REACTION OF 3-OXODIHYDROTHIONAPHTHENES WITH ARYL DIAZONIUM CHLORIDES AND ARYL ISOTHIOCYANATES

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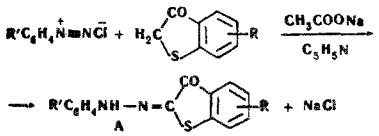
The reaction of 3-oxodihydrothionaphthenes with aryl diazonium chlorides gives 2-arylhydrazono-3-oxodihydrothionaphthenes. By oxidation of the latter with hydrogen peroxide in glacial acetic acid, new 2-arylhydrazonodihydrothionaphthene-(3)-one-1, 1-dioxides are synthesized. Condensation of aryl isothiocyanates with 3-oxodihydrothionaphthenes in tetrahydrofuran gives 2-(arylthiocarbamyl)-3-oxodihydrothionaphthenes; cyclization of the latter with ω-bromoacetophene leads to the synthesis of 4-phenyl-3-aryl-2-(3'-oxodihydrothionaphthylidene-2')-Δ^4-thiazolines.

The reaction of 3-oxodihydrothionaphthenes with aryl diazonium chlorides has been but little studied [1, 2]. Recently aryl derivatives of 2-methyldihydrothionaphthen-(3)-one-1, 1-dioxide have been synthesized [3].

The literature does not describe addition reactions between aryl isothiocyanates and 3-oxodihydrothionaphthenes followed by cyclization of the coupling products with ω-bromoacetophenone to Δ^4-thiazoline derivatives, or oxidation of 2-arylhydrazono-3-oxodihydrothionaphthene-1, 1-dioxides.

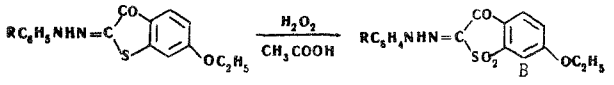


R = 6·C_2H_5O; 4,5-Benzo

We have now prepared a number of 2-arylhydrazono-3-oxodihydrothionaphthenes (A) by reacting 6-ethoxy- and 4, 5-benzo-3-oxodihydrothionaphthenes with aryl diazonium chlorides (Table 1). Coupling is effected in aqueous sodium acetate solution or pyridine.

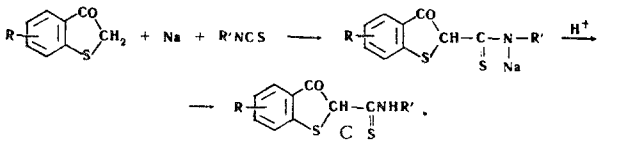
The structure of the 2-arylhydrazonodihydrothionaphthen-(3)-ones is proved by the way in which they are synthesized, and by IR spectrum data [sharp characteristic absorption bands of bonds: N—H (3200–3240), C=O (1655–1670), C=N (1590–1600 cm^{-1})]. The UV spectra of these compounds have 3–4 absorption maxima in the 270–450 mμ region.

For a number of 2-phenyl substituted hydrazones of 6-ethoxy-3-oxodihydrothionapthenes it is shown that hydrogen peroxide in glacial acetic acid oxidizes them to 2-arylhydrazonodihydrothionapthen-(3)-one-1, 1-dioxides (B) (Table 2).



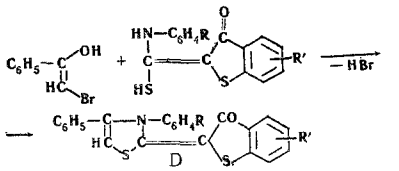
The IR spectra of these compounds have sharp absorption bands of symmetric and asymmetric vibrations of the SO_2 group (1165–1135 and 1305–1345 cm^{-1}).

3-Oxodihydrothionaphthenes also react with aryl isothiocyanates in tetrahydrofuran solution in the presence of sodium, to give 2-(arylthiocarbamyl)-3-oxodihydrothionaphthenes (C) (Table 3), the equations being



Under our conditions there were no products formed by addition of two molecules of aryl isothiocyanate to a 3-oxodihydrothionaphthene. Yields of type C compounds are low 2–38%, possibly because 3-oxodihydrothionaphthenes are readily oxidized to the corresponding thioindigo dyes. The UV absorption plots of the compounds show absorption maxima at 277–295, 305–340, and 416–425 mμ (in ethanol).

Condensation of 2-(arylthiocarbamyl)-3-oxodihydrothionaphthenes with ω-bromoacetophenone in ethanol leads to cyclization to the corresponding 4-phenyl-3-aryl-2-(3'-oxodihydrothionaphthylidene-2')-Δ^4-thiazoline (D) (Table 4).

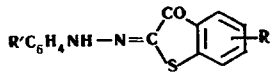


Type D compounds are characterized by UV absorption spectra with 4 absorption maxima, at 245–250, 304–306, 340–342 and 438–442 mμ (in ethanol).

EXPERIMENTAL

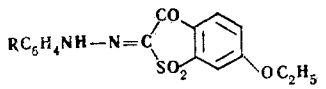
2-p-Tolylhydrazono-6-ethoxy-3-oxodihydrothionaphthene (IV). 2.1 g (0.02 mole) p-toluidine in 15 ml 17% HCl was diazotized at 0°–5° C with a solution of 1.4 g (0.02 mole) $NaNO_2$ in 15 ml water. The diazo solution was filtered and quickly added with stirring to a cooled solution of 3.9 g (0.02 mole) 6-ethoxy-3-oxodihydrothionaphthene in 60 ml pyridine plus 15 ml water containing 12 g NaOAc. The solution turned reddish-orange, and a precipitate soon started to form. The products were stirred for 4–5 hr, 100 ml water added, then kept for 2 hr, and the reddish-orange precipitate filtered off, washed with water, and dried, yield 3.2 g, mp 194°–195° (ex AcOH), λ_{max}, mμ (ε): 274 ($1.67 \cdot 10^4$), 346 ($0.62 \cdot 10^4$), 360 ($1.22 \cdot 10^4$), 448 ($1.75 \cdot 10^4$).

Table 1



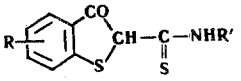
Compound	R	R′	Mp, ° C	Formula	N, % Found	N, % Calculated	Yield, %
I	6-C_2H_5O	H	162 —163	$C_{16}H_{14}N_2O_2S$	9.20; 8.96	9.39	6
II		*o*-CH_3	145	$C_{17}H_{16}N_2O_2S$	8.80; 8.60	8.97	49
III		*m*-CH_3	146 —147	$C_{17}H_{16}N_2O_2S$	9.28; 9.13	8.97	49
IV		*p*-CH_3	194 —195	$C_{17}H_{16}N_2O_2S$	8.55; 8.51	8.97	52
V		*o*-CH_3O	186	$C_{17}H_{16}N_2O_3S$	8.60; 8.45	8.53	52
VI		*p*-CH_3O	152 —153	$C_{17}H_{16}N_2O_3S$	8.47; 8.28	8.53	48
VII		*p*-C_2H_5O	167	$C_{18}H_{18}N_2O_3S$	8.13; 7.94	8.18	51
VIII		*o*-Cl	157	$C_{16}H_{13}ClN_2O_2S$	8.38; 8.36	8.42	37
IX		*m*-Cl	179 —180	$C_{16}H_{13}ClN_2O_2S$	8.35; 8.25	8.42	38
X	4,5-Benzo	H	172 —172.5	$C_{18}H_{12}N_2OS$	9.13; 9.15	9.20	36
XI		*o*-CH_3O	198 —199	$C_{19}H_{14}N_2O_2S$	8.38; 8.35	8.38	19
XII		*o*-OC_2H_5	178.5—179	$C_{20}H_{16}N_2O_2S$	7.87; 7.83	8.04	32
XIII		*p*-CH_3O	196 —197	$C_{19}H_{14}N_2O_2S$	8.05; 8.00	8.38	46
XIV		*p*-CH_3	198 —199	$C_{19}H_{14}N_2OS$	8.72; 8.69	8.80	52
XV		*p*-Cl	242 —243	$C_{18}H_{11}ClN_2OS$	8.10; 7.93	8.27	18

Table 2



Compound	R	Mp, ° C	Formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %
XVI	*o*-CH_3	229	$C_{17}H_{16}N_2O_4S$	59.50; 59.34	4.70; 4.65	59.29	4.68	29
XVII	*p*-CH_3	245—246	$C_{17}H_{16}N_2O_4S$	58.97	4.67	59.29	4.68	32
XVIII	*o*-CH_3O	252—253	$C_{17}H_{16}N_2O_5S$	56.71; 56.88	4.11; 4.25	56.66	4.48	42
XIX	*p*-CH_3O	232	$C_{17}H_{16}N_2O_5S$	56.82; 56.84	4.60; 4.65	56.66	4.48	11
XX	*m*-Cl	229—230	$C_{16}H_{13}ClN_2O_4S$	53.05	3.61	52.68	3.59	46
XXI	*p*-Cl	260—262	$C_{16}H_{13}ClN_2O_4S$	53.04	3.46	52.68	3.59	61

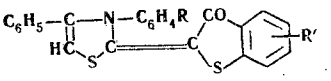
Table 3



Compound	R	R′	Mp, ° C	Formula	S, %		Yield, %
					Found	Calculated	
XXII	6-C_2H_5O	CH_2=$CHCH_2$	169.5—171	$C_{14}H_{15}NO_2S_2$	21.23; 21.10	21.85	2
XXIII		C_6H_5	200—201	$C_{17}H_{15}NO_2S_2$	19.32; 19.31	19.47	2
XXIV		o-$CH_3OC_6H_4$	183—184	$C_{18}H_{17}NO_3S_2$	17.75; 17.66	17.84	6
XXV		p-$CH_3C_6H_4$	185	$C_{18}H_{17}NO_2S_2$*	18.68; 18.59	18.67	2
XXVI		p-BrC_6H_4	193—194	$C_{17}H_{14}BrNO_2S_2$	15.72; 15.62	15.75	14
XXVII	4, 5-Benzo	C_6H_5	196—197	$C_{19}H_{13}NOS_2$	18.80; 18.74	19.11	38

*Found: N 4.08; 4.07%. Calculated N 4.08%. λ_{max} mμ(ε): 277 ($1.34 \cdot 10^4$), 304 ($2.28 \cdot 10^4$), 416 ($1.3 \cdot 10^4$).

Table 4



Compound	R	R′	Mp, ° C (ex EtOH)	Formula	Found, %			Calculated, %			Yield, %
					C	H	S	C	H	S	
XXVIII	H	6-OC_2H_5	269—271	$C_{25}H_{19}NO_2S_2$	—	—	14.85 14.85	—	—	14.92	77
XXIX	o-OCH_3	6-OC_2H_5	223—224	$C_{26}H_{21}NO_3S_2$	67.77 67.60	4.31 4.23	13.96 13.91	67.94	4.60	13.95	79
XXX	p-Br	6-OC_2H_5	251—253	$C_{25}H_{18}BrNO_2S_2$*	59.25 59.23	2.69 2.57	12.61 12.42	59.06	3.56	12.61	88
XXXI	H	4,5-Benzo	299—302	$C_{27}H_{17}NOS_2$	74.91 74.98	3.90 3.89	14.54 14.52	74.45	3.91	14.72	65

*Found: Br 15.92; 16.08%. Calculated Br 15.72%.

Compounds **I–XV** (Table 1) were prepared similarly. They formed reddish-orange to cherry-colored crystals with a metallic glitter, readily soluble in most organic solvents when heated, less soluble in n-hexane, petrol ether, and ether; insoluble in formamide and water. When treated with conc. H_2SO_4 the arylhydrazones gave an intense violet color which disappeared on dilution with water, or on making alkaline.

2-p-Tolylhydrazono-6-ethoxy-3-oxodihydrothionaphthene-1,1-dioxide (XVII). 1 g (0.003 mole) hydrazone IV was suspended in 30 ml glacial AcOH at 45°, and 8 g H_2O_2 added. The mixture was left for 3 weeks at room temperature, and the yellowish-orange precipitate filtered off and dried. Recrystallization from glacial AcOH gave minute yellowish-orange crystals with a metallic glitter. Yield 0.35 g (32%), mp 245°–246° C (ex AcOH), λ_{max}, mμ (ε): 250–260 (inflection) ($0.84 \cdot 10^4$) and 436 ($2.38 \cdot 10^4$).

Compounds **XVI–XXI** (Table 2) were prepared similarly. They formed pale-yellow to yellowish-orange crystals. They were readily soluble in many organic solvents when heated, but only slightly soluble in water.

2-p-Bromophenylthiocarbamyl-6-ethoxy-3-oxodihydrothionaphthene (XXVI). 0.24 g (0.01 g-at) finely cut Na was added to a solution of 2.9 g (0.01 mole) 6-ethoxy-3-oxodihydrothionaphthene in 100 ml tetrahydrofuran. The mixture was heated on a water-bath until the Na had almost completely dissolved, 2.1 g (0.01 mole) p-bromophenylisocyanate added, and the whole left at room temperature for 72 hr, with periodical shaking. The solvent was completely evaporated off, and the viscous oily residue was treated with 70–90 ml water, the whole well ground, and then filtered. The filtrate was made slightly acidic with AcOH. After some time the product, at first viscous and oily, crystallized. The solid was filtered off, washed with water, and dried. Yield 0.6 g (14%), mp 191°–192° C (ex EtOH-dioxane). λ_{max}, mμ (ε): 294 ($2.2 \cdot 10^4$), 340 ($1.1 \cdot 10^4$), 425 ($4.9 \cdot 10^4$).

Compounds **XXII–XXVII** (Table 3) were prepared similarly. They formed grayish-yellow or yellowish-green crystals. They were soluble in alkalies and many organic solvents.

4-Phenyl-3-(p-bromophenyl)-2-(3-oxodihydrothionaphthylidene-2′)-Δ^4-thiazoline (XXX). A mixture of 0.2 g (0.5 mmole) XXVI and 0.1 g (0.5 mmole) ω-bromoacetophenone in 15 ml EtOH was refluxed on a water-bath for 4–5 hr, then left for 12 hr at room temperature. The grayish-yellow precipitate with a metallic glitter was filtered off, washed with EtOH, then with ether, and dried, yield 0.22 g (88%), mp 251°–253° C (ex EtOH-Me_2CO 5:1). λ_{max}, mμ (ε): 249 ($1.5 \cdot 10^4$), 306 ($1.1 \cdot 10^4$), 339 ($1.34 \cdot 10^4$), 442 ($2.92 \cdot 10^4$).

Compounds **XXVIII–XXXI** (Table 4) were prepared similarly. UV spectra were measured with a SF-4 spectrophotometer, and IR spectra with a UR-10 automatic double beam spectrophotometer (Zeiss, Jena). Prisms: KBr, NaCl, and LiF. The compounds were tabletted with KBr (1:100).

REFERENCES

1. P. Friedlaender, Monatsch, **30**, 353, 1909.
2. K. Auwers and F. Arndt, Ann. **381**, 299, 1911.
3. B. Eistert and M. Regitz, Chem. Ber., **96**, 2290, 1963.

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