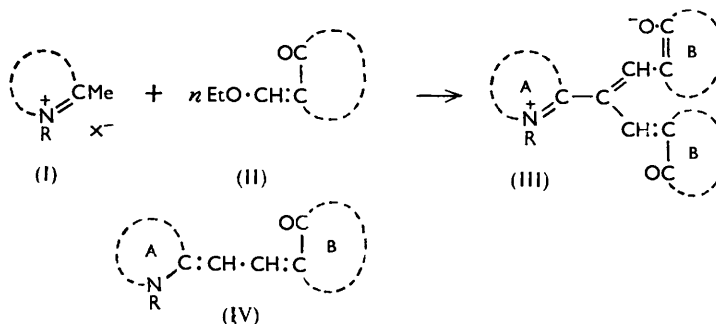


580. *Trinuclear Dyes Related to Oxonols. Part II.\* Formation and Absorption Spectra.*

By R. A. JEFFREYS.

Several new trinuclear dyes are described. Steric and electronic limitations to the formation of trinuclear dyes from methyl-substituted heterocyclic quaternary salts and ethoxymethylene derivatives of ketomethylene heterocyclic compounds are formulated. These dyes, and similar ones prepared by Hamer, Rathbone, and Winton,<sup>1</sup> are considered to be chain-substituted mesoionic oxonols.

In previous papers<sup>2,3</sup> it was shown that trinuclear dyes (III) related to oxonols may be produced, together with dimethinmerocyanines (IV), by reaction of heterocyclic quaternary salts possessing a reactive methyl group (cf. I) with ethoxymethylene keto-heterocyclic compounds (cf. II) in basic media. The reaction was confined to quaternary salts derived



from benzimidazole, perimidine, and pyridine, and ethoxymethylene derivatives of 3-alkyl-2-thiothiazolid-4-one and 2-ethylthiothiazol-5-one. Dyes containing 3-phenylisooxazol-5-one, 1 : 3-diethyl-2-thiobarbituric acid, and 2-phenyloxazol-5-one rings have now been made.

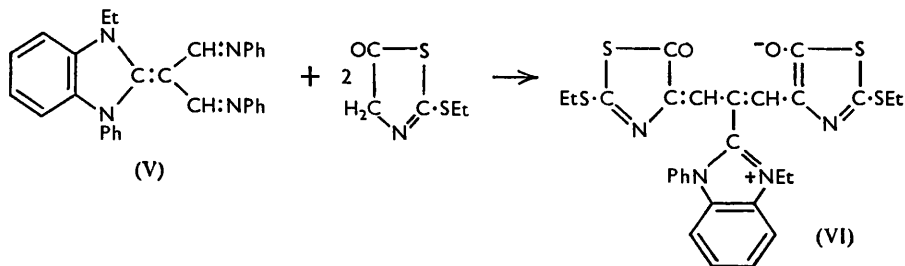
\* The paper in *Compt. rend. XVIIth Congr. Int. Chim. Ind.*, 1954, Vol. III, p. 618, is regarded as Part I.

<sup>1</sup> Hamer, Rathbone, and Winton, *J.*, 1949, 1113.

<sup>2</sup> Jeffreys, *Compt. rend. XVIIth Congr. Int. Chim. Ind.*, 1954, Vol. III, p. 618.

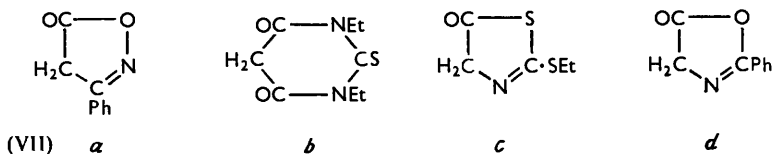
<sup>3</sup> Jeffreys, *J.*, 1955, 2394.

An alternative synthesis of one dye has confirmed the structure (III). The intermediate (V), of the type described by Hamer *et al.*<sup>1</sup> and kindly supplied by Dr. F. M. Hamer, condensed with two equivalents of 2-ethylthiothiazol-5-one to give the trinuclear compound (VI), identical with a sample prepared from the 2-methyl heterocyclic quaternary salt and two equivalents of the 4-ethoxymethylene derivative of the thiazolone (VIIc).



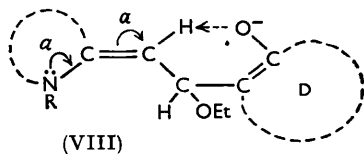
**Dye Formation.**—A trinuclear dye is formed only when the quaternary salt is derived from a heterocyclic base with a strong  $-M$  effect;<sup>2</sup> the yields of dyes are in order of  $-M$  effects of the participating heterocycles (*e.g.*, benzimidazole dye no. 19, 49%; perimidine dye, 20%; and pyridine dye no. 21, 11%).

The choice of keto-heterocyclic ring systems available for dye formation is restricted to those strongly  $+M$  heterocycles which form ethoxymethylene derivatives.<sup>4</sup> Quaternary salts from 2-methylbenzimidazole and 4-methylpyridine were condensed with two molecular equivalents of the ethoxymethylene derivatives of (VIIa—d). Whereas 1:3-dimethyl- or 1:3-diethyl-benzimidazolium salt provided trinuclear dyes with derivatives of (VIIa—c), 1-ethyl-2-methyl-3-phenylbenzimidazolium iodide formed the required dye only in the case of (VIIc). It is considered that steric factors prevent trinuclear-dye formation with (VIIa and b) since these nuclei each have two substituent atoms or groups which would be adjacent to the conjugated trimethin chain, and these together with the 1-ethyl-3-phenyl



groups of the benzimidazolium salt hinder the approach of a second ethoxymethylene molecule to the  $\alpha$ -carbon atom. Trinuclear dyes with 4-pyridyl nuclei were isolated only from the products of reactions involving derivatives of (VIIc and d). Again, steric hindrance or high solubility of the product prevented formation or isolation of the dyes containing the nuclei (VIIa and b).

Attempts to prepare trinuclear dyes (III) from the related dimethinmerocyanines (IV) with (a) ethoxymethylene derivatives (II), or (b) diethoxymethyl acetate and ketomethylene heterocyclic compounds (VII), failed. Since the dyes (IV) are therefore eliminated as intermediates, it is considered that compounds of type (III) are formed by way of intermediates such as (VIII).



So long as the ethoxy-group on the  $\beta$ -carbon atom is retained, a compound of type (VIII) has the structure of a methylene base with a nucleophilically reactive  $\alpha$ -carbon atom (arrows *a*), and can react with a second molecule of ethoxymethylene derivative. It is interesting that the ease of formation of trinuclear dye, as measured by the yields, is in the reverse order of the "availability" of the methylene base from the respective quaternary salts (I) and may be a guide to the reactivity of the methylene bases.<sup>5</sup>

<sup>4</sup> Knott, *J.*, 1954, 1482.

<sup>5</sup> Brooker, Dent, Heseltine, and Van Lare, *J. Amer. Chem. Soc.*, 1953, **75**, 4335.

*Absorption Spectra.*—The trinuclear dyes described have high extinction coefficients (Table 1), implying a planar resonance system. It has been shown<sup>2</sup> that, to satisfy this condition, one of the heterocyclic nuclei must be twisted from the plane of dye resonance,

TABLE 1. *Absorption maxima (a) (in m $\mu$ ) and molecular extinction coefficients (b) ( $\times 10^{-4}$ ) in various solvents.*

Dye no.	Component B		Benzene		MeOH		Aq. MeOH (1:2)																																																																																																																																																																																																
	a	b	a	b	a	b	a	b																																																																																																																																																																																															
<i>Dimethinmerocyanines (IV).</i>																																																																																																																																																																																																							
(i) $\Lambda = 1\text{-R-3-R'-benzimidazolin-2-ylidene.}$																																																																																																																																																																																																							
	1-R	3-R'																																																																																																																																																																																																					
1	Me	Me	VIIa	460	6.0	412	3.8	390	1.9																																																																																																																																																																																														
2	Et	Ph	VIIa	475	8.1	431	3.3	416	1.9																																																																																																																																																																																														
3	Me	Me	VIIb	460	—	416	—	407	—																																																																																																																																																																																														
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4	Et	Ph	VIIb	472	7.7	422	2.1	426	3.6																																																																																																																																																																																														
				i454		i440		i438																																																																																																																																																																																															
5	Et	Et	VIIc	511	—	470	—	453	—																																																																																																																																																																																														
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6	Et	Ph	VIIc	518	8.2	494	5.7	488	5.1																																																																																																																																																																																														
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7	Me	Me	VII d	511	—	482	—	470	—																																																																																																																																																																																														
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(ii) $\Lambda = 1\text{-ethyl-1:4-dihydropyridin-4-ylidene.}$																																																																																																																																																																																																							
8	—	—	VIIa	545	—	477	1.6	460	1.5																																																																																																																																																																																														
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9	—	—	VIIb	535	—	480	—	460	—																																																																																																																																																																																														
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10	—	—	VIIc	546	—	530	—	515	—																																																																																																																																																																																														
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11	—	—	VII d	542	—	550	—	528	—																																																																																																																																																																																														
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12*	1-Ethyl-1:4-dihydroquinol-4-ylidene		3-Ethyl-2-thiothiazolid-4-one		569 <sup>b</sup>	—	614 <sup>b</sup>	—	605 <sup>b</sup>																																																																																																																																																																																														
					604		577		i569																																																																																																																																																																																														
13*	3-Ethylbenzothiazolin-2-ylidene		,, ,,		513 <sup>b</sup>	—	526 <sup>b</sup>	—	533 <sup>b</sup>																																																																																																																																																																																														
14*	3-Ethylbenzothiazolin-2-ylidene		3-Ethyl-2-thio-oxazolid-4-one		487	—	498	—	503																																																																																																																																																																																														
15	3-Methylthiazolidin-2-ylidene		,, ,,		442	—	450	—	460																																																																																																																																																																																														
16*	5-Chloro-3-ethylbenzothiazolin-2-ylidene		3-Ethyl-1-phenyl-2-thiohydantoin		485	—	508	—	518																																																																																																																																																																																														
<table border="1"> <thead> <tr> <th>Dye no.</th> <th>Components A, B as in no.</th> <th>Benzene a</th> <th>Benzene b</th> <th>MeOH a</th> <th>MeOH b</th> <th>Aq. MeOH (1:2) a</th> <th>Aq. MeOH (1:2) b</th> <th><math>\Delta\lambda_{\max.}</math></th> <th>Related trimethinnoxonol *</th> </tr> </thead> <tbody> <tr> <td colspan="10"><i>Trinuclear dyes (III).</i></td> </tr> <tr> <td>17</td> <td>1</td> <td>496</td> <td>—</td> <td>488</td> <td>6.5</td> <td>488</td> <td>6.3</td> <td>— 8</td> <td>530<sup>c</sup></td> </tr> <tr> <td></td> <td></td> <td>i470</td> <td></td> <td>i466</td> <td></td> <td>i466</td> <td></td> <td></td> <td></td> </tr> <tr> <td>18</td> <td>3</td> <td>464</td> <td>—</td> <td>460</td> <td>5.0</td> <td>463</td> <td>—</td> <td>— 1</td> <td>536</td> </tr> <tr> <td>19</td> <td>5</td> <td>564</td> <td>3.0</td> <td>565</td> <td>11.8</td> <td>567</td> <td>—</td> <td>3</td> <td>595<sup>a</sup></td> </tr> <tr> <td></td> <td></td> <td>i536</td> <td></td> <td>i530</td> <td></td> <td>i533</td> <td></td> <td></td> <td>i562</td> </tr> <tr> <td>20</td> <td>6</td> <td>570</td> <td>10.8</td> <td>568</td> <td>10.1</td> <td>572</td> <td>9.9</td> <td>2</td> <td>595<sup>a</sup></td> </tr> <tr> <td></td> <td></td> <td>i532</td> <td></td> <td>i534</td> <td></td> <td>i538</td> <td></td> <td></td> <td>i562</td> </tr> <tr> <td>21</td> <td>10</td> <td>565</td> <td>6.6</td> <td>574</td> <td>5.4</td> <td>580</td> <td>8.3</td> <td>15</td> <td>595<sup>a</sup></td> </tr> <tr> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>i562</td> </tr> <tr> <td>22</td> <td>11</td> <td>562</td> <td>—</td> <td>554</td> <td>—</td> <td>545</td> <td>—</td> <td>— 17</td> <td>—</td> </tr> <tr> <td></td> <td></td> <td>i528</td> <td></td> <td>i516</td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>23<sup>1</sup></td> <td>12</td> <td>559</td> <td>—</td> <td>587</td> <td>—</td> <td>595</td> <td>—</td> <td>36</td> <td>613<sup>c</sup></td> </tr> <tr> <td>24<sup>1</sup></td> <td>13</td> <td>514</td> <td>—</td> <td>538</td> <td>—</td> <td>561</td> <td>—</td> <td>47</td> <td>613<sup>c</sup></td> </tr> <tr> <td>25<sup>1</sup></td> <td>14</td> <td>493</td> <td>—</td> <td>503</td> <td>—</td> <td>520</td> <td>—</td> <td>27</td> <td>—</td> </tr> <tr> <td>26<sup>1</sup></td> <td>15</td> <td>455</td> <td>—</td> <td>510</td> <td>—</td> <td>530</td> <td>—</td> <td>75</td> <td>—</td> </tr> <tr> <td></td> <td></td> <td>i491</td> <td></td> <td>i470</td> <td></td> <td>446</td> <td></td> <td></td> <td></td> </tr> <tr> <td>27<sup>1</sup></td> <td>16</td> <td>504</td> <td>—</td> <td>513</td> <td>—</td> <td>523</td> <td>—</td> <td>19</td> <td>—</td> </tr> </tbody> </table>										Dye no.	Components A, B as in no.	Benzene a	Benzene b	MeOH a	MeOH b	Aq. MeOH (1:2) a	Aq. MeOH (1:2) b	$\Delta\lambda_{\max.}$	Related trimethinnoxonol *	<i>Trinuclear dyes (III).</i>										17	1	496	—	488	6.5	488	6.3	— 8	530 <sup>c</sup>			i470		i466		i466				18	3	464	—	460	5.0	463	—	— 1	536	19	5	564	3.0	565	11.8	567	—	3	595 <sup>a</sup>			i536		i530		i533			i562	20	6	570	10.8	568	10.1	572	9.9	2	595 <sup>a</sup>			i532		i534		i538			i562	21	10	565	6.6	574	5.4	580	8.3	15	595 <sup>a</sup>										i562	22	11	562	—	554	—	545	—	— 17	—			i528		i516						23 <sup>1</sup>	12	559	—	587	—	595	—	36	613 <sup>c</sup>	24 <sup>1</sup>	13	514	—	538	—	561	—	47	613 <sup>c</sup>	25 <sup>1</sup>	14	493	—	503	—	520	—	27	—	26 <sup>1</sup>	15	455	—	510	—	530	—	75	—			i491		i470		446				27 <sup>1</sup>	16	504	—	513	—	523	—	19	—
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i = Inflection. \* In pyridine or MeOH. <sup>a</sup> Hamer and Winton, *J.*, 1949, 1126. Jeffreys and Knott, *J.*, 1952, 4632. <sup>c</sup> Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Cressman, and Dent, *J. Amer. Chem. Soc.*, 1951, 73, 5332.

and the dyes therefore behave as trimethinoxonols, or as chain-substituted dimethinmerocyanines. The electronic analysis given in Part I resulted in the formulation of the dyes as mesoionic oxonols, with the third heterocyclic nucleus (A in III) at an angle to the plane of dye resonance.

The small shifts of absorption maximum with solvent ( $\Delta\lambda_{\max}$ ) confirm this conception in the case of dyes containing benzimidazole and pyridine nuclei. The absorption maxima of the other dyes (III) (prepared by the method of Hamer *et al.*<sup>1</sup>) possessing heterocyclic nuclei (A, B) with weaker  $+M$  and  $-M$  effects, show greater changes of  $\lambda_{\max}$  with solvent. With the exception of the quinoline dye no. 23, all of these have absorption maxima at longer wavelengths than their related dimethinmerocyanines in the same solvent, and it is concluded<sup>2</sup> that they have the oxonol configuration. Trinuclear dye no. 23, derived from 3-ethyl-2-thiothiazolid-4-one and 4-methylquinoline may be compared with the corresponding known trimethinoxonol, and the related merocyanine dye no. 12. The latter merocyanine exhibits only small changes of  $\lambda_{\max}$  with change of solvent and is probably almost energetically symmetrical.<sup>6</sup> A further  $+M$  substitution in this system, giving dye no. 23, will reduce the energy of the mesoionic contributing structure and stabilize the oxonol configuration of the molecule. The trinuclear dyes of Table 1 are therefore considered as oxonols. However, it is to be expected that  $\Delta\lambda_{\max}$  will be larger for dyes with weaker  $\pm M$  heterocyclic nuclei, since stabilization of the mesoionic extreme structures by a polar solvent will be more pronounced than that of dyes possessing heterocyclic nuclei with strong  $-M$  and  $+M$  effects. Examples of this bathochromic increase in  $\Delta\lambda_{\max}$  with increased  $+I$  effect of the cationic heterocyclic nucleus are: benzimidazole dyes (1—8  $m\mu$ ) < benzothiazole dyes (27—47  $m\mu$ ) < thiazoline dye (75  $m\mu$ ).

The 2-phenyloxazol-5-one 4-pyridyl dye (no. 22) is anomalous in formation and absorption (hypsochromic  $\Delta\lambda_{\max}$ ) but the absorption maximum of the related trimethinoxonol is unknown.

#### EXPERIMENTAL

Microanalyses are by Mr. C. B. Dennis of these Laboratories.

*5-Ethoxymethylene-1:3-diethyl-2-thiobarbituric Acid.*—1:3-Diethyl-2-thiobarbituric acid (50 g.) and ethyl orthoformate (125 c.c.) in acetic anhydride (500 c.c.) were heated on the steam-bath for 1 hr. The oil left after evaporation under reduced pressure was extracted with hot

TABLE 2. *Dimethinmerocyanine dyes (IV).*

No.	Method of prep. <sup>a</sup>	Cryst. from <sup>b</sup>	Form <sup>c</sup>	Yield (%)	M. p.	Formula	Found (%)	Required (%)
1	B	P-D	Yellow Lf	72	260° <sup>e</sup>	C <sub>20</sub> H <sub>17</sub> O <sub>2</sub> N <sub>3</sub>	C, 71.4, H, 5.3 N, 12.4	72.5, 5.1 12.7
2	C	M-D	Brown Pr	30	253	C <sub>26</sub> H <sub>21</sub> O <sub>2</sub> N <sub>3</sub>	C, 76.6, H, 5.3 N, 10.3	76.6, 5.2 10.3
3	B	P-M	Yellow N	65	>315	C <sub>19</sub> H <sub>22</sub> O <sub>2</sub> N <sub>4</sub> S	N, 15.0, S, 8.4	15.1, 8.6
4	C	M	Yellow N	36	272	C <sub>25</sub> H <sub>26</sub> O <sub>2</sub> N <sub>4</sub> S	C, 67.0, H, 6.0 N, 12.6, S, 7.3	67.3, 5.8 12.6, 7.2
5	D <sup>d</sup>	B-L	Red N	—	175	C <sub>18</sub> H <sub>21</sub> ON <sub>3</sub> S <sub>2</sub>	S, 18.1	17.8
6	C <sup>d</sup>	B-L	Maroon Lf	18	138	C <sub>22</sub> H <sub>21</sub> ON <sub>3</sub> S <sub>2</sub>	C, 64.6, H, 5.3 N, 10.1, S, 15.7	64.8, 5.2 10.3, 15.7
7	A, E	P-D	Maroon N	40, 60	258	C <sub>20</sub> H <sub>17</sub> O <sub>2</sub> N <sub>3</sub>	C, 72.5, H, 5.1 N, 12.6	72.5, 5.6 12.7
8	A, C	M-D	Orange S	—, 55	160 <sup>f</sup>	C <sub>18</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub> , MeOH	C, 69.6, H, 6.0 N, 8.6	70.4, 6.2 8.6
9	C	P-M	Maroon N, gold reflex	12	309 <sup>e</sup>	C <sub>17</sub> H <sub>21</sub> O <sub>2</sub> N <sub>3</sub> S	N, 12.7, S, 9.7	12.7, 9.7
10	A	No solid isolated.			Absorption measurements carried out on solutions.			
11	A	B-L	Purple	34	172	C <sub>18</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub>	C, 73.0, H, 5.5 N, 9.4	74.0, 5.5 9.6

<sup>a</sup> See text. <sup>b</sup> B, benzene; D, ether; E, ethanol; L, light petroleum (b. p. 60—80°); M, methanol; P, pyridine. <sup>c</sup> Lf, leaflets; N, needles; S, sponge; P, plates; Pr, prisms. <sup>d</sup> Together with trinuclear dye. <sup>e</sup> Decomp. <sup>f</sup> Shrinks at 115°. <sup>g</sup> Shrinks at 212°.

ligroin (b. p. 60—80°), and the extract was chilled and filtered. The *product* (35 g., 55%), recrystallized from ligroin as a straw-coloured powder, m. p. 63° (Found: N, 11.2; S, 12.7.

<sup>6</sup> Ref. c, Table 1.

$C_{11}H_{16}O_3N_2S$  requires N, 10.9; S, 12.5%), partly decomposing on recrystallization or storage.

*Dimethinmerocyanines* (Table 2).—These dyes were prepared from the 2-2'- or 2-4'-anilino-vinyl heterocyclic quaternary salt (1 mol.) and ketomethylene heterocyclic compound (1 mol.) with acetic anhydride (1 mol.) and triethylamine (2 mols.) in ethanol (method A) or in pyridine (method B), by refluxing the solution for  $\frac{1}{4}$  hr.

TABLE 3. *Trinuclear oxonol dyes* (III) (footnotes of Table 2 apply).

No.	Method of prep. <sup>a</sup>	Cryst. from <sup>b</sup>	Form <sup>c</sup>	Yield (%)	M. p.	Formula	Found (%)	Required (%)
17	E	P-M	Orange P	40	293° <sup>e</sup>	$C_{30}H_{22}O_4N_4$	N, 11.1	11.2
18	C, D	M-D	Orange P	51	305° <sup>e</sup>	$C_{28}H_{32}O_4N_4S_2$	C, 57.9, H, 5.8 N, 14.5, S, 11.1	58.0, 5.5 14.5, 11.0
19	C	P-E	Green Pr	49	247	$C_{24}H_{26}O_2N_4S_4$	N, 10.6, S, 24.4	10.6, 24.2
20	C <sup>d</sup>	P-M	Green Pr	21	261			
21	C	P-D	Gold L	11	215	$C_{20}H_{21}O_2N_3S_4$	N, 9.1, S, 28.0	9.1, 27.6
22	E	P-M	Green, N, gold lustre	9	277° <sup>e</sup>	$C_{28}H_{21}O_4N_3$	C, 72.2, H, 4.7 N, 9.0	72.6, 4.5 9.1

Trinuclear oxonol dyes and some dimethinmerocyanines were obtained from the reaction of a 2- or 4-methyl heterocyclic quaternary salt (1 mol.) with an ethoxymethylene derivative of a ketomethylene heterocyclic compound (2 mols.) and triethylamine (2 mols.) in boiling ethanol for  $\frac{1}{2}$  hr. (method C), in ethanol at 20–40° for 1 hr. (method D), or in boiling pyridine for  $\frac{1}{2}$  hr. (method E). Method D involved the use of only 1 mol. each of ethoxymethylene derivative and triethylamine, to favour formation of the dimethinmerocyanine.

In all cases the yield of crude dye was improved by the addition of a few drops of water to the cooled reaction solution.

*Anhydro-1-ethyl-2-[1-(2-ethylthio-5-hydroxythiaz-4-ylmethylene)-2-(2-ethylthio-5-oxothiazolin-4-ylidene)ethyl]-3-phenylbenziminazolinium hydroxide* (VI) (dye no. 20).—2-(1-Ethyl-3-phenylbenziminazolin-2-ylidene)-1:3-di(phenylimino)propane (V) (0.6 g.) and 2-ethylthiothiazol-5-one (prepared from 0.6 g. of *N*-ethylthiothiocarbonylglycine<sup>7</sup>) with anhydrous sodium acetate (0.6 g.) in acetic anhydride (8 c.c.) were refluxed at 140–150° for 7 min. Ether (20 c.c.) was added to the cooled mixture, which was then filtered and distilled in a vacuum; a little methanol was added to the residue, which solidified. It was filtered off, washed with a little methanol, and recrystallized from pyridine-methanol as bright green prisms (0.2 g., 25%), m. p. 261°, identical with a sample prepared by method C above (Found: C, 58.0; H, 4.7; N, 9.6; S, 22.4.  $C_{28}H_{26}O_2N_4S_4$  requires C, 58.1; H, 4.5; N, 9.7; S, 22.2%).

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<sup>7</sup> Aubert, Knott, and Williams, *J.*, 1951, 2185.