

**On phthalides and 1,3-indandiones. XLIX.**  
**Preparation of 3-arylmethylene-4,7-dithia-4,5,6,7-**  
**-tetrahydrophthalides and 2-aryl-4,7-dithia-4,5,6,7-**  
**-tetrahydro-1,3-indandiones**

P. HRNČIAR

*Department of Organic Chemistry, Faculty of Natural Sciences, Komenskij University,  
801 00 Bratislava*

Received 24 May 1971

*Dedicated to Professor S. Stankoviansky on his 65th birthday*

3-Arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides, prepared by condensation of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride with arylacetic acids, were rearranged with sodium methanolate to give 2-aryl-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones. 3-(1-Naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide underwent substitution chlorination, bromination, and nitration in position 4, whereas 3-(2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide in position 1 of the naphthalene ring.

In our preceding papers referring to the Gabriel modification of Perkin synthesis we used variously substituted phthalic anhydride [1–4] and cinchomeric anhydride [5] as starting material. Now, we wish to report the use of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride as the carbonyl component. The reaction of this compound with phenylacetic acid was already described [6].

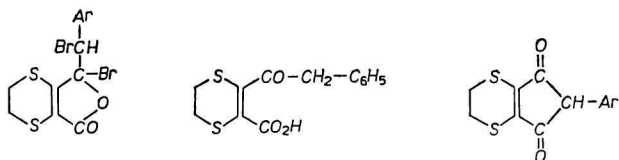
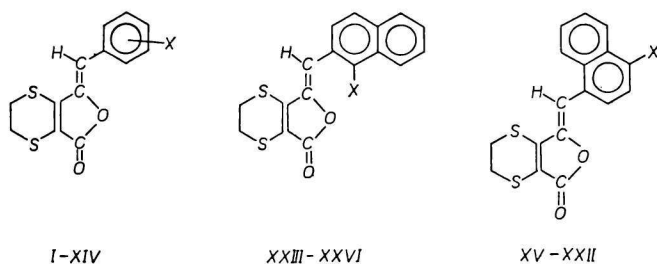
To prepare variously substituted 3-arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides, which served for the investigation of the substituent transfer effects and also for the synthesis of 2-aryl-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones, we treated the above-mentioned anhydride either with *meta*- and *para*-substituted phenylacetic acids or with 4-substituted 1-naphthylacetic and 2-naphthylacetic acids. This reaction was carried out under the conditions of Gabriel modification of Perkin synthesis similar to those employed in the reaction of phthalic anhydride with the mentioned acids *i.e.* in the presence of catalytic amounts of potassium acetate. It has been shown advantageous to carry out the reaction at a temperature by 20–25°C lower (180–210°C) than that used for condensation of phthalic anhydride with these acids [1]. 3,6-Dithia-3,4,5,6-tetrahydrophthalic anhydride decomposes above 220°C before it is capable to react with the proper arylacetic acid. The yield is in substance the same as when using phthalic anhydride. Also in this very case, *trans*-3-arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides (*I–XIII*, *XV–XVII*, *XXIII*) are the reaction products [7, 8] similarly as with phthalic anhydride since the presence of a *cis* isomer could not be proved even chromatographically.

The condensation of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride with *p*-aminophenylacetic acid does not proceed; therefore *p*-aminobenzal-4,7-dithia-4,5,6,7-tetrahydrophthalide (*XIV*) was prepared by reduction of the nitro derivative *XIII* analogously.

gously to the naphthal derivative *XXI*. In both cases the reduction with tin(II) chloride in acetic acid was shown to be quite convenient.

It has been found that 3-(4-X-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalides (*XVIII*–*XX*) and 3-(1-X-2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalides (*XXIV*–*XXVI*) (X = Cl, Br, NO<sub>2</sub>) can be well achieved from *XV* and *XXIII* by substitution chlorination, bromination or nitration on naphthalene ring. This method is more advantageous than that from the proper chloro-, bromo-, and nitronaphthylacetic acid. The chlorination was carried out under similar reaction conditions as with 1-naphthalphthalide and 2-naphthalphthalide [8, 9] avoiding thus the addition to the C=C double bond. The compounds *XV* and *XXIII* behaved differently when brominated: *XXIII* similarly as *I* underwent with one molequivalent of bromine an addition bromination at room temperature (substances *XXVII* and *XXIX*), whereas *XV* a substitution bromination on the naphthalene ring in position 4 (substance *XIX*). With *XXIII* the substitution bromination could be carried out at the naphthalene ring only in a higher-boiling chlorobenzene. Upon bromination with two molequivalents of bromine the compound *XV* underwent first substitution and then addition bromination (*XXVIII*). The different behaviour of *XV* and *XXIII* upon bromination could be explained mostly in steric terms. The central C=C double bond of *XV* is more hindered (the second benzene ring of naphthalene is in the *ortho*-position) than that of *XXIII*, where the second benzene ring is in the *meta*-position. This steric hindrance is enhanced in *XXIV*–*XXVI* with which the addition bromination to the C=C double bond does not take place at all, whereas with *XVI*–*XXII* such a bromination occurs. Under the conditions given for the substitution chlorination and bromination of *XV* and *XXIII* the substitution chlorination and bromination of *I* does not take place.

The nitration of *XV* and *XXIII* was carried out with concentrated nitric acid in chloroform. The nitration of *I* proceeds under these reaction conditions only in a low yield (10%). Comparing the substitution reactions of *I* with those of *XV* and *XXIII* one



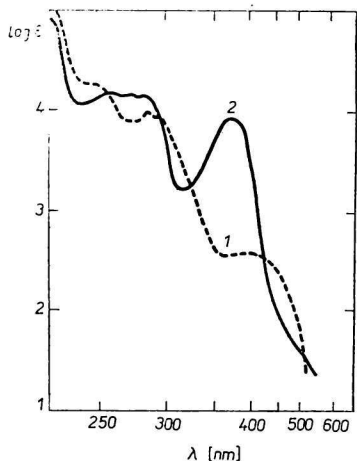
Scheme I

(1)

is entitled to say that an important role — in addition to the positive electromeric effect of the C=C double bond — plays also the electron density of aromatic systems, which is higher with naphthalene, this being reflected in the easier course of substitution reactions with *XV* and *XXIII*.

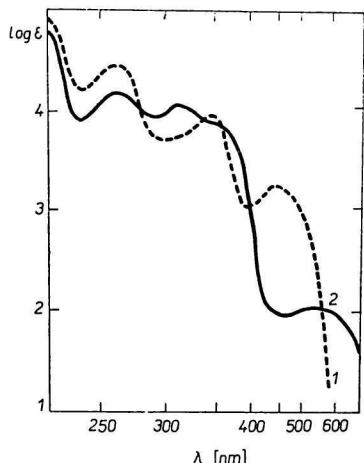
An experimental evidence that the halogen or nitro group entered the naphthalene ring was brought forward analogously with the comparable derivatives of 1-naphthalphthalide and 2-naphthalphthalide [7, 8], *i.e.* by oxidation of *XVIII*–*XX* and *XXIV*–*XXVI* with potassium dichromate in acetic acid to furnish the proper naphthoic acid. The compounds *XV* and *XXIII* were unambiguously identified as being substituted in the position 4 and 1 at the naphthalene ring, respectively (Scheme 1).

That the chlorination, bromination, and nitration proceeded could be seen also in the infrared spectra of the substances obtained. All phthalides prepared by condensation of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride with arylacetic acids reveal a characteristic band of the CO stretching vibration in the 1725–1771  $\text{cm}^{-1}$  range. The position of this band is shifted somewhat lower when compared with analogous benzalphthalides and naphthalphthalides what can be rationalized by an enhanced conjugation between the carbonyl group and the C=C double bonds system [9]. The absorption band of these substances in the 1650–1660  $\text{cm}^{-1}$  region is indicative of the central double bond. The position of this band is for the same reason also shifted towards lower frequencies when contrasted with benzalphthalides. Substituted phthalides display similar characteristic bands of those bonds. The band indicative of the central double bond disappears after bromination of *I*, *XV*, and *XXIII*. Synthesized dithiaphthalides show a stretching C=C double bond vibration of dithiacyclohexene ring at 1518–1535  $\text{cm}^{-1}$ . This position was ascribed to the dithiacyclohexene ring on the basis of comparison between spectra of *I*–*XXV* with that of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride.



*Fig. 1.* Electronic spectrum (in methanol).

1. 2-(1-naphthyl)-1,3-indandione;
2. 2-(1-naphthyl)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandione.



*Fig. 2.* Electronic spectrum in methanolic  $10^{-2}$  N-NaOH.

1. 2-(1-naphthyl)-1,3-indandione;
2. 2-(1-naphthyl)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandione.

The absorption band at  $1556\text{ cm}^{-1}$  in the latter is associated with the  $\text{C}=\text{C}$  double bond, this being in accordance with [10]. The lower frequency of this band is again caused by the expanded conjugation.

It is noteworthy that the addition of bromine to the double  $\text{C}=\text{C}$  bond of dithia-cyclohexene ring does not proceed even with a threefold excess of bromine.

The cleavage of the lactone ring of 3-arylmethylene-4,7-dithia-4,5,6,7-tetrahydro-phthalides proceeded under the same reaction conditions as with benzal-phthalides. *o*-Arylacetyl-3,5-dithia-3,4,5,6-tetrahydrobenzoic acids (XXX) are the reaction products, as evidenced by hydrolysis of I.

The rearrangement of 3-arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides to 2-aryl-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (XXXI–XLII) was carried out by sodium methoxide in methyl alcohol. The above-mentioned dithiaindandiones, like indandiones, are formed also by direct condensation of one moleivalent of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride with one moleivalent of arylacetic acid and three moleivalents of triethylamine in acetic anhydride as was the case with the preparation of indandiones XXXI, XLI, XLII.

2-Aryl-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones thus synthesized display a strong doublet associated with the asymmetric and symmetric vibration of carbonyl groups. The position of the asymmetric band, which is more intensive, is in the  $1680\text{--}1694\text{ cm}^{-1}$  and that of the symmetric in the  $1730\text{--}1732\text{ cm}^{-1}$  region. These vibrations are shifted by  $20\text{--}25\text{ cm}^{-1}$  towards wavelength shorter than the adequate carbonyl vibrations of analogous 2-aryl-1,3-indandiones [11]. The double bond of dithiacyclohexene ring of XXXI–XLII is seen in the  $1530\text{--}1539\text{ cm}^{-1}$  region. Diethyl 3,6-dithia-3,4,5,6-tetrahydrophthalate is reported to have the  $\text{C}=\text{C}$  double bond at  $1550\text{ cm}^{-1}$  [10].

Indandiones XXXI–XLII have in their electronic spectra bands due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions shifted towards lower wavelengths when contrasted with those of the corresponding 2-aryl-1,3-indandiones. Dithiaindandiones, which were prepared, display in alkaline medium little intense band at  $500\text{--}700\text{ nm}$  absent in 2-aryl-1,3-indandiones. This band might be, however, associated with the  $n \rightarrow \pi^*$  transition of *d*-electrons of sulfur (Figs. 1, 2).

## Experimental

Synthesized substances and their characteristic data are listed in Tables 1–3. Melting points were determined according to Kofler.

Infrared spectra were recorded in nujol with a UR-20 double-beam spectrophotometer with an NaCl prism. Electronic spectra were taken with a 450 Perkin–Elmer apparatus in the  $215\text{--}750\text{ nm}$  range. The concentration of the investigated substances was  $10^{-3}\text{ M}$  in dry methanol.

### *3-Arylmethylene-4,7-dithia-4,5,6,7-tetrahydrophthalides (I–XVII, XXIII)*

3,6-Dithia-3,4,5,6-tetrahydrophthalic anhydride (3.8 g, 0.02 mole), arylacetic acid (0.02 mole) and freshly fused potassium acetate (0.3 g) were placed in a 100-ml flask equipped with a thermometer and a water outlet tube and heated at  $190\text{--}210^\circ\text{C}$  for 2–4 hours. The reaction mixture was poured into ethanol (50 ml) and the crude product was crystallized either from ethanol or from the mixture of ethanol and chloroform.

Table 1

## 3-(X-Benzal)-4,7-dithia-4,5,6,7-tetrahydrophthalides

Compound	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C]	$\bar{\nu}(\text{C}=\text{O})$ [cm <sup>-1</sup> ]	$\bar{\nu}(\text{C}=\text{C})^a$ [cm <sup>-1</sup> ]
				% C	% H	% S	% X				
<i>I</i>	H	C <sub>13</sub> H <sub>10</sub> S <sub>2</sub> O <sub>2</sub>	262.1	59.54	3.82	24.42		69	150–152	1760	1649
<i>II</i>	3-F	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> F	281.1	59.63	3.65	24.69		68	143–144	1756	1532
				55.64	3.38	22.93					1539
<i>III</i>	4-F	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> F	281.1	55.70	3.21	22.86		66	191–193	1758	1659
				55.48	3.51	22.49					1539
<i>IV</i>	3-Cl	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> Cl	296.5	52.65	3.03	21.58	11.89	63	163–165	1760	1655
				52.69	2.93	21.73	11.61				1535
<i>V</i>	4-Cl	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> Cl	296.5	52.65	3.03	21.58	11.89	61	190–192	1761	1649
				52.78	3.21	21.32	11.68				1527
<i>VI</i>	4-Br	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> Br	340.9	45.73	2.63	18.65	23.98	62	192–194	1761	1649
				45.68	2.96	18.71	23.68				1528
<i>VII</i>	3-I	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> I	389.9	40.21	2.32	16.51	32.73	63	192–194	1760	1651
				40.38	2.61	16.81	32.65				1535
<i>VIII</i>	4-I	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> I	389.9	40.21	2.31	16.51	32.73	61	197–199	1761	1652
				40.60	2.28	16.48	32.98				1529
<i>IX</i>	3-CH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>2</sub>	276.1	60.85	4.15	23.15		43	151–153	1760	1653
				61.10	4.31	23.28					1531
<i>X</i>	4-CH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>2</sub>	276.1	60.85	4.15	23.95		39	177–179	1761	1652
				60.74	4.03	22.96					1529
<i>XI</i>	3-OCH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>3</sub>	292.1	57.52	4.13	21.91		48	117–119	1750	1658
				57.74	4.28	22.16					1532
<i>XII</i>	4-OCH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>3</sub>	292.1	57.52	4.13	21.91		46	166–168	1752	1650
				57.39	4.28	21.64					1520
<i>XIII</i>	4-NO <sub>2</sub>	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>4</sub> N	307.1	50.81	2.30	20.80	4.54	51	278–280	1771	1652 <sup>b</sup>
				50.93	2.21	20.61	4.68				1529
<i>XIV</i>	4-NH <sub>2</sub>	C <sub>13</sub> H <sub>11</sub> S <sub>2</sub> O <sub>2</sub> N	277.1	56.25	2.63	23.08	5.05	81	250–252	1725	1650
				56.34	2.84	22.68	4.73				1520

a) First value characteristic of the central double bond, the second of the dithiocyclohexene ring double bond.

b)  $\bar{\nu}_{\text{as}}(\text{NO}_2)$  1515;  $\bar{\nu}_{\text{s}}(\text{NO}_2)$  1338.

Table 2  
 3-(4-X-1-Naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalides (XV–XXII)  
 and 3-(1-X-2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalides (XXIII–XXVI)

Com- pound	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C]	$\tilde{\nu}(\text{C}=\text{O})$ [cm <sup>-1</sup> ]	$\tilde{\nu}(\text{C}=\text{C})^a$ [cm <sup>-1</sup> ]
				% C	% N	% S	% X				
XV	H	C <sub>17</sub> H <sub>12</sub> O <sub>2</sub> S <sub>2</sub>	312.2	65.35	3.85	20.47		61	191–193	1762	1648
XVI	4-CH <sub>3</sub>	C <sub>18</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	326.2	65.91	3.92	20.86		39	174–176	1753	1533
XVII	4-OCH <sub>3</sub>	C <sub>18</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	342.2	66.27	4.29	19.65		49	161–163	1760	1638
XVIII	4-Cl	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub> Cl	346.6	63.25	4.21	18.76		78	219–221	1761	1521
XIX	4-Br	C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> S <sub>2</sub> Br <sub>2</sub>	391.1	63.38	4.39	18.38		69	229–231	1762	1646
				59.05	3.23	18.61	10.35				
XX	4-NO <sub>2</sub>	C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> S <sub>2</sub> N	357.2	52.16	2.82	16.37	20.43	81	230–231	1762	1639
				51.93	3.11	16.05	19.96				
XXI	4-NH <sub>2</sub>	C <sub>17</sub> H <sub>13</sub> O <sub>2</sub> S <sub>2</sub> N	327.2	58.47	3.07	17.92	3.83 N	84	228–230	1731	1640 <sup>b</sup>
				58.25	3.21	17.65	3.41 N				
XXII	4-NHCOCH <sub>3</sub>	C <sub>19</sub> H <sub>15</sub> O <sub>3</sub> S <sub>2</sub> N	357.2	62.37	3.51	19.55	4.28 N	91	241–243 (dec.)	1764	1642
				62.68	3.63	19.81	4.18 N				
XXIII	H	C <sub>17</sub> H <sub>12</sub> O <sub>2</sub> S <sub>2</sub>	312.2	63.55	4.21	17.95	3.92 N	73	197–199	1764	1647
				63.18	4.60	17.58	3.68 N				
XXIV	1-Cl	C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> S <sub>2</sub> Cl	346.5	65.35	3.85	20.47		68	219–221	1774	1654
				65.13	4.11	20.61					
XXV	1-Br	C <sub>17</sub> H <sub>11</sub> O <sub>2</sub> S <sub>2</sub> Br	391.1	58.88	3.17	18.82	10.23	63	226–228	1760	1653
				59.21	3.43	18.38	10.61				
XXVI	1-NO <sub>2</sub>	C <sub>17</sub> H <sub>11</sub> O <sub>4</sub> S <sub>2</sub> N <sub>2</sub>	357.2	52.16	2.82	16.37	20.43	75	220–272	1767	1671
				52.38	2.51	16.20	20.87				
				58.47	3.07	17.92	3.83 N			1767	1651 <sup>c</sup>
				58.21	3.43	17.68	3.65 N				1529

a) First value characteristic of the central double bond, the second of the dithiocyclohexene ring double bond.

b)  $\tilde{\nu}_{\text{as}}(\text{NO}_2)$  1515;  $\tilde{\nu}_{\text{s}}(\text{NO}_2)$  1329.

c)  $\tilde{\nu}_{\text{as}}(\text{NO}_2)$  1529;  $\tilde{\nu}_{\text{s}}(\text{NO}_2)$  1345.

Table 3

2-(X-Phenyl)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (XXXI–XL),  
 2-(1-naphthyl)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandione (XLI),  
 and 2-(2-naphthyl)-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandione (XLII)

Compound	X	Formula	M	Calculated/found				Yield [%]	M.p. [°C]	$\bar{\nu}(\text{C}=\text{O})^a$ [cm <sup>-1</sup> ]	$\bar{\nu}(\text{C}=\text{C})^b$ [cm <sup>-1</sup> ]
				% C	% H	% S	% X				
XXXI	H	C <sub>13</sub> H <sub>10</sub> S <sub>2</sub> O <sub>2</sub>	262.1	59.54	3.82	24.42		93	162–163	1964	1523
				59.38	3.61	24.05				1733	
XXXII	3-F	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> F	281.1	55.70	3.21	22.86		95	133–135	1679	1526
				55.96	2.98	22.61				1732	
XXXIII	4-F	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> F	281.1	55.70	3.21	22.86		94	151–153	1674	1523
				56.13	3.61	22.73				1735	
XXXIV	4-Cl	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> Cl	296.6	52.65	3.03	21.58	11.89	95	187–189	1679	1524
				52.31	3.28	21.63	11.76			1732	
XXXV	4-I	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>2</sub> Cl	389.9	40.21	2.32	16.51	32.73	94	188–190	1676	1523
										1730	
XXXVI	4-CH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>2</sub>	276.1	60.85	4.15	23.15		91	156–158	1684	1523
				61.12	4.38	22.81				1730	
XXXVII	3-OCH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>3</sub>	292.1	57.52	4.13	21.91		92	113–115	1682	1526
				57.35	4.31	27.63				1730	
XXXVIII	4-OCH <sub>3</sub>	C <sub>14</sub> H <sub>12</sub> S <sub>2</sub> O <sub>3</sub>	292.1	57.52	4.13	21.91		93	127–129	1683	1519
				57.38	4.51	22.28				1730	
XXXIX	4-NO <sub>2</sub>	C <sub>13</sub> H <sub>9</sub> S <sub>2</sub> O <sub>4</sub> N	307.1	59.81	2.30	20.80	4.54 N	90	193–195	1696	1523
				50.54	2.61	20.61	4.38			1734	
XL	4-NH <sub>2</sub>	C <sub>13</sub> H <sub>11</sub> S <sub>2</sub> O <sub>2</sub> N	277.1	56.25	2.63	23.08	5.05 N	85	189–191	1680	1519
				56.31	2.97	22.64	5.35 N			1731	
XLI		C <sub>17</sub> H <sub>12</sub> O <sub>2</sub> S <sub>2</sub>	312.2	65.35	3.85	20.47		95	201–203	1690	1526
				65.64	3.99	20.63				1730	
XLII		C <sub>17</sub> H <sub>12</sub> O <sub>2</sub> S <sub>2</sub>	312.2	65.35	3.85	20.47		95	188–189	1694	1523
				65.18	4.11	20.18				1733	

a) First value characteristic of the asymmetric vibrations, the second of the symmetric vibrations.

b) Dithiocyclohexene ring double bond.

*3-(4-Chloro-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XVIII)*  
 and *3-(1-chloro-2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XXIV)*

Freshly distilled sulfuryl chloride (2 g) was added to a solution of XV or XXIII (0.01 mole) in chloroform (30 ml). The reaction mixture was heated to 30°C and allowed to stand for 30 minutes. Then ethanol (50 ml) was added and the desired product was crystallized from the ethanol—chloroform mixture.

*3-(4-Bromo-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XIX)*  
 and *3-(1-bromo-2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XXV)*

One molequivalent of bromine was added to a solution of XV or XXIII (0.01 mole) in chloroform (30 ml) at room temperature or in chlorobenzene (30 ml) at boiling point. After 30 minutes ethanol (40 ml) was added to the reaction mixture and crystals obtained were recrystallized from the mixture chloroform—ethanol.

*3-(4-Nitro-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XX)*  
 and *3-(1-nitro-2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XXVI)*

Nitric acid (6 ml,  $d = 1.5$ ) was added during 10 minutes to a solution of XV or XXIII (0.01 mole) in chloroform (30 ml) at increased temperature. After cooling ethanol was added and the separated product was crystallized from acetic acid.

*3-(4-Aminobenzal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XIV)*  
 and *3-(4-amino-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XXI)*

Hydrogen chloride was passed through a mixture of tin(II) chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ; 10 g), acetic acid (100 ml) and XIII or XX (0.01 mole) at 60°C for 2 1/2 hours. The reaction mixture was poured into water (150 ml) after cooling. The separated salt was washed with ammonia and the base crystallized from chloroform—ethanol mixture.

*3-(4-Acetamino-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide (XXII)*

The substance XXI (0.7 g, 0.002 mole) was refluxed with acetic anhydride (10 ml) and acetic acid (30 ml) for 90 minutes. The crude product separated after cooling was recrystallized from acetic acid.

*3-(Benzal)-4,7-dithia-4,5,6,7-tetrahydrophthalide dibromide (XXVII),*  
*3-(4-bromo-1-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide dibromide (XXVIII),*  
 and *3-(2-naphthal)-4,7-dithia-4,5,6,7-tetrahydrophthalide dibromide (XXIX)*

One molequivalent of bromine was added to a solution of I, XV, or XXIII (0.005 mole) in chloroform (30 ml). After 30 minutes ethanol (50 ml) was added to the reaction mixture. Light-yellow crystals were filtered off and recrystallized from the mixture chloroform—ethanol.

For XXVII: yield 79%, m.p. 136—138°C.

For  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{S}_2\text{Br}_2$  (421) calculated: 37.00% C, 2.36% H, 15.17% S, 37.76% Br; found: 36.81% C, 2.83% H, 15.46% S, 37.28% Br;  $\bar{\nu}(\text{C}=\text{O})$  1755  $\text{cm}^{-1}$ ,  $\bar{\nu}(\text{C}=\text{C})$  1541  $\text{cm}^{-1}$  (of dithiacyclohexene ring).

For XXVIII: yield 69%, m.p. 194—196°C.

For  $\text{C}_{17}\text{H}_{11}\text{O}_2\text{S}_2\text{Br}_3$  (550.7) calculated: 37.05% C, 1.89% H, 11.64% S, 43.50% Br; found 36.72% C, 2.30% H, 11.30% S, 42.98% Br;  $\bar{\nu}(\text{C}=\text{O})$  1772  $\text{cm}^{-1}$ ,  $\bar{\nu}(\text{C}=\text{C})$  1569  $\text{cm}^{-1}$ .

For XXIX: yield 79%, m.p. 165—168°C.

For  $\text{C}_{17}\text{H}_{12}\text{O}_2\text{S}_2\text{Br}_2$  (472.1) calculated: 43.18% C, 2.55% H, 13.23% S, 33.89% Br; found: 42.78% C, 2.68% H, 12.33% S, 33.58% Br;  $\bar{\nu}(\text{C}=\text{O})$  1760  $\text{cm}^{-1}$ ,  $\bar{\nu}(\text{C}=\text{C})$  1531  $\text{cm}^{-1}$ .



*2-Phenylacetyl-3,6-dithia-1-cyclohexenecarboxylic acid (XXX)*

A mixture consisting of the substance *I* (0.5 g, 0.002 mole) and 10% aqueous sodium hydroxide (30 ml) was refluxed 20 minutes. After cooling the solution was filtered and acidified with 10% hydrochloric acid to pH 2. The product *XXX*, which crystallized during few hours was recrystallized from the benzene—petrol mixture.

Yield 67%, m.p. 120—121°C.

For  $C_{13}H_{12}O_3S_2$  (280.1) calculated: 55.56% C, 4.28% H, 22.80% S; found: 55.21% C, 4.51% H, 22.51% S;  $\bar{\nu}(C=O)$  1731  $cm^{-1}$ ,  $\bar{\nu}(C=C)$  1525  $cm^{-1}$ .

*2-Aryl-4,7-dithia-4,5,6,7-tetrahydro-1,3-indandiones (XXXI—XLII)**Method A*

The appropriate phthalide (0.005 mole) was added to a 2% methanolic solution of sodium methoxide (50 ml) and refluxed for 1 hour, during which the colour of the reaction mixture turned violet or dark green. The solution, while hot, was filtered and after cooling acidified with 20% hydrochloric acid to pH 2. The crude product was crystallized from ethanol, toluene or acetic acid.

*Method B* (used for preparation of *XXXI*, *XLI*, *XLII*)

A mixture of 3,6-dithia-3,4,5,6-tetrahydrophthalic anhydride (0.02 mole), arylacetic acid (0.02 mole), acetic anhydride (0.1 mole), and dry triethylamine (0.06 mole) was heated under reflux at 125—130°C for 45 minutes. Volatile components were then distilled off under diminished pressure (water ejector) and 96% ethanol (20 ml) was added. The solution was heated to boiling point, poured into 2% sodium hydroxide (500 ml) and stirred at 30°C for 6—8 hours. The reaction mixture was filtered and the filtrate acidified with 20% hydrochloric acid to pH 2. The crude product was crystallized from ethanol (yield about 50%).

*Acknowledgements.* I wish to express my thanks to Dr E. Greipelová and Dr M. Livař (Institute of Chemistry, Komenský University, Bratislava) for analyses and electronic spectra, and to Dr A. Perjéssy (Department of Organic Chemistry, Komenský University, Bratislava) for measurement of infrared spectra.

## References

- Hrnčiar, P., *Chem. Zvesti* **16**, 96 (1962).
- Hrnčiar, P., *Chem. Zvesti* **17**, 668 (1963).
- Hrnčiar, P. and Joniak, D., *Chem. Zvesti* **20**, 336 (1966).
- Hrnčiar, P. and Kuruc, L., *Chem. Zvesti* **21**, 267 (1967).
- Hrnčiar, P., *Chem. Zvesti* **19**, 365 (1965).
- Hahn, W. E. and Radzyńkiewicz, R., *Łodz. Towarz. Nauk, Wydział III, Acta Chim.* **10**, 31 (1965).
- Furdík, M. and Hrnčiar, P., *Chem. Zvesti* **12**, 464 (1958).
- Furdík, M. and Hrnčiar, P., *Chem. Zvesti* **14**, 44 (1960).
- Perjéssy, A. and Hrnčiar, P., *Collect. Czech. Chem. Commun.* **37**, 1708 (1972).
- Schweizer, H. R., *Helv. Chim. Acta* **52**, 2221 (1969).
- Perjéssy, A. and Hrnčiar, P., *Tetrahedron* **27**, 6159 (1971).

Translated by Z. Votický