

THE SYNTHESSES OF SOME NOVEL 2-METHYL-2-SUBSTITUTED-PHENYLAZO-1, 3-INDANDIONES

NERMİN ERTAN, TAHSİN UYAR

Department of Chemistry, Gazi University, Ankara, Turkey.

(Received May 27, 1994; Accepted June 29, 1994)

ABSTRACT

The preparation of a series of 2-Methyl-2-substituted phenylazo-1, 3- indandiones by coupling of 2-Methyl-1, 3-indandione with substituted anilines is reported. The effects of various substituents on the absorption spectra are discussed.

INTRODUCTION

The coupling reactions of aromatic diazonium salts with active methinyl compounds such as substituted β -diketones and β -keto esters are known as Japp-Klingemann reactions and the products are aliphatic carbon arylazo compounds (1, 2). The products of the Japp-Klingemann reaction have been employed in the syntheses of amino acids and indoles. When the Japp-Klingemann reaction is applied to the cyclic β -keto esters and diketones, the ring is opened in the second stage of the process (3, 4). In contrast to β -keto esters, 1, 3-diketones have not been extensively employed in the Japp-Klingemann reaction. Recently, we have reported (5) that the coupling products of 2-Acetyl-1, 3-indandione with diazotizing anilines are 2-substitutedphenylazo-1, 3-indandiones and readily lose the acetyl group in aqueous media instead of opening the five-membered ring. It is the purpose of the present work to establish whether the five-membered ring is opened in 2-alkyl substituted indandiones. 2-Methyl-1, 3-indandione was chosen as coupling component. A series of some novel aliphatic azo compounds were prepared by coupling 2-Methyl-1, 3-indandione with substituted anilines and the substituent effects on the absorption spectra of compounds were investigated.

EXPERIMENTAL

2-Methyl-1, 3-indandione was prepared by the method given in the literature (6). The substituted anilines were of chemical grade and they were diazotized by the usual methods.

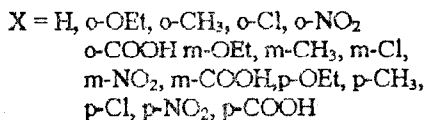
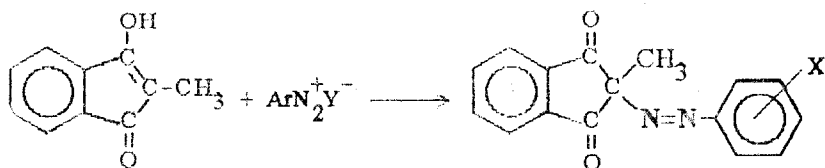


Figure 1. 2-Methyl-2-substitutedphenylazo-1, 3-indandiones.

IR spectra were determined in KBr with a Perkin-Elmir 1330 spectrophotometer. ¹HNMR spectra were recorded with Varian EM 60 in CDCl₃. The ultraviolet spectra were measured on a Bousch and Lomb Spectronic 2000 spectrophotometer. Microanalyses were carried out at Hewlett Packard Microanalysis Instrument.

General Procedure

Since all the compounds were prepared in a similar manner, only the preparation of the unsubstituted compounds will be given in detail.

Preparation of 2-Methyl-2phenylazo-1,3-indandione

2-Methyl-1,3-indandione (0,80 g, 0,005 mole) was dissolved in a solution of potassium hydroxide (0,28 g, 0,005 mole) in water (2 ml). The resulting solution was cooled in an ice-salt bath to 0-5° and was treated with a cold solution of the benzendiazonium chloride prepared by diazotizing aniline (0,005 mole) in 1,25 ml conc. hydrochloric acid and 2 ml water with sodium nitrite (0,389 g, 0,005 mole). The solution of diazonium salt was buffered with sodium acetate (0,41 g, 0,005 mole) and was slowly added to the vigorously stirred solution. After the addition was completed, the mixture was stirred for further 30 minutes. The precipitated yellow solid was collected and washed thoroughly with cold water and dried. Crystallization from ethanol gave yellow needles. The yield is 95 %, m.p. 96° (dec).

The compounds prepared, their m. ps and spectral data are listed in Table 1.

Table 1. Spectral Data of 2-Methyl-2-Substitutedphenylazo-1, 3-Indandiones.

Compounds No.	Substituent	IR, cm^{-1} (in KBr)		^1H NMR, ppm (in CDCl_2 or DMSO)	$\lambda_{\text{m}}^{\text{ab}}$ (nm) (in CHCl_3)
		$\nu_{\text{N}} = \text{N}$	$\nu_{\text{C}} = \text{O}$		
1	H	1950	1705, 1745	1.6 (3H, s _a), 7.1 (4H, m ^b), 7.7 (4H, m)	237, 253, 285
2	o-OEt	1595	1710, 1750	1.4 (3H, t _a), 1.8 (3H, 2s), 4.1 (2H, q ^d), 7.0-8.1 (8H, m)	238, 250, 325
3	o-CH ₃	1595	1705, 1750	1.9 (3H, s), 2.5 (3H, s), 7.4 (4H, m), 8.2 (4H, m)	235, 253, 285
5	o-COOH	1590	1650, 1745	1.8 (3H, s), 7.6-3 (8H, m)	382, 255-
6	o-NO ₂	1590	1705, 1745	1.7 (3H, s), 7.6-8.6 (8H, m)	237, 253, 295
7	m-CH ₃	1592	1705, 1745	1.8 (3H, s), 2.30 (3H, s), 7.5 (4H, m), 8.2 (4H, m)	240, 250, 286
8	m-Cl	1580	1710, 1750	1.7 (3H, s), 7.4 (4H, m), 8.0 (4H, m)	242, 258, 234
9	m-COOH	1590	1690-1710	1.8 (3H, s), 7.7-8.4 (8H, m)	237, 256, 280
10	m-NO ₂	1590	1705, 1745	1.7 (3H, s), 7.7-8.7 (8H, m)	237, 253-
11	p-OEt	1595	1715, 1750	1.4 (3H, t), 1.8 (3H, s), 4.0 (2H, q), 6.9-8.1 (8H, m)	238, 249, 323
12	p-CH ₃	1595	1710, 1750	1.8 (3H, s), 2.4 (3H, s), 7.1-8.2 (8H, m)	237, 252, 296
13	p-Cl	1595	1710, 1720	1.7 (3H, s), 7.6 (4H, m), 8.1 (4H, m)	237, 254, 293
14	p-COOH	1580	1650-1750	1.9 (3H, s), 7.7-8.3 (8H, m)	238, 257, 285
15	p-NO ₂	1590	1710, 1750	1.7 (3H, s), 7.7-8.6 (8H, m)	239, 259, 289

a Singlet, b multiplet, c triplet, d quartet.

RESULTS AND DISCUSSION

The infrared, ^1H NMR, ultraviolet spectral characteristics and elemental analyses of 2-Methyl-2-substitutedphenylazo-1,3-indandiones were given in Table 1 and Table 2. Figure 2 shows the ^1H NMR, spectrum of the p-OEt substituted compound.

Table 2. Elemental Analyses of 2-Methyl-2-Substitutedphenylazo-1, 3-Indandiones.

Compound No.	Substituent	Molecular formula	C, %		H, %		N, %		m.p. (°C)
			Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	H	$\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2$	72.73	73.29	4.55	5.04	10.60	10.28	96 dec.
2	o-OEt	$\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_2$	70.13	69.05	5.19	5.11	9.09	9.38	97-98
3	o- CH_3	$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$	73.38	73.19	5.03	5.16	10.07	9.76	116-118
4	o-Cl	$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$	64.32	63.97	3.69	3.83	9.39	8.94	120-122
5	o-COOH	$\text{C}_{17}\text{H}_{12}\text{O}_4\text{N}_2$	66.23	66.61	3.89	4.03	9.09	8.86	168-170
6	o- NO_2	$\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}_3$	62.13	61.89	3.96	3.96	13.59	13.22	143-144
7	m- CH_3	$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2$	73.38	74.01	5.03	5.06	10.07	9.87	133-134
8	m-Cl	$\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_2\text{Cl}$	64.32	64.42	3.69	4.01	9.39	9.03	138-140
9	m-COOH	$\text{C}_{17}\text{H}_{12}\text{O}_4\text{N}_2$	66.23	65.98	3.89	4.11	9.09	8.89	169-170
10	m- NO_2	$\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}_3$	62.13	62.57	3.56	3.91	13.59	13.15	158-160
11	p-OEt	$\text{C}_{16}\text{H}_{16}\text{O}_3\text{N}_2$	70.13	69.95	5.19	5.25	9.09	8.81	96.97
12	p- CH_3	$\text{C}_{17}\text{H}_{14}\text{O}_2\text{N}_2$	73.38	73.64	5.03	5.24	10.07	9.93	113-114
13	p-Cl	$\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}_3\text{Cl}$	64.32	63.91	3.69	4.01	9.39	8.98	118-120
14	p-COOH	$\text{C}_{17}\text{H}_{12}\text{O}_4\text{N}_2$	66.23	66.05	3.89	4.12	9.09	8.91	164-165
15	p- NO_2	$\text{C}_{16}\text{H}_{11}\text{O}_4\text{N}_3$	62.13	61.96	3.56	3.59	13.59	13.21	161-162

The infrared spectrum of all compounds (1-15) have intense carbonyl bands in the region of 1705-1750 cm^{-1} . ^1H NMR spectra of compounds studied exhibit a CH_3 singlet at about 1,7 ppm (from TMS). This singlet and all the spectral evidence indicate that in the coupling reactions the five-membered ring is not opened.

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 (7-9).

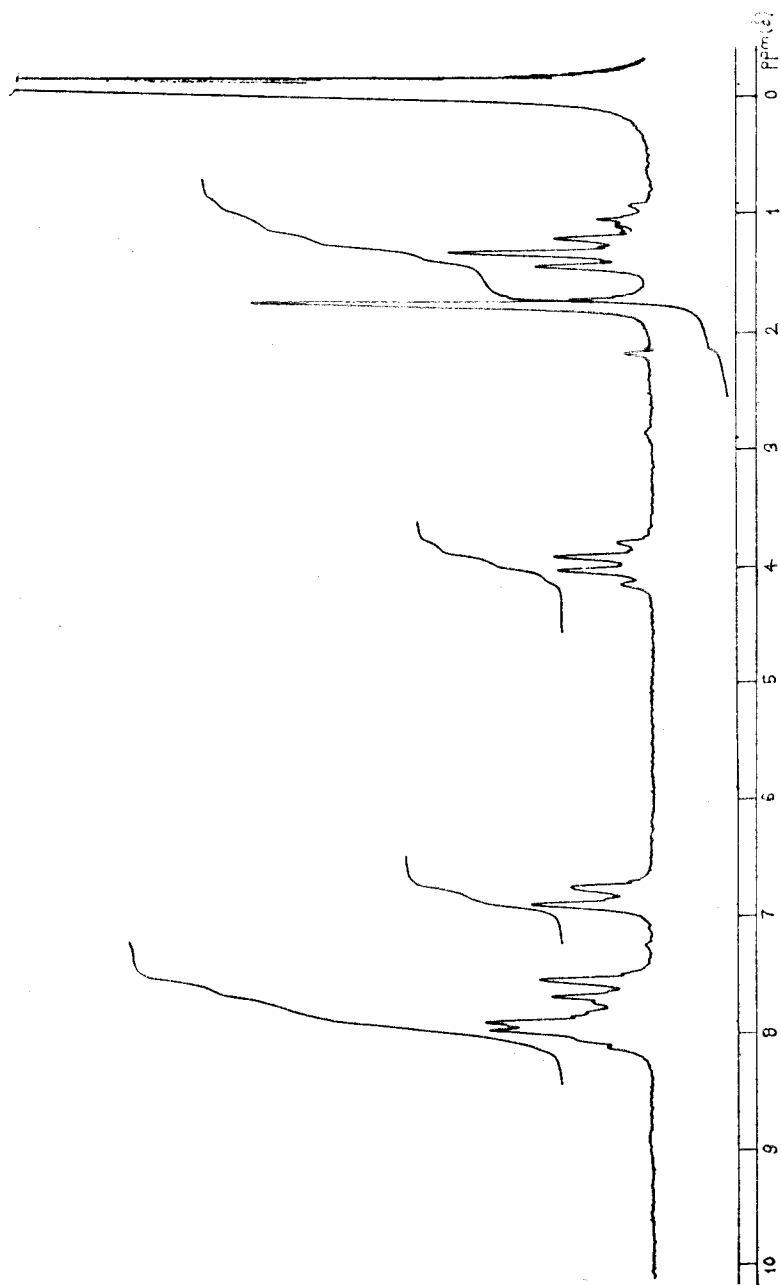
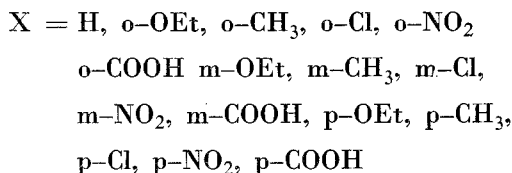


Figure 2. The ^1H NMR spectrum of 2-Methyl-2-(4'-ethoxyphenylazo)-1,3-indandione.

The absorption spectra of compounds prepared recorded in chloroform generally exhibit three maxima. Depending on the substituents, they lie in the ranges 237–242 nm, 249–259 nm and 280–325 nm (Table 1). Introduction of electron donor substituents into the diazo moiety leads to a strong bathochromic shift in the longest wavelength absorption band while electron acceptor substituents exert no significant influence except NO₂ group which causes bathochromic shifts at o-, m- and p-positions. These results are in agreement with those of phenylazopyrazolones (10) and arylazoformaldoximes (11).



REFERENCES

1. PHILLIPS, R.R., *Organic Reactions* Vol. 10, John Wiley and Sons, New York, 1959, Chapter 2.
2. SANDLER, A. and KARO, F., *Organic Functional Group Preparations*, Vol. II. Academic Press, New York, 1971, Chapter 14.
3. Linstead and Wang, *J. Chem. Soc.*, 1937, 807.
4. FEOFILAKTOV and IVANOV., *J. Gen. Chem. U.S.S.R.*, 13 (1943) 457; [*C. A.*, 38, 3255, 1944].
5. HOCALOĞLU, N., UYAR, T. and TÜRKER, L., *Dyes and Pigments* 12 (1990) 187.
6. WISLICENUS, W. and KÖTZLE, A., *Ann.*, 252 (1889) 72; [*C.A.*, 60, 14516 f].
7. SAKHARE, L. and GUDRİNİENCE, E., *Zh. Org. Khim.*, 2 (1966) 674.
8. PUCKETT, S.A., GREENSLEY, M.K. and POUL, I.C., *J. Chem. Soc., Perkin II*, 1 (1977) 847.
9. DUBENKO, R.G., KONSHEVA, V.D., Nelyuev, V.M. and PEL'KIS, P.S., *Zh. Org. Khim.*, 15 (7) (1979) 1483; [*C.A.*, 91 (1979) 174975r].
10. NIKOLOV, P., FRATEV, F. and STOYANOV, S., *Z. Naturforsch.*, 36 a (1981) 191.
11. SHAWALİ, A.S. and ALTHAHOU, B.M., *Tetrahedron*, 33 (1977) 1625.