

ON PHTHALIDES AND INDANDIONES. XXXVIII.*

ALKYLATION OF 2-(1-X-2-NAPHTHYL)-1,3-INDANDIONE
IN ETHANOL AND IN DIMETHYLFORMAMIDE

P. HRNČIAR and F. SZEMES

*Department of Organic Chemistry,
Komenský University, Bratislava*

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It was established that on alkylation of 2-(1-X-2-naphthyl)-1,3-indandione by primary halo-hydrocarbons only C-alkyl derivatives are formed if $X = H$, but a mixture of C-alkyl and O-alkyl derivatives if $X = Cl, Br, NO_2$; on reaction with isopropyl iodide a mixture of C-isopropyl and O-isopropyl derivatives has been obtained if $X = H$, but when $X = Cl, Br, NO_2$ O-isopropyl derivative was obtained exclusively. The yields of the alkylation in ethanol and in dimethylformamide are compared. On reaction with diazomethane, when $X = H$, C-methyl and O-methyl derivatives were obtained, while in other cases only O-methyl derivatives could be isolated. The infrared and ultraviolet spectra of the prepared substances are interpreted.

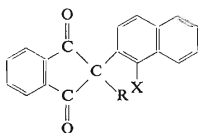
On alkylation of 2-phenyl-1,3-indandione with primary halo-hydrocarbons only C-alkyl derivatives are obtained¹⁻³. In contrast to this we observed in a previous paper⁴ that on methylation of 2-(1-naphthyl)-1,3-indandione with methyl iodide in ethanol O-methyl derivatives were obtained in addition to C-methyl derivatives. Similarly, on alkylation of 2-phenyl-1,3-indandione substituted at the position 2 of the phenyl group both C-alkyl and O-alkyl derivatives have been formed⁵⁻⁷. If the alkyl groups are bulky (for example the tert-butyl group) O-alkyl derivatives are formed exclusively⁶.

In this paper we report on the results of the alkylation of 2-(1-X-2-naphthyl)-1,3-indandione ($X = H, Cl, Br, NO_2$) (I-IV) not yet carried out. We were interested in the role of sterical effect during the alkylation of 2-(2-naphthyl)-1,3-indandione (I) as compared with the alkylation of 2-phenyl-1,3-indandione and 2-(1-naphthyl)-1,3-indandione. Further, we are investigating the influence of the substituent in position 1 of the naphthalene nucleus on the course of the substitution.

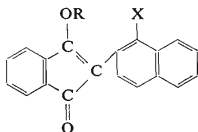
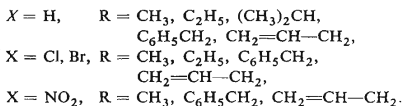
Base catalysed alkylation of derivatives of 1,3-indandione is a typically nucleo-

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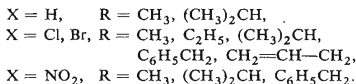
philic substitution with two centers of nucleophilicity. Therefore, it is possible to assume that on alkylation of 2-(1-X-2-naphthyl)-1,3-indandione both C-alkyl and O-alkyl derivatives will be formed (Scheme 1).



V-XX



XXI-XXXV



The methylation and the benzylation of substances I-IV was carried out in absolute ethanol and dimethylformamide. As may be seen from the results given in Table I alkylation in ethanol under catalysis with sodium ethoxide gave in both cases lower yields than in the case of alkylations in dimethylformamide in the presence of potassium carbonate. This was especially true of substances II-IV. The mentioned effect is probably produced by the fact that in ethanol in the presence of ethoxide ions a competing reaction between the halohydrocarbon and the ethoxide ions may take place. This view is supported by the fact that the pH value is decreased more than would correspond to the reaction of the indandione anion and the halohydrocarbon. It is also possible that in the aprotic solvent (dimethylformamide) the solvation of the nucleophilic reagent is decreased, *i.e.* that of compounds I-IV, in contrast to the protic solvent - ethanol. It is true that the substitution of the protic solvent by an aprotic one did not affect the percentage of the ratio of the C-alkyl derivative and the O-alkyl derivative to such an extent as was determined by Kurcs and co-

workers⁸ during the ethylations of ethyl acetoacetate (in protic solvents the percentage of O-ethyl derivatives was lower than in polar aprotic solvents), but preliminary experiments have shown that the alkylation of 2-aryl-1,3-indandiones in dimethylformamide can be carried out even in the absence of a catalyst. However, the yields were much lower (up to 40%).

As regards alkylation with primary alkyl halides, it can be safely supposed that this is a reaction following a S_N2 mechanism both in absolute ethanol and in dimethylformamide. Of course, the general rule that nucleophilic reagents with two centers of nucleophilicity, such as the anions of the corresponding 1,3-indandiones in this case, react in the reactions of the S_N2 type primarily with the less electronegative atom, is valid only for 2-(2-naphthyl)-1,3-indandione (*I*) unsubstituted at position 1 of the naphthyl residue. Reaction of this indandione with primary halohydrocarbon gave C-alkyl derivatives only. When 2-(2-naphthyl)-1,3-indandione substituted in the position 1 ($X = \text{Cl}, \text{Br}, \text{NO}_2$) was alkylated, O-alkyl derivatives were formed in addition to C-alkyl derivatives. The former are predominant in the majority of cases, and in the case of the ethylation with ethyl iodide, they are practically the only products (see Table I). On the basis of the comparison of the yields of the reaction it could be concluded that the reaction took place better with methyl iodide than with ethyl iodide. The yields dropped still more in the case of isopropyl iodide. In the reaction with isopropyl iodide compound *I* alone gives in addition to C-isopropyl derivative *XII* also O-isopropyl derivative *XXVII*. This fact can be explained by sterical effect. Benzylation with benzyl chloride gave only slightly lower yields than methylation with methyl iodide. In this connection the yields of the alkylation with allyl chloride are strikingly low.

When comparing the results of alkylation of *II* and *III*, compound *II* always gave a larger proportion of C-alkyl derivative, and *vice versa*, compound *III* gave predominantly the O-alkyl derivative. Thus, the magnitude of the effective volume of the halogen atom has an influence on the ratio of the C-alkyl and O-alkyl derivatives formed. On the basis of the results of the alkylation of nitro derivative *IV* it can be stated that in addition to the sterical effect the course of the alkylation is also influenced by electronic effects because in the case of compound *IV*, which generally gives lower yields of alkylation, the C-alkylation is relatively stronger than in the case of *II* and *III* although the effective volume of the nitro group is somewhere in between that of chlorine and bromine.

When comparing the results of the alkylation of 2-(1-X-2-naphthyl)-1,3-indandione with those of the alkylation of 2-(2-X-phenyl)-1,3-indandione⁵ it can be observed that in the case of the naphthyl derivative the steric effect of the substituent is more pronounced, *i.e.* O-alkyl derivatives are formed in greater yields, while the total reactivity of these two types of indandiones is approximately equal. The results of the measurement of the reaction rate of the methylation of these indandiones⁹ also points to this conclusion. Steric hindrance of the naphthalene nucleus during the

alkylations of the carbon atom is more pronounced in 2-(1-naphthyl)-1,3-indandione than in 2-(2-naphthyl)-1,3-indandione. On alkylation of the former, O-alkyl derivatives are formed in addition to C-alkyl derivatives⁴.

Methylations of substances *I–IV* were also carried out with diazomethane in diethyl ether. Methylation of compound *I* gave both C-methyl and O-methyl derivative, similarly as in the case of 2-phenyl-1,3-indandione. With compounds *II–IV* O-methyl derivatives were obtained exclusively.

In order to confirm the structures of the products formed on alkylation we measured their IR spectra and compared them with those of the starting 2-(1-X-2-naphthyl)-1,3-indandiones. On the basis of the absorption bands in the spectra measured in nujol it can be stated that the original indandiones occur under these conditions only in their keto form. In the region of stretching vibrations of the carbonyl groups these original substances show a strong double absorption band which results from the coupling of the vibrations of two equivalent carbonyl groups¹⁰. The position of the stronger absorption band is at $1710–1714\text{ cm}^{-1}$ and that of the weaker band is at $1742–1753\text{ cm}^{-1}$. 2-Alkyl-2-(1-X-2-naphthyl)-1,3-indandiones also have a similar absorption in the carbonyl region. The maxima of stronger bands are situated in the $1705–1718\text{ cm}^{-1}$ zone and those of weaker ones in the $1742–1753$

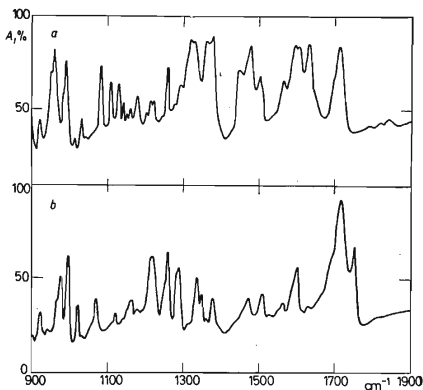


FIG. 1

Infrared Spectrum

a 2-Methyl-2-(1-chloro-2-naphthyl)-1,3-indandione (*VI*), *b* 1-methoxy-2-(1-chloro-2-naphthyl)-1-inden-3-one (*XXII*).

cm^{-1} region (see Table II). Substances formed by O-alkylation, *i.e.* 1-alkoxy-2-(1-X-2-naphthyl)-1-inden-3-ones have spectra different from the starting compounds and also C-alkylated indandiones. In the IR spectra of these compounds only one band is present in the carbonyl region the intensity of which is low in comparison with the preceding group. Valter and Nejland¹⁰ proved that the integrated intensity of the absorption band of the keto form of 1,3-indandiones is double that of the carbonyl band of the enol form. The position of this band is between 1701–1712 cm^{-1} . The differing intensity of these bands can be well seen in the infrared spectrum of compound VI (XII) (Fig. 1). The spectra of this group of substances also display strong absorption bands at 1621–1630 cm^{-1} due to stretching vibration of the double bond in the five-membered indene ring.

TABLE I

Yields of C-Alkyl and O-Alkyl Derivatives after Alkylation of 2-(1-X-2-Naphthyl)-1,3-indandiones in Dimethylformamide (first number) and in Ethanol (after methylation and benzylation, second number)

X	Alkylating agent	Total yield, %		Ratio C : O
		C-derivative	O-derivative	
H	CH ₃ J	97 (70)	0 (0)	∞ (∞)
Cl		45 (23)	16 (15)	2.81 (1.5)
Br		35 (22)	42 (19)	0.83 (0.9)
NO ₂		92 (19)	0.5 (0.2)	184 (95)
H	C ₆ H ₅ CH ₂ Cl	99 (75)	0 (0)	∞ (∞)
Cl		23 (5)	22 (3)	1.04 (1.66)
Br		18 (7.3)	37 (4.5)	0.84 (1.62)
NO ₂		14 (7.8)	2 (0)	7 (∞)
H	CH ₂ =CH-CH ₂ Cl	46	0	∞
Cl		10	28	0.35
Br		8	35	0.23
NO ₂		19	0.2	95
H	(CH ₃) ₂ CHJ	63	19	3.31
Cl		0	74	0
Br		0	79	0
NO ₂		0	31	0
H	CH ₃ CH ₂ J	80	0	∞
Cl		0.5	72	0.07
Br		0.2	71	0.02

The groups of C-alkyl and O-alkyl derivatives also differ substantially in mutual steric orientation of the aromatic systems. As all C-alkyl derivatives prepared from the same indandione have substantially identical spectra, and because the same is true of the prepared O-alkyl derivatives, we investigated the electronic spectra only in the case of C-methyl and O-methyl derivatives. In the molecule of 2-methyl-2-(1-X-naphthyl)-1,3-indandiones both aromatic nuclei (benzene and naphthalene) are oriented out of plane, while in the molecule of 1-methoxy-2-(2-naphthyl)-1-inden-3-one (XXI) the planar orientation of the aromatic residues is possible (conjugation of the indene and the naphthalene nuclei). However, when the hydrogen atom at position 1 of the naphthyl residue is substituted by a larger substituent, such a planar orientation of the two aromatic residues is no longer possible. This is then manifested by the changes in the conjugation of the corresponding $\pi - \pi'$ electronic systems, accompanied by changes in the position and the intensity of the bands in the electronic spectra.

In the spectra of the investigated compound bands of $\pi \rightarrow \pi^*$ transitions appear in the 220–270 nm and 350–500 nm regions, further probably also bands of $n \rightarrow \pi^*$ transitions in the 270–320 nm region. In the spectrum of 1-methoxy-2-(2-naphthyl)-1-inden-3-one a distinct bathochromic shift is observable, when compared with the spectrum of 2-methyl-2-(2-naphthyl)-1,3-indandione (compare Figs 2 and 3). This shift

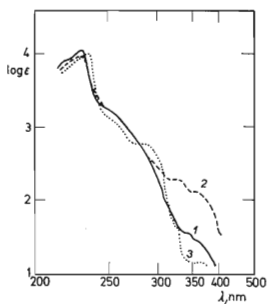


FIG. 2

Ultraviolet Spectra of Methanolic Solutions
 1 2-Methyl-2-(2-naphthyl)-1,3-indandione;
 2 2-methyl-2-(1-nitro-2-naphthyl)-1,3-indandione;
 3 2-methyl-2-(1-chloro-2-naphthyl)-1,3-indandione.

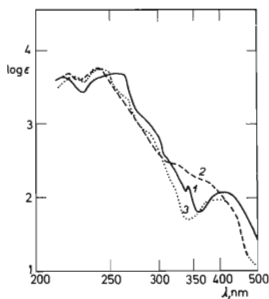


FIG. 3

Ultraviolet Spectra of Methanolic Solutions
 1 1-Methoxy-2-(naphthyl)-1-inden-3-one;
 2 1-methoxy-2-(1-nitro-2-naphthyl)-inden-3-one;
 3 1-methoxy-2-(1-chloro-2-naphthyl)-inden-3-one.

is due to a strong mutual influence of $\pi \rightarrow \pi$ transitions of aromatic nuclei (through the five-membered ring). A similar bathochromic shift is observed also in the case of O-methyl derivatives, when compared with C-methyl derivatives, even when the naphthalene nucleus is substituted in position 1 by a halogen atom or by the nitro group. A similar shift was also observed in the case of 1-methoxy-2-(2-X-phenyl)-1-inden-3-one⁵. For 1-methoxy-2-(2-naphthyl)-1-inden-3-one, as well as for its halo-derivatives the band at 400 nm ($\epsilon = 1000$) is characteristic. It is dependent on the $\pi \rightarrow \pi^*$ transition of the whole conjugated system. The position of this band in the case of the nitro derivative is shifted to a shorter wave-length. It is also less intense, probably due to a strong $-I$ effect of the nitro group. On the other hand, when 2-methyl-2-(1-nitro-2-naphthyl)-1,3-indandione (VIII) is compared with 2-methyl-2-(2-naphthyl)-1,3-indandione (V) a strong bathochromic shift is observed in the spectrum of the former in the 300–400 nm region (at $\epsilon = 1000$).

The substituent at position 1 of the naphthalene nucleus (Cl, Br, NO_2) influences both bands (at 220–270 nm and 350–500 nm) in a hypsochromic way (see Fig. 3). It should be mentioned that a bathochromic shift in the 350 nm region is observed in the spectrum of 1-methoxy-2-(1-nitro-2-naphthyl)-1-inden-3-one (XXIV) when compared with 1-methoxy-2-(2-naphthyl)-1-inden-3-one (XXI), in contrast to what is observed with halogen substituted derivatives. However, when comparing with 2-methyl-(1-nitro-2-naphthyl)-1,3-indandione (VIII) a hypsochromic shift took place even in this region.

EXPERIMENTAL

Analytical data and the melting points of newly prepared compounds are listed in Table II.

Preparation of 2-(1-X-2-Naphthyl)-1,3-indandiones I–IV

(X = H, Cl, Br, NO_2)

The starting 2-(1-X-2-naphthyl)-1,3-indandiones were prepared by rearrangement of corresponding (1-X-2-naphthal)phthalides effected with sodium methylate in methanol, according to¹¹.

Alkylation of 2-(1-X-2-Naphthyl)-1,3-indandiones

A. *In ethanol*: To a solution of 0.2 g (0.01 gramatom) of sodium in 300 ml of ethanol 0.05 mol of the corresponding indandione were added, followed, after five minutes, by 0.01 mol of halo-hydrocarbon. The reaction mixture was refluxed for 4–4 1/2 hours. The end of the reaction is shown by the change of the intensely red coloration of the solution to orange and by the dropping of the pH of the medium to 7. After cooling the reaction solution is filtered and ethanol and excess halo-hydrocarbon are distilled off. The crude product is dissolved in benzene and chromatographed on alumina (Brockmann II, Reanal, Budapest). 2-Alkyl-2-(1-X-2-naphthyl)-1,3-indandione (V–XX) is eluted first, followed by 1-alkoxy-2-(1-X-2-naphthyl)-1-inden-3-one (XXI–XXXV). The R_F values of the C- and O-methyl derivatives, measured on a thin layer of alumina are the following: for compound V 0.62, VI 0.48, VII 0.42, VIII 0.36, XXI 0.38, XXII 0.42, XXIII 0.36, XXIV 0.28. As 2-alkyl derivatives are colourless we used for their detection

TABLE II

Analytical Data of 2-R-2-(1-X-2-Naphthyl)-1,3-indandiones (compounds I—XX) and 1-RO-2-(1-X-2-Naphthyl)-1-inden-3-ones (compounds XXI—XXXV)

Compound	X R	M.p., °C (Kofler)	Formula (m.w.)	Calculated/Found			ν_{CO} cm^{-1}
				% C	% H	% X	
I	H	173	$\text{C}_{19}\text{H}_{11}\text{O}_2$	—	—	—	1 710
	H		(271·2)	—	—	—	1 752
II	Cl	222	$\text{C}_{19}\text{H}_{10}\text{ClO}_2$	—	—	—	1 714
	H		(305·7)	—	—	—	1 753
III	Br	209—210	$\text{C}_{19}\text{H}_{10}\text{BrO}_2$	—	—	—	1 713
	H		(350·2)	—	—	—	1 752
IV	NO_2	174—175	$\text{C}_{19}\text{H}_{10}\text{NO}_4$	—	—	—	1 714
	H		(316·3)	—	—	—	1 753
V	H	131	$\text{C}_{20}\text{H}_{14}\text{O}_2$	83·92	4·96	—	1 708
	CH_3		(286·3)	84·12	5·13	—	1 745
VI	Cl	197	$\text{C}_{20}\text{H}_{13}\text{ClO}_2$	74·76	4·08	11·05	1 716
	CH_3		(320·3)	75·00	4·21	11·02	1 751
VII	Br	231	$\text{C}_{20}\text{H}_{13}\text{BrO}_2$	65·77	3·59	21·80	1 716
	CH_3		(365·2)	65·90	3·75	22·00	1 751
VIII	NO_2	236—238	$\text{C}_{20}\text{H}_{13}\text{NO}_4$	75·52	3·95	4·23(N)	1 718
	CH_3		(331·3)	74·95	4·25	3·72(N)	1 751
IX	H	94	$\text{C}_{11}\text{H}_{16}\text{O}_2$	83·97	5·37	—	1 708
	C_2H_5		(300·3)	83·76	5·23	—	1 748
X	Cl	178	$\text{C}_{21}\text{H}_{15}\text{ClO}_2$	75·34	4·52	19·59	1 714
	C_2H_5		(334·8)	75·61	4·63	10·92	1 750
XI	Br	196	$\text{C}_{21}\text{H}_{15}\text{BrO}_2$	66·50	3·98	21·07	1 714
	C_2H_5		(379·2)	66·75	4·15	20·83	1 750
XII	H	224—226	$\text{C}_{22}\text{H}_{18}\text{O}_2$	84·63	5·51	—	1 712
	$(\text{CH}_3)_2\text{CH}$		(314·8)	84·31	6·01	—	1 784
XIII	H	135	$\text{C}_{26}\text{H}_{18}\text{O}_2$	86·10	5·00	—	1 711
	$\text{C}_6\text{H}_5\text{CH}_2$		(362·4)	86·42	4·87	—	1 747
XIV	Cl	268	$\text{C}_{26}\text{H}_{12}\text{ClO}_2$	78·69	4·31	8·93	1 713
	$\text{C}_6\text{H}_5\text{CH}_2$		(396·8)	78·51	4·35	8·85	1 746
XV	Br	278	$\text{C}_{26}\text{H}_{17}\text{BrO}_2$	70·76	3·88	18·11	1 711
	$\text{C}_6\text{H}_5\text{CH}_2$		(441·2)	71·00	3·90	17·82	1 745
XVI	NO_2	278	$\text{C}_{26}\text{H}_{17}\text{NO}_4$	76·64	4·20	3·43(N)	1 711
	$\text{C}_6\text{H}_5\text{CH}_2$		(407·4)	77·20	4·65	3·76(N)	1 748
XVII	H	58	$\text{C}_{22}\text{H}_{16}\text{O}_2$	84·59	5·16	—	1 707
	$\text{CH}_2=\text{CH}-\text{CH}_2$		(312·3)	84·42	5·31	—	—
XVIII	Cl	124	$\text{C}_{22}\text{H}_{15}\text{ClO}_2$	76·19	4·36	10·22	1 711
	$\text{CH}_2=\text{CH}-\text{CH}_2$		(346·8)	75·96	4·23	10·11	1 745
XIX	Br	150	$\text{C}_{22}\text{H}_{15}\text{BrO}_2$	67·53	3·86	20·45	1 713
	$\text{CH}_2=\text{CH}-\text{CH}_2$		(381·3)	67·33	3·75	20·10	1 750
XX	NO_2	154	$\text{C}_{22}\text{H}_{15}\text{NO}_4$	73·94	4·23	3·91(N)	1 708
	$\text{CH}_2=\text{CH}-\text{CH}_2$		(367·3)	73·73	4·32	3·72(N)	1 750

TABLE II

(Continued)

Compound	X R	M.p., °C (Kofler)	Formula (m.w.)	Calculated/Found			ν_{CO} cm^{-1}	$\nu_{\text{C}=\text{C}}$ cm^{-1}
				% C	% H	% X		
XXI	H	95	$\text{C}_{20}\text{H}_{14}\text{O}_2$	83.92	4.96	—	—	—
	CH_3		(286.3)	83.75	4.90	—	1 712	1 624
XXII	Cl	83–85 ^a	$\text{C}_{20}\text{H}_{13}\text{ClO}_2$	74.76	4.08	11.05	1 712	1 630
	CH_3	64–66 ^a	(320.8)	74.43	4.04	11.00		
XXIII	Br	135 ^a	$\text{C}_{20}\text{H}_{13}\text{BrO}_2$	65.77	3.59	21.88	1 702	1 626
	CH_3	114–116 ^a	(365.2)	65.65	3.33	20.98		
XXIV	NO_2	208	$\text{C}_{20}\text{H}_{13}\text{NO}_2$	75.52	3.95	4.23(N)	1 707	1 627
	CH_3		(331.3)	75.32	3.75	4.12(N)		
XXV	Cl	150	$\text{C}_{21}\text{H}_{15}\text{ClO}_2$	75.34	4.52	10.59	1 701	1 623
	C_2H_5		(334.8)	75.21	4.62	10.16		
XXVI	Br	134	$\text{C}_{21}\text{H}_{15}\text{BrO}_2$	66.50	3.98	21.07	1 706	1 624
	C_2H_5		(379.25)	66.33	3.77	21.02		
XXVII	H	oil	$\text{C}_{22}\text{H}_{18}\text{O}_2$	84.63	5.55	—	1 715	1 625
	$(\text{CH}_3)_2\text{CH}$		(314.4)	84.42	6.02			
XXVIII	Cl	159	$\text{C}_{22}\text{H}_{17}\text{ClO}_2$	75.75	4.91	10.16	1 703	1 624
	$(\text{CH}_3)_2\text{CH}$		(348.8)	75.64	4.75	9.94		
XXIX	Br	158	$\text{C}_{22}\text{H}_{17}\text{BrO}_2$	67.18	4.36	20.32	1 704	1 623
	$(\text{CH}_3)_2\text{CH}$		(393.3)	66.92	4.23	20.25		
XXX	NO_2	196	$\text{C}_{22}\text{H}_{17}\text{NO}_2$	73.52	4.77	3.89(N)	1 704	1 621
	$(\text{CH}_3)_2\text{CH}$		(359.4)	73.62	4.80	4.03(N)		
XXXI	Cl	207	$\text{C}_{26}\text{H}_{17}\text{ClO}_2$	78.69	4.31	8.93	1 705	1 624
	$\text{C}_6\text{H}_5\text{CH}_2$		(396.8)	78.90	4.52	8.85		
XXXII	Br	198	$\text{C}_{26}\text{H}_{17}\text{BrO}_2$	60.76	3.88	18.11	1 704	1 623
	$\text{C}_6\text{H}_5\text{CH}_2$			71.01	3.80	17.82		
XXXIII	NO_2	196–198	$\text{C}_{26}\text{H}_{17}\text{NO}_4$	76.64	4.20	3.43(N)	1 703	1 623
	$\text{C}_6\text{H}_5\text{CH}_2$		(407.4)	77.32	4.25	3.67(N)		
XXXIV	Cl	152–154	$\text{C}_{22}\text{H}_{15}\text{ClO}_2$	76.19	4.36	10.22	1 705	1 623
	$\text{CH}_2=\text{CH}-\text{CH}_2$		(346.8)	75.80	4.62	10.01		
XXXV	Br	145–147	$\text{C}_{22}\text{H}_{15}\text{BrO}_2$	67.53	3.86	20.43	1 706	1 624
	$\text{CH}_2=\text{CH}-\text{CH}_2$		(391.3)	67.80	3.70	20.10		

^a These substances had polymorphous properties; when crystallised from benzene–light petroleum mixtures of various proportions the substances had different melting points, but the IR spectra and the results of elemental analyses were identical.

a saturated solution of 2,4-dinitrophenylhydrazine in 0.1M-HCl, or spraying with nitration mixture. The eluate of the C-derivative is evaporated almost to dryness and then crystallised from benzene–light petroleum (1 : 1). A similar procedure is also adopted for the O-derivative which is recrystallised from benzene–light petroleum (1 : 20).

B. *In dimethylformamide*: To 30 ml dimethylformamide 0.0025 mol of the corresponding 2-(1-X-2-naphthyl)-1,3-indandione were added followed by 0.64 g (0.005 mol) of anhydrous potassium carbonate, 0.05 mol of halo-hydrocarbon and the reaction mixture is heated with stirring on a water bath for 3 hours. Dimethylformamide is distilled off *in vacuo* and the dry residue is boiled twice with 60 ml of benzene, the solution is filtered, concentrated to 30 ml and chromatographed on alumina. Further procedure was as under A.

C. *With diazomethane*: To 0.005 mol of the corresponding 2-(1-X-2-naphthyl)-1,3-indandione in 30 ml of ether diazomethane (0.01 mol) in 30 ml of ether is added at room temperature. The mixture is stirred and allowed to stand at room temperature for one hour. Ether is then distilled off and the residue is dissolved in 40 ml of benzene and chromatographed on alumina. Further procedure was as under A. On methylation of 2-(2-naphthyl)-1,3-indandione (I) we obtained in addition to O-derivative (XXI) (62% yield) also the C-methyl derivative (V) (10% yield). In the case of other indandiones only O-derivatives were obtained in 80–90% yields.

Spectroscopic Measurement

Infrared spectra of new substances were measured on a double-beam model UR-20 spectrophotometer (with a NaCl prism) in the 700–2000 cm^{-1} region. The apparatus was calibrated using a polystyrene foil. The samples were suspended in nujol (4 mg of substance in 15 mg nujol). The spectrum of nujol was compensated.

Electronic spectra were measured on a Perkin-Elmer spectrometer (with a prism), model 450, in the 215–750 nm region. Ethanolic solutions of the investigated substances had the following concentrations: 10^{-3}M , 10^{-4}M , $5 \cdot 10^{-5}\text{M}$. The width of the cells was 0.50 cm and 1.00 cm.

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REFERENCES

1. Nathanson F.: Ber. 26, 2576 (1893).
2. Gheorghiu C.: J. Prakt. Chem. (2) 146, 193 (1936).
3. Furdík M., Hrnčiar P., Vačoková V.: Acta Fac. Rerum. Nat. Univ. Comenianae (Chimia) III, 1117 (1959).
4. Hrnčiar P.: Acta Fac. Rerum Nat. Univ. Comenianae (Chimia) XII, 273 (1968).
5. Hrnčiar P., Štekláč M., Livař M., Cipinová H.: Chem. zvesti 23, 597 (1969).
6. Bruynes C. A., Rekker R. F., Nauta W. T.: Rec. Trav. Chim. 85, 1529 (1969).
7. Hrnčiar P., Szemes F.: Chem. zvesti, in press.
8. Kurcs A. L., Masias A., Genkina N. K., Beletskaja I. P., Reutov O. A.: Izv. Akad. Nauk SSSR 187, 807 (1969).
9. Hrnčiar P., Szemes F.: Unpublished results.
10. Valter S. P., Nejland O. J.: Izv. Akad. Nauk Latv. SSR, Ser. Chim. 1964, 185.
11. Furdík M., Hrnčiar P.: Chem. zvesti 14, 44 (1960).

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