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Dimethin and Tetramethin Merocyanines Derived from Thiazolones

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Preparations of dimethin and tetramethin merocyanines from the fixed acidic nucleus, 2-benzylthio-thiazolone, and various variable basic nuclei, like quinoline-4, quinoline-2, pyridine-2, pyridine-4, benzoxazole, benzothiazole, and 4-phenyl -2-methylthiazole, are described.

With the help of the absorption data, certain generalisations on the influence of structural changes on absorption and the relative acidity of the thiazolone nucleus have been made.

The photographic sensitising properties of these dyes have also been studied.

The present work describes the preparation of dimethin and tetramethin merocyanines derived from the fixed acidic nucleus, 2-benzylthio-thiazolone, and various variable basic nuclei like quinoline-4, quinoline-2, benzothiazole, benzoxazole, etc.

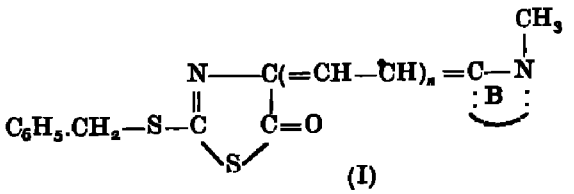
The dimethin merocyanines were prepared by condensing the ethoxymethylene derivative of 2-benzylthio-thiazolone with various heterocyclic compounds in absolute ethanol in presence of triethylamine.

The ethoxymethylene intermediate was prepared by the reaction of the *N*-dithiocarbobenzyloxyglycine with ethyl orthoformate in acetic anhydride.

The tetramethin merocyanines were prepared by condensing methoxyallylidene derivative of 2-benzylthio-thiazolone with various heterocyclic nuclei in absolute ethanol in presence of triethylamine.

The methoxyallylidene derivatives of thiazolone was prepared by the reaction of *N*-dithiocarbobenzyloxyglycine with 1,3,3-trimethoxypropene in acetic anhydride.

The dimethin and tetramethin merocyanines conform to structure (I).



(I)

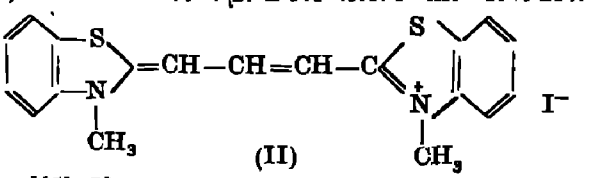
$n = 1$ (dimethin).
$n = 2$ (tetramethin).

The sensitising properties of the merocyanines prepared have been studied. The results of sensitisation studies indicate that most of the merocyanines derived from thiazolone sensitise a silver-bromo-iodide paper, the range of maximum sensitisation being close

to the region of maximum absorption of the dye concerned (Fig. 1, No. 1,2,3,4). It was observed that the merocyanines, containing the basic nuclei pyridine-4, pyridine-2, are poor sensitisers. The most powerful sensitisers among the dimethin and tetramethin merocyanines derived from 2-benzylthio-thiazolone are those derived from quinoline-4, benzothiazole, and 4-phenylthiazole.

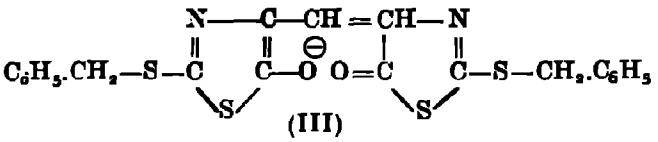
FIG. 1

The relative acidity of the thiazolone nucleus, as compared to rhodanine and thiohydantoin, has also been evaluated with the help of the "Deviation factor". Brooker[1] has postulated that in a series of merocyanines, containing the same basic nucleus, the deviation will be highest for the least acidic nucleus and as the acidity is increased, the deviation is correspondingly increased. Deviation is considered as the difference between the absorption maximum of the dye concerned and the mean value of the absorption maximum of the corresponding symmetrical cyanine and oxonol. Deviation is calculated as illustrated here by taking the case of the merocyanines derived from 2-methylbenzothiazole and the acidic nucleus, 2-benzylthio-thiazolone. The absorption maximum of the symmetrical cyanine, derived from benzothiazole (II), is 565 mμ and that of the oxonol derived from 2-benzylthio-thiazolone (III) is 520 mμ. The merocyanine (I), composed of both the nuclei, however, absorbs at 520 mμ. Deviation is therefore 22.5 mμ.



(II)

1. *J. Amer. Chem. Soc.*, 1951, **73**, 5332.



(III)

As already reported[2], the deviations of merocyanines, derived from the basic nucleus 2-methylbenzothiazole and the acidic nuclei rhodanine and thiohydantoin, are 33.5 mμ and 67.5 mμ respectively. The least deviation in the case of thiazolone nucleus shows that thiazolone is more acidic than rhodanine, which in turn is more acidic than thiohydantoin.

The higher acidity of the thiazolone nucleus, as compared to rhodanine and thiohydantoin, can also be arrived at by way of resonance theory[3].

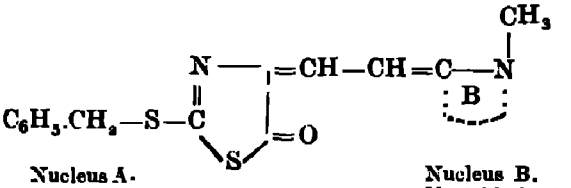
EXPERIMENTAL

N-Dithiocarbobenzyloxyglycine was prepared by the method of Aubert *et al.*[4] with slight modifications from glycine (15 g.), CS_2 (15.2 g.), and KOH (22.4 g.) in water (50 ml). It was crystallised from ethanol. m.p. 132°, yield 65%.

4-Ethoxymethylene-2-benzylthio-thiazolone was prepared by the method of Knott[5] with slight modifications from *N*-dithiocarbobenzyloxyglycine (2.0 g.), acetic anhydride (10 ml), and ethyl orthoformate (3.5 ml).

Dimethin Merocyanines.—Equimolecular quantities of the preceding compound and the quaternary heterocyclic compound were dissolved in minimum amount of absolute ethanol. After addition of an equimolecular quantity of triethylamine, the reaction mixture was heated for 5 to 10 min. on a steam bath. The solvent was removed by distillation when a pasty mass was deposited, which solidified on keeping in contact with methanol. It was finally crystallised from ethanol. The analytical data and properties of these dimethin merocyanines are recorded in Table I.

TABLE I



Nucleus A.
Benzylthio-thiazolone.

Nucleus B.
Variable basic nuclei.

Nature of B.	Yield.	M.P.	$\lambda_{max.}$	% Carbon.		% Hydrogen.	
				Found.	Reqd.	Found.	Reqd.
Benzoxazole	35%	178°	490 mμ	63.20	63.15	4.12	4.21
Benzothiazole	49	196°	530	60.48	60.61	4.12	4.04
Quinoline-2	42	143°	549	67.48	67.58	4.72	4.61
Quinoline-4	35	206° (d)	502	67.38	67.58	4.59	4.61
Pyridine-2	62	181°	510	63.42	63.52	4.81	4.70
Pyridine-4	45	218° (d)	532	63.41	63.52	4.84	4.70

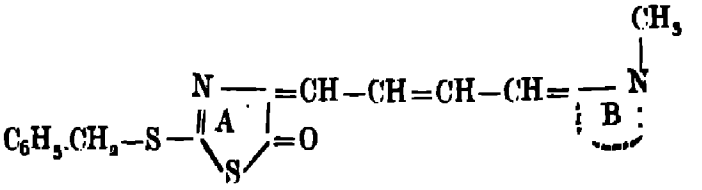
N.B. (d) denotes decomposition.

2. Rout *et al.*, this *Journal*, 1960, **37**, 613.
3. Rout *et al.*, *ibid.*, 1959, **36**, 625.
4. *J. Chem. Soc.*, 1951, 2188.
5. *Ibid.*, 1954, 1485.

4-Methoxyallylidene-2-benzylthio-thiazolone was obtained by refluxing *N*-dithiocarbobenzyloxyglycine (2.0 g.), acetic anhydride (10 ml), and 1,3,3-trimethoxypropene (4 ml) in an oil bath at 130° for 30 min. Removal of the solvents resulted in deposition of an oil. This was washed several times with light petroleum (40-60°) and finally a brown solid was obtained, which was used directly for the synthesis of the dye; m.p. 75°, yield 45%.

Tetramethin Merocyanines.—Equimolecular quantities of the preceding compound and the quaternary heterocyclic compound were dissolved in minimum amount of absolute ethanol. After addition of an equimolecular quantity of triethylamine, the reaction mixture was heated for 10 to 15 min. in a steam bath. On removal of the solvent by distillation, a pasty mass was deposited, which solidified on keeping in contact with methanol. It was finally crystallised from ethanol. The analytical data and properties of the tetramethin merocyanines are recorded in Table II.

TABLE II



Nature of B.	Yield.	M.P.	$\lambda_{max.}$	% Carbon. Found.	% Carbon. Reqd.	% Hydrogen. Found.	% Hydrogen. Reqd.
Benzothiazole	32 %	198°	625 mμ	62.50	62.56	3.98	4.26
Benzoxazole	55	207° (d)	590	65.20	65.03	4.22	4.43
Quinoline-2	45	164°	650	69.11	69.23	4.72	4.81
Quinoline-4	45	201° (d)	685	69.18	69.23	4.77	4.81
Pyridine-2	50	178°	605	65.47	65.57	4.77	4.92

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