VELOCITY OF REARRANGEMENT
OF ortho-SUBSTITUTED 3-(X-BENZAL)PHTHALIDES
INTO 2-(X-PHENYL)-1,3-INDANEDIONES AND STUDY
OF ortho-EFFECT

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Velocity of the second order rearrangement of ortho-substituted 3-(X-benzal)phthalides into respective 2-(X-phenyl)-1,3-indanediones by action of methanolic sodium methoxide has been studied spectrophotometrically. The values of logarithm of the rate constant obtained by extrapolation of the concentration dependences to zero concentration of methoxide have been correlated with σ, σ^0, σ^+, $\mathscr{F}$, $\mathscr{R}$, and E_s constants of the substituents and with the Charton v constant for the ortho-substituted derivatives. The obtained dependences log k vs the mentioned constants have been compared with the corresponding dependences of the rearrangement of the meta- and para-substituted 3-(X-benzal)phthalides into the respective 3-(X-phenyl)-1,3-indanediones. Transmission of the substituent effect on the reaction centre is almost the same from ortho and from para positions. Possible ortho-effect and steric hindrance of the substituents have been followed.

The previous papers[1−3] dealt with influence of X on rate and mechanism of rearrangement of meta and para-substituted 3-(X-benzal)phthalides (further denoted as meta- and para-substituted benzalphthalides), 3-(4′-X-1′-naphthal)phthalides and meta- and para-substituted 3-(X-benzal)cinchomerides into the respective derivatives of 2-(X-phenyl)-1,3-indanedione (further denoted as para- and meta-substituted indanediones) and 5-aza-1,3-indanediones, respectively, by action of methanolic sodium methoxide. For the correlation the rate constants were obtained by extrapolation of linear dependences log k vs ionic strength (methoxide concentration) to zero ionic strength. In the mentioned reports dependence between log k and the Taft σ^0 or the Hammett $\sigma_{m,p}$ constants was found. The paper[4] deals with characteristics of the long-wave band, with dependence between extent of conjugation and intensity of the band, with dependence of the long-wave band position and the substituent character, and with possible correlation of wave-number of this band with the Hammett substituent constants type $\sigma_{UV, K-ortho}$ in the series of ortho- and para-substituted indanediones, benzalphthalides and benzaldithiaphthalides. Position of this band in some derivatives was calculated by quantum-chemical calculations of spectra of substituted benzalphthalides using the SCF MO CI method in PPP approximation[5].

Preparation of the *ortho*-substituted benzalphthalides with the aim of study of the *ortho*-effect[4,6] made us to investigate effect of the substituent X on the reaction centre in the rearrangement of the *ortho*-substituted benzalphthalides into *ortho*-substituted indanediones.

EXPERIMENTAL

The procedures and data treatment are given in detail elsewhere[2]. The *ortho*-, *meta*- and *para*-substituted benzalphthalides were prepared according to refs[4,6] and purified by column chromatography and crystallization. The melting points agreed with the literature data[4,6]. Methanol was dried over magnesium and rectified with a 30 plates column. The spectra were measured in visible region (700—360 nm) using an automatic system consisting of a Perkin–Elmer spectrophotometer model 450, a DDR-1C apparatus for recording of the spectra and time data of the corresponding absorbances in numerical form on punched tape. The spectral and time data were converted to rate constants with a Siemens 4004/150 computer.

Experimental Conditions and Treatment of Results

Time dependence of the spectra of the reaction mixture was recorded within the whole visible region and recorded numerically near the absorption maximum (435 nm) using 1 cm cells at $20.0 \pm 0.1°C$. The limit absorbance values of the reaction mixture were reached either in the proper kinetic measurement, or they were measured separately after a longer time (twice in each experiment) the cell being filled with the rest of the reaction mixture kept in thermostat at the given reaction temperature. When following the reactions we measured 60 to 100 absorbance data within 75 nm in the vicinity of the absorption maximum of the reaction product in visible region. From the absorbance-time records (A_{ig} and T_{ig} matrices) of the individual records i at the chosen wavelengths $g = 1, 2 \ldots 5$ evaluated by the computer we selected the vectors A_i and T_i at the constant g. These data were used for calculation of the second order rate constant using the relation

$$k = \frac{2.303}{(a-b)\,T_i} \log \frac{A_{\lim} - A_i \cdot (b/a) - A_p(1 - (b/a))}{A_{\lim} - A_i},$$

where k (mol^{-1} dm^3 s^{-1}), a and b (mol dm^{-3}), $A_{\lim}$ and A_p stand for the rate constant, initial methoxide and phthalide concentrations, absorbances at the wave-number g at the time $T \to \infty$ and $T = 0$, respectively, the last value being determined by extrapolation in the dependence A_i *vs* T_i. The $A_{\lim}$ values corresponding the resulting concentration of indanedione anion were within the interval 1·4 to 1·6. Accuracy of the absorbance and time measurements was ± 0.001 and 0·5 s, respectively, standard deviation of the rate constant was 0·5 to 2%. Number of records in the individual measurements was 15 to 40. The other experimental conditions are given in Table I.

As the rearrangement rate constant of the studied compound series depended on ionic strength (methoxide concentration), we calculated the log k value extrapolated to zero methoxide concentration for each derivative. Slope of dependence log k *vs* a was positive and slightly increased with increasing substituent constant (from value 0·5 to 2·2). The substituent constants σ were taken from ref[7], σ^0 from ref[8], σ^+ from ref[9], and ν from ref[10–15]. The two-parameter correlations were calculated with a Siemens 4004/150 computer. The σ^* and E_s constants were taken from ref[12], $\mathscr{F}$ and $\mathscr{R}$ from ref[13].

RESULTS AND DISCUSSION

UV spectra of the starting phthalides *I* show a marked long-wave band in the region 330 nm, connected with $\pi \rightarrow \pi^*$ transition of the whole conjugated system. Existence of this band and its position are due to participation of the phenyl ring in conjugation with the phthalide residue. Then the substituents in the phenyl ring affect position of this band, too. Changes in the band position of the other substituted benzal-phthalides are less marked than those of the *para*-substituted derivatives. Also molar absorptivities of the *para*-substituted derivatives have higher values which is obviously due to change in the transition moment[4]. Dependence of the band position on the substituent constants σ could not be evaluated quantitatively[4]. In contrast to anions of the rearrangement products *III*, the starting phthalides *I* have no absorption band in visible region. The relatively constant value of the molar absorptivity of the band of the reaction product *III* (Table I) obviously indicates weak influence of substituents on the values of the transition moment of the respective transition, indicating also that concentration of the reaction product in the reaction equilibrium is close to that of 2-(X-phenyl)-1,3-indanedione *III* anion, which corresponds to quantitative course of the reaction. Molar absorptivity of the long-wave band of the *ortho*--substituted derivatives shows even smaller changes in dependence on substituents than that of the *para*-substituted derivatives (Table I). Not even the *o*-nitro derivative shows higher molar absorptivity as compared with the other derivatives, which contrasts with the *p*-nitro derivative having much higher absorptivity value.
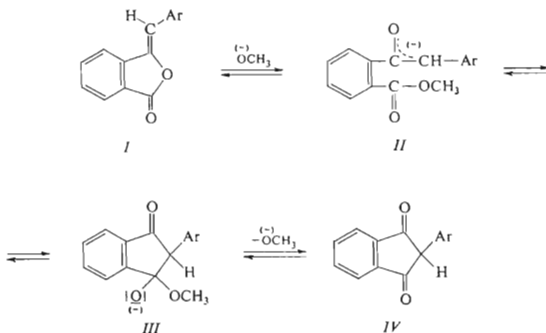
The constant shift of the band maximum of the rearrangement product towards lower wavelengths by about 25 nm (in the series of the *ortho*-substituted derivatives)

is obviously due to lowering of conjugation of the phenyl ring with the rest of the molecule, which is due to steric affect of the *ortho* substituents or, possibly, to other interactions with the carbonyl group. This is markedly seen with the nitro derivatives, where the reaction rate is much higher with the *para*-derivative than with the *ortho*--derivative (Table I).

On basis of the refs[2,3] giving detailed rearrangement mechanism of the *meta*- and *para*-substituted derivatives it is presumed that the rate-limiting step of the rearrangement consists in cyclization of the C-anion of the ester *II*. As it is seen from

TABLE I

Rate Constants (log k) and Spectral Data of Reaction Product *III* of Rearrangement of X-Benzal-phthalides *I*

Compound[a]	X	log k^b	S (log k)	CH_3ONa mol dm^{-3}	λ_{max} nm	ε_{max} mol^{-1} dm^3 cm^{-1}
1	H	−2·491	0·022	0·006—0·10	461	1 595
2	2′-OCH$_3$	−3·219	0·028	0·006—0·10	440	2 122
3	2′-CH$_3$	−2·755	0·012	0·006—0·10	437	2 107
4	2′-F	−2·257	0·037	0·006—0·10	436	2 129
5	2′-Cl	−1·988	0·016	0·006—0·10	430	2 142
6	2′-Br	−1·927	0·009	0·006—0·10	430	2 023
7	2′-I	−1·866	0·019	0·006—0·10	428	2 133
8	2′-NO$_2$	−1·342	0·012	0·006—0·05	418	2 158
9	4′-NH$_2$	−2·909^c	0·000	0·05 —0·21	475	1 510
10	4′-OCH$_3$	−2·686^c	0·011	0·02 —0·10	472	1 690
11	4′-CH$_3$	−2·586^c	0·012	0·01 —0·10	465	1 810
12	4′-F	−2·280^c	0·016	0·006—0·10	463	1 830
13	4′-Cl	−1·904^c	0·017	0·006—0·03	460	1 830
14	4′-Br	−1·842^c	0·024	0·006—0·03	459	1 850
15	4′-I	−1·796^c	0·000	0·006—0·05	458	1 810
16	4′-NO$_2$	−0·571^c	0·048	0·002—0·006	439	23 300
17	3′-CH$_3$	−2·460^d	—	—	—	—
18	3′-OCH$_3$	−2·360^c	0·060	0·01 —0·10	461	1 810
19	3′-F	−1·815^c	0·038	0·006—0·03	457	1 870
20	3′-Cl	−1·636^d	—	—	—	—
21	3′-Br	−1·659^c	0·049	0·006—0·03	454	1 810
22	3′-NO$_2$	−0·996^c	—	—	—	—

[a] Initial concentration 7·5 . 10^{-4}M; [b] for zero methoxide concentration; [c] taken from ref.[2]; [d] taken from ref.[1].

the measurement results of the rearrangement rate of the *ortho*-substituted phthalides (Table I) the rearrangement velocity depends on the substituent character, which is similar with the case of *meta*- and *para*-substituted derivatives. From comparison of log k_0 it is seen that the reaction rate in the series of *ortho*- and *meta*-substituted derivatives is somewhat lower than that of the corresponding *para*-substituted derivatives (Table II).

Satisfactory common correlation of log k of the *ortho*-, *meta*- and *para*-substituted derivatives are found with the σ and σ^0 constants (Table II). Omission of the 2-OCH$_3$, 4-NH$_2$, and 4-NO$_2$ derivatives in the correlations has no substantial effect on the correlations results. These results justify the conclusion that the substituent effect is transferred from the *ortho* position in about the same way as that from the *para* position. The only exception is nitro group showing significantly greater difference between the reaction rates of the *para* and *ortho* isomers. *o*-Nitrobenzalphthalide or anion of methyl 2-((2-nitrophenyl)acetyl)benzoate exhibit a weaker M- effect than anions of methyl 2-((4-nitrophenyl)acetyl)benzoate or 2-((4-nitro-1-naphthyl)-acetyl)benzoate in which the effect causes the free electron pair to be shifted from

TABLE II
Statistical Results of One-Parameter Linear Dependences

Correlation	Compound[a]	ϱ	S, ϱ	log k_0	S, log k_0	r
	o-X	1·728	0·242	—2·455	0·089	0·946
	p-X	1·667	0·202	—2·179	0·026	0·952
σ	*m*-X	1·972	0·149	—2·429	0·105	0·986
	o-, *m*-, *p*-X	1·671	0·139	—2·310	0·097	0·937
	o-X	1·747	0·265	—2·554	0·139	0·937
	p-X	1·963	0·147	—2·349	0·054	0·981
σ^0	*m*-X	1·951	0·098	—2·400	0·067	0·994
	o-, *m*-, *p*-X	1·875	0·133	—2·399	0·114	0·959
	o-X	1·269	0·141	—2·234	0·001	0·965
	p-X	1·043	0·207	—1·969	0·083	0·885
σ^+	*m*-X	1·978	0·116	—2·413	0·079	0·991
	o-, *m*-, *p*-X	1·107	0·122	—2·088	0·016	0·896

[a] For *o*-X we used the corresponding σ constants of the *p*-substituents; *o*-X = *ortho*-substituted 3-(X-benzal)phthalides, *m*-X = *meta*-substituted 3-(X-benzal)phthalides; *p*-X = *para*-substituted 3-(X-benzal)phthalides.

carbon to oxygen atoms of the nitro group, as we explained in the report[3]. This statement is also confirmed by the measured values of electronic spectra of anions of the given esters. The o-derivatives give good correlation results with the σ^+ constants (Table II). With exception of o-methoxy derivative, they also correlate well with the σ^0 constants ($r = 0.969$). The best correlation results with the σ, σ^0 and σ^+ constants are obtained from the *meta* derivatives ($r = 0.986$; 0.994; and 0.991, respectively), which is obviously due to their lowest disturbation of the aromatic system. As the correlation results of log k of the *ortho* derivatives with the respective σ_p, σ_p^0 and σ_p^+ constants gave a relatively low correlation coefficient, we tried the correlations with the σ_m, σ_m^+ and σ_I constants which involve but small part of mesomeric effect. Unsatisfactory results of these correlations ($r = 0.853$; 0.894 and 0.758, respectively) obviously indicate that the *ortho* derivatives also show M-effect (with the halogen substituents). We have already shown that sterical hindrance deviates nitro group from the plane of phenyl nucleus whereby conjugation is disturbed and mesomeric effect is less important. This presumption is also confirmed by two-parameter correlation of log k of the *ortho*-substituted derivatives with E_s and σ^* constants taken from ref.[12]

$$\log k = -2.648 - 0.095E_s + 1.596\sigma^* ,$$

where $r = 0.942$; $s = 0.156$; $n = 7$. The computation program is modified to eliminate the most deviating points. After elimination of the nitro derivative $r = 0.997$; $s = 0.005$; $n = 6$. The second eliminated derivative was the iodo derivative. The methyl derivative was not eliminated due probably to operation of its hyperconjugation effect. From the given correlation it follows that the *ortho* derivatives also exhibit sterical effects to a small extent, as elimination of the points agrees with size order of the substituents. Of course, the correlation results with the Charton sterical v constants[15] and with E_s constants[12,26] were unsatisfactory ($r = 0.579$ and 0.714, respectively). When using $\mathscr{F}$ and $\mathscr{R}$ constants[13] we obtained the following results for the two-parameter correlation and extended Hammett equation of the *ortho*-substituted derivatives;

$$\log k = -2.476 \pm 0.171 + (0.993 \pm 0.223)\mathscr{F} + (1.660 \pm 0.634)\mathscr{R} ,$$

where

$$r = 0.920 ; \qquad s = 0.262 ; \qquad n = 8 .$$

After elimination of o-methoxy derivative (which has the strongest mesomeric effect in the given series) it was obtained:

$$\log k = -2.517 \pm 0.087 + (0.979 \pm 0.113)\mathscr{F} + (0.901 \pm 0.390)\mathscr{R} ,$$

where

$$r = 0.968 \; ; \quad s = 0.054 \; ; \quad n = 7 \, .$$

From this equation it follows that contributions of inductive and mesomeric effects are almost identical in contrast to the foregoing equation in which resonance effect was predominant.

Even though these two-parameter correlations have no decisive value due to small number of points, it is interesting to compare the order of elimination of the individual derivatives of the given series with the use of E_s and σ^* or $\mathscr{F}$ and $\mathscr{R}$ constants.

The correlation results of $\log k$ vs σ and σ^0 constants of the substituents X allow to make the conclusion that the substituent effects are transferred from the *ortho* position approximately in the same way as those from the *para* position. The slopes ϱ are positive also in case of the *ortho*-substituted derivatives, and values at the ordinate axis of the correlations do not substantially differ with the *ortho*, *meta* and *para* derivatives.

From the comparison of these values obtained from linear correlation $\log k_0$ vs σ and σ^0 constants (Table II) it can be stated that the rearrangement mechanism of the *ortho*-substituted benzalphalides is identical with that of *m*- and *p*-substituted benzalphthalides.

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