)	82.87 82.51	10.64 10.65	212.5 261.5 (4.16)

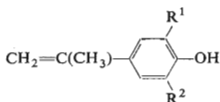
<sup>a</sup> Crystallization solvents: *I* hexane–benzene, *II*–*VIII* hexane, *IX* methanol. <sup>b</sup> Determined by hydrogenation on PtO<sub>2</sub> under normal pressure in the case of phenols *I*–*VIII* in ethanol, in the case of *IX* in glacial acetic acid. <sup>c</sup> According to ref. <sup>7</sup>, m.p. 85°C. <sup>d</sup> According to ref. <sup>4</sup>, m.p. 43–44°C. <sup>e</sup> 1,1,3,3-Tetramethylbutyl.

band intensities confirm the structure of the 4-isopropenylphenols (Table II). The NMR parameters of the isopropenyl group of all the 4-isopropenylphenols under investigation depend very little on the alkyl substituents present in the aromatic nucleus, and the coupling constants values of this group are identical with the coupling constants values of the isopropenyl group of  $\alpha$ -methylstyrene<sup>17</sup>. However, the effect of the substituent appears in the aromatic part of the spectrum. The chemical shifts and coupling constants of protons at positions 3,5,6 of 2-alkyl-4-isopropenylphenols were determined by an analysis of the three-spin unsymmetrical system ABC. The chemical shifts of the protons at the position ortho with respect to the substituent can be affected by the magnetic anisotropy of the substituent, its electronegativity, effects of the electric field, and steric effects<sup>18</sup>.

In the case of 2-methyl-4-isopropenylphenols, some indications of an interaction between the protons of the methyl group and the aromatic nucleus appear in the NMR spectra in the region of the aromatic and methyl protons. The effects of the long-range coupling<sup>19</sup> are most pronounced in the case of 2,6-dimethyl-4-isopropenylphenol, where instead of a singlet a septet is formed on the aromatic band, and a trip-

TABLE II

NMR Data of 4-Isopropenylphenols



The solutions measured were 0.5M in  $\text{CDCl}_3$  in the presence of 4-nitroso-N,N-dimethylaniline.

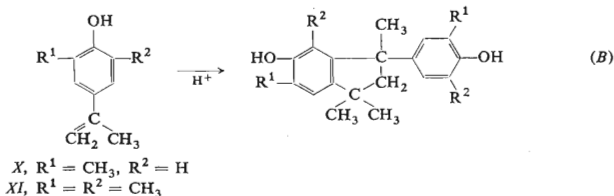
Phenol <sup>a</sup>	Chemical shifts (relative intensities <sup>b</sup> )				H-3	H-5	H-6	OH	$J_{56}^c$	$J_{35}^c$
	$\text{CH}_3^d = \text{CH}_{trans}^e = \text{CH}_{cis}^e$	$\text{R}^1, \text{R}^2$								
<i>I</i>	7.92	4.77	5.05		2.69	2.69	3.23	4.15	9.0	—
<i>II</i>	7.92	4.77	5.07	7.78(3)	2.76	2.84	3.32	5.12	8.9	2.0
<i>III</i>	7.93	4.78	5.09	8.18(3) 7.40(2)	2.78	2.85	3.38	5.45	8.5	2.1
<i>V</i>	7.93	4.85	5.11	8.63(9)	2.72	2.98	3.59	5.43	7.6	2.0
<i>VI</i>	7.92	4.83	5.12	9.28(9) 8.58(6) 8.10(2)	2.58	2.84	3.47	5.44	7.6	2.1
<i>VII</i>	7.93	4.77	5.06	7.79(6)	2.90	2.90	—	5.38	—	—
<i>VIII</i>	7.89	4.78	5.06	7.78(3) 8.59(9)	2.74	2.91	—	5.26	—	2.3
<i>IX</i>	7.87	4.78	5.10	8.56(18)	2.71	2.71	—	4.82	—	—

<sup>a</sup> Cf. Table I. <sup>b</sup> Unit relative intensity is not given. <sup>c</sup> Long-range coupling constants of compounds *II* and *VII* cf. p. 1990. <sup>d</sup> Relative intensity of the isopropenyl methyl group of all compounds is 3. <sup>e</sup> Referred to the methyl group.

let appears on the methyl band, the distances of the multiplet components being 0.65 c/s. The long-range couplings of the other 2-methyl-4-isopropenylphenols manifest themselves prevalingly in a broadening of the corresponding lines. From an analysis of the spin systems  $AA'X_3X_3$  and  $ABCX_3$ , involving protons of the aromatic nucleus and methyl group of 2,6-dimethyl- and 2-methyl-4-isopropenylphenol, it follows that the long-range coupling constants  $J_{CH_3-H_{ortho}}$  and  $J_{CH_3-H_{para}}$  have the same signs and approximately the same value  $-0.65$  c/s, whereas the coupling constant  $J_{CH_3-H_{meta}}$  has a value of  $+0.3$  c/s, and thus a sign opposite to that of  $J_{CH_3-H_{ortho}}$  and  $J_{CH_3-H_{para}}$  (cf. ref.<sup>20-22</sup>). The established values of the long-range coupling constants of 2-methyl-4-isopropenylphenols confirm the small dependence of these constants on a further substitution of the benzene nucleus, already observed with the derivatives of toluene<sup>23-25</sup>.

All the 4-isopropenylphenols prepared in the present work polymerize spontaneously, which makes more difficult their purification by crystallization; this is probably the reason why the melting points quoted in the literature<sup>3-7</sup> for 4-isopropenylphenol differ so much ( $70-85^\circ\text{C}$ ). The stability of the monomer increases with the increasing hindrance of the hydroxyl group: the non-substituted 4-isopropenylphenol and its 2-alkyl derivatives with a small alkyl polymerize most readily; 2-alkyl-4-isopropenylphenols with a bulky alkyl, and particularly 2,6-dialkyl-4-isopropenylphenols polymerize much slower. At the same time, copolymers with oxygen are probably formed, since we observed the formation of 3,5-ditert-butyl-4-hydroxyacetophenone while attempting to recrystallize a polymer formed from 2,6-ditert-butyl-4-isopropenylphenol. The polymerization could be suppressed by adding 4-nitroso-N,N-dimethylaniline.

The reaction product obtained when hydrogen chloride is acting upon 4-isopropenylphenols depends on substituents  $R^1$  and  $R^2$ . From 2-methyl- and 2,6-dimethyl-4-isopropenylphenol in a toluene solution, derivatives of 5-indanol are formed by dimerization. (The dimer formation with an indane skeleton has been described in the cases of styrene<sup>26</sup>,  $\alpha$ -methylstyrene<sup>27</sup>, and the derivatives thereof<sup>27,28</sup>.) The same derivatives were isolated also in the acid-catalyzed alkylation of 4-chlorophenol and 2,6-ditert-butylphenol with 2-methyl- or 2,6-dimethyl-4-isopropenylphenol<sup>1</sup>:



The dimerization of 2-methyl-4-isopropenylphenol allows the formation of two structure isomers; it follows from the NMR spectrum that the isolated indanol has a structure *X* which arises by cyclisative alkylation at a sterically better accessible carbon atom. The NMR spectra confirm the structure of both prepared 1,1,3-trimethyl-3-(4-hydroxyphenyl)-5-indanols (Table III). The assignment of the methyl and methylene groups in the spectra was carried out by comparison with the NMR spectrum of 1,1,3-trimethyl-3-phenylindane (dimer of  $\alpha$ -methylstyrene). It follows from an analysis of the spectra that protons in the methylene group are non-equivalent and the geminal coupling constant of the compound *X*,  $J = 12.5$  c/s can be compared with the geminal coupling constant of the dimer of  $\alpha$ -methylstyrene,  $J = 13.1$  c/s. In the case of compound *XI*, the quadruplet corresponding to the methylene group is partly overlapped by the lines of methyl groups bound to the aromatic nucleus. In the spectrum of the aromatic part of both compounds the lines of aromatic and hydroxylic protons overlap. An addition of hydrochloric acid to the solutions under investigation allows the discrimination of the positions of lines of the aromatic and hydroxylic protons. In the case of the compound *X* the position of the methyl group on the aromatic nucleus was confirmed on the grounds of an analysis of the aromatic spin systems AB and ABC (protons in positions 4,7,2',5,6'), which in part overlap.

TABLE III

Chemical Shifts (Relative Intensities) in the NMR Spectra of the 1,1,3-Trimethyl-3-phenylindane Derivatives

Measured 0.5M solutions in pyridine.

Compound	CH <sub>3</sub> gem.	CH <sub>3</sub>	CH <sub>2</sub>	CH <sub>3</sub> on the nucleus	H <sup>a</sup>	OH <sup>a</sup>
<i>X</i> <sup>b</sup>	8.88 (3)	8.36 (3)	8.01 (1) <sup>c</sup>	7.70 (3)	3.67 (1) <sup>d</sup>	2.85 (1)
	8.83 (3)		7.54 (1)	7.54 (3)	3.14 (1)	2.74 (1)
<i>XI</i> <sup>a</sup>	8.72 (3) 8.67 (3)	8.20 (3)	7.82 (1)	7.81 (3)	3.30 (3)	3.69 (1)
			7.58 (1)	7.68 (6)		
				7.56 (3)		
<i>XII</i> <sup>e</sup>	9.08 (3)	8.44 (3)	7.96 (1) <sup>f</sup>	—	—	—
	8.80 (3)		7.68 (1)			

<sup>a</sup> Solutions in dioxane (in the case of compound *XI* 0.35M). <sup>b</sup> Cf. p. 7. <sup>c</sup>  $J_{gem} = 12.5$  c/s. <sup>d</sup> For protons in positions 4,7,2',3',6', resp.;  $J_{2,3'} = 8.6$  c/s,  $J_{2,6'} = 2.4$  c/s,  $J_{4,7} = 1$  c/s. <sup>e</sup> 1,1,3-Trimethyl-3-phenylindane. <sup>f</sup>  $J_{gem} = 13.1$  c/s.

In the ABC system, coupling constants  $J_{AB} = 8.6$  c/s and  $J_{BC} = 2.4$  c/s were established, and in the AB system the constant  $J_{AB} = 1$  c/s was found, which indicates that the protons in the AB system must necessarily be in the position *para*.

4-Isopropenylphenol and 2-*tert*-butyl-4-isopropenylphenol yield compounds of a molecular weight higher than corresponds to a dimer. The structure thereof has not been investigated.

### EXPERIMENTAL

The samples for analysis were chromatographically uniform; they were dried *in vacuo* 0.5–1 Torr over  $P_2O_5$  at room temperature for 12 hours. The melting points were determined on the Boetius block, the boiling points were established by distillation. The ultraviolet spectra of ethanolic solutions were measured with a CF4R (Optica, Milano) apparatus, the infrared spectra were recorded with a UR-10 (Zeiss, Jena) apparatus in KBr discs, and a JNM-3-60 (JEOL) spectrometer (60 Mc, resolution  $10^{-8}$ ) was employed for measurements of the NMR spectra, which were then calibrated by the side bands method and by means of hexamethyldisiloxane as an internal standard ( $\tau = 9.95$ ); the analysis of the NMR spectra was carried out using a Minsk 22 computer. The molecular weights were determined osmotically in the gas phase in benzene solutions.

*Chemicals used.* Commercial 4,4'-isopropylidenebisphenol (Spolek pro chemickou a hutní výrobu), m.p. 153–156°C, and 4,4'-isopropylidenebis(2-methylphenol) (Lachema), m.p. 132–135°C; the other 4,4'-isopropylidenebisphenols used were prepared according to ref.<sup>1,2</sup> Other materials prepared were methyl 3,5-ditert-butyl-4-hydroxybenzoate<sup>29</sup>, m.p. 165.5–166.5°C, 3,5-ditert-butyl-4-hydroxyacetophenone<sup>30</sup>, m.p. 146–148.5°C, and 1,1,3-trimethyl-3-phenylindane<sup>27</sup>, m.p. 34–35°C.

#### Alkaline Cleavage of 4,4'-Isopropylidenebisphenols

A mixture of the chosen 4,4'-isopropylidenebisphenol and solid sodium hydroxide (1%, procedure A) or sodium (0.2–0.3%, procedure B) or butyllithium (1.75%, procedure C) was heated at a pressure 2–15 Torr (in the case of cleavage of tetraalkylated bisphenols 30–50 Torr) in a bath, whose temperature was gradually increased to approx. 250°C. A mixture of the corresponding phenol and 4-isopropenylphenol obtained by distillation was then fractionated by vacuum fractional distillation on a 15 cm Vigreux column. The products were recrystallized from hexane, or from the mixture hexane–benzene, and ditert-butyl derivative was recrystallized from methanol. The results are summarized in Table I.

#### Acidic Cleavage of 4,4'-Isopropylidenebis(2,6-ditert-butylphenol)

A mixture of 4.5 g of 4,4'-isopropylidenebis(2,6-ditert-butylphenol) and 0.17 g *p*-toluenesulphonic acid was heated at a pressure 9 Torr in a bath the temperature of which was gradually increased up to 250°C. In the distillate, 2-*tert*-butylphenol, 4-*tert*-butylphenol, 2,4-ditert-butylphenol, and a trace of phenol were discovered by means of paper chromatography.

#### 2,6-Ditert-butyl-4-isopropenylphenol

To a solution of the Grignard reagent in ether, prepared in the usual manner from 27.6 g methyl iodide (0.194 mol) and 6 g magnesium (0.25 g-atom), a solution of 12.4 g 3,5-ditert-butyl-4-

hydroxyacetophenone (0.05 mol) in 250 ml dibutyl ether was added in two hours under stirring. On adding the whole amount of the solution, the reaction mixture was stirred for another four hours (a precipitate appeared after two hours), and then left to stand overnight. After a hydrolysis with a solution of 125 g ammonium chloride in 375 ml water, sucking off of the inorganic salts, extraction with water and removing ether by distillation, the residue was distilled *in vacuo*. The yield of the crude product was 11.7 g (95%), m.p. 65–75°C; data on the pure product are in Table I.

#### Reaction of 4-Isopropenylphenols with Hydrogen Chloride

A solution of the selected 4-isopropenylphenol in toluene was saturated with dry hydrogen chloride at room temperature for 30 min. After standing for three days the solution was filtered, extracted with a solution of sodium bicarbonate and water, and the solvent was distilled off *in vacuo*. 1,1,3,6-Tetramethyl-3-(3-methyl-4-hydroxyphenyl)-5-indanol (X), m.p. 193–194.5° (toluene). For  $C_{20}H_{24}O_2$  (296.4), calculated: 81.04% C, 8.70% H; found: 81.09% C, 8.34% H; mol. weight 294. 1,1,3,4,6-Pentamethyl-3-(3,5-dimethyl-4-hydroxyphenyl)-5-indanol (XI), m.p. 160–161.5° (toluene-hexane). For  $C_{22}H_{28}O_2$  (324.5), calculated: 81.44% C, 8.70% H; found: 81.53% C, 8.80% H. The molecular weight of the product, obtained from 4-isopropenylphenol, was 370, that of the product obtained from 2-tert-butyl-4-isopropenylphenol was 411.

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