Sites of Successive Bromination of the Ambident Nucleophiles 2-Methoxy-, 2,4-Dimethoxy- and 2,4,6-Trimethoxy-benzylidenefluorenes and 2,2-Dimesityl-1-*tert*-butylethenol

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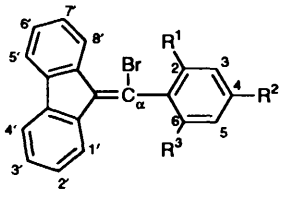
The reaction of the 2-methoxy- **2a**, 2,4-dimethoxy- **2c** and 2,4,6-trimethoxy-benzylidenefluorene **2d** with bromine in AcOH has been investigated. With compound **2a** the initial product is the α,9'-dibromide **3a** which, with excess of bromine, gives the α,5,9'-tribromo derivative **3c**. In NaOAc–AcOH compound **3a** gives both debromination to **2a** and dehydrobromination to **1a** and **3b** gives the α,5-dibromo derivative **5a**. Compounds **2c** and **2d** give successively the 5-bromo- and 3-bromo- **4b** and **4c** and the α,5-dibromo- and α,3-dibromo- **5b** and **5c** derivatives and further bromination of compound **2d** gives, first, the α,3,5-tribromo- **6** and then the α,3,5,2',7'-pentabromo- **7** derivatives. Higher sensitivity to substituents of the α-aryl ring compared with the double bond towards electrophilic bromine and accompanying increased steric shielding of the double bond account for this order. Bromination of 2,2-dimesityl-1-*tert*-butylethenol **11** gives mainly ring-brominated 2,2-dimesityl-1-*tert*-butylethanones **12–14** and several other derivatives.

For a study of nucleophilic vinylic substitution (α-bromo-2-methoxybenzylidene)fluorene **1a**, (α-bromo-2,4-dimethoxybenzylidene)fluorene **1c** and (α-bromo-2,4,6-trimethoxybenzylidene)fluorene **1d** were required.



1a; R^1 = OMe, R^2 = R^3 = H
b; R^2 = OMe, R^1 = R^3 = H
c; R^1 = R^2 = OMe, R^3 = H
d; R^1 = R^2 = R^3 = OMe

Styrenes are potentially ambident nucleophiles since electrophilic attack by bromine can take place both on the ring and at the double bond. However, ring-substituted styrenes ArCH=CHR (R = H, Me, CO_2H), with one,[1] two[2] or three[3] substituents, including 2,6-dimethoxy-,[2a] 3,4-dimethoxy- and 2,4,6-trimethyl-styrene,[3] are attacked at the double bond rather than on the ring, presumably due to the higher stability of a benzyl cation compared with an isomeric arenium ion.

This preference should be sensitive to both electronic and steric effects at both the double bond and the aromatic ring. For example, while it was first suggested that the enol derived from 2,4,6-trimethylacetophenone is brominated at the double bond,[4] it was shown later that it is mainly brominated on the ring.[5] However, the larger substrate iodine attacks the double bond.[5]

The Hammett's ρ^+-value is higher for electophilic aromatic substitution, including bromination on the ring, than is the ρ^+-value for the bromine addition to the double bond of arylethylenes.[6] Consequently, when other effects are equal, the addition of an electron-donating substituent to the ring should increase the relative percentage of ring bromination. The site of bromination of mono-, di- and tri-methoxy-substituted benzylidenefluorenes should, therefore, be influenced by both steric and electronic factors.

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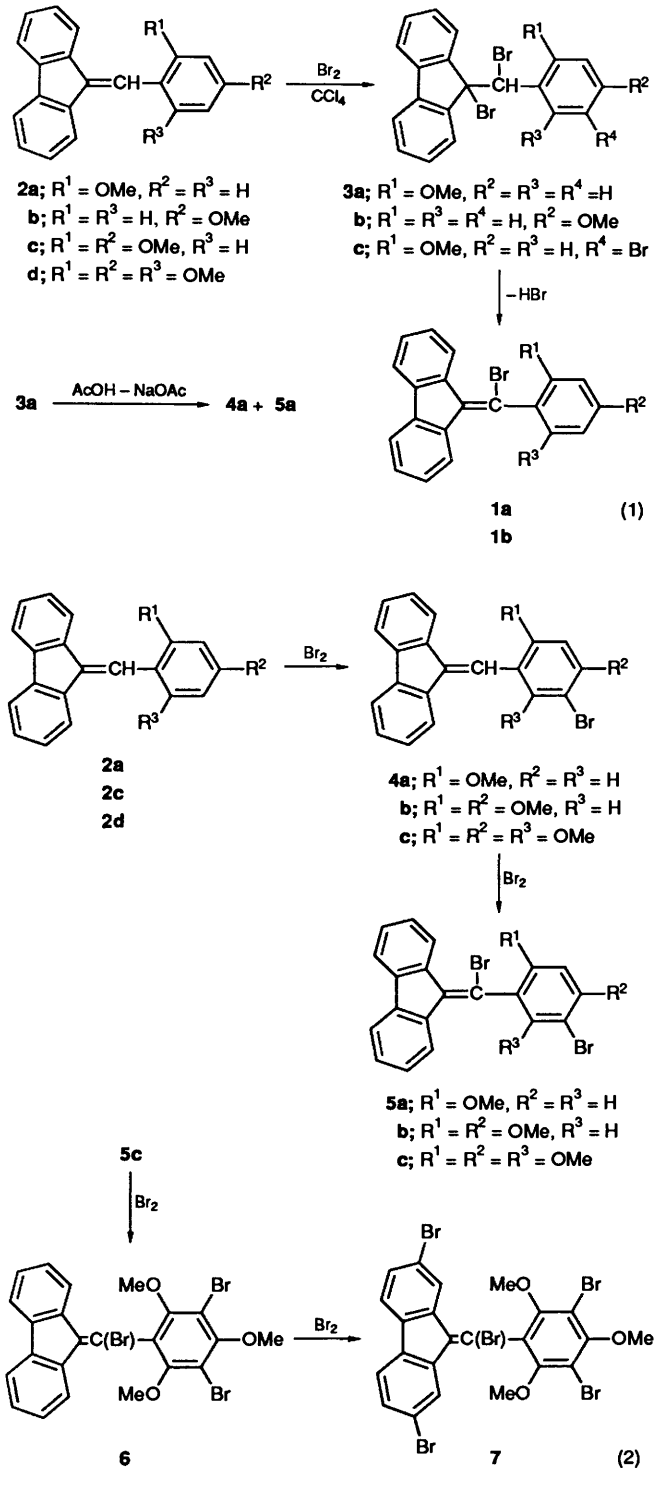
Results and Discussions

Bromination of Methoxy-substituted Arylidenefluorenes.—*para*-Substituted benzylidenefluorenes, including the *p*-methoxy derivative **2b**, add bromine to the double bond to form compound **3b**, and dehydrobromination of the adduct then gives the α-bromo derivative **1b** [equation (1)].[7] To elucidate whether the regioselectivity of attack by bromine is dependent on a steric factor we added bromine to the formally more crowded *ortho*-isomer **2a**. The ^{1}H NMR spectrum of the crude mixture showed that, on addition of less than an equimolar amount of bromine, only the α,9'-dibromide **3a** was formed. When an equimolar amount of bromine was added, compound **3a** was the main product, but ~ 20% of the α,5,9'-tribromide **3c** is formed, sometimes together with a small amount of the α,5-dibromide **5a**. However, neither **3c** nor **5a** is formed when compound **3a** is not formed, so that compound **3a** is the precursor of tribromide **3c** which, in turn, gives compound **5a**. Heating of the adducts **3a** and **3c** in AcOH–NaOAc gave the dehydrobromination products α-bromo-2-methoxy- **1a** and α,5-dibromo-2-methoxy- **5a** benzylidenefluorene, together with the debromination products **2a** and **4a**.

However, when (2,4-dimethoxybenzylidene)fluorene **2c** was brominated by an equimolar amount of bromine in refluxing AcOH, the ring-bromination product (5-bromo-2,4-dimethoxybenzylidene)fluorene **4b** was isolated in 50% yield. Reaction of monobromide **4b** with an equimolar amount of bromine in AcOH gave the α,5-dibromo derivative **5b**, *i.e.*, the product of a double-bond bromination [equation (2)].

When (2,4,6-trimethoxybenzylidene)fluorene **2d** reacts with bromine or with dioxane dibromide, mono-ring bromination to compound **4c** first takes place. With an excess of bromine the main product is the α,3,5-tribromo derivative **6** but the α,3-dibromo **5c** and the α,3,5,2',7'-pentabromo **7** derivatives were also isolated [equation (2)].

The desired mono-α-bromo derivatives **1c** and **1d** were not obtained in either of these reactions. When compound **2d** was treated with *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide and/or under irradiation, neither ring- nor double-bond bromination took place.



The structures of the bromination products can be established from the ^{1}H NMR spectra. That compounds **4b** and **5b** are the 5- and not the 3-bromo derivatives is deduced from the appearance of two 1 H aromatic singlets rather than an AB quartet. The position of the bromine in compounds **4a** and **5a** was deduced by analogy. The α-brominated species **1a**, **5a–c**, **6** and **7** are characterized by two features: (a) a strong downfield shift of the fluorenylidene 8′-H hydrogen, the closer neighbour to bromine in the ring *cis* to the latter, from $\delta \sim 7.8$ in the α-H derivatives **2** and **4** to δ 8.86–9.04 in the α-Br derivatives. This is attributed to electron withdrawal by the bromine. (b) A substantial highfield shift of 1′-H (on the ring *trans* to the bromine) from δ 7.1–7.3 in derivatives **2** and **4** to δ 6.21–6.46. This is ascribed to anisotropic shielding by the aromatic ring which probably has an appreciable torsional angle with the C=C bond due to steric repulsion between *o*-OMe and α-Br.

The change from *p*-OMe **2b** to *o*-OMe **2a** which increases the crowding near the C=C bond probably also increases the reactivity of the aryl ring to bromination, due to the presence of the unhindered *para* (*i.e.*, 5-) position. Nevertheless, exclusive addition to the double bond takes place. However, the presence of the additional 4-methoxy group in the ring of compound **2c** shifts the reaction to ring bromination. Since the steric effect around the double bond is the same for compounds **2a** and **2c**, it is the electronic effect of the added 4-methoxy group which increases the nucleophilicity of the ring much more than that of the double bond, in spite of the higher hindrance to ring bromination. This is not surprising. The Hammett's ρ-values for bromination of monosubstituted benzenes in AcOH[6a,b] or of polymethylbenzenes in $MeNO_2$[6b] are −12 and −8.1, while for addition of bromine to the double bond of styrenes in MeOH or in AcOH and for chlorination of cinnamic acids in AcOH $\rho^+ = -4.1$ to −4.3, respectively.[6c–e] The large difference in the ρ-values for the two types of reaction, coupled with the high electron-donating ability of the *p*- or *o*-MeO substituents, accounts for the shift in regioselectivity. We note that a similar effect is observed in the further bromination. The reaction of the 5-bromo-2,4-dimethoxy-substituted system **4b** with bromine results now in α-bromination to give compound **5b** rather than by attack on the ring C-3. Although a steric effect may contribute to a lower reactivity, we believe that it is the electronic effect of the 3-bromo substituent which decreases the reactivity compared with that of the double bond.

The regioselectivity in the reaction of the 2,4,6-trimethoxy-substituted system **2d** resembles that of the dimethoxy analogue **2c**. In spite of increased steric hindrance at the double bond, the first bromine attacks the ring, and the second bromine attacks the double bond of compound **4c**. Only then does the third bromine attack C-5 of the dibromide **5c**. Bromination of the fluorene ring occurs only afterwards, indicating that a 3-bromo-1-(substituted bromomethyl)-2,4,6-trimethoxyphenyl ring is still more nucleophilic than a 9′-(bromovinyl substituted)-fluorene ring.

The steric effects on the addition of bromine to the double bond, if any, are therefore masked by the strong electronic effect of the methoxy and bromine substituents. However, the initial bromination at the ring rather than at C-α in compounds **2c** and **2d** is in contrast with what is known for competition between the double bond and the aryl ring bromination of substituted styrenes,[1–3] including 2,6-dimethoxystyrene.[2a] Comparison of the latter compound with compounds **2c** and **2d** indicates that the fluorenyl moiety reduces the reactivity of the double bond, presumably by steric effects. Hence, activation (of different magnitude) of both sites by the methoxy and bromine substituents is superimposed on steric reduction of the rates by the *o*-MeO group and the fluorenyl moiety. Only when the ring is deactivated by one Br atom does the double bond of compounds **4b** and **4c** become more reactive in bromination than does the other ring position.

In the discussion above, we implicitly compared transition states leading to arenium ions and benzyl cations. However, the addition to the double bond may alternatively lead initially either to a substituted 9′-fluorenyl cation or, less likely, to a bromonium ion, rather than to the benzyl cation. Since both these latter species are less sensitive to ring-substituent effects than is the benzyl cation, the conclusions regarding substituent effects remain valid.

Bromination of Mesityl-substituted Systems.—It is of interest to compare the present results with those for bromination of mesityl-substituted systems. Whereas, 2,4,6-trimethylstyrene **8a**

adds bromine exclusively to the double bond, giving only dibromide **9** ($R^1 = R^2 = H$)[3] [equation (3)] the enol of mesitophenone **8b** gives exclusively or mainly ring bromination product **10** rather than dibromide **9**. However, iodination of compound **8b** occurs at the double bond and not at the ring. This is surprising since enols are frequently assumed to react at a close-to-diffusion-controlled rate at the double bond.[8]

$$\underset{\mathbf{8}}{MesC(R^1)=CR_2^2} \xrightarrow{Br_2} \underset{\mathbf{9}}{MesC(R^1)(Br)-C(Br)R_2^2} + \underset{\mathbf{10}}{(BrMes)C(R^1)=CR_2^2} \quad (3)$$

a $R^1 = R^2 = H$

b $R^1 = OH$, $R^2 = H$

Mes = mesityl = 2,4,6-trimethylphenyl

Steric effects at the double bond decrease the reactivity of addition of bromine, and 2,6-dimethylstyrene and compound **8a** add bromine much more slowly than expected on the basis of electronic effects evaluated from the reactions of 3- and 4-substituted styrenes.[6d]

In order to investigate whether steric effects at the double bond will direct the bromination of even an enol to the ring rather than to the double bond, the bromination of the sterically crowded stable enol 1-*tert*-butyl-2,2-dimesitylethenol **11**[9] was investigated.[10] Several products were obtained [equation (4)], and some were identified as the ring-brominated products **12–14**, and a cleavage bromination product **15**, while others were tentatively assigned, on the basis of mass spectra and analogies[11] with similar compounds, as substituted benzofurans **16** and **17**. It is important to emphasize that none of the α-bromo ketone **18**, expected to be produced from the

$$\underset{\mathbf{11}}{Mes_2C=C(OH)Bu^t} \xrightarrow[Fe,\ CCl_4]{Br_2} \underset{\mathbf{12}}{(BrMes)_2CHCOBu^t} + \underset{\mathbf{13}}{(Br_2Mes)(BrMes)CHCOBu^t} + \underset{\mathbf{14}}{(Br_2Mes)_2CHCOBu^t} + \underset{\mathbf{15}}{MesCH(Br)COBu^t} + \underset{\mathbf{16}}{\text{Me, Br, Me, MesBr, Bu}^t} + \underset{\mathbf{17}}{\text{Me, Me, Me, MesBr}_2\text{, Bu}^t} \quad (4)$$

enol formed by addition of bromine to the double bond, was observed. However, ketone **15** may be obtained by an initial bromination of the double bond, or by cleavage of compound **18**. Our interpretation of these results indicates nearly exclusive

$$\underset{\mathbf{18}}{Mes_2C(Br)COBu^t}$$

ring rather than double-bond bromination, but is complicated by the fact that substitution generates HBr which presumably isomerizes the enol(s) to the keto derivative.[10] Although unchanged substrate **11** is still present in appreciable amounts when most of the products of equation (4) are observed, the rates of the various processes are unknown. Although the product tentatively indicates that ring bromination is faster than addition to the double bond, this conclusion is not unequivocal.

Experimental

General.—M.p.s were measured on a Thomas Hoover apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were measured with a Bruker 400 MHz spectrometer, with *J* values given in Hz, and mass spectra with an MAT 311 instrument at 70 eV. Light petroleum refers to the fraction boiling in the range 40–60 °C.

9′-(2-Methoxybenzylidene)fluorene **2a**.—(*a*) A solution containing fluorene (3.3 g, 20 mmol), 2-methoxybenzaldehyde (2.7 g, 20 mmol) and Bu^{t}OK (2.2 g, 20 mmol) in Bu^{t}OH (50 cm^3) was refluxed for 5 h. The precipitate formed was filtered off, washed with water, and crystallized (EtOH) to give 9′-(2-methoxybenzylidene)fluorene **2a** (5.0 g, 88%) as a yellow, difficultly crystallizable resin, m.p. 62–64 °C; $\delta_H(CDCl_3)$ 3.87 (3 H, s, MeO), 6.98–7.10 (2 H, m, ArH), 7.02 (1 H, s, =CH), 7.26–7.43 (4 H, m, ArH), 7.60–7.73 (5 H, m, ArH) and 7.81–7.85 (1 H, m, ArH); *m/z* (50 °C) (relative abundance, assignment) 284 (12, M), 178 (17, FlCH), 120 (8, AnCH), 119 (6, AnC), 105 (6, PhCO), 88 (10), 86 (64, $C_5H_{10}O$), 84 (100, C_5H_8O) and 47 (22, C_2H_7O) (Found: C, 88.4; H, 5.8. Calc. for $C_{21}H_{16}O$: C, 88.70; H, 5.67%).

(*b*) To a solution containing fluorene (3.3 g, 20 mmol) and 2-methoxybenzaldehyde (2.7 g, 20 mmol) in toluene (50 cm^3) was added solid KOH (300 mg, 5.4 mmol) and the mixture was refluxed for 10 h in a Dean–Stark apparatus. The solvent was evaporated off to give a yellow oil (4.97 g, 83%) which by TLC was mainly title compound **2a**, although it contained several other products. Attempted crystallization from CH_2Cl_2, MeOH, EtOH, light petroleum and EtOAc resulted in a resin. Chromatography on silica [(96:4) light petroleum–EtOAc as eluent] gave compound **2a** as a yellow solid, m.p. 63–64 °C, which became an oily solid on storage.

9′-Bromo-9′-(α-bromo-2-methoxybenzyl)fluorene **3a**.—(*a*) To a solution of 9′-(2-methoxybenzylidene)fluorene **2a** (1.3 g, 4.6 mmol) in acetic acid (30 cm^3) was added bromine (0.23 cm^3, 4.6 mmol), and the colour was immediately discharged. After 10 min at room temp. the mixture was poured into water (250 cm^3), and the precipitate formed was filtered off, washed with water, and dried (2.0 g, 98%). Crystallization (EtOH) gave a 4:1 mixture (NMR) of the title compound **3a** m.p. 108–110 °C (decomp.) and 9′-(5-bromo-2-methoxybenzylidene)fluorene **4a** (together 1.4 g, 70%); $\delta_H(CDCl_3)$ 3.59 (0.6 H, s, OMe, **4a**), 3.64 (2.4 H, s, OMe, **3a**), 6.38–6.53 (3 H, m, Ar + 9′-H), 6.69 (1 H, d, *J* 8, ArH), 6.98 (1 H, t, *J* 8, ArH), 7.16–7.23 (2 H, m, ArH), 7.33–7.53 (4 H, m, ArH), 7.69–7.73 (1 H, m, ArH) and 8.15–8.19 (1 H, m, ArH); *m/z* 446, 444 and 442 (1.4, 2.6 and 1.3, M), 365 and 363 (6 and 6, M − Br), 364 and 362 (9 and 9, M − HBr), 284 (78, M − Br_2), 269 (20, M − Br_2 − Me), 253 (11, M − Br_2 − OMe) and 178 (100, $C_{14}H_{10}$) (Found: C, 56.7; H, 3.6; Br, 37.2. Calc. for $C_{21}H_{16}Br_2O$: C, 56.79; H, 3.63; Br, 35.98%).

(*b*) To a solution of 9′-(2-methoxybenzylidene)fluorene (0.69 g, 2.3 mmol) in AcOH (15 cm^3) was added a solution of bromine (0.09 cm^3, 1.7 mmol) in AcOH (10 cm^3). The colour of bromine disappeared after 5 min at room temperature. The mixture was poured into water (150 cm^3), and the precipitate formed was filtered off, washed with water and dried, to leave a light yellow solid (750 mg), m.p. range 98–124 °C; $\delta_H(CDCl_3)$: two methoxy signals at δ 3.67 (**3a**) and δ 3.57 (**1a**) in a 3:1 ratio. Chromatography on silica with 96:4 light petroleum–ethyl acetate as eluent gave compound **3a** as a very light yellow solid (500 mg, 66%), m.p. 128–128.5 °C; $\delta_H(CDCl_3)$ 3.67 (3 H, s, OMe), 6.44–6.53 (3 H, m, ArH + HC=?), 6.66–6.71 (1 H, m, ArH), 6.95–7.03 (1 H, m, ArH), 7.18–7.23 (2 H, m, ArH), 7.35–7.55 (4 H, m, ArH), 7.70–7.74 (1 H, m, ArH) and 8.16–8.20 (1 H, m, ArH); *m/z* 446, 444 and 442 (6, 13 and 7, M), 284 (100, M − Br_2), 269 (12, M − Br_2 − OMe − CH_2) and 201 and 199 (24 and 23, $MeOC_6H_4C_6H_4$) (Found: C, 57.1; H, 3.6. Calc. for $C_{21}H_{16}Br_2O$: C, 56.78; H, 3.63%).

9'-Bromo-9'-(α,5-dibromo-2-methoxybenzyl)fluorene **3c**.—To a solution of compound **3a** (0.45 g, 0.1 mmol) in AcOH (25 cm^3) was added bromine (0.062 cm^3, 12 mmol). After the mixture had been stirred for 3 h, a solid had separated out. After filtration, the solid was washed with water and dried to give title compound **3c** as a solid (25 mg, 5%), m.p. 140 °C; $\delta_H(CDCl_3)$ 3.63 (3 H, s, OMe), 6.33–6.39 (2 H, m, ArH), 6.68–6.69 (1 H, m, 6- or 9'-H?), 7.04–7.09 (1 H, m, ArH), 7.19–7.24 (2 H, m, ArH), 7.35–7.58 (4 H, m, ArH), 7.66–7.71 (1 H, m, ArH) and 8.15 (1 H, d, *J* 8, ArH); *m/z* (110 °C) 526, 524, 522 and 520 (1.2, 4, 4 and 1.2, M), 445, 444, 443, 442, 441 and 440 (4, 5, 8, 8, 4 and 3, M − Br and M − HBr), 364 and 362 (60 and 61, M − 2Br), 282 (9, Fl=CAn − 2H?), 268 (37, Fl=CAn − Me?), 239 (43), 178 (100, FlMe) and 163 (12, Fl) (Found: C, 48.3; H, 2.9; Br, 46.1. Calc. for $C_{21}H_{15}Br_3O$: C, 48.22; H, 2.89; Br, 46.83%).

Water (150 cm^3) were added to the solution. The solid thus obtained was filtered off and dried. Crystallization from EtOH gave a further crop of pure tribromide **3c** (435 mg, total yield 88%), m.p. 140 °C.

9'-(α-Bromo-2-methoxybenzylidene)fluorene **1a**.—A solution containing 9'-bromo-9'-(α-bromo-2-methoxybenzyl)fluorene **3a** (165 mg, 0.37 mmol) in AcOH (10 cm^3)–NaOAc (31 mg, 0.37 mmol) was refluxed for 90 min, then poured into water (100 cm^3), and the precipitate thus formed was filtered off, washed with water and dried to give a solid (111 mg) which was a mixture of starting material **3a** and compound **2a** according to ^1H NMR spectroscopy [$\delta_H(CDCl_3)$ 3.81 (2.3 H, s, OMe, **3a**), 3.87 (0.5 H, s, MeO, **1a**), 4.09 (0.2 H, s, OMe) and 6.21–8.93 (12 H, m, ArH)]. Crystallization from EtOH gave 9'-(α-bromo-2-methoxybenzylidene)fluorene **1a** as a yellow solid (52 mg, 39%), m.p. 117–118 °C; $\delta_H(CDCl_3)$ 3.81 (3 H, s, MeO), 6.23 (1 H, d, *J* 8, ArH), 6.83–6.91 (1 H, m, ArH), 7.05–7.51 (7 H, m, ArH), 7.62–7.75 (2 H, m, ArH), 8.88–8.89 (1 H, m, dd, *J* 1.5, ArH); *m/z* (90 °C) 364 and 362 (47 and 50, M), 268 (79, M − Br − Me), 178 (45, $FlCH_2$), 165 (77, FlH) and 28 (100, CO) (Found: C, 69.4; H, 4.15; N, 21.4. Calc. for $C_{21}H_{15}BrO$: C, 69.43; H, 4.16; N, 22.00%).

Reflux of compound **3a** in AcOH for 90 min gave a **3a**:**2a** mixture in 97% yield.

9'-(α,5-Dibromo-2-methoxybenzylidene)fluorene **5a**.—A solution of the tribromide **3c** (340 mg, 0.65 mmol) in AcOH (20 cm^3)–NaOAc (54 cm^3, 0.65 mmol) was refluxed for 90 min. The mixture was poured into water (130 cm^3), and the precipitate thus formed was filtered off, washed with water, and dried to give a ~1:5 mixture of a compound with $\delta_H(CDCl_3)$ 3.65, which was tentatively assigned as 9'-(5-bromo-2-methoxybenzylidene)fluorene **4a** (which was not investigated further) and 9'-(α,5-dibromo-2-methoxybenzylidene)fluorene **5a**, $\delta_H(CDCl_3)$ 3.78 (2.5 H, s, OMe, **5a**), 3.85 (0.5 H, s, OMe, **4a**), 6.31 (1 H, d, *J* 8, FlH), 6.94 (2 H, d, *J* 8.5, ArH), 7.29–7.74 (7 H, m, ArH) and 8.86 (1 H, approx. d, *J* 8, FlH). Crystallization from EtOH gave pure compound **5a** as crystals (221 mg, 77%), m.p. 189 °C; $\delta_H(CDCl_3)$ 3.78 (3 H, s, OMe), 6.30 (1 H, d, *J* 8, 1'-H), 6.94 (2 H, d, *J* 8.5, or 2 s, Anisyl H), 7.19–7.75 (7 H, m, 6 × FlH + AnH) and 8.85 (1 H, d, *J* 8, 8'-H); $\delta_C(CDCl_3)$ 56.17 (OMe), 113.12, 113.75, 118.85, 119.32, 119.47, 124.04, 126.24, 127.12, 127.17, 128.28, 129.23, 132.41, 132.99, 133.51, 137.14, 137.71, 137.98, 139.88, 141.23 and 155.16; *m/z* (120 °C) 444, 442 and 440 (12, 26 and 14, M), 364 and 362 (8 and 10, MH − Br), 348 and 346 (20 and 22, M − Br − Me), 268 (19), 253 (10), 239 (23), 165 (100, FlH) and 126 (16) (Found: C, 57.3; H, 3.3; Br, 35.8. Calc. for $C_{21}H_{14}Br_2O$: C, 57.04; H, 3.19; Br, 36.15%).

9'-(2,4-Dimethoxybenzylidene)fluorene **2c**.—A solution consisting of fluorene (5 g, 30 mmol), 2,4-dimethoxybenzaldehyde (5 g, 30 mmol) and Bu^{t}OK (3.3 g, 30 mmol) in refluxing Bu^{t}OH (50 cm^3) was stirred for 4 h. The precipitate formed was filtered off, washed with water, and crystallized from EtOH to give 9'-(2,4-dimethoxybenzylidene)fluorene **2c** (9.0 g, 95%), m.p. 109 °C; $\delta_H(CDCl_3)$ 3.85 and 3.87 (6 H, 2 s, MeO), 6.44 (2 H, m, 3- and 5-H), 7.06 (1 H, t, 2'-H), 7.22 (3 H, m, fluorenylidene H), 7.54 (1 H, d, 6-H) and 7.64 and 7.75 (3 H and 2 H, m, fluorenylidene H); $\delta_C(CDCl_3)$ 55.11 and 55.22 (Me), 98.19, 104.11, 117.86, 119.25, 119.47, 120.16, 123.85, 123.91, 126.31, 126.64, 127.45, 127.87, 131.76, 134.68, 136.72, 138.59, 139.71, 140.82, 158.77 and 161.37; *m/z* 314 (87, M), 271 (34, M − CH − CH_2O), 238 (45, M − CH_2 − 2 MeO), 226 (35, M − 2 CH − 2 MeO) and 178 (100, $C_{14}H_{10}$) (Found: C, 84.3; H, 5.9. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77%).

Bromination of 9'-(2,4-Dimethoxybenzylidene)fluorene **2c**.—To a solution of compound **2c** (0.63 g, 2 mmol) in AcOH (10 cm^3) was added Br_2 (0.11 cm^3, 2 mmol) and the reaction mixture was heated until evolution of HBr had ceased. The mixture was poured into water (150 cm^3) and the precipitate was filtered off and dried. Three cystallizations from EtOH gave pure 9'-(5-bromo-2,4-dimethoxybenzylidene)fluorene **4b** (0.42 g, 50%), m.p. 154–156 °C; $\delta_H(CDCl_3)$ 3.88 and 3.98 (6 H, 2 s, MeO), 6.54 (1 H, s, 3-H), 7.11 (1 H, t, 2'-H), 7.31 (3 H, m, 1-, 4'- and 5'-H), 7.55 (1 H, s, α-H), 7.68 (3 H, m, 3'-, 6'- and 7'-H), 7.78 (1 H, d, 8'-H) and 7.82 (1 H, s, 6-H); $\delta_C(CDCl_3)$ 55.88 and 56.34 (MeO), 96.25, 101.60, 119.16, 119.43, 119.66, 120.34, 121.99, 124.01, 126.69, 126.83, 127.91, 128.32, 134.63, 135.94, 136.50, 138.94, 139.50, 141.12, 156.95 and 158.14; *m/z* 394 and 392 (70 and 71, M), 283 (21, M − Br − CH_2O), 255 (15), 240 (19), 226 (28) and 178 (100, $C_{14}H_{10}$) (Found: C, 66.9; H, 4.5; Br, 20.6. Calc. for $C_{22}H_{17}BrO_2$: C, 67.19; H, 4.39; Br, 20.32%).

Bromination of Compound **4b**.—Compound **4b** (0.6 g, 1.52 mmol) was dissolved in AcOH (10 cm^3), Br_2 (0.09 cm^3, 1.6 mmol) was added, and the reaction mixture was heated until evolution of HBr had ceased. After work-up as above, crude 9'-(α,5-dibromo-2,4-dimethoxybenzylidene)fluorene **5b** (0.85 g, 80%) was obtained. Purification by PLC, followed by crystallization from EtOH, gave pure compound **5b**, m.p. 160–162 °C; $\delta_H(CDCl_3)$ 3.82 (3 H, s, 2-MeO), 4.02 (3 H, s, 4-MeO), 6.40 (1 H, d, 1'-H), 6.61 (1 H, s, 3-H), 6.93 (1 H, t, 2'-H), 7.25 (1 H, t, 3'-H), 7.40 (2 H, m, 6'- and 7'-H), 7.47 (1 H, s, 6-H), 7.65 (1 H, d, 4'-H), 7.71 (1 H, d, 5'-H) and 8.86 (1 H, d, 8'-H), $\delta_C(CDCl_3)$ 56.31 and 56.44 (MeO), 97.17, 102.48, 119,27, 119,43, 119.62, 124.08, 125.00, 126.26, 127.06, 127.16, 128.18, 129.11, 133.67, 137.37, 137.78, 138.19, 139.79, 141.21, 156.60 and 157.71; *m/z* 474, 472 and 470 (16, 32 and 16, M), 393 and 391 (22 and 20, M − Br), 378 and 376 (11 and 11, M − Br − Me) and 165 (100, fluorenyl) (Found: C, 55.4; H, 3.25; Br, 34.3. Calc. for $C_{22}H_{16}Br_2O_2$: C, 55.96; H, 3.42; Br, 33.85%).

9'-(2,4,6-Trimethoxybenzylidene)fluorene **2d**.—A solution containing 2,4,6-trimethoxybenzaldehyde (2 g, 10 mmol), fluorene (1.66 g, 10 mmol) and Bu^{t}OK (1.12 g, 10 mmol) in refluxing ^{t}BuOH (30 cm^3) was stirred for 20 h. After disappearance of both reagents (TLC) the precipitate was filtered off, washed with water (50 cm^3), dried, and crystallized from 2:1 $CHCl_3$–EtOH to give 9'-(2,4,6-trimethoxybenzylidene)-fluorene **2d** (3.2 g, 93%), m.p. 197–198 °C; $\delta_H(CDCl_3)$ 3.73 (6 H, s, 2- and 6-MeO), 3.90 (3 H, s, 4-MeO), 6.23 (2 H, s, 3- and 5-H), 7.10 (1 H, d, 1'-H), 7.28 (3 H, m, 2'-, 6'- and 7'-H), 7.31 (1 H, t, 3'-H), 7.42 (1 H, s, α-H), 7.67 (1 H, d, 4'-H), 7.70 (1 H, d, 5'-H) and 7.84 (1 H, m, 8'-H); $\delta_C(CDCl_3)$ 55.34 and 55.55 (MeO), 90.60, 107.27, 118.46, 119.07, 119.29, 120.48, 124.61, 126.40, 126.67, 127.40, 127.53, 136.93, 137.79, 139.00, 139.80, 140.51, 159.07 and 161.71; *m/z* 344 (100, M), 178 (44, $C_{14}H_{10}$) and 166 (20, $C_{13}H_{10}$) (Found: C, 79.1; H, 5.8. Calc. for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85%).

Bromination of 9'-(2,4,6-Trimethoxybenzylidene)fluorene.—(a) *With an equimolar amount of bromine.* To a solution of dioxane dibromide, obtained by addition of bromine (0.05 cm^3, 1 mmol) to 1,4-dioxane (10 cm^3) was added compound **2d** (0.34 g, 1 mmol). The mixture was heated for *ca.* 1 h, until evolution of HBr had ceased, and then was poured into water (100 cm^3) and the precipitate formed (0.4 g, 95%) was filtered off and dried. Crystallization from EtOH gave 9'-(3-bromo-2,4,6-trimethoxybenzylidene)fluorene **4c**, m.p. 192–193 °C; $\delta_H(CDCl_3)$ 3.63 (3 H, s, 6-MeO), 3.74 (3 H, s, 2-MeO), 4.00 (3 H, s, 4-MeO), 6.42 (1 H, s, 5-H), 7.10 and 7.33 (1 H and 4 H, m, fluorenylidene H), 7.42 (1 H, s, α-H) and 7.69 and 7.85 (2 H and 1 H, m, fluorenylidene H); $\delta_C(CDCl_3)$ 55.86, 56.43 and 61.13 (MeO), 90.52, 92.43, 98.38, 113.48, 117.23, 119.32, 119.46, 120.53, 124.39, 126.81, 126.88, 127.99, 128.20, 137.26, 138.26, 139.28, 140.73, 156.97, 157.41 and 157.86; *m/z* 404 and 402 (66 and 65, M), 247 and 245 [25 and 26, $C_6HBr(OMe)_3$], 227 (26), 214 (17), 178 (100, $C_{14}H_{10}$) and 165 (27, fluorenyl) (Found: C, 65.6; H, 4.4; Br, 18.7. Calc. for $C_{23}H_{19}BrO_3$: C, 65.26; H, 4.52; Br, 18.88%).

(b) *With an excess of bromine.* To a solution of compound **2d** (0.67 g, 2 mmol) in AcOH (20 cm^3) was added bromine (0.3 cm^3, 6 mmol). The reaction mixture was refluxed for *ca.* 2 h until evolution of HBr had ceased and was then worked up as above. Chromatography on a silica column with 7:3 light petroleum–$CHCl_3$ as eluent gave three compounds.

(i) 9'-(α,3-Dibromo-2,4,6-trimethoxybenzylidene)fluorene **5c** (120 mg, 0.24 mmol, 12% based on **2d**), m.p. 186–188 °C; $\delta_H(CDCl_3)$ 3.74 and 3.77 (6 H, 2 s, 2- and 6-MeO), 4.01 (3 H, s, 4-MeO), 6.44 (1 H, s, 5-H), 6.46 (1 H, d, 1'-H), 6.96 (1 H, t, 2'-H), 7.25 (1 H, t, 3'-H), 7.42 and 7.69 (2 H, m, fluorenylidene H) and 8.92 (1 H, d, 8'-H); no splitting of signals was observed with the chiral shift reagent (+)-Yb^{III} Resolve-Al, although a downfield shift of some of the signals by 0.02 ± 0.05 ppm/10 mg of the shift reagent was observed; $\delta_C(CDCl_3)$ 56.45, 56.83 and 61.19 (MeO), 92.99, 98.60, 119.35, 119.40, 119.65, 123.59, 126.46, 127.07, 127.37, 128.25, 129.10, 137.84, 138.26, 138.34, 138.86, 139.80, 141.26, 155.70, 156.73 and 158.60; *m/z* 504, 502 and 500 (21, 41 and 20, M), 423 and 421 (45 and 44, M – Br), 408 and 406 (8, M – Br – Me) and 166 (100, $C_{13}H_{10}$) (Found: C, 55.0; H, 3.5; Br, 31.6. Calc. for $C_{23}H_{18}Br_2O_3$: C, 55.01; H, 3.61; Br, 31.82%).

(ii) 9'-(α,3,5-Tribromo-2,4,6-trimethoxybenzylidene)fluorene **6** (0.45 g, 0.7 mmol, 35% based on **2d**), m.p. 190 °C; $\delta_H(CDCl_3)$ 3.76 (6 H, s, 2- and 6-MeO), 4.01 (3 H, s, 4-MeO), 6.35 (1 H, d, 1'-H), 6.99 (1 H, t, 2'-H), 7.27 (1 H, t, 3'-H), 7.44 (2 H, m, 6'- and 7'-H), 7.68 (2 H, m, 4'- and 5'-H) and 8.91 (1 H, d, 8'-H); $\delta_C(CDCl_3)$ 61.01 and 61.39 (MeO), 110.18, 114.23, 119.61, 119.66, 123.74, 126.52, 127.24, 127.65, 128,84, 129.17, 129.61, 137.58, 137.85, 138.85, 140.06, 141.46, 152.72 and 157.06; *m/z* 584, 582, 580 and 578 (18, 53, 53 and 19, M), 503, 501 and 499 (13, 25 and 13, M – Br) and 165 (100, fluorenyl) (Found: C, 47.4; H, 2.9; Br, 41.75. Calc. for $C_{23}H_{17}Br_3O_3$: C, 47.54; H, 2.95; Br, 41.25%).

(iii) 2',7'-Dibromo-9'-(α,3,5-tribromo-2,4,6-trimethoxybenzylidene)fluorene **7** (85 mg, 0.11 mmol, 5.5% based on **2d**), m.p. 227–228 °C; $\delta_H(CDCl_3)$ 3.81 (6 H, s, 2- and 6-MeO), 4.02 (3 H, s, 4-MeO), 6.22 (1 H, d, 1'-H), 7.36–7.62 (4 H, m, fluorenylidene H) and 9.04 (1 H, d, 8'-H); $\delta_C(CDCl_3)$ 61.28 and 61.53 (MeO), 110.23, 117.32, 120.87, 121.42, 121.56, 127.16, 128.21, 129.42, 131.65, 132.56, 137.03, 137.74, 138.84, 139.15, 154.59 and 157.83; *m/z* 742, 740, 738, 736, 734 and 732 (7, 34, 68, 69, 34 and 7, M – 2 H) and 325, 323 and 321 (51, 100 and 53, $C_6Br_2(OMe)_3$ – 2 H) (Found: C, 38.0; H, 2.2; Br, 54.2. Calc. for $C_{23}H_{15}Br_5O_3$: C, 37.39; H, 2.05; Br, 54.07%).

(c) *With NBS.* No reaction was found to occur when compound **2d** (1.09 g, 3 mmol), NBS (0.54 g, 3 mmol) and a catalytic amount of benzoyl peroxide in CCl_4 (20 cm^3) were refluxed for 35 h. Substrate **2d** was recovered unchanged.

Reaction of Enol **11** *with Bromine.*—(a) To a stirred mixture of 1-*tert*-butyl-2,2-dimesitylethenol **11**[9] (336 mg, 1 mmol) and granular (60 mesh) iron (15 mg, 0.25 mmol) in CCl_4 (10 cm^3) was added dropwise a solution of bromine (0.2 cm^3, 4 mmol) in CCl_4 (5 cm^3) in the dark at 20 °C. The mixture turned brown immediately. After addition of 1 mmol of Br_2 the mixture was stirred for 2.5 h. TLC analysis showed five spots (including starting material **11**) after 1.5 h. After addition of the remaining 3 mmol of Br_2 and stirring of the mixture for a further 105 min, enol **11** had completely disappeared (TLC) and four spots remained. 10% aq. $Na_2S_2O_3$ (100 cm^3) was added to the dark red mixture until the complete disappearance of the colour of bromine. Water (50 cm^3) and CCl_4 (30 cm^3) were added, the solution was filtered, and the organic layer was separated, dried ($MgSO_4$) and evaporated, to leave a crude yellow oil (209 mg).

Flash chromatography on a silica column with 7:3 light petroleum–CH_2Cl_2 as eluent gave four solid fractions totalling 186 mg.

Fraction 1 (25 mg), m.p. 119–126 °C, gave, after fractional crystallization from 2:1 CH_2Cl_2–light petroleum, sulfur (from the thiosulfate) and an organic fraction (8 mg) with the following spectral properties: ν_{max}(Nujol)/cm^{-1} no characteristic peak > 1400; $\delta_H(CDCl_3)$ 1.17 (9 H, s, Bu^t), 1.86, 1.98, 2.19, 2.44, 2.48 and 2.51 (18 H, 6 s, 6 × Me) and 6.99 (1 H, s, MesH); *m/z* (CI, isobutane) 495, 493, and 491 (100, MH^+, protonated benzofuran) and 414 (M – Br).

Fraction 2 (3 mg), m.p. 108–110 °C, contained material sufficient only for mass and ^1H NMR spectra: $\delta_H(CDCl_3)$ 1.18 (9 H, s, Bu^t), 1.85, 2.26, 2.29, 2.48, 2.51 and 2.71 (18 H, 6 s, 6 × Me) and 7.12 (1 H, s, MesH); *m/z* (EI) 494, 492 and 490 (47, 97 and 22, M), 479, 477 and 475 (62, 100 and 55, M – Me), 413 (30) and 412 and 410 (24 and 22, M – HBr); (CI) 494, 492 and 490 (56, 100 and 49, M), 478, 476 and 474 (9, 13 and 6, M – CH_3 – H), 447 (16), 444 (10), 415 (12), 412 (21), 334 (8), 330 (9), 312 (20), 278 (13) and 256 (11). Tentative assignment of the compounds of fractions 1 and 2: isomeric 3-dibromomesityl-2-*tert*-butyl-4,6,7-trimethylbenzofuran **17** and 5-bromo-3-bromomesityl-2-*tert*-butyl-4,6,7-trimethylbenzofuran **16**.

The third fraction, a transparent oil (150 mg), solidified to a solid, m.p. 100–103 °C. Crystallization from 1:2 light petroleum–methanol gave a solid, m.p. 104 °C, which was identified as bis(3-bromo-2,4,6-trimethylphenyl)methyl *tert*-butyl ketone **12**, ν_{max}(Nujol)/cm^{-1} 1690vs (C=O); $\delta_H(CDCl_3)$ 1.15 (9 H, s, Bu^t), 1.94, 2.07, 2.26, 2.34, 2.35 and 2.36 (18 H, 6 s, *o*- and *p*-Me), 5.75 (1 H, s, CH, does not disappear on addition of D_2O) and 6.86 and 6.91 (2 H, 2 s, MesH); $\delta_C(CDCl_3)$ 21.4, 21.4, 22.7, 22.8, 24.1 and 28.5 (Me), 45.9 and 57.9 (CH, CMe_3), 127.0, 128.0, 131.3, 131.4, 132.1, 135.1, 136.6, 136.7, 137.1, 137.2, 137.4 and 137.9 (Ar) and 215.6 (C=O); *m/z* (EI, 100 °C) 496, 494 and 492 (0.5, 0.9 and 0.5, M), 411, 409 and 407 (75, 100 and 75, M – Br – 2 H_2), 316 and 314 [18 and 19, BrMesC(Mes) – H_2], 250 (13, Mes_2C), 249 (15, Mes_2C – H), 235 (63, Mes_2C – Me), 85 (27, Bu^{t}CO) and 57 (94, Bu^t); *m/z* (CI, MeOH) 415 and 413 (31 and 27, MH – Br – 2 H, benzofuran derivative), 296 and 294 (100 and 58, Bu^{t}CO-CH_2MesBr) and 216 (50, Bu^{t}COCHMes); *m/z* (CI, NH_3) 514, 512 and 510 (47, 100 and 42, MNH_4), 408 (24) and 296 (100) (Found: C, 58.15; H, 6.0; Br, 30.2. Calc. for $C_{24}H_{30}Br_2O$: C, 58.30; H, 6.07; Br, 32.39%).

Fraction 4 (8 mg), m.p. 88–90 °C; ν_{max}(Nujol)/cm^{-1} 1700vs (C=O) and 1595 (C=C); $\delta_H(CDCl_3)$ 1.06 (9 H, s, Bu^t), 2.25, 2.26 and 2.32 (9 H, 3 s, 3 × Me), 6.24 and 6.25 (1 H, s, CH) and 6.85 (2 H, s, MesH); *m/z* (CI, CH_4) 297 and 295 (2.8 and 2.1, MH), 217 (100, Bu^{t}COCHMes), 189 (7, Bu^{t}CHMes) and 161 (7). Tentative assignment: MesCH(Br)COBu^t **15**.

(b) To a stirred mixture of enol **11** (504 mg, 1.5 mmol) and granular (60 mesh) iron (29 mg, 0.5 mmol) in CCl_4 (15 cm^3) was added dropwise a solution of bromine (0.6 cm^3), 12 mmol) in

CCl_4 (15 cm^3) in the dark at room temperature. TLC after 6 h still showed the presence of starting material **11**. Bromine (4 cm^3, 3.2 mmol) was then added and the mixture was stirred for 27 h, when starting material **11** had completely disappeared and four strong and four weak spots were observed by TLC. 5% aq. $Na_2S_2O_3$ (2 × 50 cm^3) was added and, after disappearance of the colour of bromine, the organic phase was separated, washed with water (2 × 25 cm^3), dried and evaporated. The remaining light yellow oil (500 mg), which showed in its ^1H NMR spectrum six *tert*-butyl signals, was chromatographed on a silica column with 4:1 light petroleum–CCl_4 as eluent. Each of the first two fractions turned to be a mixture of several compounds, both by NMR and by the wide range of the m.p. The third fraction was chromatographed on a preparative TLC plate, with 4:1 light petroleum–CH_2Cl_2 as eluent, and gave the known $(Br_2Mes)_2CHCOBu^t$, **14** (136 mg, 14%), m.p. 190–191 °C, with ^1H NMR and IR spectra identical with those described earlier.[10]

Repeated chromatography of the fourth fraction gave a further crop of compound **14** (20 mg, 2%) and a solid (178 mg, 20%), m.p. 110–111 °C, which after crystallization (MeOH) was identified as $(Br_2Mes)(BrMes)CHCOBu^t$, **13**, ν_{max}(Nujol)/cm^{-1} 1700 (C=O); $\delta_H(CDCl_3)$ 1.12 (9 H, s, ^{t}Bu), 1.92, 2.24, 2.26, 2.35 and 2.71 (18 H, 5 s, 6 × Me), 5.83 (1 H, s, CH) and 6.37 (1 H, s, ArH); *m/z* (90 °C) 490, 488, 486 and 484 (12, 34, 34 and 12, M − Bu^t − H), 268 (18), 85 (36) and 57 (100, Bu^t); (CI, isobutane) 574, 572 and 570 (0.29, 0.58 and 0.34, MC_2H_2) and 374 (100) (Found: C, 50.2; H, 4.8. Calc. for $C_{24}H_{29}Br_3O$: C, 50.29; H, 5.09%).

The fifth fraction (108 mg), m.p. 110–111 °C, contained some of the tribromo ketone **13** and was not separated further.

Fraction 6 was an oil which solidified on storage. Crystallization from 1:1:1 MeOH–CH_2Cl_2–$CHCl_3$ gave a compound (8 mg), m.p. 62–67 °C, with spectral properties ascribed to $BrMesCH(Br)COBu^t$: ν_{max}(Nujol)/cm^{-1} 1700 (C=O); $\delta_H(CDCl_3)$ 1.05 (9 H, s, ^{t}Bu), 2.34, 2.39 and 2.44 (9 H, 3 s, 3 × Me), 6.22 (1 H, s, CH) and 6.97 (1 H, s, ArH); *m/z* 376 (0.06, M), 297 and 295 (14 and 14, M − Br), 290 (6), 240 (6), 238 (6), 131 (8), 85 (12) and 57 (100, ^{t}Bu). The compound was impure according to its analysis (Found: C, 49.2; H, 5.2. Calc. for $C_{15}H_{20}Br_2O$: C, 47.90; H, 5.36%).

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