

Reactions of 2-halo-2-(Y-phenyl)-1,3-indandiones with anions of C-acids

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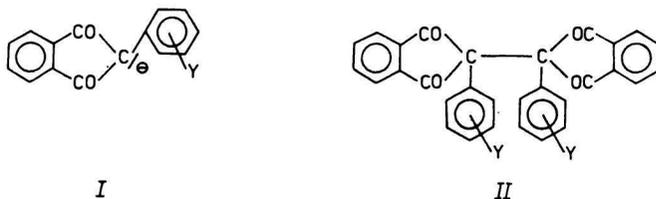
Reactions of 2-X-2-(Y-phenyl)-1,3-indandiones (X = Cl, Br; Y = H, *p*-NO₂, *p*-CH₃O, *m*-CH₃O) with anions of acetylacetone, ethyl malonate nitromethane, and 2-nitropropane were carried out. It was found that the starting indandione was converted during the reaction into the anion of 2-(Y-phenyl)-1,3-indandione (*I*) and bis-2-(Y-phenyl)-1,3-indandione (*II*). The ratio of the products *I* and *II* was dependent on X, C-acid, and the solvent.

Были осуществлены реакции 2-X-2-(Y-фенил)-1,3-индандионов (X = Cl, Br; Y = H, *p*-NO₂, *p*-CH₃O, *m*-CH₃O) с анионами ацетилацетона, этилмалоната, нитрометана и 2-нитропропана. Было найдено, что исходный индандион превращается в ходе реакции в анион 2-(Y-фенил)-1,3-индандиона (*I*) и бис-2-(Y-фенил)-1,3-индандиона (*II*). Отношение продуктов *I* и *II* зависит от X, C-кислоты и растворителя.

It is known that 2-halo-2-phenyl-1,3-indandiones afford with primary amines 2-R-amino-2-phenyl-1,3-indandiones [1—4]. We assume that the exchange of the halogen by alkylamine cannot be considered a nucleophilic substitution regarding the nature of the structural groupings in the molecule of the starting compound. Especially the reactions of 2-bromo-2-(4-nitrophenyl)-1,3-indandione with aniline and *o*- and *p*-anizidine, which gave the appropriate 2-arylamino-2-(nitrophenyl)-1,3-indandiones [4, 5] already at room temperature, affirmed our assumption. It was found further that in the reaction of 2-halo-2-(4-nitrophenyl)-1,3-indandione with diethylamine and *p*-aminobenzoic acid besides the substituted derivative, also bis-2-(4-nitrophenyl)-1,3-indandione was formed. This was the main product when the reaction was carried out with diisobutylamine, triethylamine or 2-naphthylamine [6]. Substitution reaction proceeded also between 2-halo-2-phenyl-1,3-indandiones and alkali thiocyanates [7]. When this reaction was carried out at higher temperature, besides 2-thiocyanato-2-(X-phenyl)-1,3-indandiones also bis-2-(Y-phenyl)-1,3-indandiones, which could represent also the main reaction product, were formed [8]. Ozol and coworkers [6] assumed on the basis of the results obtained in the reaction of

the mentioned 2-bromo-2-(4-nitrophenyl)-1,3-indandione with amines that substitution of halogen with alkylamino (arylamino) group in 2-halo-2-(Y-phenyl)-1,3-indandiones was a complicated mechanism where the first step was the bromination of amines on nitrogen with 2-bromo-2-(X-phenyl)-1,3-indandione as the bromination agent. To enlarge our knowledge on the properties of 2-chloro(bromo)-2-(Y-phenyl)-1,3-indandiones (Y = H, 4-NO₂, 3-OCH₃, 4-OCH₃) we carried out the reactions of these compounds with the following anions of C-acids: acetylacetone, ethyl malonate, nitromethane, 2-nitropropane. It is to be noted that the reactions of 2-halo-2-(Y-phenyl)-1,3-indandiones with C-acids were not studied so far.

We found that the starting 2-halo-2-(Y-phenyl)-1,3-indandione was converted in the presence of C-anions at the conditions mentioned in Experimental into two products: anion of 2-(Y-phenyl)-1,3-indandione (*I*) and bis-2-(Y-phenyl)-1,3-indandione (*II*) (Scheme 1)



Scheme 1

Isolation of the products *I* and *II* indicates that in the presence of C-anions the halogen is split off either as a cation or in the atomic form. As can be seen from the results presented in Table 1, the ratio of the products *I* and *II* changes in dependence on the nature of Y and the used C-anion. The electron-accepting NO₂ group on phenyl favours the cleavage of the halogen as a cation while the electron-releasing methoxy group in the position 4 on phenyl favours the cleavage of atomic chlorine (bromine). The effect of the substituent on the ratio of the formed products *I* and *II* corresponds to its electron properties and its position on phenyl because the amount of the product *II* decreases in the following order: *p*-OCH₃ < H < *m*-OCH₃ < *p*-NO₂. In the reaction of 2-bromo-2-(4-nitrophenyl)-1,3-indandione with the anion of acetylacetone in ethanol only one product, viz. 2-(4-nitrophenyl)-1,3-indandione, was isolated after acidifying the reaction mixture. On the basis of the results of gas chromatography and mass spectrometry of the separated products we assume that 2-bromo-2-(4-nitrophenyl)-1,3-indandione acted on acetylacetone as an electrophilic bromination agent. As bromoform and ethyl acetoacetate were proved to be present in the

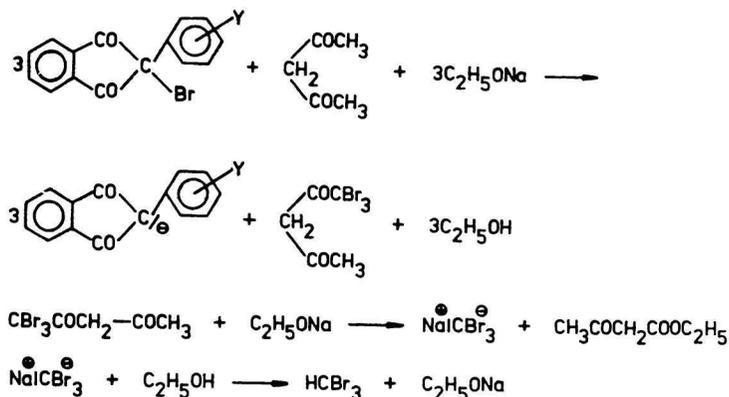
Table 1

 Dependence of yields (%) of 2-(Y-phenyl)-1,3-indandione (*I*) and bis-2-(Y-phenyl)-1,3-indandione (*II*) on C-acid

Starting compound		Acetylacetone		Ethyl malonate		Nitromethane		2-Nitropropane	
X	Y	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
Bromine	4-Nitro	90	—	70	15	70	15	70	15
Chlorine	4-Nitro	85	—	60	30	60	30	—	—
Bromine	4-Nitro	79	15	—	—	—	—	—	—
Bromine	H	68	20	15	80	—	—	—	—
Chlorine	H	58	31	—	—	—	—	—	—
Chlorine	3-Methoxy	45	38	—	98	—	—	—	—
Bromine	3-Methoxy	51	30	—	—	—	—	—	—
Bromine	4-Methoxy ^a	42	31	—	97	—	97	41	37
Chlorine	4-Methoxy	35	43	—	97	—	—	—	—

a) In xylene.

reaction products we assume that the methyl group of acetylacetone and its anion, respectively, was brominated. The formation of these products can be expressed by the following reactions (Scheme 2).



Scheme 2

The results in Table 1 show that the ratio of products *I* and *II* depends also on the used C-anion. With ethyl malonate, from 2-bromo-2-(4-nitrophenyl)-1,3-indandione also the product *II* was formed. Similar results gave also nitromethane and 2-nitropropane. The other effects are clear from the results presented in Table 1. It is to be noted further that the reaction proceeded differently when it was carried out without a C-anion, only in alcohol in the

presence of alcoholate. In this case neither *I* or *II* was formed [9]. The reaction of 2-chloro-2-(4-nitrophenyl)-1,3-indandione with the anion of acetylacetone was carried out also in xylene. The reaction proceeded analogously, only the ratio of products changed in favour of *II*. Products of nucleophilic substitution were not observed in these cases. Because the used C-anions are stronger nucleophilic reagents, it could not be assumed that 2-R-amino-2-phenyl-1,3-indandiones were formed from 2-chloro(bromo)-2-phenyl-1,3-indandiones by a nucleophilic substitution.

Experimental

Infrared spectra were measured on a Specord 75 spectrometer in the region of 500—3500 cm^{-1} using NaCl optics. The apparatus was calibrated by polystyrene foil, samples were measured in Nujol.

Mass spectra were measured on a GC/MS System 111 Variant MAT spectrometer using a column of 35% SE-30 on Superlioport; carrier gas was nitrogen, temperature gradient 20°C min^{-1} .

The starting 2-chloro- and 2-bromo-2-phenyl-1,3-indandiones were prepared after [1]; 2-chloro-2-(3-methoxyphenyl)-1,3-indandione and 2-chloro-2-(4-methoxyphenyl)-1,3-indandione were prepared by chlorination with sulfuryl chloride [10]; 2-bromo-2-(3-methoxyphenyl)-1,3-indandione and 2-bromo-2-(4-methoxyphenyl)-1,3-indandione were prepared by bromination with *N*-bromosuccinimide [11]; 2-chloro-2-(4-nitrophenyl)-1,3-indandione and 2-bromo-2-(4-nitrophenyl)-1,3-indandione were prepared after [12].

Reaction of 2-X-2-(Y-phenyl)-1,3-indandione with sodium salt of acetylacetone (Y = H, 3-OCH₃, 4-OCH₃, 4-NO₂; X = Cl, Br)

Into a three-necked 250 ml flask provided with a mechanic stirrer, reflux, and a separating funnel, dry ethanol (50 ml) and sodium (0.015 mol) were added. After the formation of the alcoholate, acetylacetone (0.01 mol) was added and then the starting indandione (0.01 mol) dissolved in dry ethanol (50 ml) was added slowly (1 h) at 40°C.

When Y = NO₂, a dark-red precipitate was formed, separated and dissolved in water. After acidifying with hydrochloric acid, 2-(4-nitrophenyl)-1,3-indandione was obtained; m.p. 214—217°C in accordance with the literature [12].

When X = H, 3-OCH₃, 4-OCH₃, a white precipitate of bis-2-(X-phenyl)-1,3-indandione was formed and crystallized from ethanol.

Bis-2-phenyl-1,3-indandione, m. p. 226—228°C in accordance with the literature [8].

Bis-2-(3-methoxyphenyl)-1,3-indandione, m.p. 230—232°C.

For C₃₂H₂₂O₆ (502.52) calculated: 76.48% C, 4.41% H; found: 76.31% C, 4.50% H; $\nu(\text{CO}) = 1710, 1734 \text{ cm}^{-1}$.

Bis-2-(4-methoxyphenyl)-1,3-indandione, m.p. 253—255°C.

For C₃₂H₂₂O₆ (502.52) calculated: 76.48% C, 4.41% H; found: 76.55% C, 4.30% H; $\nu(\text{CO}) = 1706, 1734 \text{ cm}^{-1}$.

The solvent was distilled off and the residue was extracted into benzene. The insoluble part was dissolved in water and after acidifying 2-(Y-phenyl)-1,3-indandione (Y = H, 3-OCH₃, 4-OCH₃) was obtained.

2-Phenyl-1,3-indandione, m.p. 144—145°C in accordance with the literature [1]; 2-(4-methoxyphenyl)-1,3-indandione, m.p. 153—154°C in accordance with the literature [13]; 2-(3-methoxyphenyl)-1,3-indandione, m.p. 117—118°C in accordance with the literature [14].

After evaporation the benzene extract was separated by gas-liquid chromatography and on the basis of mass spectra the following compounds were determined in the extract when 2-bromo-2-(Y-phenyl)-1,3-indandione was taken into the reaction: bromoform, ethyl acetoacetate, and the unreacted acetylacetone.

Analogous procedure was used in the reaction of 2-X-2-(Y-phenyl)-1,3-indandione with ethyl malonate, nitromethane, and 2-nitropropane. However, we failed to identify the bromination product in benzene extract.

Reaction of 2-bromo-2-(4-nitrophenyl)-1,3-indandione with acetylacetone in xylene

Into the prepared potassium salt of triphenylmethanol (1.5 g) in dry xylene (25 ml) acetylacetone (0.33 g; 3 mmol) and then 2-bromo-2-(4-nitrophenyl)-1,3-indandione (1.2 g; 1.5 mmol) dissolved in dry xylene (30 ml) were added from a separating funnel. The reaction mixture was stirred for 4 h at 40°C. The red-brown precipitate — potassium salt of 2-(4-nitrophenyl)-1,3-indandione — was separated and dissolved in water. After acidifying with hydrochloric acid 2-(4-nitrophenyl)-1,3-indandione (0.7 g, 79%) was obtained. The supernatant was evaporated and fractionated on silica gel using benzene and ethyl acetate (20:1) as eluent. The first portion obtained was triphenylmethanol and the second one contained bis-2-(4-nitrophenyl)-1,3-indandione; yield 0.15 g (17%), m.p. 252—254°C. The residue was not identified.

For C₃₀H₁₆N₂O₈ (532.45) calculated: 67.65% C, 3.02% H, 5.04% N; found: 67.49% C, 3.12% H, 4.95% N; $\nu(\text{CO}) = 1716, 1742 \text{ cm}^{-1}$.

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