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Synthesis of Specifically Tritiated Xylenols, Indanols, Tetrahydronaphthols and Their Methyl Ethers*

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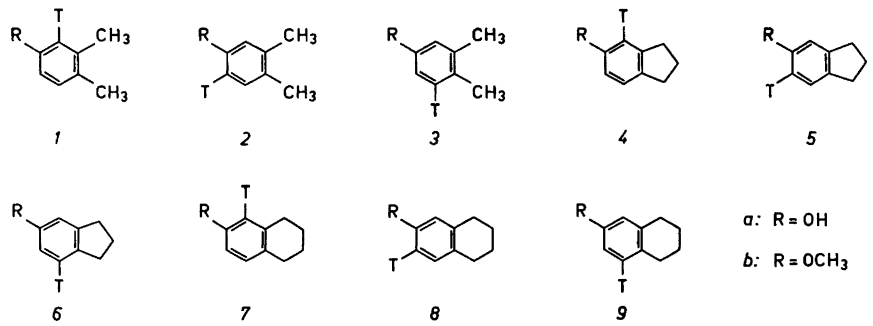
3,4-Dimethylphenol, 5-indanol, and 6-tetralol, specifically tritiated in the aromatic rings, have been synthesised together with their corresponding methyl ethers. Some of the tritiated phenols were obtained from the corresponding labelled methoxy compounds by demethylation with BBr_3. No appreciable loss of radioactivity occurred in this reaction. Bromination of 2-*t*-butyl-4,5-dimethylphenol in acetic acid yielded 2,4-dibromo-6-*t*-butyl-3,4-dimethylhexa-2,5-dien-1-one (*12*) as the main product.

As part of our study of the directing effect of annulated rings in aromatic systems, we have determined the rate of tritium exchange of specifically labelled 3,4-dimethylphenol, 5-indanol, 1,2,3,4-tetrahydro-6-hydroxynaphthalene (6-tetralol), and the corresponding methyl ethers. In this paper, we describe the synthesis of the tritium labelled compounds used (*1* – *9*). The kinetic studies are described in an accompanying paper.**



* The directing effect of annulated rings in aromatic systems. VI. Part V, see Ref. 5.
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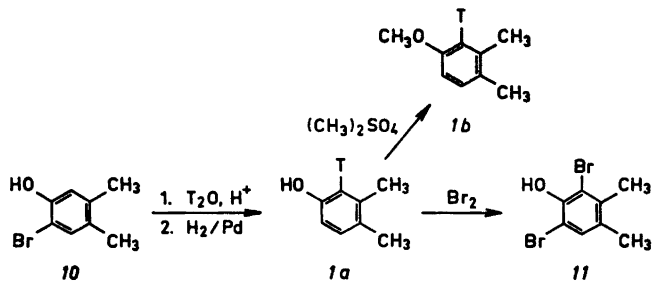
Specifically tritiated compounds are often prepared from the appropriate bromo derivatives, which are converted to Grignard reagents and then hydrolyzed with tritiated water.[1,2] Specific labelling of phenolic compounds by this method can only be achieved when the hydroxy group is suitably protected. Since many of the tritiated compounds described here are phenols, we have developed a method whereby the corresponding specifically tritiated methoxy compounds are facilely demethylated with BBr_3 to the corresponding phenols without appreciable loss of radioactivity.

Xylene derivatives. 3,4-Dimethylphenol-2-[^{3}H] (*1a*), 3,4-dimethylphenol-6-[^{3}H] (*2a*), and the corresponding methyl ethers *1b* and *2b*, were prepared, starting from 2-bromo-4,5-dimethylphenol (*10*). When the bromophenol *10* was treated with tritiated water under mild acid catalysis, tritium was introduced in the *ortho* position to the hydroxyl group. Removal of bromine by catalytic dehalogenation then afforded the phenol *1a*. Work by Best and Wilson,[3] and others [4] indicate that only hydrogens *ortho* or *para* to the hydroxyl



Scheme 1

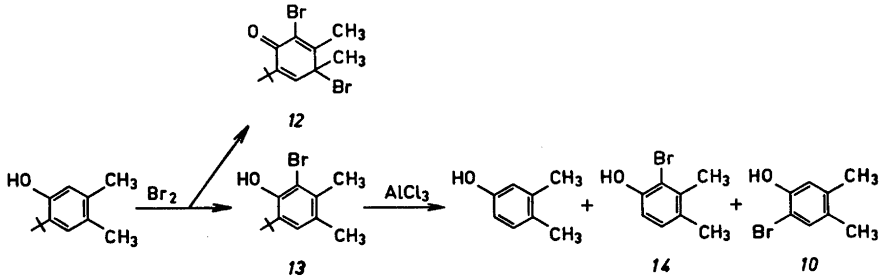
group in phenols are exchanged. We could show that no tritium substitution had occurred in the *meta* position to the hydroxyl group by converting *1a* to 2,6-dibromo-3,4-dimethylphenol (*11*), which was found to be devoid of radioactivity (Scheme 1). The methoxy compound *1b* was then obtained from *1a* by methylation under anhydrous conditions, using dimethyl sulphate in toluene in the presence of sodium carbonate. The 6-tritiated compounds *2a* and *2b* were obtained *via* the Grignard reagent according to standard methods.

A synthetic route to *1a via* 2-bromo-3,4-dimethylphenol was also explored with the results summarized in Scheme 2. Since direct bromination of 3,4-dimethylphenol yields predominantly 2-bromo-4,5-dimethylphenol,[5] the more reactive 2-position was first blocked with a tertiary butyl group. Bromination of this phenol in acetic acid gave two products. Mass spectrum of the main component shows the molecular ion at *m/e* 336, indicating that dibromination of the protected phenol had occurred. The IR-spectrum shows no OH-absorption, but instead an unexpected band appears at 1650 cm^{-1}, indicating an unsaturated ketone.[6] The UV-spectrum shows a strong band at λ_{max} (hexane) 257 nm ($\varepsilon = 11\,800$). These results suggest that the main product is a cyclohexadienone derivative of structure *12*. This compound would have an UV-absorption around 250 nm, while a linearly conjugated cyclohexadienone

structure is expected to absorb in the region 320 – 340 nm.[7] The structure *12* was confirmed by NMR-spectrum which shows a one-proton singlet at $\delta = 6.85$ ppm, representing a vinylic proton. The two methyl groups appear as singlets at $\delta = 2.40$ and 1.95 ppm, and the tertiary butyl group gives rise to a singlet at $\delta = 1.25$ ppm.

The second product obtained in the bromination was identified as 2-bromo-6-*t*-butyl-3,4-dimethylphenol (*13*) by its IR, UV, and NMR spectra, described in the experimental section.

Attempts to remove the protecting *t*-butyl group by heating *13* with *p*-toluenesulphonic acid according to Dean *et al.*[8] gave either no reaction or, after prolonged heating, black polymeric products. Dealkylation with $AlCl_3$ in benzene [9] gave a dark oil, from which three products were isolated, identified as 3,4-dimethylphenol, 2-bromo-3,4-dimethylphenol (*14*), and 2-bromo-4,5-



Scheme 2

dimethylphenol (*10*). The two latter compounds were formed in an approximate ratio of 1:2, indicating a rearrangement of the bromine from the less reactive to the more reactive position in the dimethylphenol. Similar rearrangements and disproportionations of aromatic bromo compounds have been observed, and particularly studied by O'Bara *et al.*[10] Although the two bromo compounds could be separated by preparative TLC,[5] this method was not deemed suitable for the preparation of larger quantities of *1a*.

3,4-Dimethylphenol-5-[^{3}H] (*3a*) was prepared from 2,6-dibromo-3,4-dimethylphenol (*11*) by treatment with tritiated water in trifluoroacetic acid at 80°C and subsequent catalytic dehalogenation. Milder conditions (H_2SO_4 in ethanol or P_2O_5, T_2O, and BF_3 according to Yavorsky and Gorin [11]) gave no tritium introduction. The corresponding methoxy compound *3b* was prepared by methylation of *3a* under anhydrous conditions, as described above.

Indane derivatives. Bromoindanols were used in the synthesis of the indane derivatives *4* – *6*. Bromination of 5-indanol in CCl_4 at 0°C gives almost exclusively 6-bromo-5-indanol.[5] To prepare the corresponding 4-bromo-5-indanol, the more reactive 6-position was blocked by a *t*-butyl group before bromination, following the procedure of Dean *et al.*[8] The specifically tritiated indanols *4a* and *5a*, and their methyl ethers *4b* and *5b* were then prepared from the corresponding bromo ethers *via* Grignard reagents as described above. 5-Methoxyindane-7-[^{3}H] (*6b*) was obtained from 4,6-dibromo-5-methoxyindane by the

method used in the preparation of *3a*. Demethylation of *6b* with BBr_3 afforded 5-indanol-7-[^{3}H] (*6a*).

Tetralin derivatives. Bromination of 6-tetralol in CCl_4 at 0° yields predominantly 5-bromo-6-tetralol,[5] which can be purified from the 7-bromo isomer by recrystallization. The 5-[^{3}H]-compounds *7a* and *7b* were obtained from the 5-bromo derivative *via* the Grignard reagents, as above.

To obtain *8a*, attempts were made to synthesize 7-bromo-6-tetralol by blocking the more reactive 5-position of 6-tetralol with a *t*-butyl group and then converting this derivative to *8a via* bromination, dealkylation and tritiation *via* the Grignard reagent as indicated above for *1a*. However, butylation of 6-tetralol gave only 7-*t*-butyl-6-tetralol, probably due to the steric hindrance of the 5-position. Compound *8a* was finally obtained from 5-bromo-6-tetralol, using tritiated water and mild acid catalysis as described for *1a*. The ether *8b* was then prepared from *8a* by methylation as before. The 8-[^{3}H]-derivatives *9a* and *9b* were formed from 6-tetralol by the same series of reactions as described for the corresponding indane derivatives *6a* and *6b*.

EXPERIMENTAL

General comments. Melting points were determined with calibrated Anschütz thermometers in an electrically heated metal block. Infrared absorption spectra were measured on a Perkin-Elmer 237 spectrophotometer, and ultraviolet absorption spectra were measured with a Beckman DK-2 spectrophotometer. Nuclear magnetic resonance spectra were measured in $CDCl_3$-solutions with a Varian Associates A 60 spectrometer. Chemical shifts are expressed in δ ppm relative to tetramethylsilane. Mass spectra were obtained with an LKB 9000 instrument at 70 eV. Molecular weights were determined with a Hitachi Perkin-Elmer Model 115 Molecular Weight Apparatus, using benzene as solvent. Thin layer chromatography was performed, using silica gel G plates of 0.3 mm (analytical) and 1 mm (preparative) thickness. The plates were activated by heating at 130°C for 1.5 h and stored in a dry cabinet until used.

The radioactivity of the synthesized compounds was determined by liquid scintillation counting (Packard Tri-Carb Model 3375) after purification to constant activity. The chemical identity of each substance was determined by spectral and chromatographical comparison with authentic samples.

2-Bromo-4,5-dimethylphenol. 3,4-Dimethylphenol (10 g; 82 mmol) in CCl_4 (400 ml) was treated with a solution of bromine (13.1 g; 82 mmol) in CCl_4 (100 ml) at 0°, and the solution was left standing overnight at room temperature. The solvent was evaporated *in vacuo* and the solid residue crystallized twice from light petroleum, affording 13.1 g (79 %) of 2-bromo-4,5-dimethylphenol, m.p. 77 – 78° (lit.[12] 76 – 79°). TLC showed that the product was free of 2-bromo-3,4-dimethylphenol. NMR: $\delta = 7.10$ and 6.72 ppm (s, 1H each, Ar*H*), 5.15 ppm (broad, 1H, O*H*) and 2.15 ppm (s, 6H, ArCH_3).

2-Bromo-4,5-dimethylphenol-6-[^{3}*H*]. To a solution of 2-bromo-4,5-dimethylphenol (3 g; 15 mmol) in dry tetrahydrofuran (10 ml) and H_3PO_4 (0.2 ml; 89 %) was added tritiated water (10 μl, sp. act. 5 C/ml). The mixture was heated in a sealed ampoule at 80° overnight. After cooling, ether (20 ml) was added and the solution washed with saturated $NaHCO_3$-solution, dried (Na_2SO_4) and evaporated *in vacuo*. The residue was redissolved in methanol (2 ml) and evaporated to remove exchangeable tritium. The solid phenol was used in the next step without further purification.

3,4-Dimethylphenol-2-[^{3}*H*] (*1a*). The above tritiated bromophenol (3 g; 15 mmol) was dissolved in ethanol (15 ml), KOH (1 g) was added, and the mixture hydrogenated at atmospheric pressure over Pd-C at room temperature, until TLC showed that no bromo compound remained. After filtration and evaporation, the product was purified by preparative TLC (ether:light petroleum, 1:5). This yielded 1.5 g (83 %) of the tritiated dimethylphenol *1a*. Sp. act. 0.8 μC/mmol. A small sample of this compound (50 mg; 0.41 mmol) was treated with bromine (118 mg; 1.02 mmol) in CCl_4 (5 ml) in the presence of Na_2CO_3.

The 2,6-dibromo-3,4-dimethylphenol formed, isolated by preparative TLC, showed no significant radioactivity, indicating that no tritium had entered the 5-position during the acid catalyzed tritiation.

3,4-Dimethylanisole-2-[^3H] (*1b*). Compound *1a* (0.5 g; 4.1 mmol) in dry toluene (5 ml) was stirred overnight at 80° with dimethyl sulphate (1.0 g; 8.2 mmol) in the presence of anhydrous sodium carbonate (1.4 g; 8.2 mmol). After filtration, the product was purified by preparative TLC (ether:light petroleum, 1:20), affording 0.5 g (89 %) of the ether. Sp. act. 0.6 μC/mmol.

2-t-Butyl-4,5-dimethylphenol. 3,4-Dimethylphenol (10 g; 82 mmol) was dissolved in phosphoric acid (115 ml; 89 %) by heating the mixture at 80°. *t*-Butanol (30.4 g; 410 mmol) was added and the mixture stirred at 80° for 3 h. After cooling, water (400 ml) was added and the mixture extracted with ether. The ether extract was washed with aqueous NaOH (2 × 30 ml, 1 N) to remove unreacted starting material, and then with NaCl-solution. After drying (Na_2SO_4) and evaporation, the solid residue was crystallized from light petroleum to yield 13.5 g (92 %) of white crystals, m.p. 45 – 46° (lit.[13] 46°).

2,4-Dibromo-6-t-butyl-3,4-dimethylhexa-2,5-dien-1-one (*12*) *and 2-bromo-6-t-butyl-3,4-dimethylphenol* (*13*). Bromine (48 g; 300 mM) was slowly added to a solution of 2-*t*-butyl-4,5-dimethylphenol (35 g; 200 mmol) in acetic acid (150 ml) and the solution stirred at room temperature for 6 h, by when a heavy precipitate had formed. Water (700 ml) was added, and the solid was filtered, washed with water until the filtrate was neutral, and dried. TLC of the solid material (ether:light petroleum, 1:10) indicated two products of R_F-values 0.71 and 0.49. The material was dissolved in 500 ml of light petroleum and kept at −25° overnight. A bright yellow substance (24 g) precipitated, shown by TLC to be the more polar of the two reaction products. Recrystallization from light petroleum gave an analytically pure product, m.p. 72 – 74°. This was identified by its spectral data, discussed above, as compound *12*. (Found: C 43.2; H 4.77; Br 47.4. Calc. for $C_{12}H_{16}Br_2O$: C 42.9; H 4.81; Br 47.6. Mol. wt. 336.) Mass spectrum shows significant peaks at *m/e* (rel. int. %): 336 M^+ (< 1); 255 (34); 243 (79); 241 (100); 215 (22); 213 (24); 162 (33). The molecular weight was independently determined to 321 using the molecular weight apparatus described above.

The filtrate from the crystallization was concentrated to a small volume and placed on a column of Al_2O_3 (500 g) and eluted with 1000 ml of ether: light petroleum (1:100). This yielded 18.5 g of the less polar of the reaction products in pure form, m.p. 40 – 42° (from EtOH:H_2O, 9:1). It was identified as 2-bromo-6-*t*-butyl-3,4-dimethylphenol by the following spectral data: λ_{max} (hexane) 276 nm (ε = 10 500). NMR δ = 6.97 ppm (s, 1H, Ar*H*), 5.80 ppm (broad, 1H, OH), 2.30 ppm and 2.25 ppm (s, 3H each, ArCH_3) and 1.40 ppm (s, 9H, *t*-butyl). Mass spectrum shows prominent peaks at *m/e* (rel. int. %): 258 (23) $M^{+\cdot}$, 256 (24), 243 (98), 241 (100), 215 (24), 213 (25), 162 (45). (Found: C 56.2; H 6.52. Calc. for $C_{12}H_{17}BrO$: C 56.0; H 6.68.)

2-Bromo-4,5-dimethylanisole. 2-Bromo-4,5-dimethylphenol (6.3 g; 31 mmol) was methylated with dimethyl sulphate in alkali,[14] affording 5.8 g (87 %) of the ether, m.p. 47 – 48° (lit. [15] 30 – 32°), NMR: δ = 7.23 and 6.65 ppm (s, 1H each, Ar*H*), 3.81 ppm (s, 3H, $-OCH_3$), 2.18 and 2.15 ppm (s, 3H each, ArCH_3).

3,4-Dimethylanisole-6-[^3H] (*2b*). A Grignard reagent was prepared from 2-bromo-4,5-dimethylanisole (3.0 g; 14 mmol) and magnesium (0.68 g; 28 mmol) in dry ether (30 ml). The solution was stirred for 2 h to complete the reaction, whereafter 1 ml of tritiated water (sp. act. 20 mC/ml) was added dropwise and the stirring continued for another hour. Water (20 ml) was then added, the ether layer separated, and the water layer extracted with ether (3 × 10 ml). The combined extract was dried (Na_2SO_4) and evaporated *in vacuo*. TLC revealed the presence of unreacted bromo compound. The mixture of products was therefore catalytically dehalogenated over 10 % Pd-C as described for *1a*, and purified on preparative TLC (ether:light petroleum 1:20). This yielded 1.0 g (53 %) of the tritiated anisole *2b*. Sp. act. 14.2 μC/mmol.

3,4-Dimethylphenol-6-[^3H] (*2a*). To the tritiated anisole *2b* (0.1 g; 0.73 mmol) was added dropwise BBr_3 (62 mg; 0.25 mmol), causing a vigorous reaction. After about 2 min, saturated $NaHCO_3$-solution (1 ml) was slowly added and the mixture extracted with ether (3 × 1 ml). The extract was subjected to preparative TLC (ether:light petroleum 1:5), and the phenolic material was isolated. Yield 76 mg (84 %), sp. act. 13.9 μC/mmol.

2,6-Dibromo-3,4-dimethylphenol-5-[^3H]. 2,6-Dibromo-3,4-dimethylphenol [16] (8 g) in trifluoroacetic acid (20 ml) was treated with tritiated water (10 μl, sp. act. 5 C/ml) in a

sealed ampoule at 80° for 3 h. The solution was then poured into saturated $NaHCO_3$-solution (300 ml) and extracted with ether. The ether extract was dried (Na_2SO_4) and evaporated, and the residue redissolved in methanol (10 ml) and evaporated to remove exchangeable tritium. The solid product was used in the next step without further purifications.

3,4-Dimethylphenol-5-[^3H] (*3a*). This compound was prepared from the above dibromo phenol by catalytic dehalogenation as described for *1a*. Sp. act. 0.6 μC/mmol.

3,4-Dimethylanisole-5-[^3H] (*3b*). This compound was prepared from *3a* by the method described for *1b*. Sp. act. 0.5 μC/mmol.

5-Methoxyindane-4-[^3H] (*4b*). 4-Bromo-5-methoxyindane [8] (1 g; 4.4 mmol) was converted to the corresponding Grignard reagent and treated with tritiated water (1 ml, 20 μC/ml) as described for *2b*, affording 0.4 g of *4b* (65 %). Sp. act. 39.1 μC/mmol.

5-Indanol-4-[^3H] (*4a*). The above tritiated ether *4b* was demethylated with BBr_3 as described for *2a*. Sp. act. 26.9 μC/mmol.

5-Methoxyindane-6-[^3H] (*5b*). This compound was prepared from 6-bromo-5-methoxyindane [17] (2 g; 8.8 mmol) *via* the Grignard reagent as described for *2b*. Sp. act. 7.6 μC/mmol.

5-Indanol-6-[^3H] (*5a*). Demethylation of *5b* (100 mg; 0.6 mmol), using the method described for *2a*, afforded 72 mg (80 %) of *5a*. Sp. act 6.5 μC/mmol.

4,6-Dibromo-5-indanol. 5-Indanol (2 g; 14.9 mmol) was treated with bromine (5.5 g; 34.3 mmol) in CCl_4 at 0° for 3 h, washed with saturated $NaHCO_3$ solution, dried (Na_2SO_4) and evaporated. The crude product was placed on a silica gel column (100 g) and eluted with 200 ml of ether:light petroleum (1:20). This gave 3.2 g (73 %) of product, m.p. 31 – 32° (light petroleum). (Found: C 37.3; H 2.90. Calc. for $C_9H_8Br_2O$: C 37.0; H 2.77.) ν_{max} (KBr) 3520 cm^{-1}. NMR: $\delta = 7.24$ ppm (s, 1H, Ar*H*), 5.70 ppm (broad, 1H. OH), 3.2 – 2.7 ppm (m, 4H, $ArCH_2$), 2.3 – 1.8 ppm (m, 2H, $-CH_2$-).

4,6-Dibromo-5-methoxyindane. The above dibromoindanol (2 g; 6.9 mmol) was methylated with dimethyl sulphate (2.2 g; 17.1 mmol) in alkaline solution.[14] After crystallization from light petroleum, 1.8 g (86 %) of product, m.p. 28 – 29°, was obtained. (Found: C 40.2; H 3.24. Calc. for $C_{10}H_{10}Br_2O$: C 39.2; H 3.30). NMR: $\delta = 7.26$ ppm (s, 1H, Ar*H*), 3.82 ppm (s, 3H, $-OCH_3$), 3.1 – 2.3 ppm (m, 4H, $ArCH_2$-), 2.3 – 1.7 ppm (m, 2H, $-CH_2$-).

4,6-Dibromo-5-methoxyindane-7-[^3H]. This compound was obtained from the above methoxyindane (1 g; 3.3 mmol) by reaction with tritiated water (10 μl, sp. act. 5 C/ml) in trifluoroacetic acid (10 ml) as described for 2,6-dibromo-3,4-dimethylphenol-5-[^{3}H].

5-Methoxyindane-7-[^3H] (*6b*). 4,6-Dibromo-5-methoxyindane-7-[^{3}H] (750 mg; 2.4 mmol) was catalytically dehalogenated as described for *1a*, giving 290 mg (81 %) of product. Sp. act. 5.0 μC/mmol.

5-Indanol-7-[^3H] (*6a*). Demethylation of *6b* (100 mg, 0.6 mmol) with BBr_3 (55 mg; 0.2 mmol) as described for *2a* afforded 65 mg (72 %) of *6a*. Sp. act. 3.2 μC/mmol.

5-Bromo-6-tetralol and methylether. Bromination of 6-tetralol gave 5-bromo-6-tetralol as main product.[5] Repeated crystallization from light petroleum gave pure 5-bromo-6-tetralol, m.p. 75 – 76° (lit.[18] 74°). Methylation of this bromophenol with dimethyl sulphate gave 5-bromo-6-methoxytetralin, m.p. 38 – 39° (lit.[19] 38 – 39°). NMR: The two aromatic protons give an AB-pattern centered at $\delta = 6.83$ ppm ($J = 9$ cps, $\delta_A = 6.98$ ppm, and $\delta_B = 6.68$ ppm), 3.84 ppm (s, 3H, $-OCH_3$), 2.9 – 2.5 ppm (m, 4H, $ArCH_2$-), 2.0 – 1.5 ppm (m, 4H, $-CH_2$-).

6-Methoxytetralin-5-[^3H] (*7b*). The methyl ether above (1.3 g; 5.4 mmol) was converted to the Grignard reagent and treated with tritiated water (1 ml, 20 mC/ml) as described for *2b*. Sp. act. 26.4 μC/mmol.

6-Tetralol-5-[^3H] (*7a*). The tritiated ether *7b* was demethylated with BBr_3 as described for *2a*. Sp. act. 26.2 μC/mM.

6-Tetralol-7-[^3H] (*8a*). 5-Bromo-6-tetralol [18] (1.2 g, 5.3 mmol) was treated with tritiated water under acid catalysis as described for 2-bromo-4,5-dimethylphenol-2-[^3H]. Catalytic dehalogenation as by *1a* gave 700 mg (92 %) of product. Sp. act. 1.9 μC/mmol. No significant radioactivity could be detected in the product obtained after dibromination of *8a*, showing that no significant tritiation had occurred in the 8-position of 5-bromo-6-tetralol.

6-Methoxytetralin-7-[^3H] (*8b*). The tritiated phenol *8a* (400 mg; 2.8 mmol) was methylated with dimethyl sulphate as described for *1b*. Sp. act. 0.6 μC/mmol.

5,7-Dibromo-6-methoxytetralin. 5,7-Dibromo-6-tetralol [18] (1 g; 3.3 mmol) was methylated with dimethyl sulphate (1 g; 8.2 mmol) in alkaline solution,[14] affording 0.86 g (82 %) of product, m.p. 76 – 77° (light petroleum). (Found: C 41.2; H 3.91. Calc. for $C_{11}H_{12}Br_2O$: C 41.3; H 3.79.) NMR: $\delta = 7.21$ ppm (s, 1H, Ar*H*), 3.82 ppm (s, 3H, $-OCH_3$), 2.8 – 2.5 ppm (m, broad, 4H, $ArCH_2$-), 2.0 – 1.5 ppm (m, broad, 4H, $-CH_2$-).

6-Methoxytetralin-8-[^3H] (*9b*). Acid catalyzed tritiation of 5,7-dibromo-6-methoxytetralin (700 mg; 2.2 mmol), as described for 2,6-dibromo-3,4-dimethylphenol-5-[^{3}H], followed by catalytic dehalogenation (see *1a*) gave 250 mg (77 %) of *9b*. Sp. act. 11.5 μC/mmol.

6-Tetralol-8-[^3H] (*9a*). Demethylation of *9b* (74 mg; 0.5 mmol) with BBr_3, as described for *2a*, yielded 64 mg (94 %) of *9a*. Sp. act. 11.1 μC/mmol.

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