449. Oxonols Derived from Azol-5-ones.

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A number of symmetrical and unsymmetrical oxonol dyes derived from 2substituted thiazol-5-ones and 2-phenyloxazol-5-one has been prepared for test as photographic sensitizers. Di-(2-phenyl-4-oxazol-5-one)methinoxonol is readily attacked by aniline to give, probably, α -benzamido- β -(5-hydroxy-2phenyl-4-oxazolyl)acrylanilide. The reaction of 4-ethoxymethylene-2-phenyloxazol-5-one and 2-benzylthiothiazol-5-one leads to a colourless chromotropic product which is isomeric with the required oxonol. It sensitizes a silver halide emulsion to visible light in the same way as related normal oxonols.

OXONOLS (dyes obtained by linking two heterocyclic keto-methylene nuclei by a methin group) are in many instances rather poor photographic sensitizers. Although this may be due partly to their poor adsorption on the grain the chief reason is probably because, in general, steric hindrance prevents coplanarity of the two nuclei. This is shown in the Figure for di-(3-methyl-1-phenyl-4-pyrazol-5-one)methinoxonol (Knorr, *Annalen*, 1887, **238**, 137). Similarly the trimethinoxonols are overcrowded molecules, although less so than the methinoxonols. In order that oxonols may be planar one or both of the positions marked ***** in the Figure must be unsubstituted, *i.e.*, must be hetero-atoms. Suitable nuclei are, *e.g.*, **3**-ethylrhodanine and 2-diphenylamino-5-thiazol-4-one (Brooker, U.S.P. 2,241,238).



Recently Cook, Harris, and Shaw (J., 1949, 1435) obtained oxonols of type (I; R = R' = SR'') which also fulfil the required condition, and Davis and Levy (J., 1949, 2179) obtained thionols of type (II) in which planarity may be achieved by opening of the chain angle

(I)
$$R \downarrow_{N} - CH - \downarrow_{N} R'$$
 $Ph \downarrow_{N} - CH - \downarrow_{N} CS$ (II)

Since dyes (I; R = R' = SEt or SBz) have now been found to be powerful orthosensitizers further examples have been synthesised. The oxygen analogue, di-(2-ethoxy-4thiazol-5-one)methinoxonol (I; R = R' = OEt) was readily obtained from 2-ethoxythiazol-5-one and its 4-ethoxymethylene derivative (Aubert, Knott, and Williams, *J.*, 1951, 2185) in alcoholic triethylamine. Unsymmetrical oxonols (I; $R = O \cdot C_{16}H_{33}$, R' = SEt; $R = S \cdot C_8H_{17}$, R' = NHAc; etc.) were also obtained in this way. The absorption characteristics of the anions of these oxonols (see Experimental) show that in (I; R = R' =SEt) replacement of first one and then both SEt by OEt causes a progressive hypsochromic shift.

In the oxazolone series (cf. Davis and Levy, *loc. cit.*) a number of oxonols (III) were obtained which in some cases behave abnormally. The symmetrical oxonol di-(2-phenyl-4-oxazol-5-one)methinoxonol (III; A = 2-phenyl-4-oxazolone), whilst stable as its anion and in inert solvents, is rapidly decolorized in alcoholic solution. This is attributed to ring opening (cf. Davis and Levy, *loc. cit.*) by addition of ethanol. The same effect is obtained on addition of aniline to the benzene solution of the dye, giving α -benzamido- β -(5-hydroxy-2-phenyl-4-oxazolyl)acrylanilide (IV). On the other hand the oxonol (V; $R = CH_2Ph$) is colourless, has a low melting point, and gives a red melt. It sensitizes a silver chloride emulsion with λ_{max} . At 530 m μ . It dissolves in hot acetone or benzene to an orange-red

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 ψ -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 prisms, m. p. 146°, after two crystallizations from methanol (Found : N, 9:35; S, 21·4. $C_{11}H_{12}O_4N_2S_2$ requires N, 9:35; S, 21·3%); λ_{max} 472 (450) mµ 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·C₁₄H₂₉).—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. C₂₃H₃₆O₃N₂S₃ requires N, 5·8; S, 19·85%); λ_{max} . 492 (470) mµ in methanolic triethylamine.

[2-Ethylthio-4-thiazol-5-one][2-n-octylthio-4-thiazol-5-one]methinoxonol (I; R = SEt, R' = S·C₈H₁₇) was obtained similarly from N-dithiocarbethoxyglycine (1·8 g.) and N-dithiocarbe-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. C₁₇H₂₄O₂N₄S₄ requires S, 30·8%). λ_{max} 519 (492) mµ in methanolic triethylamine.

[2-n-Dodecylthio-4-thiazol-5-one][2-ethylthio-4-thiazol-5-one]methinoxonol (I; R = SEt, R' = S·C₁₂H₂₅), obtained and isolated similarly, formed purple needles, m. p. 55°, from acetone (Found : S, 27·3. $C_{21}H_{32}O_2N_2S_4$ requires S, 27·1%); λ_{max} 520 (490) m μ in methanolic triethylamine.

[2-Acetamido-4-thiazol-5-one][2-n-octylthio-4-thiazol-5-one]methinoxonol (I; R = NHAc, $R' = S \cdot C_8 H_{17}$).—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. $C_{17}H_{23}O_3N_3S_3$ requires N, 10·15; S, 23·2%); λ_{max} . 497 (484) mµ in methanolic triethylamine.

[3-Carboxymethyl-2-thio-5-thiazolid-4-one][2-phenyl-4-oxazol-5-one]methinoxonol.—4-Ethoxymethylene-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 2N-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 actone treatment (Found: N, 7.45; S, 17.6. $C_{15}H_{10}O_5N_2S_2$ requires N, 7.75; S, 17.7%); λ_{max} , 434 (520i) m μ 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%). λ_{max} . 433 (523) m μ 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; 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%); λ_{max} 504 (480i) m μ in methanolic triethylamine.

Di-(2-phenyl-4-oxazol-5-one)methinoxonol.—2-Phenyloxazol-5-one (0.8 g.), 4-ethoxymethylene-2-phenyloxazol-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. C₁₉H₁₂O₄N₂ 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; λ_{max} , 498 m μ in methanolic triethylamine, 520 m μ in benzene.

The red benzene solution faded on addition at 70° of a few drops of aniline. The colourless α -benzamido- β -(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 C₂₅H₁₉O₄N₃ 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 = CH₂Ph). --4-Ethoxymethylene-2-phenyloxazol-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; N, 7·1; S, 16·25%); λ_{max} . 496 mµ 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%); λ_{max} . 469 m μ in methanolic triethylamine.

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