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CHLORINE SUBSTITUTED 2-(4'-DIMETHYLAMINOPHENYL)INDAN-1,3-DIONES AND THEIR DIMERS

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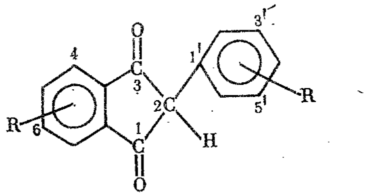
Cyclic β-diketones, the best known representative of which is 2-phenylindan-1,3-dione (Ia) and also its derivatives having substituents on the aromatic rings on the second carbon atom have various biological and chemical activities [1, 2].

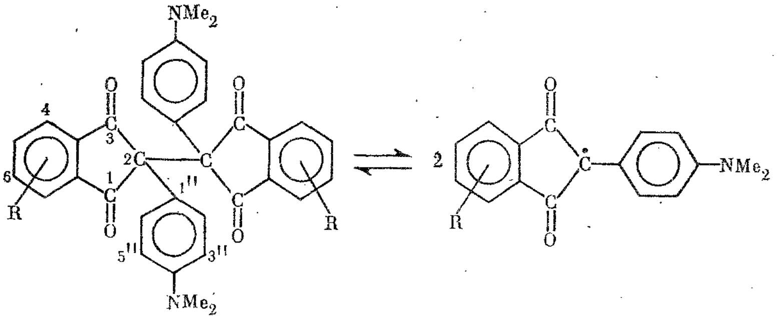
It has been shown that the introduction of a Cl atom into the phenyl or phthaloyl ring appreciably influences the nature of the biological action of the preparation [3].



(Ia-d)

R = R' = H (a); R = 4-Cl, R' = 4'-N(Me)$_2$ (b); R = 5-Cl, R'$_1$= 4'-N(Me)$_2$ (c); R = H, R' = 4'-N(Me)$_2$ (d)

In work [4] was established the strong inhibiting action of 2-(4'-dimethylaminophenyl)-indan-1,3-dionic free radicals generated by the decomposition of the dimer 2,2'(bis(4"-dimethylaminophenyl)indan-1,3-dione (IIa) in the low temperature oxidation reactions of hydrocarbons.



(IIa-c)

R = H (a), 4-Cl (b), 5-Cl (c).

In the work in question new 2-arylindan-1,3-diones (Ib, c) containing chlorine in the phthaloyl ring and the corresponding dimers (IIb, c) were synthesized.

Normally halogen substituted 2-arylindan-1,3-diones are obtained by an anhydride condensation method, i.e., heating the corresponding halophthalic anhydride in an arylacetic

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TABLE 1. IR-Spectra of Polychromic Molecules (Ib, c)

Compound	1500-1800 cm^{-1} interval	2200-2800 cm^{-1} interval
4-Chloro-2-(4'-dimethylaminophenyl)indan-1,3-dione. Red form	1510 o.s, 1536 s, 1581 m, 1601 m, 1646 m, 1704 o.w.	2200–2750 wide
The same*	1510 o.s; 1533 o.s, 1581 s, 1601 s, 1646 m, 1704 s, 1740 m	2480, 2573, 2702
5-Chloro-2-(4'-dimethylaminophenyl)indan-1,3-dione Red form	1510 o.s, 1570 o.s, 1610 m, 1660 s, 1704 m	2400–2750 wide
The same*	1502 o.s., 1526 o.s, 1553 s, 1600 s, 1650 s, 1704 m, 1740 w	2433, 2550, 2600–2730 wide
Black form	1510 s, 1570 s, 1610 o.s, 1650 s, 1704 w	2400–2750 wide
The same	1508 o.s, 1566 o.s, 1600 o.s, 1650 s, 1704 s, 1740 m	2400–2750 wide

*Measurements carried out after storage of the compounds for one year.

acid in an Ac_2O solution in the presence of Et_3N [4, 5]. (Ib, c) were obtained by a Dieckmann condensation according to an improved method [8]. For the synthesis of (Ib, c) the difficulty obtainable 4-chlorophthalide (III) and 5-chlorophthalide (IV) are necessary. Therefore in work [9] a method of synthesis of (IV) from 4-chlorophthalimide or 5-aminophthalide, which are obtainable in a few steps, is reported. We have proposed a new synthesis of chlorophthalides (IIIa, b) and (IV) in one step from the availalbe 3-chlorophthalic and 4-chlorophthalic anhydrides [10].

On reduction of 3-chlorophthalic anhydride by Zn dust in a mixture of HCl and AcOH a mixture of isomeric phthalides (IIIa, b) is formed.

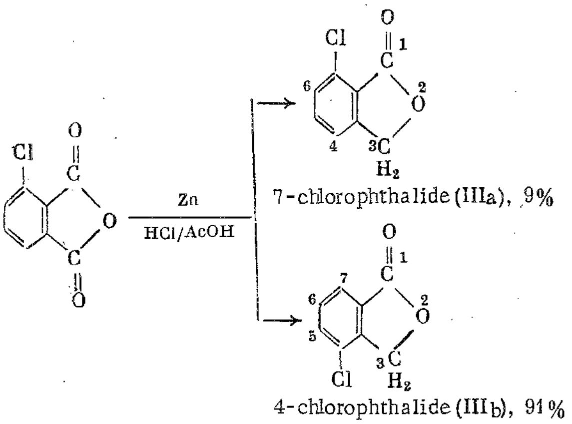
According to the GLC data the predominant compound in the mixture is the 4-chlorophthalide (IIIb) but the compound formed on longer standing is assigned the 7-chlorophthalimide (IIIa) structure. The compounds obtained were not separated inasmuch as both the isomeric phthalides (IIIa, b) form (Ib) on condensation.

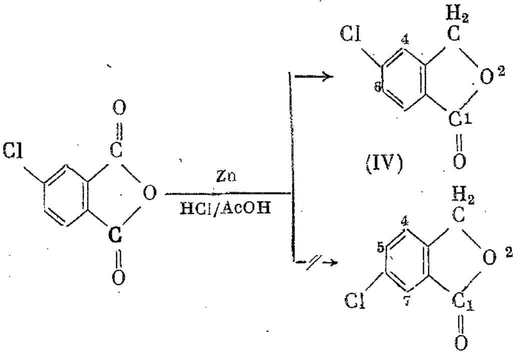
The reduction of 4-chlorophthalic anhydride under analogous conditions proceeds regioselectively with the formation of 5-chlorophthalide (IV), the structure of which was established by the PMR method.

The condensations of phthalides (IIIa, b) and (IV) with dimethylaminobenzaldehyde proceed smoothly with the formation of (Ib) and (Ic), which crystallize out of AcOH, forming bright red crystals. On heating to 90-100°C the red crystals of (Ic) change to a black color. On crystallizing from alcohol shining black crystals are formed. A similar occurrence of polychromism was found for compound (Id); in work [11] conditions are provided for obtaining three modifications: yellow, red, black. (See following page).

The red modifications of (Ib, c) and the black modification of (Ic) were studied by the IR spectroscopy method and the data obtained shown in the table. On comparison of the IR spectra obtained with the spectra of polymorphic modifications of (Id) it is evident that the spectra of the red modifications of (Ib, c) resemble the spectrum of the red modification of (Id) and that of the black modification of (Ic) resembles that of the black modification of (Id). Therefore the red modifications of (Ib, c) are internal salts and the black modification of (Ic) is a complex of an internal salt and the enol form [11]. On storage of (Ib, c) absorption bands appear in the IR spectra at 1704 and 1740 cm^{-1} ascribed to the antisymmetric and symmetric stretching vibrations of the carbonyl group. Thus (Ib and c) on standing gradually go over to the thermodynamically stable diketo form.

Dimers (IIb, c) were obtained by oxidizing basic aqueous-alcoholic solutions of (Ib, c) by ammonium persulfate [12]. They are compounds with bright yellow colors. The IR spec-





tra of these compounds is characterized by the intensity of the two absorption maxima of the carbonyl group at 1700 and 1737 cm^{-1}.

Solutions of dimers (IIb, c) in organic solvents as well as dimer (IIa) change to a yellow color caused by absorption of free radicals generated by the decomposition of (IIa, b, c).

EXPERIMENTAL

IR spectra were obtained on a Specord 76-IR spectrophotometer in KBr tablets; the PMR spectra on the Bruker WM-250 (250 MHz) in $CDCl_3$ with TMS as internal standard. GLC was carried out in Tsvet-5 chromatograph with a flame ionization detector, nitrogen flow rate 40 ml/min, column 700 × 3 mm with 15% squalane on Chromatone N-AW-DMCS (0.20-0.25 mm), temperature 160°C.

5-Chloro and 7-Chlorophthalides (IIIa, b). To a mixture of 73 g (0.4 moles) 3-chlorophthalic anhydride, 600 ml glacial AcOH, 320 ml conc. HCl and 100 ml of water was added 174 g (2.7 moles) of Zn dust with stirring during the course of 1 h. The mixture was stirred for 14 h at 90-95°C, filtered, neutralized with a saturated solution of Na_2CO_3 to pH 5. The residue was filtered off. Obtained 58.0 g (85%) of white crystals, mp 72-74°C (heptane). Found: C 56.46; H 3.02. $C_8H_5O_2Cl$. Calculated: C 57.00; H 2.99%. IR spectrum (ν, cm^{-1}): 1757 (C=O). PMR spectrum (δ, ppm) 5.31 s (CH_2), 7.3-7.9 m (aromatic H).

5-Chlorophthalide (IV). Analogously 55 g (0.3 moles) of 4-chlorophthalic anhydride in a mixture of 450 ml glacial AcOH, 240 ml conc. HCl, 75 ml of water was reduced by 130 g (2 moles) of Zn dust. Yield of (IV) 31.5 g (62%), mp 150-151°C (heptane) (compare mp 151.5°C [12]). Found: C 57.21; H 2.95%. $C_8H_5O_2Cl$. Calculated: C 57.00; H 2.99%. IR spectrum (ν, cm^{-1}) 1745 (C=O). PMR spectrum (δ, ppm): 5.32 s (CH_2), 7.53 s (H^4), 7.55 d (H^6, $J_{6,7}$ = 9 Hz), 7.89 d (H^7, $J_{7,6}$ = 9 Hz).

4-Chloro-2-(4'-Dimethylaminophenyl)Indan-1,3-dione (Ib). In 8 ml of dry ethyl acetate was dissolved on warming 2.43 g (0.015 moles) of a mixture of phthalides (IIIa, b) and 2.24 g (0.015 moles) of p-dimethylaminobenzaldehyde. A solution of MeONa was added (from 1.6 g (0.07 moles) of Na and 23 ml of MeOH), refluxed for 1 h, the solvent removed, the residue dissolved in 150 ml of water, treated with activated carbon, and filtered. The filtrate was acidified with HCl to pH 5. The precipitate of red color (sometimes formed with an admixture of the black modification) was filtered off. Yield of (Ib) 3.74 g (87%), mp. 167-168°C (AcOH), red crystals. R_f = 0.15 (Silufol; benzene/ethyl acetate (2:1)). Found: C 67.54;

H 4.74%. $C_{17}H_{14}O_2NCl$. Calculated: C 68.12; H 4.71%. PMR spectrum (δ, ppm): 2.96 s (CH_3), 4.23 s (H^2), 6.85 d ($H^{3'}$ and $H^{5'}$, J_o = 9 Hz); 7.10 d ($H^{2'}$ and $H^{6'}$, J_o = 9 Hz), 7.8 m (H^5 and H^6), 7.97 d (H^7, $J_{7,6}$ = 6 Hz).

5-Chloro-2-(4'-Dimethylaminophenyl)Indan-1,3-dione (Ic). In 18 ml dry ethyl acetate was dissolved, with heating, 4.86 g (0.03 moles) of 5-chlorophthalide (IV) and 4.48 g (0.03 moles) of p-dimethylaminobenzaldehyde, a solution of MeONa (from 3.2 g (0.14 moles) of Na and 46 ml MeOH) was added, the mixture refluxed 1 h, and worked up in a manner analogous to that of the previous synthesis. Yield of (Ic) 7.35 g (85%), mp 149-151°C (AcOH), red crystals. R_f = 0.12 (Silufol; benzene/ethyl acetate (2:1)). Found: C 68.14; H 4.96%. $C_{17}H_{14}O_2NCl$. Calculated: C 68.12; H 4.71%. PMR Spectrum (δ, ppm): 292 s (CH_3), 4.18 s (H^2), 6.69 d ($H^{3'}$ and $H^{5'}$, J_o = 9 Hz), 7.01 d ($H^{2'}$ and $H^{6'}$, J_o = 9 Hz), 7.83 d.d (H^6, $J_{6,7}$ = 9, $J_{6,4}$ = 2 Hz), 8.0 m (H^4 and H^7). On crystallization of (Ic) from alcohol, shining black crystals are formed, mp 154-155°C.

2,2'-Bis[4-Chloro-2(4"-Dimethylaminophenyl)Indan-1,3-dione] (IIb). In a solution of 0.6 g (15 mmoles) of NaOH in 15 ml water and 10 ml alcohol was dissolved with heating 0.6 g (2 mmoles) of (Ib). A hot solution of 0.90 g (4 mmoles) of ammonian persulfate in 15 ml water was added. The yellow precipitate was filtered off. Obtained 0.50 g (84%) of (IIb). It was crystallized from chloroform with addition of ethanol, mp 207-208°C dec R_f = 0.90 (Silufol; benzene/ethyl acetate (2:1)). Found: C 67.70; H 4.58%. $C_{34}H_{26}O_4N_2Cl_2$. Calculated: C 68.35; H 4.39%. PMR spectrum (δ, ppm): 2.95 s (CH_3), 6.62 d ($H^{3''}$ and $H^{5''}$, J_o = 9 Hz), 7.00 d ($H^{2''}$ and $H^{6''}$, J_o = 9 Hz), 7.6 m (H^5 and H^6), 7.8 m (H^7).

2,2'-Bis[5-Chloro-2-(4"-Dimethylaminophenyl)Indan-1,3-dione] (IIc). The (Ic), 0.6 g (2 mmoles) was oxidized in the same way as the above. Obtained 0.51 g (86%) in the form of a yellow powder. Crystallized from chloroform with the addition of ethanol, mp 202-203°C dec. R_f = 0.95 (Silufol; benzene/ethyl acetate (2:1)). Found: C 68.28; H 4.45%. $C_{34}H_{26}O_4N_2Cl_2$. Calculated: C 68.35; H 4.39. PMR spectra (δ, ppm), 2.95 s (CH_3), 6.61 d ($H^{3''}$ and $H^{5''}$, J_o = 9 Hz). 7.00 d ($H^{2''}$ and $H^{6''}$, J_o = 9 Hz), 7.66 d (H^6, $J_{6,7}$ = 9 Hz), 7.8 m (H^4 and H^7).

CONCLUSIONS

1. The possibility of using the Dieckmann condensation to obtain chlorosubstituted 2-(4"-dimethylaminophenyl)indan-1,3-diones has been shown.

2. We have discovered thermochromic behavior in the chlorosubstituted dimers which we obtained.

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