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, n.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.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

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)-thianaplthenone-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 1912.1 Weston and Suter² 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)³ was obtained.⁴ The treatment of IIa with phenylhydrazine gave the hydrazone of 3(2H)-thianaphthenone-1,1-dioxide (IIIb).5

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.^{5,6}

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,7 under-

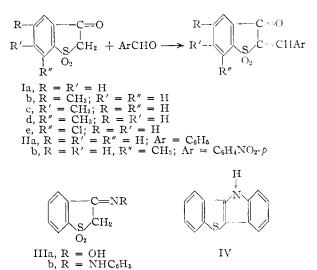
(1) M. Lanfry, Compt. rend., 154, 519 (1912).

A. W. Weston and C. M. Suter, This JOURNAL, 61, 389 (1039).
 D. H. Hartough, "Compounds with Condensed Thiophene

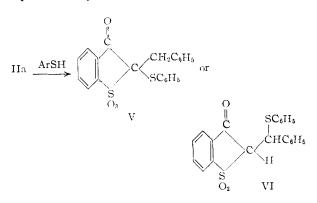
Rings," Interscience Publishers, Inc., New York, N. Y., 1954, p. 166. (4) This reaction is similar to that of hydroxylamine hydrochloride with 2-benzylideneindan-1,3-dione; cf. A. Mustafa and A. H. E. Harhash, THIS JOURNAL, 78, 1649 (1956).
(5) E. W. McClelland and J. L. D'Silva, J. Chem. Soc., 227 (1932).

(6) C. E. Dagliesh and F. G. Mann, ibid., 653 (1947).

(7) A. Mustofa. ibid., 1370 (1951).



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 α,β -unsaturated compounds,⁸ structure VI is preferable. The fact that the adduct dissolves in cold aqueous sodium hydroxide solution with a yellow color and is liberated upon neutralization with ice-cold, dilute hydrochloric acid is also in accord with structure VI. When VI was heated above its melting point for a few minutes and then cooled, the styryl derivative IIa was regenerated. The ease of removal of the addend indicates that the substance is the result of simple addition and that no unexpected reaction has occurred. Attempts to oxidize VI with hydrogen peroxide in glacial acetic acid over a water-bath also led to the formation of IIa.⁹

a water-bath also led to the formation of IIa.⁹ Reaction of Aromatic Thiols with 3(2H)-Thianaphthenone-1,1-dioxides (I).—It is generally accepted that a ketone and a thiol react in the presence of an acid catalyst to form a mercaptal,¹⁰ although scattered reports in the literature indicate that certain cyclic ketones, e.g., 4-cholesten-3-one¹¹ and other ketosteroids,¹² yield unsaturated sulfides (enol thioethers).

Recently,¹³ it was observed that 2-methyl-1indanone and 2-methyl-1-tetralone react with thiophenol, under the conditions of the mercaptal reaction, to produce phenyl-2-methyl-3-indenyl sulfide and phenyl-2-methyl-3,4-dihydro-1-naphthyl sulfide, respectively.

We have investigated the reaction of aromatic thiols with 3(2H)-thianaphthenone-1,1-dioxides (I) in the presence of anhydrous zinc chloride and hydrogen chloride and have obtained colorless products, believed to have structure VII. Under these experimental conditions, 2-methyl-3(2H)-thianaphthenone-1,1-dioxide (IX) did not react with thiols.

Desoxybenzoin¹⁴ is known to form an unsaturated sulfide when treated with thiophenol. By analogy, a similar mechanism may be presented for the formation of VII, involving the addition of one mole of thiol to form a hemimercaptal followed by elimination of water to give the unsaturated sulfide VII.

The unsaturated sulfides VII, listed in Table II, are oxidized readily by hydrogen peroxide in glacial acetic acid to give the corresponding sulfones,¹² listed in Table III.

When VIIa was treated with aqueous sodium hydroxide and zinc dust, 2,3-dihydrothianaph-thene-1,1-dioxide and thiophenol were obtained.¹⁵

Experimental

3(2H)-Thianaphthenone-1,1-dioxides.—The new 3(2H)-

(8) T. Posner, Ber., **35**, 809 (1902); B. H. Nicolet, THIS JOURNAL, **53**, 3066 (1931); P. S. Bailey and J. C. Smith, J. Org. Chem., **21**, 709 (1956); R. M. Ross and F. W. Raths, THIS JOURNAL, **73**, 129 (1951);
R. M. Ross, H. L. Bushey and R. J. Rolih, *ibid.*, **73**, 540 (1951); R. M. Ross, *ibid.*, **71**, 3458 (1949).

(9) ω-p-Dinitrostyrene thiol adducts behaved similarly when treated with hydrogen peroxide under the same conditions; cf. A. Mustafa, A. H. E. Harhash and M. Kamel, *ibid.*, **77**, 3860 (1955).

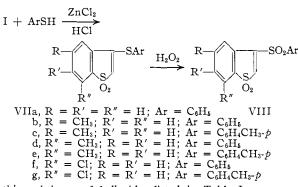
(10) E. Baumann, Ber., 18, 883 (1885).

(11) S. Bernstein and L. Dorfman, THIS JOURNAL, 68, 1152 (1946).
 (12) G. Rosenkranz, S. Kaufmann and J. Romo, *ibid.*, 71, 3689 (1949).

(13) E. Campaigne and R. D. Moss, ibid., 76, 1269 (1954).

(14) E. Campaigne and J. R. Leal, ibid., 76, 1272 (1954).

(15) Cf. the reduction of thianaphthene-1,1-dioxide by zinc dust and aqueous sodium hydroxide to yield 2,3-dihydrothianaphthene-1,1-dioxide; F. Challenger and P. H. Clapham, J. Chem. Soc., 1615 (1948).



thianaphthenone-1,1-dioxides listed in Table I were prepared from the corresponding 3(2H)-thianaphthenones which were obtained by known procedures.¹⁶ A solution of 5 g. of the thianaphthenone in 30 ml. of glacial acetic acid was treated with 25 ml. of 30% hydrogen peroxide, and the reaction mixture was heated (steam-bath) for 1 hr., with the exception of 6-methyl- and 7-methyl-3(2H)-thianaphthenone, whereby oxidation was complete in 5 minutes. The reaction products, which separated on cooling, were crystallized from a suitable solvent as colorless crystals; they gave no color with concentrated sulfuric acid and a yellow color in alcoholic sodium hydroxide.

in alcoholic sodium hydroxide. **Condensation of:** (a) 3(2H)-**Thianaphthenone**-1,1-dioxide (Ia) with Benzaldehyde.—A mixture of 1 g. of Ia¹⁷ and 2 ml. of benzaldehyde was heated for 3 hr. over an oil-bath (140° temperature of bath). The reaction mixture was cooled to room temperature and triturated with 5 ml. of cold ethyl alcohol. The resulting pale yellow solid was crystallized from alcohol; m.p. 148° (yellow melt).

Anal. Caled. for $C_{15}H_{10}O_3S$: C, 66.66; H, 3.70; S, 11.85. Found: C, 66.32; H, 3.61; S, 11.56.

This 2-benzylidene derivative IIa was soluble in benzene but difficultly soluble in ether, cold alcohol and acetic acid. It developed a yellow color in concentrated sulfuric acid.

A solution of 0.5 g. of IIa in 20 ml. of glacial acetic acid was treated with 2 g. of sodium acetate and 0.5 g. of hydroxylamine hydrochloride. The reaction mixture was refluxed for 3 hr., cooled and then poured into ice-cold water. The resulting substance was crystallized from dilute acetic acid (m.p. $24\delta^{\circ}$) and identified as the oxime of 3(2H)thianaphthenone-1,1-dioxide (IIIa)³ by a mixed m.p. determination with a sample of IIIa, obtained by the reaction of hydroxylamine hydrochloride with Ia under similar experimental conditions.

(b) 7-Methyl-3(2H)-thianaphthenone-1,1-dioxide (Id)
(b) 7-Methyl-3(2H)-thianaphthenone-1,1-dioxide (Id)
with p-Nitrobenzaldehyde.—A mixture of 1 g. of Id and 1 g. of the aldehyde was heated at 160° for 2 hr. The solid residue obtained after cooling was washed thoroughly with hot benzene and then crystallized from nitrobenzene as yellow crystals (IIb), m.p. 265°. IIb was difficultly soluble in most organic solvents and gave an orange solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{16}H_{11}NO_5S;\ C,\ 58.36;\ H,\ 3.34;\ N,\ 4.26;\ S,\ 9.72.$ Found: C, 57.97; H, 3.31; N, 4.03; S, 9.39.

Reaction of Thiophenol on IIa.—One g. of IIa was mixed with a slight excess over the calculated amount of the thiol in a test-tube, and the reaction mixture was heated at 100° for 3 hr. The cooled reaction mixture was triturated with boiling light petroleum (b.p. $30-50^{\circ}$, 50 ml.) when the oily reaction product turned into solid powder. It was filtered, washed with hot light petroleum and crystallized from benzene; m.p. 138° , yield *ca.* 88%.

Anal. Calcd. for $C_{21}H_{16}O_3S_2$: C, 66.31; H, 4.21; S, 16.84. Found: C, 66.77; H, 4.50; S, 16.49.

The thiol adduct formed colorless crystals, dissolved readily in hot benzene but was difficultly soluble in cold

(16) 5-Methyl-: D. S. Tarbell, D. K. Fukushima and H. Dam, THIS JOURNAL, **67**, 1643 (1945); 6-methyl-: A. Mustafa and S. M. A. D. Zayed, *ibid.*, **78**, 6174 (1956); 7-methyl- and 7-chloro-: C. E. Dalgliesh and F. G. Mann, J. Chem. Soc., 893 (1945); and 2-methyl-3(2H)thianaphthenone: C. Hansch and W. A. Blondon, THIS JOURNAL, **70**, 1561 (1948).

(17) F. G. Bordwell, B. B. Lampert and W. H. McKellin, *ibid.*, 71, 1702 (1949).

TABLE I

NEW SULFONES (I)

3(2H)-Thia- naphthenone- 1,1-dioxide	M.p.,ª °C.	Vield, %	Formula	Carbo Calcd.	on, % Found	Hydro Calcd.	gen, % Found	Sulfı Calcd.	ır, % Found	
Ib	202	42	$C_9H_8O_3S$	55.10	54.83	4.08	3.99	16.32	15,81	
Ic	190	48	$C_9H_8O_3S$	55.10	55.30	4.08	4.02	16.32	16.01	
Iđ	187	45	$C_9H_8O_3S$	55.10	54.73	4.08	4.09	16.32	15,88	
Ie	227	56	C ₈ H ₅ O ₃ SCl ^b	44.34	43.82	2.31	2.31	14.78	15.06	
IX ^e	Above 360	54	$C_9H_8O_3S$	55.10	54.92	4.08	4.01	16.32	16.03	

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

Table II

3-Arylmercaptothianaphthene-1,1-dioxides (VII)

5-MRILMERCHFIOTHIANAFHHENE-1,1-DIOAIDES (VII)										
3-Aryl- mercapto- deriv.	М.р., <i>^а</i> °С.	Yield, $\%$	Color with concd. H2SO4	Formula	Carbo Calcd.	n, % Found	Hydro Calcd.	gen, % Found	Sulfu Caled.	r, % Found
VIIa	128	81	Yellow	$C_{14}H_{10}O_2S_2$	61.31	61.01	3.65	3,57	23.36	23.12
VIIb	126	79	Orange	$\mathrm{C_{15}H_{12}O_2S_2}$	62.50	62.39	4.16	4.00	22.22	21.98
VIIc	144	72	Deep red	$C_{16}H_{14}O_2S_2$	63.57	63.21	4.63	4.53	21.19	20.96
VIIđ	122	74	Yellow	$C_{15}H_{12}O_2S_2$	62.50	62.43	4.16	4.43	22.22	21.74
VIIe	124	71	Orange	$C_{16}H_{14}O_2S_2$	63.77	63.77	4.63	4.93	21.19	21.24
VIIf	134	82	Yellow	$C_{14}H_9O_2S_2Cl^b$	54.46	53.91	2.91	3.16	20.74	20.25
VIIg	142	76	Orange	$\mathrm{C_{15}H_{11}O_2S_2Cl^c}$	55.81	55.47	3.41	3.31	19.84	19.43
4 411 0141				1.1 (1.11.51.5	1 10.07	10.1.1	C1 11	01. f1	10.00	

^a All melting points are uncorrected. ^b Calcd., Cl, 11.51; found, 10.95. ^c Calcd., Cl, 11.01; found, 10.82.

Table III

OXIDATION PRODUCTS OF 3-ARVLMERCAPTOTHIANAPHTHENE-1,1-DIOXIDE (VIII)

Oxidation	M.p.,ª	Yield,		Carbon, %		Hydrogen, %		Sulfur, %	
products	°Č.	%	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
VIIIa	155	77	$C_{14}H_{16}O_4S_2$	54.90	54.63	3.27	3.12	20.91	20.28
VIIIb	184	68	$C_{15}H_{12}O_4S_2$	56, 25	55.99	3.75	3.63	20.00	20.10
VIIIc	190	66	$C_{16}H_{14}O_4S_2$	57,48	17.09	4.19	4.00	19.16	19.76
VIIId	130	81	$C_{15}H_{12}O_4S_2$	56.25	55.98	3.75	3.66	20.00	19.67
VIIIe	158	78	$C_{16}H_{14}O_4S_2$	57.48	57.09	4.19	4.15	19.16	18.87
VIIIf	285	83	$C_{14}H_9O_4S_2Cl^b$	49.34	48.97	2.64	2.54	18.79	17.97
VIIIg	210	75	$C_{15}H_{11}O_4S_2Cl^c$	50.77	50.08	3.10	2.87	18.05	17.67
All melting r	nointe are	117007700	ted & Caled Cl	10.42 · found	1 11 10	Caled (1 10.01.	found 9.88	

All melting points are uncorrected. b Caled., Cl, 10.42; found, 11.10. Caled., 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(2H)-Thianaphthenone-

Reaction of Aromatic Thiols with 3(2H)-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. $40-60^\circ$, ca. 60 ml.). The resulting solid was filtered and crystallized from a suitable solvent.

The 3-arylmercapto 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-aryImercapto 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-Phenylmercaptothianaphthene-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.¹⁵ 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 to be thiophenol (n.p. and mixed m.p. determination with an authentic sample of phenyl thiobeuzoate).

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