

Synthesis of *o*-Substituted Phenols by Criegee Rearrangement of Benzylic Hydroperoxides

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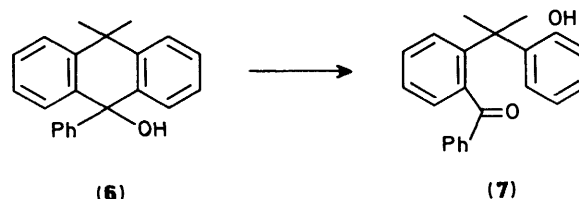
9-Phenylthioxanthren-9-ol, 10,10-dimethyl-9-phenyl-9,10-dihydroanthracen-9-ol, and 9-arylfluoren-9-ols undergo Criegee-type rearrangements when treated with hydrogen peroxide and acid to generate substituted benzophenones from the first two substrates, and monoesters of biphenyl-2,2'-diol from the fluorenes *via* subsequent Bayer-Villiger oxidation of the intermediate 2'-aroylbiphenyl-2-ol. 5-Phenyl-10,11-dihydrodibenzocyclohepten-5-ol and its dehydroderivative gave the corresponding heptanone and heptenone on treatment with acid and hydrogen peroxide. Prolonged reaction of the 5-phenyldibenzohepten-5-ol afforded products arising from oxidation of the double bond.

The rearrangement of 9-aryl-9-hydroxyxanthenes with acidified hydrogen peroxide has been developed as a synthetic route to hydroxylated aromatics.^{1,2} The suggestion³ that these reactions proceed by a Criegee-type rearrangement of the hydroperoxides has recently been confirmed,⁴ and evidence for the dominance of electronic factors over conformational restraints presented. 9-Aryl-10-phenyl-9,10-dihydroacridin-9-ols rearrange similarly upon treatment with hydrogen peroxide in the presence of acid to substituted triphenylamines.⁵ We now report the reaction of analogous ring systems with hydrogen peroxide and acid.

The acid-catalysed reaction of 9-phenylthioxanthren-9-ol (1) with hydrogen peroxide gave the previously unreported 2-benzoylphenyl 2-hydroxyphenyl sulphoxide (2) as the major product together with the sulphone dialkyl peroxide (3), thioxanthren-9-one (4), and thioxanthren-9-one 10,10-dioxide (5) (Scheme 1). Formation of small amounts of the thioxanthenes (4) and (5) is probably due to protonation or oxidation of the sulphide group, which then inhibits the rearrangement. Support

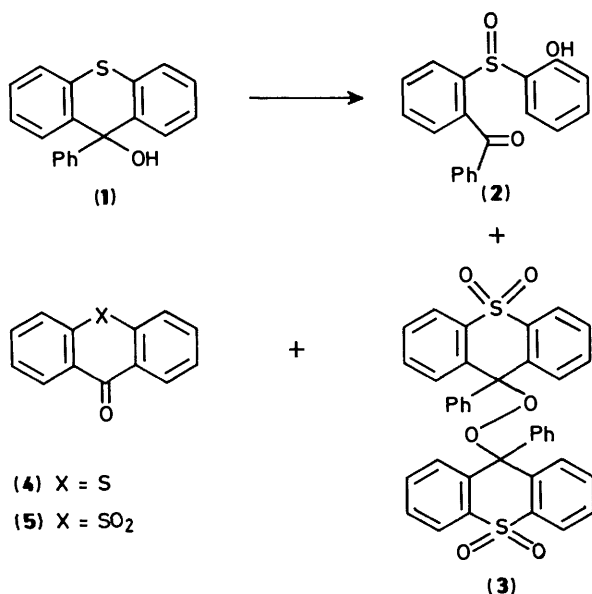
for this proposal is the formation of the thioxanthone dioxide (5) as the only ketonic product when 9-phenylthioxanthren-9-ol 10,10-dioxide was treated with acid and hydrogen peroxide.

It was established that the heteroatom is not essential for the rearrangement by treating 10,10-dimethyl-9-phenyl-9,10-dihydroanthracen-9-ol (6) with acid and hydrogen peroxide to give 2-(2-benzoyl- $\alpha\alpha$ -dimethylbenzyl)phenol (7) (80%). The

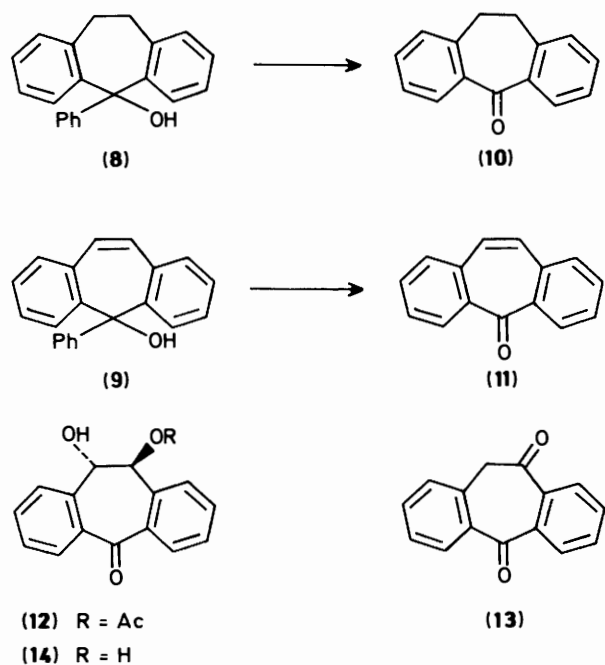


absence of detectable amounts of 10,10-dimethylantrone from this reaction mixture demonstrates that even the weakly electron-donating alkyl bridge promotes participation of the nuclear phenyl rings over the 9-phenyl substituent in the rearrangement.

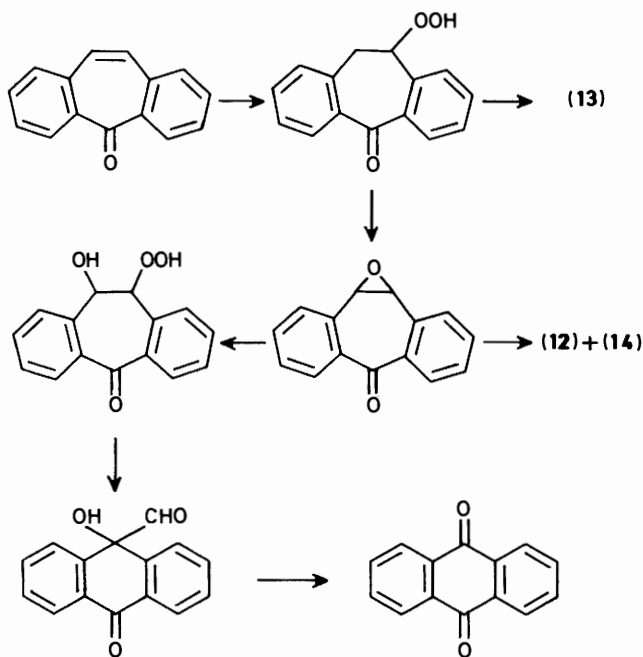
With the 5-phenyldibenzocyclohepten-5-ols (8) and (9) it has been found that dibenzocycloheptene ring is unaffected by acidified hydrogen peroxide and that the 5-phenyl substituent migrates under these conditions. The formation of 10,11-dihydrodibenzo[*a,d*]cyclohepten-5-one (10) and 5*H*-dibenzo[*a,d*]cyclohepten-5-one (11), from the acid and hydrogen peroxide rearrangement of 5-phenyl-10,11-dibenzocycloheptenol (8) and 5-phenyldibenzocyclohepten-5-ol (9) respectively, is attributed to either the difference in energies of the conformers or the relatively high energy required for the formation of the intermediate or transition state in the rearrangement reaction. In both these substrates models indicate that the pseudo-equatorial hydroperoxides, which are formed from the alcohols, should be significantly lower in energy. When the reaction of the dibenzocycloheptene (9) was allowed to proceed for a prolonged period, anthraquinone and a compound which is proposed to be 10-acetoxy-11-hydroxy-10,11-dihydrodibenzo[*a,d*]cyclohepten-5-one (12) were obtained. Although the i.r. and n.m.r. spectra of the cycloheptenone (12) were in accord with a structure, in which the substituents are *trans* to each other, since chromatography of the compound led to its partial decomposition it could not be obtained sufficiently pure for



Scheme 1.

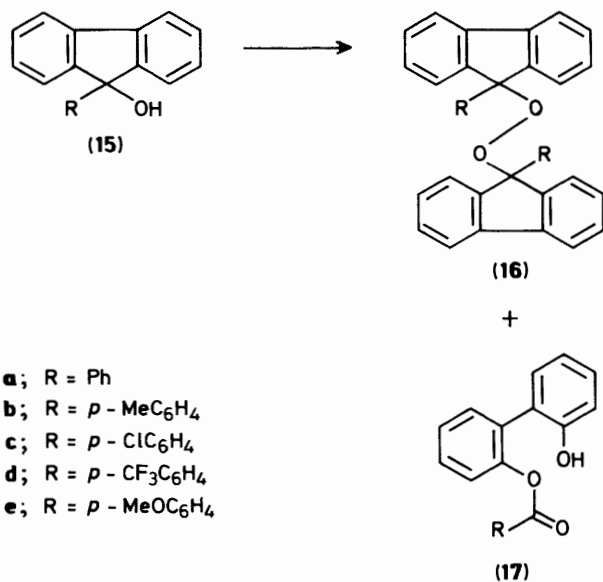


elemental analysis. In a separate experiment the ketone (11) on treatment with acid and hydrogen peroxide, afforded anthraquinone and 10,11-dihydrodibenzo[*a,d*]cycloheptene-5,10-dione (13) contaminated with 10,11-dihydroxy-10,11-dihydrodibenzo[*a,d*]cyclohepten-5-one (14). Treibs and Klinkhammer⁶ reported a similar ring contraction of the keto diol (14) to anthraquinone on oxidation with hot nitric acid. The ring contraction, which probably occurs *via* a ketol, is rationalised in Scheme 2.



In contrast to the dibenzocycloheptene system it was found that the five-membered ring in 9-arylfuoren-9-ols (15a–d) underwent fragmentation to afford 2'-aryloxybiphenyl-2-ols when treated with acidified hydrogen peroxide. 9-Phenylfluoren-9-ol (15a) afford the dialkyl peroxide (16a) as the major product,

together with 2'-benzyloxybiphenyl-2-ol (17a). The high yield of the peroxide (16a) is indicative of the formation of the 9-phenylfluoren-9-yl carbocation which is trapped by 9-phenylfluoren-9-yl hydroperoxide. With the 9-arylfuorenols (15b–d) the major products were the corresponding 2'-aryloxybiphenyls (17b–d). The formation of the aryloxybiphenyls (17a–d) and the absence of the corresponding benzophenones is due to a facile Bayer–Villiger rearrangement. The presence of two lowfield protons in the ¹H n.m.r. spectra, as well as the occurrence of the arylacylium ions in the mass spectra, confirm the mode of rearrangement. Only when the 9-aryl substituent was *p*-methoxyphenyl did the 9-substituent migrate in preference to the fluorene ring opening since the major products in separate experiments were fluorenone and benzocoumarin respectively. This result is in accord with rearrangements of 9-arylxanthenes⁴ under the same conditions. In one oxidation the major product was fluorenone whereas in a duplicate experiment further oxidation afforded benzocoumarin by a Baeyer–Villiger rearrangement, as well as fluorenone and a small amount of 2'-(*p*-methoxyphenyl)biphenyl-2-ol (17e). The more facile rearrangement of the fluorenyl ring system in compounds (15a–d) is most probably due to the higher energy of the HOMO of the fluorenyl system which interacts more effectively with the antibonding orbital of the peroxy group. Even though yields are not optimised, this study demonstrates that oxidative cleavage of 9-arylfuoren-9-ols is a route for the synthesis of the previously unreported mono-esters of biphenyl-2,2'-diol.



Experimental

I.r. spectra were recorded on a Perkin-Elmer spectrometer, Model 297. 60 MHz ¹H N.m.r. spectra were obtained on a Perkin-Elmer R12A spectrometer with TMS as internal reference. U.v.–visible spectra were run on a Varian Series 634 spectrometer. M.p.s were determined on a Kofler hot-stage and are uncorrected.

Reactions of Tertiary Alcohols with 30% Aqueous Hydrogen Peroxide in Acid Medium.—General procedure. The alcohol (6–8 mmol), dissolved in a mixture of conc. sulphuric acid (5 cm³) and glacial acetic acid (25 cm³), was treated with 30% aqueous hydrogen peroxide (25 cm³) and the mixture stirred at ambient temperature for between 4 h and 5 days. The products were either isolated by filtration and crystallisation from ethanol or benzene–light petroleum, or the mixture was extracted with

dichloromethane ($3 \times 50 \text{ cm}^3$), and the extract washed with saturated aqueous potassium hydrogen carbonate ($2 \times 20 \text{ cm}^3$), water ($2 \times 30 \text{ cm}^3$), dried (Na_2SO_4), and evaporated. Preparative layer chromatography (p.l.c.) (silica gel; C_6H_6 or CH_2Cl_2) of the residue afforded the crystalline products, which were recrystallised from ethanol or benzene-petroleum ether.

(a) 9-Phenylthioxanthene-9-ol (**1**) gave bis(9-phenyl-10,10-dioxothioxanthene-9-yl) peroxide (**3**) (11%) as a white precipitate, m.p. 175–176 °C [lit.,⁷ m.p. 238–239 °C (decomp.)]; $\nu_{\text{max.}}$ (Nujol) 1 200, 1 115, 930, 860, 765, and 720 cm^{-1} ; m/z 289 (M^+ /2) (Found: C, 70.7; H, 4.4. Calc. for $\text{C}_{38}\text{H}_{26}\text{O}_6\text{S}_2$: C, 71.0; H, 4.1%). Separation of the reaction mixture by p.l.c. (SiO_2 ; C_6H_6) afforded 2-benzoylphenyl 2-hydroxyphenyl sulphoxide (**2**) (52%), m.p. 152–153 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 200, 1 660, 1 030 (w, S=O), and 995 cm^{-1} (s, S=O);⁸ δ (CDCl_3) 6.50–8.40 (13 H, m) and 10.00 (1 H, s, –OH, exchangeable in D_2O); m/z 322 (M^+), 245 ($M - 77$), 229 ($M - \text{C}_6\text{H}_4\text{OH}$), 213 ($M - 109$), 181, 105, and 77 (Found: C, 70.5; H, 4.6. $\text{C}_{19}\text{H}_{14}\text{SO}_3$ requires C, 70.8; H, 4.4%), thioxanthene-9-one-10,10-dioxide (**5**) (5%), and thioxanthene (**4**) (5%). Compounds (**4**) and (**5**) were identical with authentic compounds (m.p., i.r., and n.m.r. spectra).

(b) 9-Phenylthioxanthene-9-ol 10,10-dioxide gave, after p.l.c. (SiO_2 ; CH_2Cl_2), thioxanthene-9-one 10,10-dioxide (**5**) (57%), identical with the authentic compound (m.p., i.r., and n.m.r. spectra).

(c) 10,10-Dimethyl-9-phenyl-9,10-dihydroanthracene-9-ol (**6**) treated by the above general procedure for two days, gave, after p.l.c. (SiO_2 ; CH_2Cl_2), a solid which crystallised from dichloromethane-light petroleum as white needles of 2-(2-benzoyl- α,α -dimethylbenzyl)phenol (**7**) (80%), m.p. 171–172 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 550, 3 350, 1 665, and 1 600 cm^{-1} ; δ (CDCl_3) 1.73 (6 H, s), 4.72 (1 H, s, exchangeable in D_2O), 5.93–6.25 (1 H, m), 6.40–6.85 (2 H, m), and 6.93–7.82 (10 H, m); m/z 316 (M^+), 301 ($M - \text{Me}$), 286 ($M - 2\text{Me}$), 239 ($M - \text{C}_6\text{H}_5$), 105, 77, and 28 (Found: C, 83.6; H, 6.3. $\text{C}_{22}\text{H}_{20}\text{O}_2$ requires C, 83.5; H, 6.4%).

(d) 5-Phenyldibenzo[*a,d*]cyclohepten-5-ol (**8**) gave, after p.l.c. (SiO_2 ; C_6H_6), 10,11-dihydrodibenzo[*a,d*]cyclohepten-5-one (**10**) (46%), identical with an authentic sample.

(e) (i) 5-Phenyldibenzo[*a,d*]cyclohepten-9-ol (**9**) on treatment with acidic 30% H_2O_2 for 4 h, gave a white precipitate which crystallised from ethanol as 5*H*-dibenzo[*a,d*]cyclohepten-5-one (**11**) (79%), identical (m.p., i.r., and n.m.r. spectra) with an authentic sample.

(ii) The above experiment was repeated with an extension of the reaction time to 4 days. P.l.c. separation of the reaction mixture gave a yellow band, which on elution (CH_2Cl_2 -ethanol) afforded a crystalline solid which recrystallised from acetone as anthraquinone (34%), m.p. 282–284 °C (sublim.) [lit.,⁹ m.p. 286 °C (sublim.)]. The eluates of a t.l.c. band at R_f 0.1–0.2 were rechromatographed (SiO_2 ; 50% ether-light petroleum) to give, at R_f 0.6, impure *trans*-10-acetoxy-11-hydroxy-10,11-dihydrobenzo[*a,d*]cyclopenten-5-one (**12**) (10.5%); $\nu_{\text{max.}}$ (CHCl_3) 3 600, 3 420, 1 740, 1 660, and 1 605 cm^{-1} ; δ (CDCl_3) 1.82 (3 H, s), 3.41 (1 H, s), 5.1 (1 H, d, J 6.67 Hz), 6.15 (1 H, d, J 6.67 Hz), and 7.1–8.05 (8 H, m). However, the compound could not be obtained pure enough for elemental and mass spectral analysis.

(f) 5*H*-Dibenzo[*a,d*]cyclohepten-5-one (**11**), under the same conditions as in (e) (ii), after chromatographic separation of the products (p.l.c.; SiO_2 ; CHCl_3) gave a band which was eluted and shown by h.p.l.c. analysis [μ -Porasil eluted with hexane-dioxane (1 400:10 v/v); 1.0 $\text{cm}^3 \text{ min}^{-1}$] to contain anthraquinone (16%) and starting material (27%). The band at R_f 0.1 gave a white solid, which crystallised from acetone as an inseparable mixture of 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene-5,10-dione (**13**) and the diol (**14**), m.p. 106–110 °C; $\nu_{\text{max.}}$ (Nujol) 3 400 and 1 660 cm^{-1} ; δ (CD_3COCD_3) 4.8 (1 H, br s), 5.02 (2 H,

s), and 7.1–7.8 (8 H, m); m/z 240.1 (M^+ , diol), 222.1 (M^+ , diketone), 194 ($M - \text{CO}$), 166 ($M - 2\text{CO}$), and 152 ($M - 2\text{CO}$, CH_2) ($M = M^+$, diketone).

(g) Anthrone (500 mg, 2.57 mmol) in acetic acid (25 cm^3) and conc. sulphuric acid (5 cm^3) was stirred with 30% H_2O_2 at ambient temperature for 5 days. Water (50 cm^3) was added and the precipitate was filtered off, washed with water, and air-dried. The light-yellow product crystallised from acetone to afford anthraquinone (480 mg, 89.5%) identical with an authentic specimen (m.p. and i.r.).

(h) 9-Phenylfluorene-9-ol (**15a**) gave bis-9-phenylfluorene-9-yl peroxide (**16a**) (53%), m.p. 192–193 °C (lit.,¹⁰ m.p. 193 °C); δ (CDCl_3) 7.00–7.80 (26 H, m); m/z 541.1 (M^+), 257.1 ($M/2$), and 241.2 (Found: C, 70.7; H, 3.9. Calc. for $\text{C}_{38}\text{H}_{26}\text{O}_2$: C, 70.3; H, 4.0%) and white prisms which crystallised from dichloromethane-light petroleum to give 2'-benzoyloxy-biphenyl-2-ol (**17a**) (27%), m.p. 93–94 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 570, 3 320, 1 735, and 1 605 cm^{-1} ; δ (CDCl_3) 5.25 (1 H, s, exchangeable in D_2O), 6.7–7.7 (11 H, m) and 7.8–8.1 (2 H, m); m/z 290 (M^+), 185 ($M - 105$), 105, and 77 (Found: C, 78.7; H, 4.9. $\text{C}_{19}\text{H}_{14}\text{O}_3$ requires C, 78.6; H, 4.8%). In a repeat experiment (**17a**) was obtained in 39% yield.

(i) 9-(4-Tolyl)fluorene-9-ol (**15b**) gave benzocoumarin (3.5%) and fluorenone (4.5%) which were identical with authentic material (m.p., i.r., and n.m.r. spectra) and a white solid which recrystallised from dichloromethane-light petroleum as needles of 2'-(4-toluyloxy)biphenyl-2-ol (**17b**) (65%), m.p. 143–144 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 570s, 3 300br, 1 740s, and 1 620 cm^{-1} ; δ (CDCl_3) 2.35 (3 H, s), 5.23 (1 H, s, exchangeable in D_2O), 6.12–7.62 (10 H, m), and 7.65–8.02 (2 H, d, part of AA'BB' system); m/z 304.3 (M^+), 185.1 ($M - 119$), 119.1 (100%), and 91.2 (Found: C, 79.3; H, 5.4. $\text{C}_{20}\text{H}_{16}\text{O}_3$ requires C, 78.9; H, 5.3%).

(j) 9-(4-Chlorophenyl)fluorene-9-ol (**15c**) gave 2'-(4-chlorobenzoyloxy)biphenyl-2-ol (**17c**) (40%), m.p. 145–146 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 570, 3 300, 1 740, and 1 602 cm^{-1} ; δ (CDCl_3) 5.13 (1 H, s, exchangeable in D_2O), 6.60–7.60 (10 H, m), and 7.70–8.05 (2 H, d, part of AA'BB' system); m/z 324.1 (M^+), 289.1 ($M - \text{Cl}$), 139 (100%), 111, and 75 (Found: C, 70.7; H, 3.9. $\text{C}_{19}\text{H}_{13}\text{ClO}_3$ requires C, 70.3; H, 4.0%). A gummy material was isolated from the reaction mixture by t.l.c. (SiO_2 ; C_6H_6) and shown to be peroxidic (HOAc-KI test). It was shown (h.p.l.c.) to consist of 9-(4-chlorophenyl)fluorene-9-ol (**15c**) and probably 9-(4-chlorophenyl)fluorene-9-yl hydroperoxide.

(k) 9-(4-Trifluoromethylphenyl)fluorene-9-ol (**15d**) gave, after crystallisation from light petroleum, crystals of 2-(4-trifluoromethylbenzoyloxy)biphenyl-2-ol (**17d**) (45%), m.p. 124–125 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 570s, 3 300br, 1 745s, and 1 590 cm^{-1} ; δ (CDCl_3) 5.45 (1 H, s, OH) and 6.5–8.1 (12 H, m); m/z 358 (M^+), 339 ($M - \text{F}$), 173 ($\text{CF}_3\text{C}_6\text{H}_4\text{CO}$), and 145 (Found: C, 67.15; H, 3.8. $\text{C}_{20}\text{H}_{13}\text{F}_3\text{O}_3$ requires C, 67.06; H, 3.63%).

(l) (i) 9-(4-Methoxyphenyl)fluorene-9-ol (**15e**) gave fluorenone (56%), identical (m.p., i.r., and n.m.r. spectra) with an authentic sample.

(ii) 9-(4-Methoxyphenyl)fluorene-9-ol (**15e**), in a repeat experiment, gave fluorenone (17%) and benzocoumarin (31%), identical with authentic specimens, as well as 2-(4-methoxybenzoyloxy)biphenyl-2-ol (**17e**) (3%), m.p. 134–135 °C; $\nu_{\text{max.}}$ (CHCl_3) 3 560, 3 400br, 2 850, 1 735s, 1 615, and 850 cm^{-1} ; δ (CDCl_3) 3.81 (3 H, s), 5.23 (1 H, s, exchangeable in D_2O), 6.65–7.60 (10 H, m), and 7.80–8.10 (2 H, d, part of AA'BB' system); m/z 320.1 (M^+), 135, 107.2, 92.1, and 76.9 (Found: C, 75.3; H, 5.1. $\text{C}_{20}\text{H}_{16}\text{O}_4$ requires C, 75.0; H, 5.0%).

Synthesis of 9-Arylfluorene-9-ols (15a–e).—The 9-arylfluorene-9-ols (**15**) were synthesized by a published procedure.¹¹

(i) 9-Phenylfluorene-9-ol (**15a**) (89%), had m.p. 84–85 °C (lit.,¹¹ m.p. 85 °C); $\nu_{\text{max.}}$ (CHCl_3) 3 600s, 3 400br, and 1 605 cm^{-1} ; δ (CDCl_3) 2.45 (1 H, s, OH), 7.20–7.60 (11 H, m), and

7.60–7.90 (2 H, m); m/z 258 (M^+), 241 ($M - OH$), 181, and 152.

(ii) 9-(4-Tolyl)fluoren-9-ol (**15b**) (42%), had m.p. 81–83 °C (lit.,¹¹ m.p. 84–85 °C); $\nu_{\max.}$ (CHCl₃) 3 600s, 3 400br, 1 610, and 1 595 cm⁻¹; δ (CDCl₃) 2.20 (3 H, s), 2.40 (1 H, s, exchangeable in D₂O), 6.80–7.40 (10 H, m), and 7.40–7.72 (2 H, m); m/z 272 (M^+ , 100%), 255 ($M - OH$), 239, 181, and 152.

(iii) 9-(4-Chlorophenyl)fluoren-9-ol (**15c**) (70%), had m.p. 89–91 °C (lit.,¹¹ m.p. 91–92 °C); $\nu_{\max.}$ (CHCl₃) 3 600s, 3 400br, 1 610, and 1 590 cm⁻¹; δ (CDCl₃) 2.50 (1 H, s, OH), 6.90–7.40 (10 H, m), and 7.40–7.60 (2 H, m); m/z 292 (M^+), 275 ($M - OH$), 257 ($M - Cl$), 181 ($M - C_6H_4Cl$, 100%), and 152.

(iv) 9-(4-Trifluoromethylphenyl)fluoren-9-ol (**15d**) (62%), had m.p. 64–66 °C; $\nu_{\max.}$ (CHCl₃) 3 600s, 3 400br, 1 622, and 1 610 cm⁻¹; δ (CDCl₃) 2.50 (1 H, s, OH) and 7.05–7.72 (12 H, m); m/z 326.1 (M^+), 309 ($M - 17$), 181 ($M - C_7H_4F_3$, 100%), and 152 (Found: C, 74.05; H, 4.1. C₂₀H₁₃F₃O requires C, 73.62; H, 4.02%).

(v) 9-(4-Methoxyphenyl)fluoren-9-ol (**15e**) (80%), had m.p. 91–92 °C (lit.,¹² m.p. 85–86 °C); $\nu_{\max.}$ (CHCl₃) 3 600s, 3 430br, 2 850s, 1 615, and 1 590 cm⁻¹; δ (CDCl₃) 2.82 (1 H, s, OH), 3.52 (3 H, s), 6.51–6.65 (2 H, d, part of AA'BB' system), 7.00–7.35 (8 H, m), and 7.35–7.70 (2 H, m); m/z 288 (M^+ , 100%), 271 ($M - OH$), 257 ($M - OCH_3$), 228, 202, and 181 ($M - C_6H_4OCH_3$).

9-Phenylthioxanthen-9-ol 10,10-Dioxide.—9-Phenylthioxanthen-9-ol (20 g, 68.9 mmol) on oxidation with chromium trioxide by a published procedure⁷ gave a solid which crystallised from acetone–light petroleum as prisms of the title compound (16.32 g, 74%), m.p. 216–217 °C (lit.,¹³ m.p. 214–216 °C); $\nu_{\max.}$ (Nujol) 3 460 and 1 600 cm⁻¹; δ (CD₃COCD₃) 5.9 (1 H, s, OH), 7.0–7.5 (5 H, m), 7.5–7.9 (4 H, m), and 7.9–8.4 (4 H, m); m/z 322 (M^+), 305 ($M - OH$), 258 ($M - SO_2$), 245 ($M - 77$), 229 (100%, $M - C_6H_5$, O), 181 ($M - C_6H_5$, SO₂), 152, 105, 78, 77, and 28 (Found: C, 71.0; H, 4.45. Calc. for C₁₉H₁₄O₃S: C, 70.81; H, 4.34%).

9-Phenylthioxanthen-9-ol (**1**).—By a general procedure,¹⁴ thioxanthone (50 g, 236 mmol) gave, after crystallisation from benzene–light petroleum, the title compound 9-phenylthioxanthen-9-ol (**1**) (56.2 g, 87%), m.p. 101–102 °C (lit.,¹⁵ m.p. 102–104 °C); $\nu_{\max.}$ (CHCl₃) 3 600s, 3 370br, 1 600, and 1 585 cm⁻¹; δ (CDCl₃) 2.30 (1 H, s, exchangeable in D₂O), 6.30–7.55 (11 H, m), and 7.75–8.10 (2 H, m); m/z 290 (M^+), 273 ($M - 17$), 213 ($M - 77$, 100%), 184 and 77.

5-Phenyldibenzo[a,d]cyclohepten-9-ol (**9**).—Dibenzo[a,d]cyclohepten-5-one (50 g, 245 mmol) was converted by a Grignard reaction¹⁶ into the title compound (**9**) (15.3 g, 74%), m.p. 150–151 °C (lit.,¹⁶ m.p. 150 °C); $\nu_{\max.}$ (CHCl₃) 3 600s, 3 400br, and 1 600 cm⁻¹; δ (CDCl₃) 2.22 (1 H, s, OH), 6.50–7.65 (13 H, m), and 8.05–8.35 (2 H, m); m/z 284 (M^+), 207 ($M - 77$), 178 (100%), 152, 105, and 77.

5-Phenyl-10,11-dihydrodibenzo[a,d]cyclohepten-5-ol (**8**).—Under the same conditions as above, 10,11-dihydrodibenzo[a,d]cyclohepten-5-one (44.8 g, 215 mmol), gave the title compound (**8**) (30 g, 49%), m.p. 150–151 °C (lit.,⁶ m.p. 151 °C); $\nu_{\max.}$ (CHCl₃) 3 600, 3 390br, and 1 600 cm⁻¹; δ (CDCl₃) 2.28 (1 H, s), 2.68–2.90 (4 H, m), 6.85–7.73 (11 H, m), and 7.93–8.20 (2 H, m); m/z 286 (M^+), 269 ($M - OH$), 209 ($M - C_6H_5$), 181 (100%), 165, 152, 131, and 77.

Thioxanthen-9-one 10,10-Dioxide (**5**).—Thioxanthone (9.9 g, 46.6 mmol) in acetic acid (100 cm³) and 3M aqueous sulphuric acid (100 cm³) was treated with potassium permanganate (30 g), and the mixture warmed at 70 °C for 30 min with occasional shaking. The cooled mixture was decolourised with sodium metabisulphate, diluted with water (1 000 cm³) and filtered. Crystallisation of the precipitate from ethanol, afford the title compound (**5**) 7.2 g (63%), m.p. 187–188 °C (lit.,¹⁷ m.p. 187 °C); $\nu_{\max.}$ (CHCl₃) 1 680, 1 600, and 1 585 cm⁻¹; δ (CDCl₃) 7.5–8.0 (4 H, m) and 8.0–8.5 (4 H, m); m/z 244 (M^+), 196 (100%), 168, 151, 136, and 76.

Acknowledgements

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References

- J. D. Loudon, J. R. Robertson, J. N. Watson, and S. D. Aiton, *J. Chem. Soc.*, 1950, 55.
- J. D. Loudon and J. D. Scott, *J. Chem. Soc.*, 1953, 269.
- D. E. Bissing, C. A. Matuszak, and W. E. McEwen, *J. Am. Chem. Soc.*, 1964, **86**, 3824; J. D. Loudon, *Progr. Org. Chem.*, eds J. W. Cook and W. Carruthers, Butterworths (London), 1961, **5**, 46; P. D. Bartlett and J. D. Cotman, *J. Am. Chem. Soc.*, 1950, **72**, 3095; W. Dilthey, F. Quint, and H. Dierichs, *J. Prakt. Chem.*, 1938, **151**, 25.
- J. Koorts, B. Taljaard, and A. Goosen, *S. Afr. J. Chem.*, 1987, **40**, 237.
- B. Staskun, S. A. Glover, A. Goosen, C. W. McClelland, B. Taljaard, and F. R. Vogel, *S. Afr. J. Chem.*, 1985, **38**, 121.
- W. Treibs and H. J. Klinkhammer, *Chem. Ber.*, 1951, **84**, 671.
- M. Gomberg and E. C. Britton, *J. Am. Chem. Soc.*, 1921, **43**, 1945.
- L. J. Bellamy, 'The Infra-red Spectra of Complex Molecules', J. Wiley, London, 1960, p. 359.
- M. Philips, *Chem. Rev.*, 1929, **1**, 125.
- M. Basse, E. Bunzel, and A. G. Davies, *J. Chem. Soc.*, 1955, 2550.
- A. F. Cockerell and J. F. Lamper, *J. Chem. Soc. B*, 1971, 503.
- T. W. Toone, E. Lee-Ruff, and A. C. Hopkinson, *Can. J. Chem.*, 1975, **53**, 1635.
- M. M. Coombs, *J. Chem. Soc.*, 1958, 4200.
- S. A. Glover, A. Goosen, C. W. McClelland, B. Taljaard, and F. R. Vogel, *S. Afr. J. Chem.*, 1984, **37**, 164.
- W. T. Bowie and M. R. Feldman, *J. Am. Chem. Soc.*, 1971, **99**, 4721.
- M. Gomberg and L. H. Cone, *Justus Liebigs Ann. Chem.*, 1909, **370**, 142.
- A. Lapworth, *J. Chem. Soc.*, 1898, **73**, 404.

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