Dyes and Pigments **12** (1990) 187–195

The Syntheses of some Novel 2-Substituted Phenylazo-1,3-indandiones

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(Received 29 November 1988; accepted 10 January 1989)

ABSTRACT

The synthesis of various novel 2-substituted phenylazo-1,3-indandiones (which are potential dyestuffs) by the Japp–Kligemann coupling reaction is reported. Ultraviolet–visible absorption spectra of the compounds were examined in various solvents and the compounds in solution exhibited azo–hydrazone tautomerism. The effects of various substituents on these equilibria are discussed.

INTRODUCTION

The coupling reactions of aromatic diazonium salts with compounds having active methine hydrogen, such as 2-substituted-1,3-diketones and β-ketoesters, are known as Japp–Kligemann reactions and the products are aliphatic carbon–arylazo compounds.[1–3] For many years, it was believed that phenylhydrazones were the only stable products of Japp–Kligemann reactions in which azo compounds were thought to be the intermediates, and their rate of conversion has been observed to be increased by bases.[4] Various azo compounds have been obtained as stable substances in these coupling reactions.[5,6]

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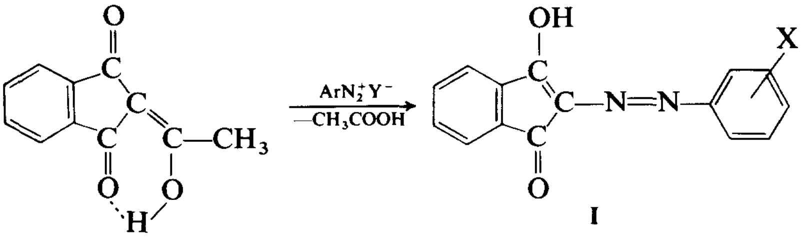
Dyes and Pigments 0143-7208/90/$03·50 © 1990 Elsevier Science Publishers Ltd, England. Printed in Great Britain

In this present work, the isolation and characterization of the azo compounds obtained through a series of Japp–Kligemann reactions from 2-acetyl-1,3-indandione (at carbon-2) and the diazonium salts of various *o*-, *m*- and *p*-substituted anilines have been achieved.



I

X = H, *o*-Cl, *m*-Cl, *p*-Cl
o-Br, *m*-Br, *p*-Br
o-COOH, *m*-COOH, *p*-COOH
o-NO_2, *m*-NO_2, *p*-NO_2
o-CH_3, *m*-CH_3, *p*-CH_3
o-OCH_2CH_3, *p*-OCH_2CH_3

Since the products obtained (**I**) are potential dyestuffs, the effects of substituents on the visible absorption spectra and the tautomerism of the 2-substituted phenylazo-1,3-indandiones were considered.

EXPERIMENTAL

The synthesis of 2-acetyl-1,3-indandione was carried out as described in the literature[7] (m.p. 110–111°C). All the substituted aromatic amines used in the present work were diazotized by the usual methods.[8,9]

The coupling reactions of 2-acetyl-1,3-indandione with various diazonium salts were carried out as described by Yao & Resnick.[5] All the chemicals were purified prior to use in syntheses.

General procedure

Since all the compounds were prepared in a similar manner,[5] only the preparation of some representative substituted compounds will be given in detail.

Preparation of 2-phenylazo-1,3-indandione

2-Acetyl-1,3-indandione (0·94 g, 0·005 mol) was dissolved in 4·5 ml pyridine and 10 ml water, and the solution was cooled to 0–5°C in an ice bath. A diazonium solution, prepared by dissolving 0·465 g (0·005 mol) of aniline in

1·25 ml conc. HCl and 2·25 ml water, cooling to 0°C, and adding a saturated aqueous solution of 0·38 g sodium nitrite, was then added slowly with stirring. During the addition of the diazonium salt, the solution turned orange and an orange solid gradually precipitated. The mixture was stirred for 1 h in an ice bath and then filtered and the residue washed several times with ice–water. Recrystallization from ethanol gave orange needle-like crystals; yield 62%, m.p. 192–194°C.

Preparation of 2-(2-chlorophenylazo)-1,3-indandione
o-Chloroaniline (0·637 g, 0·005 mol) was diazotized and coupled with 0·94 g (0·005 mol) 2-acetyl-1,3-indandione in the above manner. Recrystallization from ethanol yielded orange needles, m.p. 233–236°C.

Preparation of 2-(4-bromophenylazo)-1,3-indandione
p-Bromoaniline (0·86 g, 0·005 mol) was diazotized and coupled with 2-acetyl-1,3-indandione. Recystallization from benzene yielded orange crystals, m.p. 247–251°C.

Preparation of 2-(4-nitrophenylazo)-1,3-indandione
p-Nitroaniline (0·69 g, 0·005 mol) was diazotized and coupled as above. Recrystallization from acetic acid yielded orange needles, m.p. 318–321°C.

Preparation of 2-(4-methylphenylazo)-1,3-indandione
A solution of the diazonium chloride from 0·535 g (0·005 mol) of *p*-toluidine in 1·25 ml conc. HCl and 2·25 ml water was added at 0°C to one of 0·94 g of 2-acetyl-1,3-indandione in 4·5 ml pyridine and 10 ml water. The mixture was kept overnight at 0°C and the orange solid was filtered off and crystallized from ethanol, m.p. 209–211°C.

The elucidation of structures of the compounds synthesized were carried out using a Perkin–Elmer 377 infrared spectrometer, a Varian EM 360 ^{1}H-NMR spectrometer and a Kratos MS-30 mass spectrometer. The UV–Vis absorption spectra were recorded on a Perkin–Elmer–Hitachi 220 UV–Vis spectrometer.

RESULTS AND DISCUSSION

Table 1 shows some experimental and spectral data for the products obtained from the coupling reactions of 2-acetyl-1,3-indandione with various substituted phenyldiazonium salts. All the spectral evidence indicates that, in the above coupling reactions, the azo compounds initially

TABLE 1

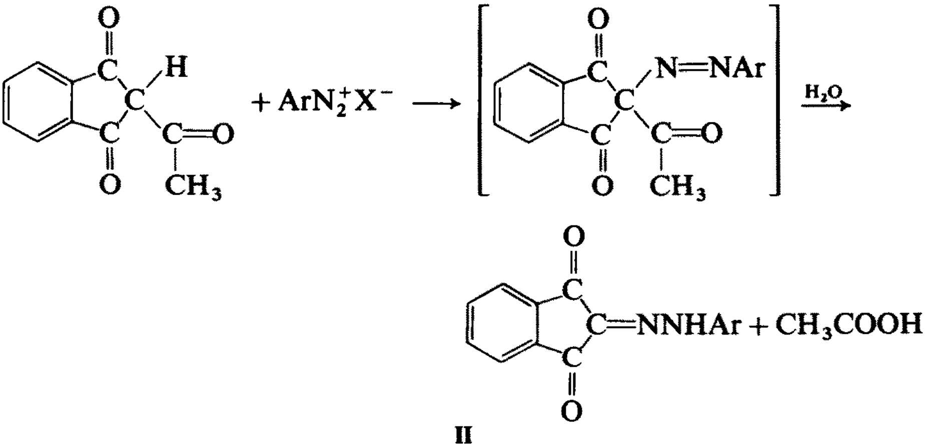
Experimental and Spectral Data of 2-Substituted Phenylazo-1,3-indandiones

No.	*X (substituent)*	*Absorption spectrum*		*Mass spectrum*		*H-NMR spectrum*			*M.p. (°C)*	*Crystallization solvent*
		Azo–enol[a] $\nu OH(cm^{-1})$	*Hydrazone*[a] $\nu OH(cm^{-1})$	M^+ *(m/e)*	*Relative intensity (%)*	*Aromatic H* δ *(ppm)*[b]	*Solvent*	CH_3 δ *(ppm)*[b]		
1	H	3 100–2 950	1 570	250	99·55	7·20–7·70 (9H) m	CDCl$_3$	—	192–194	Ethanol (95·5%)
2	*o*-Cl	3 200–2 800	1 570	284	18·36	7·30–7·81 (8H) m	CDCl$_3$	—	233–236	Ethanol (95·5%)
3	*m*-Cl	3 200–3 000	1 571	284	62·10	7·18–7·75 (8H) m	CDCl$_3$	—	228–230	Ethanol
4	*p*-Cl	3 200–2 900	1 572	284	45·93	7·25–7·81 (8H) m	CDCl$_3$	—	244–246	Ethanol
5	*o*-Br	3 200–2 900	1 570	327	29·33	7·15–7·84 (8H) m	TFA	—	246–249	Ethanol
6	*m*-Br	3 200–2 900	1 555	327·99	44·99	7·22–7·82 (8H) m	TFA	—	238–240	Ethanol
7	*p*-Br	3 200–2 900	1 570	327	34·99	7·25–7·92 (8H) m	TFA	—	247–251	Benzene
8	*o*-COOH	3 400–2 700	1 575	294	64·10	7·82–8·25 (8H) m	DMSO	—	284–287	Ethanol
9	*m*-COOH	3 400–2 700	1 570	294	72·33	7·82–8·21 (8H) m	DMSO	—	301–305	Acetic acid (glacial)
10	*p*-COOH	3 200–2 300	1 570	294	64·42	7·86–8·50 (8H) m	DMSO	—	347(dec)	Acetic acid
11	*o*-NO$_2$	3 200–2 950	1 560	295	36·99	5·02–6·50 (8H) m	TFA	—	293–296	Acetic acid
12	*m*-NO$_2$	3 150–2 900	1 570	295	70·01	7·21–7·98 (8H) m	TFA	—	302–305	Acetic acid
13	*p*-NO$_2$	3 150–2 900	1 570	295	88·41	7·25–7·98 (8H) m	TFA	—	318–321	Acetic acid
14	*o*-CH$_3$	3 200–2 900	1 570	264	100·00	7·10–7·65 (8H) m	CDCl$_3$	2·5 (3H) s	191–194	Ethanol
15	*m*-CH$_3$	3 200–3 000	1 590	264	100·00	7·61–8·40 (8H) m	CDCl$_3$	2·55 (3H) s	193–196	Ethanol
16	*p*-CH$_3$	3 100–2 800	1 575	264	88·85	7·22–7·72 (8H) m	CDCl$_3$	2·3 (3H) s	209–211	Ethanol
17	*p*-OEt	3 100–2 900	1 575	—	—	6·80–8·01 (8H) m	CDCl$_3$	1·35 (3H) s 4·01 (2H) d 13·5 (N—H)	188–190	Ethanol
18	*o*-OEt	3 200–3 000	1 590	—	—	6·8–8·21 (8H) m	CDCl$_3$	1·57 (3H) s 4·21 (2H) d 13·7 (N—H)	158–160	Ethanol

[a] In KBr.

[b] From TMS.

Abbreviations: m, multiplet; s, singlet; d, doublet.



II

formed (**II**) readily lose the acetyl group in aqueous media instead of opening the five-membered ring.

Figure 1 shows the ^{1}H-NMR spectrum of the *m*-CH$_3$-substituted compound.

It has been reported that in order to obtain an azo compound, C-2 in the indandione moiety should have a substituent such as methyl, carboethoxy or benzoyl, all of which undergo elimination less readily compared with the acetyl group.[10–13]

The absorption spectra of compounds **1–18** recorded in chloroform generally exhibit two maxima. Depending on the substituents, they lie in the

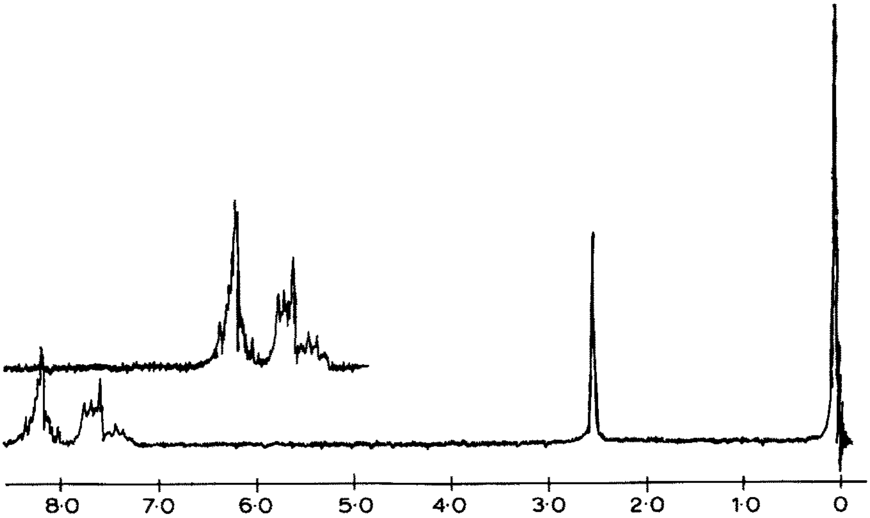


Fig. 1. The ^{1}H-NMR spectrum of 2-(3-methylphenylazo)-1,3-indandione in CDCl$_3$.

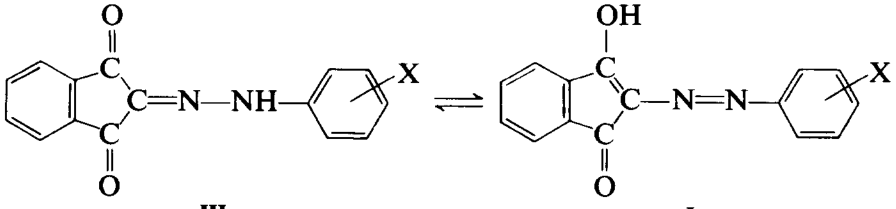
TABLE 2
The Visible Absorption Maxima of 2-Substituted Phenylazo-1,3-indandiones

No.	*X*	λ_{max}[a] *(nm)*	
		Azo	*Hydrazone*
1	H	404	432
2	*o*-Cl	404	434
3	*m*-Cl	400	426
4	*p*-Cl	404	436
5	*o*-Br	404	435
6	*m*-Br	403	431
7	*p*-Br	406	437
8	*o*-COOH	407	431
9	*m*-COOH	399	428
10	*p*-COOH	405	436
11	*o*-NO_2	413	425
12	*m*-NO_2	396	S[b]
13	*p*-NO_2	408	S[b]
14	*o*-CH_3	S[b]	441
15	*m*-CH_3	406	436
16	*p*-CH_3	402	438
17	*o*-OCH_2CH_3	S[b]	449
18	*p*-OCH_2CH_3	S[b]	454

[a] In $CHCl_3$.
[b] S, shoulder.

ranges 396–413 nm and 425–454 nm (Table 2). Figure 2 shows the absorption spectra of representative compounds of the series X = H, *p*-NO_2, *m*-NO_2 and *o*-NO_2.

Although, for *o*-CH_3, *p*-NO_2, *m*-NO_2, *o*-OEt and *p*-OEt-substituted compounds there exists essentially a single maximum, the peaks are flanked by shoulders. It is known that two maxima are observed for compounds exhibiting azo–hydrazone tautomerism.[14-17] Of these peaks, the one at the shorter wavelength is assigned to the azo tautomer. It has been reported that the hydrazone form is more stable than the azo tautomer.[16-19]



III **I**

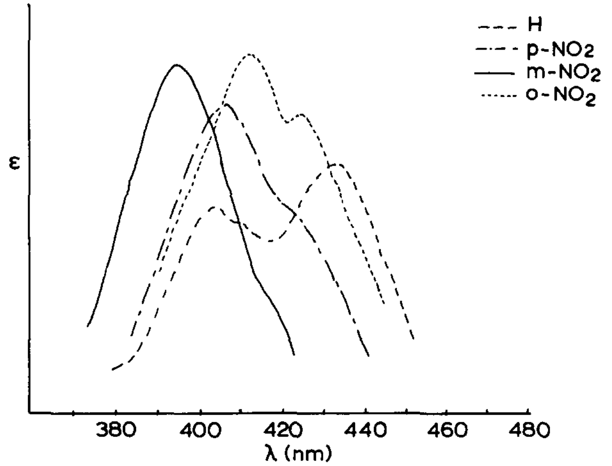


Fig. 2. The visible absorption spectra of 2-substituted phenylazo-1,3-indandiones.

Infrared spectra (in KBr) of compounds **1–18** have C=N and N=N stretching bands at about 1570 cm^{-1} and 1450 cm^{-1} respectively. Moreover, an enol —OH band in the region of 2700–3400 cm^{-1} indicates the presence of the azo tautomer.

^{1}H-NMR spectra supply further evidence for the existence of tautomeric equilibria. The spectrum of 2-phenylazo-1,3-indandione (X = H) recorded in $CDCl_3$ exhibits an N—H (broad) peak at 13–14 ppm (from TMS) and an azo–enol O—H peak at 1·85 ppm.

Furthermore, the visible absorption patterns of the compounds are changed with solvents. Since the tautomeric equilibria strongly depend on the nature of the media[16,20] the behaviour of 2-phenylazo-1,3-indandione (X = H) in various solvents was studied. The spectrum of 2-phenylazo-1,3-indandione in chloroform shows an absorption region consisting of two coalescent bands at about 404 and 432 nm, whereas in toluene and methanol the intensity of the former band is increased and that of the latter reduced (Fig. 3). Thus, the absorption curves almost pass through an isosbestic point, characteristic of equilibria.

As is seen from Table 2, in the azo tautomers the presence of *p*-substituted electron acceptor groups in the diazo residue results in a bathochromic shift, whilst electron donor substituents give a hypsochromic shift. On the other hand, in the azo-hydrazone tautomers, electron acceptor substituents cause a slight bathochromic effect whilst electron donor substituents exert a strong bathochromic effect.

In the *m*-substituted compounds, electron acceptor substituents cause hypsochromic shifts in both of the tautomers. However, this effect is much more pronounced in the azo tautomers.

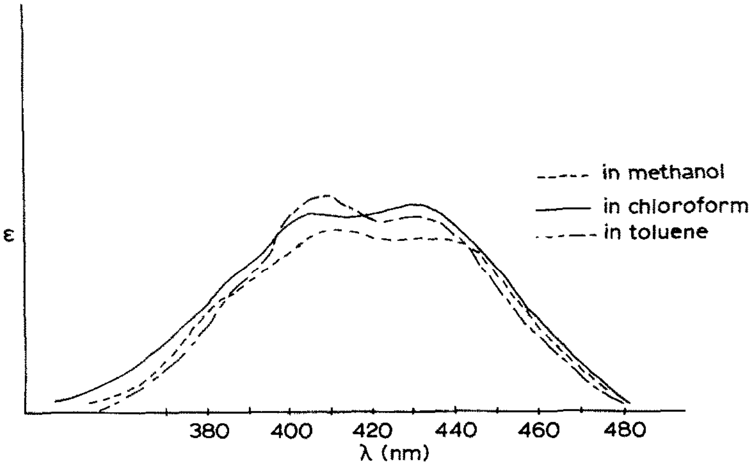


Fig. 3. The visible absorption spectra of 2-phenylazo-1,3-indandiones.

The UV–vis spectra of compounds **1–18** suggest that the tautomeric equilibrium is considerably affected by various substituents in the diazo residue. The intensity of the bands varies in accordance with the character of the substituent present in the diazonium residue. The presence of electron-withdrawing groups increases the intensity of the azo band at the expense of the azo-hydrazone band. The *p*-OEt, *o*-OEt substituted derivatives in chloroform all exist mainly in the hydrazone form. Comparison of the spectra in $CHCl_3$ confirms that the concentration of the azo-hydrazone tautomer increases in the order m-NO_2 < p-NO_2 < m-Cl < o-NO_2 < o-Cl < p-Cl ~ m-CH_3 < o-CH_3 < p-CH_3 ~ H < p-OEt < o-OEt.

ACKNOWLEDGEMENT

The authors thank Dr Alan Marshall and C. R. Weisenberger of Johnston Laboratory, Ohio State University, for the mass spectral analyses.

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