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ON PHTHALIDES AND INDANDIONES. XLII.*

ALKYLATION OF 2-(1-NAPHTHYL)-1,3-INDANDIONE

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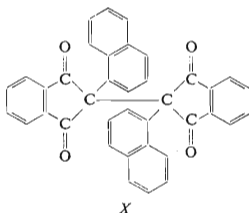
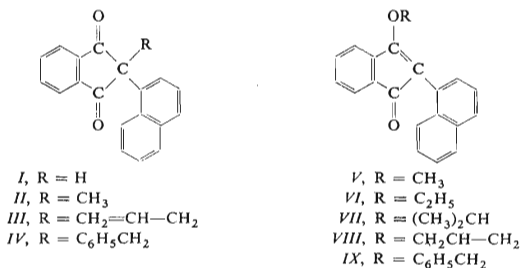
When the anions of 2-phenyl-1,3-indandione and 2-(2-naphthyl)-1,3-indandione are alkylated with primary alkyl halides in various solvents C-alkyl derivatives^{1,2} are formed exclusively. In a previous work³ Hrnčiar found that on methylation of the anion of 2-(1-naphthyl)-1,3-indandione (*I*) with methyl iodide in ethanol O-methyl derivative is formed in addition to the C-methyl derivative. Therefore we were interested in the question to what extent the sterical effect (drop in nucleophilicity) at the C-atom in the position 2 of *I* would be observable during the alkylations with other alkyl halides, in comparison with 2-phenyl-1,3-indandione and 2-(2-naphthyl)-1,3-indandione. The alkylations were carried out in protic and in aprotic solvents having various dielectrical constants (methanol, ethanol, dimethylformamide, dimethyl sulfoxide, acetone, dichloromethane). For the formation of anion *I* in alcoholic medium we made use of alcoholate, while in other solvents potassium carbonate was employed.

From the results given in Table I it is evident that the anion of compound *I* affords in all solvents on alkylation with methyl iodide, benzyl chloride, benzyl iodide, allyl bromide, and allyl chloride a mixture of C-alkyl and O-alkyl derivatives. After ethylation with ethyl bromide and ethyl iodide only the O-ethyl derivative *VI* could be isolated. In alkylations of the anion of 2-phenyl-1,3-indandione and 2-(2-naphthyl)-1,3-indandione with the mentioned primary halo hydrocarbons C-alkyl derivatives were obtained exclusively. When anion *I* reacted with isopropyl iodide, again O-isopropyl derivative *VII* is formed exclusively.

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In paper² it is mentioned that alkylations of the anion of 2-(2-naphthyl)-1,3-indandione in methanol take place with very low yields. Similarly, on alkylation of anion *I* in this medium, as well as in methanol, low yields were observed. Relatively low yields were observed also in dimethyl sulfoxide where they are lowered by the competitive reaction of dimethyl sulfoxide with alkyl halogenides⁴, similarly as in the case of alcohols as solvents. The alkylations took place best in acetone and in dimethylformamide. While in acetone (also in methanol and ethanol) the total yields of alkylation decrease from methyl iodide, over ethyl iodide, to isopropyl iodide, alkylations in dimethylformamide were best with isopropyl iodide. Alkylations in dichloromethane did not take place at all.

When comparing the percentual ratio of the formation of C-alkyl derivatives and O-alkyl derivatives in various solvents, we obtained similar results as in paper², *i.e.* the C : O ratio was highest in dimethylformamide and dimethyl sulfoxide, and lowest again in acetone. This is true not only for the alkylation with methyl iodide, but also for that with allyl chloride, allyl bromide, benzyl chloride, and benzyl iodide. In methanol and ethanol the C : O ratio of alkyl derivatives was approximately equal, which is in accordance with the paper⁵ where the authors found that on methylation of the anion of 1,3-cyclohexanedione with methyl iodide in alcohols of different dielectric constant the percentual ratio of the formation of C-methyl and O-methyl derivatives was practically equal. It is surprising that on ethylation of compound *I* the O-ethyl derivative *VI* is obtained exclusively, although, for example, when the anion of 2-(1-bromo-2-naphthyl)-1,3-indandione³ was ethylated, C-ethyl derivative was obtained in low yield in addition to O-ethyl derivative. Similarly, Crispin and coworkers⁶ obtained on ethylation of the anion of 2-methyl-1,3-cyclohexanedione and 2-methyl-1,3-cyclopentanedione with ethyl iodide in methanol also



SCHEME 1

C-ethyl derivative in addition to O-ethyl derivatives. In the case of 2-methyl-1,3-cyclohexanedione the former was the main product of reaction. In the case of compound *I* the nucleophilicity of the carbon in the position 2 decreased in comparison with 2-phenyl-1,3-indandione and 2-(2-naphthyl)-1,3-indandione in consequence of steric hindrance.

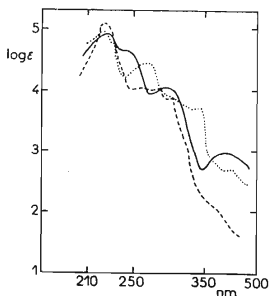


FIG. 1
Electronic Spectra in Methanol
Compound *I* ·····, compound *II* -----,
compound *V* - · - · - ·

In dimethylformamide and in dimethyl sulfoxide the methylation was carried out even without potassium carbonate. Methylation in dimethylformamide without potassium carbonate took place with 20% conversion and a C-methyl: O-methyl derivative ratio similar to that when carbonate was present. When methylation was carried out in dimethyl sulfoxide in the absence of a catalyst we also obtained bis-2-(1-naphthyl)-1,3-indandione (*X*) in addition to compounds *II* and *V*. When the reaction was carried out without the catalyst elementary iodine also separated, which was not observed in the presence of potassium carbonate.

In order to confirm the structure of the alkylation products we measured their IR spectra and compared them with the spectra of compound *I*. In nujol compound *I* is present in its keto form exclusively. In the region of stretching vibrations of carbonyl groups *I* displays a strong double absorption peak resulting from the coupling between the vibrations of two equivalent carbonyl groups⁶. The position of the stronger peak is at 1712 cm^{-1} and that of the weaker peak at 1751 cm^{-1} . The prepared 2-alkyl-2-(1-naphthyl)-1,3-indandione *II-IV* absorb in the region of carbonyl stretching vibrations in an analogous manner. The maxima of stronger bands are in the $1708\text{--}1716\text{ cm}^{-1}$ region while weaker bands are in the $1748\text{--}1752\text{ cm}^{-1}$ region (Table II). Infrared spectra differing from those of the starting compound have 1-alkoxy-2-(1-naphthyl)-1-inden-3-ones *V-IX*. In their spectra only one band is observed in the region of the carbonyl group stretching vibration the intensity of which is decreased in comparison with the previous group of substances. Valter and Nejlund⁷ demonstrated that the integrated intensity of the absorption band of the keto form represents the double value of the integrated intensity of the carbonyl group band of the enol form. The position of the CO-group band in compounds *X-IX* is at $1701\text{--}1709\text{ cm}^{-1}$. In the spectra of these compounds strong absorption bands at $1624\text{--}1631\text{ cm}^{-1}$ occur which belong to the stretching vibration of the C=C double bond in the five-membered indene ring.

C-alkyl and O-alkyl derivatives differ also in their electronic spectra. In the molecule of derivatives *II-IV* both aromatic rings (benzene and naphthalene) are in a non-planar orientation, while in the molecules of derivatives *V-IX* the planar orientation of the aromatic systems is possible. All C-alkyl derivatives *II-IV* have practically identical spectra. This is also true of O-alkyl derivatives *V-IX*. In the 220–270 nm region and 350–500 nm region bands of $\pi-\pi^*$ transitions are present, while in the 270–320 nm region the bands of $n-\pi^*$ transitions probably occur. From the spectra in Fig. 1 a bathochromic shift of the spectrum of compounds *V-IX* in comparison with compounds *II-IV* is evident. This shift is a consequence of a strong mutual interaction of $\pi-\pi^*$ electronic systems of aromatic nuclei through the unsaturated five-membered ring. For substances *V-IX* the strong band at 420 nm ($\epsilon = 1000$) is characteristic, which is connected with the $\pi-\pi^*$ electronic transition of the whole conjugated system.

EXPERIMENTAL

Alkylation of 2-(1-Naphthyl)-1,3-indandione

A. In methanol (ethanol): To an alcoholate solution prepared from 0.2 g (0.01 gramatom) of sodium in 300 ml of methanol (or ethanol) 0.005 mol of *I* were added followed, after 5 minutes, by 0.01 mol of the corresponding halo hydrocarbon. The reaction mixture was heated at $40^\circ\text{C} \pm 1^\circ$ for 8 hours. After cooling the solution is filtered and the filtrate distilled to eliminate the solvent and the excess halo hydrocarbon. The crude product was dissolved in chloroform and chro-

TABLE I

Results of Alkylation of the Anion of 2-(1-Naphthyl)-1,3-Indandione in Various Solvents
The first number represents the total yield in %, the second is the C : O ratio of alkylation.

Reagent	Dimethyl- formamide	Dimethyl sulfoxide	Acetone	Methanol	Ethanol
CH ₃	65.8	36.3	82.1	30.7	26.5
	3	2.84	0.42	1.77	1.63
C ₂ H ₅ Br	59.3	30.4	72.6	6.5	7.1
C ₂ H ₅ I	63.5	35.9	76.1	10.3	8.6
(CH ₃) ₂ CHI	76.3	35.8	28.3	3.1	traces
CH ₂ =CH—CH ₂ Cl	20.8	8.1	41.2	—	—
	2.44	2.57	1.27		
CH ₂ =CH—CH ₂ Br	35.4	28.3	62.6	13.1	5.1
	2.03	2.22	1.5	1.5	1.27
C ₆ H ₅ CH ₂ Cl	68.7	34.8	42.1	23.8	31.8
	1.77	2.2	0.72	1.63	1.82
C ₆ H ₅ CH ₂ I	89.2	36.6	68.3	29.6	30.6
	10.8	8.22	4.26	2.70	3

matographed on alumina (Brockmann II, Reanal, Budapest; column height 30 cm, diameter 2 cm). 2-Alkyl-2-(1-naphthyl)-1,3-indandione *II-IV* was eluted first (approx. 4 cm before the yellow band), which is colourless, followed by 1-alkoxy-2-(1-naphthyl)-1-inden-3-one *V-IX*. The eluate of the C-derivative is evaporated almost to dryness and the residue recrystallised from benzene-light petroleum (1 : 1). A similar procedure was carried out also in the case of the O-derivative which was crystallised from a benzene-light petroleum mixture (1 : 20).

B. In dimethylformamide (dimethyl sulfoxide, acetone): To a mixture of 30 ml of the solvent, 0.64 g (0.005 mol) of anhydrous potassium carbonate, and 0.68 g (0.0025 mol) of *I*, which was allowed to stand for 5 minutes, 0.01 mol of halo hydrocarbon was added and the mixture was heated at $40^{\circ}\text{C} \pm 1^{\circ}$ for 4 hours. The solvent was evaporated and the dry residue boiled twice with 40 ml of chloroform. The solution was filtered and evaporated to 25 ml and then chromatographed on alumina. Further working up as under *A*.

TABLE II

Properties of the 2-R-2-(1-Naphthyl)-1,3-indandiones *II-IV* and 1-R-O-2-(1-Naphthyl)-1-inden-3-ones *V-IX* Prepared

Compound	Formula (M.w.)	M.p., °C (Kofler)	Calc./Found		$\nu(\text{CO})$ cm^{-1}	$\nu(\text{C}=\text{C})$ cm^{-1}
			% C	% H		
<i>II</i>	$\text{C}_{20}\text{H}_{15}\text{O}_2$ (286.3)	152–154	83.92	4.96	1 716	—
			83.85	4.99	1 752	—
<i>III</i>	$\text{C}_{22}\text{H}_{19}\text{O}_2$ (312.4)	121–122	84.59	5.16	1 713	—
			84.68	5.26	1 749	—
<i>IV</i>	$\text{C}_{26}\text{H}_{19}\text{O}_2$ (362.4)	201–202	86.16	5.00	1 708	—
			85.95	5.18	1 742	—
<i>V</i>	$\text{C}_{20}\text{H}_{15}\text{O}_2$ (286.3)	145–146	83.92	4.96	1 701	1 631
			83.90	5.11		
<i>VI</i>	$\text{C}_{21}\text{H}_{17}\text{O}_2$ (300.4)	124–125	83.97	5.37	1 702	1 624
			83.80	5.53		
<i>VII</i>	$\text{C}_{24}\text{H}_{19}\text{O}_2$ (314.4)	135–136	84.03	6.09	1 708	1 624
			83.93	5.92		
<i>VIII</i>	$\text{C}_{22}\text{H}_{17}\text{O}_2$ (312.4)	87–88	84.59	5.16	1 708	1 625
			84.68	5.32		
<i>IX</i>	$\text{C}_{26}\text{H}_{19}\text{O}_2$ (362.4)	132–133	86.16	5.00	1 709	1 626
			86.13	5.23		

Spectroscopic Measurements

The infrared spectra were measured on a two-beam prism UR-20 model spectrophotometer, in the $700-2000\text{ cm}^{-1}$ range (NaCl optics). The apparatus was calibrated using a polystyrene foil. The samples were prepared in nujol, 4 mg substance per 15 mg nujol.

Electronic spectra were measured on a prism Perkin-Elmer spectrophotometer, model 450, in 215–750 nm region, in methanol. Concentrations: $1 \cdot 10^{-3}\text{M}$, $1 \cdot 10^{-4}\text{M}$, $1 \cdot 5 \cdot 10^{-5}\text{M}$. Cell widths: 0.50 cm and 1.00 cm.

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**AROMATIC DIAZO
AND AZO COMPOUNDS. LXXXVII.*****FORMATION OF 3-BENZENEAZOPYRIDINE
FROM SULPHITE ADDUCT**

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Previously we described¹ the preparation of the azo compound *IV* which is formed by coupling benzenediazonium chloride with the adduct of pyridine and three molecules of sodium hydrogen sulphite (*I*), the azo compound *II* being probably formed first whereupon a rapid spontaneous splitting off of one sulphite molecule follows. The subject of the present paper is a study of splitting off of the two remaining sulphite molecules with the aim of obtaining 3-benzeneazopyridine (*VI*).

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