SYNTHESIS AND THERMAL REARRANGEMENT OF OXYGEN HETEROCYCLIC SPIRANS

N. Foroughifar

Department of Chemistry, Teacher's Training University of Arak, Arak, Islamic Republic of Iran

Abstract

Thermal rearrangement of spirans (14) and (31) yields the xanthones (16, 34) and diphenylmethane (15, 32), respectively. The structure for xanthone (16), isolated from thermolysis, has been established by reduction to xanthene (20) followed by reoxidation to give xanthone (16). Alternatively, methylation of the diphenylmethane (15) followed by heating with selenium dioxide also yields xanthone (16). The transformation of the diphenylmethane (15) into xanthone (16) occurs by heating with selenium dioxide either with or without solvent.

Introduction

The spiran (1), on thermolysis in decalin at 190°C, was recovered unchanged. By contrast, when the spiran (2) was heated in either dodecane at the b. p., or in dimethyl sulphoxide held at 160°C for 5h, the hydroxy-spiran (3) was found [1].

Shode [2] and Tajbakhsh [3] therefore heated the spirans (4) and (5) without solvent. They separated four products from the resulting melt of spiran (4), which were assigned the structures (6), (7), (8), and (9). Three products (10), (11), and (12) were obtained from spiran (5). A further product was isolated from (5) and was assigned the bixanthyl structure (13) although all attempts to purify this product completely were unsuccessful.

It was thus demonstrated that changing a tert-butyl substituent to a methyl substituent in the spiran had little effect on the types of products isolated on thermolysis although significant differences were noted in the relative yields of these products. One of the aims of the work described in this paper was to determine the factors which affect the yield and distribution of the products, with particular regard to the effect of changing the substituents.

Furthermore, it was hoped that information could be obtained on the mechanism by which spirans undergo thermal rearrangement. The initial compound chosen for study was the trityl-substituted spiran (14).

Results and Discussion

The known 2-methyl 4-tritylphenol was produced from commercially available 2-methylphenol by reaction with triphenylmethanol [4].

Heating the resulting 2-methyl-4-tritylphenol with acidic aqueous formaldehyde solution under reflux gave, after crystallization from acetic acid-chloroform, the desired diphenylmethane (15) in 48% yield. The synthesis of the desired spiran (14) was achieved by oxidation of the diphenylmethane (15). The spectral data for this product were consistent with its structure.

The spiran (14) was heated neat at 180-185°C for 3h. From the resulting melt, which was shown by TLC to be a complex mixture of products, three products were isolated and identified as (i) xanthone (16) (20%), (ii) diphenylmethane (15) (18%), and (iii) triphenylmethane (17)(25%).
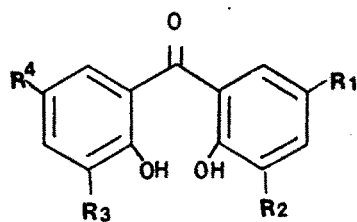
(2)

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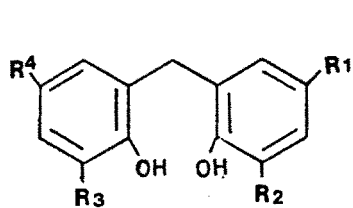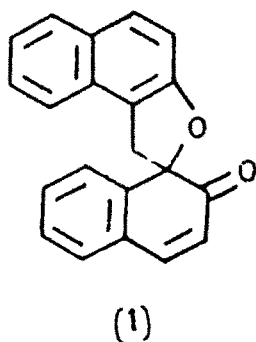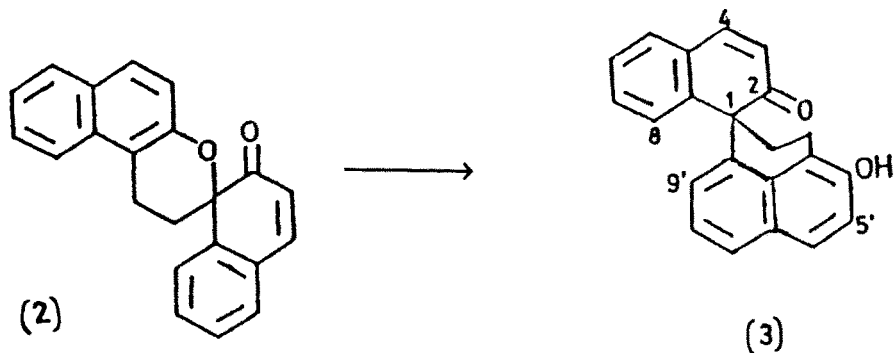
7) $R^1=R^2=R^3=R^4=$t-Bu
11) $R^1=R^4=$t-Bu, $R^2=R^3=$Me
15) $R^1=R^4=$CPh$_3$, $R^2=R^3=$Me
32) $R^1=R^4=$Me, $R^2=R^3=$t-Bu
39) $R^1=R^4=$Me, $R^2=R^3=$H
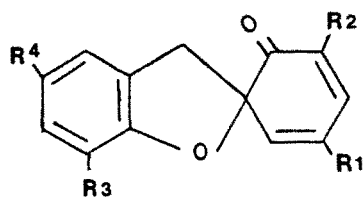
4) $R^1=R^2=R^3=R^4=$t-Bu
5) $R^1=R^4=$t-Bu, $R^2=R^3=$Me
14) $R^1=R^4=$CPh$_3$, $R^2=R^3=$Me
31) $R^1=R^4=$Me, $R^2=R^3=$t-Bu

8) $R^1=R^2=R^3=R^4=$t-Bu
12) $R^1=R^4=$t-Bu, $R^2=R^3=$Me
18) $R^1=R^4=$CPh$_3$, $R^2=R^3=$Me
35) $R^1=R^4=$Me, $R^2=R^3=$t-Bu
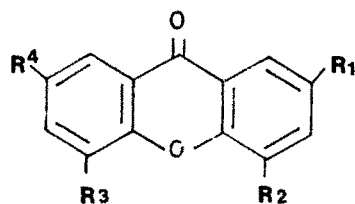
6) $R^1=R^2=R^3=R^4=$t-Bu
10) $R^1=R^4=$t-Bu, $R^2=R^3=$Me
16) $R^1=R^4=$CPh$_3$, $R^2=R^3=$Me
22) $R^1=R^2=R^3=R^4=$H
34) $R^1=R^4=$Me, $R^2=R^3=$t-Bu
38) $R^1=R^4=$Me, $R^2=R^3=$H
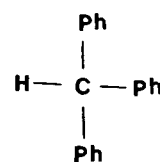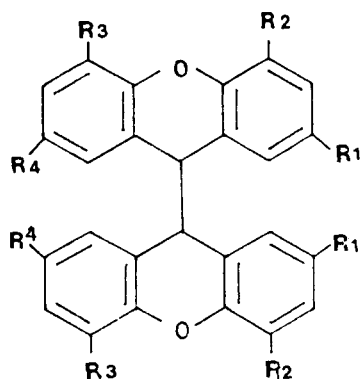
9) $R^1 = R^2 = R^3 = R^4 = t\text{-}Bu$
13) $R^1 = R^4 = t\text{-}Bu$, $R^2 = R^3 = Me$
19) $R^1 = R^4 = CPh_3$, $R^2 = R^3 = Me$
27) $R^1 = R^2 = R^3 = R^4 = H$
36) $R^1 = R^4 = Me$, $R^2 = R^3 = t\text{-}Bu$

(17)

Again, the structure of these compounds was apparent from their spectral data. Further evidence is provided by the fact that the xanthone (16) was heated under reflux in isopropanol with sodium borohydride to give, after two days, the xanthene (20) in good yield. The structure of the xanthene (20) was confirmed from its spectral data.
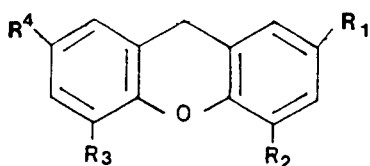
20) $R^1 = R^4 = CPh_3$, $R^2 = R^3 = Me$
21) $R^1 = R^2 = R^3 = R^4 = H$
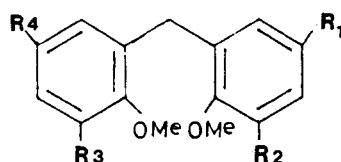
23) $R^1 = R^4 = CPh_3$, $R^2 = R^3 = Me$
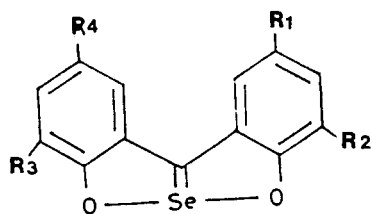
24) $R^1 = R^4 = t\text{-}Bu$, $R^2 = R^3 = Me$
25) $R^1 = R^2 = R^3 = R^4 = t\text{-}Bu$
26) $R^1 = R^4 = CPh_3$, $R^2 = R^3 = Me$
37) $R^1 = R^4 = Me$, $R^2 = R^3 = t\text{-}Bu$
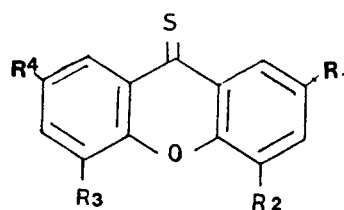
28) $R^1 = R^2 = R^3 = R^4 = H$
29) $R^1 = R^4 = CPh_3$, $R^2 = R^3 = Me$
30) $R^1 = R^4 = t\text{-}Bu$, $R^2 = R^3 = Me$

Stirring a solution of the xanthene (20) in a mixture of tert-butanol and DMSO (1:4) in the presence of potassium tert-butoxide under an atmosphere of oxygen resulted in its quantitative conversion to the xanthone (16). An alternative approach in order to establish unambiguously the validity of the structure (16). Treatment of the diphenylmethane (15) with an excess of methyl iodide gave, after work up, the desired dimethylated derivative (23) in good yield. Its structure was apparent from spectral data. Heating the product (23) neat with selenium dioxide at 240-260°C for 2h gave, after work up, 16% of the xanthone (16) together with 30% of recovered starting material (23) and a number of other uncharacterizable products.

An intimate mixture of the diphenylmethane (15) and selenium dioxide was heated at 210-220°C for 3h, from which, after separation of the melt, the xanthone (16) (24%) was obtained together with another product in approximately (17%) as a yellow solid. It was noted that this minor product was somewhat unstable in the presence of air, being slowly converted into the xanthone (16). On the basis of the spectral evidence available for this product, it was not possible to draw a plausible structure. It is unfortunate that none of the desired benzophenones (18) could be obtained from the reactions of selenium dioxide with either of the diphenylmethanes (15) or (23).

The xanthone (16) was heated in xylene solution with excess P_2S_5 to give the desired xanthione (29) (68%) as greenish-yellow crystals, m.p. 197-199°C, as well as 25% of unreacted starting xanthone (16). Stirring a mixture of the xanthione (29) with zinc dust, and concentrated HCl in AcOH gave the starting xanthione (29) in 40% yield together with the xanthone (16) in 30% yield. No trace of the desired bixanthyl (19) could be detected in this reaction.

In view of the results obtained from the thermal rearrangement of the spiran (14) it was decided to extend this work to another spiran in order to attempt to shed light on the factors which affect the product obtained in these reactions. The known spiran (31) [10] was chosen for this study. The diphenylmethane (32) required for the preparation of the spiran (31) was obtained by the standard procedure [10].

Spiran (31) was heated neat at 180-185°C for 3h and the resulting melt was purified by extensive chromatography to give only two isolated products, which were identified as xanthone (34) (3%) and diphenylmethane (32) (25%). It is of interest to note that, as was the case for the spiran (14), neither the benzophene (35) nor the bixanthyl (36) could be detected in the reaction mixture.

As was the case with the xanthone (16) heating an intimate mixture of the compound (32) with selenium dioxide at 140°C for 1h gave, after work up and chromatography, approximately 15% of a yellow tar which resisted all attempts at crystallization, together with two other fractions which were each shown by ^{1}H-NMR to contain a mixture of products including the starting material (32). No trace of any of the desired xanthone (34) could be detected in the crude reaction mixture. The above yellow tar was tentatively assigned the structure (37) from its spectral data.

Shode [2] reported that treatment of the diphenylmethane (17) with selenium dioxide gives the analogous selenium containing compound (25) as the only isolable product.

In an attempt to establish the structure (34) by conversion into the known [5] compound 2-7, dimethylxanthone (38), the diphenylmethane (32) was heated under reflux in a mixture of benzene and nitromethane in the presence of aluminium trichloride according to the literature [11]. Separation of the product mixture by TLC gave 44% of the known [11] diphenylmethane (39), together with a number of other products as an intractable mixture. Unfortunately, the amount of the xanthone (38) obtained from the thermolysis of the spiran (31) was not sufficient to enable the reaction to be profitably performed on this compound.

The results obtained from the thermolysis of the spiran (31) provided little mechanistic information. Thus, apart from diphenylmethane (32), the only product isolated was the xanthone (34) and that only in a paltry 3% yield. It would appear that, under the conditions required to effect thermal rearrangement of the spiran (31), most of the products which are potentially possible are unstable and decompose to polymeric materials and/or fragmentation products.

Experimental Section

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. I. R. spectra were recorded on a Perkin-Elmer 157G spectrophotometer. ^{1}H-NMR spectra were obtained on a Perkin-Elmer R34 220 MHz spectrometer using tetramethylsilane as the internal standard. Thin and thick-layer chromatography was conducted on glass plates coated with Merck silica gel G, the plates were dried at 100°C for 1h. The products were visualized either by UV illumination or by spraying with ceric sulphate solution (ca. 5% in 1M sulphuric acid) followed by heating. Hopkin and Williams silica gel and aluminium oxide were used for column chromatography.

Standard work up of reaction extracts involved washing the organic solvent with water until the

washings were neutral, and drying the solvent with anhydrous $MgSO_4$. The drying agent was filtered off and the organic solvent evaporated under vacuum.

Bis (2-hydroxy-3-tert -butyl-5-methylphenyl) methane (32)

A suspension of 2-tert-butyl-4-methylphenol (100 g, 0.6 mol) in a mixture of conc. hydrochloric acid (20 g, 0.55 mol) and 37% aqueous formaldehyde solution (20 g, 0.66 mol) was stirred at room temperature for 24h. The reaction mixture was filtered, the residual solid washed with water and crystallised from acetic acid, giving the desired product (32) (65 g, 63%) as colourless crystals, m.p. 133-134°C (Found M^+, 340. $C_{23}H_{32}O_2$ requires M, 340), λ_{max} (CHCl$_3$) 3500-3800, 2840, 1715Cm^{-1}, δ(CDCl$_3$) 6.93 (4H, s, 2x H-C$_4$, 2 x H-C$_6$), 5.3-6.3 (2H, bs, 2 x OH), 3.86 (2H, S, CH2), 2,23 (6H, s, 2 x CH3), and 1.37 (18H, s, 2 x t-Bu).

Spiro [7-tert-butyl-5-methylbenzofuran-2(3H), 1'-(3'-tert-butyl-5'-methylcyclohexa-3', 5'-dien-2'-one)] (31)

Method A: To a cooled (-5°C) solution of compound (32) (7.0 g, 20 mmol) in methanol (80 ml) 10% aqueous NaOCl solution (3.0 g, 0.04 mol) was added dropwise. The resulting yellow-red solution was stirred for 24h and then diluted with ethyl acetate and saturated aqueous sodium metabisulphite solution. The layers were separated and standard work up of the organic layer gave a reddish-yellow oil, which was purified by column chromatography on silica gel using ligroin as eluant. The yellow fractions eluted first from the column was further purified by TLC using ethyl acetate: ligroin = 1:9 as eluant and the maior band (Rf=0.8) collected and crystallised from methanol to give the desired product (31) (1.7 g, 24%) as yellow crystals, m.p. 119-121°C (lit [10]: m.p. 119-122°C) (Found: M^+. 338. $C_{23}H_{30}O_2$ requires M, 338), V_{max} (Nujol) 1710 and 855Cm^{-1}; δ(CDCl$_3$) 6.1-6.9 (4H, m, H-C$_4$, H-C$_6$, H-C$_4$', H-C$_6$'), 3.20 (2H, AB, JAB 17Hz, H$_2$-C$_3$), 2.23 (3H, s, CH$_3$-C$_5$), 1.89 (3H, s, CH$_3$-C$_5$') and 1.35 (9H, s) and 1.15 (9H, s) (2 x t-Bu).

Upon standing, these pale yellow crystals began to lose their colour due to partial conversion into the dimer (33) [10]. Signals arising from the dimer (33) were present in the ^{1}H-NMR spectrum of compound (31).

Method B: Attempted oxidation of diphenylmethane (32) (2.0 g, 5.8 mmol) with excess, basic aqueous potassium fericyanide was unsuccessful and yielded only unchanged starting material.

Thermolysis of Spiran (31)

The spiran (31) (1.0 g, 2.95 mmol) was heated without solvent at 180-182°C for 3h. The cooled dark brown melt was then separated by preparative TLC using ethyl acetate: ligroin=1:9 as eluant into two broad fractions.

The product with higher Rf value was crystallised from methanol to give 4,5-di-tert-butyl-2,7-dimethyl-(9H)-xanthen-9-one (34) (30 mg, 3%) as colourless crystals, m. p. 196-199°C (Found: M^+ 336. $C_{23}H_{23}O_2$ requires M, 336), λ_{max} (CHCl$_3$) 2930, 1715, 1610 and 1170Cm^{-1}; δ(CDCl$_3$), 8.12 (2H, d, 2Hz, H-Cl, H-C$_3$), 7.58 (2H, d, 2Hz, H-C$_3$, H-C$_3$), 2.45 (6H, s, 2 x CH$_3$), 1.63 (18H, s, 2 x t-Bu). Treatment of a small portion of this compound (34) with either concentrated H_2SO_4[9, 10] or Dimroth's reagent [11] (this name is proposed for a saturated solution of boric acid in acetic anhydride) produced in both cases a yellow fluorescence under UV illumination. The product with the lower Rf value was crystallised from acetic acid/ water, to give compound (32) (250 mg, 25%) as a colourless solid, m. p. 133-134°C, which was identified by comparison with authentic material (TLC, ^{1}H-NMR and mixed m. p.). Both fractions also contained a large number of minor bands which were not investigated further.

Removal of tert-butyl Groups from the diphenylmethane (32)

A solution of compound (32) (0.60 g, 1.76 mmol) and aluminium chloride (0.50 g, 3.74 mmol) in a mixture of nitromethane (3 ml) and benzene (30 ml) was heated under reflux for 22h. Extraction with ether, followed by a standard work-up gave a yellow solid which was separated by preparative TLC using ethyl acetate: ligroin=1:9 as eluant. The product with the lower Rf value was crystallised from acetone to give bis(2-hydroxy-5-methylphenyl) methane (39) (100 mg, 44%) as colourless crystals, m. p. 126-128°C (lit[11]: 127-128°C) (Found: $^+$M, 228. $C_{15}H_{16}O_2$ requires M, 228) δ(CDCl$_3$) 7.05 (2H, d, 1.5Hz, 2 x H-C$_6$), 6.80 (2H, dd, 8 and 1.5Hz, 2 x H-C$_4$), 6.71 (2H, d, 8Hz, 2 x H-C$_3$), 3.80 (2H, s, CH$_2$), 2.18 (6H, s, 2 x CH$_3$).

Reaction of diphenylmethane (32) with selenium dioxide

A mixture of compound (32) (1.0 g, 2.94 mmol) and selenium dioxide (1.0 g, 8.96 mmol) was heated at 140°C for 1h, in the absence of solvent. After cooling, the residue was diluted with water and extracted into ether, standard work up gave a red dark solid which was separated by preparative TLC using acetone-

ligroin = 1:9 as eluant into three fractions:

Fraction 1: (Rf: 0.9) gave the product (37) as a yellow tar (150 mg) which resisted all attempts at crystallisation [Found ^+M, 416. $C_{23}H_{28}O_2Se$ requires M, 416 (for ^{80}Se)], $\delta(CDCl_3)$ 8.23 (2H, d, 2Hz, H-C_1 and H-C_8), 7.38 (2H, d, 2Hz, H-C_3 and H-C_6), 2.54 (6H, s, 2 x CH_3), 1.53 (18H, s, 2xt-Bu).

Fraction 2: (Rf: 0.7) gave, after crystallisation from methanol, starting material (32).

Fraction 3: (Rf: 0.5) gave a dark red tar which was shown by ^{1}H-NMR to contain a number of products and it was not investigated further.

An examination of the crude product mixture from this reaction by TLC failed to reveal the presence of the xanthone (34).

2-methyl-4-tritylphenol

Concentrated sulphuric acid (15 ml) was added dropwise to a stirred solution of triphenylmethanol (26.0 g, 0.10 mol) and 2-methylphenol (10.0 g, 0.09 mol) in acetic acid (90 ml) at room temperature. After two days, the mixture was diluted with water. The resulting solid was dried and recrystallised from acetic acid to give 2-methyl-4-tritylphenol (21.0 g, 50%) as pale pink crystals, m. p. 181-183°C (lit[4]: 180-181°C) (Found: M^+, 350. calculated for $C_{26}H_{22}O$ M, 350), λ_{max} (CHCL$_3$) 3600, 3300-3500 1505Cm^{-1}, $\delta(CDCl_3)$ 7.10-7.28(15 H, m, trityl), 6.93 (1H, d, 2Hz, H-C_3), 6.87 (1H, dd, 8, 2Hz, H-C_5), 6.58 (1H, d, 8Hz, H-C_6), 2.12 (3H, S, CH3).

Bis (2-hydroxy-3-methyl-5-tritylphenyl) methane (15)

A mixture of 2-methyl-4-tritylphenol (10.0 g, 0.028 mol), concentrated hydrochloric acid (18 g), and aqueous formaldehyde solution (13.2 g, 0.44 mol) was heated under reflux for 24h. The reaction mixture was filtered and the product crystallised from acetic acid-chloroform to give product (15) (4.9 g, 48%) as colourless crystals, m. p. 251-253°C (Found: M^+, 712.3327. $C_{53}H_{44}O_2$ requires M, 712.3343), λ_{max} (Nujol) 3300-3550, 755Cm^{-1}, $\delta(CDCl_3/C_5 D_5 N)$ 6.8-7.3 (34H, m, 2 x trityl, 2 x H-C_4, 2 x H-C_6), 3.77 (2H, s, CH_2), 2.12 (6H, s, 2 x CH_3).

Spiro [7-methyl-5-tritylbenzofuran-2 (3H), 1'-(3'-methyl-5'-tritylcyclohexa-3', 5'-dien-2'-one)] (14)

To a stirred solution of compound (15) (20.0 g, 0.028 mol) in boiling benzene (150 ml), a solution of potassium ferricyanide (100 g, 0.3 mol) and potassium hydroxide (60 g, 1.07 mol) in water (800 ml) was added slowly under nitrogen at room temperature. After the addition, the solution was stirred for 3h. The

reaction mixture was then extracted with ether, the standard work up of which yielded a yellow solid which was purified by column chromatography on silica gel using chloroform: ligroin=1:24 eluant. Crystallisation from acetone, gave the desired product (14) (10.0 g, 50%) as yellow crystals, m. p. 118-119°C (Found: C, 89.8, H, 5.7, M^+, 710, $C_{53}H_{42}O_2$ requires C, 89.6; H, 5.9%, M. 710), λ_{max} (CHCl$_3$) 3000-3100, 1680 and 640Cm^{-1}, $\delta(CDCl_3)$ 7.0-7.4 (30H, m, 2 x trityl), 6.74 (1H, s) and 6.72 (1H, s) (H-C_4, H-C_6), 6.45 (1H, d, 2Hz, H-C_6'), 6.33 (1H, d, 2Hz, H-C_4'), 3.35 and 3.04 (2H, AB system, JAB 16Hz, CH_2), 2.10 (3H, s, CH_3-C_7), 1.74 (3H, S, CH_3-C_3').

Thermolysis of Spiran (14)

The spiran (14) (3.0 g, 4.2 mmol) was heated without solvent at 180-185°C for 3h. The resulting red liquid solidified on cooling and analytical TLC using chloroform; ligroin=1:1 as eluant revealed it to contain a number of distinct compounds. The mixture was separated into three broad fractions by column chromatography using chloroform: ligroin=1:4 as eluant:

Fraction 1: This was again separated by preparative TLC using chloroform: ligroin=1:4 as eluant, Rf 0.8 gave after crystallisation from methanol, triphenylmethane (17) (250 mg, 25%) as colourless crystals, m. p. 89-90°C (lit[12],:92°C) (Found: M^+, 244, calculated for $C_{19}H_{16}M$, 244). This compound was shown by ^{1}H-NMR, TLC comparison and mixed m. p. to be identical to an authentic sample.

Fraction 2: This was further separated by preparative TLC using chloroform: ligroin=3:2 as eluant, Rf 0.5 showed a bright blue fluorescence under UV. After recrystallisation from ethyl acetate this gave 4,5-dimethyl-2, 7-ditrityl-(9H)-xanthen-9-one (16) (0.60 g, 20%) as pale yellow crystals, m. p. 242-243°C (Found: C, 89.9; H, 5.55; M^+, 708. $C_{53}H_{40}O_2$ requires C, 89.8; H, 5.6; M, 708), λ_{max} (CHCl$_3$) 3060, 2920, 1655, 1610Cm^{-1}; $\delta(CDCl_3)$ 8.12 (2H, d, 2Hz, H-C_1, H-C_8), 7.38 (2H, d, H-C_3, H-C_6), 7.05-7.33 (30H, m, 2 x trityl) and 2.40 (6H, s, 2 x CH_3). Treatment of a small portion of the xanthone (16) with either concentrated sulphuric acid [8, 9] or Dimroth's reagent [8, 9] produced in each case a yellow fluorescence under UV illumination.

Fraction 3: This was further separated by preparative TLC using chloroform as eluant, Rf 0.2 was a colourless solid (0.33 g) which, after further purification by preparative TLC using chloroform: ethyl acetate = 1:1 as eluant, gave diphenylmethane (15) (0.20 g, 7%) as a colourless solid, which was shown by ^{1}H-NMR, TLC and m. p. comparison to be identical to an authentic sample.

Reaction of diphenylmethane (15) with selenium dioxide (i) neat

An intimate mixture of compound (15) (0.35 g, 0.49 mmol) and selenium dioxide (50 mg, 0.45 mmol) was heated at 240-250°C for 2h. The red melt was allowed to cool to room temperature, diluted with water and extracted into ether in the standard way. The residual red tar was separated by preparative TLC using chloroform: ligroin = 1:1 as eluant into two fractions, the higher Rf gave, after crystallisation from chloroform-methanol, an unknown compound x (60 mg) as a yellow crystalline solid, m. p. 138-140°C (Found: M$^+$, 788. C$_{53}$H$_{40}$O$_2$Se requires M, 788), λ_{max} (CHCl$_3$) 2920, 1655, 1500Cm^{-1}; δ(CDCl$_3$) 11.31 (2H, s, exchangeable with D$_2$O) 9.64 (2H, s), 7.0-7.3 (30H, m), and 2.15 (6H, s). The lower Rf gave 4,5-dimethyl-2, 7-ditrityl (9H)-xanthen-9-one (16) (120 mg, 35%) as a colourless crystalline solid which was identified by comparison with authentic material TLC and ^{1}H-NMR).

4,5-dimethyl-2,7-ditrityl-(9H)-xanthen-9-one (16)

A mixture of potassium tert-butoxide (100 mg), tert-butyl alcohol (10 ml), dimethyl sulphoxide (20 ml), and 4,5-dimethyl-2,7-ditrityl-(9H)-xanthene (20) (100 mg, 0.14 mmol) was stirred under an oxygen atmosphere at room temperature. After 20h, water (10 ml) was added and the mixture was worked up with ether in the standard way to give a yellow solid (100 mg, 98%) which was shown by ^{1}H-NMR comparison with an authentic sample to consist solely of the desired product (16).

4,5-dimethyl-2,7-ditrityl-(9H)-xanthene-9-thione (29)

Attempted preparation of 9-(4', 5'-dimethyl-2', 7'-ditrityl-(9H)-xanth-9'-yl)-4,5-dimethyl-2,7-ditrityl-(9H)-xanthene (19).

A mixture of 4,5-dimethyl-2,7-ditrityl-(9H)-xanthene-9-thione (29) (100 mg, 0.14 mmol), concentrated hydrochloric acid (5 ml), and zinc dust (0.30 g) in acetic acid (10 ml) was heated on a steam bath for 18h. After cooling, the mixture was worked up with water (10 ml) and extracted into ether in the standard way to give a residue which was separated by preparative TLC using chloroform: ligroin=2:3 as eluant into two fractions. The higher Rf gave xanthone (16) (60 mg, 61%) as a colourless solid which was identified by ^{1}H-NMR and TLC comparison with authentic material. The lower Rf gave the starting xanthione (29) (25 mg, 25%) as a greenish-yellow solid which was identified by ^{1}H-NMR and TLC comparison with au-

thentic material. The reaction was repeated as above, both at room temperature with concentrated hydrochloric acid and by warming on a steam bath with dilute hydrochloric acid. The crude residual product after work up as above was shown by TLC to consist in each case solely of a mixture of the xanthone, (16) and the xanthione (29).

4,5-dimethyl-2, 7-ditrityl-(9H)-xanthene (20)

A solution of xanthone (16) (100 mg, 0.14 mmol) and sodium borohydride (50 mg, 1.4 mmol) in isopropanol (5 ml) was heated under reflux for 2 days. The reaction mixture was treated with dilute hydrochloric acid and extracted into chloroform. The chloroform extract was worked up in the standard way to give a solid which was purified by preparative TLC using ethyl acetate-ligroin=1:19 as eluant, followed by crystallisation from methanol giving 4,5-dimethyl-2, 7-ditrityl-(9H)-xanthene (20) (75 mg, 76%) as colourless crystals, m. p.=108-110°C (Found: M$^+$, 694.3221, C$_{53}$H$_{42}$O requires M, 694.3238), λ_{max} (CHCl$_3$) 2800-3100, 1595, 1500, 1440Cm^{-1}; δ(CDCl$_3$) 7.03-7.42 (30H, m, 2 x trityl), 6.83 (2H, s) and 6.75 (2H, s) (H-C$_1$, H-C$_3$, H-C$_6$, H-C$_8$), 3.74 (2H, s, CH$_2$), and 2.24 (6H, s, 2 x CH$_3$).

Reaction of bis (2-methoxy-3-methyl-5-tritylphenyl) methane (23) with selenium dioxide

An intimate mixture of compound (23) (0.40 g, 0.54 mmol) and selenium dioxide (50 mg, 0.54 mmol) was heated at 240-260°C for 2h. The mixture was then allowed to cool to room temperature, treated with water (30 ml), and extracted into ether, the regular work up of which gave a yellow solid which was separated by preparative TLC using chloroform: ligroin=1:1 as eluant into three fractions.

Fraction 1: Rf 0.8 gave after crystallisation from ethyl acetate, 4,5-dimethyl-2, 7-ditrityl-(9H)-xanthen-9-one (16) (60 mg, 16%) as colourless crystals, m. p. 242-243°C, which were identified by ^{1}H-NMR and TLC comparison with authentic material.

Fraction 2: Rf 0.6 gave the starting diphenylmethane (23) (120 mg, 30%) as a colourless crystalline solid which was identified by ^{1}H-NMR and TLC comparison with authentic material.

Fraction 3: Rf 0.4 gave a colourless solid (80 mg) which was shown by analytical TLC to contain several components. All attempts to isolate a characterisable compound from this product were unsuccessful and it was not investigated further.

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