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NEW SPIROBIINDANETETROLS FROM 3-TERT.ALKYLPYROCATECHOLS

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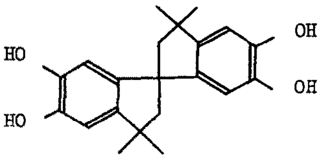
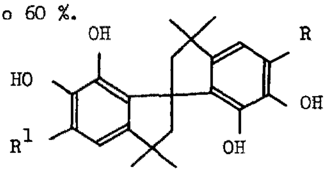
Spirobiindanols are formed by acid-catalysed condensation of some phenols with a ketone. The details of the reaction mechanism are not known yet. The reaction is generally carried out by boiling the two components for several hours in the presence of acetic and hydrochloric acids. Under these conditions, pyrocatechol and acetone react[1] to form 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-5,6,5′,6′-tetrol (I) with a yield of 50 to 60 %.



I



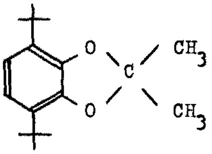
II ($R = R^1 = H$)

III (R = tert.Butyl, $R^1 = H$)

IV ($R = R^1$ = tert.Butyl)

The substance for which we are proposing structure II, i.e. 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-6,7,6′,7′-tetrol [m.p. 253°C (toluene; measured under argon) found 74.35 % C, 7.18 % H, calculated for $C_{21}H_{24}O_4$ (340.4): 74.09 % C, 7.11 % H; acetate m.p. 171°C (dilute ethanol), found 68.52 % C, 6.47 % H, calculated for $C_{29}H_{32}O_8$ (508.6): 68.49 % C, 6.34 % H] was prepared by refluxing 3-tert.butylpyrocatechol (0.1 mole) with acetone (0.15 mole) in a mixture of acetic acid (60 ml) and hydrochloric acid (20 ml) for 35 hours, the yield being 13.7 %. In the first phase of the reaction, 5,5′-di-tert.butyl-3,3,3′,3′-tetramethyl-1,1′-spirobiindane-6,7,6′,7′-tetrol (IV) is formed [m.p. 214.5-216.5° (heptane), found 76.98 % C, 9.16 % H, calculated for $C_{29}H_{40}O_4$ (452,6) 76.95 % C, 8.91 % H] which can be isolated in a yield of 3.1 % by cooling the reaction mixture after refluxing for 7 hours.

During the condensation reaction, several by-products are formed: of these, 2,2-dimethyl-4,7-di-tert.butyl-1,3-benzodioxole (V) [m.p. 112°C (methanol), b.p. 110°C/1 Torr, found 78.09 % C, 10.06 % H, calculated for $C_{17}H_{26}O_2$ (262.4) 77.82 % C, 9.99 % H] was isolated and identified (yield 2.03 %) and the substance III was identified by chromatographic means. The derivative V was prepared as a model substance by condensing 3,6-di-tert.butylpyrocatechol with acetone in acetic acid and hydrochloric acid, the component mixture being allowed to stand overnight at room temperature.



V

The substance II is also formed by condensation of 3-tert.pentylpyrocatechol with acetone. It was found by means of paper chromatography with standards (Table 1) that substance III differs from substance II by a value of ΔR_{Mg} corresponding to a tert.butyl group bound in the ortho position with respect to the hydroxyl group. Substance IV differs in the same way from substance III. In acid medium (e.g. under condensation conditions) the substance IV is easily dealkylated to form substance III and later II. On the other hand, substance III and later IV are formed from substance II by alkylation with tert.butyl alcohol catalysed with sulphuric acid.

TABLE 1

R_F and ΔR_{Mg} Values of Prepared and Model[a] Substances

System[b]	I_1S_1				I_2S_2			
Substance	IX	X	II	III	III	IV	XI	XII
R_F	0.10	0.83	0.15	0.86	0.09	0.61	0.13	0.67
ΔR_{Mg}	-1.64		-1.58		-1.20		-1.13	

[a] IX 3-methylpyrocatechol, X 3-methyl-6-tert.butylpyrocatechol, XI 4-tert.octylpyrocatechol, XII 4-tert.octyl-6-tert.butylpyrocatechol. [b] Impregnation: I_1 20 % formamide, I_2 40 % dimethylformamide. Solvents: S_1 benzene-chloroform (2:1), S_2 heptane-diisopropyl ether (4:1).

From the intensity and position of lines in NMR spectra (Table 2; Spectrometer Model JNM-3-60, operating at 60 Mc/s; hexamethyldisiloxane as internal standard, $\tau = 9.95$) and from the fact, that the substance IV differs from substance II by two tert.butyl groups it follows that the substance II contains four methyl, two methylene, four hydroxyl groups and two hydrogen atoms on an aromatic ring. Substance IV contains, besides two tert.butyl groups, four methyl, two methylene, four hydroxyl groups and two hydrogen atoms on an aromatic ring. In substance II the fact that two hydrogen atoms are adjacent is supported by the measured interaction constant J_{ortho} = 7.9 c/s in CD_3CN and J_{ortho} = 8.1 c/s in dioxane. In agreement with this, the substance II can be tert.butylated in the ortho position with respect to the hydroxyl, whereas substance I cannot. Also, for steric reasons this would not be possible in case the second vicinal position were occupied by an alkyl, small as it maybe. It is known, for example, that neither 3,5-dimethylphenol[2] nor 2,5-dimethylhydroquinone[3] cannot be tert.butylated on the ring.

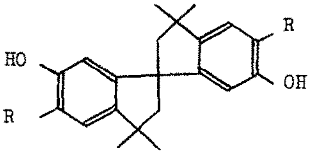
TABLE 2

Chemical Shifts in NMR Spectra[a]

Substance, Conc., Solvent		Shift			
		CH_3	CH_2	H_{arom}	OH
I	0.5 M in dioxane	8.76 8.71 (6)	7.83 (2)	3.87 (1) 3.48 (1)	2.92 2.90 (2)
	0.25 M in pyridine	8.73 (6)	7.68 (2)	b	b
II	0.2 M in dioxane	8.75 8.68 (6)	b	3.55 3.45 (2)	3.96 (1) 2.91 (1)
	0.25 M in pyridine	8.59 8.48 (6)	7.68 7.06 (2)	b	b
	CD_3CN (saturated solution)	8.75 8.69 (6)	7.82 7.64 (2)	3.45 3.29 (2)	c
IV	$CDCl_3$ (saturated solution)	8.70 8.59 (15)	7.66 (2)	3.28 (1)	5.72 (1) 4.43 (1)
	0.2 M in pyridine	8.62 8.54 (6) 8.45 (9)	7.73 7.27 (2)	b	b

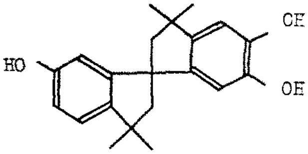
[a] line intensities in parentheses; [b] signals are overlapped by solvent signals; [c] signals are suppressed by proton exchange

In the attempt to obtain more evidence for the structure II, 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-6,6′-diol (VI) was oxidised with Fremy salt. After reduction with sodium dithionite, however, only 3,3,3′,3′-tetramethyl-1,1′-spirobiindane-5,6,6′-triol (VIII) [m.p. 227-9°C (toluene-hexane; measured under argon) found 77.79 % C, 7.56 % H, calculated for $C_{21}H_{24}O_3$ (324.4) 77.75 % C, 7.46 % H] and substance I were isolated from the reaction mixture. Furthermore, the derivative VI was alkylated with isobutylene under catalysis with $BF_3.Et_2O$ in benzene suspension at 70°C and 5,5′-di-tert.butyl-3,3,3′,3′-tetramethyl-1,1′-spirobiindane-6,6′-diol (VII) [m.p. 283°C (heptane), found 83.12 % C, 9.75 % H, calculated for $C_{29}H_{40}O_2$ (420.6) 82.81 % C, 9.59 % H] was isolated with a yield of 69 %. The attempt at oxidising the last substance to a pyrocatechol derivative IV, however, has not meet as yet with success.



VI (R = H)

VII (R = tert.butyl)



VIII

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