

**Alkylation of 1-Benzhydryl-2-methyl-2-thiopseudourea.**—1-Benzhydryl-2-methyl-2-thiopseudourea, 7.68 g. (0.03 mole), and methyl iodide, 6.4 g. (0.045 mole), were refluxed in 100 ml. of acetone with 2 g. (0.015 mole) of potassium carbonate for 4 hr. Some inorganic material was filtered off and the acetone filtrate was evaporated down *in vacuo* at room temperature to leave a thick oil residue. The residue was taken up in chloroform and the chloroform solution filtered to remove more inorganic solids. The

chloroform was then evaporated down *in vacuo* at room temperature and the residue taken up in a little isopropyl alcohol. Upon addition of dilute hydriodic acid to the isopropyl alcohol solution, 4.0 g. of a solid hydroiodide salt, m.p. 162–164°, precipitated. Two recrystallizations from an isopropyl alcohol-ether mixture gave a product, m.p. 173–174°, which was identical in every way with 1-benzhydryl-2,3-dimethyl-2-thiopseudourea hydroiodide.

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## Reactions with Mercaptans. IV. Reaction of Aromatic Thiols with 3(2H)-Thianaphthenone-1,1-dioxides and 2-Benzylidene-3(2H)-thianaphthenone-1,1-dioxide

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The condensation reaction of 3(2H)-thianaphthenone-1,1-dioxides (I) with aromatic aldehydes has been investigated, *e.g.*, 3(2H)-thianaphthenone-1,1-dioxide condenses with benzaldehyde to give 2-benzylidene-3(2H)-thianaphthenone-1,1-dioxide (IIa). The latter undergoes an addition reaction with thiophenol, yielding the thiol adduct believed to have structure VI. Aromatic thiols react with 3(2H)-thianaphthenone-1,1-dioxides, in the presence of anhydrous zinc chloride and hydrogen chloride, to yield the corresponding unsaturated sulfides VII which are readily oxidized to the sulfone derivatives VIII.

Aldehyde condensation products of 3(2H)-thianaphthenone-1,1-dioxide (Ia) have not previously been prepared, although Ia has been known since 1912.<sup>1</sup> Weston and Suter<sup>2</sup> were unable to condense benzaldehyde with Ia in an alkaline medium.

We obtained well-defined crystalline products by the reaction of benzaldehyde with Ia and by that of *p*-nitrobenzaldehyde with 7-methyl-3(2H)-thianaphthenone-1,1-dioxide (Id). The analytical data indicate that one molecule of aldehyde condenses with one molecule of the thianaphthenone-1,1-dioxide with the elimination of one molecule of water.

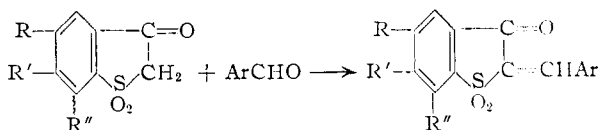
The structural assignments for these products are based on their participation in known reactions. When 2-benzylidene-3(2H)-thianaphthenone-1,1-dioxide (IIa) was treated with hydroxylamine hydrochloride, the corresponding oxime of 3(2H)-thianaphthenone-1,1-dioxide (IIIa)<sup>3</sup> was obtained.<sup>4</sup> The treatment of IIa with phenylhydrazine gave the hydrazone of 3(2H)-thianaphthenone-1,1-dioxide (IIIb).<sup>5</sup>

2-Benzylidene-3(2H)-thianaphthenone reacted with phenylhydrazine to give [10H]-thianaphtheno-[3,2-*b*]-indole (IV), *via* the Fischer indole ring closure of the resulting phenylhydrazone of 3(2H)-thianaphthenone.<sup>5,6</sup>

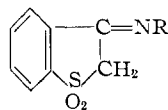
We have also studied the addition, *e.g.*, of benzenethiol, to the double bond at position 2 which is conjugated with the unsaturated group in 2-arylidene-3(2H)-thianaphthenone-1,1-dioxides.

IIa, like the 2-arylideneindan-1,3-diones,<sup>7</sup> under-

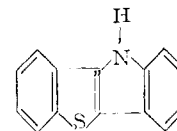
- (1) M. Lanfry, *Compt. rend.*, **154**, 519 (1912).
- (2) A. W. Weston and C. M. Suter, *THIS JOURNAL*, **61**, 389 (1939).
- (3) D. H. Hartough, "Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, p. 166.
- (4) This reaction is similar to that of hydroxylamine hydrochloride with 2-benzylideneindan-1,3-dione; *cf.* A. Mustafa and A. H. E. Harhash, *THIS JOURNAL*, **78**, 1649 (1956).
- (5) E. W. McClelland and J. L. D'Silva, *J. Chem. Soc.*, 227 (1932).
- (6) C. E. Dagliesh and F. G. Mann, *ibid.*, 653 (1947).
- (7) A. Mustafa, *ibid.*, 1370 (1951).



- Ia, R = R' = H  
 b, R = CH<sub>3</sub>; R' = R'' = H  
 c, R' = CH<sub>3</sub>; R = R'' = H  
 d, R'' = CH<sub>3</sub>; R = R' = H  
 e, R'' = Cl; R = R' = H  
 IIa, R = R' = R'' = H; Ar = C<sub>6</sub>H<sub>5</sub>  
 b, R = R' = H, R'' = CH<sub>3</sub>; Ar = C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>-*p*

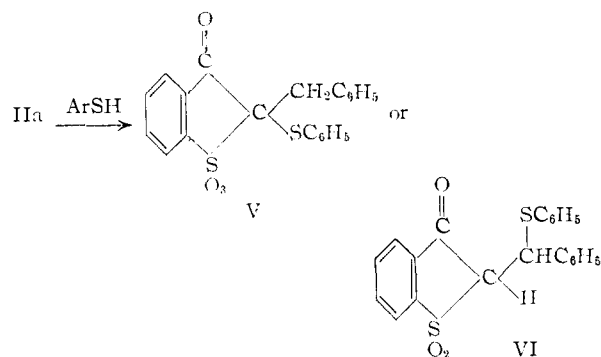


- IIIa, R = OH  
 b, R = NHC<sub>6</sub>H<sub>5</sub>



IV

goes addition reaction with thiophenol in absence of a catalyst to give a colorless adduct which can be represented by V or VI.



In view of the well-established mechanism for the addition of thiols to analogous  $\alpha,\beta$ -unsaturated



TABLE I  
NEW SULFONES (I)

3(2 <i>H</i> )-Thianaphthenone-1,1-dioxide	M.p., <sup>a</sup> °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Sulfur, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Ib	202	42	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> S	55.10	54.83	4.08	3.99	16.32	15.81
Ic	190	48	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> S	55.10	55.30	4.08	4.02	16.32	16.01
Id	187	45	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> S	55.10	54.73	4.08	4.09	16.32	15.88
Ie	227	56	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> SCl <sup>b</sup>	44.34	43.82	2.31	2.31	14.78	15.06
IX <sup>c</sup>	Above 360	54	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> S	55.10	54.92	4.08	4.01	16.32	16.03

<sup>a</sup> Melting points are uncorrected. <sup>b</sup> Calcd., Cl, 16.39; found, 16.01. <sup>c</sup> 2-Methyl-3(2*H*)-thianaphthenone-1,1-dioxide.

TABLE II

## 3-ARYLMERCAPTOTHIANAPHTHENE-1,1-DIOXIDES (VII)

3-Arylmercaptoderiv.	M.p., <sup>a</sup> °C.	Yield, %	Color with concd. H <sub>2</sub> SO <sub>4</sub>	Formula	Carbon, %		Hydrogen, %		Sulfur, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
VIIa	128	81	Yellow	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub> S <sub>2</sub>	61.31	61.01	3.65	3.57	23.36	23.12
VIIb	126	79	Orange	C <sub>15</sub> H <sub>12</sub> O <sub>2</sub> S <sub>2</sub>	62.50	62.39	4.16	4.00	22.22	21.98
VIIc	144	72	Deep red	C <sub>16</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	63.57	63.21	4.63	4.53	21.19	20.96
VIIId	122	74	Yellow	C <sub>15</sub> H <sub>12</sub> O <sub>2</sub> S <sub>2</sub>	62.50	62.43	4.16	4.43	22.22	21.74
VIIe	124	71	Orange	C <sub>16</sub> H <sub>14</sub> O <sub>2</sub> S <sub>2</sub>	63.77	63.77	4.63	4.93	21.19	21.24
VIIIf	134	82	Yellow	C <sub>14</sub> H <sub>9</sub> O <sub>2</sub> S <sub>2</sub> Cl <sup>b</sup>	54.46	53.91	2.91	3.16	20.74	20.25
VIIIf	142	76	Orange	C <sub>15</sub> H <sub>11</sub> O <sub>2</sub> S <sub>2</sub> Cl <sup>c</sup>	55.81	55.47	3.41	3.31	19.84	19.43

<sup>a</sup> All melting points are uncorrected. <sup>b</sup> Calcd., Cl, 11.51; found, 10.95. <sup>c</sup> Calcd., Cl, 11.01; found, 10.82.

TABLE III

## OXIDATION PRODUCTS OF 3-ARYLMERCAPTOTHIANAPHTHENE-1,1-DIOXIDE (VIII)

Oxidation products	M.p., <sup>a</sup> °C.	Yield, %	Formula	Carbon, %		Hydrogen, %		Sulfur, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
VIIIa	155	77	C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> S <sub>2</sub>	54.90	54.63	3.27	3.12	20.91	20.28
VIIIb	184	68	C <sub>15</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub>	56.25	55.99	3.75	3.63	20.00	20.10
VIIIc	190	66	C <sub>16</sub> H <sub>14</sub> O <sub>4</sub> S <sub>2</sub>	57.48	17.09	4.19	4.00	19.16	19.76
VIIId	130	81	C <sub>15</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub>	56.25	55.98	3.75	3.66	20.00	19.67
VIIIe	158	78	C <sub>16</sub> H <sub>14</sub> O <sub>4</sub> S <sub>2</sub>	57.48	57.09	4.19	4.15	19.16	18.87
VIIIIf	285	83	C <sub>14</sub> H <sub>9</sub> O <sub>4</sub> S <sub>2</sub> Cl <sup>b</sup>	49.34	48.97	2.64	2.54	18.79	17.97
VIIIIf	210	75	C <sub>15</sub> H <sub>11</sub> O <sub>4</sub> S <sub>2</sub> Cl <sup>c</sup>	50.77	50.08	3.10	2.87	18.05	17.67

<sup>a</sup> All melting points are uncorrected. <sup>b</sup> Calcd., Cl, 10.42; found, 11.10. <sup>c</sup> Calcd., Cl, 10.01; found, 9.88.

ether, ethyl alcohol and acetic acid. It dissolved in aqueous sodium hydroxide (10%) with yellow color and gave an orange yellow solution in cold concentrated sulfuric acid.

**Action of Heat on the Thiol Adduct VIII.**—Two tenths g. of VIII was heated in a dry test-tube at 140° for 20 minutes (bath-temp.). The adduct melted and then turned into a somewhat solid substance. The cooled reaction mixture was crystallized from ethyl alcohol; m.p. 148° (identified as IIa, m.p. and mixed m.p.).

**Reaction of Aromatic Thiols with 3(2*H*)-Thianaphthenone-1,1-dioxides. General Procedure.**—To a solution of one gram of the sulfone derivative in the least amount of cold acetic acid, 1 g. of the thiol and 5 g. of powdered anhydrous zinc chloride are added. The reaction mixture was saturated with dry hydrogen chloride gas for 4 to 5 hr., stoppered and kept aside overnight at room temperature. It was poured into three times its volume of ice-cold water and extracted with benzene. The benzene layer was washed with water, dried over anhydrous sodium sulfate and evaporated. The oily residue was treated with cold petroleum ether (b.p. 40–60°, ca. 60 ml.). The resulting solid was filtered and crystallized from a suitable solvent.

The 3-arylmecapto derivatives VII, listed in Table II, formed colorless crystals which were readily soluble in cold benzene and chloroform but sparingly soluble in alcohol, acetic acid and ether. When treated with concentrated sulfuric acid, they gave yellow solutions which changed to orange and finally violet on standing for a few minutes. VIIa in acetone solution decolorized potassium permanganate, and in chloroform solution it decolorized bromine dissolved in chloroform.

**Oxidation of VII to the Sulfones VIII. General Procedure.**—A suspension of 1 g. of the 3-arylmecapto derivative VII in 20 ml. of glacial acetic acid was treated with 4 ml. of 30% hydrogen peroxide and 5 ml. of acetic anhydride. The reaction mixture was heated on a boiling water-bath for 1 hr., cooled, poured into 100 ml. of ice-cold water and kept at room temperature overnight. The resulting solid was collected by filtration, washed with water, dried and crystallized from a suitable solvent.

The oxidation products VIII, listed in Table III, formed colorless crystals and gave no color when treated with cold sulfuric acid; they dissolved readily in glacial acetic but were sparingly soluble in ether and cold ethyl alcohol.

**Reduction of 3-Phenylmercaptanthianaphthene-1,1-dioxide (VII).**—VIIa (0.7 g.) was treated with 50 ml. of aqueous sodium hydroxide (8%) and 10 g. of zinc dust according to the procedure described by Challenger.<sup>15</sup> The reaction mixture was refluxed for 2 hr., during which the solid VIIa changed into an oil. The cooled reaction mixture was diluted with water and extracted with benzene. After the benzene extract had been dried and evaporated, it was treated with cold petroleum ether (b.p. 40–60°, ca. 50 ml.) and the resulting solid crystallized from petroleum ether (b.p. 80–100°) as colorless crystals, m.p. 91°, which were identified as 2,3-dihydrothianaphthene-1,1-dioxide by mixed melting point determination.<sup>15</sup> The aqueous alkaline reaction mixture gave, on acidification, an oil which was proved to be thiophenol (m.p. and mixed m.p. determination with an authentic sample of phenyl thiobenzoate).

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