

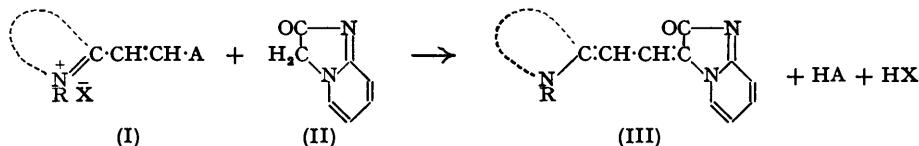
672. *The Abnormalities of Dyes Derived from 3:7a-Diazaindan-2-one.**

By EDWARD B. KNOTT.

3:7a-Diazaindan-2-one (II) has been employed in condensations to yield dimethinmerocyanines (III), solutions of which show a hypsochromic absorption shift on increasing the solvent polarity. These dyes are reactive towards cyclic keto-methylene compounds, yielding oxonols. In the formation of these dimethinmerocyanines from the diazaindanone and 2-substituted vinyl derivatives (I) of cyclic ammonium salts the formation of bis-(3:7a-diaza-1-indan-2-one)methinoxonol (IV) is observed when the diazaindanone is used in excess. The reason for the strongly dipolar nature of the dyes (III) is discussed, together with the possible mechanism of the reactions.

DIMETHINMEROCYANINES, which were discovered by Kendall (B.P. 428,222; 428,360) and independently by Brooker and his collaborators (cf. Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, and White, *J. Amer. Chem. Soc.*, in the press) may be obtained by the condensation of a 2-substituted vinyl derivative of a cyclic quaternary ammonium salt (I) with a keto-methylene compound, in the presence of a base. The group A is usually an anilino-, acetanilido-, or alkylthio-residue. A variety of keto-methylene compounds has been employed in this condensation but 3:7a-diazaindan-2-one* (II) which gives dimethinmerocyanines of type (III) has not hitherto been used.† Various dyes have now been obtained from this substance, and their properties are of interest.

For these condensations the hydrohalide of (II) (Reindel, *Ber.*, 1924, 57, 1381) was employed as it is more conveniently handled than the less stable base or sodium salt (see also Chichibabin, *ibid.*, p. 2072; Reindel and Rausch, *Ber.*, 1925, 58, 393). It was noteworthy that even when



an excess of triethylamine was used to bind the acid the dyes were always obtained as the hydrohalides. The dye bases differ from known dyes of this class in possessing much greater water solubility, particularly on heating. They are also quite insoluble in non-polar solvents and exceedingly easily soluble in polar organic solvents, the dyes thus behaving as strongly polar molecules.

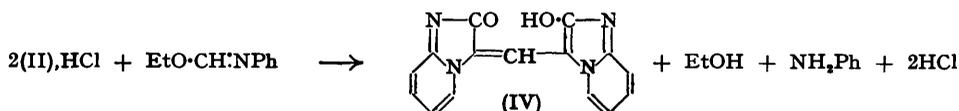
In a condensation of 2-2'-acetanilidovinylbenzoxazole ethiodide with the hydrochloride of (II) in alcoholic triethylamine, an excess of the hydrochloride was inadvertently used and, contrary to experience in a previous experiment using molar quantities of reactants, a dye crystallized during the refluxing, the normal dye being obtained from the filtrate. The alcohol-insoluble dye was very soluble in aqueous sodium carbonate or ammonia and was precipitated by acid, thus possessing the reverse characteristics of the normal dimethinmerocyanine. It proved to be the oxonol, bis-1-(3:7a-diazaindan-2-one)methinoxonol ‡ (IV), as shown by its analysis and preparation from (II) and ethylisofromanilide. Acidification of the hot, aqueous

* This compound (II) was originally named pyrimidazolone (Reindel, *Ber.*, 1924, 57, 1381). Allen and van Allan (*J. Org. Chem.*, 1948, 13, 599) pointed out, however, that the name pyrimidazole has been applied to several ring systems and renamed the compound 3a-azaindol-2-one. Dr. Allen suggested (privately) that a more satisfactory name would be 1:3a-diazaindan-2-one in which the parent hydrocarbon is taken as the basis. This is not completely satisfactory since pyrimidazolone is not derived from indane but from the 7aH-isomer. The Editor has suggested 3:7a-diazaindan-2-one as the name which allows no ambiguity, in which case the presence of the 7a-nitrogen atom shows that there has been a shift of hydrogen from the 3-position of indane to the 7a-position. It will be noted that the numbering now starts from the methylene carbon and not from the methin carbon as in the name suggested by Dr. Allen.

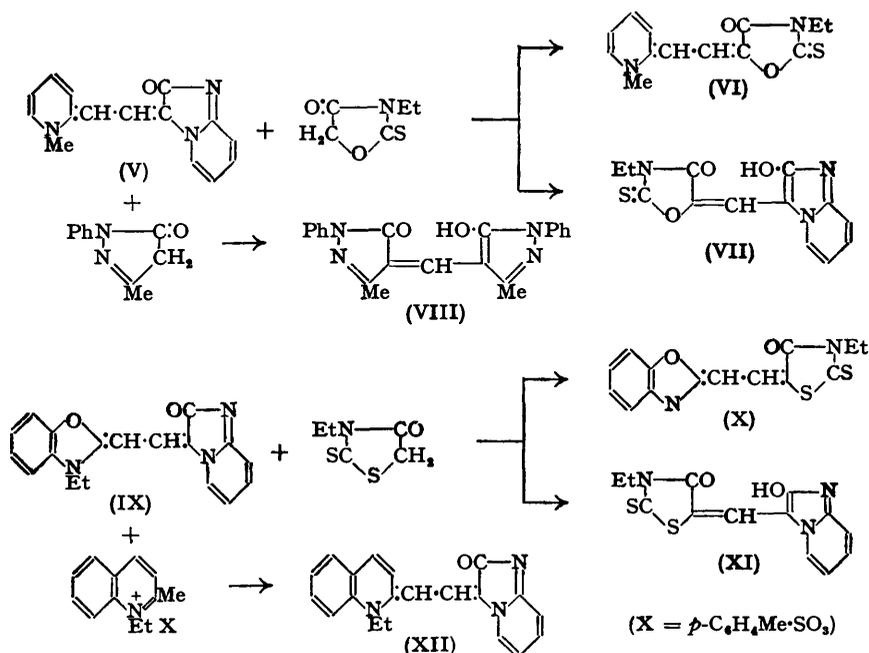
† Since this paper was written van Dormael (*Bull. Soc. chim.*, 1949, 58, 167) has published similar condensations with this nucleus.

‡ For the oxonol nomenclature, see Hamer and Winton, *J.*, 1949, 1126.

alkaline solution of the oxonol with acetic acid gave the crystalline dihydrate but, when an excess of concentrated hydrochloric acid was used for acidification, the hydrochloride dihydrate obtained which was readily hydrolysed by water to the dihydrate.



The yield of the oxonol was increased considerably when two mols. of the salt of (II) were employed for one of the quaternary salt (I). The same product was obtained irrespective of the nature of (I), although the yields varied from case to case, being particularly low when the dimethinmerocyanine formed a sparingly soluble hydrohalide which was precipitated from the alcoholic solution during refluxing. This fact seemed to indicate that the oxonol was formed by reaction of the second mol. of (II) with the dimethinmerocyanine. 2-Anilino-vinyl derivatives (I; A = NPh) of the quaternary salt gave a higher yield of oxonol than did the 2-acetanilido-vinyl analogues (I; A = NPhAc). The probability that the oxonol was formed from the normal dyes was heightened by the fact that these latter are attacked not only by (II) to give (IV), but also by other compounds containing a reactive methylene or methyl group, even in the absence of a base, to give unsymmetrical oxonols, dimethinmerocyanines, and in one case a symmetrical oxonol. These reactions are typified by the following:



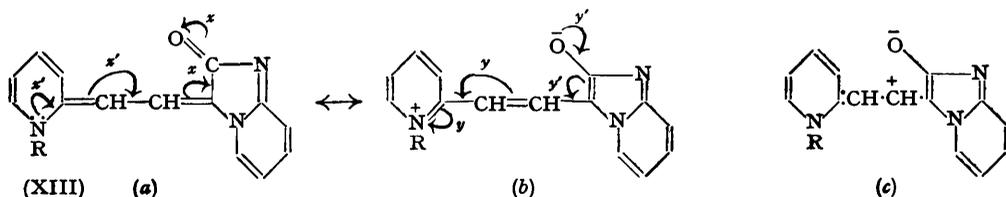
The yields of the oxonols (VII) and (XI) were higher than those of the dimethinmerocyanines.

The alcohol-soluble potassium salt of the oxonol (IV) is also reactive, yielding unsymmetrical oxonols on treatment with reactive keto-methylene compounds:



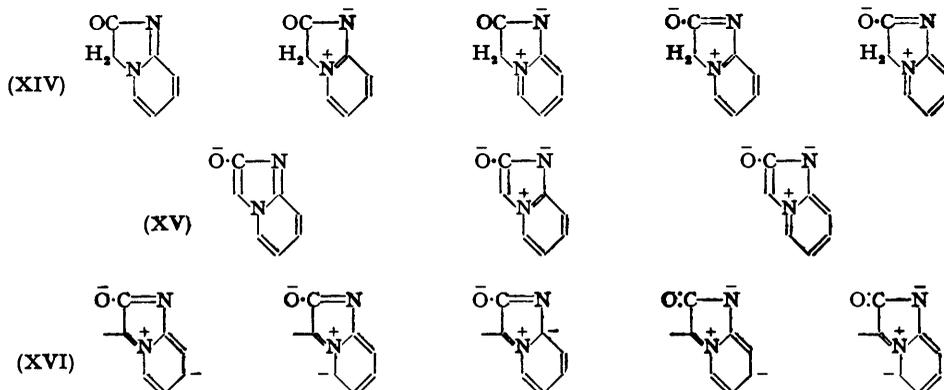
The Dipolar Nature of the Dimethinmerocyanines.—The abnormal behaviour of the dyes derived from (II) shows this nucleus to differ considerably from the normal type of cyclic keto-methylene compound. The behaviour as strongly polar molecules of the dimethinmerocyanines (III) indicates that there is a strong electron attraction by the nucleus from the rest of the

molecule, *i.e.*, the polar, extreme structure (*e.g.*, XIIIb) in these dyes appears to be of greater significance than usual.



This strong polarity appears in hypsochromic shifts when the polarity of the solvents is increased. This is the reverse of the usual bathochromic shifts shown by non-ionic dyes under such influences. The theoretical explanation of such a reversal was given by Förster (*Z. Elektrochem.*, 1939, 45, 572) (see also Brooker *et al.*, *J. Amer. Chem. Soc.*, in the press; Knott, *J.*, in the press). It occurs in those dyes in which the energy level of the dipolar extreme structure (*e.g.*, XIIIb) is of the same order as, or lower than, the level of the classical structure (*e.g.*, XIVa). Increasing solvent polarity then favours still more the dipolar structure, causing an increase in the non-degeneracy of the resonance system (*e.g.*, XIIIa \leftrightarrow XIIIb), with a resultant hypsochromic shift.

If one considers the two extreme structures of the dye (XIIIa, b) it is apparent that the pyridinium ion which constitutes the left-hand side of the molecule in (b) will be more stable than the dihydropyridine moiety in (a), since in the former, full Kekulé resonance is possible. However such a consideration applies in the case of any *merocyanine*; consequently the behaviour of (XIII) as a strong dipole indicates that the energy of the right-hand moiety of (a), on acquisition of an electron to give the reduced form as in (b), does not increase to the same extent as it does in other cases. It is, of course, feasible that the energy of the nucleus actually decreases on reduction. The higher $+M$ effect of this nucleus, compared with others, may be explained by consideration of the number of contributing structures in the net-uncharged and net-negatively charged form.* If structures involving formal bonds are omitted then the net-uncharged form is stabilized by five important contributing structures, (XIV). On the other hand the net-negatively



charged nucleus is stabilized only by three structures of this type (XV). There is, however, a further set of five stabilizing structures (XVI) which can contribute only to the net-negatively charged rings. The contributions by structures (XVI) may be of sufficient importance to account for the behaviour of the nucleus. Even if the energy of the net-negatively charged form is not greatly different from the energy of the net-uncharged form of the nucleus it may be sufficient, in conjunction with the increased stabilization of the left hand side of the molecule (XIIIb), to increase the polarity relative to analogous dyes containing other ketonic nuclei.

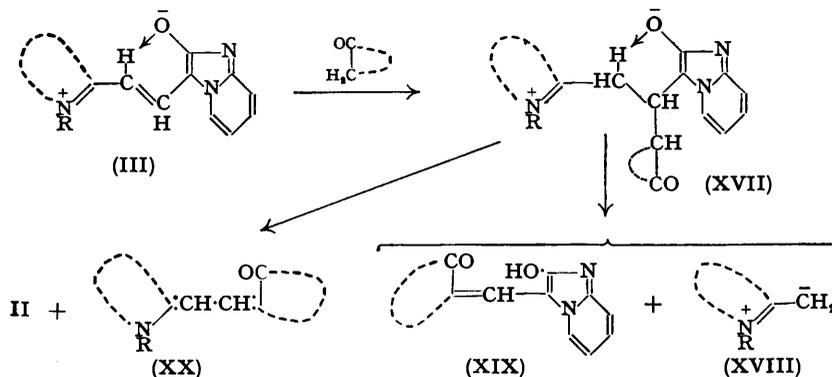
The Mechanism of Oxonol Formation from the Dimethinmerocyanines.—Although the isolation of intermediate products has not been possible it seems reasonable to assume that the formation of oxonols from these dimethinmerocyanines depends primarily on the attack by the nucleophilic carbon atom of the methylene group on the electrophilic β -carbon atom of the chain of the dye. If the two extreme structures (a) and (b) of the dye (XIII) are considered, then the

* For some of these considerations the author is indebted to Dr. L. G. S. Brooker.

electromeric processes involved in (a) are denoted by x and in (b) by y . The mesomeric processes in each case are represented by $x'-x$ and $y-y'$. The electrophilic strength of the β -carbon atom will depend, not only on the polarisability of the molecule in the field of the attacking molecule represented by x and y , but also on the charge on the β -carbon atom in the hybrid arising from such excited structures as (XIIIc). In these neutralized systems the β -carbon activity will thus increase as the ratio $x : x'$ or of $y : y'$ of the shifts increases. The activity of these dyes, compared with other dimethinmerocyanines, may thus be attributed to the high $+M$ effect, *i.e.*, electron affinity, of the right hand nucleus.

The same consideration explains the electrophilic nature of the β -carbon atom in the β -substituted vinyl derivative (I) to which the dimethinmerocyanines are closely related.

The attack on the dye (III) by a keto-methylene compound is then pictured as follows. The unstable intermediate (XVII) expels either the methylene base (XVIII) to give the oxonol (XIX), or (II) to give the second dimethinmerocyanine (XX). The expulsion of (XVIII) requires no



transfer of proton and this may be the reason why the oxonol is the main product. The formation of small quantities of the dye (XX), which requires the transfer of a proton to the diazaindenol anion, may be facilitated by hydrogen bonding between the active α -chain-hydrogen and the oxygen atom. The formation of the symmetrical oxonol (VIII) from (V) and 3-methyl-1-phenylpyrazolone which is known to have a highly active, nucleophilic carbon atom is possibly a result of further attack on the unsymmetrical oxonol (XIX) with the elimination of (II). The feasibility of this is indicated by the formation of (VIII) from (IV) and 3-methyl-1-phenylpyrazolone.

EXPERIMENTAL.

Microanalyses are by Drs. Weiler and Strauss, Oxford. M.p.s are uncorrected.

3 : 7a-Diazaindan-2-one hydrochloride was obtained from 2-imino-1 : 2-dihydro-1-pyridylacetic acid (Reindel, *Ber.*, 1924, 57, 1381) by refluxing it with an equal part of concentrated hydrochloric acid for 15 minutes, concentrating the mixture in an open dish on the steam-bath until it was viscous, and then adding an excess of *isopropyl* alcohol. After being washed with the same solvent, the required salt was obtained as cream-coloured crystals. The hydrobromide was obtained by heating a solution of 2-bromoacetamidopyridine (Chichibabin, *ibid.*, 1925, 58, 393) in *n*-butanol on the steam-bath for 4 hours, by which time the quaternisation was complete and the salt, a brown crystalline mass, had separated.

[3 : 7a-Diaza-1-indan-2-one][1-ethyl-2-quinoline]dimethinmerocyanine (XII).—2'-Acetanilidovinyl-quinoline ethiodide (4.44 g., 0.01 mol.) was dissolved in hot ethanol (50 c.c.) and a solution of 3 : 7a-diazaindan-2-one hydrobromide (2.15 g., 0.01 mol.) in ethanol (50 c.c.) was added, followed by triethylamine (2.8 c.c., 0.02 mol.). After 2 minutes' boiling the dye *hydriodide*, m. p. 300°, separated as golden crystals. It was purified by being boiled several times with ethanol (Found : N, 9.5; I, 27.5. C₂₀H₁₈ON₃I requires N, 9.5; I, 28.85%). The base was obtained by dissolving the salt in alcoholic triethylamine and precipitating with water. After drying in air it was dissolved in ethanol, and ether was run into the hot solution until crystallisation commenced. The dye, m. p. 266°, collected after the solution had cooled, formed purple needles with a green reflex (Found : N, 13.6. C₂₀H₁₇ON₃ requires N, 13.3%), λ_{\max} 562 (in methanol), 543 m μ . (in aqueous methanol).

[3 : 7a-Diaza-1-indan-2-one][3-ethyl-2-benzoxazole]dimethinmerocyanine (IX).—2'-Acetanilidovinyl-benzoxazole ethiodide (4.34 g.), 3 : 7a-diazaindan-2-one hydrobromide (2.15 g.), triethylamine (2.8 c.c.) and ethanol (25 c.c.) were refluxed together for 30 minutes. Triethylamine and alcohol were partly removed by distillation and, on cooling, the *hydrobromide* (4 g.) crystallised. It formed red needles, m. p. 202°, from ethanol (Found : N, 10.5; Br, 20.65. C₁₈H₁₆O₂N₃Br requires N, 10.9; Br, 20.7%). The base was obtained as yellow flakes on addition of aqueous sodium carbonate to the warm aqueous

solution of the salt, followed by chilling. It is very difficult to filter. It formed orange crystals, m. p. 269°, from water (Found : N, 13.6. $C_{18}H_{16}O_2N_2$ requires N, 13.8%), λ_{max} 502 m μ . (in methanol).

[3 : 7a-Diaza-1-indan-2-one][3-ethyl-2-benzthiazole]dimethinmerocyanine, was obtained as a very insoluble salt on refluxing for 30 minutes a mixture of the diazaindanone hydrobromide (2.15 g.), 2-2'-acetanilidovinylbenzthiazole ethiodide (4.5 g.), triethylamine (2.8 c.c.), and ethanol (25 c.c.). The base was released as for the previous dye, and obtained as red needles or small green crystals, m. p. 271°, from ethanol-ether (Found : N, 12.6; S, 9.95. $C_{18}H_{16}ON_2S$ requires N, 13.1; S, 10.0%), λ_{max} 532 m μ . (in methanol). The hydrobromide was obtained as red needles, m. p. 309°, by dissolving the base in ethanol and adding a solution of hydrobromic acid in acetic acid (Found : N, 10.4. $C_{18}H_{16}ON_2Br$ requires N, 10.45%).

[3 : 7a-Diaza-1-indan-2-one][3-ethyl-2-thiazolidine]dimethinmerocyanine.—A mixture of 2-2'-acetanilidovinylthiazoline ethiodide (4 g.), the diazaindanone hydrobromide (2.15 g.), triethylamine (2.8 c.c.), and ethanol (25 c.c.) was refluxed for 30 minutes and concentrated to half volume. On chilling, a mixture (4 g.) of purple needles and orange rosettes was obtained. The base was extremely soluble in water and was not isolated. The hydrobromide was obtained as orange rosettes, m. p. 236°, by dissolving the crude product in hot alcohol and adding a solution of hydrobromic acid in acetic acid (Found : N, 11.4; Br, 22.0. $C_{14}H_{14}ON_2SBr$ requires N, 11.85; Br, 22.6%), λ_{max} 479 m μ . (in methanol).

[3 : 7a-Diaza-1-indan-2-one][1-methyl-2-pyridine]dimethinmerocyanine (V).—2-2'-Anilino vinylpyridine methiodide (3.5 g.) was heated under reflux for 30 minutes with acetic anhydride (10 c.c.), then chilled, and the acetanilidovinyl derivative precipitated with ether. The oil was washed with ether and refluxed with 3 : 7a-diazaindan-2-one hydrobromide (2.15 g.), triethylamine (2.8 c.c.), and ethanol (25 c.c.) for 30 minutes. The hydrobromide commenced to crystallise after a few minutes. It (2.7 g.) formed a purple powder, m. p. 268°, from methanol (Found : N, 12.5. $C_{18}H_{14}ON_2Br$ requires N, 12.65%). The base was obtained as purple needles, m. p. 261°, from water. It contained water of crystallisation, removed at 110° (Found : N, 16.4. $C_{18}H_{13}ON_2$ requires N, 16.7%), λ_{max} 525 (in methanol), 464 m μ . (in water).

[3 : 7a-Diaza-1-indan-2-one][1-ethyl-4-pyridine]dimethinmerocyanine was obtained similarly from 4-2'-anilino vinylpyridine ethiodide (3.7 g.). The hydriodide (2 g.) formed fine purple hairs, m. p. 267°, from methanol (Found : N, 10.1. $C_{18}H_{16}ON_2I$ requires N, 10.7%), and the base dihydrate, red needles from water (Found : N, 14.1. $C_{18}H_{16}ON_2 \cdot 2H_2O$ requires N, 13.95%), λ_{max} 542 m μ . (in methanol).

Bis-(3 : 7a-diaza-1-indan-2-one)methinoxonol (IV).—(a) 3 : 7a-Diazaindan-2-one hydrochloride (3.4 g., 0.02 mol.), ethanol (200 c.c.), and triethylamine (2.8 c.c.) were heated to effect dissolution, and ethylisoformanilide (1.5 g., 0.01 mol.) added. A brick-red solid (2.5 g.), m. p. 300°, separated. For purification this oxonol was boiled several times with ethanol (Found : C, 64.6; H, 3.5; N, 20.1. $C_{16}H_{10}O_2N_4$ requires C, 64.75; H, 3.6; N, 20.5%). After its dissolution in boiling aqueous ammonia and then neutralisation with acetic acid, rose-coloured needles of the dihydrate separated on cooling (Found : C, 57.1; H, 4.5; N, 17.5. $C_{15}H_{10}O_2N_4 \cdot 2H_2O$ requires C, 57.35; H, 4.5; N, 17.65%). The addition of excess of concentrated hydrochloric acid to the ammoniacal solution of the base gave orange needles of the hydrochloride dihydrate (Found : Cl, 10.1. $C_{15}H_{10}O_2N_4 \cdot HCl \cdot 2H_2O$ requires Cl, 10.15%). Further typical experiments are as follows.

(b) 2-2'-Acetanilidovinylbenzoxazole ethiodide (8.7 g., 0.01 mol.), the diazaindanone hydrochloride (4.3 g., 0.0125 mol.), ethanol (20 c.c.), and triethylamine (2.8 c.c., 0.02 mol.) were refluxed for 30 minutes. The oxonol (2.2 g.) was obtained as a brick-red crystalline powder (Found : C, 64.4; H, 3.75; N, 20.2%). The filtrate gave the normal dimethinmerocyanine salt on concentration.

(c) 2-2'-Anilino vinylthiazoline methiodide (3.6 g., 0.01 mol.), the diazaindanone hydrochloride (3.4 g., 0.02 mol.), ethanol (20 c.c.), and triethylamine (2.8 c.c., 0.02 mol.) were refluxed for 10 minutes. The whole solidified to a brick-red crystalline mass. The oxonol (3.9 g.) was converted into the dihydrate (Found : C, 56.95; H, 4.55; N, 18.4%) and hydrochloride dihydrate (Found : Cl, 9.85%).

(d) The compound (IX) (3.41 g., 0.01 mol.), 3 : 7a-diazaindan-2-one hydrochloride (1.7 g., 0.01 mol.) triethylamine (1.4 c.c., 0.01 mol.) (may be omitted), and ethanol (20 c.c.) were refluxed for 1 hour. The oxonol (2.4 g., 86.5%) separated during this time (Found : N, 20.3%).

Reactions of Dimethinmerocyanines.—(a) The cyanine (V) (2.5 g.), 3-ethyl-4-keto-2-thio-oxazolidine (1.45 g.), and ethanol (15 c.c.) were refluxed for 3 hours. The solid which separated was boiled with aqueous sodium carbonate, leaving purple needles undissolved. The latter (0.2 g.) formed metallic spears, m. p. 254° from pyridine (Found : C, 59.8; H, 5.5; N, 10.4. Calc. for $C_{13}H_{14}O_2N_2S$: C, 59.6; H, 5.35; N, 10.7%). It is [3-ethyl-4-keto-2-thio-5-oxazolidine][2-methyl-1-pyridine]dimethinmerocyanine (VI). The filtrate from the reaction mixture gave an orange precipitate on addition of water : this was obtained as orange-brown crystals (1.9 g.), m. p. 292° (decomp.), from aqueous sodium carbonate and is [3 : 7a-diaza-1-indan-2-one][3-ethyl-4-keto-2-thio-5-oxazolidine]methinoxonol (VII) (Found : N, 14.4; S, 8.5. $C_{13}H_{11}O_3N_2S$ requires N, 14.4; S, 8.7%).

(b) The base (IX) (3.05 g.), treated similarly, gave the analogous [3-ethyl-2-benzoxazole][3-ethyl-4-keto-2-thio-5-oxazolidine]dimethinmerocyanine (0.95 g.) (Found : C, 61.2; H, 5.05; N, 8.25; S, 10.1. Calc. for $C_{17}H_{16}O_2N_2S$: C, 60.8; H, 5.05; N, 8.85; S, 9.75%). The filtrate gave 2.1 g. of the oxonol formed as recorded in (a) (Found : C, 54.25; H, 3.85%).

(c) The base (IX) (3.05 g., 0.01 mol.), 3-ethylrhodanine (1.6 g., 0.01 mol.), and ethanol (20 c.c.) were refluxed for 2 hours. After 10 minutes, crystals commenced to form. After cooling, the solid (2.4 g.), which was a mixture, was collected, and the oxonol removed by boiling 2N-sodium carbonate. The residue (0.5 g.) formed yellow needles, m. p. 230°, from ethanol (Found : C, 57.5; H, 4.75; N, 10.0; S, 19.06. Calc. for $C_{18}H_{14}O_2N_2S_2$: C, 57.55; H, 4.7; N, 9.65; S, 19.3%). It is [3-ethyl-2-benzoxazole][3-ethyl-4-keto-2-thio-5-thiazolidine]dimethinmerocyanine (X). The carbonate extract, together with the dye precipitated by water from the reaction mixture filtrate, gave 2.5 g. of [3 : 7a-diaza-1-

indan-2-one[3-ethyl-4-keto-2-thio-5-thiazolidine]methinoxonol (XI), which formed a steel-grey crystalline powder, m. p. 300°, from formamide (Found: C, 51.15; H, 3.95; N, 13.5; S, 20.95. $C_{13}H_{11}O_2N_2S_2$ requires C, 51.1; H, 3.6; N, 13.8; S, 21.0%).

(d) The oxonol (IV) (2.5 g., 0.01 mol.), 3-methyl-1-phenylpyrazolone (1.74 g., 0.01 mol.), and ethanol (20 c.c.) were refluxed for 1½ hours. On dilution with water a yellow precipitate was given which on recrystallisation from ethanol formed yellow needles (1.1 g.), m. p. 175° alone or mixed with an authentic specimen of (VIII) (Found: N, 15.3. Calc. for $C_{21}H_{18}O_2N_4$: N, 15.6%).

(e) The base (IX) (3.05 g., 0.01 mol.), quinaldine ethotoluene-*p*-sulphonate (3.43 g., 0.01 mol.), and ethanol (25 c.c.) were refluxed together for 2 hours. The purple solution was then poured into water and the dimethinmerocyanine (XII) collected; it formed purple needles (1.1 g., 35%) with a green reflex, m. p. 265°, identical with the product obtained earlier (Found: N, 13.4%).

Reactions of the Oxonol (IV).—(a) The oxonol (1.4 g., 0.005 mol.) and 3-ethyl-4-keto-2-thio-oxazolidine (0.75 g., 0.005 mol.) were suspended in a solution of potassium hydroxide (0.6 g.) in alcohol (30 c.c.) and refluxed for 1 hour. The resultant clear solution was acidified with dilute hydrochloric acid, and the precipitate recrystallised from aqueous sodium carbonate. It formed orange-brown crystals (1.05 g., 77.5%), m. p. 292° (decomp.), identical with (VII) obtained earlier (Found: S, 9.4%).

(b) The oxonol (1.4 g.), 3-methyl-1-phenylpyrazolone (0.87 g., 0.005 mol.), and a solution of potassium hydroxide (0.4 g.) in alcohol (30 c.c.) were refluxed for 1 hour. The clear, hot solution was acidified, and the orange crystals (1.3 g.) were collected on cooling. They were repeatedly extracted with isopropyl ether, to give 0.45 g. (50%) of the ether-soluble oxonol (VIII), m. p. 176° alone or mixed with an authentic specimen (Found: N, 15.4%).

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