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EXTREMELY REACTIVE CARBON–CARBON DOUBLE BONDS—I[1]

REACTIONS WITH 2-(9-XANTHYLIDENE)-, 2-(9-THIOXANTHYLIDENE)-, AND 2-(9-FLUORENYLIDENE)-INDANE-1, 3-DIONE. A CONTRIBUTION ON THE STRUCTURE AND REACTIVITY OF NON-PLANAR C–C DOUBLE BONDS

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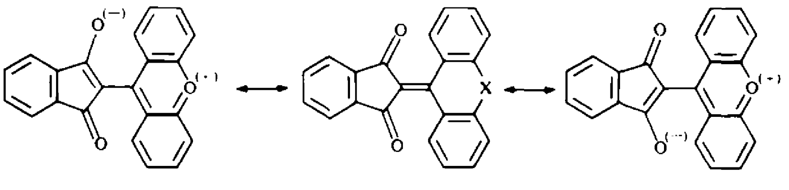
Abstract—The compounds in the title (*cf* **1a**, **1b** and **2**) react with various reagents, often under mild conditions, mostly by breaking of the central double bond. According to X-ray diffraction the central double bond of 2 - (9 - xanthylidene)indane - 1, 3 - dione is inclined by 47.2°. The relationship between the structure and reactivity of the compounds in the title is discussed.

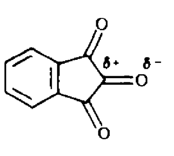
Three circumstances led us to investigate the structure and reactivity of the above compounds in detail (i) The unusual reactions of sterically hindered (overcrowed) ethylene, which we formerly referred to as ethylene with "anomalous behaviour", have long been of interest to us;[1] however, whereas the compounds of this type which we have studied hitherto are symmetrical about their central double bond, there are different substituents at the double bond of the 2-methyleneindane-1, 3-dione derivatives **1a**, **1b** and **2**. (ii) During the course of a series of investigations of cyclic 1,2,3-tricarbonyl compounds in recent years we have repeatedly reported the unique reactivity of the middle carbonyl group in indane-1, 2, 3-trione (**3**),[2] in which the polarity is fixed in the sense of **3**; the 2-methyleneindane-1,3-dione derivatives **1a**, **1b** and **2** now studied have, as the possible polar limiting structures **1a**′ and **1a**″ show, a polarity opposite to that of the 2-position of the initial double bond system. (iii) We had already published[3,5] syntheses for the three compounds **1a**, **1b** and **2**.

The preparation of **1a** and **1b** by condensation of the corresponding 9,9-dichloroxanthane with indane-1,3-dione (**7**) was described as long ago as 1955.[3] Both compounds are deeply coloured. The action of thionyl chloride on **1a** followed by hydrolysis yields xanthone (*cf.* **4**: S is replaced by O).[3]



1a **1b**

X = O **1a**: nearly black, violet in solution
X = S **1b**: red-brown, orange-red in solution



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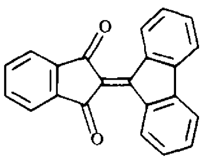


2

2 was first prepared in 1966 by the action of fluorenone imine (**20**) on indane-1, 3-dione (**7**).[4] We obtained **2** by the Wittig reaction of indane-1, 2, 3-trione (**3**) with 9-fluorenylidene triphenylphosphorane.[5]

Experiments with **1a**, **1b** *and* **2**

These three compounds reacted with a wide variety of substances and proved to be extremely reactive. In 14 of the 21 reactions described reaction products which showed a preceding breaking of the central double bond could be isolated.

Table 1 lists the experiments described and the products isolated. Appropriate literature references are given for all the known products. The constitutions of the hitherto unknown compounds **11a**, **11b**, **14a**, **14b**, **17**, **21** and **22** are given in accordance with their analyses and spectral data.

Table 1.

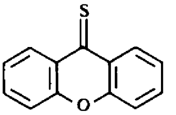
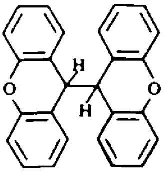
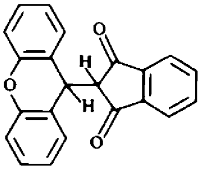
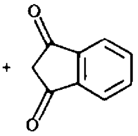
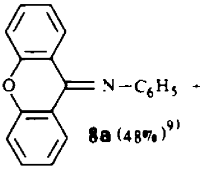
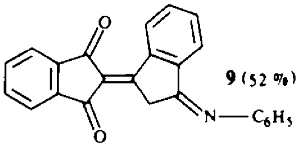
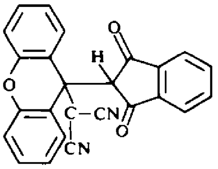
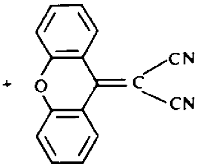
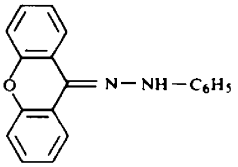
No.	Reagents	Reaction conditions	Reaction products (yield)
Experiments with **1a**			
1	Schwefel	270°C; 20 min	 **4** (35%)[6]
2	zinc/glacial acetic acid	120°C	 **5a** (51%)[7]
3	C_6H_5-SH	100°C, 10 h	 +  **6** (55%)[31] **7** (12%)[8] + $C_6H_5-S-S-C_6H_5$
4	$NaBH_4$	20°C; $(CH_3)_2CHOH$; 12 h	**6** (~100%) $\xrightarrow[(5)]{200°C;\ air;\ 2\ h}$ **1a** (41%)
6	$C_6H_5-NH_2$	20°C; 12 h	 +  **8a** (48%)[9] **9** (52%)[10]
7	$NC-CH_2-CN$	20°C; pyridine; 12 h	 +  **11a** (42%) **10** (8%)[11]
8	$C_6H_5-NH-NH_2$	20°C; CH_3OH; 12 h	 **12** (38%)[12]

Table 1. (*Contd*).

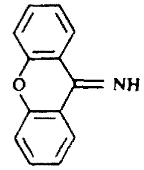
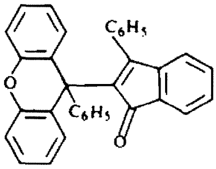
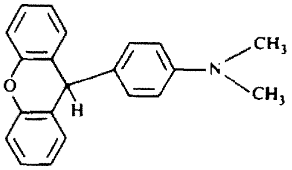
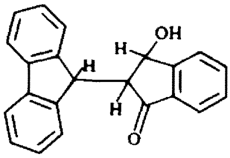
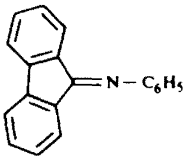
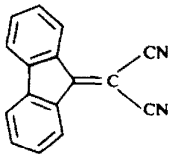
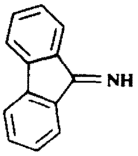
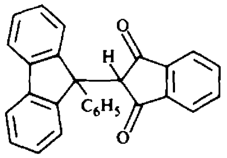
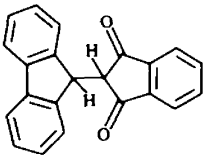
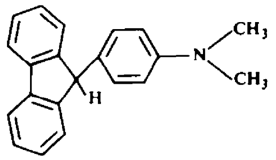
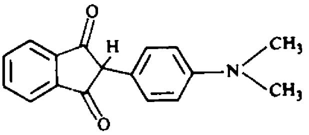
No.	Reagents	Reaction conditions	Reaction products (yield)	
9	NH_3	20°C; H_2O; 48h	 **13** (50%)[13]	
10	C_6H_5MgBr	Ether/C_6H_6; 2 h reflux	 **14a** (20%)	
11	$C_6H_5-N(CH_3)_2$	150°C; 2 h	 **15** (13%)[14] + $C_{34}H_{30}N_2O_4$ **16** (22%)	
Experiments with **1b**				
12	zinc / acetic acid glacial	120°C	**5b** (16%)[15]	In the formulae of **5b, 8b, 11b** and **14b** the ring oxygen in the corresponding compounds (**5a**, etc) is replaced by sulpher.
13	$C_6H_5-NH_2$	100°C; 1 h	**8b** (17%)[16]	
14	$NC-CH_2-CN$	20°C; pyridine; 12 h	**11b** (51%)	
15	C_6H_5MgBr	ether/C_6H_6; 3 h reflux	**14b** (21%)	
Experiments with **2**				
16	zinc/glacial acetic acid	120°C	 **17** (79%)	
17	$C_6H_5-NH_2$		 **18** (49%)[17]	
18	$NC-CH_2-CN$	20°C; pyridine	 **19** (60%)[18]	
19	NH_3	20°C; H_2O	 **20** (73%)[19]	

Table 1. (*Contd*).

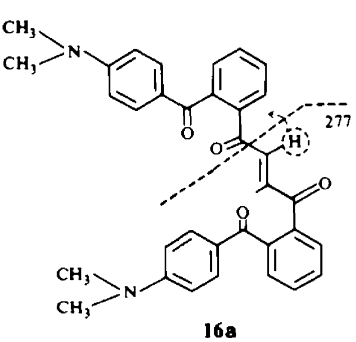
No.	Reagents	Reaction conditions	Reaction products (yield)
20	C_6H_5MgBr	Ether/C_6H_6; 2 h unter Rückfluß	 **21** (33%)
21	C_6H_5-SH	150 °C; 5 h	 + $C_6H_5-S-S-C_6H_5$ **22** (75%)
22	$C_6H_5-N(CH_3)_2$	150 °C; 4 h	 + **16** (31%) **23** (13%)[20]

The constitution of reaction product **16** is uncertain. The analysis of this red compound corresponds to the formula $C_{17}H_{15}NO_2$ (265.3). The most abundant fragment in the mass spectrum (which is also the base peak) is at *m/e* 277. High resolution gives 277.1103 ($C_{18}H_{15}NO_2$). We therefore conclude that **16** must have the empirical formula $[C_{17}H_{15}NO_2]_n$ with $n \geq 2$. A dimer of the empirical formula $C_{34}H_{30}N_2O_4$ (530.6) is probable. **16** is not identical with the known derivative of indane-1, 3-dione **24** ($C_{17}H_{15}NO_2$). As for the constitution of **16**, we think that only two structures need consideration, **16a** and **16b**, which can be preferred above a precursor of type **16c**.

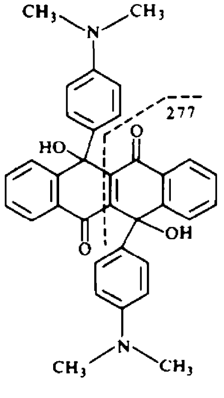
Of the two possibilities, we prefer **16b**, since (i) the base



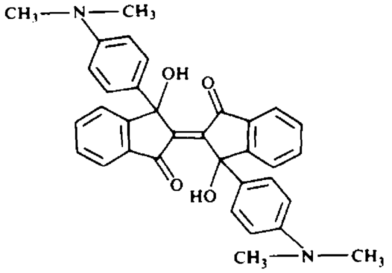
24[21]



16a



16b



16c

peak in the mass spectrum at m/e 277 is explicable *without* the H-migration necessary in **16a** (cracking into the fragments shown); (ii) the appearance of a peak at m/e 260 (17%) is consistent with the fragment of mass number 277 (detachment of OH; seldom encountered in the mass spectra of ketones); (iii) the strong bands for a tertiary OH-group found at 1188 and 1370 cm^{-1} in the IR spectrum (KBr) of **16** and the very weak carbonyl bands at 1708 and 1662 cm^{-1} are consistent only with **16b**; and (iv) signals for aromatic protons are found in three ranges in the ^1H-NMR spectrum of **16** (CF_3COOH): $\delta = 7.89$ and 8.67, $W^{1/2} = 5$ Hz, 8H, p-$(CH_3)_2NC_6H_4$, and $\delta = 8.02$–8.32, m, 10H, of which 2H t-OH.

Attempts to convert **1a** with the following compounds (reaction temperatures in °C) were unsuccessful and gave back the starting materials: benzaldehyde (190), 9-diazofluorene (150), phenanthrenequinone (80), diphenyl disulphide (150), boron trifluoride in methanol (60), 2, 3-dimethylbutadiene (60).

On the other hand, conversion of **1a** with triphenylmethane, 9-phenylfluorene, urea, and phenol gave mixtures of substances inseparable by "DC".

The differences in behaviour of the compounds **1a**, **1b**, and **2** with the same reagents are striking.

Hydrogenation. **1a** was smoothly hydrogenated by $NaBH_4$ to **6**, but the keto-groups are attacked, although normally $NaBH_4$ reacts with ketones and hydrogenates olefinic double bonds only in exceptional instances[22] (*cf* Reaction 4).

The hydrogenation of C–C double bonds with thiophenol as hydrogen donor has not been described before to our knowledge (*cf* Reactions 3 and 21). The partial hydrogenolyses of the central double bond of **1a** would be detected by the isolation of **7**, *cf* Reaction 3.

Reduction of **1a** or **1b** with zinc in glacial acetic acid yields the bixanthyls **5a** or **5b** respectively, *cf* Reactions 2 and 12. Dimerisations under reducing conditions are known in the xanthene series, e.g. the synthesis of **5a** from xanthydrol with zinc in glacial acetic acid.[23] On the other hand, **2** does not give any product from the breaking of the central double bond but instead yields **17** from the hydrogenation of the double bond and one of the carbonyl groups, *cf* Reaction 16.

Solvolysis. The conversions (Table 1) of **1a**, **1b** and **2** with aniline (*cf* Reactions 6, 13 and 17), phenylhydrazine (*cf* Reaction 8), ammonia (*cf* Reactions 9 and 19), and malonodinitrile (*cf* Reactions 7, 14 and 18) can be regarded formally as solvolysis of a C–C double bond. With the exception of the reaction of **1b** with malonodinitrile (Reaction 14) in every instance products from the breaking of the central double bond can be isolated.

Grignard reactions **1a** and **1b** react with phenylmagnesium bromide by 1, 2- and 1, 4-addition, whereas **2** takes up only 1 mol under 1, 4-addition (*cf* Reactions 10, 15 and 20).

Conversion with NN-dimethylaniline. Unusual reaction products are obtained from the reaction of **1a** or **2** with NN-dimethylaniline. In both instances reaction product **16** is obtained from the indane-1, 3-dione part of the starting compound; its constitution was discussed above. The *NN*-dimethylaminophenyl-derivatives **15** and **23** are obtained from the xanthene or fluorene part of the initial compound (*cf* Reactions 11 and 22). Both these take up 1 mol *NN*-dimethylaniline at the central double bond connecting the ring system of the initial compound after it has been broken.

Cleavage with sulphur. **1a** undergoes cleavage when fused with sulphur. We can isolate xanthione (**4**) (*cf* Reaction 1). This reaction is analogous to the cleavage of bixanthylene with sulphur, described earlier.[1a]

X-Ray diffraction of **1a** (Tables 2–4 have been deposited *with the Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, UK*)

1a ($C_{22}H_{12}O_3$) is orthorhombic (space group $Pbcn$) with lattice constants $a = 724.4(1)$, $b = 1265.4(1)$, $c = 1668.3(2)$ pm, $Z = 4$, $D_x = 1.41$ g cm^{-3}. The line intensities were measured on a Syntex $P2_1$ diffractometer in the θ-2θ procedure using monochromatic CuKα radiation ($\lambda = 154.178$ pm). A correction for absorption ($\mu = 0.67$ mm^{-1}) was not made. After data reduction there were 986 independent reflections ($3.0 \leqslant 2\theta \leqslant 130°$) with $F_0^2 \geqslant 2.0\sigma(F_0^2)$. The structure was solved by direct methods and refined to $R = 0.048$, $R_w = 0.044$. Weighting was given by the equation $w = k(\sigma^2(F_0) + 0.0002F_0^2)^{-1}$. The function $\Sigma W\Delta^2$ was minimized. The positions of all the hydrogen atoms could be located in the difference synthesis and were freely refined with individual isotropic temperature factors. All the other atoms had anisotropic temperature factors. The atomic parameters obtained are listed in Tables 2 and 3. The equivalent isotropic temperature factors U_{eq} of the atoms other than hydrogen in Table 2 have been calculated by the equation

$$U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i{}^* a_j{}^* \bar{a}_i.\bar{a}_j.$$

Figure 1 shows a perspective representation of the molecular structure of **1a**. The molecule shows a crystallographic C_2–symmetry, in which the atoms O(1), C(7) and C(8) are situated on the twofold axis. As was expected from steric considerations, the molecule is not planar. The two halves of the molecule are inclined at 47.2° to the twofold axis. The C(7)–C(8) double bond is especially long, 140.5(4) pm. From the lengths of the neighbouring C–C bonds C(6)–C(7) and C(8)–C(9) [145.0(2) and 147.3(3) respectively] it can be deduced that the π-electrons of the C(7)–C(8) bond are partly involved in the conjugated systems of both halves of the molecule.

Reaction mechanism

As follows from the X-ray diffraction analysis of the **1a** structure, the polar limiting structures **1a′** and **1a″** are of great importance in the description of the molecule **1a**. The central double bond of **1a** is therefore polarised and suitable reagents can be added. Reaction products **11a** and **11b** (*cf* Reactions 7 and 14) show that such additions take place.

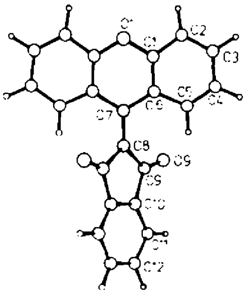


Fig. 1. Molecular structure of **1a**

We assume that addition (eqn 1) is also the first step in the cleavage reactions with ammonia, aniline and phenylhydrazine. The resulting intermediate products can only decompose into the end-products in a six-centre reaction according to equation (2). Such fragmentations in a six-membered ring with hydrogen transfer are known in the literature.[24]

Only in Reaction 6 and always in this case could we isolate a derivative of the indane-1, 3-dione (**7**). Bi-indone anil (**9**) is known to be formed from **7** and aniline.[25]

It would seem to be conclusive that the conversion with malononitrile can also be explained in terms of this mechanism, as the formation of compounds **10** and **19** demonstrates.

The conversions of **1a** and **2** with *NN*-dimethylaniline must result from quite another mechanism. The formation of **16**, which must result from the indane-1, 3-dione residue and *NN*-dimethylaniline and which (as already discussed) is at least a dimer, makes it probable that a radical intermediate stage plays a part here.

Bent C–C *double bonds*

Non-planar (bent C–C double bonds are mentioned repeatedly in the literature but have only been identified by X-ray diffraction in a few instances. A bathochromic shift is assigned to the bending. For the so-called "thermochromic ethylenes" ($\Delta^{10,10'}$-bianthrone (**28**), $\Delta^{10,10'}$-bixanthene (**29**)) the coloured high-temperature form (B-form) is given a constitution in which the central double bond is bent to a considerable extent,[26] in contrast to the low-temperature form (A-form). However, a proof of this is still lacking. On the other hand, the bending of the central double bond of $\Delta^{9,9'}$-bifluorene (**25**) has been proved.[27] As we have lately shown,[28] **25** is able to withdraw hydrogen from fluorene (**26**) in the melt (250°). The addition of 2H to **25** and the removal of one H from each of two molecules of **26** yield two molecules of 9, ion 9'-bifluorene (**27**), *cf* e.g. (3). Unlike **26**, the product is stable up to 750° and does *not* give up any hydrogen.[32] The acceptor-compound **25** is stable also in the temperature range used.[32] We trace back these unalogous reactions to the bent double bond in **25**. The above-mentioned thermochromic ethylenes react in this respect like **25**.[29]

Pinck and Hilbert described the breaking of the central double bond in **25** by amines to give **26** and the corresponding 9-iminofluorenes.[30]

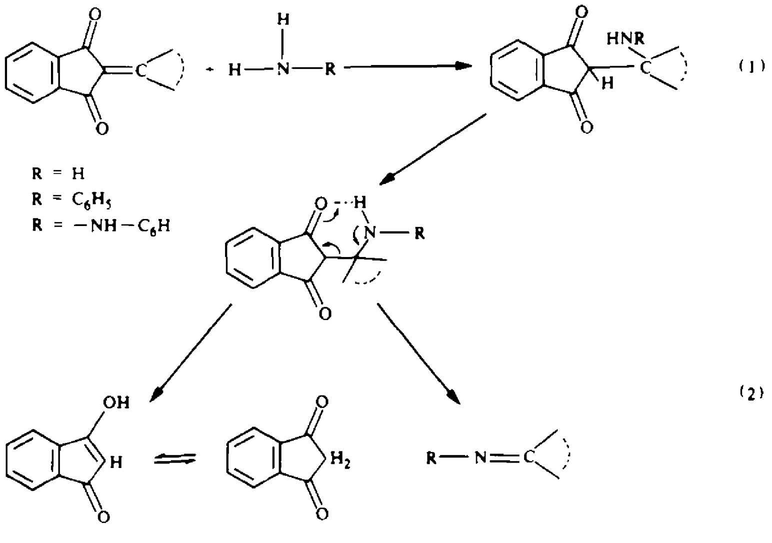
This situation is also indicated by the addition of phenylmagnesium bromide to the central double bond of **25**.[33]

The significantly higher reactivity of the compounds now investigated, **1a**, **1b** and **2**, when compared with the thermochromic ethylenes mentioned above agrees with the finding, that the two halves of the molecules are inclined at 47.2° to the two fold axis and that this is accompanied by strong polarisation. These facts have a strong mutual influence on the factors which determine the reactivity of the double bond.

Our investigations on C–C double bonds with extreme reactivity are continuing.

EXPERIMENTAL

Melting point apparatus (Dr. Tottoli of Büchi) m.ps not corrected. IR spectra: Perkin-Elmer PE 621. ^{1}H-NMR spectra: Varian HA 100 and Bruker HX 90 with tetramethylsilane as internal standard. Mass spectra: Varian MAT CH 74 at 70 eV.



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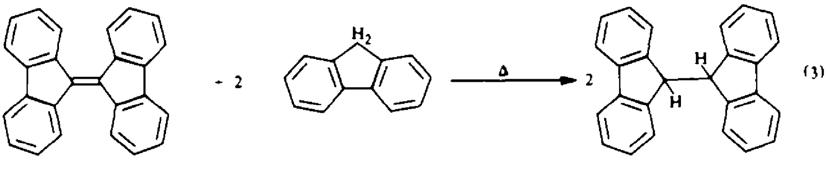
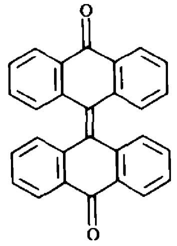


25 26 27



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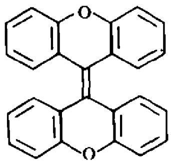

29

The syntheses of the starting compounds followed published methods: 2-(9-xanthylidene)indane-1,3-dione[3] (**1a**), 2-(9-thioxanthylidene(indane-1,3-dione (**1b**) and 2-(9-fluorenylidene)-indane-1,3-dione[4] (**2**).[5]

Experiments with 2 - (9 - xanthylidene)indane - 1, 3 - dione (**1a**)

Reaction with sulphur. 0.5 g of **1a** (1.5 mmol) and 0.5 g of flowers of sulphur were mixed intimately and the mixture heated at 270°C for 20 min out of contact with air. After the melt had cooled it was extracted with benzene, the benzene phase filtered, and the solvent distilled off under vacuum. Chromatography on a Kieselgel column with CCl_4 as eluant, followed by recrystallisation from petroleum ether (90–100°) yielded xanthione (**4**) as violet needles, m.p. 157–158°, which were identified from the mp when mixed with the authentic substance. Yield 110 mg (35%).

Reaction with zinc/glacial acetic acid. 1 g of **1a** (3.1 mmol) in glacial acetic acid (25 ml) was heated to 120°. Zinc dust (total: 1 g) was added to this mixture in successive small portions, during which its colour turned from violet to yellow. The mixture was filtered, the residue washed with benzene, the washing also filtered, and the combined filtrates concentrated to *ca.* 15 ml on the hot water-bath under vacuum. A yellowish product crystallized on cooling; this was filtered off with suction and recrystallised from ethanol: 350 mg bixanthyl (**5a**) (31%), m.p. 203–204°. Identified from a mixed specimen.

Reaction with thiophenol. 1 g of **1a** (3.1 mmol) plus 2 ml thiophenol was heated for 10 h at 100° in a sealed flask, during which the initially deep violet solution gradually became paler and ultimately was only faintly violet. The excess of thiophenol was distilled off under the vacuum from a water-jet pump and the residue fractionated on a Kieselgel column (eluant: CH_2Cl_2). Fraction 1 was obtained as a colourless substance, which after recrystallisation from ethanol was identified (mixed specimen) as diphenyl disulphide (m.p. 61°). Fraction 2 was a yellow substance, which crystallised from ethanol in thin yellow (almost colourless) needles and from its spectra (^{1}H-NMR, IR, MS) as 2 - (9 - xanthyl)indane - 1, 3 - dione (**6**), m.p. 143–145°. Yield 550 mg (55%). IR (KBr): 3030 (C–H, aromat.), 2915, 1850 (C–H, aliphat.), 1745, 1710 (C=O), 1598, 1575, 1487 (C=C, aromat) cm^{-1}; NMR ($CDCl_3$): $\delta = 3.33$ (d, J = 3 Hz, 1H, 9 - xanthyl - H), 5.01 (d, J = 3 Hz, 1H, H in position 2 of the indanedione system), 6.75–7.23 (m, 8H, arom. protons of the xanthyl residue), 7.53–7.87 (m, 4H, arom. protons of the indanedione system); MS: *m/e* 326 (8, M^+), 182 (62, xanthene$^+$), 181 (100, xanthyl$^+$), 163 (10, M^{2+}), 152 (26, $C_{12}H_8^+$). Calc for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32; Found: C, 80.92, H, 4.54%. The substance obtained as Fraction 3 was recrystallised from petroleum ether (90–100°) and identified (mixed specimen) as indane-1, 3-dione (**7**), m.p. 131°. Yield 60 mg (12%).

Reaction with sodium tetrahydroborate. 300 mg of $NaBH_4$ was added to 500 mg of **1a** (1.5 mmol) in 50 ml isopropyl alcohol and the mixture stirred overnight at room temperature. The solvent was then distilled off at room temperature under vacuum and the residue hydrolysed with dil HCl and the hydrolysate extracted with benzene. The benzene phase was separated, washed with H_2O until neutral, and then dried over Na_2SO_4. After the solvent had been distilled off at room temperature under vacuum, *ca* 500 mg crude product remained. This was washed with a little ethanol and recrystallised from the same solvent: yellowish needles, m.p. 146–147°. The product is identical with substance **6** obtained on treating **1a** with PhSH (mixed specimen).

Dehydration of **6**. 100 mg of **6** (0.3 mmol) was heated at 200° in an open test-tube in an oil-bath for 2 h (violet coloration). After cooling, 2 ml benzene was added and filtered off under suction. The violet crude product thus obtained was recrystallised from xylene. 2 - (9 - Xanthylidene)indane - 1, 3 - dione (**1a**) was obtained, m.p. 227–228° (identified from mixed m.p. with an authentic specimen). Yield 40 mg (41%).

Reaction with aniline. 1 g (3.1 mmol) of **1a** was added to 2.5 ml freshly distilled aniline and the mixture stirred overnight at room temperature. It was then diluted with benzene (100 ml) and extracted thrice with HCl (1 : 1) (15 ml each).

The combined HCl extract was filtered, neutralised with Na_2CO_3, made strongly alkaline with KOH pellets and the resulting mixture extracted repeatedly with benzene. The combined benzene extract was washed with H_2O until neutral, dried over Na_2SO_4, and the solvent removed at room temperature in a vacuum. A dark brown oil remained, from which yellow crystals separated on standing overnight. A little methanol was added, then removed under suction and the yellow product recrystallised from CH_3OH to give xanthone anil (**8a**), m.p. 133° (identified from mixed specimen). Yield 400 mg (48%).

The benzene solution remaining after the extraction with HCl (see above) was washed with H_2O until neutral and dried over Na_2So_4. The solvent was distilled off at room temperature in a vacuum, the deep blue residue dissolved in a mixture of 1 ml glacial acetic acid and 20 ml acetone, 4 ml H_2O added, and the filtrate allowed to stand overnight for the acetone to evaporate. Deep blue crystals were deposited which were filtered off with suction and recrystallised as described above: 110 mg (52%) Bindone anil (**9**) m.p. 216–218° (comparison of spectrum with that of authentic substance).

Reaction with malonodinitrile. 1 g (3.1 mmol) of **1a** and 0.7 g malonodinitrile were added to 2 ml dry pyridine and the mixture stirred overnight at room temperature. The deep blue mixture was diluted with $CHCl_3$ and filtered; the yellow residue left on the filter was washed with $CHCl_3$ and crystallised from ethanol to give 2 - (9 - dicyanomethyl - 9 - xanthyl)indane - 1, 3 - dione (**11a**) as yellow crystals, m.p. *ca* 215°. Yield 500 mg (42%). IR (KBr): $\nu = 3410$, 3325 (OH), 2205 (CN), 1715, 1670 (C=O), 1625 (C=C), 1603 cm^{-1} (arom). ^{1}H-NMR (DMSO-d_6): $\delta = 2.50$ (DMSO), 3.25 (H_2O), 6.9–7.6 (m, arom H + NC–CH–CN + OH). **11a** is an enol even in the solid state. MS: *m/e* 390 (32, M^+), 361 (100, M^+–H, –CO), 324 (38, M^+–malono-dinitrile), 323 (64, M^+–H–malono-dinitrile). Calc for $C_{25}H_{14}N_2O_3$: C, 76.92; H, 3.61; N, 7.18; Found: C, 76.96; H, 3.62; N, 7.28%.

The $CHCl_3$ filtrate was evaporated at room temperature in vacuum and the residue was chromatographed on Kieselgel with CH_2Cl_2. The greenish yellow substance thus obtained was recrystallised from benzene: 9-xanthylidenemalodinitrile, m.p. 239–241° (mixed specimen). Yield 60 mg (8%).

Reaction with phenylhydrazine. 600 mg (1.9 mmol) of **1a** and 400 mg (3.7 mmol) of phenylhydrazine in 30 ml dry methanol were stirred overnight at room temperature. The yellow precipitate was filtered off under suction and crystallised from ethanol to give 300 mg (38%) xanthone phenylhydrazone (**12**) as yellow crystals, m.p. 155° (mixed specimen).

Reaction with ammonia. A mixture of 300 mg (0.9 mmole) of **1a** and 25 ml conc. aqueous ammonia was stirred at room temperature for 2 days, during which a colourless substance was precipitated. This was filtered off with suction, dried, and crystallised from petroleum ether (90–100°): 80 mg xanthone imine (**13**) as colourless needles, m.p. 128–130° (mixed specimen).

Reaction with phenylmagnesium bromide. 80 ml dry benzene and 500 mg (1.5 mmol) of **1a** were added to the Grignard reagent from 300 mg (12.3 mmol) Mg, 1.9 g (12.3 mmol) bromobenzene, and 20 ml ether, the ether distilled off from the reaction micture, and the residue heated for 3 h under reflux. The adduct was hydrolysed with aqueous NH_4Cl, the organic phase separated, the aqueous phase extracted with ether, the combined extract washed with H_2O until neutral, and dried over Na_2So_4. After the solvent had been distilled off at room temperature in a vacuum a brown syrup was left. 10 ml methanol were added and the mixture stirred, whereupon a yellow precipitate formed. This was filtered off under suction and crystallised from ethanol: 90 mg (20%) 2 - (9 - phenyl - 9 - xanthyl) - 1 - phenylind - 3 - en - (2) -

one (**14a**) as yellow needles. m.p. *ca* 205°. IR (KBr): 3050. 3020 (C–H. arom.), 1713 (C=O). 1597. 1572. 1487 (C=C. arom.) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 6.5–7.5$ (m. arom. H). MS: *m/e* 462 (67. M^+), 385 (100. $M^+–C_6H_5$), 257 (26. 9-phenylxanthyl$^+$). Calc. for $C_{34}H_{22}O_2$: C. 88.29; H. 4.79; Found. C. 88.35; H. 4.68%.

Reaction with NN-*dimethylaniline.* 500 mg of **1a** and 5 ml of *NN*-dimethylaniline were heated in a closed flask at 150° for 2 h with stirring. The excess of the reagent was distilled off in a vacuum and the black residue purified by chromatography on Kieselgel (eluant: CH_2Cl_2). Fraction 1 was a colourless compound. m.p. 156–158° (from ethanol). which was identified (by a mixed m.p. with the authentic compound) as *p* - (9 - xanthyl) - *NN* - dimethylaniline (**15**). Yield 60 mg (13%).

Fraction 2 contained a red compound. which was crystallised from isopropyl alcohol. M.p. 198–201°. Yield 90 mg (22%). IR (KBr): $\nu = 1708$, 1662 (C=O). 1610. 1595 (C=C. arom.), 1555. 1515. 1440. 1370. (tert. OH). 1345. 1325. 1188 cm^{-1} (tert. OH). NMR (CF_3COOH): $\delta = 3.60$ (s. 12 H. N–CH_3). 7.80–8.50 (m. 14 H, arom. H), 8.60–8.80 (m. 4H, arom. H): MS: *m/e* 277 (100. $C_{18}H_{15}NO_2^+$. high-resolution: Calc: 277.1103; Found 277.1103). 276 (74. 277–H). 260 (17. 277–OH). 248 (7. 276–CO). 233 (31. 277–N(CH_3)$_2$). 220 (9. 248–CO). 205 (25. 233–CO). 189 (12). 178 (27). 177 (25. 205–CO). 176 (48. 220–N(CH_3)$_2$). 165 (16). 151 (22. $C_{14}H_9^+$). Calc for $C_{34}H_{30}N_2O_4$: C. 76.96; H. 5.70; N. 5.28: Found: C. 77.18; H. 5.54; N. 4.90%.

Experiments with 2 - (9 - thioxanthylidene) indane - 1, 3 - dione (**1b**)

Reaction with zinc/glacial acetic acid. 1 g (2.9 mmol) of **1b** in 25 ml glacial acetic acid were reacted at 120° with 1 g zinc as described for bixanthyl (see above) and the mixture was treated similarly. After the combined filtrate had been concentrated on a hot water-bath a yellow substance crystallised on cooling. This was recrystallised from xylene to give 90 mg (16%) bithioxanthyl (**5b**). m.p. > 300°. Identified by spectra-comparison with the authentic substance.

Reaction with aniline. 1 g (2.9 mmol) **1b** and 3 ml of freshly distilled aniline were heated in a closed vessel at 100° for 1 h. After cooling, the reaction mixture was treated as for the conversion of **1a** with aniline. A black oil was left, which crystallised on standing overnight. It was mixed with a little methanol and the mixture was filtered with suction to give a greenish substance. This was recrystallised from ethanol as yellow needles, m.p. 152° (mixed specimen). Yield 150 mg (17%) thioxanthone anil (**8b**).

Reaction with malonodinitrile. 500 mg (1.45 mmol) **1b**. 500 mg malonodinitrile and 1 ml pyridine were stirred overnight at room temperature. The mixture was diluted with benzene, filtered and the residue washed with benzene. 450 mg of a yellowish product were obtained; this was recrystallised twice from ethanol to give brownish yellow crystals. m.p. 255° (decomp.). Yield: 300 mg (51%) of 2 - (9 - dicyanomethyl - 9 - thioxanthyl)indane - 1, 3 - dione (**11b**). IR(KBr): = 3540, 3450, 3340 (OH). 2218 (C–N), 1717. 1673 (C=O), 1627. 1607, 1590 (C=C. arom.) cm^{-1}. ^{1}H-NMR: $\delta =$ 1.09 (t, 3H, J = 7 Hz. CH_3 ethanol), 3.53 (q, J = 7 Hz) and 3.47 (q, J = 7 Hz, 2H together. CH_2 ethanol). 4.19 (t. 1H. J = 5 Hz. OH), 7.0–7.6 (m, 14H, arom. H + NC–CH–CN + OH). MS: *m/e* = 406 (34, M^+), 377 (24, M^+–H–CO). 362 (22. M^+–44), 345 (22), 340 (74, M^+-mallonodinitrile). 339 (100. M^+–H-malonodinitrile). 66 (88. malonodinitrile$^+$). **11b** crystallises with a molecule of alcohol and is an enol Calc for $C_{25}H_{14}N_2O_2S \cdot C_2H_5OH$: C, 71.66: H, 4.45: N, 6.19: S, 7.09; Found: C, 71.53; H, 4.63: N, 6.15: S. 7.08%.

Reaction with phenylmagnesium bromide. 525 mg (1.5 mmol) of **1b** were treated with the Grignard reagent of 300 mg of Mg and 1.9 g bromobenzene in 20 ml ether. The yellow substance deposited after the addition of methanol was chromatographed on Kieselgel with CH_2Cl_2, and the yellow zone eluted first was collected. After this fraction had been recrystallised from ethanol. 150 mg (21%) of 2 - (9 - phenyl - 9 - thioxanthyl) - 1 - phenylind - 3 - en - (2) - one (**14b**) was obtained as yellow crystals, m.p. 255–257°. IR (KBr): 3053. 3020 (C–H, arom.). 1713 (C=O). 1608. 1593. 1560 (C=C. arom.) cm^{-1}. ^{1}H-NMR ($CDCl_3$): = 6.5–7.5 (m. arom. H). MS: *m/e* 478 (35. M^+). 401 (19. M^+–C_6H_5), 273 (100, 9 - phenyl - 9 - thioxanthyl$^+$). 239 (12). 77 (12, phenyl$^+$). Calc for $C_{34}H_{22}OS$: C. 85.32: H. 4.63: S. 6.70: Found: C. 85.41; H. 4.69; S. 6.74%.

Reactions with 2 - (9 - fluorenylidene(indane - 1, 3 - dione (**2**)

Reaction with zinc glacial acetic acid. Zinc dust (500 mg) was added in small successive portions to 300 mg (0.97 mmol) of **2** in 10 ml glacial acetic acid with constant stirring during which the red solution was decolorised. The mixture was filtered. the residue extracted several times with benzene. and the combined filtrate extracted thrice with H_2O. The organic phase was separated and dried over Na_2SO_4. After distilling off the solvent at room temperature in a vacuum 310 mg of a colourless solid remained. A few ml of ether were added and the mixture filtered. Recrystallisation from petroleum ether (90–100°) gave 240 mg (79%) of 1-hydroxy 2 - (9 - fluorenyl)indan - 3 - one (**17**). m.p. 180–181°. ^{1}H-NMR (DMSO-d_6): = 3.33 (dd. 1H. J = 2.8 Hz and 7 Hz. H–C–O). 4.10 (d. 1H. J = 2.8 Hz. C–O–H). 5.09 (dd. 1H. J = 7 Hz and 5 Hz. H(2) Indan.). 5.58 (d. 1H. J = 5 Hz. 9 - Fluorenyl - H). 6.3–7.4 (m. 12H, arom. H). IR (KBr): 3620–3160 (O–H). 3100–3000 (arom. C–H). 2940–2840 (aliph. C–H). 1750–1670 (C=O), 1620–1560 cm^{-1} (C=C): MS: *m/e* 312 (28. M^+). 295 (25. M^+–OH). 294 (100. M^+–H_2O). 293 (38. M^+–H–H_2O). 265 (52. 293–CO). 165 (82, 9-fluorenyl$^+$): Calc for $C_{22}H_{16}O_2$: C. 84.59: H. 5.16: Found: C. 84.74; H. 5.31%.

Reaction with aniline. 1 g (3.2 mmol) **2** and 10 ml freshly distilled aniline were heated at 110° for 2 h. After distilling off the solvent in a vacuum the residue was chromatographed on Kieselgel with CH_2Cl_2, and the yellow zone eluted first was collected. The red oil remaining after distilling off the solvent gave 400 mg (49%) fluorenone anil, (**18**) m.p. 87–88° (mixed m.p. with an authentic specimen).

Reaction with malonodinitrile. A mixture of 200 mg (0.65 mmol) **2**. 200 mg malondinitrile. 1 ml pyridine. and 3 ml benzene was allowed to stand overnight at room temperature. The deep blue solution was diluted with 20 ml benzene. then extracted thrice with 10 ml H_2O and the organic phase dried over Na_2SO_4. The solvent was distilled off at room temperature in a vacuum and the residue purified by chromatography on a Kieselguhr column with CH_2Cl_2 as eluant. The orange-red fraction eluted initially was collected. 90 mg of 9 - fluorenylidenemalonodinitrile (**19**) was obtained as bright red crystals. m.p. 229–231° (identification by spectrum comparison with the authentic substance).

Reaction with ammonia. 500 mg (1.6 mmol) of **2** with 30 ml conc. aqueous ammonia were stirred overnight at room temperature. The precipitate which had formed was filtered off under suction and dried. The product (270 mg) was a pale yellow substance which crystallised from petroleum ether (90–100°) as yellowish. almost colourless, needles. m.p. 123–124° and from mixed specimens with the authentic substance was identified as 9-iminofluorene (**20**). Yield 210 mg (73%).

Reaction with phenylmagnesium bromide. Benzene (80 ml) and 476 mg (1.5 mmol) of **2** were added to the Grignard reagent from 300 mg (12.3 mmol) Mg. 1.92 g (12.2 mmol) bromobenzene, and 20 ml ether. The ether was distilled off from the mixture. which was then refluxed for 3 h. The mixture was hydrolysed with aqueous NH_4Cl solution. the organic phase separated. the aqueous phase extracted twice with ether and the combined extract washed with H_2O until neutral. The organic phase was separated and dried over Na_2SO_4. After the solvent had been distilled off in a vacuum a reddish yellow syrup remained. Methanol was added and the mixture stirred at room temperature, whereupon a colourless substance was precipitated. This was filtered off with suction and recrystallised from ethanol: 190 mg (33%, referred to **2**) 2 - (9 - phenyl - 9 - fluorenyl)indane - 1. 3 - dione (**21**), m.p. 248–250°. ^{1}H-NMR: (DMSO-d_6): $\delta = 5.13$ (s, 1H. H–C), 7.0–7.4 (m, 11H, arom, H), 7.6–7.9 (m, 6H. arom. H). IR (KBr): 3100–3000 (arom. C–H). 2920–2860 (aliph. C–H), 1780–1740 (C=O), 1720–1670 (C=O), 1610–1580 cm^{-1} (C=C). MS: *m/e* 386 (20. M^+), 241 (100, 9-phenylfluorenyl$^+$). 240 (32. 241–H). 239 (26. 240–H). 104 (14). 76 (14). Calc for $C_{28}H_{18}O_2$ (386.45): C. 87.03; H, 4.69; Found: C. 86.88; H. 4.66%.

Reaction with thiophenol. 500 mg (1.6 mmol) of **2** and 5 ml of thiophenol were heated in a closed flask at 150° for 5 h. After the thiophenol had been distilled off in vacuum the residue was chromatographed on Kieselguhr with CH_2Cl_2. Diphenyl disulphide was obtained as Fraction 1. The second fraction was a reddish oil, which crystallised on standing. Recrystallisation from ethanol gave 370 mg (74.6%) 2 - (9 - fluorenyl)indane - 1, 3 - dione (**22**) as slightly yellowish needles. ^{1}H-NMR: $\delta = 3.83$ (d, H, J = 3 Hz, $>$C–H), 4.77 (d, H, J = 3 Hz, C–H), 7.00–7.40 (m, 6H, arom.), 7.60–7.95 (m, 6H, arom.); IR(KBr): 1740, 1710 (C=O), 1600, 1585 (C=C, arom.) cm^{-1}; MS: *m/e* 310 (52, M^+), 281 (30, M^+–H, –CO), 265 (12), 252 (16, $C_{20}H_{12}^+$), 178 (18), 177 (16), 165 (100, 9-fluorenyl$^+$), 104 (44, C_6H_4–CO^+), 76 (32, $C_6H_4^+$), 58 (14, $C_3H_6O^+$): Calc for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55; Found: C, 85.01; H, 4.49%.

Reaction with NN-*dimethylaniline*. 500 mg of **2** and 5 ml of *NN*-dimethylaniline were heated in a closed flask at 150° for 4 h with stirring. The excess of reagent was distilled off in a vacuum and the residue purified by chromatography on Kieselgel (eluent: dichloromethane). After evaporation, fraction 1 gave a brown oil from which colorless crystals deposited, recrystallised from ethanol to give 60 mg (13%) *p* - (9 - fluorenyl) - *NN* - dimethylaniline (**23**), m.p. 156–157° (mixed specimen with the authentic compound). Evaporation of fraction 2 gave a residue which recrystallised from isopropyl alcohol, gave 130 mg (31%) **16** (mixed m.p. with an authentic specimen).

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