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Robin G.F. Giles [a c], Ivan R. Green [b] & J. Alexandre X. Pestana [a]

[a] Department of Organic Chemistry, University of Cape Town, Rondebosch, 7700, South Africa

[b] Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa

[c] School of Mathematical and Physical Sciences, Murdoch University, WA, 6150

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SYNTHESIS OF E-3-HYDROXYMETHYL-1-METHOXY-4-(1'-PENTENYL)BENZENE

Robin G.F. Giles,[a#] Ivan R. Green[b*], and J. Alexandre X. Pestana[a]

[a] Department of Organic Chemistry, University of Cape Town, Rondebosch, 7700, South Africa.

[b] Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa.

ABSTRACT: The title compound with exclusively the **E**-geometry has been synthesized by two independent routes. When this compound was reacted with cerium(IV) ammonium nitrate, it was found that oxidative cyclisation to the corresponding 4-hydroxybenzopyrans did not occur. This further defines the structural parameters required for such oxidative cyclisations.

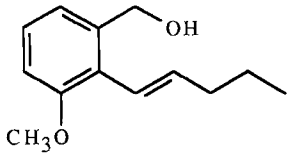
Present address: School of Mathematical and Physical Sciences, Murdoch University, WA, 6150.
* To whom correspondence should be addressed.

We have previously established the novel cyclisations of 2-alkenyl-3-hydroxyalkyl-1,4-dimethoxynaphthalenes[1,2,3] and benzenes[4] to afford the corresponding pyran derivatives using either cerium(IV) ammonium nitrate or potassium *t*-butoxide in dimethylformamide. Use of the former reagent leads to oxidative cyclisation and also occurs without the 4-methoxy substituent although the 1-alkoxy group was found to be essential. Thus compound **1** was readily converted into the pair of isomeric 4-hydroxybenzopyranols **2** and **3**. This information on the minimum structural requirements for the cyclisation enabled a mechanism to be formulated in which the 1-alkoxy substituent stabilised charges which developed on the benzilic carbon *ortho* to it through resonance. It still remained however, to ascertain whether this was the only influence that was exerted by this alkoxy group, or if it also provided a site for coordination to the metal oxidant. In order to distinguish between these two possibilities, the compound **4**, isomeric with **1**, has now been synthesised as follows.

At the outset it was apparent that the usual methods that we[4] and others[5] had developed would not yield the synthetic target **4** since the obvious starting amide **5** would yield the 1,2,3-trisubstituted amide **6** and not the required 1,3,4-trisubstituted analogue **7*** upon lithiation followed by methylation.[4]

Earlier successful acylations with premixed trifluoroacetic anhydride and alkyl carboxylic acids[6] persuaded us to treat 3-methylanisole **8** with a 1:1 mixture of pentanoic acid and trifluoroacetic anhydride. In this way the *ortho*-pentanoylanisole **9** (22%) and the required *para*-isomer **10** (77%) were formed. The latter product could be purified from the mixture through crystallisation.

* For clarity and consistency, the numbering of all the benzene derivatives will start at the methoxy ring carbon and hence will be considered as anisole derivatives.



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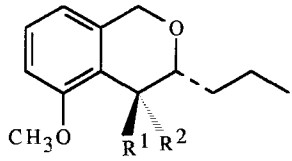
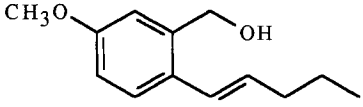


2 R^1 = OH; R^2 = H
3 R^1 = H; R^2 = OH



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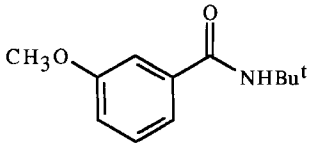

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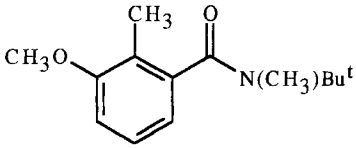

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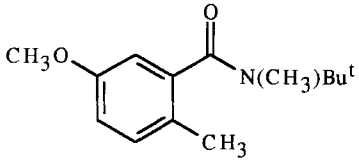

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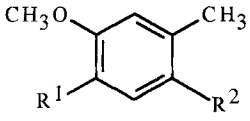
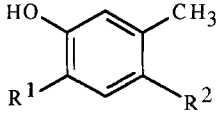


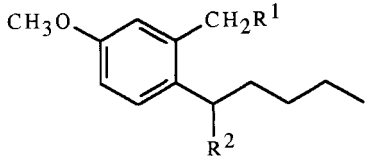
8 R^1 = R^2 = H
9 R^1 = $CO(CH_2)_3CH_3$; R^2 = H
10 R^1 = H; R^2 = $CO(CH_2)_3CH_3$



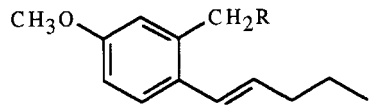
11 R^1 = $CO(CH_2)_3CH_3$; R^2 = H
12 R^1 = H; R^2 = $CO(CH_2)_3CH_3$

As a consequence of minor ambiguities in assigning individual structures **9** and **10** to the products of acylation an alternative route for their synthesis was sought. Thus *meta*-cresyl valerate was treated with boron trifluoride etherate to yield the two expected phenols which were easily separated chromatographically. The major product, phenol **11** (85%), was formed by *ortho* migration while the minor product, phenol **12** (2%) resulted from *para* migration. ^{1}H n.m.r. spectroscopy confirmed the known phenol **11**[7] as the major product by a signal at δ 12.44 for the hydrogen-bonded phenolic group while 3-H appeared as an *ortho* coupled doublet at δ 7.64 (*J* 8 Hz); 4-H appeared as a doublet of doublets at δ 6.70 (*J* 8 and 2 Hz) and 6-H appeared as a *meta* coupled doublet at δ 6.75 (*J* 2 Hz). Conversion of phenols **11** and **12** into the respective anisoles **9** and **10** was accomplished in the usual way. Unambiguous structural assignments could now be made for anisoles **9** and **10**.

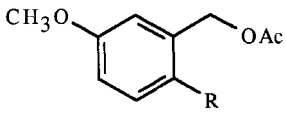
Clemmensen reduction of ketone **10** yielded the expected pentylanisole **13**. Bromination of this anisole using N-bromosuccinimide was complicated by the fact that there are two benzilic positions for bromination to occur. As indeed our objective was to convert anisole **13** into the dibromo derivative **14** many different attempts were made to effect this. In all cases the product of monobromination, **15**, whose initial formation was favoured through selective resonance stabilisation of the intermediate radical by the *para*-methoxy substituent was always produced as a by-product together with **14**. An effective separation of product **15** from the reaction mixture was not feasible but since its presence did not interfere with the subsequent reactions, its derivative was removed at the next stage.



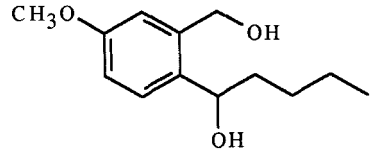
13 $R^1 = R^2 = H$
14 $R^1 = R^2 = Br$
15 $R^1 = H$; $R^2 = Br$



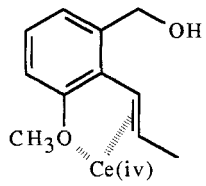
16 R = Br
17 R = H



18 R = H
19 R = $CO(CH_2)_3CH_3$
20 R = $COCH_3$



21



22

Optimum bromination was achieved using 2.5 mol N-bromosuccinimide per mole of pentylanisole **13**. The resulting mixture of products **14** and **15** was subjected to stereoelectively *trans*- dehydrobromination conditions with boiling lutidine to yield a mixture of the **E**-olefins **16** and **17**. These were chromatographically separated and bromide **16** was hydrolysed with 20% aqueous sodium hydroxide to afford the required **E**-olefine **4** in an overall yield of 12% from ketone **10**.

In an alternative synthetic procedure for **E**-olefin **4**, acetate **18**[8] was pentanoylated with premixed pentanoic acid and trifluoroacetic anhydride to yield the pure keto acetate **19** in 28% yield. This yield was significantly lower than that for the acetylation of acetate **18** under similar conditions to give **20** in 46% yield. Keto acetate **19** was reduced quantitatively with lithium aluminium hydride to the corresponding diol **21**. The signals of both hydrogens of the hydroxyl groups of diol **21** appeared at δ 3.50 in the ^{1}H n.m.r. spectrum while the two diastereotopic methylene hydrogens of the hydroxymethyl group appeared as two doublets at δ 4.53 and δ 4.69 (J 12 Hz). Treatment of diol **21** with phosphorous tribromide yielded the unstable dibromide **14** as the major bromination product prepared earlier. Dehydrobromination as before yielded exclusively the **E**-pentenyl anisole **16** which was converted into the **E**-olefin **4** as before.

Compound **4** was subjected to reaction with two molar equivalents of cerium(IV) ammonium nitrate in an attempt to achieve oxidative cyclisation to the corresponding 4-hydroxypyran derivatives.[4]

Decomposition of the starting materials was observed without isolation of any identifiable product. This confirms that, for the substituents considered, the

minimum structural requirements are to have a 1-alkoxy-2-alkenyl-3-(1'-hydroxyalkyl)benzene.

It is likely that the first step in such reactions, therefore, is the co-ordination of cerium(IV) to both the alkoxy oxygen and also the double bond of the *ortho* alkenyl substituent, as shown in structure **22**. This is then followed by a single electron transfer to afford a radical cation as previously formulated.[4]

EXPERIMENTAL

M.p.s. were determined on a Kofler hot-stage apparatus. All ^1H n.m.r. spectra were measured for solutions in ^2H-chloroform with tetramethylsilane as internal reference using either Varian XL-100 or Brucker WH-90 spectrometers; IR spectra were measured for Nujol mulls using a Perkin-Elmer 983 spectrophotometer. Preparative layer chromatography (PLC) was performed on glass plates coated with Merck Kieselgel 60 F_{254}; column chromatography refers to dry packed columns of the same gel (70-230 mesh). Hexane refers to that fraction boiling in the range of 60-80°C. The phrase 'residue obtained upon work-up' refers to the material remaining when an organic extract was separated, dried ($MgSO_4$), and evaporated under reduced pressure.

1-*Methoxy*-5-*methyl*-2-(1'-*pentanoyl*)*benzene* 9 and 1-*methoxy*-3-*methyl*-4-(*1'-pentanoyl*)*benzene* 10

METHOD A:

m-Methoxytoluene (5.10 g; 41.8 mmol) was added at once to a premixed solution of trifluoroacetic anhydride (17.64 g; 84 mmol) and valeric acid (8.57 g;

84 mmol) and the thick mixture was stirred under nitrogen at room temperature for 3.5 h. Methanol (100 ml) was added and stirring was continued for a further 1 h after which time the reaction mixture was thrown into saturated sodium hydrogen carbonate (400 ml) and this solution was extracted with dichloromethane (3 x 100 ml). The extract was washed with water and the residue obtained upon work-up was recrystallised from light petroleum to give pure arylvalerophenone **10** (4.42 g; 51%) as colourless crystals, m.p. 52-53 °C; ν_{max} 1671 cm^{-1}; δ_H 0.94 (3H, t, *J* 7 Hz, 5'-CH_3), 1.39(2H, m, *J* 7 Hz, 4'-CH_2), 1.69(2H, m, *J* 7 Hz, 3'-CH_2), 2.54(3H, s, 3-CH_3), 2.87(2H, t, *J* 7 Hz, 2'-CH_2), 3.83(3H, s, OCH_3), 6.68-6.84(2H, m, 2- and 6-*H*), and 7.74(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 76.0; H, 8.9%; M^+ 206. Calc. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8%; M 206). The mother liquors were shown to contain a 1:1 mixture of **9** and **10** which was not possible to separate using the many systems that were attempted.

METHOD B

(i) m-Cresyl valerate (1.06 g; 5.44 mmol) was added to freshly distilled boron trifluoride etherate (6 ml) and the resultant solution stirred and heated at 110 °C under nitrogen for 4 h. After cooling, the mixture was thrown into water (150 ml) and the aqueous mixture was extracted with ethyl acetate. The residue obtained upon work-up was chromatographed using ethyl acetate - hexane (1:4) as eluent. The first fraction to be eluted was phenol **11** (900 mg, 85%) b.p. 122-123 °C (3 mmHg), m.p. 16 °C [lit.,[7] b.p. 121-125 °C (3 mmHg); lit.,[9] m.p. 16 °C], and this was followed by the second fraction phenol **12** (24 mg, 2%) as colourless prisms, m.p. 88-89 °C (lit.,[7] m.p., 88-89 °C).

(ii) **1-*Methoxy*-3-*methyl*-4-(1'-*pentanoyl*)*benzene* 10**. Phenol **12** (17 mg; 0.09 mmol) was dissolved in anhydrous acetone (30 ml) containing potassium carbonate (48 mg; 0.27 mmol) and dimethyl sulphate (34 mg; 0.27 mmol) and heated under reflux for 2 h. The cooled solution was filtered and the filtrate evaporated to an oil which was dissolved in ether (80 ml) and washed with conc. ammonia (2 x 10 ml), dilute hydrochloric acid (20 ml) and water to ultimately yield the valerophenone **10** (19 mg; 97%) as colourless cubes m.p. 52-53.5 °C (from hexane) identical to the material prepared earlier.

(iii) **1-*Methoxy*-5-*methyl*-2-(1'-*pentanoyl*)*benzene* 9**. Phenol **11** (68 mg; 0.35 mmol) was converted as above into the corresponding methyl ether **9** (76 mg, 97%) as an oil; ν_{max} (film) 1667 cm^{-1}; δ_H 0.92(3H, t, *J* 7 Hz, 5'-C*H*$_3$), 1.17-1.87(4H, m, 3'- and 4'-C*H*$_2$), 2.18(3H, s, 3-C*H*$_3$), 2.96(2H, t, *J* 7 Hz, 2'-C*H*$_2$), 3.88(3H, s, OC*H*$_3$), 6.6-7.0(2H, m, 4-and 6-*H*), and 7.61(1H, d, *J* 8 Hz, 3-*H*). (Found: C, 75.8; H, 8.9%; M^+ 206. Calc. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8%; M 206).

1-*Methoxy*-3-*methyl*-4-*pentylbenzene* 13. Ketone **10** (5.17 g; 25.1 mmol) in toluene (15 ml) was added to a vigorously stirred mixture of hydrochloric acid (70 ml of 6 M solution) and zinc amalgam (15 g) and heated under reflux for 72 h. After cooling, the liquids were decanted from the zinc amalgam, diluted with water (100 ml) and neutralised with saturated sodium hydrogen carbonate. Ether extraction yielded a residue which was chromatographed using hexane as eluent to afford the dialkylanisole **13** (2.24 g; 55% based on recovered starting material) as an

oil. δ_H 0.96(3H, t, *J* 6 Hz, 5'-C*H*$_3$), 1.44(6H, m, 2'-,3'-, and 4'-C*H*$_2$), 2.32(3H, s, 3-C*H*$_3$), 2.58(2H, t, *J* 8 Hz, 1'-C*H*$_2$), 3.82(3H, s, OC*H*$_3$), 6.7-6.8(2H, m, 2- and 6-*H*), and 7.10(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 81.3; H, 10.6%; M^+ 192. Calc. for $C_{13}H_{20}O$: C, 81.2; H, 10.5%; M 192). Later fractions yielded starting material (800 mg; 15%).

E-3-*Bromomethyl*-1-*methoxy*-4-(1'-*pentenyl*)*benzene* 16 and E-1-*methoxy*-3-*methyl*-4-(1'-*pentenyl*)*benzene* 17. Dialkylanisole **13** (501 mg; 2.61 mmol) in anhydrous carbon tetrachloride (30 ml) was treated with N-bromosuccinimide (1.16 g; 6.5 mmol) and benzyl peroxide (50 mg) and stirred under reflux for 1 h. The cooled solution containing compound **14** and **15** was filtered to remove the succinimide, the filtrate was stripped of solvent the residue was treated with dry lutidine (10 ml) and the derived solution was then heated under reflux for 30 min. This was cooled and filtered to remove the lutidine hydrobromide salt and the filtrate stripped of solvent to leave a residue that was treated with hydrochloric acid (40 ml of a 1 M solution) and extracted with dichloromethane. The residue obtained upon work-up was chromatographed (PLC) using hexane as eluent to yield the **E**-olefin **16** (140 mg; 20%) as an unstable oil. δ_H 0.97 (3H, t, *J* 7 Hz, 5'-C*H*$_3$), 1.47(2H, sextet, *J* 7 Hz, 4'-C*H*$_2$), 2.20(2H, q, *J* 7 Hz, 3'-C*H*$_2$), 3.38(3H, s, OC*H*$_3$), 4.50(2H, s, 3-C*H*$_2$), 6.06(1H, dt, *J* 16 and 7 Hz, 2'-C*H*), 6.65(1H, d, *J* 16 Hz, 1'-C*H*), 6.79(1H, dd, *J* 8 and 3 Hz, 6-H), 6.86(1H, d, *J* 3 Hz, 2-*H*), and 7.41(1H, d, *J* 8 Hz, 5-*H*). [M^+ 270 and 268 (1:1)]. The second band that was isolated was the **E**-olefin **17** (137 mg; 28%) as an oil; δ_H 0.94(3H, t, *J* 8 Hz, 5'-C*H*$_3$), 1.14-1.76(4H, m, 3'-and 4'-C*H*$_2$), 2.29(3H, s, 3-C*H*$_3$), 3.74(3H, s, OC*H*$_3$), 5.94(1H, dt, *J* 17 and 7

Hz, 2'-C*H*), 6.50(1H, d, *J* 17 Hz, 1'-C*H*), 6.62-6.80(2H, m, 2- and 6-*H*), and 7.34(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 82.0; H, 9.4%; M^+ 190. Calc. for $C_{13}H_{18}O$: C, 82.1; H, 9.5%; M 190).

E-3-*Hydroxymethyl*-1-*methoxy*-4-(1'-*pentenyl)benzene* 4. Bromo-olefin **16** (102 mg; 0.38 mmol) in toluene (3 ml) was added to aqueous sodium hydroxide (20 ml of a 5 M solution). The resultant mixture was stirred under reflux for 80 h, cooled and acidified with dilute hydrochloric acid, and extracted with dichloromethane. The residue obtained upon work-up was chromatographed (PLC) using ethyl acetate - hexane (5:95) as eluent. The alcohol **4** (47 mg; 60%) was obtained as an oil; ν_{max} (film) 3360 cm^{-1}; δ_H 0.96(3H, t, *J* 7 Hz, 5'-CH_3), 1.49(2H, m, *J* 7 Hz, 4'-CH_2), 1.89(1H, br s, OH, D_2O exchangeable), 1.98(2H, q, *J* 7 Hz 3'-CH_2), 3.88(3H, s, OCH_3), 4.68(2H, s, 3-CH_2), 6.00(1H, dt, *J* 16 and 7 Hz, 2'-C*H*), 6.55(1H, d, *J* 16 Hz, 1'-C*H*), 6.78 (1H, dd, *J* 8 and 3 Hz, 6-*H*), 6.90(1H, d, *J* 3 Hz, 2-*H*), and 7.37(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 75.7; H, 9.0%; M^+ 206. Calc. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.7%; M 206).

3-*Acetoxymethyl*-4-*acetyl*-1-*methoxybenzene* 20. Acetate **18**[8] (390 mg; 2.17 mmol) was added at once to a mixture of glacial acetic acid (195 mg; 3.25 mmol) and trifluoroacetic anhydride (832 mg; 3.96 mmol) and the resulting mixture was stirred at room temperature for 48 h under nitrogen. Dichloromethane (40 ml) was then added and the organic layer was washed with saturated sodium hydrogen carbonate (2 x 20 ml) and water. The residue obtained on work-up was chromatographed using ethyl acetate - hexane (3:7). The first fraction to be eluted was starting material **18** (96

mg; 25%) followed by the keto-acetate **20** (223 mg; 46%) as white needles, m.p; 69.5-70.5 °C (from hexane); ν_{max} 1733 and 1652 cm^{-1}; δ_H 2.17(3H, s, OCOCH_3), 2.57(3H, s, COCH_3), 3.88(3H, s, OCH_3), 5.51 (2H, s, 3-CH_2), 6.88(1H, dd, *J* 8 and 3 Hz, 6-*H*), 7.05 (1H, d, *J* 3 Hz, 2-*H*), and 7.86(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 64.8; H, 6.3%; M^+ 222. Calc. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.4%; M 222).

3-Acetoxymethyl-1-methoxy-4-(1'-pentanoyl)benzene **19**. Acetate **18** (7.43 g; 41.3 mmol) was added at once to a mixture of valeric acid (21 g; 202 mmol) and trifluoroacetic acid (42.5 g; 202 mmol) and the resulting mixture was stirred at room temperature for 72 h under nitrogen. Work-up was as described for anisole **20**. The residue was chromatographed using ethyl acetate - hexane (3:7) as eluent. The first fraction to be eluted was starting material **18** (1.05 g; 14%) followed by the product keto-acetate **19** (3.05 g; 28%) as white crystals m.p. 42.5-43 °C (from hexane). ν_{max} 1736 and 1664 cm^{-1}; δ_H 0.95(3H, t, *J* 7 Hz, 5'-CH_3), 1.21-1.98 (4H, m, 3'- and 4'-CH_2), 2.16(3H, s, OCOCH_3), 2.91(2H, t, *J* 7 Hz, 2'-CH_2), 3.88(3H, s, OCH_3), 5.49(2H, s, 3-CH_2), 6.87(1H, dd, *J* 8 and 3 Hz, 6-*H*), 7.06(1H, d, *J* 3 Hz, 2-*H*), and 7.84(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 68.1; H, 7.7%; M^+ 264. Calc. for $C_{15}H_{20}O_4$: C, 68.2; H, 7.6%; M 264).

3-Hydroxymethyl-1-methoxy-4-(1'-hydroxypentyl)benzene **21**. Keto-acetate **19** (750 mg; 2.84 mmol) in dry ether (5 ml) was dripped into a stirred slurry of lithium aluminium hydride (4 mol equivalents) in dry ether at room temperature and the resulting mixture was stirred for a further 30 minutes. After the usual work-up the residue was chromatographed using

ethyl acetate - hexane (2:3) to give the diol **21** (636 mg; 100%) as an oil; ν_{max} (film) 3430 cm^{-1}; δ_H 0.89(3H, t, *J* 6 Hz, 5'-C*H*$_3$), 1.12(4H, m, 3'-and 4'-C*H*$_2$), 1.80(2H, br m, 2'-C*H*$_2$), 3.30(2H, br s, 2 x OH, D_2O exchangeable), 3.80(3H, s, OC*H*$_3$), 4.53 and 4.69(1H each, d, *J* 12 Hz, 3-C*H*$_2$), 4.78(1H, t, *J* 7 Hz, 1'-C*H*), 7.83(1H, dd, *J* 8 and 3 Hz, 6-*H*), 7.89(1H, br s, 2-*H*), and 8.32(1H, d, *J* 8 Hz, 5-*H*). (Found: C, 69.4; H, 9.1%; M^+ 224. Calc. for $C_{13}H_{20}O_3$: C, 69.7; H, 9.0%; M 224).

E-3-*Hydroxymethyl*-1-*methoxy*-4-(1'-*pentenyl*)*benzene* 4 and E-3-*bromomethyl*-1-*methoxy*-4-(1'-*pentenyl*)*benzene* 16. Diol **21** (128 mg; 0.57 mmol) was added at once to dry benzene (1 ml) containing phosphorous tribromide (0.7 mol equivalents) and the resulting solution was stirred under nitrogen for 2 h at room temperature after which time the solvent was stripped from the reaction mixture. Lutidine (10 ml) was added and the solution heated under reflux for 40 min, then cooled and sodium hydroxide (1 ml of a 1.25 M solution) was added. The resultant solution was stirred under reflux for a further 15 min, cooled and poured into hydrochloric acid (1.5 M solution until acid to litmus) and extracted with dichloromethane. The residue obtained upon work-up was chromatographed (PLC) using ethyl acetate - hexane (3:7) as eluent to yield the bromoanisole **16** (26 mg, 16%) identical to the material described earlier followed by the alcohol **4** (20 mg, 17%).

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