

# Synthesis of new derivatives of 2-thio-1,3-indandione

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2-Alkylthio- and 2-arylthio-1,3-indandiones were prepared by new synthetic procedure from 2-bromo-1,3-indandione, ethyl 2-bromo-1,3-indandione-2-carboxylate, and sulfides and thiolates of alkali metals.

Получены 2-алкилтио- и 2-арилтио-1,3-индандионы посредством нового синтетического метода, исходя из 2-бром-1,3-индандиона, этил-2-бром-1,3-индандион-2-карбоксилата и сульфидов или тиолатов щелочных металлов.

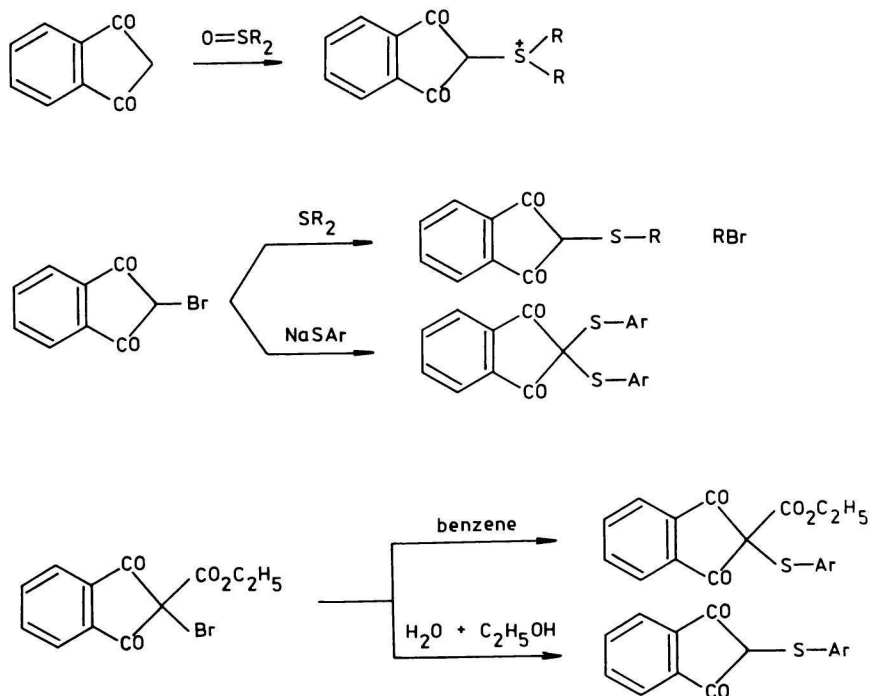
Continuing the syntheses of 1,3-indandione derivatives [1, 2], we focused our attention on the preparation of 2-sulfonium-1,3-indandionylides. Dibenzylsulfonium-1,3-indandionylide, dimethylsulfonium-1,3-indandionylide, and diethylsulfonium-1,3-indandionylide were prepared from dialkyl sulfoxides and 1,3-indandione by the procedure according to *Hochrainer* [3]. The reactions of 1,3-indandione with diphenyl sulfoxide, 4-nitrophenyl-4-methylphenyl sulfoxide, and 3-(phenylsulfinylmethylene)phthalide did not take place, only the starting compounds were isolated in each case.

The reaction of dialkyl or diaralkyl sulfides with 2-bromo-1,3-dicarbonyl compounds represents another way for the preparation of ylides of sulfur. *Hochrainer* prepared by this method sulfoniumylides of diesters of 1,3-dicarboxylic acids [4]. We found that this procedure with 2-bromo-1,3-indandione resulted in 2-alkylthio- and 2-aralkylthio-1,3-indandiones and not in 2-substituted sulfonium-1,3-indandionylides. The by-product of this reaction was bromoalkane. The reaction is significant for large-scale preparation of 2-alkylthio- and 2-aralkylthio-1,3-indandiones, since the yield of this reaction varies about 60 %.

We attempted to prepare 2-alkylthio- and 2-arylthio-1,3-indandiones by the reaction of 2-bromo-1,3-indandione with sodium benzyl sulfide, sodium methyl sulfide, and sodium thiophenolate. However, only the reaction with sodium thiophenolate afforded sulfur-containing indandione derivatives, namely 2,2-bis(phenylthio)-1,3-indandione and diphenyl disulfide.

The further starting compound for the preparation of 2-thio derivatives of 1,3-indandione was ethyl 2-bromo-1,3-indandione-2-carboxylate. In the reaction with sodium arenethiolate in addition to the main product, sodium salt of ethyl 1,3-indandione-2-carboxylate (60—75 %), 2-arylthio derivative of 1,3-indandione was isolated in 25—40 % yield. In this way, ethyl 2-phenylthio-1,3-indandione-2-carboxylate and ethyl 2-(4-methylphenylthio)-1,3-indandione-2-carboxylate were obtained in anhydrous benzene and 2-phenylthio-1,3-indandione and 2-(4-methylphenylthio)-1,3-indandione in aqueous-ethanolic medium.

The review of the reactions and reaction products is presented in Scheme 1.



Scheme 1

The results obtained are in agreement with the knowledge on the reactions of 2-bromo derivatives of 1,3-indandiones, both initial and 2-substituted. For example, *Flatov* [5] found that bromine can be split off from 2-bromo-1,3-indandione as a cation or a radical in dependence on the reaction conditions. Similar conclusions were arrived at by *Hrnčiar* [6] in studies of 2-aryl-2-halo-1,3-indandiones.

## Experimental

Infrared spectra were measured in paraffin oil on a Specord 75 IR (Zeiss, Jena) spectrophotometer in the range of 400—4000  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra of the compounds prepared were measured in DMSO (saturated solutions) on a Tesla BS 487 A spectrometer at  $\nu = 80$  MHz using tetramethylsilane as standard.

### *Dibenzylsulfonium-1,3-indandionylide (I)*

The mixture of 1,3-indandione (6.8 mmol) and dibenzyl sulfoxide (11 mmol) in acetic anhydride (5  $\text{cm}^3$ ) was stirred at 80 °C for 7 h under conditions excluding air moisture. To the cooled mixture diethyl ether (3  $\text{cm}^3$ ) was added dropwise and the precipitate was recrystallized from methanol. M.p. = 184 °C, yield = 63 %.

For  $\text{C}_{23}\text{H}_{18}\text{O}_2\text{S}$  ( $M_r = 358$ )  $w_i$ (calculated): 77.08 % C, 5.03 % H, 8.95 % S;  $w_i$ (found): 77.18 % C, 5.10 % H, 9.07 % S.  $^1\text{H}$  NMR:  $\delta_i$ /ppm: 7.10—7.82 (14H, m), 4.62—5.22 (4H, q). IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1600, 1645;  $\nu(\text{C}-\text{H})$  3000—3020;  $\nu(\text{C}-\text{H})$  710.

### *Diethylsulfonium-1,3-indandionylide (II)*

The mixture of 1,3-indandione (6.8 mmol) and diethyl sulfoxide (20 mmol) in acetic anhydride (3.5  $\text{cm}^3$ ) was stirred at 80 °C for 8 h under conditions excluding air moisture. After evaporation of the solution *in vacuo*, the precipitate was recrystallized from methanol. M.p. = 139—141 °C, yield = 72 %.

For  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}$  ( $M_r = 234$ )  $w_i$ (calculated): 66.68 % C, 5.98 % H, 13.66 % S;  $w_i$ (found): 66.74 % C, 5.81 % H, 13.42 % S.  $^1\text{H}$  NMR:  $\delta_i$ /ppm: 7.4 (4H, s), 3.7—3.1 (4H, m), 1.2—1.0 (6H, m). IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1600, 1625;  $\nu(\text{C}=\text{C})$  1575;  $\nu(\text{C}-\text{H})$  2975;  $\nu(\text{C}-\text{H})$  720;  $\nu(\text{C}-\text{S})$  625.

### *Dimethylsulfonium-1,3-indandionylide (III)*

The procedure was similar as with the compound II. Yield = 78 %, m.p. = 188—191 °C, crystallization from acetone.

For  $\text{C}_{11}\text{H}_{10}\text{O}_2\text{S}$  ( $M_r = 206$ )  $w_i$ (calculated): 64.07 % C, 4.85 % H, 15.53 % S;  $w_i$ (found): 64.13 % C, 4.98 % H, 15.65 % S.  $^1\text{H}$  NMR:  $\delta_i$ /ppm: 7.43 (4H, s), 3.0 (6H, s).

### *2-Benzylthio-1,3-indandione (IV)*

The mixture of 2-bromo-1,3-indandione (6.6 mmol), dibenzyl sulfide (8 mmol), and nitromethane (5  $\text{cm}^3$ ) was stirred at 90 °C for 5 h. After cooling of the reaction mixture diethyl ether (3  $\text{cm}^3$ ) and petroleum ether (3  $\text{cm}^3$ ) were added dropwise. The precipitate was

recrystallized from the mixture of methanol—ether (volume ratio = 1 : 1). Yield  $\approx$  60 %, m.p. = 184 °C.

For  $C_{16}H_{12}O_2S$  ( $M_r = 268$ )  $w_i$ (calculated): 71.63 % C, 4.47 % H, 11.96 % S;  $w_i$ (found): 71.50 % C, 4.15 % H, 11.89 % S.  $^1H$  NMR:  $\delta$ ,/ppm: 7.85 (4H, s), 7.075 (5H, s), 3.82 (2H, s). IR:  $\tilde{\nu}/cm^{-1}$ :  $\nu(C=O)$  1690, 1725;  $\nu(C=C)$  1580;  $\nu(C-H)$  750;  $\nu(C-S)$  650—700.

### 2-Ethylthio-1,3-indandione (V)

The procedure was similar as with the compound IV. The reaction temperature 40 °C, yield = 45 %, m.p. = 192—194 °C.

For  $C_{11}H_{10}O_2S$  ( $M_r = 206$ )  $w_i$ (calculated): 64.07 % C, 4.85 % H, 15.53 % S;  $w_i$ (found): 64.23 % C, 4.64 % H, 15.39 % S.  $^1H$  NMR:  $\delta$ ,/ppm: 0.93 (3H, t), 2.55 (2H, q), 7.93 (4H, s). IR:  $\tilde{\nu}/cm^{-1}$ :  $\nu(C=O)$  1690, 1728;  $\nu(C=C)$  1580;  $\nu(C-H)$  2940.

### 2-Propylthio-1,3-indandione (VI)

The procedure was similar as with the compound IV. M.p. = 179—182 °C.

For  $C_{12}H_{12}O_2S$  ( $M_r = 220$ )  $w_i$ (calculated): 65.45 % C, 5.45 % H, 14.54 % S;  $w_i$ (found): 65.69 % C, 5.37 % H, 14.12 % S.  $^1H$  NMR:  $\delta$ ,/ppm: 0.87 (3H, t), 1.5 (2H, q), 2.65 (2H, t), 3.02 (1H, s), 7.85 (4H, s). IR:  $\tilde{\nu}/cm^{-1}$ :  $\nu(C=O)$  1692, 1734;  $\nu(C=C)$  1580;  $\nu(C-H)$  2940.

### 2,2-Bis(phenylthio)-1,3-indandione (VII)

The mixture of 2-bromo-1,3-indandione (4.4 mmol) and sodium thiophenolate (4.5 mmol) in ether (40  $cm^3$ ) was stirred at room temperature for 10 h. Ether was distilled off *in vacuo* and the distillation residue was dissolved in water. The insoluble portion was recrystallized from ethanol. Yield = 65 %, m.p. = 143—146 °C. Ethanol was distilled off from the filtrate to give diphenyl disulfide (yield = 20 %). M.p. = 53—54 °C,  $^1H$  NMR:  $\delta$ ,/ppm: 7.13—7.62 (m).

For  $C_{21}H_{14}O_2S_2$  ( $M_r = 362$ )  $w_i$ (calculated): 69.59 % C, 3.89 % H, 17.63 % S;  $w_i$ (found): 69.86 % C, 3.86 % H, 17.58 % S.  $^1H$  NMR:  $\delta$ ,/ppm: 7.78 (4H, s), 7.25 (10H, s).

### Ethyl 2-phenylthio-1,3-indandione-2-carboxylate (VIII)

To the mixture of sodium thiophenolate (6.7 mmol) in benzene (60  $cm^3$ ) ethyl 2-bromo-1,3-indandione-2-carboxylate (7 mmol) was added within 20 min. The mixture was stirred for 4 h at 25 °C, boiled, filtered immediately, and washed with hot benzene. The insoluble portion was sodium salt of ethyl 1,3-indandione-2-carboxylate. Yield  $\approx$  60 %, decomposition at 300 °C.

To the benzene filtrate evaporated to 10 cm<sup>3</sup> the mixture (10 cm<sup>3</sup>) of diethyl ether—petroleum ether (volume ratio = 1 : 1) was added and the white precipitate was recrystallized from the mixture of ether—petroleum ether. Yield ≈ 30 %, m.p. = 107—110 °C. For C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>S (*M<sub>r</sub>* = 326) *w<sub>i</sub>*(calculated): 66.25 % C, 4.29 % H, 9.83 % S; *w<sub>i</sub>*(found): 66.47 % C, 4.24 % H, 9.66 % S. IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1715 w, 1740 s, 1775 sh;  $\nu(\text{C}=\text{C})$  1610.

For sodium salt of ethyl 1,3-indandione-2-carboxylate IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{C})$  1550, 1560;  $\nu(\text{C}=\text{O})$  1625, 1680. <sup>1</sup>H NMR:  $\delta$ ,/ppm: 7.36 (4H, s), 3.90—4.17 (2H, q), 1.07—1.25 (3H, t).

### *Ethyl 2-(4-methylphenylthio)-1,3-indandione-2-carboxylate (IX)*

The procedure was similar as with the compound VIII. Yield = 38 %, m.p. = 118—120 °C. For C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>S (*M<sub>r</sub>* = 340) *w<sub>i</sub>*(calculated): 67.05 % C, 4.71 % H, 9.42 % S; *w<sub>i</sub>*(found): 67.39 % C, 4.85 % H, 10.05 % S. IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1715, 1760 s, 1770 sh;  $\nu(\text{C}=\text{C})$  1590.

### *2-Phenylthio-1,3-indandione (X)*

To the solution of sodium thiophenolate (6.7 mmol) in 50 % ethanol (50 cm<sup>3</sup>) ethyl 2-bromo-1,3-indandione-2-carboxylate (7 mmol) was added within 20 min at 25 °C with stirring. After addition the reaction mixture was refluxed for 2 h. Then ethanol was distilled off and the reaction mixture was cooled and acidified with HCl. The precipitate was crystallized from ethanol or benzene. Yield = 22 %, m.p. = 92 °C.

For C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>C (*M<sub>r</sub>* = 254) *w<sub>i</sub>*(calculated): 70.84 % C, 3.96 % H, 12.61 % S; *w<sub>i</sub>*(found): 70.84 % C, 3.66 % H, 12.28 % S. IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1720, 1753 (CHCl<sub>3</sub>).

### *2-(4-Methylphenylthio)-1,3-indandione (XI)*

The procedure was similar as with the compound X. Yield = 25 %, m.p. = 145—146 °C. For C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>S (*M<sub>r</sub>* = 268) *w<sub>i</sub>*(calculated): 71.63 % C, 4.47 % H, 11.93 % S; *w<sub>i</sub>*(found): 71.80 % C, 4.22 % H, 11.62 % S. IR:  $\tilde{\nu}/\text{cm}^{-1}$ :  $\nu(\text{C}=\text{O})$  1730, 1680;  $\nu(\text{C}=\text{C})$  1575. <sup>1</sup>H NMR:  $\delta$ ,/ppm: 0.90 (3H, s), 6.75—7.87 (9H, m).

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