10-Thia-anthracenes. Part 3.[1] A Re-examination of the Reaction of 9-Phenylthioxanthylium Salt and Phenyl-lithium

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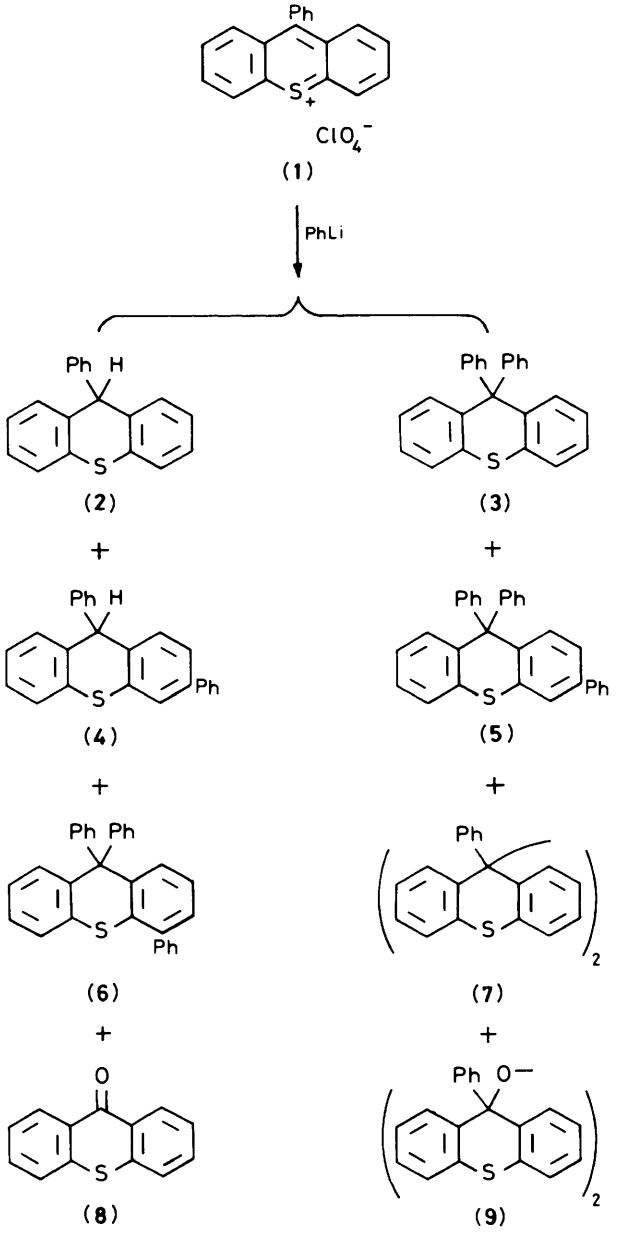
Reaction of 9-phenylthioxanthylium salt (**1**) with phenyl-lithium afforded eight compounds, 9-phenyl- (**2**), 9,9-diphenyl- (**3**), 3,9-diphenyl- (**4**), 3,9,9-triphenyl-(**5**), and 4,9,9-triphenyl-thioxanthene (**6**), 9,9′-diphenyl-9,9′-bithioxanthenyl (**7**), thioxanthone (**8**), and 9,9′-diphenyldithioxanth-9-yl peroxide (**9**). Their structures were determined by comparison with the authentic samples. Six samples, (**3**)—(**6**), 2,9,9-triphenyl- (**30**), 9-(biphenyl-4-yl)-9-phenylthioxanthene (**31**) were independently synthesized in order to determine the structures of two pairs of positional isomers, 3,4, and 5,6. A radical mechanism contributed to the reaction of compound (**1**) with phenyl-lithium.

It had been thought that thiabenzenes had the ylene structure following Price and Suld's claim to have synthesized them in 1961 by the reactions of thiopyrylium salts with phenyl-lithium.[2] The thiabenzenes prepared by the method were brown amorphous solids exhibiting broad aromatic signals in their n.m.r. spectra.[1–3] In related work we treated 10-aryl-9-phenylthioxanthenium salts with bases,[4] the ylidic intermediates so generated then undergoing ready intramolecular 1,4-sigmatropic rearrangement.[5]

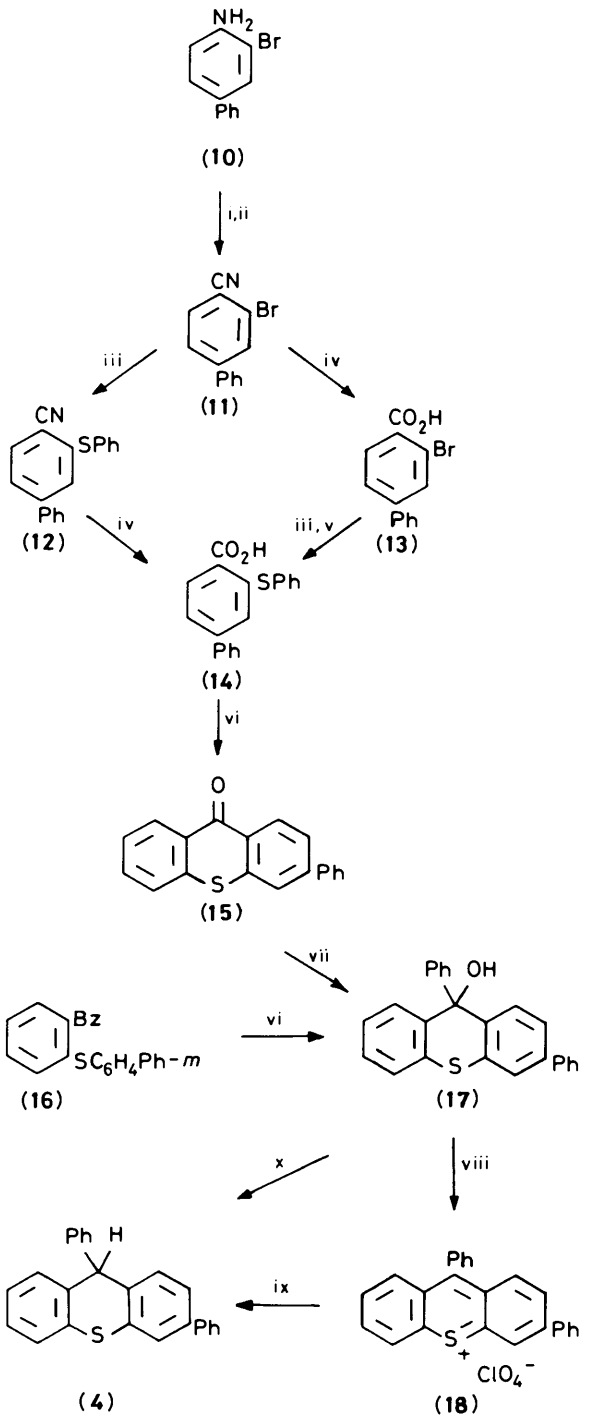
Mislow *et al.* pointed out the contradiction of these results and showed, on the basis of their similarity with acyclic sulphonium ylides, that thiabenzenes were, in fact, ylides: thus (*a*) both are stabilized by substituents or solvents which delocalize electronic charge; (*b*) both show marked upfield shifts of protons on carbons α to sulphur in their n.m.r. spectra; (*c*) both undergo thermal Stevens rearrangements; (*d*) both show stable pyramidal features at sulphur with a barrier to pyramidal inversion of at least 23 kcal/mol.[6] They also showed that the stable brown powders alleged to be 10-thia-anthracenes were, without exception, oligomeric materials of undetermined composition and structure.[6b] Independently, Hortmann *et al.* reported that thiabenzenes were ylidic compounds.[7]

We have re-examined the reaction of 9-phenylthioxanthylium perchlorate (**1**) with phenyl-lithium[3] and describe here our results.

Product Separation from the Reaction of 9-Phenylthioxanthylium Salt (**1**) *with Phenyl-lithium.*—A brown amorphous solid was prepared by the method of Price *et al.*[3] and its mass spectra were measured. Since the electron impact (e.i.) mass spectrum showed peaks with *m/z* values higher than the molecular weight of 9,10-diphenyl-10-thia-anthracene, the field desorption (f.d.) mass spectrum, in which the fragmentation peaks are much less than those of the e.i. ones, was measured.[1] The presence of molecular ion peaks implied that the product was a mixture of several thioxanthenes and, consequently, their separation was carried out by column, t.l.c., and high-performance liquid chromatography. Eight products were thus isolated: 9-phenyl- (**2**) (2.7%), 9,9-diphenyl- (**3**) (10.2%), 3,9-diphenyl- (**4**) (2.8%), 3,9,9-triphenyl- (**5**) (1.1%), 4,9,9-triphenyl-thioxanthene (**6**) (4.2%), 9,9′-diphenyl-9,9′-bithioxanthenyl (**7**) (0.5%), thioxanthone (**8**) (0.9%), and 9,9′-diphenyl-dithioxanth-9-yl peroxide (**9**) (0.6%) (see Scheme 1).[8] The structures of other, minor products (M^+, 622, 698, and 774) were not determined. Five known compounds, (**2**)—(**3**) and (**7**)—(**9**) were identical with authentic samples. Three new compounds, (**4**)—(**6**) were identified with unambiguously synthesized samples.



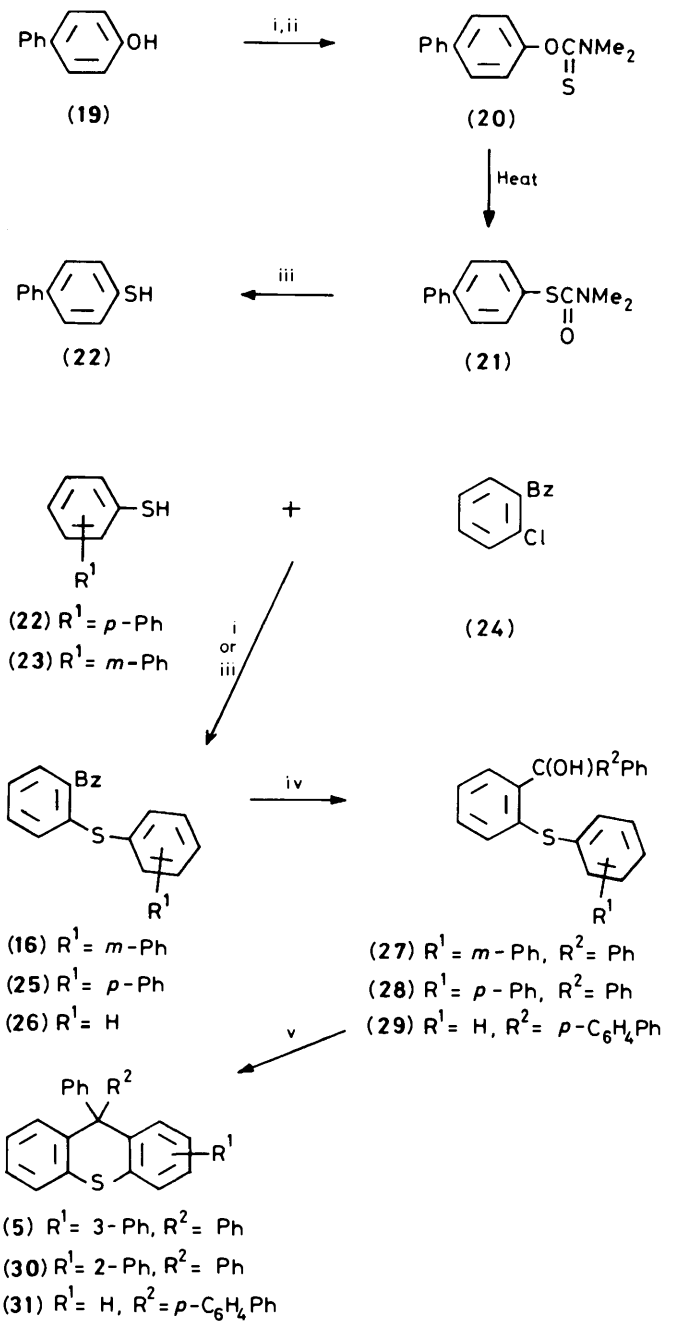
Scheme 1.



Scheme 2. *Reagents and conditions:* i, $NaNO_2$–HCl; ii, $Cu_2(CN)_2$; iii, PhSNa; iv, NaOH; v, K_2CO_3; vi, PPA; vii, PhMgBr; viii, $HClO_4$; ix, $LiAlH_4$; x, HCO_2H–Na_2CO_3

Independent Synthesis of Authentic Samples.—Scheme 2 outlines the synthetic route for 3,9-diphenylthioxanthene (**4**). Diazotization and subsequent cyanation of 4-amino-3-bromobiphenyl (**10**) provided 3-bromo-4-cyanobiphenyl (**11**) and treatment of this with sodium benzenethiolate gave (**12**), which was hydrolysed to yield the carboxylic acid (**14**). An alternative procedure involving hydrolysis of (**11**) and replacement of the bromo group of (**13**) could be applied to the synthesis of (**14**). The carboxylic acid (**14**) was cyclized with polyphosphoric acid (PPA) to give 3-phenylthioxanthone (**15**) and a Grignard reaction of this with phenylmagnesium bromide afforded 3,9-diphenylthioxanthenol (**17**). The latter was also prepared by cyclization of *o*-(biphenyl-3-ylthio)benzophenone (**16**) with PPA, no Smiles rearrangement occurring.[9] The desired compound (**4**) was derived directly from thioxanthenol (**17**) by formic acid reduction or *via* the thioxanthylium salt (**18**).

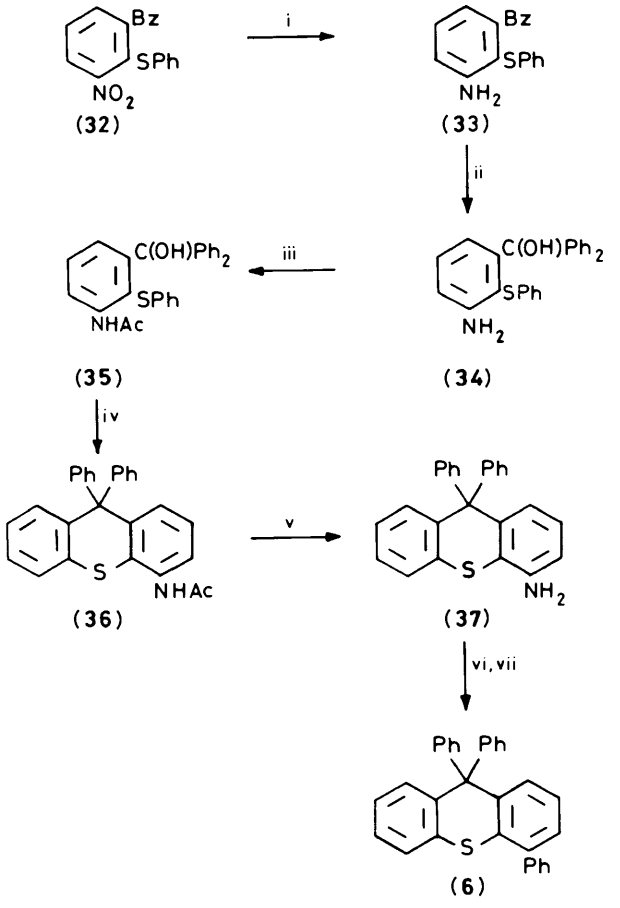
Next, 3,9,9-triphenyl- (**5**), 2,9,9-triphenyl- (**30**), and 9-biphenyl-4-yl-9-phenyl-thioxanthene (**31**) were prepared (see Scheme 3). 4-Phenylbenzenethiol (**22**) was prepared from 4-phenylphenol (**19**) by a sequence of steps involving a Newman–Kwart rearrangement and hydrolysis. Thus the phenol (**19**) was treated with *N*,*N*-dimethylthiocarbamoyl chloride to give *o*-biphenyl-4-yl *N*,*N*-dimethylthiocarbamate (**20**) (91.0%) thermal rearrangement of which at 260 °C afforded *S*-biphenyl-4-yl *N*,*N*-dimethylthiocarbamate (**21**) in quantitative yield. Hydro-



Scheme 3. *Reagents and conditions:* i, NaH; ii, $ClC(S)NMe_2$; iii, KOH; iv, R^2MgBr; v, H_2SO_4 in AcOH

lysis of (**21**) was conducted with potassium hydroxide just before its reaction with 2-chlorobenzophenone (**24**). Thus, the chloro group of (**24**) was substituted by the sodium salt of (**22**) or (**23**) to give the *o*-(biphenylylthio)benzophenone derivative (**16**) or (**25**), respectively. Grignard reaction of *o*-(arylthio)benzophenones (**16**), (**25**), or (**26**) yielded triphenylmethanol derivatives (**27**)—(**29**). Treatment of (**27**)—(**29**) with a catalytic amount of sulphuric acid afforded the cyclized products (**5**), (**30**), and (**31**) in good yields. No Smiles rearrangement products were obtained from these cyclizations.[9]

An independent synthesis of 4,9,9-triphenylthioxanthene (**6**) is shown in Scheme 4. Selective reduction of a nitro group with



Scheme 4. *Reagents and conditions:* i, $SnCl_2$–$NaBH_4$; ii, PhMgBr; iii, Ac_2O; iv, HBF_4 in AcOH; v, HCl; vi, $NaNO_2$–HCl; vii, C_6H_6–NaOH

stannous chloride–sodium borohydride[10] was applied to the reduction of 3-nitro-2-(phenylthio)benzophenone (**32**). 3-Amino-2-(phenylthio)benzophenone (**33**) thus obtained was treated with an excess of phenylmagnesium bromide (5.5 equiv.) to give the aminotriphenylmethanol derivative (**34**). Since the triphenylmethanol (**34**) having a free amino group failed to cyclize with PPA or concentrated sulphuric acid, the amino group was protected by the acetyl group. 3-Acetamido-2-(phenylthio)phenyldiphenylmethanol (**35**) cyclized easily to give 4-acetamido-9,9-diphenylthioxanthene (**36**) (90.6%). Deacetylation of (**36**) led to the 4-aminothioxanthene derivative (**37**). 4,9,9-Triphenylthioxanthene (**6**) was prepared (31.4%) by diazotization of (**37**), followed by the coupling reaction with benzene under alkaline conditions.

Reaction Mechanism.—Reaction of (**1**) with phenylmagnesium bromide produced 9,9-diphenylthioxanthene (**3**) (51%)[11] whereas reaction with phenyl-lithium afforded the eight products shown in Scheme 1. This difference may be attributed to the difference in the mode of chemical bonding.[12] Phenyl-lithium has more ionic character than phenylmagnesium bromide and would cause a redox reaction with 9-phenylthioxanthylium salt (**1**) more easily. Accordingly the radical concentration in the reaction mixture of (**1**) and phenyl-lithium is higher than that of (**1**) and phenylmagnesium bromide, although the radical (**38**) was detected in both reaction mixtures.[11] It has been indicated that alkyl-lithium–alkyl halide coupling reactions involve radicals generated by a redox process.[13]

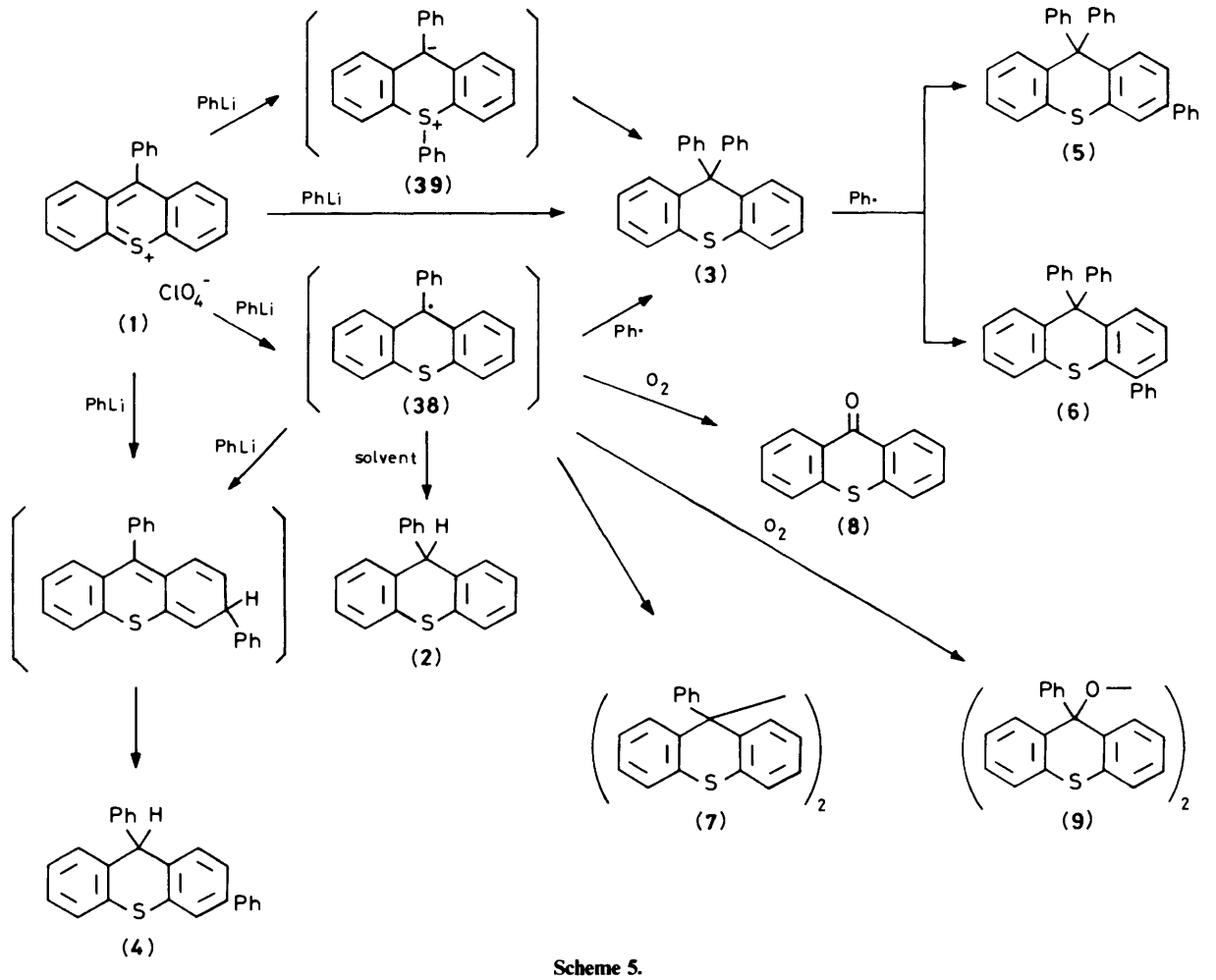
The formation of products (**2**)—(**9**) is explained by the mechanism depicted in Scheme 5. 9,9-Diphenylthioxanthene (**3**) could be produced *via* three pathways, nucleophilic attack of phenyl-lithium at the 9-position of (**1**), rearrangement of the ylide (**39**), and/or radical coupling of (**38**) with a phenyl radical. 3,9-Diphenylthioxanthene (**4**) could be formed *via* nucleophilic attack and/or radical attack at the 3-position of (**1**). When the radical (**38**) was generated from (**1**) and zinc powder in ether, 9-phenylthioxanthene (**2**), 9,9′-diphenyl-9,9′-bithioxanthenyl (**7**), thioxanthone (**8**), and 9-phenylthioxanthyl peroxide (**9**) were obtained.[11] Therefore, the radical (**38**) is a common intermediate for formation of these compounds. Although (**8**) was obtained from the reaction in which (**38**) was generated, formation mechanism of (**8**) from (**38**) cannot be explained clearly yet.

Although nitration of compound (**1**) takes place at the 4-position,[14] its phenylation here is unpredictable, reaction indices (by MO calculations) showing that the 4-position has large super delocalizability for electrophilic reactions and low frontier electron densities for nucleophilic reactions.[15] It is also reported that the electron density of the radical (**38**) is low at the 4-position.[11] In view of this, it seems that the diphenylation of (**1**) proceeds as follows: the first phenylation of (**1**) occurs at the 9-position to give 9,9-diphenylthioxanthene (**3**): this then undergoes radical phenylation at the 3- or 4-position to give the diphenylated products (**5**) or (**6**), respectively. In fact, 9,9-diphenylthioxanthene (**3**) was phenylated with 1 equiv. of phenylazotriphenylmethane in benzene to give 3,9,9-triphenyl- (**5**) and 4,9,9-triphenyl-thioxanthene (**6**) (3.4 and 3.5% respectively).

Experimental

All m.p.s were determined on a Yanagimoto micromelting point apparatus and are uncorrected. I.r. spectra were recorded on a JASCO IRA-1 spectrometer. N.m.r. spectra were measured on a Hitachi R-20-B spectrometer with tetramethylsilane as an internal standard. E.i. and f.d. mass spectra were recorded on a JEOL JMS-D-300 and JEOL JMS-O1SG-2 spectrometers, respectively.

Reaction of 9-Phenylthioxanthylium Perchlorate (**1**) *with Phenyl-lithium.*[3]—An ethereal solution of 0.97M-phenyl-lithium (28.0 ml) was added to a suspension of (**1**) (2.0 g) in dry ether (50 ml) under nitrogen. The reaction mixture was stirred for 5 h at room temperature and decomposed with cold aqueous ammonium chloride. The organic layer was separated and the aqueous layer was extracted with ether. The extracts were dried ($MgSO_4$) and evaporated to dryness at 20—25 °C under reduced pressure. The residual solid was chromatographed on alumina using hexane and then ether as eluants. The hexane fraction gave biphenyl and the ether fraction afforded a brown amorphous solid (650 mg). The brown solid was purified by column chromatography on silica gel using hexane, benzene–hexane (1:10 or 1:5), benzene, and ether. The hexane fraction gave 9-phenylthioxanthene (**2**) and 9,9-diphenylthioxanthene



Scheme 5.

(**3**). The benzene–hexane (1:10) fraction gave (**3**) and 9,9′-diphenyl-9,9′-bithioxanthenyl (**7**). The benzene–hexane (1:5) fraction gave a mixture of 3,9-diphenylthioxanthene (**4**), 3,9,9-triphenylthioxanthene (**5**), and 4,9,9-triphenylthioxanthene (**6**). The benzene fraction gave thioxanthone (**8**) and 9,9′-diphenyldithioxanth-9-yl peroxide (**9**). The ether fraction gave an amorphous solid (150 mg), whose i.r. spectrum showed S–O absorption at 1 040 cm^{-1} (KBr). Some of the fractions of hexane to benzene were still mixtures of the products and they were repeatedly subjected to preparative t.l.c. using benzene–hexane. Isolated compounds were (**2**) (25 mg, 1.7%), (**3**) (172 mg, 9.1%), (**4**) (43 mg, 2.3%), (**5**) (25 mg, 1.1%), (**6**) (95 mg, 4.2%), (**7**) (8 mg, 0.5%), (**8**) (10 mg, 0.9%), and (**9**) (10 mg, 0.6%). Known compounds, (**2**),[3] (**3**),[3] (**7**),[11] (**8**),[16] and (**9**),[11] were identified by mixed melting point tests and comparison of their i.r. spectra with those of authentic samples. Physicochemical data of new compounds (**4**)—(**6**) were as follows: (**4**), m.p. 135 °C; colourless prisms from hexane; δ($CDCl_3$) 5.36 (1 H, s, 9-H), and 7.0—7.85 (17 H, m, ArH) (Found: C, 85.4; H, 5.2. $C_{25}H_{18}S$ requires C, 85.7; H, 5.2%); (**5**), m.p. 212 °C; colourless prisms from benzene–hexane; δ($CDCl_3$) 6.7—7.75 (m, ArH) (Found: C, 87.0; H, 5.2. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%); (**6**), m.p. 192 °C; colourless prisms from benzene–hexane; δ($CDCl_3$) 6.7—7.5 (17 H, m, ArH), and 7.38 (5 H, br s, 4-Ph) (Found: C, 87.3; H, 5.2. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%). The amorphous solid obtained from the ether fraction was reduced with lithium aluminium hydride (200 mg) and separated again by preparative t.l.c. on silica gel using benzene–hexane (1:10). The compounds thus separated were (**2**) (15 mg, 1.0%), (**3**) (20 mg, 1.1%), and (**4**) (10 mg, 0.5%).

3-Bromo-4-cyanobiphenyl (**11**).—According to the procedure by Supniewski and Salzbery,[17] the cuprous cyanide solution was prepared from sodium cyanide (18.1 g) and cupric sulphate pentahydrate (23.1 g) and was covered with benzene (50 ml). The mixture was stirred and cooled to 5 °C. The finely powdered 4-amino-3-bromobiphenyl (**10**) hydrochloride (13.9 g) was suspended in concentrated hydrogen chloride (7.5 ml) and a small amount of ice, and diazotized with a concentrated solution of sodium nitrite (3.5 g). The solution of the diazonium salt was neutralized (Congo Red) using solid sodium hydrogen carbonate, filtered and added to the vigorously stirred solution of cuprous cyanide. The reaction mixture was stirred for 3.5 h. The benzene layer was separated, washed with aqueous sodium carbonate and water, dried ($MgSO_4$), evaporated and the residue distilled (b.p. 180—188 °C/3 mmHg). The distillate solidified and was recrystallized from ethanol to give yellow needles (3.8 g, 30.0%), m.p. 88—90 °C; $\nu_{max.}$ 2 240 cm^{-1} (CN) (Found: C, 60.3; H, 3.1; N, 5.3. $C_{13}H_8BrN$ requires C, 60.5; H, 3.1; N, 5.4%).

4-Cyano-3-phenylthiobiphenyl (**12**).—A mixture of (**11**) (2.0 g), anhydrous sodium carbonate (2.46 g), and benzenethiol (1.6 g) in hexamethylphosphoric triamide (HMPA) (10 m.) was stirred and heated at 100 °C for 6.5 h after which it was poured into water and extracted with ether. The extract was washed with dilute aqueous sodium hydroxide and water, then dried ($MgSO_4$). Evaporation of the solvent gave crystals which when recrystallized from ether–light petroleum afforded pale yellow needles (1.71 g, 74.2%), m.p. 90—92 °C; $\nu_{max.}$ 2 240 cm^{-1} (CN) (Found:

C, 79.4; H, 4.6; N, 4.7. $C_{19}H_{13}NS$ requires C, 79.4; H, 4.6; N, 4.9%).

2-*Bromo*-4-*phenylbenzoic Acid* (**13**).—A mixture of (**11**) (3.5 g), 40% aqueous sodium hydroxide (13 ml) and ethanol (40 ml) was refluxed for 7 h and then cooled. The reaction mixture was poured into water and acidified with concentrated hydrochloric acid (*ca.* 15 ml). The precipitate was filtered off, dried, and recrystallized from ethanol to give yellow plates (1.54 g, 41.2%), m.p. 178—180 °C; $\nu_{max.}$ 3 250—2 300 (OH) and 1 690 cm^{-1} (CO) (Found: C, 56.3; H, 3.3. $C_{13}H_9BrO_2$ requires C, 56.3; H, 3.1%).

4-*Phenyl*-2-(*phenylthio*)*benzoic Acid* (**14**).—(*a*) A mixture of the biphenyl (**12**) (1.87 g), 20% aqueous sodium hydroxide (7 ml), and ethanol (35 ml) was refluxed for 28 h and then cooled. Ethanol was removed under reduced pressure and the reaction mixture then poured into water and acidified with concentrated hydrochloric acid. The precipitate was filtered off, dried, and recrystallized from ethanol to give colourless needles (1.07 g, 53.5%), m.p. 253—255 °C; $\nu_{max.}$ 3 00—2 800 (OH) and 1 680 cm^{-1} (CO) (Found: C, 74.3; H, 4.5. $C_{19}H_{14}SO_2$ requires C, 74.5; H, 4.6%).

(*b*) Potassium 2-bromo-4-phenylbenzoate was prepared from the acid (**13**) (1.44 g) and anhydrous potassium carbonate (0.5 g) and sodium benzenethiolate from benzenethiol (1.2 g) and sodium hydride (50% in mineral oil; 0.35 g). The potassium salt of (**13**), sodium benzenethiolate, and copper powder (0.05 g) was heated at 220 °C for 30 min after which the mixture was extracted with 5% aqueous sodium hydroxide. The extract was acidified with concentrated hydrochloric acid and the precipitate was filtered off and recrystallized from ethanol to give colourless needles (0.68 g, 42.7%), m.p. 253—255 °C. The i.r. spectrum of the sample was identical with that of a sample obtained from the method (*a*).

3-*Phenylthioxanthone* (**15**).—Polyphosphoric acid [(PPA); prepared from phsphorus pentaoxide (5 g) and 85% phosphoric acid (2.5 ml)] and the acid (**14**) (1.5 g) were stirred and heated at 170 °C for 2.5 g. The mixture was then cooled and poured into water and extracted with benzene. The extract was washed with aqueous sodium carbonate and water, and dried ($MgSO_4$), and evaporated, and the residual solid recrystallized from benzene–hexane to give yellow needles (0.715 g, 50.6%), m.p. 165—167 °C; $\nu_{max.}$ 1 623 cm^{-1} (CO); $\delta(CDCl_3)$ 7.3—7.9 (10 H, m, ArH) and 8.58—8.87 (2 H, m, 1,8-H) (Found: C, 78.95; H, 4.13. $C_{19}H_{12}OS$ requires C, 79.1; H, 4.2%).

3,9-*Diphenylthioxanthenol* (**17**).—(*a*) To a stirred ethereal solution of phenylmagnesium bromide [prepared from bromobenzene (1.6 g) and magnesium (0.25 g)] was added a solution of (**15**) (1.5 g) in benzene. The ether was then removed and the reaction mixture refluxed for 10 h with stirring; subsequently it was decomposed with aqueous ammonium chloride. The organic layer was separated, the aqueous layer extracted with benzene, and the combined extracts were dried ($MgSO_4$) and concentrated. The residue was chromatographed on a silica gel column with dichloromethane–hexane (1:2) as eluant to give a solid which upon recrystallization from ether–hexane afforded colourless prisms (1.3 g, 68.2%), m.p. 144—145 °C; $\nu_{max.}$ 3 440 cm^{-1} (OH); $\delta(CDCl_3)$ 2.83 (1 H, s, OH), 6.8—7.75 (15 H, m, ArH), and 7.83—8.13 (2 H, m, 1,8-H) (Found: C, 81.7; H, 5.0. $C_{25}H_{18}OS$ requires C, 81.9; H, 4.95%).

(*b*) *o*-(Biphenyl-3-ylthio)benzophenone (**16**) (1 g) was added to PPA [prepared from phosphorus pentaoxide (4 g) and 85% phosphoric acid (2.5 ml)] and the mixture was stirred and heated at 100 °C for 2 h; it was then poured into ice–water and extracted with benzene. The extract was washed with aqueous sodium carbonate and water, dried (K_2CO_3), and evaporated and the residue purified by column chromatography on silica gel. Elution with benzene–hexane (1:1) gave an oil which, with time, solidified and was recrystallized from hexane–ether to give colourless rhombs (9.7 g, 70%), m.p. 144—145 °C. This sample was identical with a sample prepared from the method (*a*).

3,9-*Diphenylthioxanthylium Perchlorate* (**18**).—Perchloric acid (70%; 0.2 ml) was added with stirring to a solution of the thioxanthenol (**17**) (0.4 g) in ether (20 ml) and acetic acid (1 ml) and the mixture stirred for 30 min. The precipitate was filtered off, rinsed with ether, and recrystallized from acetic acid to afford red plates (0.4 g, 81.6%), m.p. 294—295 °C (decomp.); $\nu_{max.}$ 1 100 cm^{-1} (ClO_4^-) (Found: C, 66.8; H, 3.8. $C_{25}H_{17}ClO_4S$ requires C, 66.9; H, 3.8%).

3,9-*Diphenylthioxanthene* (**4**).—(*a*) A mixture of the thioxanthenol (**17**) (0.3 g) in formic acid (99%; 30 ml) containing a trace of sodium carbonate was refluxed until the red colour disappeared. The mixture was then poured into water, extracted with benzene, and the extract washed with aqueous sodium carbonate and water, dried (K_2CO_3), and evaporated. The residue was purified by preparative t.l.c. on silica gel using benzene–hexane (3:10) as eluant and then recrystallized from hexane to give colourless needles (0.2 g, 66.7%), m.p. 135 °C; $\delta(CDCl_3)$ 5.36 (1 H, s, 9-H) and 6.95—7.85 (17 H, m, ArH) (Found: C, 85.7; H, 5.1. $C_{25}H_{18}S$ requires C, 85.7; H, 5.2%).

(*b*) Compound (**18**) (0.3 g) was added to a suspension of lithium aluminium hydride (0.2 g) in dry ether (10 ml) and the mixture was stirred for 1 h at room temperature. It was then decomposed with water and the organic layer was separated; the aqueous layer was then extracted with ether. The combined extracts were dried ($MgSO_4$) and concentrated and the residue was recrystallized from hexane. The sample was identical with a sample prepared by the method (*a*).

o-*Biphenyl*-4-*yl* N,N-*Dimethylthiocarbamate* (**20**).—Sodium hydride (50% in mineral oil; 3.07 g) was added in small portions to a solution of 4-phenylphenol (10.9 g) in dimethylformamide (DMF) (80 ml). After hydrogen evolution had ceased the solution was cooled to 10 °C and a solution of *N*,*N*-dimethylthiocarbamoyl chloride (10.5 g) in DMF (40 ml) was added all at once to the solution. The mixture was heated at 80 °C for 1 h and then poured into 1% aqueous sodium hydroxide (300 ml). The aqueous solution was saturated with sodium chloride and extracted with a mixture of benzene–hexane (4:1). The extract was washed with water, dried ($MgSO_4$), and evaporated. The residual solid was recrystallized from benzene–hexane to give colourless plates (15.0 g, 91.0%), m.p. 145 °C; $\nu_{max.}$ 1 560—1 515 cm^{-1} (CS); $\delta(CDCl_3)$ 3.34 (3 H, s, Me), 3.46 (3 H, s, Me), 7.0—7.75 (7 H, m, ArH), and 7.12 (2 H, d, *J* 8.5 Hz, ArH) (Found: C, 70.1; H, 5.9; N, 5.4. $C_{15}H_{15}NOS$ requires C, 70.0; H, 5.9; N, 5.4%).

S-*Biphenyl*-4-*yl* N,N-*Dimethylthiocarbamate* (**21**).—Compound (**20**) (5 g) was heated for 45 min at 260 °C under nitrogen and the product was recrystallized from benzene–hexane to give colourless prisms, m.p. 142 °C, in quantitative yield; $\nu_{max.}$ 1 665 cm^{-1} (CO); $\delta(CDCl_3)$ 3.05 (6 H, s, Me), 7.2—7.7 (4 H, m, ArH), and 7.57 (5 H, br s, Ph) (Found: C, 70.2; H, 5.9; N, 5.3. $C_{15}H_{15}NOS$ requires C, 70.0; H, 5.9; N, 5.4%).

3-*Phenylbenzenethiol* (**23**).—A suspension of 3-aminobiphenyl hydrochloride [prepared from 3-aminobiphenyl (10 g), water (30 ml), and concentrated hydrochloric acid (11 ml)] was cooled to 0—5 °C and a solution of sodium nitrite (4.3 g) in water (10 ml) was added dropwise during 2 h. The diazonium salt solution was stirred for 30 min and then added to a solution

of potassium xanthate (14.2 g) in water (18 ml) at 40—45 °C. The reaction mixture was stirred for 30 min at that temperature, cooled, and extracted with ether. The extract was washed with 5% aqueous sodium hydroxide and water, dried ($CaCl_2$), and concentrated under reduced pressure. An ethereal solution of the residue was added to a suspension of lithium aluminium hydride (2.5 g) in dry ether and the mixture was carefully decomposed with water and then 10% sulphuric acid (60 ml). The mixture was extracted with ether and the extract washed with water, dried ($MgSO_4$), and concentrated. The residue was distilled under reduced pressure to give a colourless oil (6.1 g, 55.4%), b.p. 135—139 °C/0.7 mmHg; $\nu_{max.}$ 2 570 cm^{-1} (SH). For conversion into biphenyl-3-yl 2,4-dinitrophenyl sulphide, the thiol (**23**), as its sodium salt [prepared by mixing a solution of (**23**) (85 mg) in methanol (5 ml) and a solution of sodium hydroxide (100 mg) in water (2 ml)] was treated with a solution of 2,4-dinitrofluorobenzene (85 mg) in methanol (5 ml). The reaction mixture was stirred at room temperature for 10 min and then warmed on a water-bath for 5 min, poured into water, and extracted with chloroform. The extract was dried (K_2CO_3) and concentrated and the residue chromatographed on silica gel using benzene–hexane (1:1) as eluant to give yellow crystals which upon recrystallization from ethanol afforded biphenyl-3-yl 2,4-dinitrophenyl sulphide as yellow prisms (113 mg), m.p. 117 °C; $\nu_{max.}$ 1 520 and 1 355 cm^{-1} (NO_2) (Found: C, 61.5; H, 3.4; N, 7.9. $C_{18}H_{12}N_2O_4S$ requires C, 61.4; H, 3.4; N, 7.95%).

2-(*Biphenyl-3-ylthio*)*benzophenone* (**16**).—Sodium 3-phenylbenzenethiolate was prepared from (**23**) (1.86 g) in ether (30 ml) and sodium hydride (50% in mineral oil; 0.48 g). The solution of sodium 3-phenylbenzenethiolate in HMPA (30 ml) was added to a solution of 2-chlorobenzophenone (**24**)[18] (2.165 g) in HMPA (20 ml) at 150 °C and the reaction mixture was stirred at 150 °C for 8 h, poured into water, and extracted with ether. The extract was washed with water, dried (K_2CO_3), and evaporated to afford an oil. The oil was used for the next experiment without further purification; $\nu_{max.}$ 1 680 cm^{-1} (CO).

2-(*Biphenyl-4-ylthio*)*benzophenone* (**25**).—A mixture of the thiocarbamate (**21**) (3.5 g) and potassium hydroxide (1.15 g) in methanol (15 ml) was refluxed for 3 h under nitrogen. A solution of 2-chlorobenzophenone (**24**) (2.5 g) in DMF (40 ml) was then added to the solution of potassium 4-phenylbenzenethiolate thus prepared and methanol was removed. The mixture was heated at 120 °C for 1 h and then DMF was removed under reduced pressure. The residue was dissolved in chloroform and the solution was washed with water, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on silica gel to give di(biphenyl-4-yl) disulphide (1.85 g, 73.4%) from a hexane–benzene (5:1) fraction and 2-(biphenyl-4-ylthio)benzophenone (**25**) (1.0 g, 20.1%) as a colourless oil from a hexane–benzene (5:3) fraction.

2-(*Phenylthio*)*benzophenone* (**26**).—To a solution of sodium benzenethiolate [prepared from benzenethiol (6.1 g) and sodium hydride (60% in mineral oil; 2.2 g)] in DMF (70 ml) was added a solution of 2-chlorobenzophenone (**24**) (10 g) in DMF (70 ml). The mixture was refluxed for 3 h, poured into water, and then extracted with benzene–hexane (4:1). The extract was washed with water, dried ($MgSO_4$), and evaporated and the residue was chromatographed on silica gel using benzene–hexane (10:2) as eluant to give a yellow oil (11.2 g, 83.6%).

o-(*Biphenyl-3-ylthio*)*phenyl*(*diphenyl*)*methanol* (**27**).—An ethereal solution of the benzophenone (**16**) (1.0 g) was added to a solution of 0.75M phenyl-lithium (5 ml) and the mixture was stirred for 1 h at room temperature. It was then decomposed with water and the organic layer was separated and the aqueous layer extracted with ether. The combined extracts were dried (K_2CO_3) and concentrated and the residue was purified by column chromatography on silica gel using benzene–hexane (1:1) as eluant to give colourless crystals. Recrystallization of the product from benzene–hexane afforded colourless needles (1.0 g, 82.4%), m.p. 132 °C; $\nu_{max.}$ 3 390 cm^{-1} (OH) (Found: C, 83.8; H, 5.4. $C_{31}H_{24}OS$ requires C, 83.75; H, 5.4%).

o-(*Biphenyl-4-ylthio*)*phenyl*(*diphenyl*)*methanol* (**28**).—To an ethereal solution of phenylmagnesium bromide [prepared from bromobenzene (2.1 g) and magnesium (0.4 g) in dry ether (40 ml)] was added gradually a solution of the benzophenone (**25**) (1.0 g) in dry ether (20 ml). The mixture was refluxed for 5 h after which work-up afforded an oily product. This was chromatographed on silica gel using benzene–hexane (3:5) as eluant to give colourless crystals, recrystallization of which from benzene–hexane gave colourless plates (0.8 g, 65.9%), m.p. 102—103 °C; $\nu_{max.}$ 3 440 cm^{-1} (OH) (Found: C, 83.7; H, 5.5. $C_{31}H_{24}OS$ requires C, 83.75; H, 5.4%).

Biphenyl-4-yl-o-(*phenylthio*)*phenyl*(*phenyl*)*methanol* (**29**).—To a solution of biphenyl-4-ylmagnesium bromide [prepared from 4-bromobiphenyl (4.7 g) and magnesium (0.6 g)] in a mixture of dry ether (40 ml) and dry THF (40 ml) was added a solution of the benzophenone (**26**) (2.9 g) in dry THF (30 ml). The reaction mixture was refluxed for 3 h, worked up, and the product separated by column chromatography on silica gel using hexane–benzene (1:1) as eluant. Recrystallization of the crystalline product from benzene afforded colourless prisms (2.0 g, 45.0%), m.p. 153 °C; $\nu_{max.}$ 3 435 cm^{-1} (OH) (Found: C, 83.8; H, 5.6. $C_{31}H_{24}OS$ requires C, 83.75; H, 5.4%).

3,9,9-*Triphenylthioxanthene* (**5**).—A solution of the methanol (**27**) (0.3 g) in acetic acid (20 ml) containing 70% perchloric acid (1 drop) was heated on a water-bath for 3 h, cooled, and poured into water. The mixture was extracted with benzene and the extract was washed with water, aqueous sodium carbonate, and water, and then dried (K_2CO_3) and evaporated. The residue was purified by preparative t.l.c. on silica gel using benzene–hexane (3:10) as an eluant to give a crystalline product which upon recrystallization from benzene–hexane afforded colourless prisms (0.18 g, 62.5%), m.p. 212 °C; δ($CDCl_3$) 6.6—7.75 (m, ArH) (Found: C, 87.4; H, 5.3. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%).

2,9,9-*Triphenylthioxanthene* (**30**).—A solution of the methanol (**28**) (0.2 g) in acetic acid (20 ml) containing concentrated sulphuric acid (1 drop) was heated for 1 h on a water-bath. The solution was worked up in a similar way to that used for compound (**5**) and the product was recrystallized from benzene–hexane to afford colourless prisms (0.18 g, 93.8%), m.p. 202—203 °C; δ($CDCl_3$) 6.7—7.7 (m, ArH) (Found: C, 87.2; H, 5.2. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%).

9-(*Biphenyl-4-yl*)-9-*phenylthioxanthene* (**31**).—Compound (**29**) (0.1 g) was cyclized in a similar way to that employed for compound (**30**) and recrystallization of the product from hexane–benzene afforded colourless prisms (0.085 g, 88.6%), m.p. 245 °C (Found: C, 87.2; H, 5.2. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%).

3-*Amino*-2-(*phenylthio*)*benzophenone* (**33**).—To a solution of stannous chloride [prepared by passing hydrogen chloride gas into a suspension of stannous chloride dihydrate (40 g) in acetic acid (120 ml)] was added a solution of 3-nitro-2-(phenylthio)benzophenone (**32**)[14] (4 g) in acetic acid (100 ml); hydrogen chloride gas was then passed through the mixture for

2 h. The mixture was set aside overnight and then concentrated under reduced pressure to afford a residue which was decomposed with 20% aqueous sodium hydroxide solution (100 ml) and extracted with benzene. The extract was dried (K_2CO_3), evaporated, and the residue purified by column chromatography on silica gel using benzene–hexane (1:1) as an eluant. Recrystallization of the resulting crystalline product from benzene–hexane afforded colourless prisms (2.7 g, 74.1%), m.p. 116—117 °C; $\nu_{max.}$ 3 450, 3 350 (NH_2), and 1 660 cm^{-1} (CO) (Found: C, 74.7; H, 5.0; N, 4.5. $C_{19}H_{15}NOS$ requires C, 74.7; H, 4.95; N, 4.6%).

(*b*) Stannous chloride dihydrate (21.8 g) and the benzophenone (**32**) (4.68 g) were dissolved in ethanol (325 ml) with stirring at 60 °C and sodium borohydride (365 mg) was gradually added to the solution. After 1 h the reaction mixture was poured into water (500 ml) and extracted with benzene and the extract washed with 10% aqueous sodium hydroxide (200 ml × 2) and water, dried, and evaporated. The residue was recrystallized from benzene–hexane to give colourless prisms (4.0 g, 93.9%), which were identical with those prepared by method (*a*).

3-*Amino*-2-(*phenylthio*)*phenyl*(*diphenyl*)*methanol* (**34**).—To a solution of phenylmagnesium bromide [prepared from bromobenzene (22.6 g) and magnesium (3.5 g) in dry ether (150 ml)] was added a solution of the benzophenone (**33**) (8 g) in dry ether (50 ml). The mixture was stirred and refluxed for 5 h, decomposed with aqueous ammonium chloride, and extracted with benzene. The extract was dried (K_2CO_3), evaporated, and the residual solid purified by column chromatography on silica gel using benzene–hexane (2:1) as eluant. Recrystallization of the resulting crystalline product from benzene–hexane afforded colourless prisms (7.5 g, 74.7%), m.p. 170 °C; $\nu_{max.}$ 3 440 (OH, NH_2) and 3 350 cm^{-1} (NH_2) (Found: C, 78.55; H, 5.4; N, 3.4. $C_{25}H_{21}NOS$ requires C, 78.3; H, 5.5; N, 3.65%).

3-*Acetamido*-2-(*phenylthio*)*phenyl*(*diphenyl*)*methanol* (**35**).—Compound (**34**) (5 g) was dissolved in hot benzene (50 ml) and the solution was cooled to room temperature. Acetic anhydride (5 ml) was then added and the mixture allowed to stand overnight. It was then poured into water and the precipitate was filtered off, dried, and recrystallized from chloroform–ether to afford colourless prisms (5.4 g, 97.3%), m.p. 177 °C; $\nu_{max.}$ 3 430 (OH), 3 230 (NH), 1 690, and 1 670 cm^{-1} (CO) (Found: C, 75.95; H, 5.4; N, 3.4. $C_{27}H_{23}NO_2S$ requires C, 76.2; H, 5.45; N, 3.3%).

4-*Acetamido*-9,9-*diphenylthioxanthene* (**36**).—Compound (**35**) (5 g) was dissolved in hot acetic acid (100 ml) and hydrofluoroboric acid (42%) (2 ml) was added to the solution. The mixture was refluxed for 2 h, poured into water, and the precipitate filtered off, rinsed with water, and dried. Upon recrystallization from chloroform–ether it gave colourless prisms (4.34 g, 90.6%), m.p. 197 °C; $\nu_{max.}$ 3 200 (NH) and 1 650 cm^{-1} (CO) (Found: C, 79.9; H, 5.2; N, 3.4. $C_{27}H_{21}NOS$ requires C, 79.6; H, 5.2; N, 3.4%).

4-*Amino*-9,9-*diphenylthioxanthene* (**37**).—Compound (**36**) (4.2 g) was dissolved in hot ethanol (150 ml) and concentrated hydrochloric acid (30 ml) was added to the solution. The resulting mixture was refluxed for 5 h and then poured into water and the resulting precipitate filtered off, rinsed with dilute ammonium hydroxide, and dried. Upon recrystallization from benzene–hexane it gave colourless prisms (3.2 g, 83.2%), m.p. 260 °C; $\nu_{max.}$ 3 460 and 3 370 cm^{-1} (NH_2) (Found: C, 82.2; H, 5.1; N, 3.8. $C_{25}H_{19}NS$ requires C, 83.2; H, 5.2; N, 3.8%).

4,9,9-*Triphenylthioxanthene* (**6**).—Concentrated hydrochloric acid (1 ml) was added dropwise to a solution of the thioxanthene (**37**) (1.0 g) in DMF (15 ml) and the mixture was cooled to 0 °C in an ice-bath and diazotized with a solution of sodium nitrile in water (2 ml). The mixture was then stirred for 30 min and added to benzene at 5 °C. Dilute aqueous sodium hydroxide [prepared from sodium hydroxide (0.35 g) in water (2 ml)] was added to the mixture with vigorous stirring, the temperature being kept below 10 °C. The mixture was then stirred at that temperature for 4 h and then at room temperature for 1 day. The benzene layer was separated, the aqueous layer extracted with benzene, and the combined extracts were thrice washed with water and then dried. The solvent was evaporated off and the residue chromatographed on silica gel using hexane–benzene (5:2) as eluant. The less polar fraction gave 9,9-diphenylthioxanthene (**3**) (110 mg, 11.5%) and the polar fraction gave 4,9,9-triphenylthioxanthene (**6**) (366 mg, 31.4%). Recrystallization of (**6**) from benzene–hexane afforded colourless prisms, m.p. 192 °C; δ($CDCl_3$) 6.7—7.5 (17 H, m, ArH) and 7.38 (5 H, br s, 4-Ph) (Found: C, 87.2; H, 5.2. $C_{31}H_{22}S$ requires C, 87.3; H, 5.2%).

Radical Phenylation of 9,9-*Diphenylthioxanthene* (**3**) *with Phenylazotriphenylmethane*.—A mixture of thioxanthene (**3**) (350 mg) and phenylazo(triphenyl)methane[19] (70 mg) was stirred at 45 °C under nitrogen. Every 12 h further aliquots (× 4) of phenylazo(triphenyl)methane (70 mg) were added to the mixture. Separation of the reaction mixture was effected by repeated preparative t.l.c. on silica gel using hexane–benzene (10:1). Products were 3,9,9-triphenylthioxanthene (**5**) (13 mg, 3.4%), 4,9,9-triphenylthioxanthene (**6**) (15 mg, 3.5%), and (**3**) (304 mg, 86.9%).

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