Perimidine Dyes and Intermediates.

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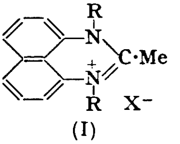
[Reprint Order No. 6049.]

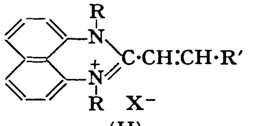
Intermediates, cyanine and *mero*cyanine dyes, all possessing a perimidine ring, have been prepared. The dihydroperimidine ring system has strong electron-releasing powers, indicated by the reversal of Kundt's rule in some *mero*cyanines. An abnormal condensation between 2-methylperimidinium salts and ethoxymethylene-keto-heterocyclic intermediates provides trinuclear *mero*cyanines, which may be considered as chain-substituted mesoionic oxonols.

ONE of the strongest electron-releasing ($-M$) heterocyclic systems used in the preparation of cyanine and *mero*cyanine dyes is benziminazoline (cf. Brooker, Keyes, Sprague, Van Dyke, Van Lare, Van Zandt, White, Cressman, and Dent, *J. Amer. Chem. Soc.*, 1951, **73**, 5332). Perimidine is related to benziminazole through its structural isomers the naphthiminazoles, and a comparison of the properties of related dyes was therefore of interest.

Low yields of pure 1-alkyl-2-methylperimidine intermediates were obtained, with some difficulty, by fusing 2-methylperimidine with alkyl toluene-*p*-sulphonates, followed by basification of the resulting salts. They were readily quaternized by fusion with alkyl esters on the steam-bath, forming 1 : 3-dialkyl-2-methylperimidinium salts (I). The intermediate (I) condensed with *O*-ethyl*iso*formanilide (at elevated temperatures) to form 2-2′-anilinovinyl intermediates (II; R′ = NHPh); with *p*-dimethylaminobenzaldehyde (in pyridine with a drop of piperidine) to form a 2-*p*-dimethylaminostyryl dye (II; R′ = $C_6H_4{\cdot}NMe_2$); with a 3-ethyl-2-ethylthiobenzothiazolium salt to form a lemon-yellow monomethincyanine (III); and with 2-2′-acetanilidovinyl heterocyclic salts (in ethanol in the presence of triethylamine) to form various trimethincyanines (IV; see Table 2). The 2-2′-anilinovinyl intermediates (II; R′ = NHPh) reacted with ketomethylene heterocyclic compounds to give dimethin*mero*cyanines (V).



(I)



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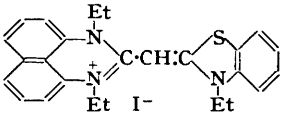

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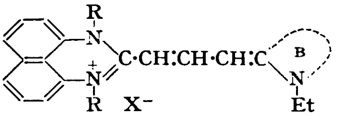

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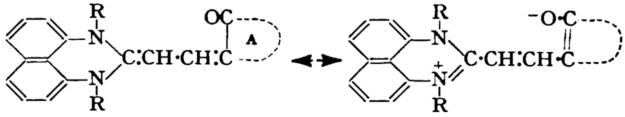
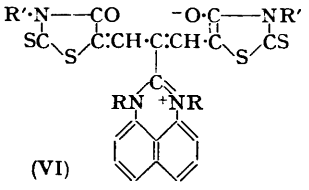


(Va) (Vb)



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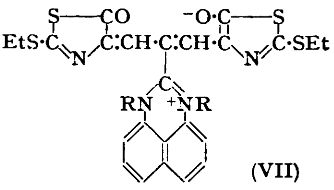

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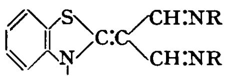
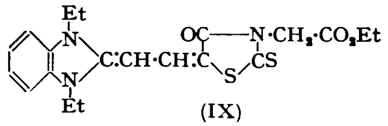


(VIII)



(IX)

In an alternative method of preparing the last dyes, 2-methylperimidinium salts (I) were condensed with ethoxymethylene-keto-heterocyclic compounds in alcoholic triethylamine according to a known general synthesis (Kendall and Fry, B.P. 544,647; Cook, Harris, and Shaw, *J.*, 1949, 1435; Aubert, Knott, and Williams, *J.*, 1951, 2185). In each reaction two dyes were formed and, in three reactions, pairs of dyes were isolated. The lighter dye of each pair was a *mero*cyanine (V), and the deeper one proved to be a trinuclear dye (VI, VII). Dyes of type (VI) possessing nuclei other than perimidine have been described by Hamer, Rathbone, and Winton (*J.*, 1949, 1113), who used dianilo-intermediates (VIII) in their syntheses.

TABLE 1. *Absorption maxima* (mμ) *of dyes in various solvents* (*i* indicates an inflection).

	Benzene	MeOH	Aq. MeOH (1 : 2)
V*a*; R = Me, A = 3-allyl-2-thiothiazolid-4-one	476*i*, 498	482*i*, 502	482*i*, 503
V*a*; R = Et, A = 3-ethoxycarbonylmethyl-2-thiothiazolid-4-one	477*i*, 503	484*i*, 505	483*i*, 505
V*a*; R = Me, A = 2-ethylthiothiazol-5-one	495	476	466
V*a*; R = Me, A = 3-methyl-2-thiothiazolid-5-one	497*i*, 523	508	495
IX	488*i*, 513	488*i*, 508	500
VI; R = Me, R′ = allyl	525*i*, 547	520*i*, 542	517*i*, 541
VI; R = Et, R′ = $EtO_2C{\cdot}CH_2$	522*i*, 545	512*i*, 536	512*i*, 536
VII; R = Me	529*i*, 570	535*i*, 566	541*i*, 572
VII; R = Et	—	530*i*, 569	—

The strong electron-releasing power of the dihydroperimidine nucleus is indicated by a reversal of Kundt's rule for some derived *mero*cyanine dyes (cf. Brooker *et al.*, *loc. cit.*). Thus, in solvents of increasing polarity and dipole moment (see Table 1), hypsochromic shifts of 10—19 mμ occur for perimidine dyes possessing strongly $+M$ thiazol-5-one and thiazolid-5-one rings, whereas the corresponding thiazolid-4-one dyes (weaker $+M$ effect) show small bathochromic shifts. The benziminazole dye with a thiazolid-4-one ring (IX), however, exhibits hypsochromic shifts of 5 and 8 mμ, indicating the still stronger $-M$ effect of the benziminazoline nucleus compared with that of dihydroperimidine.

The trinuclear dyes (VI, VII) show relatively small changes of $\lambda_{max.}$ with change of solvent polarity; their structures and absorption are discussed elsewhere (Jeffreys, Compt. rend. 17e Congrès Intern. de Chimie Industrielle, 1955).

EXPERIMENTAL

Absorption maxima are recorded for MeOH solutions unless otherwise stated. Light petroleum had b. p. 60—80°.

1-*Ethyl-2-methylperimidine.*—2-Methylperimidine (1·8 g.) and ethyl toluene-*p*-sulphonate (2·0 g.) were fused together at 140° for 45 min. The product was dissolved in water, and the solution treated with aqueous ammonia. The precipitate was extracted with light petroleum, and recrystallized from the same solvent as yellow-green prisms (0·9 g., 43%), m. p. 115° (Found: N, 13·2. $C_{14}H_{14}N_2$ requires N, 13·3%).

1 : 2-*Dimethylperimidine.*—2-Methylperimidine (5·5 g.) and methyltoluene-*p*-sulphonate (5·6 g.) were heated together on the steam-bath for 0·5 hr. The product was dissolved in ethanol and poured into aqueous sodium carbonate. The precipitated *perimidine* was filtered off, dried, and distilled, the fraction boiling at 196—200°/6 mm. being collected and recrystallized from ligroin–benzene as pale yellow needles, m. p. 159° (2 g., 34%) (Found: N, 14·2. $C_{13}H_{12}N_2$ requires N, 14·3%).

1 : 3-Diethyl-2-methyl- and 1 : 2 : 3-trimethyl-perimidinium toluene-*p*-sulphonate (I) were easily obtained as water-soluble solids by heating 1 : 2-dialkylperimidines (1 mol.) with the appropriate alkyl toluene-*p*-sulphonates (1 mol.) on the steam-bath for 0·5 hr. and were not further purified.

2-2′-*Anilinovinyl*-1 : 3-*dimethylperimidinium Toluene*-p-*sulphonate* (II; R = Me, R′ = NHPh, X = toluene-*p*-sulphonate).—1 : 2 : 3-Trimethylperimidinium toluene-*p*-sulphonate (5·1 g.) and *O*-ethyl*iso*formanilide (2·1 g.) were heated together at 140° for 1 hr. Ethanol was added to the gum, and the solid which formed recrystallized from ethanol–ether as a yellow powder (4·5 g., 77%), m. p. 216° (decomp.) (Found: N, 8·7; S, 6·7. $C_{28}H_{27}O_3N_3S$ requires N, 8·7; S, 6·6%).

2-2′-*Anilinovinyl*-1 : 3-*diethylperimidinium Iodide* (II; R = Et, R′ = NHPh, X = I).—1 : 3-Diethyl-2-methylperimidinium toluene-*p*-sulphonate (4·1 g.) and *O*-ethyl*iso*formanilide (1·5 g.) were heated together at 140° for 2 hr. and the resulting gum dissolved in ethanol. This solution was poured into aqueous potassium iodide. The *product* was filtered off and recrystallized from ethanol–ether as dark brown prisms (3 g., 64%), m. p. 233° (decomp.) (Found: N, 9·1; I, 27·4. $C_{23}H_{24}N_3I$ requires N, 9·0; I, 27·1%).

TABLE 2. [1 *or* 3-*Ethyl-2-B*][1 : 3-*dialkyl-2-perimidine*]*trimethincyanine dyes* (IV).
(*i* indicates an inflection.)

Heterocycle B	R	X	Appearance	M. p.	$\lambda_{max.}$ (mμ)	Formula	Found (%)	Reqd. (%)
Benzoxazoline	Et	ClO_4	Orange-brown [a]	212°	458*i*, 482	$C_{27}H_{28}O_5N_3Cl$	N, 8·2	8·2
Benzothiazoline	Me	I	Bronze [b]	233	499	$C_{25}H_{24}N_3SI$	N, 7·9	8·0
							S, 6·1	6·1
							I, 24·3	24·2
1 : 2-Dihydroquinoline	Me	I	Indigo [c]	252	510*i*, 539	$C_{27}H_{26}N_3I$	N, 8·0	8·1
							I, 24·3	24·4

[a] Needles from methanol–ether. [b] Needles from pyridine–ether. [c] From methanol, after chromatography on alumina.

2-p-*Dimethylaminostyryl*-1 : 3-*dimethylperimidinium Iodide* (II; R = Me, R′ = *p*-$Me_2N{\cdot}C_6H_4$, X = I).—1 : 2 : 3-Trimethylperimidinium toluene-*p*-sulphonate (2·6 g.) and *p*-dimethylaminobenzaldehyde (1 g.) in pyridine (40 c.c.) with piperidine (2 drops) were refluxed for 2 hr. and the solution poured into aqueous potassium iodide. The precipitated *dye* recrystallized from pyridine–methanol as orange needles (0·1 g.), m. p. 257° (decomp.), $\lambda_{max.}$ 439 mμ (Found : N, 9·0; I, 27·1. $C_{23}H_{24}N_3I$ requires N, 8·9; I, 27·1%).

[3-*Ethyl-2-benzothiazole*][1 : 3-*diethyl-2-perimidine*]*methincyanine Iodide* (III).—1 : 3-Diethyl-2-methylperimidinium toluene-*p*-sulphonate (1·2 g.) and 3-ethyl-2-ethylthiobenzothiazolium toluene-*p*-sulphonate (1·2 g.) with triethylamine (0·4 c.c.) in ethanol (8 c.c.) were refluxed for 30 min., and the solution was poured into aqueous potassium iodide. The *dye* was filtered off and recrystallized from ethanol as a fluffy yellow powder (0·1 g.), m. p. 207°, $\lambda_{max.}$ 385 mμ (Found : N, 8·0. $C_{25}H_{25}N_3SI$ requires N, 8·0%).

TABLE 3. *Dimethin*mero*cyanine dyes* (V, IX). (*i* indicates an inflection.)

No.	Nucleus A, dye (V)	R	Appearance	Yield (%)	M. p.	$\lambda_{max.}$ (mμ)	Formula	Found (%)	Reqd. (%)
1	3-Ethyl-2-thio-oxazolid-4-one	Et	Chocolate prisms	48	203°	480	$C_{22}H_{23}O_2N_2S$	N, 10·7	10·7
2	2-Ethylthiothiazol-5-one	Me	Red needles	7	212	476	$C_{20}H_{19}ON_3S_2$	C, 63·1 H, 5·3 N, 10·9 S, 16·7	63·0 5·0 11·0 16·8
3	3-Allyl-2-thiothiazolid-4-one	Me	Magenta needles	10	217	482*i*, 502	$C_{21}H_{19}ON_3S_2$	S, 16·3	16·3
4	3-Ethoxycarbonylmethyl-2-thiothiazolid-4-one	Et	Maroon prisms	14	208	484*i*, 505	$C_{24}H_{25}O_3N_3S_2$	N, 9·1 S, 13·7	9·0 13·7
5	3-Methyl-2-thiothiazolid-5-one	Me	Maroon	35	282	508	$C_{19}H_{17}ON_3S_2$	N, 11·4 S, 17·4	11·4 17·4
6	Dye (IX) …………	Et	Brown leaflets	30	184	488*i*, 508	$C_{20}H_{23}O_2N_2S_2$	N, 10·0 S, 15·4	10·1 15·4

Prepared from 2-2′-anilinovinylperimidinium salt (1 mol.), ketomethylene heterocyclic compound (1 mol.), acetic anhydride (1 mol.), and triethylamine (2 mols.). From pyridine.

TABLE 4. *Trinuclear dyes* (VI, VII). In the dimethin*mero*cyanine dye reactions (see above) trinuclear dyes were sometimes formed and were isolated, together with the dinuclear dyes, or as the sole reaction products. Dye mixtures (2/9, 3/7, 4/8) were separated by fractional crystallization.

No.	Dye	R	R′	Appearance	Yield (%)	M. p.	Formula	Found (%)	Required (%)
7	VI	Me	C_3H_5	Red-brown needles [a]	7	216°	$C_{28}H_{24}O_2N_4S_4$	S, 22·2	22·2
8	VI	Et	$CH_2{\cdot}CO_2Et$	Maroon leaflets [a]	19	184	$C_{32}H_{32}O_6N_4S_4$	C, 55·4; H, 4·8; N, 8·1; S, 18·4	55·2; 4·6; 8·1; 18·4
9	VII	Me	—	Bronze plates [b]	25	299	$C_{26}H_{24}O_2N_4S_4$	C, 56·4; H, 4·3; N, 10·0; S, 23·3	56·5; 4·3; 10·1; 23·2
10	VII	Et	—	Gold needles [c]	20	261	$C_{28}H_{28}O_2N_4S_4$	S, 22·0	22·1

From pyridine–methanol–ether. From pyridine–ethanol. [c] From ethanol.

Trimethincyanines (Table 2).—Three trimethincyanines were prepared by condensing together the 2-methylperimidinium and 2-2′-acetanilidovinyl heterocyclic quaternary salts in ethanol, with triethylamine to remove the acid liberated.

*Dimethin*mero*cyanines* (see Tables 3 and 4).—Unless otherwise stated, these were prepared in ethanol, from 2-methyl-heterocyclic quaternary salts (1 mol.) and ethoxymethylene derivatives of ketomethylene heterocyclic compounds (2 mols.) in the presence of triethylamine (2 mols.).

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[*Received, January 20th*, 1955.]