SYNTHESIS AND STUDIES IN THE LIGHT FASTNESS OF AZO DYES

BY

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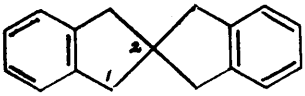
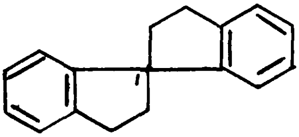
SUMMARY

The aim of the work was to prepare polycyclic systems of types (A), (B) or (C) in which two or more aromatic rings are linked *via* the tetrahedral carbon atom of a spiro system and to use these as intermediates for the synthesis of azo-dyestuffs in which the aromatic nuclei are further linked to suitable chromophoric groups. Such spiro-intermediates have not, to our knowledge, been previously used for this purpose. It was considered that the derived dyestuffs, in which two planar chromophores are held at right angles and insulated from one another by a tetrahedral carbon atom, might show interesting and unusual properties.



(A)



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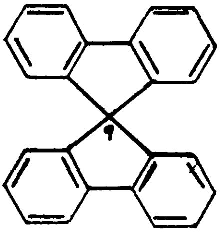


(C)

In practice, it was found that the spiro-2:2'-bisindane systems of type (A) were not readily prepared and while some compounds incorporating the spiro-1:1'-bisindane system (B) could be obtained relatively easily, they were not readily converted into dyestuffs.

The spiro-9:9'-bifluorene system (C) was eventually chosen as the most convenient for the present work and the derived 2,2'-diamino compound was diazotised and coupled with a variety of 2-hydroxynaphthoic acid anilides. The resulting red dyestuffs were found to have a better light fastness than the corresponding non-spiro dyes prepared from 2-aminofluorene.

INTRODUCTION

When a dyed fabric is exposed to light it absorbs radiation in the spectral region of 2000-8000 A° and undergoes some complex photochemical reactions resulting in a change of the brightness, purity and less frequently the hue[1]. Although the exact mechanism of the reactions involved is not yet clearly understood, it is generally accepted that photochemical breakdown of dye molecules in normal fading involves oxygen and moisture from the atmosphere[1,2,3,4](and references therein). Obviously this degradation of dye molecules by radiation energy will to some extent depend on their area of exposure to light and atmosphere. If the dye is dispersed in the substrate as single molecules or ions the area exposed will be greater than if the dye is in the form of clusters or aggregates; consequently more fading will result.

Much work has been done to determine the state of dispersion of dyes in the fibre[5-11]. Recent work appears to show that many if not most water-soluble dyes exist on the fibre in the form of aggregates[10,11]. The dye molecule on coming into contact with the solid surface of the material loses its protective shell of water, and the short range van der Waals forces then come into operation, uniting the molecules into larger units or aggregates (Fig.1). The size of these aggregates differs from one dye to another and may range from two to several hundred molecules, although little is known of their exact size. The evidence is obtained from optical microscopic examination of dyed wool[5,6], from X-ray diffraction tests on dyed wool fibres[7] and acidic oxycellulose and alginic acid[8], from electron microscopic examination of direct dyed regenerated cellulose films[9] and from many other spectroscopic and optical tests[10,11].

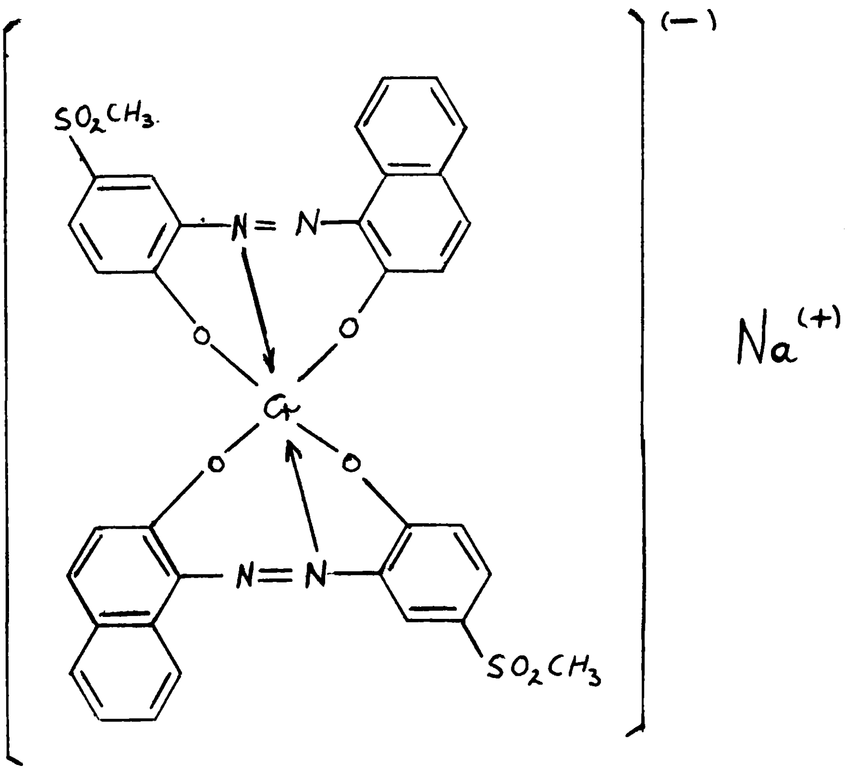
In the case of water-insoluble dyes aggregation can be expected and it has long been known that they exist on the fibre as clusters of amorphous particles or actual crystals [13,14].

Kayser[12] was the first to connect the increase in the fastness to light of azoic dyeings with a change in the degree of aggregation brought about by soaping. Bean and Rowe[13] and Baxter et al[14] observed that treatment such as soap-boiling or steaming which caused the crystal growth of such dyes to be sufficiently pronounced to be visible under the microscope, increased the resistance to fading. Similar results were obtained by Sumner and Vickerstaff[15] on vat dyes. Baxter and Giles[14] by their study of a number of dyes, both water-soluble and insoluble, confirmed that light fastness is increased with increase in the degree of aggregation.

Weissbein and Coven[9] studied the light fastness of nine different dyes and observed by electron micrography that there were aggregated particles in cellulose films dyed with dyes of good fastness (Fig.1), but none could be detected in those dyed with dyes of poor fastness e.g. Sky Blue FF.

Quite recently Wan Shik Ha[16] found the fading rate curves of cotton fabrics dyed with Diphenyl Fast Red 5BLN, Diphenyl Fast Blue RL, and Solar Yellow BG supported the conclusions of Baxter and Giles[14] for the effect of aggregation on the light fastness of dyes.

The 2:1-metal complex dyes are distinguished by their high light fastness. Schetty[17] gives a full account of their chemistry and mentions that they show very high light fastness on most diverse substrates. Giles and McEwan[18] attributed their high fastness to their tendency to form a micelle of unusual structure and proposed a possible mechanism for the formation of the micelle. In these dyes, for example, Irgalan Brown Violet DL:



IRGALAN BROWN VIOLET DL

the two planar azo-dye molecules are held at right angles to each other by a "spiro" atom of chromium[17,21](Fig.2). The principal aggregating force is assumed to be the tendency of the hydrophobic portions of these planar units to escape from water and achieve the closest side-by-side contact with neighbouring groups. The short range van der Waals forces come into operation and the aromatic nuclei appear to be stacked side-by-side. The most likely form of an aggregate on these assumptions is a unique type of micelle consisting of interlocked molecules with surface "fins" of aromatic nuclei, as shown in Fig.3.

Weissbein and Coven[9] confirmed by electron micrography that there are aggregates of the copper complex of Sky Blue FF (C.I. 24410) in dyed regenerated cellulose film. They, and also others[19,20,22] compared the fading rate of this dye with that of its uncomplexed form and found that the latter fades much more rapidly than the former.

Despite their better light fastness properties, the metal-complex dyes have a great disadvantage in that the presence of the chelating metal atom produces darker and duller shades with a loss of tinctorial strength in some cases. It was considered probable that if the central metal atom were replaced by a tetrahedral carbon atom, it should be possible to obtain a dye with the fastness of the metal-complex dyes but without the corresponding dullness of shade. The following is an account of the syntheses of some molecules of this type and a study of their light fastness properties.

Present work: fading[23]

The light fastness of the dyes was studied by dyeing Cellophane films to different depths (cf. Ref.24, Sec.A13) and exposing them to light from a mercury vapour lamp until the dye was appreciably faded. Fading rate curves were drawn by plotting the optical density values as ordinate and time as abscissa. It is normally observed that initial fading is somewhat irregular, but after some time a steady curve is obtained. It is also noted[22] that a dye which tends to form aggregates often gives higher optical density values in the beginning such that the curve first rises to a maximum before fading steadily[22,25]. On the other hand a dye with a lesser tendency to aggregate gives a descending curve right from the start.

Giles *et al*[14] introduced "Characteristic Fading" (CF) curves which have been used successfully over the past few years to demonstrate the light fastness properties of dyes in a simple and precise manner. In these curves (Fig.4) the logarithm of the time, t_f, required for a given percentage loss of dye (usually, for convenience, 10%) is plotted against the logarithm of the initial concentration, Co, of the dye in the substrate. Generally as stated the time for 10% fading is taken as the t_f value and plotted as ordinate, since a 10% loss approximates to the amount of fading used in practice for assessing fastness. It is clear that, as a result of any treatment which increases the light fastness of the dye, the CF curve will be raised to a higher level. Similarly any process which decreases the fastness should lower the height of the curve[26]. Here, the results will be compared by drawing the characteristic fading curves.

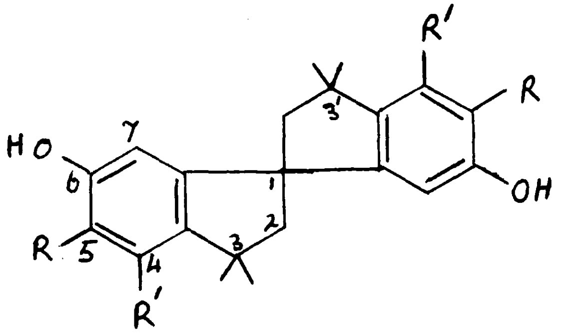
Spiro Compounds

As mentioned in the previous section the presence of a spiro structure involving a chelating metal atom in dye molecules improves their light fastness, but tends to produce dull shades, and because of this undesirable property the use of these dyes is to some extent limited in the textile industry. It was considered that a molecule of similar spatial configuration, but having a tetrahedral carbon atom in place of the metal atom, might have the same high light fastness resulting from the tendency of this structure to aggregate in the fibre but without its having the dull shade.

In view of possible practical applications the parent spiro compounds should be stable chemically and be such that they can be easily converted into dyes by incorporation of a suitable chromophore and applied to the fibre without degradation. Some aliphatic spirans, e.g. spiro alkanes, do not fulfil this requirement. On the other hand many spiro aromatic systems have been prepared in the past, some of which can be considered as suitable parent substances for conversion into spiro-dyes. Some of these spiro systems are reviewed below.

1:1' -Spiro bisindanes

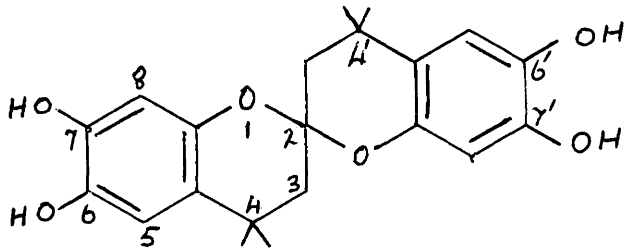
Baker and his colleagues[27-35] have described how a series of substituted derivatives of 1,1'-spiro bisindane may be readily prepared by condensing suitable phenols with simple aliphatic ketones. Thus the condensation product from two moles of catechol and three moles of acetone in the presence of acetic acid and hydrochloric acid was shown to be 5,6,5',6' -tetrahydroxy-3,3,3',3'-tetramethyl-bis-1,1'-spiro indane (I,R = OH,R' = H)[27,28,36].



(I)

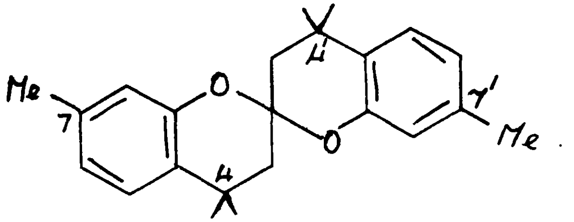
Similarly from o-cresol the corresponding spiro bisindane (I, R=Me, R' = H) was obtained, while pyrogallol afforded the hexahydroxy compound (I, R=R' = OH)[30].

With hydroxyquinol, however, a spiro chroman resulted. A structural study[28] of this condensation product revealed that it contained only four free hydroxyl groups and it was shown to be the tetrahydroxy-4,4,4',4' - tetramethyl-bis-2,2'-spiro chroman (II)[29].



(II)

Similar spiro chromans were obtained from m- and p-cresol, thus m-cresol gave 4,4,7,4',4',7'- hexamethyl-bis-2,2'-spiro chroman (III) and p-cresol gave the isomeric 4,4,6,4',4',6'- hexamethyl-bis-2,2'-spiro chroman (IV)[29]



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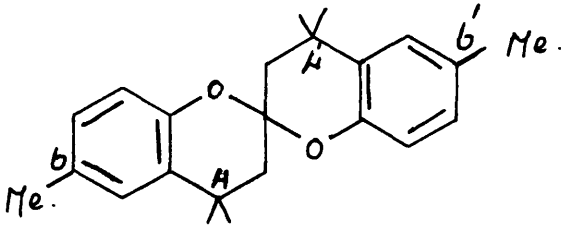
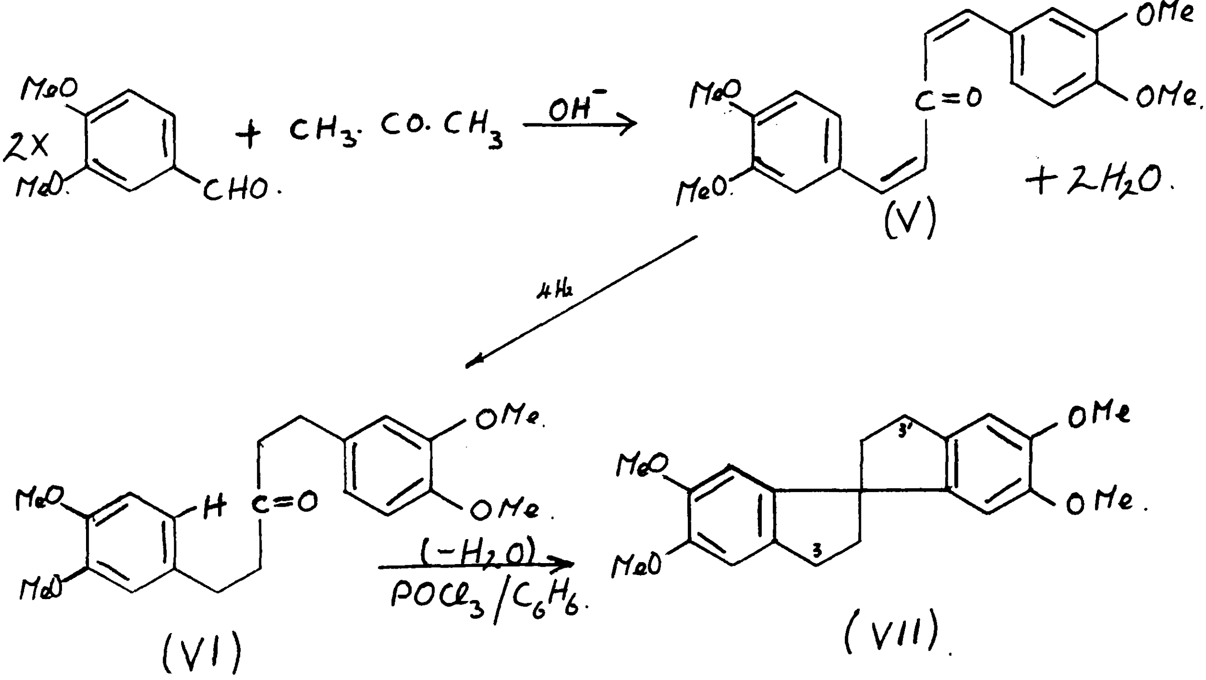


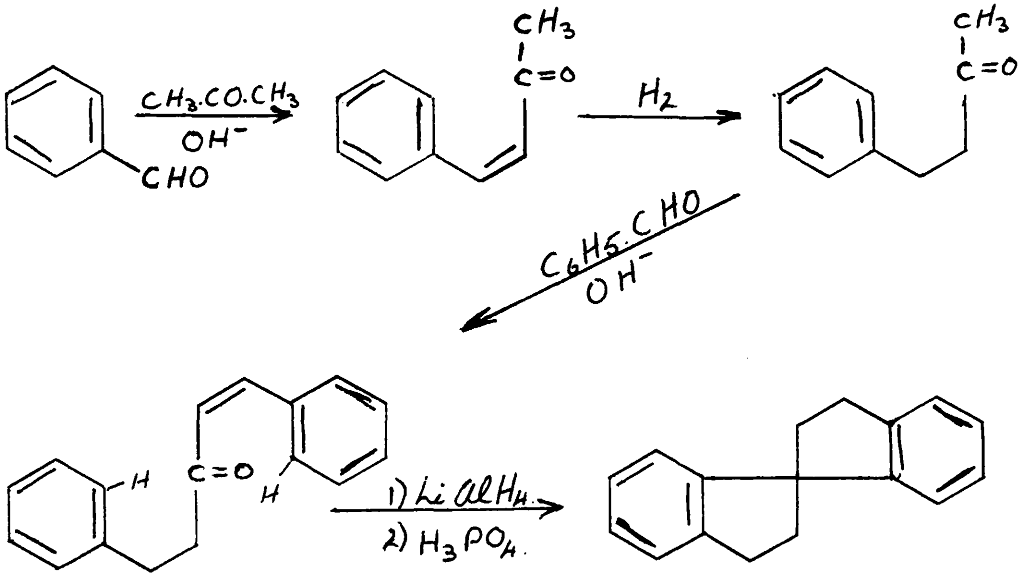
(IV)

Some 1,1'-spiro bisindanes with unsubstituted 3,3' - positions were prepared by base-catalysed condensation of acetone with an aromatic aldehyde, followed by reduction and dehydration with phosphorous oxychloride or phosphoric acid. Thus Baker[33,34,35] has synthesised 5,6,5',6' - tetramethoxy-1,1' - spiro bisindane (VII) from veratraldehyde and acetone as follows:



The yellow condensation product (V) from veratraldehyde and acetone is reduced catalytically to the symmetrical diveratrylacetone (VI) which undergoes cyclodehydration to the spiro compound (VII) when boiled with phosphorus-oxychloride in benzene[35].

Stetter and Reishl[37] have described similar reactions starting from benzaldehyde which led to an unsubstituted 1,1 - spiro bisindane (VIII):



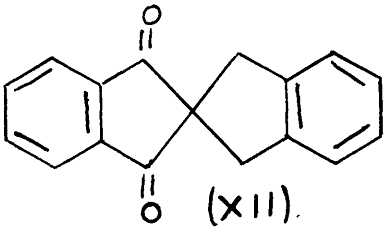
(VIII)

Of the available spiro 1,1' - bisindanes therefore the hydroxy compounds of type (I) prepared by Baker could apparently be obtained in a one-step process from readily available starting materials and, provided they could be made to couple satisfactorily with diazonium salts, they might well be ideal parent compounds for the preparation of spiro-dyes. The preparation of two examples of this type and subsequent tests on them are discussed in the sequel.

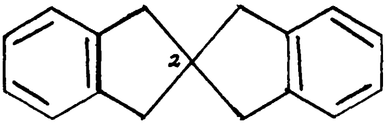
2,2' - Spiro bisindanes (XI)

Spiro bisindanes linked at the 2-position were also considered as likely parent hydrocarbons for conversion into possible light-fast dyes since, because of their linear spiro structure, steric influence between groups in the derived amino compounds should be at a minimum and they should couple with appropriate phenolic components satisfactorily.

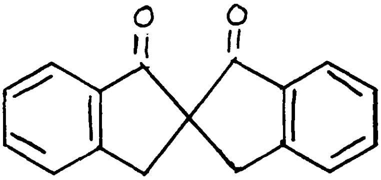
According to the literature[38] it should be possible to obtain the 2,2'-spiro bisindane (XI) from either of the two spiro diketones (XII) and (XIII)



(XII).



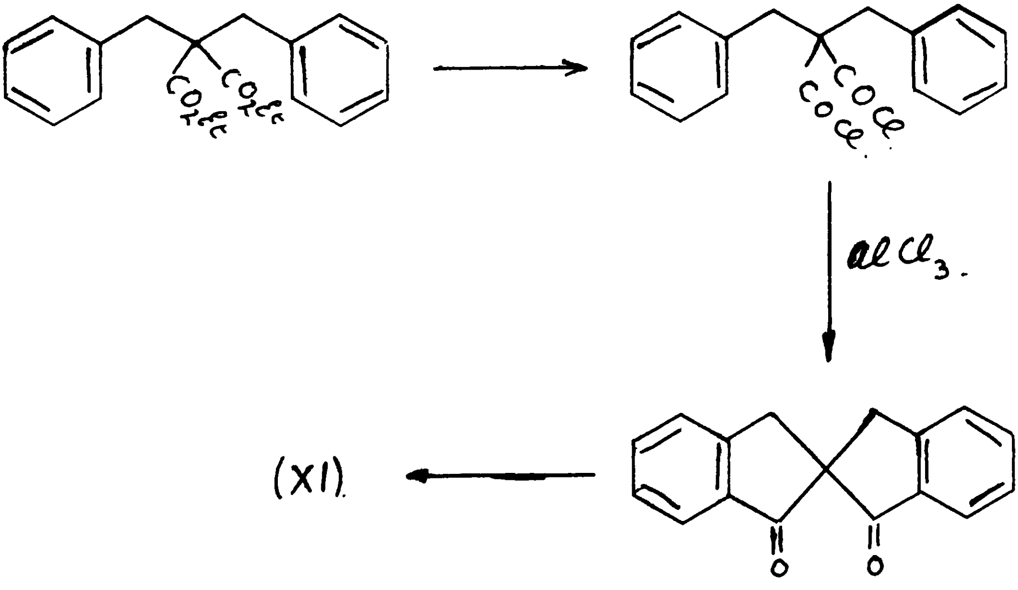
(XI)



(XIII).

Fecht[38] in 1907 claimed to have obtained the diketone (XII) by the reaction of indane-1,3-dione with o-oxylylene dibromide in the presence of sodium ethoxide. However, Radulescu[39] repeated these experiments and in 1925[40] concluded that the supposed diketone (XII) does not in fact have a spiro structure. More recently Carolan[41] attempted to obtain diketone (XII) by various modifications of the methods of Fecht and Radulescu, but unfortunately without success. Carolan also attempted to make the alternative diketone (XIII) for conversion into the hydrocarbon (XI).

The preparation of the diketone (XIII) was first reported by Radulescu[42] in 1911, starting from dibenzyl malonic ester by the following route in 60% yield, and the spiro hydrocarbon was later obtained from it by Leuchs[43].



(XI)

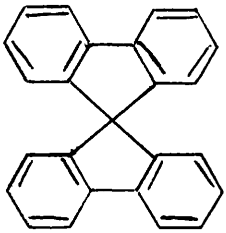
(XIII)

Ingold and Wilson[44], in 1934, had occasion to repeat this series of reactions but had difficulty in obtaining the relatively high yield claimed by Radulescu. They found that if ferric chloride is used in the cyclisation step more reproducible results are possible but yields are still relatively poor. Carolan followed this modified procedure and eventually obtained the dione (XIII) in only very low yield. He considered that the reaction conditions were still too severe and suggested that a milder condensing agent might be found if time were available which would effect the double ring closure.

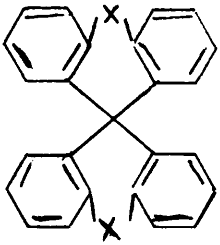
In view of the apparent difficulties experienced by these previous workers in making the spiro 2,2' - bisindane (IX) it was considered that this was unsuitable as a basis for preparing spiro dyes and attention was therefore concentrated on spiro aromatic systems which could be obtained relatively easily in the minimum of steps from readily available starting materials.

Spiro Bifluorenes and Related Compounds

Under this class we can consider those spiro compounds such as (XIV) derived from fluorenone itself and those in which an additional group is interposed between the biphenyl system as in compounds derived from xanthenone (XV, X=O), anthrone ($X=CH_2$) or acridone (X=NH).



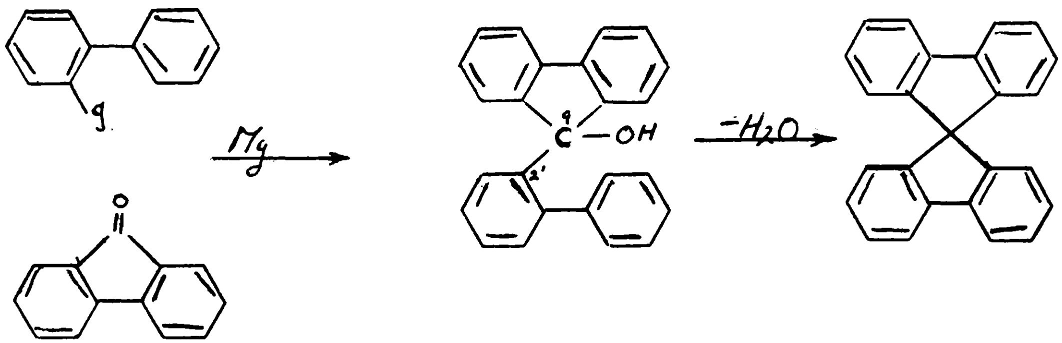
(XIV)



(XV)

(where X = CH_2, O, or NH)

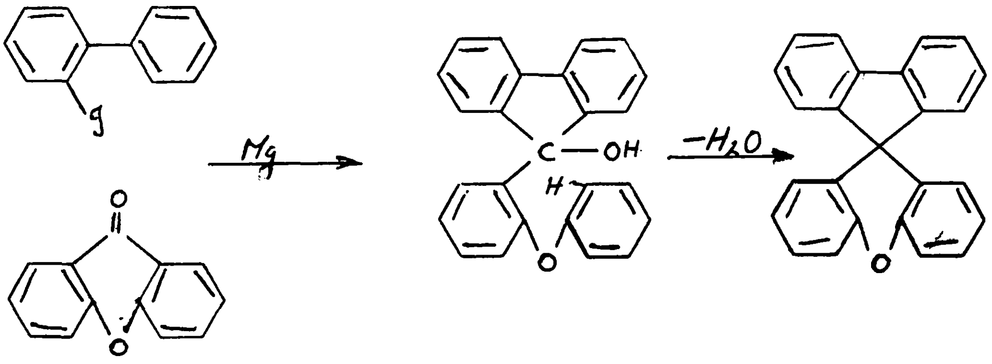
Clarkson and Gomberg[45], by acid catalysed dehydration of 9-(2'-biphenyl)-9-fluorenol (XVI), obtained 9,9' - spiro bifluorene (XIV). The carbinol was prepared by a Grignard reaction involving _o_-iodo-biphenyl and fluorenone.



(XVI)

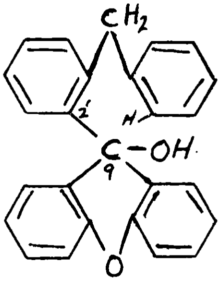
(XIV)

They also prepared a number of similar spirans in the course of their studies on the rate of ring closure of the related carbinols. Thus derivatives of (XV) (X=O) were among the spirans prepared by them. Similarly the xanthenol (XVII) synthesised from o-iodobiphenyl and xanthenone when boiled under reflux with a mixture of acetic acid and acetyl chloride underwent ring closure to the spiran (XVIII).

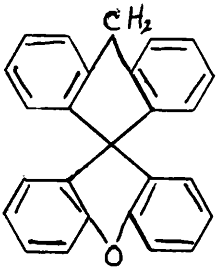


(XVII). (XVIII).

In an analogous manner the spiran (XX) was obtained via the intermediate 9-(2'-benzylphenyl)-9-xanthenol (XIX).

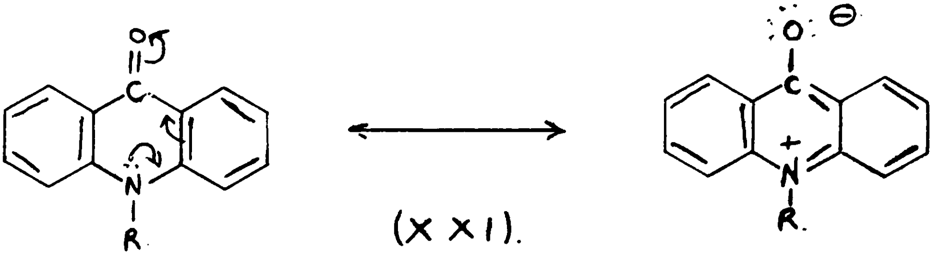


(XIX).



(XX).

Derivatives of type (XV; X = NH), having a spiro bis-dihydroacridine ring system have not been described in the literature. It is unlikely that they could be prepared in a manner analogous to that which gives rise to the spiro bifluorenes since possible starting materials such as acridone (XXI, R = H) or N-methyl acridone (XXI, R = Me) do not show ketonic properties but behave as vinylogous amides[46] and would not undergo the required Grignard reaction.



(XXI).

Of the systems available therefore, that containing the spiro-bifluorene structure (XIV) appeared to be the most attractive and work on the synthesis and the use of this material will be described in a later section.

EXPERIMENTAL

Dyeing

The dyeings were made on normal commercial Cellophane film of thickness 0.001 inch. The films were scoured with soap (5 g/l. solution at the boil for 15 minutes) and dyed according to the procedure (A 13) recommended for viscose rayon dyeing[47]. After dyeing, the films of different shade depths were soaped in Lissapol N solution (2g./l.), (I.C.I. Ltd.) for 15 minutes, rinsed thoroughly with water, mounted on the outside surface of a large beaker with rubber bands on both edges, and left overnight to dry into a smooth film without wrinkles, and without significant shrinkage.

Rectangular slides of suitable dimensions were cut from photographic glass. A sheet of the same size as the dyed film was placed between two glass slides and the whole held together by gummed tape.

Slides were marked with lead pencil on the bottom strip of gummed paper and care was taken that this side always faced the source of illumination.

Illumination

Daylight as fading agent is very slow and highly variable in intensity. For an efficient and more accurate determination of light fastness, some artificial source of light is necessary. For the present work a continuous and relatively constant emission was obtained from an Osram high pressure, mercury vapour lamp of 400 W. having an appropriate choke in series. This has an advantage over many other similar artificial light sources in that the running cost is quite low and no maintenance is required to keep it working. The lamp is held in a porcelain holder screwed to a wooden base board and surrounded by a cylindrical sheet of aluminium (17" in diameter x 15" high) fitted at vapour stream level with a 3/4 inch wide aluminium shelf on which the patterns are placed during exposure. As the source of illumination is a vertical incandescent vapour the intensity of emission is considered to be relatively constant in any lateral direction.

The lamp has a weak continuous spectrum as a background with a number of superimposed strong monochromatic bands. The five major emission lines in its spectrum are at 3650 A, 4047 A, 4358 A, 5461 A and 5780 A[48].

The temperature inside the screen was found to be constant for continuous running at 56°C.

Measurements of optical density of the slides were taken on a Unicam SP. 600 spectrophotometer. The slides were exposed to the lamp and their optical densities were measured at intervals to determine the fading. For more accurate results optical density was measured both from the front and the rear of the slide and the average of the two values was taken. Fading rate curves and CF^{14} curves were drawn.

Syntheses

5,6,5',6'-tetrahydroxy-3,3,3',3'-tetramethylbis-1,1'-spiro hydrindene (I, R = OH, R' = H). (Ref.27).

Catechol (132 g; 1 mole) in acetone (142.5 ml; 1.66 mole) and acetic acid (300 ml.), containing concentrated hydrochloric acid (240 ml.) was heated under reflux on the steam bath. After a few hours crystals began to appear and the amount slowly increased. At the end of 50 hours the mixture was allowed to cool and the solid material was collected, washed thoroughly with cold acetic acid and then with water and dried. Recrystallisation of the material from acetic acid and alcohol afforded a fine crystalline product (110g.) m.p. 314°. Baker[27] gives m.p. 315° for this compound.

Condensation of o-acetylamino-phenol with acetone.

o-Acetylaminophenol (151 g., 1 mole) in acetone (142.5 ml. 1.66 moles) and acetic acid (300 ml.), containing concentrated hydrochloric acid (240 ml.) was heated under reflux on a steam bath for a period of 50 hours. No crystals appeared and the reaction mixture had become a dark brown colour. On diluting an aliquot with water it gave only a turbid solution, which was diazotisable and coupled with β-naphthol. The total mixture was therefore neutralised with dilute sodium hydroxide and the resulting precipitate was collected, washed with 1% sodium hydroxide, then with water and dried. The product had m.p.138-143°.

6,6' -Dihydroxy-3,3,5,3'3',5'- hexamethylbis- 1,1'- spiro hydrindene (I, R = Me, R' = H) (Ref.30).

A mixture of o-cresol (100g.), acetic acid (250 ml.), acetone (75 ml.) and concentrated hydrochloric acid (190 ml.) was heated under reflux on the steam bath for 60 hours, and then poured into water. The very thick solid mass was collected, washed thoroughly with water, dried by heating under reduced pressure on the steam bath, and acetylated by boiling with acetic anhydride and pyridine (50 ml.) for 6 hours. To the hot stirred liquid, water (200 ml.) was cautiously added followed by ethanol (150 ml.) and after cooling the crystalline product was collected. This diacetyl derivative was washed with cold alcohol until white, then with water, and dried, to give the spirodiacetate (30g.).

The diacetate was hydrolysed by heating on the steam bath for 1 hour with alcohol (100 ml.) and a solution of sodium hydroxide (16g.) in water (64 ml.). The solution was diluted with water (200 ml.), and acidified with hydrochloric acid, and the white solid collected, washed, dried (yield, 20g.) and crystallised from xylene (100 ml.).

After several crystallisations the product, 6,6'-dihydroxy-3,3,5,3',3',5' - hexamethylbis-1,19-spiro hydrindene, was obtained, presmatic needles m.p. 243-245°. Baker[30] quotes m.p. 245-246° for this compound.

Condensation of Veratraldehyde with Acetone (Ref.34,35,49).

Veratraldehyde (20g.) was dissolved in alcohol (160 ml.) and acetone (3.2g.) was added. Aqueous sodium hydroxide (10%; 10 ml.) was added dropwise during a period of 15 minutes, care being taken to ensure that the temperature did not rise above 10°. The mixutre was then stirred at this temperature for a further 10 hours. During this time the product separated as an oil which solidified to give a yellow curdy precipitate. This was collected by filtration, washed with water, dried and recrystallised from methanol to give diveratralacetone (V) as yellow needles (15.5g.), m.p. 84°. Baked states that this compound exists in two different forms, m.p. 84° and m.p. 120°, and it is likely that these are in fact geometrical isomers[34].

The infrared spectrum of the compound in CH Cl$_3$ showed strong peaks at 1670cm^{-1} (dienone), 1620, 1598 and 1580cm^{-1} (Ar-CH=CH-) and 1261cm^{-1} (Ar-O-CH$_3$). The n.m.r. spectrum in COCl$_3$ showed peaks at τ 6.10 (12 protons = CH$_3$O-), 2.86 (6-aromatic protons) and doublets centred at τ 3.15 and 2.23 each equivalent to two protons (ethylenic hydrogens).

Diveratrylacetone (VI)

A solution of diveratralacetone (10.9g.) in ethyl acetate (400 ml.) was hydrogenated in the presence of platinum (from 226mg. PtO_2) at room temperature and atmospheric pressure until the theoretical uptake of hydrogen was achieved and the solution was colourless. After filtration, the solvent was evaporated and the residue crystallised from methanol to give diveratrylacetone (VI) (7.5g.), as plates, m.p. 84°. Baker[34] quotes melting point 85° for this compound. The melting point of the corresponding oxime was 139°. (Baker quotes m.p. 138.5°).

The infrared spectrum of the product (in $CHCl_3$) showed strong peaks at 1715cm^{-1}(saturated carbonyl), 1592cm^{-1} (aromatic ring), 2849cm^{-1} ($\underline{CH}_3$-O-), and 1253cm^{-1} (CH_3-O-Ar), while the n.m.r. spectrum contained peaks at τ 3.27 (6 aromatic protons), 6.18 (12 methoxyl protons) and 7.75 (multiplet due to 8 methylene protons).

Cyclodehydration of Diveratrylacetone (Ref.35).

The ketone (VI) (3.42g.) was dissolved in dry benzene (30 ml.), phosphorus oxychloride (20 ml.) was added cautiously and the mixture was boiled under reflux for 4 hours. The colour of the solution became first pink and then deep blue. The reaction mixture was then cooled and added to ice and water (120 ml.). The benzene layer was separated and the aqueous layer further extracted with the same solvent. The total benzene solution was thrice washed with dilute sodium hydroxide solution, then with water until neutral and dried over adhydrous sodium sulphate. Removal of the solvent by distillation afforded a residue and crystallisation of this from methanol (10 ml.) at 0° gave 5,6,5',6'-tetramethoxybis-1,1'-spiro indane (VII) as rosettes of needles (2.73g.), m.p. 80-81°. Baker[35] quotes m.p. 81° for the compound.

The infrared spectrum contained peaks at 1610 and 853cm^{-1} (aromatic), 2857cm^{-1} (CH_3O-) and 1253cm^{-1} (CH_3-O-Ar). The n.m.r. spectrum showed twin methoxyl peaks of equal intensity at τ 6.10 and 6.24 (six protons each), a complex multiplet centred at τ 7.45 due to the eight methylene protons, and two singlets in the aromatic region at τ 3.15 and 3.50 due to the two pairs of aromatic protons.

The condensation product of m-nitrobenzaldehyde with acetone: 3,3'-Dinitrodibenzylidine acetone (Ref.50).

To a cold solution of m-nitrobenzaldehyde (10.26g.) in ethanol (100 ml.) water was added dropwise until the solution became cloudy. More ethanol was then added until this cloudiness just disappeared and a clear solution was obtained. To this solution, acetone (1.25 ml.) was added followed by aqueous sodium hydroxide solution (10%; 10 ml.). The flask was then stoppered and shaken vigorously until precipitation of the yellow solid product was complete. The product was then filtered, washed, first with water and then with ethanol, and crystallised from acetic anhydride to give yellow needles (8.3g.), m.p. 235°. The literature[50] quotes m.p. 235 and 238° for this compound.

The infrared spectrum (in KCl) showed peaks at 1678cm^{-1} (dienone system), 1631cm^{-1} (C=C), 1597cm^{-1} (conjugated aromatic ring), 1522,1376,1346 and 740cm^{-1} (Ar-NO_2) and 839cm^{-1} (Ar-NO_2, C-N vibration).

Reduction to 3,3'-Diaminodibenzylacetone.

The unsaturated ketone, 3,3'-Dinitrodibenzylidineacetone

(8.0g.) was suspended in ethyl acetate and catalytically reduced in presence of Raney nickel at atmospheric pressure and room temperature until a colourless solution was obtained. The solvent was removed by evaporation in a stream of nitrogen and the crude oily product was acetylated.

The oily diamino compound showed absorption in the infrared at 3356cm^{-1} (NH_2), 1701cm^{-1} (saturated ketone), 1605 and 1245 cm^{-1} ($Ar-NH_2$) and 862cm^{-1} (1,3-disubstituted benzene).

3,3'-Diacetylaminodibenzylacetone.

The above product (7.5g.) in acetic anhydride (15 ml.) was heated on the steam bath for about 30 minutes and then left overnight at room temperature to complete the reaction. Water was added to decompose the anhydride and an oily product was obtained which did not dissolve readily in any solvent. It was concluded that this could not be the desired compound and perhaps some inter-molecular condensation had occurred, producing a Schiff's base type of compound. The infrared spectrum of the product exhibited peaks at 3059cm^{-1} (-NH-), 1715cm^{-1} (saturated ketone), 1672cm^{-1} ($CH_3.\underline{CO}.NH-$), 1605cm^{-1} ($CH_3.CO.\underline{NH}-$) and 1570cm^{-1} (aromatic).

Preparation of 9.9'-spiro Bifluorene:Fluorenone from Fluorene (Ref.51)

A 500 ml. three-necked flask was fitted with a dropping funnel and reflux condenser. Fluorene (20g; 1.2 moles) was placed in the flask, glacial acetic acid (40 ml.) was added and the mixture was heated to gentle boiling to give a homogenous solution. To this was added dropwise with stirring, a warm solution of sodium dichromate (60g.) in glacial acetic acid (80 ml.) and water (20 ml.) in the course of half an hour, such that the boiling of the fluorene solution was never interrupted. The solution was then refluxed for a further 2.5 hours. The deep green liquid was then poured on to ice and water (400 ml.), allowed to stand for at least two hours, filtered at the pump and washed first with water containing sulphuric acid and then with pure water until the residue on filter paper was free of chromic ion. This crude fluorenone was dried and then distilled under vacuum. The clear yellow distillate (12g.) was crystallised from a mixture of benzene and petroleum ether, m.p. 85°.

2-Aminobiphenyl (Ref.52)

2-Nitrobiphenyl was reduced to the amino-compound as follows:

(a) At first the procedure of Scarborough and Waters[52] was adopted and a solution of stannous chloride (240g.) in concentrated hydrochloric acid (240 ml.) was slowly added to a solution of 2-nitrobiphenyl (37g.) in alcohol (300 ml.). The reaction mixture was refluxed for three hours at the end of which a yellowish precipitate separated which was found to be a tin complex. This was redissolved in water and an excess of sodium hydroxide solution was added. An oil separated which on extraction with ether and evaporation of the solvent gave a brown residue (11g.) which consisted essentially of 2-aminobiphenyl. The above process was not considered satisfactory and the improved method outlined below, was eventually adopted[53].

(b) Into a round bottom flask equipped with a reflux condenser and dropping funnel, 2-nitrobiphenyl (25 g.) and granulated tin (36g.) was placed and concentrated hydrochloric acid (60 ml.) was added slowly and cautiously from the dropping funnel. The flask was heated gently until almost all the tin granules were dissolved. The reaction mixture was refluxed for a further hour. The flask was then fitted for steam distillation and the milky distillate was collected.

saturated with solid sodium chloride, and extracted with ether. On evaporation of the ethereal solution the pale brown residue crystallised to give 2-aminobiphenyl (20g.) m.p. 45°.

2-Iodobiphenyl (Ref.54)

2-Aminobiphenyl (69g; 0.42 mole) was dissolved in dilute hydrochloric acid and cooled in an ice bath to 5°. A solution of sodium nitrite (29.0g.) in water was added dropwise keeping the temperature below 10°. When diazotisation was complete the mixture was treated with a solution of potassium iodide (200g.) in water (300ml.) slowly and with continuous stirring. The low temperature was maintained for a further hour before the ice bath was removed and the mixture was allowed to stand at room temperature for a further 24 hours. The oil which separated was extracted with benzene and the extract was washed with sodium thiosulphate solution and dried over sodium sulphate. On evaporation of the solvent, the residue was distilled under reduced pressure to give 2-iodobiphenyl as a pale brown syrupy liquid, b.p. 156° at 6 mm, (95.6g. 81.3%).

9-(2-Biphenyl)-9-fluorenol (Ref.55)

Dry magnesium turnings (1.17g.) were placed in a round-bottomed flask fitted with a condenser and calcium chloride tube. Dry ether (10 ml.) was added followed by 2-iodobiphenyl (14g., 8.65 ml.). On slight warming the Grignard reaction commenced and was allowed to proceed under gentle reflux without further heating. On completion of the reaction, an ethereal solution of fluorenone (9g.) was added in small portions and the reaction mixture was boiled under reflux overnight. The yellow magnesium complex which precipitated was collected and washed with absolute ether. The solid was then stirred into ice-cold ammonium chloride solution (10%, 425 ml.) and left for two hours. The precipitate was collected and dried <u>in vacuo</u>. Recrystallisation from ethanol afforded the desired carbinol (XVI) as colourless plates (9.2g.), m.p. 174°. Clarkson & Gomberg[45] give m.p. 169-170° for this compound.

The carbinol exhibited a fairly complex infrared spectrum with strong peaks at 3534cm^{-1} (OH), 1166 and 1114cm^{-1} (tertiary alcohol), 1466 and 1443cm^{-1} (Ar-CH=CH-), 1017 and 769cm^{-1} (mono-substituted aromatic ring), 756, 745, 730 and 703 (1,2-disubstituted aromatic rings).

Cyclisation of the carbinol (XVI)

The carbinol (XVI) (9.2g.) was dissolved in boiling acetic acid (15 ml.) and one drop of concentrated hydrochloric acid was added. An immediate reaction took place and the mixture solidified. The product was collected by filtration, redissolved in ethanol and crystallised to give 9,9'-spiro bifluorene (XIV) as colourless plates (7.09g.), m.p. 198-199°. Clarkson and Gomberg[45] also quote this m.p. for the compound.

Compared with the carbinol, the spiro hydrocarbon showed a relatively simple infrared spectrum, the only intense peaks occurring at 1441cm^{-1} (aromatic C=C in plane vibrations), and 746 and 725cm^{-1} (1,2-disubstituted aromatic rings). Only aromatic protons (centred at τ 2.63) were evident in a very complex n.m.r. spectrum.

Nitration of 9,9'-spiro bifluorene (Ref.55).

A mixture of concentrated nitric acid (60 ml.), s.g. 1.42, and glacial acetic acid (60 ml.) was added dropwise to a boiling solution of the spiro-compound (6g.) in acetic acid (200 ml.) over 30 minutes and the reaction mixture was refluxed for a further 75 minutes. After cooling an equal volume of water was added and the nitration product was precipitated as a yellow powdery solid. Crystallisation of this crude product from acetic acid (100 ml.) gave 2,2'-dinitro-9,9'-spiro bifluorene (XXXVII) as yellow crystals (4.8g.) m.p. 234°. Weissburger et al[55] quote m.p. 245-249° for this compound.

The infrared spectrum of the dinitro compound contained bands at 1590cm^{-1} (conjugated aromatic rings), 1513 and 1340cm^{-1} (Ar-NO_2), and 836cm^{-1} (aromatic C-N stretching).

Reduction of 2,2'-dinitro-9,9'-spiro bifluorene (Ref.55)

(a) The dinitro compound (0.176g.) dissolved in ethanol (10ml.) was placed in a three-necked flask and iron powder (0.176g.) was added. The flask was fitted with a reflux condenser and a dropping funnel containing concentrated hydrochloric acid (1 ml.). The acid was added dropwise during 30 minutes and the mixture was refluxed for a further 30 minutes. The excess of iron was removed by filtration and the filtrate was poured into water (17.6 ml.) containing a mixture of aqueous ammonium hydroxide (0.66 ml.) and sodium potassium tartrate (0.88g.). A dark green precipitate was obtained which was perhaps an iron complex. On further addition of water to the filtrate, however, a white precipitate m.p. 174°, separated, and this was redissolved in dilute hydrochloric acid and neutralised with ammonia. A blue precipitate was obtained infra-red analysis of which indicated the presence of peaks due to a nitro group. It must be assumed that the reduction was incomplete and that other side products had been formed, an observation which is quite usual in the reduction of aromatic nitro-compounds. A modified method of reduction was therefore used.

(b) (Ref.56). To a suspension of the dinitro-spiro bifluorene (2.3g.) in ethanol (63 ml.) and water (14 ml.) a solution of crystalline calcium chloride (0.777g.) in water (1.16 moles) was added, followed by glacial acetic acid (1 ml.) and zinc dust (5g.). The mixture was refluxed vigorously for four hours before the hot solution was filtered at the water pump to remove the excess of zinc. The residue was washed with hot aqueous ethanol (80%; 4 ml.) and the combined filtrate and washings were poured into cold water (156 ml.). The resulting precipitate was collected and recrystallised to give the desired diamino spiro difluorene (XXXVIII), (1.22g. 52%), m.p. 224° and 239° (double melting point). Weissburger **et al**[55] give m.p. 244-248° with sintering at 155° for this compound.

The infrared spectrum showed peaks at 3390cm^{-1} ($-NH_2$), 1613 and 1309cm^{-1} ($Ar-NH_2$). The n.m.r. spectrum in $CDCl_3$ showed a four-proton singlet at τ 6.65 due to the primary amino groups at 2 and 2' and a doublet centred at τ 3.98 (equivalent to two protons) due to the aromatic hydrogens attached at the 1 and 1'-positions. The remainder of the aromatic region (centred at τ 2.63) was extremely complex.

Diazotisation of 2,2'-diamino-9,9'-spiro-difluorene(XXXVIII)

The diamino-spiro compound (128 mg.) was dissolved in concentrated hydrochloric acid (1 ml.) by gentle heating and the solution was cooled to 0°. An aqueous solution of sodium nitrite (52 mg.) was added slowly while stirring at 0°. The resulting ice cold diazonium solution was coupled with alkaline beta-naphthol to give a bright red product. A systematic study of the properties of this dyestuff and of other similar dyestuffs obtained by coupling the spiro compound with various beta-naphthol derivatives was then carried out by dyeing Cellophane films as mentioned above.

2-Nitrofluorene (Ref.64)

Concentrated nitric acid (27 ml. s.g. 1.42) was added dropwise with stirring over a period of 15 min. to a solution of fluorene (20g.) in glacial acetic acid at 50°. After the addition the mixture was gradually warmed to 80°. The thick paste was then cooled and the solid product was collected by filtration, washed with cold aqueous acetic acid, water and dried. Recrystallisation from acetone gave the pure 2-nitrofluorene as plates (16g.), m.p. 157-159°. Kuhn[64] gives m.p. 157-158° for this compound.

2-Aminofluorene (Ref.56-cf.ref.64)

A suspension of 2-nitrofluorene (15g.) in ethanol (410 ml.) and water (90 ml.) was treated with calcium chloride (5g.) in water (8 ml.) and glacial acetic acid (5 ml.). To this mixture, zinc dust (25g.) was added in small portions and the resulting suspension was then boiled vigorously under reflux for 4 hours. The hot liquid was filtered, the residue being washed with hot aqueous ethanol (80%) and the combined filtrate and washings were poured into cold water (1 ℓ.) The solid crystalline product was collected and recrystallised from aqueous ethanol (50%) to give 2-aminofluorene (12.5g.) as leaflets, m.p. 126-127°. (lit.[56]: 127°). The infrared spectrum showed peaks at 3425cm^{-1} (NH_2), 1621 and 1319cm^{-1} (Ar-NH_2).

DISCUSSION

Fading

In the present work, it was decided to use non-polar coupling components in order to have closest similarity with 2:1- metal complex dyes, and it was in fact found that the light fastness of the resulting azo dyes is higher than the control (non-spiro analogue). To have a better comparison, as just stated 2-aminofluorene, was also prepared as control and coupled with the same coupling component after diazotisation. The light fastness of the dye thus prepared is lower than that of the dye from spiro bifluorene and a steeper CF curve is obtained (Fig.4).

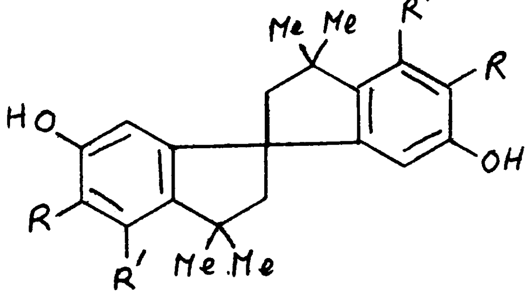
The characteristic fading curve for the spiro dye is higher than the curve for the control, 2-aminofluorene, dye indicating the higher light fastness of the former. However, the curve for the spiro dye is not as flat as was hoped on the analogy of 2:1-metal complex dyes, which could mean that the improvement in light fastness is not as great at lower depths as it is at higher depths. The cause may be due to some irregularity in the shapes of the aggregates. According to Baxter et al[14] the change in the slope of a CF curve depends on the form of dye crystal growth with increase in concentration. It is related to the rate at which the distribution of sizes of the particles change with increase in depth of dyeing. If the dye particles tend to be of uniform size or are of a small range of sizes the slope will be low and the curve flat. On the other hand if the system consists of dye particles of different sizes, with increase in dye concentration these may grow larger and also other small particles may form, resulting in a wide range of sizes giving a CF curve of high slope. In our case, perhaps due to precipitation of dye in the fibre, which may always tend to give a wide range of particle sizes, we have a CF curve with a slightly higher slope than expected. Dyeing with 2:1-metal complex dyes from aqueous solution however may tend to give a smaller range of particle sizes and thus account for the better light fastness even at low concentrations. Thus the cause of the difference may lie in the fact that in the present case the dye is a water-insoluble one, applied by coupling in situ, and therefore precipitated in the fibre, whereas the commercial metal-complex dyes are applied by dyeing, i.e. the dye is adsorbed directly into the fibre and is not insolublised at any time.

Syntheses

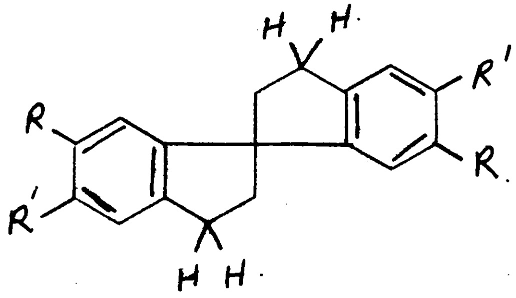
Mention was made above of suitable spiro aromatic systems for use as intermediates in the synthesis of the spiro dyestuffs. The most promising systems appeared to be:-

(i) Those derived by condensation of a phenol, such as catechol or o-cresol, with acetone in the presence of acid (ref.27,28,29). The great advantage of this process would be that the spiro intermediate is produced directly from simple starting materials and the number of synthetic stages is at a minimum. Thus catechol leads directly to the spiran I(R=OH, R'=H), while o-cresol gives the analogue I(R=Me, R'=H) directly. The disadvantage of these products would appear to lie in the presence of substituents (particularly OH) on the aromatic rings which might hinder or prevent coupling with diazonium salts.

(ii) The similarly constituted spirans of the type VIII



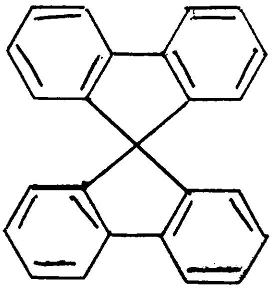
(I)



(VIII).

prepared by condensation of suitably substituted benzaldehydes with acetone, followed by reduction and spiro cyclisation of the intermediate saturated ketones[35,37].
Again it appeared that these could be prepared from readily available starting materials although the number of synthetic stages is greater and the products which possess easily oxidisable benzylic hydrogen atoms may not be as stable as the compounds of type (I).

(iii) Compounds of the spiro bifluorene type (XIV) which resemble the spiro bisindanes (I) and (VIII) in that they may be regarded as spiro bisbenzindanes. It is likely therefore that they will be somewhat more stable than compounds of types (I) and (VIII), but again while the synthetic stages involved in their preparation are relatively simple, there are a good number of them and the starting materials are not so readily available and consequently more expensive. Attempts were made to prepare and examine the properties of compounds of all three types.

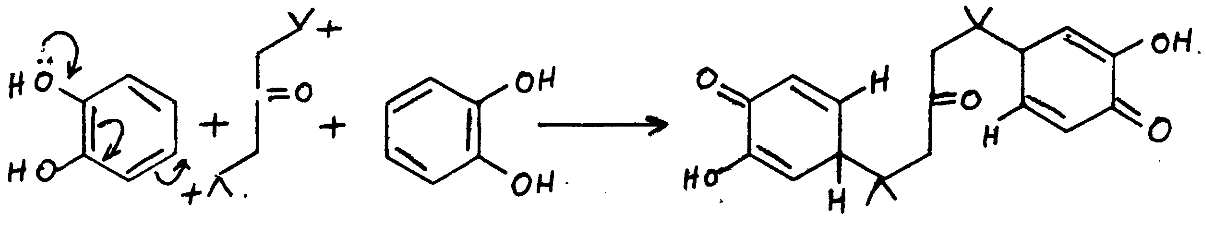

(XIV)

Compounds of type (I)

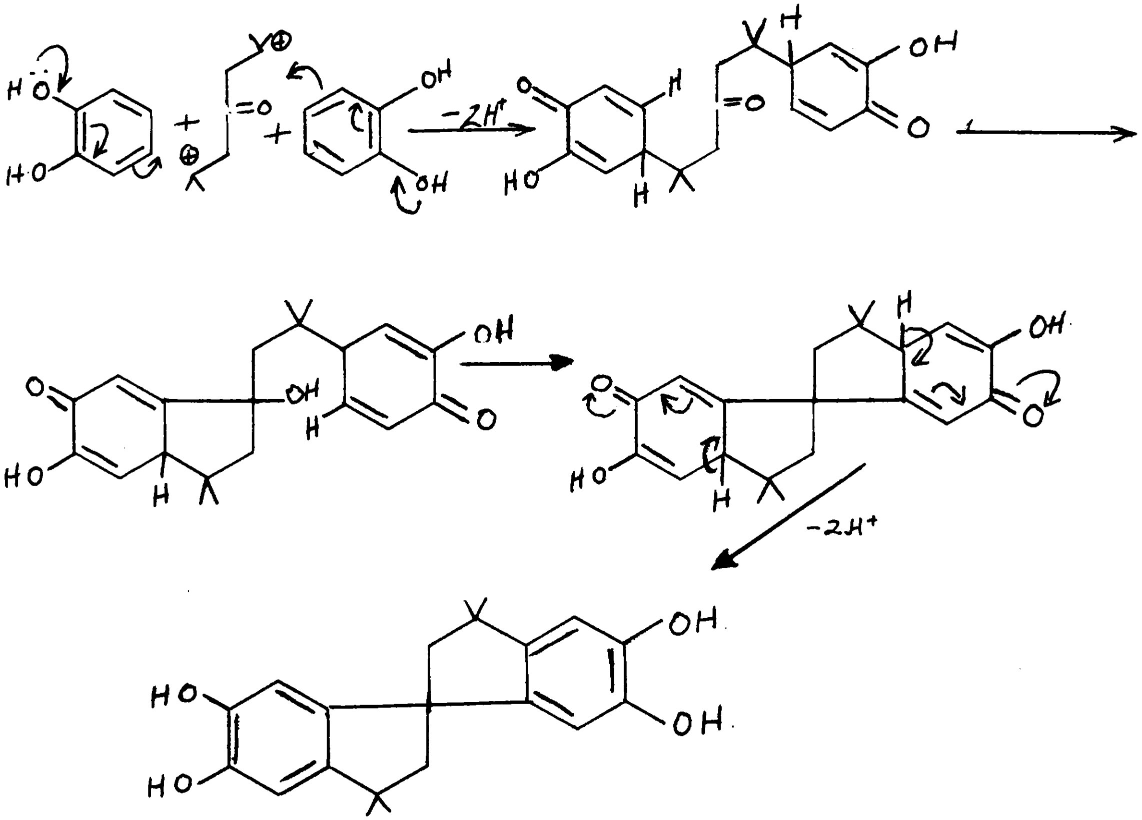
The condensation product (I,(R=OH, R'=H) derived from catechol and acetone in the presence of hydrochloric acid and acetic acid was first prepared by Fabinyi and Széki[57]. Ghiglieno[58] showed that the compound could be produced equally easily when catechol was condensed with an equivalent amount of phorone. Baker[27] reinvestigated the structure of the compound and suggested that the condensation product is probably 5,6,5',6'-tetrahydroxy-3,3,3',3'-tetramethylbis-1,1'-spiro hydrindene (I, R=OH, R'=H).

Following Baker's procedure two moles of catechol were condensed with three moles of acetone in the presence of hydrochloric acid and acetic acid and the tetrahydroxy-compound (I, R=OH, R'=H) was obtained in acceptable yield.

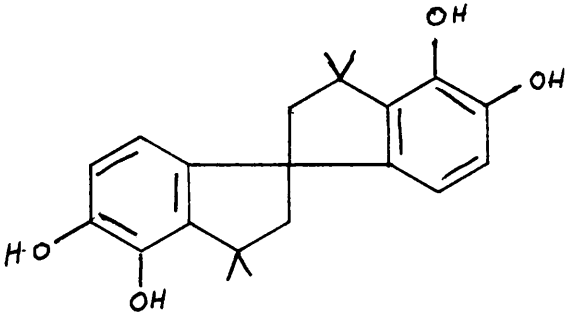
The condensation proceeds *via* electrophilic attack of a phorone carbonium ion on the position of high electron density in the catechol nucleus. The p-position seems to be



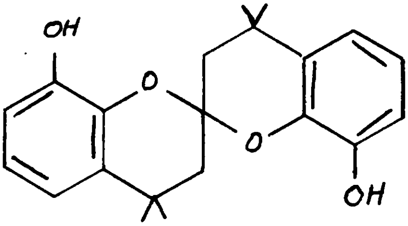
more favourable for electrophilic attack, perhaps because the electron-withdrawing inductive effect of hydroxyl-oxygen influences the adjacent o-position much more powerfully than the more distant p-position. The quasi p-quinonoid structure is likely to be more stable than the corresponding quasi o-quinonoid structure and this leads to preferential p-substitution. A possible mechanism of formation seems to be:-



The o-attack however, could give rise to the spiro indane (XXII) or the pyran (XXIII) but these have not been detected in the product from the reaction.



(XXII)

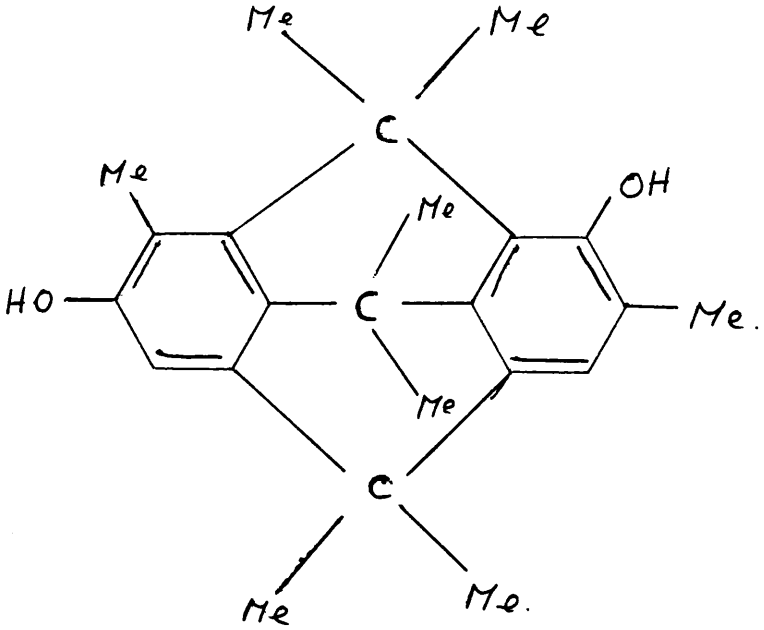


(XXIII)

Neiderl and Casty[59] carried out the analogous reaction by condensing o-cresol with acetone or phorone in presence of sulphuric acid and isolated a dihydric phenol for which they proposed the structure:

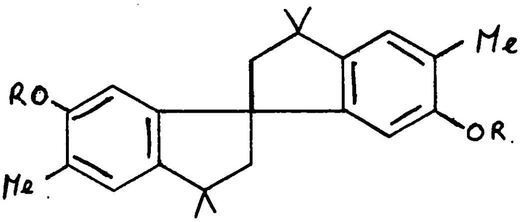
$HO.C_6H_3Me.CMe_2.CH_2.CO.CH_2.CMe_2.C_6H_3.Me.OH$ (XXIV)

Sükösd[60] carried out this condensation using hydrochloric acid and acetic acid in place of sulphuric acid and isolated the diacetyl derivative of a dihydric phenol of molecular formula $C_{23}H_{28}O_2$, for which he proposed the structure (XXV). This, as Baker points out, is stereochemically impossible[30].

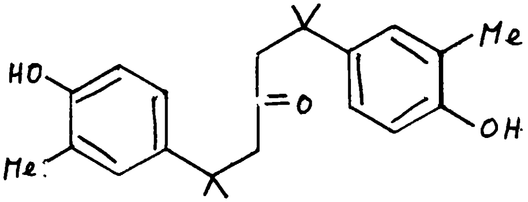


(XXV)

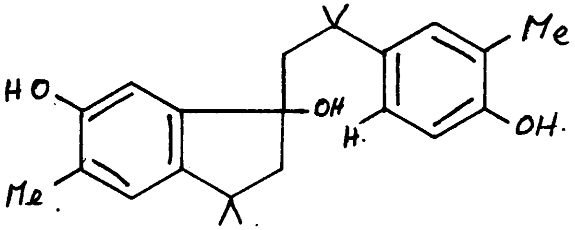
Fisher, Furlong and Grant[36] considered that the compound was probably the bis-1,1'-spiro hydrindene (XXVI, R=H) and further suggested that the product obtained by Neiderl was perhaps an intermediate in the formation of Sükösd's compound. This intermediate may be represented by (XXVII) or (XXVIII).



(XXVI)



(XXVII)

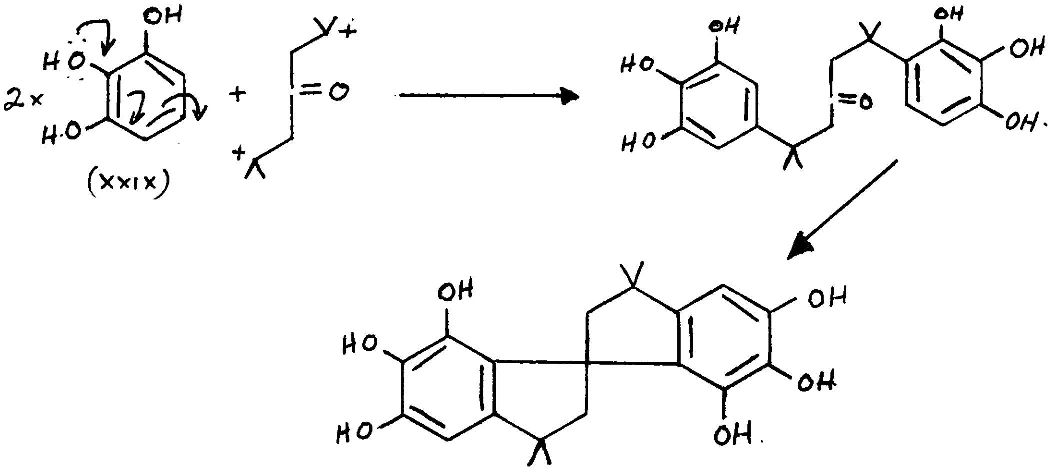


(XXVIII)

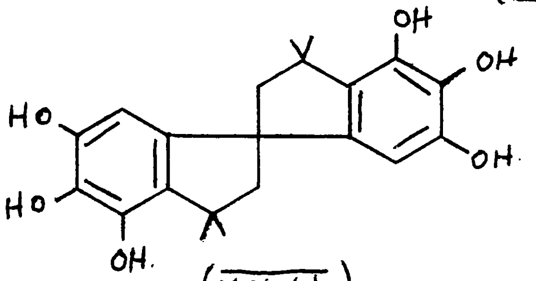
o-Cresol thus follows the same reaction course to give a substituted spiro indane.

Using the method of Baker[30] we therefore, also prepared the diacetoxy-spiran (XXVI, R=Ac) from o-cresol and from it the parent diol (XXVI, R=H).

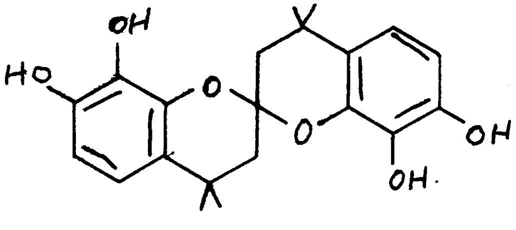
A similar product (XXX) can be obtained[29,61] from pyrogallol (XXIX) in which the o- and the p-directing groups activate the ring in such a manner that the electron density is much more enhanced at position 5 than at positions 4 and 6, due to the greater electron withdrawing inductive effects of the hydroxyl groups ortho to the latter positions. Thus the spiro indane (XXX) can be considered to arise by the following mechanism:



(XXX)



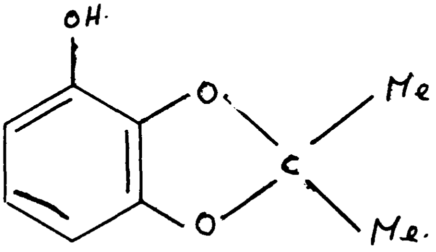
(XXXI)



(XXXII)

However, similar electrophilic attack by a phorone carbonium ion at positions 4 and 6 is also possible and this could lead to the formation of the spiro indane (XXXI) or the spiro chroman (XXXII) neither of which have been detected in the reaction product.

The condensation between pyrogallol and acetone was first carried out by Wittenberg in 1882[61] in the presence of phosphorus oxychloride. The product (m.p. 250°) was considered to be an "acetal" of pyrogallol and acetone (XXXIII) and was not at that time positively identified.

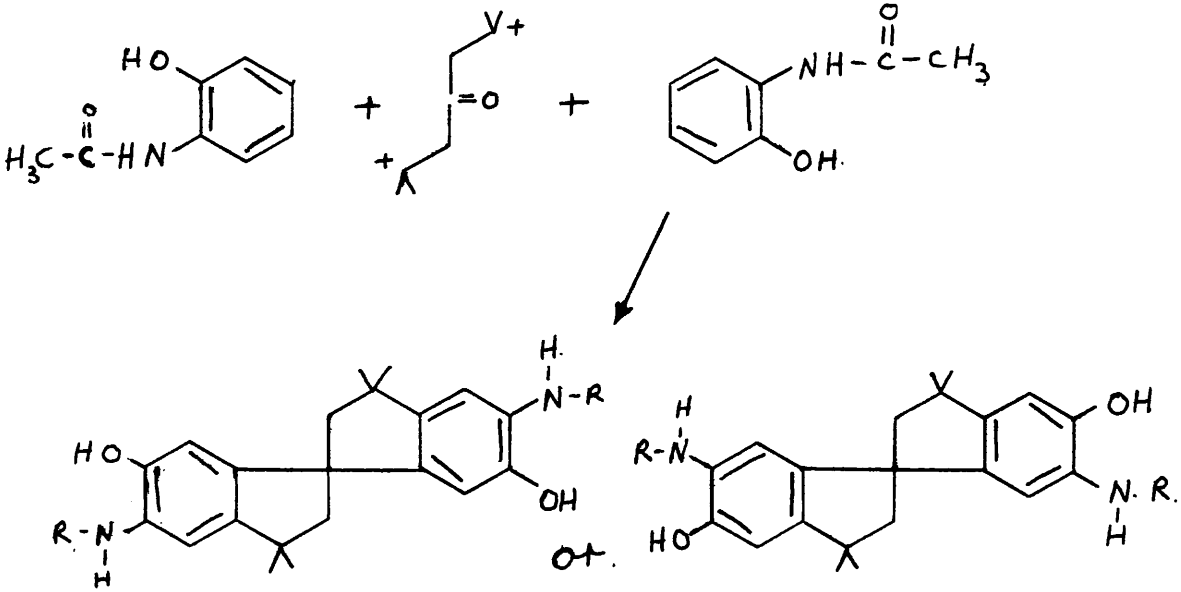


(XXXIII)

Fabinyi and Széki[57,62] obtained the same product by condensing acetone and pyrogallol in presence of acetic and hydrochloric acids and proposed a stereochemically impossible structure based on their erroneous formula for the catechol-acetone condensation product. Later Ghiglieno[58] and Fisher, Furlong and Grant[36] proposed a structure which could not account for all the properties shown by the compound. Finally Baker[29] proved that the compound is the hexahydroxy-3,3,3'3'-tetramethylbis-1,1'-spiro hydrindene (XXX).

This spiro compound did not appear very promising for our purposes because there is only one site in each aromatic ring where coupling could take place and even this cannot be of any practical value because of the steric hindrance from the neighbouring dimethyl groups. Using the two compounds (I, R=OH, R'=H) from catechol and (I, R=Me, R'=H), (i.e. XXVI, R=H) from o-cresol, efforts were made to couple the phenols with simple diazotised bases and with analogous stabilised salts. The phenols, however, were relatively insoluble in aqueous sodium hydroxide and coupling did not take place readily. The colours of the derived dyes were rather disappointing; in most cases, dull yellow colours were produced. Probably the presence of more than one hydroxyl-group in the aromatic system and the steric effects associated with the tetramethyl derivative may inhibit or reduce their tendency to couple. To overcome these difficulties it was considered worthwhile to prepare similar spiro compounds with amino-substituents in the ring and to convert these to azo dyes by diazotising and coupling with suitable aromatic hydroxy- or amino-compounds.

o-Acetylaminophenol appeared to be a suitable starting material as the acetylamino group also has electron-donating character and could thus induce electron density at the poisition para- to it in a similar way as the hydroxy-group does in catechol. Thus the condensation might be expected to take place in the following way:



The conditions of the reaction were much the same as those used by Baker[27]. However, with this particular starting material no crystals appeared in the reaction mixture and the colour of the solution became darker with the elapse of time during reflux. It is likely that the acetylamino groups would be hydrolysed in the acidic medium to give an acid soluble diamino condensation product.* On neutralising the mixture with sodium hydroxide a brownish precipitate settled. This precipitate was collected at the pump and dried. It was diazotised by the normal method using sufficient hydrochloric acid to give a strong blue colour on Congo Red paper throughout the reaction, and slowly adding 10% sodium nitrite solution, keeping the temperature always at about 0°. This diazo-solution when coupled with β-naphthol in alkaline medium gave a bright red colour. On coupling with 1-amino-8-hydroxynaphthalene, 3,6-disulphonic acid it gave a reddish blue colour. A similar blue colour was obtained by coupling the diazo-solution with 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid. The diazotised condensation product also coupled with m-phenylene diamine in acidic medium. The colours of the final dyes resulting from coupling with various end components were thus in general satisfactory. It seemed, however, interesting to examine if this condensation product, having a hydroxy- and an amino-substituent in the nucleus, could itself be used as a coupling component.

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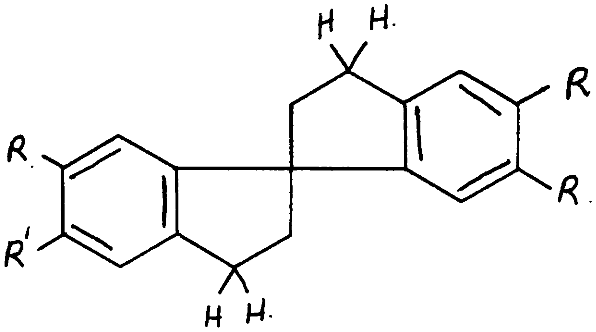
*Although there is no evidence that this product is not simply deacetylated starting material, viz: o-aminophenol.

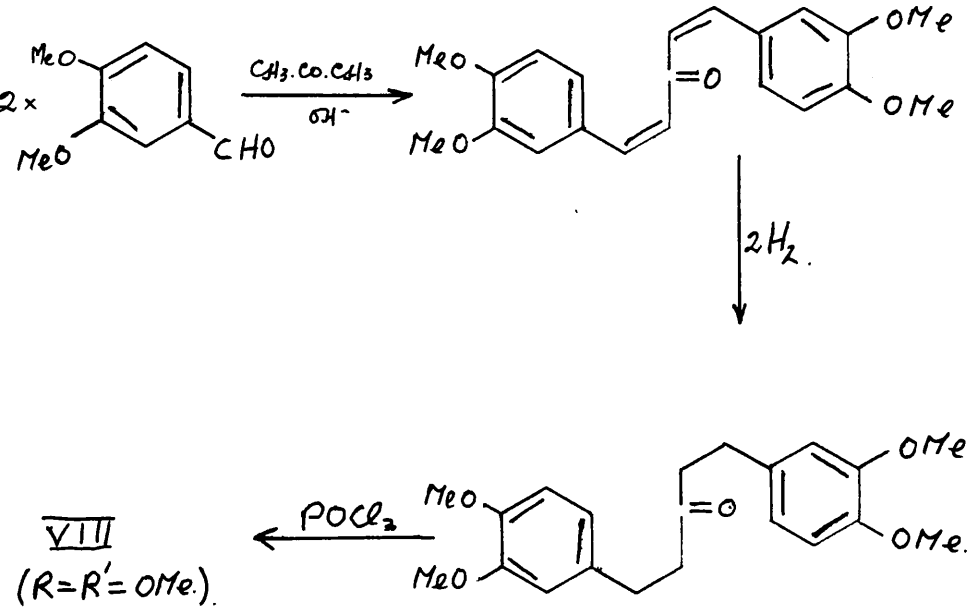
It did couple with two energetic diazo compounds, namely p-chlorobenzene diazonium chloride and p-nitrobenzene diazonium chloride, but the colours were again drab and uninteresting. One could imagine that if the amino-spiro compounds of the general type (I) are used as diazotisable bases the formation of azo dyes of interesting shades might be more likely because one can choose a coupling component with suitable strong chromophoric and auxochromic substituents. However due to shortage of time and lack of facilities further studies on this product could not be carried out.

Compounds of Type (VIII)

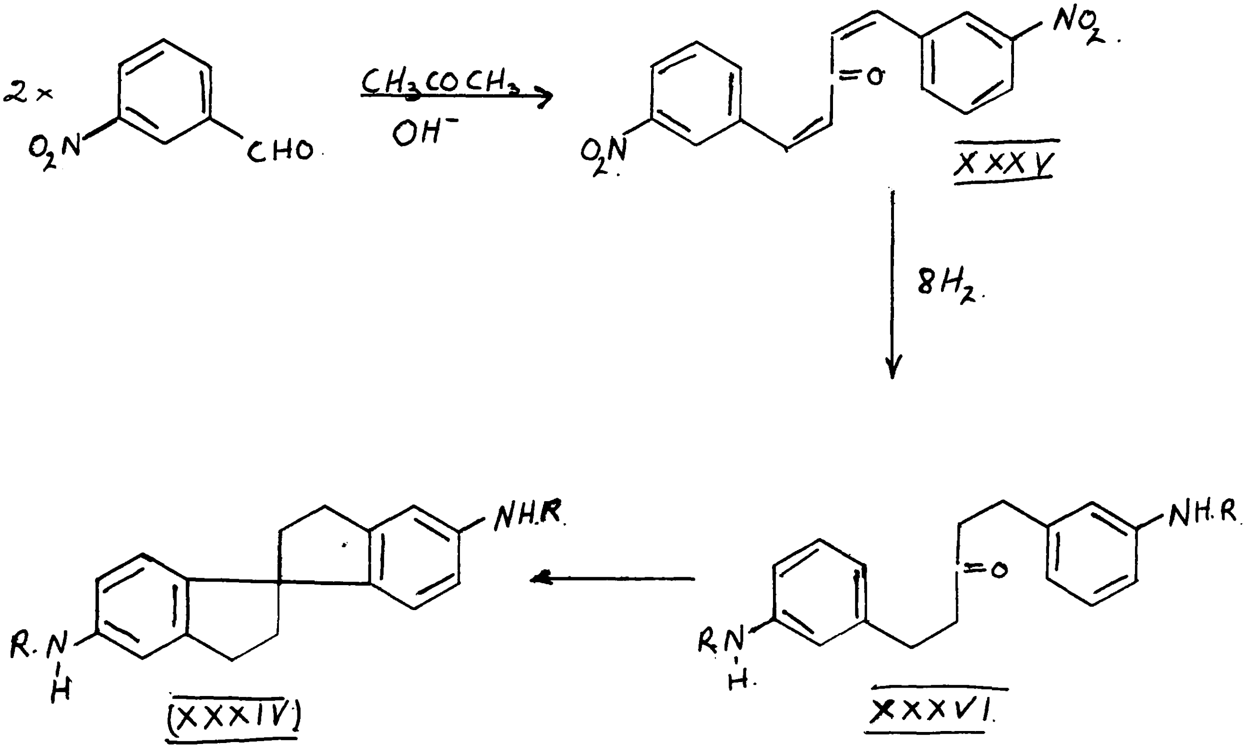


(VIII).

Attention was then turned to the preparation of the spiro bis-indanes of type (VIII) by the cyclo-dehydration procedure of Baker[35]. To gain experience of this process a series of reactions was carried out starting from veratraldehyde as follows:



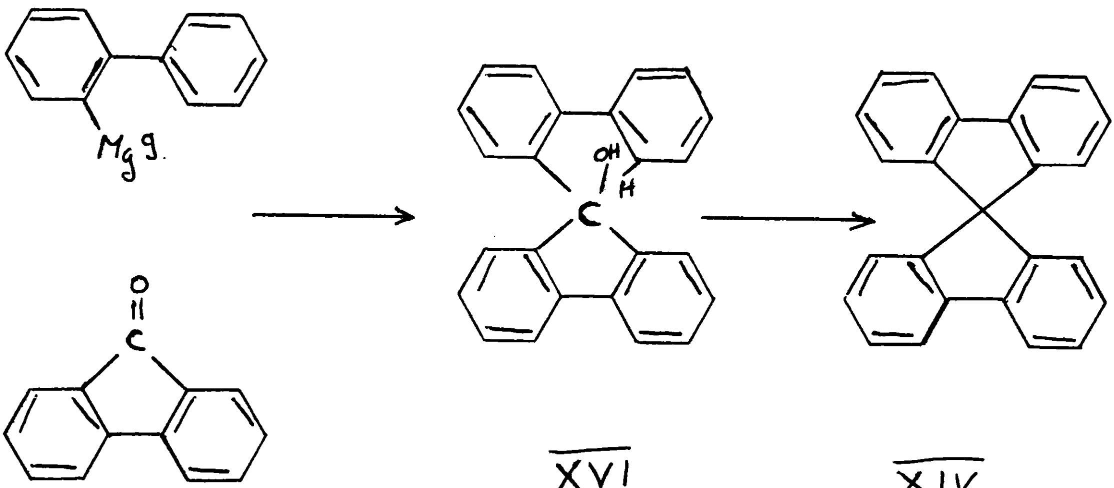
The desired tetramethoxy compound (VIII, R=R'=OMe) was obtained but in a lower yield than that claimed by Baker[35]. Nevertheless, it was considered that an attempt should be made to prepare the spiran (VIII, R=H, R'=NH_2), by a modification of this procedure, for conversion into a dyestuff <u>via</u> the corresponding bis-diazonium salt. The method selected for the preparation of (VIII, R=H, R'=NH_2, i.e. XXXIV, R=H) is summarised as follows:



Condensation of m-nitrobenzaldehyde with acetone in the presence of sodium hydroxide according to the methods of Pfeiffer and Van der lee[50] afforded the known 3,3'-dinitrodibenzalacetone (XXXV). Catalytic reduction of this compound (XXXV) brought about saturation of the two olefinic bonds giving in effect a saturated ketone and also reduced the nitro-groups to amino-groups; a necessary step if the corresponding para- positions are to be activated before the cyclodehydration. The resulting diamino-ketone (XXXVI,R=H) was obtained as an oil, the infra-red spectrum of which was in keeping with the expected structure (XXXVI ,R=H). (strong carbonyl peak at 1701cm^{-1} and peaks due to the amino-groups at 1250,1605,3226 and 3356cm^{-1}). The results in this reaction were very variable, however, and the infrared spectra indicated that the product was often contaminated with a Schiff's base, probably produced by interaction between the carbonyl and amino groups. It was hoped that purification of the product would be achieved _via_ the corresponding diacetyl compound (XXXVI, R=Ac) and while some of this was obtained (peaks at 1718cm^{-1} for C=O, 1672 cm for CO.NH, 3509,1605 and 1570cm^{-1} for NH, in the infra red spectrum), yields were poor and since our experience indicated that the cyclo-dehydration step to produce the desired spiro-compound (XXXIV, R=Ac) was also uneconomical, this route was abandoned.

Compounds of Type (XIV)-the spiro bifluorene system.

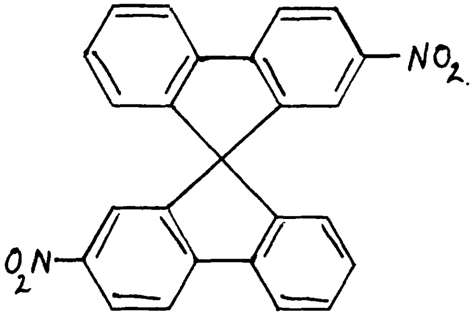
As indicated in a previous section ring systems of the spiro bifluorene type have been apparently readily prepared by the Grignard reaction involving a halo-compound (such as o-iodobiphenyl) and an appropriate tricyclic ketone (e.g. fluorenone), followed by acid catalysed dehydration of the intermediate tertiary alcohol[45].



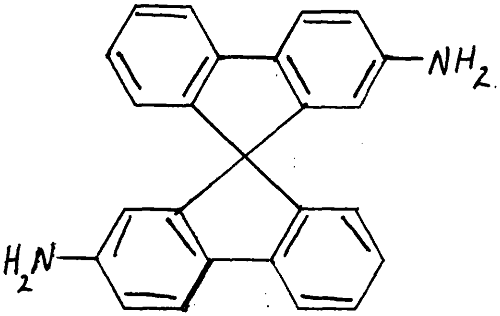
XVI

XIV

In the present work, *o*-iodobiphenyl was prepared by standard methods starting from *o*-nitrobiphenyl which was reduced either with stannous chloride according to the method of Scarborough and Waters[52] or better by means of granulated tin and hydrochloric acid[53] and the resulting *o*-amino compound was treated under Sandmeyer conditions[54] with potassium iodide. The second component, fluorenone, was prepared satisfactorily by oxidation of fluorene according to the methods described by Fieser and Huntress *et al*[51]. The Grignard reaction was carried out using the method of Clarkson and Gomberg[45] and the intermediate magnesium complex was decomposed with aqueous ammonium chloride to give the carbinol (XVI). Cyclodehydration of the latter was readily effected with hydrochloric-acetic acid and the desired hydrocarbon (XIV) so obtained was successfully nitrated with fuming nitric acid in acetic acid[55] to give the 2,2'-dinitro-derivative (XXXVII).



(XXXVII)

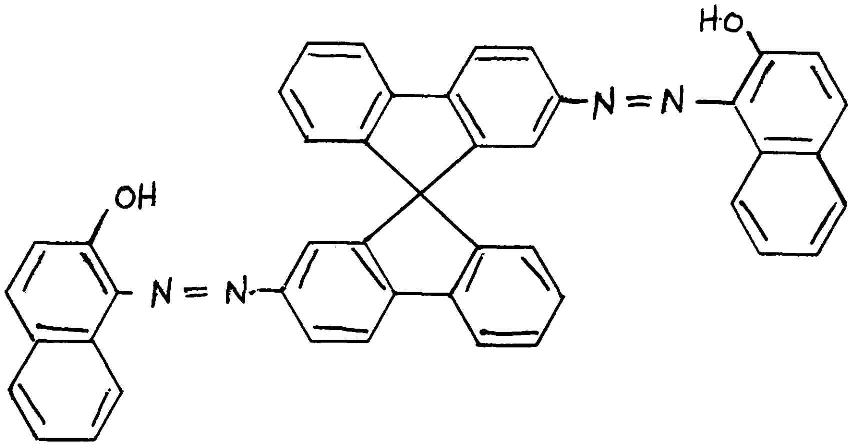


(XXXVIII)

Weissberger[55] has described conditions for the reduction of the 2,2'-dinitro compound (XXXVII) to the corresponding 2,2'-diamino-derivative (XXXVIII). These involve treatment of the nitro compound in ethanol with iron powder and hydrochloric acid and in our hands this method failed to produce satisfactory quantities of the diamine (XXXVIII). An alternative procedure was therefore sought. Neilson, Wood and Wylie[63] have described a method for the reduction of simple nitro-compounds to amines under very mild conditions. This method consists in treating a solution of the nitro-compound in methanol containing sodium borohydride with 5% palladium-charcoal catalyst.

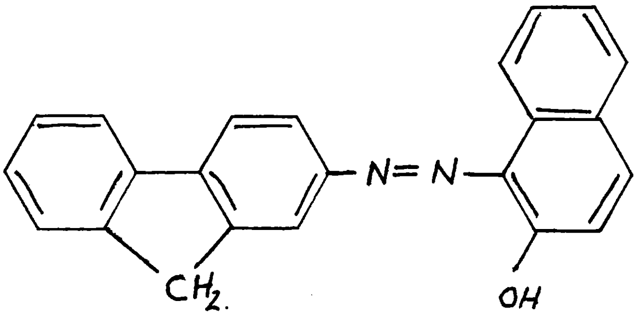
Application of this technique in the present case was ineffective, however, due to the low solubility of the nitro-compound (XXXVII) in cold methanol. The most successful method was eventually found to be a modification of that employed by Sampey and Reid[56] for the reduction of the non-spiro analogue (2-nitrofluorene). This involves the use of zinc in the presence of calcium chloride and acetic acid under reflux. Thus treatment of a suspension of the dinitro-compound (XXXVII), in ethanol, containing a strong aqueous solution of calcium chloride and glacial acetic acid, with zinc dust under reflux, gave after the usual working up process, an acceptable yield of the desired 2,2'-diamino compound (XXXVIII). Although the overall yield of the latter from fluorenone and *o*-iodobiphenyl was only about 15%, it was considered that this could be considerably improved should the derived azo dyes have the predicted properties.

Diazotisation of the diamino-compound was conducted in the usual way and the derived diazonium salt solution was coupled with an alkaline solution of β-naphthol to give a bright red dye (XXXIX). Tests for determination of the light fastness of the dyestuff were carried out and the results plotted as mentioned in an earlier section.



(XXXIX)

The dyestuff was found to be of high light fastness, as was expected. In order to test whether the high resistance to fading is due to the spiro system, it was necessary to have a similar dye of non-spiro structure, for direct comparison. The corresponding non-spiro analogue was therefore prepared from 2-aminofluorene, the latter being prepared by nitration and reduction of fluorene by the method of Kuhn[64] and Sampey[56](c.f.55). Diazotisation and coupling of the 2-aminofluorene with the same coupling component, beta-nephthol, used for the spiro system gave a similar dye (XL). This dye however did not possess such good fading resistance as the spiro analogue (see fading section for details).



(XL)

Couplings with some other components including resorcinol, meta-phenylenediamine (acidic medium), alpha-naphthylamine etc. were carried out. In each case bright colours were obtained but due to shortage of time no quantitative tests for the determination of their light fastness could be carried out.

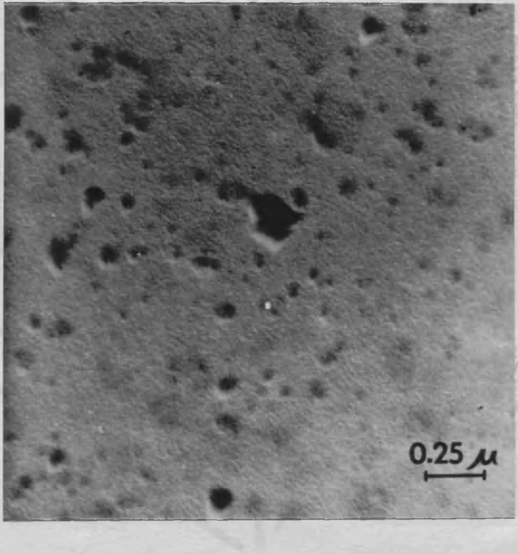


Fig.1. Electron micrograph of aggregated direct cotton dye in cellulose film (Ref.9.).

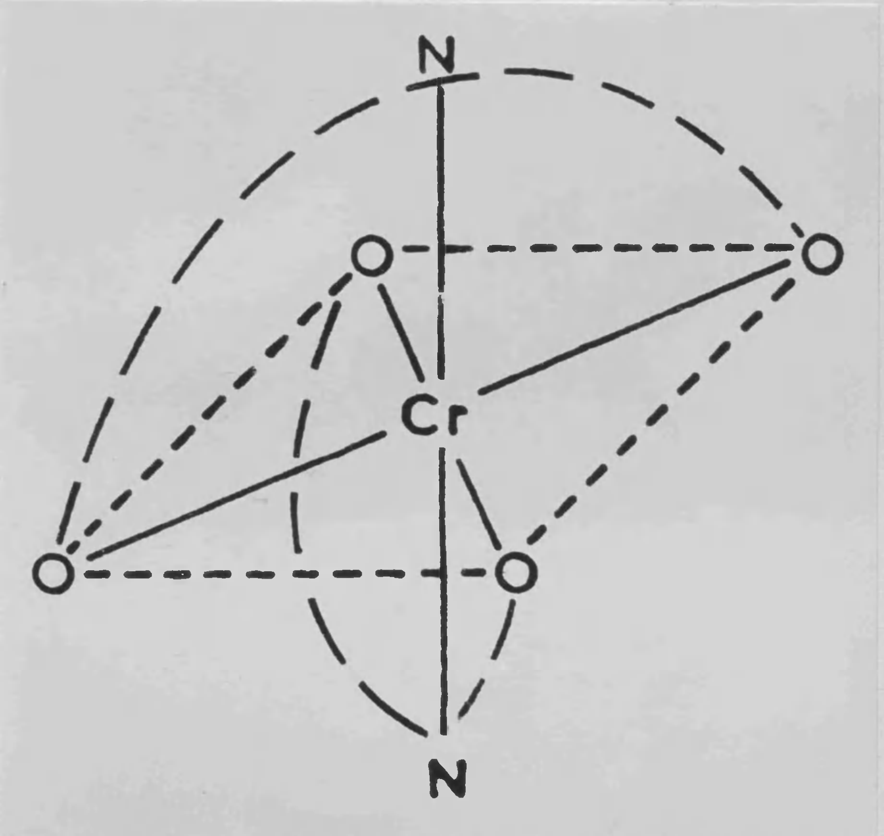


Fig. 2. Skeleton structure of 2:1, dye-metal complex.

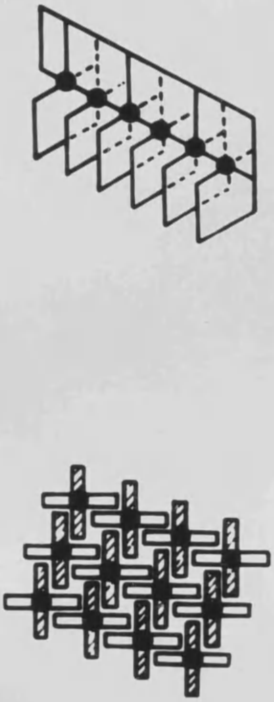


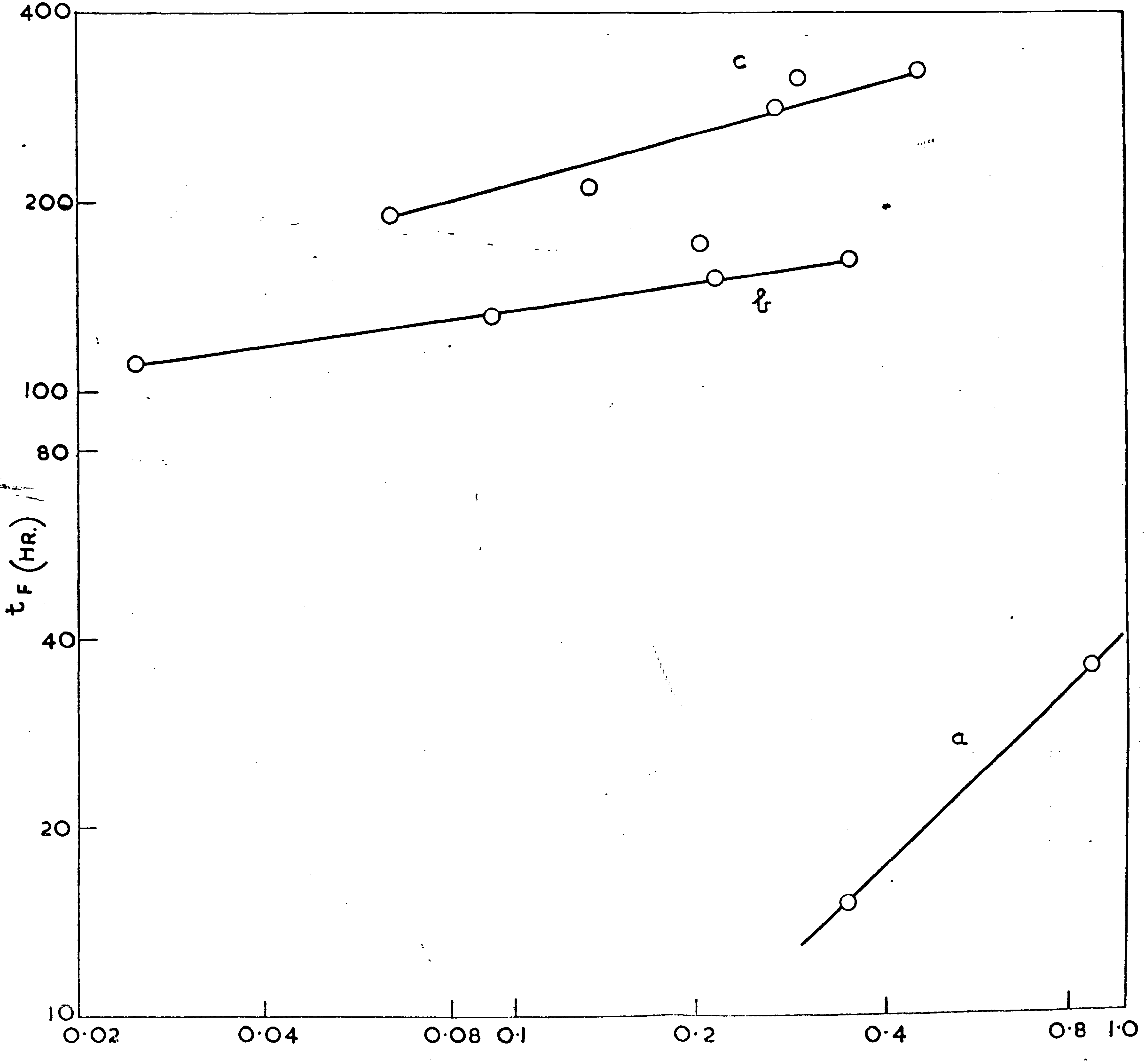
Fig. 3. Sketch of suggested micelle structure of 2:1, dye-metal complexes (Ref.18).

Fig.4. Characteristic Fading (CF) curves for insoluble azo dyes in Cellophane film. (t_f = time for 10% loss of dye by fading).

a = Aniline → Brenthol AS

b = 2-Aminofluorene → Brenthol AS

c = Diamino-spiro difluorene → Brenthol AS


400
200
100
80
40
20
10
t_F (HR.)
0·02
0·04
0·08
0·1
0·2
0·4
0·8
1·0
OPTICAL DENSITY
c
b
a

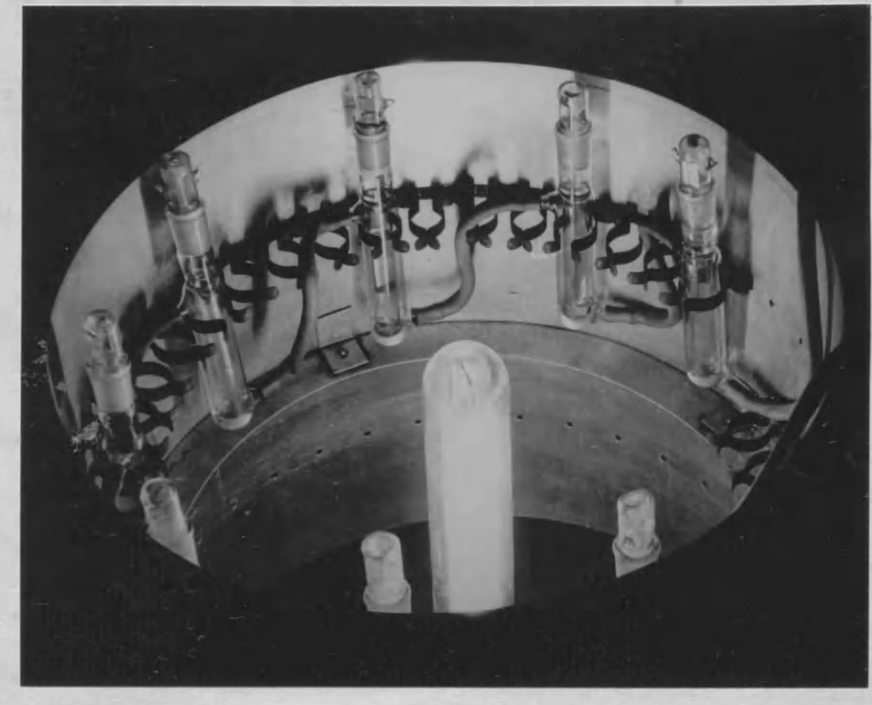


Fig.5. Fading lamp used, showing tubes for fading in controlled atmospheres when required.

REFERENCES

1. C.H. Giles and R.B. McKay, Textile Res. J., 1963, 33, 527. (a review).
2. N.F. Desai and C.H. Giles, J. Soc. Dyers Colourists, 1949, 65, 639.
3. H.R. Chipalkatti, N.F. Desai, C.H. Giles and N.Macaulay, J. Soc. Dyers and Colourists, 1954, 70, 487.
4. J.W. Cumming, C.H. Giles and A.E. McEachran, ibid, 1957, 73, 373.
5. G.L. Royer and C. Maresh, Amer. Dyestuff Reporter, 1943, 32, 181.
6. J.B. Speakman and S.G. Smith, J. Soc. Dyers and Colourists, 1936, 52, 121.
7. W.T. Askbury and J.A.T. Dawson, ibid, 1938, 54, 6.
8. J.O. Warwicker, J. Textile Inst., 1958, 49, T.148.
9. L. Weissbein and G.E. Coven, Textile Res. J., 1960, 30, 58, 62.
10. D.S.E. Campbell, D. Cathcart, C.H. Giles and S.M.K. Rahman, Trans. Faraday Soc., 1959, 55, 1631.
11. C.H. Giles, S.M.K. Rahman and D. Smith, J. Chem. Soc., 1961, 1209.
12. E. Kayser, Textilber., 1926, 7, 437.
13. P. Bean and F.M. Rowe, J. Soc. Dyers and Colourists, 1929, 45, 61.
14. G. Baxter, C.H. Giles, M.N. McKee and N. Macaulay, ibid, 1955, 71, 218.

15. H.H. Sumner, T. Vickerstaff and E. Waters, *ibid*, 1953, *69*, 181.

16. Wan Shik Ha, *Ta Han Hua Hsueh Hui Chih,* 1962, *6*, (2),104; *Chem. Abs.,* 1964, *60*, 1880.

17. G. Schetty, *J. Soc. Dyers and Colourists,* 1955, *71*, 705.

18. C.H. Giles and T.H. McEwan, *J. Chem Soc.,* 1959, 1791.

19. Y. Ishii, *J. Soc. Textile Cellulose Ind. Japan,* 1959, *15*, 56.

20. Y. Ishii and M. Shimada, *ibid,* 1960, *16*, 579.

21. E. Race, F.M. Rowe and J.B. Speakman, *J. Soc. Dyers and Colourists*, 1946, *62*, 372.

22. C.H. Giles, G. Baxter and S.M.K. Rahman, *Textile Res. J.*, 1961, *31*, 838.

23. C.H. Giles and R.B. McKay, *Textile Res. J.,* 1963, *33*, 529.

24. C.H. Giles, "Laboratory Course in Dyeing", Soc. Dyers and Colourists, Bradford, 1957.

25. C.H. Giles, *J. Applied Chem.,* 1965, *15*, 541.

26. C.H. Giles, *J. Soc. Dyers Colourists,* 1957, *73*, 127.

27. W. Baker, *J. Chem. Soc.,* 1934, 1678.

28. W. Baker and J.C. McGowan, *ibid*, 1938, 347.

29. W. Baker and D.M. Besly, *ibid,* 1939, 195.

30. W. Baker and D.M. Besly, *ibid,* 1939, 1421.

31. W. Baker and D.M. Besly, *ibid,* 1940, 1103.

32. W. Baker and J.C. McGowan, *ibid*, 1943, 486.

33. W. Baker, R.F. Curtis and J.F.W. McOmie, ibid, 1951, 76.

34. W. Baker, R.F. Curtis and M.G. Edwards, ibid, 1951, 83.

35. W. Baker and H.L. Williams, ibid, 1959, 1295.

36. C.H. Fisher, R.W. Furlong and M. Grant, J. Amer. Chem. Soc., 1936, 58, 820.

37. H. Stetter and A. Reischl, Ber., 1960, 93, 791.

38. H. Fecht, ibid, 1907, 40, 3883, 3890.

39. D. Radulescu, Chem. Abs., 1914, 8, 2874; Chem. Zentr., 1912, II, 1363; ibid, 1924, I, 2249.

40. D. Radulescu, Bull. Soc. Chim. France, 1925, 37, 916; Chem. Abs., 1926, 20, 185; 1925, 19, 494.

41. T. Carolan, Associate-ship Thesis, R.C.S.T., Glasgow, 1964.

42. D. Radulescu, Ber., 1911, 44, 1023; H. Leuchs and D. Radulescu, ibid, 1912, 45, 189; 1913, 46, 2420.

43. H. Leuchs and L. Lock, ibid, 1915, 48, 1432; H. Leuchs and G. Kowalski, ibid, 1925, 58, 2822.

44. C.K. Ingold and C.L. Wilson, J. Chem. Soc., 1934, 776.

45. R.G. Clarkson and M. Gomberg, J. Amer. Chem. Soc., 1930, 52, 2881.

46. A. Albert, "The Acridines", E. Arnold and Co., London, 1951 and 1966.

47. See Ref. 24, p.13.

48. B.S. Cooper and F.S. Hawkins, J. Soc. Dyers Colourists, 1949, 65, 586.

49. S. Sugasawa and H. Yoshikawa, J. Chem. Soc., 1933, 1583.

50. P. Pfeiffer and B. Segall, Annalen, 1928, 460, 123; J. Van de Lee, Rec. Trav. Chim., 1928, 47, 923.

51. E.H. Huntress, E.B. Hershberg and I.S. Cliff, J. Amer. Chem. Soc., 1931, 53, 2720; L.F. Feiser, "Experiments in Organic Chemistry", D.C. Heath and Co. Boston, 3rd. Edition, 1957, pp.88 and 92.

52. H.A. Scarborough and W.A. Waters, J. Chem. Soc., 1927, 89.

53. A.I. Vogel, "Textbook of Practical Organic Chemistry", Longmous, London, 3rd. Edition, p.563.

54. H. Gelman, J.E. Kirby and C.R. Kinney, J. Amer. Chem.Soc, 1929, 51, 2252.

55. J.H. Weissburger, E.K. Weissburger and F.E. Ray, ibid, 1950, 72, 4250, 4253.

56. J.R. Sampey and E.E. Reid, ibid, 1947, 69, 712.

57. R. Fabinyi and T. Széki, Ber., 1905, 38, 2307.

58. M. Ghiglieno, Atti. R. Accad. Sci. Torino, 1912, 47, 16.

59. J.B. Niederl and R. Casty, Sitzungsber. Akad. Wiss.Wien, 1928, 137, IIb, 1038.

60. J. Sűkösd, Acta Lit. Sci. Univ. Hung. Francisco-Josephinae, 1932, 2, 230; Chem. Abs., 1933, 27, 1873.

61. H. Wittenberg, J. Prakt. Chem., 1882, 26, 76.

62. Beilstein's "Handbuch der Organischer Chemie", 4th Edition, 1923, 6, 1080.

63. T. Neilson, H.C.S. Wood and A.G. Wylie, J. Chem. Soc. 1962, 371.

64. W.E. Kuhn, Org. Syn. 1933, 13, 74.