On phthalides and 1,3-indandiones. LI.
The rate of rearrangement of 3-(4-X-1-naphthylmethylene)phthalides to 2-(4-X-1-naphthyl)-1,3-indandiones

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The rate of rearrangement of eight 3-(1-naphthylmethylene)phthalides substituted in naphthalene ring at the 4 position to 2-(1-naphthyl)-1,3-indandiones with sodium methoxide in methyl alcohol was investigated spectrophotometrically. The rate constants ($\log k'$) obtained by extrapolation of the dependence of $\log k$ of the second-order reaction upon the concentration of methoxide to its zero concentration were correlated with σ substituent constants. Parameters of the regression line $\log k' = 2.155 \sigma - 2.192$ agree, within the experimental error, with the parameters of the corresponding dependence for the rearrangement of 3-(X-phenylmethylene)phthalides $\log k' = 1.886 \sigma - 2.321$.

In our previous paper [1] we compared the rate of rearrangement of *m*- and *p*-substituted 3-(X-phenylmethylene)-6-azaphthalides to 2-(X-phenyl)-5-aza-1,3-indandiones by sodium methoxide in methanol with the corresponding reaction of 3-(X-phenylmethylene)phthalides. This reaction was studied in detail by *Creamer, Fischer,* and *Vaughan* [2]. We found that the influence of nitrogen in the rearrangement of azaphthalides appears in both the increase of $\log k_0$ by a unit as compared with phthalides and the decrease in slope ϱ by 37%. On the basis of these findings and by comparing the obtained results with other papers we proposed the cyclization of a five-membered ring as the rate-determining step of rearrangement.

The present paper deals with the rate of rearrangement of 3-(4-X-naphthylmethylene)-phthalides (*A*) to 2-(4-X-1-naphthyl)-1,3-indandiones (*B*; see Scheme 1) under the same conditions as in [1]. In paper [2] the ester and pseudo ester of the *o*-phenylacetylbenzoic acid are considered as substances which are by-products as well as intermediates at the formation of indandiones from arylmethylenephthalide. Therefore we prepared ester *C-3* and pseudo ester *D-3* of 2-(1-naphthylacetyl)benzoic acid and studied the rate of rearrangement of these compounds to the derivative *B-3*.

Experimental

The working procedures and the way of the interpretation of results are thoroughly described in [1].
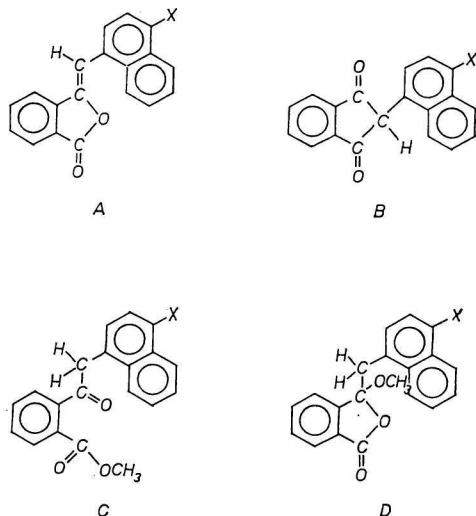
Scheme 1

Six of eight 3-(4-X-1-naphthal)phthalides under study had been already described and we prepared them by methods reported in [3—5].

3-(4-Methyl-1-naphthal)phthalides (*A*-2) and 3-(4-methoxy-1-naphthal)phthalides (*A*-1), previously not described, were prepared by the Gabriel modification of the Perkin reaction from phthalic anhydride and 4-methyl-1-naphthylacetic acid or 4-methoxy-1-naphthylacetic acid catalyzed by potassium acetate under the same conditions as employed in the preparation of other naphthalphthalides [3].

3-(4-Methyl-1-naphthal)phthalide forms bright yellow crystals from ethanol—chloroform. M.p. 184—186°C (Kofler).

For $C_{20}H_{14}O_2$ (286.11) calculated: 83.88% C, 4.93% H; found: 84.05% C, 4.98% H. Infrared spectrum (nujol): $\nu(C=O)$ 1720 cm^{-1}, $\nu(C=C)$ 1628 cm^{-1}.

3-(4-Methoxy-1-naphthal)phthalide yields yellow crystals from ethanol—chloroform. M.p. 191—193°C (Kofler).

For $C_{20}H_{14}O_3$ (302.11) calculated: 79.44% C, 4.67% H; found: 79.65% C, 4.72% H. Infrared spectrum (nujol): $\nu(C=O)$ 1720 cm^{-1}, $\nu(C=C)$ 1628 cm^{-1}.

Methyl 2-(1-naphthylacetyl)benzoate (*C*-3) was prepared from 2-(1-naphthylacetyl)-acetic acid (0.01 mole) and diazomethane (0.02 mole) in ethereal medium. Yield 80%. The ester forms colourless crystals of m.p. 78—79°C (Kofler).

For $C_{20}H_{16}O_3$ (304.12) calculated: 78.94% C, 5.26% H; found: 80.55% C, 5.31% H.

Chemical grade methanol was dried with magnesium and rectified on a column with 30 theoretical plates. A stock solution of *ca.* 1 M sodium methoxide was prepared by dissolving the appropriate amount of sodium in dry methanol. Molarity was determined by titration with 1 M sulfuric acid.

Apparatus and equipment

The changes in absorbances in dependence on time were measured by recording the spectrum in the visible region (700—360 nm) by an automatic system consisting of

Perkin—Elmer, Model 450 spectrophotometer, DDR-1C device for the spectrum recording in the digital form on punched tape and a device for the digital time recording [1]. Further processing of the records and computations were performed on a Gier (Regnezentralen) digital computer using ALGOL 60 language (modification Gieralgol IV).

Experimental conditions of rearrangement and data processing

The spectra of the reaction mixture associated with the formation of anion of the indandione B (absorption increase) were recorded as time dependent in the whole visible region and digital recording was made near the absorption maximum (440 nm). The cell thickness was 1 cm, temperature $20.0 \pm 0.1°C$. Vectors A_i and T_i (at constant wavelength g) were chosen from the records of absorbance and time (matrices A_{ig} and T_{ig}) for individual values i at selected wavelengths $g = 1, 2 \ldots 5$. These vectors were used in the calculation of the second-order rate constant according to the following relationship

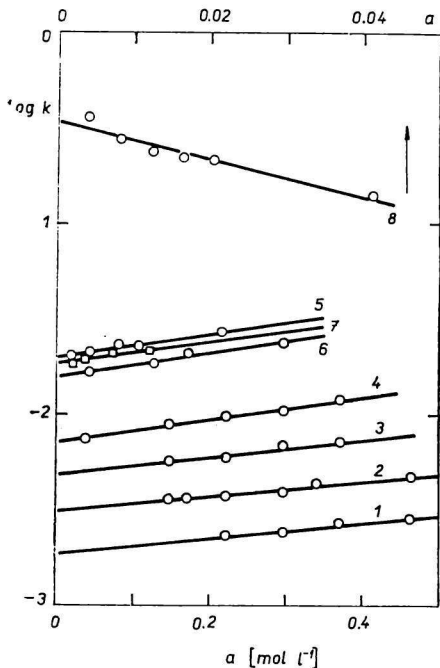$$k = -\frac{2.303}{(a-b)t} \log \frac{A_\infty - A \cdot b/a - A_0(1 - b/a)}{A_\infty - A} , \qquad (1)$$

Fig. 1. Dependence of the rate constants of rearrangement of 3-(4-X-1-naphthylmethylene)phthalides (A) to anions of 2-(4-X-1-naphthyl)-1,3-indandiones (B) on the methoxide concentration.

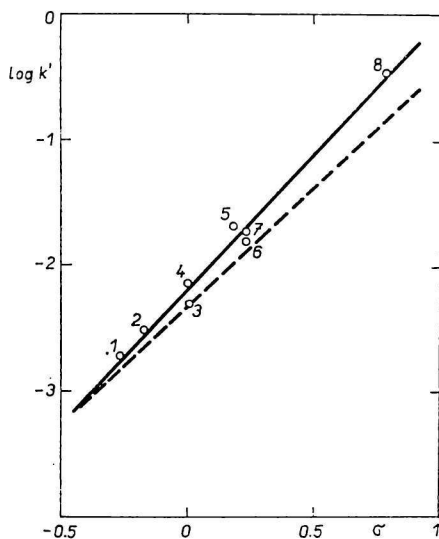The numbering of compounds is identical with that in Table 1.

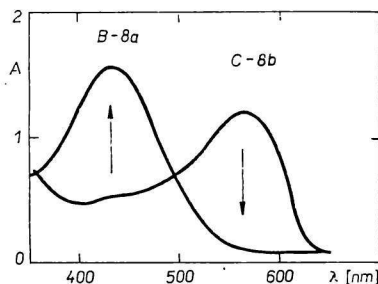Fig. 2. Dependence of the rate constants of rearrangement of 3-(4-X-1-naphthylmethylene)phthalides (———) and 3--arylmethylenephthalides (- - - -) on the σ substituent constant.

The numbering of compounds as in Table 1.

where k [mol^{-1} l s^{-1}] is the rate constant, a and b [mol l^{-1}] the initial concentration of methoxide and phthalide, respectively, A_∞ the absorbance at wavenumber g and time $t \to \infty$ (limit absorbance), A_0 the absorbance at the same wavenumber g in time $t = 0$ (A_0 obtained by extrapolation of the dependence A on t), A and t are the respective elements of vectors $\mathbf{A}_i$ and $\mathbf{T}_i$.

Fig. 3. Spectra of the reaction mixture of the rearrangement of 3-(4-nitro-1--naphthylmethylene)phthalide (A-8) in the visible region.
The spectra are denoted according to Scheme 2.

The relationship (*1*) was derived [1] from the known expression for the rate constant of the second-order reaction assuming the linear dependence of absorbance of the mixture of compounds A and B anions on their concentration. The application of this relationship to the rate constant of the second-order reaction was not verified in the mentioned case; but it was verified in the study of rearrangement of 3-(X-phenylmethylene)-phthalides [1, 2], *i.e.* the related compounds.

The A_∞ values corresponding to the final concentration of the anion of indandione B were between 1.4 and 1.6. The absorbance measurements were accurate to ± 0.001, the accuracy of the time measurements 0.5 s, standard deviation of the rate constant being $0.5-2\%$. The number of records of individual measurements $15-40$. The value of log k in each measurement was obtained as an average of five values for $g = 1, 2 \ldots 5$, calculated from experimental points A and t, for which the logarithm of fraction in relationship (*1*) was lower than 1.

Other experimental data are evident from Tables $1-3$ and Figs. $1-3$.

Results and discussion

The position of long wavelength absorption band of anion B (being formed in the rearrangement) similarly as in a series of 2-phenyl-1,3-indandiones and 2-phenyl-5-aza--1,3-indandiones [1], depends on the substituent X. If compared with these compounds, the slope of dependences of the band position upon the σ substituent constant in the case of 2-(1-naphthyl)-1,3-indandiones is approximately half. Since the band position underwent only a small change and the band was broad, we were unable to determine accurately the dependence of $\lambda_{\max}$ on σ. The molar absorptivity of the long wavelength band in dependence on substituent shows still smaller changes than with the compounds studied in [1]. Its value does not depend on the methoxide concentration. It is the nitro derivative (B-8; Table 1) that exhibits a markedly higher absorptivity, similarly as is the case with 2-phenyl-1,3-indandiones; this is certainly caused by the $-M$ effect of the nitro group, which will manifest itself in the conjugation with free electron pair of the carbon atom in the 2 position of the indandione ring (structure B-8*a* in

Table 1

Logarithms of the rate constants (log k') of the rearrangement of 3-(4-X-1-naphthal)-phthalides (A) and spectral data of the reaction products (B)

Compound (A)	X	σ	σ^0	log k [a]	S (log k') [b]	[mol CH_3ONa l^{-1}] [a]	Ayx [c]	Anion B	
								λ_{max} [nm]	ε_{max} [mol^{-1} l cm^{-1}]
1	CH_3O	-0.27	-0.12	-2.730	0.039	$0.22-0.46$	0.392	445	1834
2	CH_3	-0.17	-0.15	-2.516	0.023	$0.15-0.46$	0.396	442	1954
3	H	0.00	0.00	-2.319	0.046	$0.15-0.37$	0.457	440	1938
4	$NHCOCH_3$	0.00	0.02	-2.152	0.024	$0.04-0.37$	0.585	438	1930
5	I	0.18	0.27	-1.702	0.015	$0.02-0.2?$	0.604	435	2016
6	Cl	0.23	0.27	-1.804	0.026	$0.04-0.30$	0.624	437	2005
7	Br	0.23	0.26	-1.733	0.018	$0.02-0.12$	0.573	436	1978
8	NO_2	0.78	0.82	0.467	0.052	$0.004-0.04$	-9.906	432	5400

a) Rate constants extrapolated to the zero methoxide concentration; *b*) standard deviation of log k'; *c*) slope of dependence log $k = Ayx\ a + \log k'$.

Initial concentration of phthalides A was 7.5×10^{-4} M for $1-7$ and 2.8×10^{-5} M for 8.
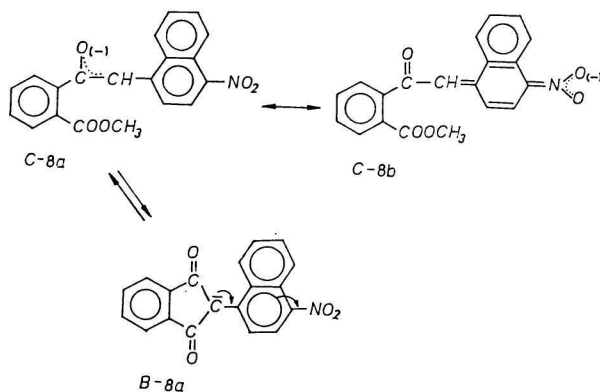
Scheme 2

Scheme 2). The starting phthalides A-$1-A$-7 do not absorb in the visible region above 400 nm; on the other hand, the nitro derivative (compound A-8) shows, when the reaction mixture is being prepared, an intense band at 563 nm. The intensity of this band decreases during reaction at the same rate as the band intensity of the anion of indandione B-8 at 432 nm increases. It concerns the conversion of anion C-8a or C-8b to B-8a anion through indandione B-8, which does not manifest itself in the spectrum (see detailed scheme of the proposed reaction mechanism in [1]).

Experimental results of the dependence of log k on a (Fig. 1) are satisfactory and provide us with sufficiently exact values of log k extrapolated to $a = 0$. Whereas with compounds $1-7$ the slope of dependence of log k on a was positive (the rate of rearrangement increases with the increasing methoxide concentration; Table 1), the slope of the nitro

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derivative (compound 8) was negative, *i.e.* the reaction rate decreased with the increasing methoxide concentration.

The negative slope of dependence of log k on a is ascribed mainly to the fact that with the increasing methoxide concentration also the interaction dipole—ion probably increases, which leads to the formation of the structure *C*-8*b*, *i.e.* to the transmission of the free electron pair and thus to the decrease in the reaction rate.

Table 2

Parameters of Hammett correlation for the rearrangement of naphthalphthalides (*A*) and benzalphthalides [1]

Compounds	Omitted points No.	ϱ	$S(\varrho)$	$\log k_0$	$S(\log k_0)$	r
			Correlation with σ			
Naphthalphthalides		2.155	0.103	−2.192	0.036	0.993
	8	2.015	0.184	−2.194	0.014	0.980
Benzalphthalides		1.886	0.109	−2.321	0.076	0.971
			Correlation with σ^0			
Naphthalphthalides		2.212	0.122	−2.306	0.059	0.991
	8	2.120	0.238	−2.303	0.049	0.970
Benzalphthalides		1.993	0.077	−2.387	0.063	0.987

Correlations of log k with σ and σ^0 constants of substituent X (Fig. 2, Table 2) justify to draw conclusion that the substituent effect on the transition state of the reaction is transferred through the naphthalene moiety in the same measure as through the benzene moiety. It becomes evident especially after eliminating the value for the nitro derivative in correlation with naphthalphthalides, when the ϱ constants in both series of compounds agree within the standard deviations. The differences in log k_0 in both series are more marked (which would be indicative of slightly higher reactivity of 1-naphthalphthalides), but only in correlation with σ^0 constants. When correlated with Taft σ^0 constants [6] the log k_0 values are again close. Since only a few compounds have been studied in a series of 1-naphthalphthalides, it cannot be rationalized that log k_0 values are different in both series.

Table 3

Rate constants of the rearrangement of methyl ester *C*-3 and pseudo ester *D*-3 of 2-(1-naphthylacetyl)benzoic acid

CH₃ONa [mol l⁻¹]	log k [mol⁻¹ l s⁻¹]		
	Ester C-3	Pseudo ester D-3	Naphthalphthalide[a] A-3
0.165	−2.2583	−2.2580	−2.2436
0.329	−2.1947	−2.1946	−2.1686

a) Calculated according to Table 1 for compound 3.

This is in line with [7]. In this paper the authors found for the dependence of the carbonyl stretching vibration of the naphthalphthalides upon the σ value a relationship $\nu(C=O) = 11.09\ \sigma + 1781.4\ \text{cm}^{-1}$ and for analogous dependence of p- and m-substituted benzalphthalides the relationship $\nu(C=O) = 12.02\ \sigma + 1782.2\ \text{cm}^{-1}$. They stated that the transmission of the substituent effects on the carbonyl group through both aromatic systems is the same. If, basing on [1, 2], we consider the cyclization of the C anion of ester C (or C-8b anion) as the rate-determining step and if we assume that the substituent X affects mainly the electron density on the carbon neighbouring naphthyl or phenyl but also on the carbonyl carbon of the ester group, then it may be stated that the replacement of phenyl by 1-naphthyl will not manifest itself either on the change of the reaction rate or on the transmission of the effects of substituents X.

The rate constants of rearrangement of ester C-3 and pseudo ester D-3 of 2-(1-naph-thylacetyl)benzoic acid to 2-(1-naphthyl)-1,3-indandione B-3 (Table 3) are very close to the constants of rearrangement of 1-naphthalphthalide A-3 to B-3. Also these values provide evidence for cyclization as the rate-determining step (a detailed scheme of the mechanism of rearrangement is in [1]).

A comparison of the thermodynamic parameters of the rearrangement of benzal-phthalides, benzalazaphthalides, 1-naphthalphthalides, and some other compounds will be the subject of a separate communication.

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