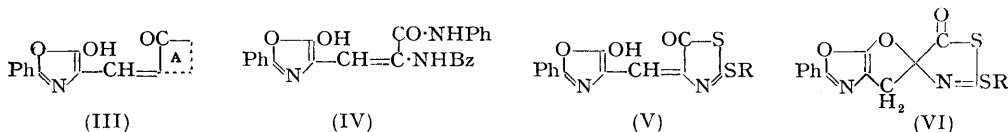




solution. An unstable red form is obtained by heating its solution in alcoholic triethylamine, and then acidifying it. This form reverts to the colourless form on recrystallization. Hot xylene solutions are pink, the colour slowly fading. Unlike normal oxonols it is insoluble in aqueous sodium hydroxide. From this property and its reversible thermo-



chromic behaviour it appears that isomerization has occurred to the spiran (VI); an oxonium  $\psi$ -base or oxonium base structure is unlikely as no salt-like properties are exhibited and treatment of a benzene solution with hydrogen chloride failed to give the oxonium chloride.

#### EXPERIMENTAL

Microanalyses are by Drs. Weiler and Strauss.

*Di-(2-ethoxy-4-thiazol-5-one)methinoxonol* (I; R = R' = OEt).—*N*-Thiocarbethoxyglycine (Aubert *et al.*, *loc. cit.*) (1.65 g.) and acetic anhydride (15 c.c.) were heated in an oil-bath at 130° for 30 minutes and the solvents removed under reduced pressure. A similar mixture containing, in addition, ethyl orthoformate (5 c.c.) was treated similarly. The two residual oils were heated under reflux in ethanol (10 c.c.) and triethylamine (2 c.c.) for 5 minutes. The yellow solution was cooled, water (50 c.c.) was added, and the clear solution was acidified with dilute hydrochloric acid. The precipitated orange oil slowly crystallized. This *oxonol* formed orange crystals, m. p. 146°, after two crystallizations from methanol (Found: N, 9.35; S, 21.4. C<sub>11</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>S<sub>2</sub> requires N, 9.35; S, 21.3%);  $\lambda_{\max}$ , 472 (450) m $\mu$  in methanolic triethylamine. This and other wave-lengths in parentheses indicate secondary peaks or inflexions (i).

[2-Ethylthio-4-thiazol-5-one][2-*n*-tetradecyloxy-4-thiazol-5-one]methinoxonol (I; R = SEt, R' = O·C<sub>14</sub>H<sub>29</sub>).—*N*-Dithiocarbethoxyglycine (1.8 g.) and acetic anhydride (10 c.c.) were heated on the steam-bath for 30 minutes and the solvents removed. 4-Ethoxymethylene-2-*n*-tetradecyloxythiazol-5-one (Aubert *et al.*, *loc. cit.*) [from *N*-thiocarbo-*n*-tetradecyloxyglycine (3.3 g.)] was added to the residue and the whole heated under reflux in ethanol (10 c.c.) with triethylamine (2 c.c.) for 3 minutes. The dye solution was set aside for 1 hour, water (50 c.c.) added, and the dye (4.2 g.) precipitated with dilute hydrochloric acid. It formed orange-brown needles, m. p. 74°, from acetone (Found: N, 5.9; S, 20.1. C<sub>23</sub>H<sub>36</sub>O<sub>3</sub>N<sub>2</sub>S<sub>3</sub> requires N, 5.8; S, 19.85%);  $\lambda_{\max}$ , 492 (470) m $\mu$  in methanolic triethylamine.

[2-Ethylthio-4-thiazol-5-one][2-*n*-octylthio-4-thiazol-5-one]methinoxonol (I; R = SEt, R' = S·C<sub>8</sub>H<sub>17</sub>) was obtained similarly from *N*-dithiocarbethoxyglycine (1.8 g.) and *N*-dithiocarbo-*n*-octyloxyglycine (Aubert *et al.*, *loc. cit.*) (2.6 g.). The red oil obtained on acidification was washed by decantation, dissolved in acetone, and chilled, to give the *methinoxonol* which formed clusters of small, violet needles, m. p. 76°, from acetone (Found: S, 31.05. C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>N<sub>4</sub>S<sub>4</sub> requires S, 30.8%);  $\lambda_{\max}$ , 519 (492) m $\mu$  in methanolic triethylamine.

[2-*n*-Dodecylthio-4-thiazol-5-one][2-ethylthio-4-thiazol-5-one]methinoxonol (I; R = SEt, R' = S·C<sub>12</sub>H<sub>25</sub>), obtained and isolated similarly, formed purple needles, m. p. 55°, from acetone (Found: S, 27.3. C<sub>21</sub>H<sub>32</sub>O<sub>2</sub>N<sub>2</sub>S<sub>4</sub> requires S, 27.1%);  $\lambda_{\max}$ , 520 (490) m $\mu$  in methanolic triethylamine.

[2-Acetamido-4-thiazol-5-one][2-*n*-octylthio-4-thiazol-5-one]methinoxonol (I; R = NHAc, R' = S·C<sub>8</sub>H<sub>17</sub>).—*N*-Dithiocarbo-*n*-octyloxyglycine (1.3 g.), ethyl orthoformate (5 c.c.), and acetic anhydride (15 c.c.) were heated for 30 minutes at 120°, and the solvent was then removed. 2-Acetamidothiazol-5-one hydrobromide (Aubert *et al.*, *loc. cit.*), (1.2 g.), ethanol (10 c.c.), and triethylamine (3 c.c.) were added and the whole was heated for 5 minutes on the steam-bath. The sticky crystalline dye obtained on acidification formed a brown crystalline powder, m. p. 228°, from acetic acid (Found: N, 10.3; S, 23.5. C<sub>17</sub>H<sub>23</sub>O<sub>3</sub>N<sub>3</sub>S<sub>3</sub> requires N, 10.15; S, 23.2%);  $\lambda_{\max}$ , 497 (484) m $\mu$  in methanolic triethylamine.

[3-Carboxymethyl-2-thio-5-thiazolid-4-one][2-phenyl-4-oxazol-5-one]methinoxonol.—4-Ethoxy-methylene-2-phenyloxazol-5-one (1.1 g.), 3-carboxymethylrhodanine (0.95 g.), ethanol (50 c.c.), and triethylamine (1.5 c.c.) were refluxed for 5 minutes after completion of solution. The orange-red solution was filtered, diluted with water (100 c.c.), and acidified with dilute sulphuric acid. The precipitated red oil solidified on cooling. It was redissolved in 2*N*-sodium carbonate,

and the solution was filtered and acidified. The red oil was then dissolved in boiling acetone and boiled until crystallisation set in. This *oxonol* formed magenta needles, m. p. 245°, after repetition of the acetone treatment (Found: N, 7.45; S, 17.6.  $C_{15}H_{10}O_5N_2S_2$  requires N, 7.75; S, 17.7%);  $\lambda_{\max}$ . 434 (520i)  $m\mu$  in methanolic triethylamine.

[3-Ethyl-2-thio-5-thiazolid-4-one][2-phenyl-4-oxazol-5-one]methinoxonol obtained similarly from 3-ethylrhodanine formed violet crystals of indefinite m. p. from benzene (Found: N, 8.3.  $C_{15}H_{12}O_3N_2S_2$  requires H, 8.45%).  $\lambda_{\max}$ . 433 (523)  $m\mu$  in methanolic triethylamine.

[3-Ethyltetrahydro-4-keto-2-thio-1-phenylglyoxaline][2-phenyl-4-oxazol-5-one]methinoxonol was obtained similarly from 3-ethyl-1-phenyl-2-thiohydantoin (1.1 g.) as greenish-red needles of indefinite m. p. from benzene (Found: C, 64.3; H, 4.3; N, 10.7; S, 8.1.  $C_{21}H_{17}O_3N_3S$  requires C, 64.5; H, 4.35; N, 10.75; S, 8.2%);  $\lambda_{\max}$ . 504 (480i)  $m\mu$  in methanolic triethylamine.

Di-(2-phenyl-4-oxazol-5-one)methinoxonol.—2-Phenylloxazol-5-one (0.8 g.), 4-ethoxymethylene-2-phenylloxazol-5-one (1.1 g.), ethanol (10 c.c.), and triethylamine (1 c.c.) were heated on the steam-bath for 5 minutes. The deep yellow solution was chilled and 0.5N-hydrochloric acid was added, giving a flocculent red precipitate (1.7 g.) of the dye. It formed dark red needles with a dark green reflex, m. p. 210° (after softening), after twice crystallizing from benzene (Found: C, 68.3; H, 3.6; N, 8.3.  $C_{19}H_{12}O_4N_2$  requires C, 68.5; H, 3.6; N, 8.45%). The colour of its acetone solution slowly faded and the yellow ethanol solution gave a yellow oil on dilution with water;  $\lambda_{\max}$ . 498  $m\mu$  in methanolic triethylamine, 520  $m\mu$  in benzene.

The red benzene solution faded on addition at 70° of a few drops of aniline. The colourless  $\alpha$ -benzamido- $\beta$ -(5-hydroxy-2-phenyl-4-oxazolyl)acrylanilide (IV) which separated formed fluffy, colourless needles, m. p. 205° (decomp. from 195°), from methanol (Found: C, 70.6; H, 4.15; N, 9.9.  $C_{25}H_{19}O_4N_3$  requires C, 70.6; H, 4.45; N, 9.9%).

Isomer of [2-Benzylthio-4-thiazol-5-one][2-phenyl-4-oxazol-5-one]methinoxonol (V; R =  $CH_2Ph$ ).—4-Ethoxymethylene-2-phenylloxazol-5-one (1.1 g.), 2-benzylthiothiazol-5-one (1.1 g.), ethanol (10 c.c.), and triethylamine (1 c.c.) were refluxed for 5 minutes. Dilution with water gave a yellow precipitate changing to a red oil on acidification. The latter solidified slowly. It formed colourless, glossy threads, m. p. 136° (red), after two recrystallizations from acetone (orange-red solution). This *isomer* is insoluble in aqueous sodium hydroxide. It dissolves in xylene to give a pink solution when hot, becoming colourless after several hours (Found: C, 60.85; H, 3.3; N, 6.9; S, 16.55.  $C_{20}H_{14}O_3N_2S_2$  requires C, 61.0; N, 3.55; S, 16.25%);  $\lambda_{\max}$ . 496  $m\mu$  in methanolic triethylamine.

Isomer of [2-n-Octylthio-4-thiazol-5-one][2-phenyl-4-oxazol-5-one]methinoxonol (V; R =  $n-C_8H_{17}$ ).—Obtained similarly, this *isomer* formed fluffy, pink needles, m. p. 108° (red), from acetone (Found: N, 6.75; S, 15.6.  $C_{12}H_{24}O_3N_2S_2$  requires N, 6.75; S, 15.4%);  $\lambda_{\max}$ . 469  $m\mu$  in methanolic triethylamine.

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