Synthesis of 1*H*-Pyrazolo[3,2-*c*]-*s*-Triazoles and Derived Azamethine Dyes

By **Joseph Bailey,** Research Division, Kodak Limited, Headstone Drive, Harrow, Middlesex HA1 4TY

The condensation of ethyl 5-hydrazino-3-methylpyrazole-4-carboxylate with various aldehydes and acid chlorides is outlined. The cyclisation of the resulting hydrazones and hydrazides, under oxidative and dehydrative conditions, respectively, gives ethyl 1*H*-pyrazolo[3,2-*c*]-*s*-triazole-7-carboxylates. Hydrolysis of these esters followed by decarboxylation of the corresponding acids, gives 1*H*-pyrazolo[3,2-*c*]-*s*-triazoles. Another method of synthesis of 1*H*-pyrazolo[3,2-*c*]-*s*-triazoles, involves the condensation of *S*-methylisothiocarbohydrazide hydroiodide with β-oxo-esters. The synthesis of a range of azamethine dyes containing the pyrazolo[3,2-*c*]-*s*-triazole nucleus is described, and the absorption properties of these dyes are discussed.

AZAMETHINE dyes formed by coupling Δ^2-pyrazolin-5-ones with an oxidised *p*-phenylenediamine are useful for forming the magenta image in multilayer colour photographs.[1] In the search for new dyes with better spectral properties, 1*H*-pyrazolo[3,2-*c*]-*s*-triazoles were required as colour couplers.

It is known that certain heterocyclic hydrazines can be used as intermediates for the preparation of more complex heterocyclic systems. Thus, 2-pyridylhydrazine can be condensed with benzaldehyde and the resulting hydrazone can be oxidised to form 3-phenyl-*s*-triazolo[4,3-*a*]pyridine.[2] *s*-Triazolo[4,3-*b*]pyridazines can be obtained by cyclisation of the products from condensing 3-pyridazinylhydrazines with either aldehydes or acid chlorides.[3]

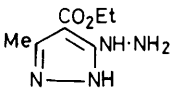
In the present investigation, analogous condensations have been carried out with a pyrazol-5-ylhydrazine as the key intermediate to obtain some 1*H*-pyrazolo-[3,2-*c*]-*s*-triazoles.

4-Ethoxycarbonyl-3-methylpyrazol-5-ylhydrazinium chloride was prepared by the method of Beyer *et al.*[4] Modifications to the described procedure were necessary to obtain pure material. Treatment of this salt in hot methanol with triethylamine afforded the free base (1).

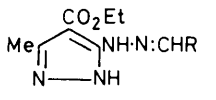
The hydrazine (1) was condensed with various aldehydes to obtain a series of hydrazones (2). Two of these hydrazones could also be obtained from the hydrazinium chloride by using a method from the literature.[4]

These hydrazones were converted, by oxidative cyclisation, into the corresponding ethyl 1*H*-pyrazolo-[3,2-*c*]-*s*-triazole-7-carboxylates (3) when treated in acetic acid with bromine in the presence of sodium acetate. Two of these esters were also obtained by treatment of the respective ethyl 5-acylhydrazino-3-methylpyrazole-4-carboxylates with phosphoryl chloride. The hydrazides required for these dehydrations were prepared from the base (1) and the appropriate acid chlorides.

The hydrolysis of ethyl pyrazole-4-carboxylates has been reported [5] to occur when the esters are heated in concentrated sulphuric acid. This method has been

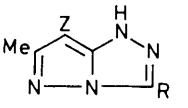


(1)



(2)

a; R = phenyl
b; R = *o*-tolyl
c; R = *p*-tolyl
d; R = mesityl
e; R = *o*-chlorophenyl
f; R = *p*-chlorophenyl
g; R = 2,6-dichlorophenyl
h; R = *o*-fluorophenyl
i; R = *p*-fluorophenyl
j; R = *o*-nitrophenyl
k; R = *p*-nitrophenyl
l; R = n-hexyl



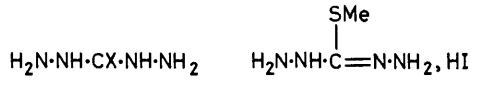
(3) Z = CO_2Et
(4) Z = CO_2H
(5) Z = H

a; R = phenyl
b; R = *o*-tolyl
c; R = *p*-tolyl
d; R = mesityl
e; R = *o*-chlorophenyl
f; R = *p*-chlorophenyl
g; R = 2,6-dichlorophenyl
h; R = *o*-fluorophenyl
i; R = *p*-fluorophenyl
j; R = *o*-nitrophenyl
k; R = *p*-nitrophenyl
l; R = n-hexyl

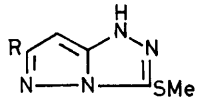
[1] J. R. Thirtle and D. M. Zwick, 'Colour Photography,' in Kirk–Othmar Encyclopedia of Chemical Technology, Wiley, New York, 1964, vol. 5, p. 812.
[2] J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 1957, 727.
[3] A. Pollak and M. Tisler, *Tetrahedron*, 1966, **22**, 2073.
[4] H. Beyer, G. Wolter, and H. Lemke, *Chem. Ber.*, 1956, **89**, 2550.
[5] J. Sandstrom, *Acta Chem. Scand.*, 1962, **16**, 2395.

applied successfully to hydrolyse a series of ethyl 1*H*-pyrazolo[3,2-*c*]-*s*-triazole-7-carboxylates to the corresponding carboxylic acids (4).

Decarboxylation occurred when these carboxylic acids were heated in dimethylaniline, resulting in the production of a range of 1*H*-pyrazolo[3,2-*c*]-*s*-triazoles (5).



(6) (7)

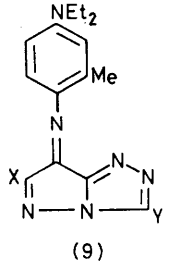


(8)

a; R = phenyl
b; R = *p*-nitrophenyl
c; R = *m*-nitrophenyl

In an attempt to find a simplified preparation of 1*H*-pyrazolo[3,2-*c*]-*s*-triazoles, thiocarbohydrazide [6] (6; X = S) was heated with ethyl acetoacetate in ethanol. However, the condensation yielded a pyrazolinone, and carbohydrazide (6; X = O) behaved similarly. On the other hand, when *S*-methylisothiocarbohydrazide hydroiodide (7) (prepared by alkylation of thiocarbohydrazide with methyl iodide) was heated with ethyl benzoylacetate the 1*H*-pyrazolo[3,2-*c*]-*s*-triazole (8a) was obtained. Likewise, ethyl *p*-nitrobenzoylacetate was condensed with the salt (7) in pentyl alcohol to give the base (8b). Analogously, ethyl *m*-nitrobenzoylacetate gave the base (8c).

A range of azamethine dyes (9) was prepared by treating the appropriate pyrazolotriazole with 4-diethylamino-2-methylaniline in alkaline solution in the presence of potassium persulphate.



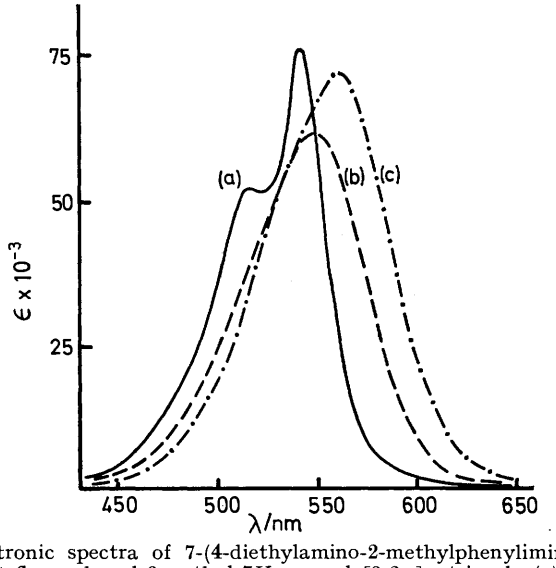
(9)

a; X = Me, Y = phenyl
b; X = Me, Y = *o*-tolyl
c; X = Me, Y = *p*-tolyl
d; X = Me, Y = mesityl
e; X = Me, Y = *o*-chlorophenyl
f; X = Me, Y = *p*-chlorophenyl
g; X = Me, Y = 2,6-dichlorophenyl
h; X = Me, Y = *o*-fluorophenyl
i; X = Me, Y = *p*-fluorophenyl
j; X = Me, Y = *o*-nitrophenyl
k; X = Me, Y = *p*-nitrophenyl
l; X = Me, Y = n-hexyl
m; X = Ph, Y = methylthio
n; X = *p*-nitrophenyl, Y = methylthio

Light Absorption Properties.—The azamethine dyes (9) absorb green light. Their absorption properties are given in Table 6. One set of absorption curves is given in the Figure, from which it is apparent that in methanol and ethyl acetate the dye has a single absorption band. However, with cyclohexane as solvent the band is resolved into a doublet. It is probable that any fine structure (in cyclohexane solution) is lost in the more polar solvents because of hydrogen bonding of the dye molecules with the solvent.

The new dyes have improved absorption properties over the corresponding pyrazolinone dyes [7] in that they have higher extinction coefficients and no secondary blue absorption, and show a sharper cut-off on the long wavelength side.

The absorption maxima of these dyes undergo marked bathochromic shifts with increasing dielectric constant of the solvent. This behaviour parallels that generally observed with non-ionic dyes, whose resonance hybrids receive the major contribution from uncharged structures. Furthermore, the extinction value for each dye



Electronic spectra of 7-(4-diethylamino-2-methylphenylimino)-3-*p*-fluorophenyl-6-methyl-7*H*-pyrazolo[3,2-*c*]-*s*-triazole (a) in cyclohexane; (b) in ethyl acetate; (c) in methanol

in methanol is greater than that obtained in ethyl acetate, and although in general the extinction value in cyclohexane at peak absorption of each dye is greater than that obtained in ethyl acetate, the total area under the absorption curve for each dye in cyclohexane is less than that for the same dye in ethyl acetate (Figure).

The action of acid on the dyes, as exemplified by compounds (9d and l), causes a bathochromic shift in $\lambda_{max.}$ probably by formation of a cationic species.

Table 6 shows that the absorptions of the dyes (9a and i) are 23 and 24 nm bathochromically displaced, respectively, in comparison with the dye (9l). This suggests that the phenyl ring in these dyes contributes to the resonance systems, and this is substantiated by the fact that the colours of dyes containing electron-withdrawing substituents such as a nitro-group in the *para*-position of a phenyl ring, *viz.* dyes (9k and n) are considerably

[6] L. F. Andrieth, E. S. Scott, and K. S. Kippur, *J. Org. Chem.*, 1954, **19**, 733.

[7] G. H. Brown, B. Graham, P. W. Vittum, and A. Weissberger, *J. Amer. Chem. Soc.*, 1951, **73**, 919.

deeper than those of the corresponding dyes without nitro-substituents. Furthermore, the *p*-chloro-substituent in the dye (9f) causes a bathochromic shift of 4 nm in comparison with the non-chlorinated dye (9a). On the other hand, the electron-donating *para*-methyl group in the dye (9c) causes a hypsochromic displacement in comparison with the corresponding unsubstituted dye (9a).

The dyes which carry a substituent in the *ortho*-position of the phenyl ring, *viz.* (9b, d, e, g, h, and j) have absorptions which are hypsochromically displaced in comparison with the parent (9a). To account for this, it is suggested that the phenyl ring is twisted from coplanarity with the heterocyclic system by steric effects. This is substantiated by molecular models.

The use of dyes and intermediates containing the pyrazolo[3,2-*c*]-*s*-triazole nucleus in photographic systems is covered by patents.[8,9]

TABLE 1

Ethyl 5-hydrazino-3-methylpyrazole-4-carboxylates (2)

Compound (2)	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N
a	167 [a,b]	84	$C_{14}H_{16}N_4O_2$	61.7	5.9		20.4	61.8	5.9		20.6
b	177 [c]	91	$C_{15}H_{18}N_4O_2$	63.1	6.5		19.5	62.9	6.3		19.6
c	185 [a]	86	$C_{15}H_{18}N_4O_2$	63.0	6.4		19.5	62.9	6.3		19.6
d	197—198 [a]	89	$C_{17}H_{22}N_4O_2$	65.2	7.1		17.8	65.0	7.0		17.8
e	212 [a]	92	$C_{14}H_{15}ClN_4O_2$	54.9	5.0	11.7	18.1	54.8	4.9	11.6	18.3
f	230—231 [a]	95	$C_{14}H_{15}ClN_4O_2$	54.9	5.1	11.7	18.2	54.8	4.9	11.6	18.3
g	204—206 [a]	80	$C_{14}H_{14}Cl_2N_4O_2$	49.0	4.0	20.6	16.3	49.3	4.1	20.8	16.4
h	174 [c]	83	$C_{14}H_{15}FN_4O_2$	58.1	5.3		19.2	57.9	5.2		19.3
i	185—186 [a]	80	$C_{14}H_{15}FN_4O_2$	57.9	5.3		19.1	57.9	5.2		19.3
j	223—225 [a]	95	$C_{14}H_{15}N_5O_2$	53.2	4.6		21.9	53.0	4.7		22.1
k	285—286 [a,d]	83	$C_{14}H_{15}N_5O_2$	53.2	4.8		22.0	53.0	4.7		22.1
l	85 [a]	67	$C_{14}H_{24}N_4O_2$	59.7	8.7		19.8	60.0	8.6		20.0

[a] From ethanol. [b] Lit. m.p. 167°. [c] From benzene. [d] Lit., m.p. 276°.

TABLE 2

Ethyl 6-methyl-1*H*-pyrazolo[3,2-*c*]-*s*-triazole-7-carboxylates (3)

Compound (3)	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N
a	175—176 [a]	86	$C_{14}H_{14}N_4O_2$	62.5	5.3		20.6	62.2	5.2		20.7
b	181 [a]	76	$C_{15}H_{16}N_4O_2$	63.1	5.7		19.6	63.3	5.6		19.7
c	236 [a]	89	$C_{15}H_{16}N_4O_2$	63.0	5.7		19.9	63.3	5.6		19.7
d	210—211 [a]	80	$C_{17}H_{20}N_4O_2$	65.6	6.6		17.8	65.4	6.4		17.9
e	176 [b]	75	$C_{14}H_{13}ClN_4O_2$	55.3	4.2	11.8	18.4	55.2	4.3	11.7	18.4
f	220 [a]	82	$C_{14}H_{13}ClN_4O_2$	55.4	4.4	11.9	18.3	55.2	4.3	11.7	18.4
g	259 [a]	88	$C_{14}H_{12}Cl_2N_4O_2$	49.3	3.3	20.8	16.2	49.6	3.5	20.9	16.5
h	179 [c]	80	$C_{14}H_{13}FN_4O_2$	58.6	4.6		19.2	58.4	4.5		19.4
i	190 [a]	76	$C_{14}H_{13}FN_4O_2$	58.6	4.6		19.5	58.4	4.5		19.4
j	231 [a]	71	$C_{14}H_{13}N_5O_4$	53.6	4.3		21.9	53.3	4.1		22.2
k	259 [d]	79	$C_{14}H_{13}N_5O_4$	53.4	4.2		22.0	53.3	4.1		22.2
l	(Oil [d])	86									

[a] From ethanol. [b] From benzene. [c] From methanol. [d] Not purified.

EXPERIMENTAL

The visible-light absorption measurements were made with a Unicam SP 800 instrument. Mass spectra were determined with an A.E.I. MS 902 instrument operating at 70 eV with a direct insertion probe.

Ethyl 5-Hydrazino-3-methylpyrazole-4-carboxylate (1).—To a stirred suspension of thiocarbohydrazide [6] (159 g) in refluxing ethanol (1.4 l) was added concentrated hydrochloric acid (435 ml) during 30 min and then ethyl 2-chloroacetoacetate (247 g) during 30 min. The mixture was heated for a further 30 min and filtered to remove sulphur. The solid which separated from the cooled filtrate was collected and treated with boiling water (1.3 l) for 5 min, and the mixture was filtered to remove more sulphur. The filtrate was evaporated to dryness under reduced pressure, and the residue recrystallised from ethanol to give 4-ethoxycarbonyl-3-methylpyrazol-5-ylhydrazinium chloride (77 g, 23%), m.p. 221°. This salt (22 g), methanol (100 ml), and triethylamine (14 ml) were heated together until the solid dissolved. The solution was chilled, and the separated solid was collected and recrystallised from methanol to give the *product* (1) (14.7 g, 80%) as plates, m.p. 177° (Found: C, 45.6; H, 6.7; N, 30.3. $C_7H_{12}N_4O_2$ requires C, 45.7; H, 6.5; N, 30.4%).

General Procedure for the Preparation of Ethyl 5-N'-Benzylidenehydrazino-3-methylpyrazole-4-carboxylates (2).—Ethyl 5-hydrazino-3-methylpyrazole-4-carboxylate (18.4 g), the appropriate aldehyde (0.1 mol), and dry benzene (300 ml) were heated under reflux for 3 h while the water formed distilled out azeotropically. The solid which separated after cooling the benzene solution was collected and recrystallised. The products were obtained as needles. In the cases of aldehydes containing nitro-groups the amount of benzene used was increased to 600 ml and the products afforded yellow needles. *Ethyl 3-N'-heptylidenehydrazino-5-methylpyrazole-4-carboxylate* was prepared similarly except

[8] J. Bailey, E. B. Knott, and P. A. Marr, B.P. 1,247,493; B.P. 1,252,418; B.P. 1,253, 933.
[9] J. Bailey, B.P. 1,334,515.

that after the reaction period was over all the benzene was removed by distillation and the residue was recrystallised. That ethanol can be used instead of benzene was exemplified by the condensation of the hydrazine with *o*-chlorobenzaldehyde in which ethanol (400 ml) was used instead of benzene. The reaction time was 2 h and the product separated from the cooled ethanol in 88% yield.

TABLE 3

6-Methyl-1*H*-pyrazolo[3,2-*c*]-*s*-triazole-7-carboxylic acids (4)

Compound (4)	Yield (%)	Formula	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N
a	89	$C_{12}H_{10}N_4O_2$	59.2	4.3		22.9	59.6	4.1		23.1
b	70	$C_{13}H_{12}N_4O_2$	60.6	4.5		21.6	60.9	4.7		21.9
c	83	$C_{13}H_{12}N_4O_2$	60.5	4.6		21.7	60.9	4.7		21.9
d	62	$C_{15}H_{16}N_4O_2$	63.0	5.4		19.5	63.4	5.6		19.7
e	95	$C_{12}H_9ClN_4O_2$	51.8	3.2	12.7	20.0	52.1	3.3	12.8	20.2
f	85	$C_{12}H_9ClN_4O_2$	51.9	3.2	12.6	19.9	52.1	3.3	12.8	20.2
g	93	$C_{12}H_8Cl_2N_4O_2$	45.9	2.6	22.6	17.8	46.3	2.6	22.8	18.0
h	77	$C_{12}H_9FN_4O_2$	55.0	3.3		21.3	55.4	3.5		21.5
i	94	$C_{12}H_9FN_4O_2$	55.2	3.6		21.3	55.4	3.5		21.5
j	73	$C_{12}H_9N_5O_4$	49.8	3.0		24.1	50.2	3.1		24.4
k	77	$C_{12}H_9N_5O_4$	50.2	3.1		24.2	50.2	3.1		24.4
l	60	$C_{12}H_{18}N_4O_2$	57.4	7.0		22.1	57.6	7.2		22.4

TABLE 4

6-Methyl-1*H*-pyrazolo[3,2-*c*]-*s*-triazoles (5)

Compound (5)	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	Cl	N	Required (%) C	H	Cl	N
a	216—217 [a]	89	$C_{11}H_{10}N_4$	66.8	5.3		27.9	66.7	5.1		28.3
b	137 [b]	65	$C_{12}H_{12}N_4$	67.7	5.9		26.2	67.9	5.7		26.4
c	230 [a]	84	$C_{12}H_{12}N_4$	67.8	5.9		26.2	67.9	5.7		26.4
d	234 [c]	93	$C_{14}H_{16}N_4$	69.8	6.8		23.3	70.0	6.7		23.3
e	184—185 [b]	83	$C_{11}H_9ClN_4$	56.8	4.1	15.1	24.0	56.8	3.9	15.3	24.1
f	264 [c]	70	$C_{11}H_9ClN_4$	56.5	3.8	15.2	24.1	56.8	3.9	15.3	24.1
g	337 [d]	87	$C_{11}H_8Cl_2N_4$	49.4	3.2	26.4	20.8	49.5	3.0	26.6	21.0
h	210 [a,f]	79	$C_{11}H_9FN_4$	61.5	4.4		25.6	61.1	4.2		25.9
i	243 [c]	78	$C_{11}H_9FN_4$	61.3	4.3		25.8	61.1	4.2		25.9
j	197 [e]	77	$C_{11}H_9N_5O_2$	54.1	3.7		28.6	54.3	3.7		28.8
k	305 [c]	83	$C_{11}H_9N_5O_2$	54.0	3.6		28.7	54.3	3.7		28.8
l	110—111 [b]	60	$C_{11}H_{18}N_4$	64.2	8.8		27.1	64.1	8.7		27.2

[a] From ethanol–water (1 : 1). [b] From light petroleum (b.p. 60—80 °C). [c] From ethanol. [d] From ethanol–light petroleum (b.p. 60—80 °C) (1 : 1). [e] From benzene–light petroleum (b.p. 60—80 °C) (2 : 1). [f] *m/e* 216 (M^+).

TABLE 5

7-(4-Diethylamino-2-methylphenylimino)-7*H*-pyrazolo[3,2-*c*]-*s*-triazoles (9)

Compound (9)	Form	M.p. (°C)	Yield (%)	Formula	Found (%) C	H	Cl	N	S	Required (%) C	H	Cl	N	S
a	Purple needles	198—199 [a]	94	$C_{22}H_{24}N_6$	71.1	6.6		22.4		71.0	6.45		22.6	
b	Green needles	170—171 [a]	85	$C_{23}H_{26}N_6$	71.1	6.6		21.5		71.5	6.7		21.8	
c	Green needles	205—206 [a]	97	$C_{23}H_{26}N_6$	71.2	6.6		22.0		71.5	6.7		21.8	
d	Red rods	159—160 [a]	96	$C_{25}H_{30}N_6$	72.1	7.1		19.9		72.5	7.25		20.3	
e	Purple needles	160—161 [a]	86	$C_{22}H_{23}ClN_6$	64.8	5.7	8.8	20.7		64.9	5.6	8.7	20.6	
f	Green needles	246 [a]	93	$C_{22}H_{23}ClN_6$	64.9	5.9	8.8	20.6		64.9	5.6	8.7	20.6	
g	Dark blue rods	305 [a]	90	$C_{22}H_{22}Cl_2N_6$	59.6	5.0	16.3	19.2		59.8	5.0	16.1	19.0	
h	Purple needles	178 [a]	90	$C_{22}H_{23}FN_6$	67.6	6.2		21.6		67.7	5.9		21.5	
i	Green platelets	227 [b]	92	$C_{22}H_{23}FN_6$	67.6	6.3		21.6		67.7	5.9		21.5	
j	Purple needles	251 [b]	89	$C_{22}H_{23}N_7O_2$	63.1	5.6		23.2		63.3	5.5		23.5	
k	Black platelets	280 [b]	91	$C_{22}H_{23}N_7O_2$	63.1	5.5		23.2		63.3	5.5		23.5	
l	Red microcrystals	73 [c]	82	$C_{22}H_{32}N_6$	70.1	8.8		21.8		69.5	8.45		22.1	
m	Black rods	194—195 [a]	92	$C_{22}H_{24}N_6S$	65.4	6.0		20.7	8.2	65.4	5.9		20.8	8.2
n	Black needles	146—147 [b]	89	$C_{22}H_{23}N_7O_2S$	58.4	5.2		21.5	7.0	58.8	5.1		21.8	7.1

[a] From methanol. [b] From ethanol. [c] Not recrystallised.

General Procedure for the Synthesis of Ethyl 6-*Methyl*-1H-*pyrazolo*[3,2-c]-s-*triazole*-7-*carboxylates* (3).—A solution of bromine (8 g) in acetic acid (40 ml) was added dropwise, during 5 min, to a stirred mixture of the appropriate ethyl 5-*N*′-benzylidenehydrazino-3-methylpyrazole-4-carboxylate (0.05 mol) and anhydrous sodium acetate (8.2 g) in acetic acid (200 ml). The mixture was stirred at room temperature for 1 h and then heated on a steam-bath for 20 min. The mixture was then cooled and poured into water (2 l) with stirring. The precipitate was filtered off, dried, and recrystallised. The products were obtained as needles, except those containing nitro-groups which were yellow needles. *Ethyl* 3-*hexyl*-6-*methyl*-1H-*pyrazolo*[3,2-c]-s-*triazole*-7-*carboxylate* separated as an oil which was extracted into ethyl acetate (3 × 200 ml); the combined extract was dried ($MgSO_4$) and concentrated to leave the product as a pale yellow oil.

Ethyl 6-methyl-3-o-tolyl-1H-pyrazolo[3,2-c]-s-triazole-7-carboxylate (3b). To a stirred solution of the hydrazine (1) (4.6 g) in dry pyridine (80 ml) was added *o*-toluoyl chloride (3.9 g) during 15 min. The solution was stirred for 1 h more, then heated at 100 °C for 1 h, cooled, and poured into water (1.5 l). The precipitate was collected, washed with water, and recrystallised from ethanol to give *ethyl 3-methyl-5-N′-o-toluoylhydrazinopyrazole-4-carboxylate* as a microcrystalline solid (4.1 g, 54%), m.p. 166—167° (Found: C, 59.7; H, 6.1; N, 18.5. $C_{15}H_{18}N_4O_3$ requires C, 59.6; H, 6.0; N, 18.6%).

This hydrazide (3 g), phosphoryl chloride (3 g), and benzene (100 ml) were heated under reflux for 6 h. The benzene was removed by distillation, the residue was treated with water (200 ml), and the solid was extracted into ethyl acetate. The extract was dried ($MgSO_4$) and concentrated and the residue was recrystallised from ethanol to give the *product* as a microcrystalline solid (1.45 g, 51%), m.p. 181°, undepressed by the product obtained from the corresponding pyrazolylhydrazone.

Ethyl 3-hexyl-6-methyl-1H-pyrazolo[3,2-c]-s-triazole-7-carboxylate (3l). The hydrazine (1) (4.6 g) was dissolved in dry pyridine (100 ml), heptanoyl chloride (3.7 g) was added during 10 min, and the solution was heated under reflux for 2 h. The solution was cooled and poured into water (1.2 l). The precipitate was collected, washed well with water, and recrystallised from 50% aqueous ethanol to give *ethyl 5-heptanoylhydrazino-3-methylpyrazole-4-carboxylate* as a microcrystalline solid (3.8 g, 51%), m.p. 145° (Found: C, 56.9; H, 8.3; N, 18.8. $C_{14}H_{24}N_4O_3$ requires C, 56.8; H, 8.1; N, 18.9%).

This hydrazide (3 g), phosphoryl chloride (1.5 g), and dry benzene (50 ml) were heated under reflux for 10 h. After removing the benzene by distillation the residue was stirred with water (200 ml) and the gum was extracted into ethyl acetate (3 × 70 ml). The combined extract was dried ($MgSO_4$) and concentrated to give the product as a yellow oil (2.5 g, 90%), which was used without purification.

General Procedure for the Preparation of 6-Methyl-1H-pyrazolo[3,2-c]-s-triazole-7-carboxylic Acids (4).—The ester (2 g) and sulphuric acid (s.g. 1.84; 16 ml) were heated together on a steam-bath for 30 min. The temperature of the mixture was 90—95 °C. The clear solution was then cooled and poured into water (200 ml). The precipitate was collected, washed with water (100 ml), and dried. The products were used without purification. (Those containing a nitro group were yellow.)

General Procedure for the Preparation of 6-Methyl-1H-pyrazolo[3,2-c]-s-triazoles (5).—The carboxylic acid (2 g) and dimethylaniline (10 ml) were heated together at 150 °C for 30 min (carbon dioxide was evolved). The temperature of the mixture was then raised to 180 °C during 15 min. The solution was then cooled and poured into light petroleum (b.p. 60—80 °C; 200 ml) and the precipitate was collected and recrystallised. The products were obtained as colourless-to-buff needles except the nitro-containing compounds, which were yellow needles.

Condensation of Thiocarbohydrazide with Ethyl Acetoacetate.—Thiocarbohydrazide (5.3 g), ethyl acetoacetate (6.5 g), and ethanol (150 ml) were heated under reflux for 4 h. The mixture was filtered and the solid was rejected. The filtrate was evaporated to dryness and the residue was recrystallised from methanol to give 3-methyl-Δ^2-pyrazolin-5-one (4 g, 82%), m.p. and mixed m.p. 216°. Carbohydrazide, treated likewise, gave the same product.

S-Methylisothiocarbohydrazide Hydroiodide (7).—Methyl iodide (18 g) was added to a stirred suspension of thiocarbohydrazide (12 g) in refluxing ethanol (400 ml), and the mixture was heated for 2 h. The resulting solution was cooled and the solid which separated was collected. A further amount was obtained by distilling ethanol (200 ml) from the filtrate. The combined crops (19.6 g, 70%) were recrystallised from ethanol to give the *product* as needles, m.p. 145° (Found: C, 9.5; H, 3.8; I, 50.9; N, 22.5; S, 12.8. $C_2H_9IN_4S$ requires C, 9.7; H, 3.6; I, 51.2; N, 22.6; S, 12.9%).

TABLE 6

Light absorption maxima (nm) of dyes (9) in various solvents

Compound (9)	Solvent *	$\lambda_{max.}$	$\varepsilon_{max.}$
a	(a)	565	67 700
	(b)	551	59 900
	(c)	544	78 300
		518	53 600
b	(a)	554	56 700
	(b)	541	52 600
	(c)	532	59 900
		506 sh	46 300
c	(a)	560	64 000
	(b)	549	61 800
	(c)	539	68 100
		516	48 700
d	(a)	549	52 600
	(a) + dil. HCl	578	75 600
	(b)	531	50 100
	(c)	520	62 000
		495 sh	39 000
e	(a)	555	60 200
	(b)	539	54 600
	(c)	524	60 200
		500 sh	38 200
f	(a)	569	68 200
	(b)	555	65 100
	(c)	548	75 600
		521	51 300
g	(a)	554	69 000
	(b)	536	62 500
	(c)	522	†
		498 sh	†
h	(a)	558	68 400
	(b)	542	61 500
	(c)	527	65 900
		500 sh	50 400
i	(a)	561	73 400
	(b)	552	65 000
	(c)	541	75 200
		516	51 700
j	(a)	560	68 400
	(b)	537	63 900
	(c)	534	†
		508 sh	†
k	(a)	577	†
	(b)	570	†
l	(a)	541	47 800
	(a) + dil. HCl	570	73 300
	(b)	528	46 400
	(c)	515	56 900
m	(a)	577	58 000
	(b)	564	53 800
	(c)	550	61 700
		525	39 800
n	(a)	596	†
	(b)	587	†

* (a) MeOH, (b) EtOAc, (c) cyclohexane. † Not measured.

3-Methylthio-6-phenyl-1H-pyrazolo[3,2-c]-s-triazole (8a).—Ethyl benzoylacetate (9.6 g) and compound (7) (12.4 g) were heated together at 110—115 °C for 25 min; during the last 5 min the volatile products were distilled off under

reduced pressure. The residue was treated with sodium carbonate solution (10%; 300 ml) and the small amount of insoluble oily material was removed by filtration. The filtrate was cooled and the solid was collected and recrystallised from benzene to give the *product* as needles (5 g), m.p. 179° (Found: C, 57.6; H, 4.2; N, 23.9; S, 13.9%; *m/e*, 230. $C_{11}H_{10}N_4S$ requires C, 57.4; H, 4.3; N, 24.3; S, 13.9%; *M*, 230).

3-*Methylthio*-6-*p*-*nitrophenyl*-1H-*pyrazolo*[3,2-c]-s-*triazole* (8b). Ethyl *p*-nitrobenzoylacetate (2.3 g) and compound (7) (2.4 g) were heated in refluxing pentyl alcohol (40 ml) for 35 min. The solution was cooled and the yellow solid (1 g) was collected and recrystallised from pentyl alcohol to give yellow *rods*, m.p. 277° (Found: C, 47.8; H, 3.4; N, 25.7; S, 11.4. $C_{11}H_9N_5O_2S$ requires C, 48.0; H, 3.3; N, 25.5; S, 11.6%).

3-*Methylthio*-6-*m*-*nitrophenyl*-1H-*pyrazolo*[3,2-c]-s-*triazole* (8c).—Ethyl *m*-nitrobenzoylacetate (2.4 g) and compound (7) (2.5 g) were heated at 120 °C for 15 min. The product was treated with aqueous sodium carbonate (10%; 80 ml) and heated until most of the solid had dissolved. The hot mixture was filtered and the yellow solid (0.8 g) which separated from the filtrate was recrystallised from benzene to give yellow *microcrystals*, m.p. 217° (Found: C, 47.7; H, 3.4; N, 25.3; S, 11.7. $C_{11}H_9N_5O_2S$ requires C, 48.0; H, 3.3; N, 25.5; S, 11.6%).

General Method for the Synthesis of 7-(4-*Diethylamino*-2-*methylphenylimino*)-7H-*pyrazolo*[3,2-c]-s-*triazoles* (9).—Potassium persulphate (0.6 g) was added to a stirred mixture of the 1*H*-pyrazolo[3,2-*c*]-*s*-triazole (1 mmol), 4-diethylamino-2-methylanilinium chloride (0.25 g), methanol (10 ml), and sodium carbonate in water (5%; 20 ml). Stirring was continued for 40 min and then water (70 ml) was added, and the dye was collected by filtration, washed with water (50 ml), dried, and recrystallised twice from either methanol or ethanol, with the exception of the dye (9l) which was extracted from the reaction mixture with benzene (50 ml); the benzene was removed by distillation to leave a dark red gum which slowly hardened.

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