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Acetylenic Analogues of the Cyanine Dyes. 2.[1] Synthesis of Isomeric Acetylenic Dyes

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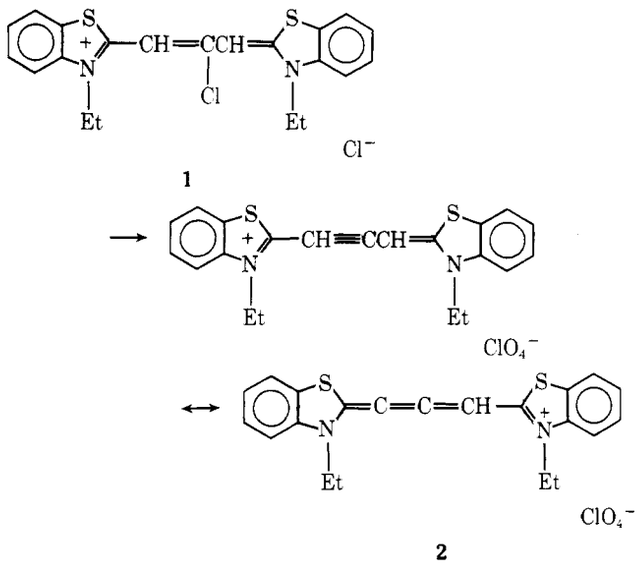
A new synthesis of acetylenic analogues of cyanine dyes is described, and the mechanism of the reaction is discussed in terms of ynenamines as reactive intermediates. This approach makes possible the separate synthesis of isomeric acetylenic dyes such as **4** and **5**.

The first examples of acetylenic cyanine analogues were described recently.[1] These compounds, which possess a formal triple bond in the conjugated system, were obtained through a reaction sequence in which the final step was the dehydrochlorination of a *meso*-chloro carbocyanine, as in the formation of **2** from **1**. This route leads to dyes of unambiguous structure only when the terminal heterocyclic nuclei are identical. In cases where this condition is not met, for example in **3**, elimination of hydrogen chloride can occur in two alternative modes to give the two isomeric dyes **4** and **5**.

We report here a new and more versatile approach, whereby dyes such as **4** and **5** may be obtained separately. One method[2] for the preparation of meso-substituted carbocyanines involves the reaction, under basic conditions, of a heterocyclic quaternary salt containing a 2-substituted propenyl group with a second quaternary salt having a suitable leaving group. Thus, reaction of the 2-chloropropenyl salt **6**[3] with the betaine **7**[4] in acetonitrile, using pyridine as condensing agent, gave the *meso*-chloro carbocyanine **1**. When triethylamine was used in place of pyridine, however, the product was the acetylenic dye **2**.[1,6]

Since **1** is not dehydrochlorinated under the conditions used to prepare **2**, it cannot be an intermediate in the formation of **2**. The reaction of 2-chloropropenyl salts with triethylamine in the absence of a second reactive quaternary salt proved to be highly illuminating. Although the reaction of **6** did not yield



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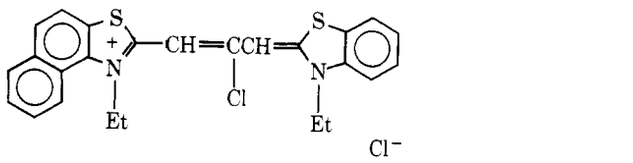

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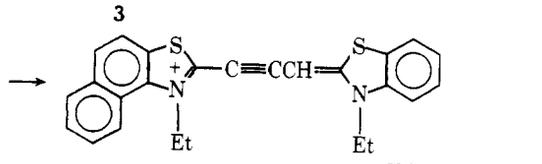

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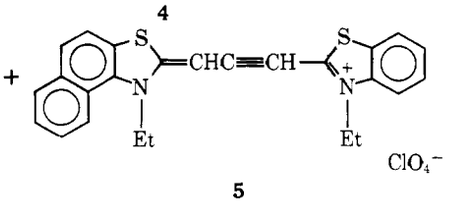
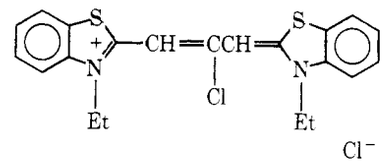
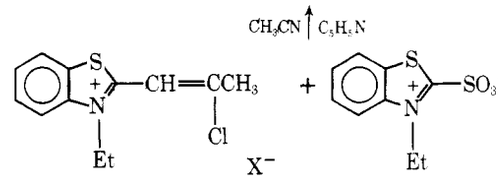


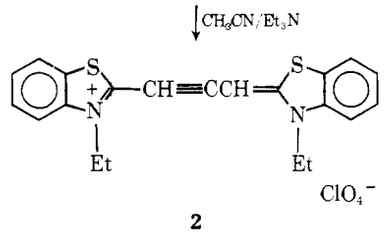
5



1

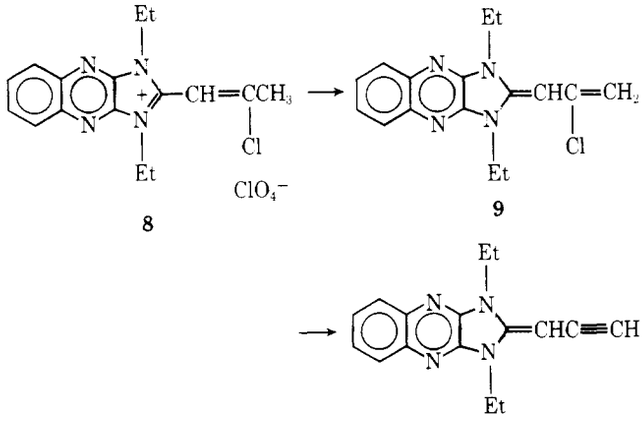


6 **7**

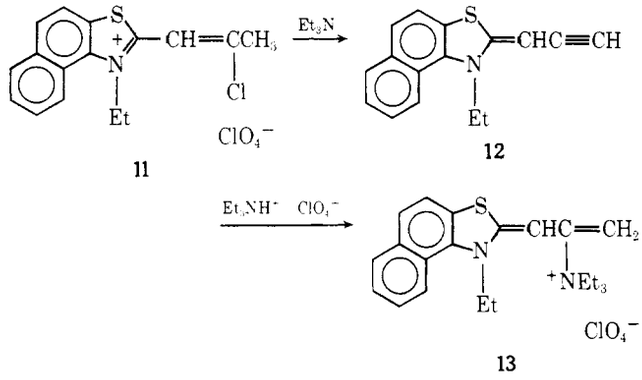


2

any readily isolated products, treatment of an acetonitrile solution of the corresponding derivative of imidazo[4,5-*b*]-quinoxaline, **8**, resulted in the rapid separation of the ynenamine[7] **10**, presumably via the dienamine **9**. When the



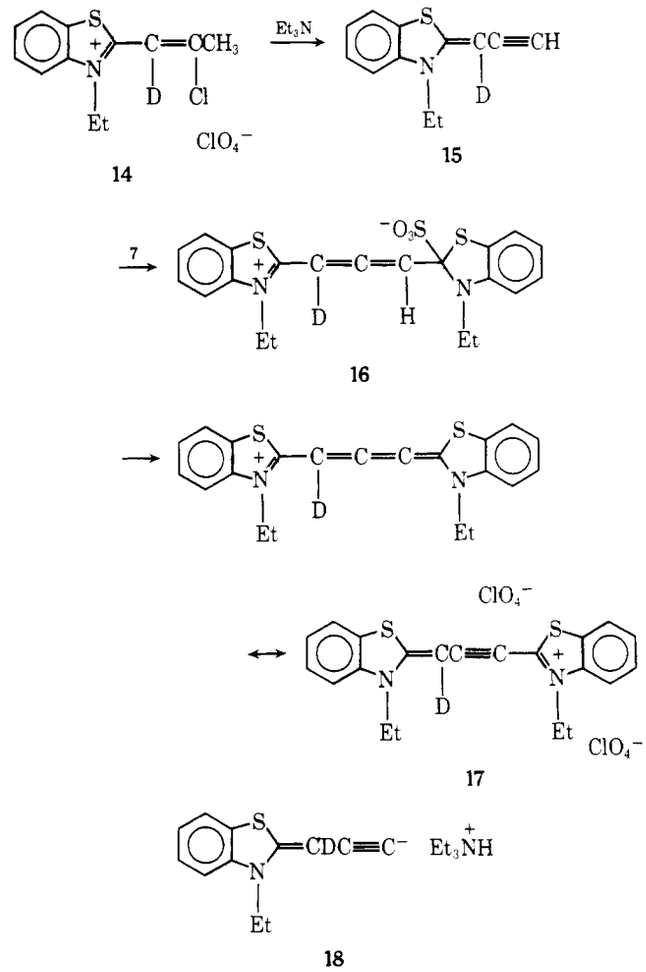
naphtho[1,2-*d*]thiazolium salt **11**[3] was allowed to react with triethylamine under the same conditions, the initially generated ynenamine **12** underwent a subsequent addition of triethylamine hydroperchlorate across the triple bond to yield the ammonium salt **13**. Replacement of triethylamine by the



more sterically hindered diisopropylethylamine, together with sodium hydride, resulted in termination of reaction at the ynenamine stage and **12** was isolated.

We believe that ynenamines such as **10** and **12** are the key intermediates in this synthesis of acetylenic dyes, for they readily react with **7** to give the same acetylenic dyes as are obtained from their parent 2-chloropropenyl salts, **8** and **11**.

Further insight into the mechanism of the dye-forming reaction was gained by replacement of **6** by its deuterium substituted analogue **14**. The reaction gave a dye in which deuterium was retained, consistent with a reaction sequence in which the deuterated ynenamine **15** adds to **7** to give an intermediate **16**. Since the loss of bisulfite from **16** to give **17** proceeds with retention of deuterium, this elimination must occur in a 1,2 rather than a 1,4 manner. Although a route involving the intermediacy of an acetylide ion **18** could also lead to retention of deuterium in the acetylenic dye, the addition–elimination sequence seems likely, since under comparable conditions the rate of exchange of the acetylenic hydrogen atom in **12** with D_2O proceeded much more slowly than the formation of **5** from **11**. It is interesting to note that reaction of **13** with **7** yields only **5**, though more slowly than in the reaction of **7** with either **11** or **12**, suggesting that in solution **13** may be in equilibrium with **12**. The slower reaction of **13** also confirms that **13** is formed from **12** and not vice versa.



Regardless of the precise details of the mechanism by which the acetylenic dyes are formed, the retention of deuterium in **17** has important implications for the synthesis of acetylenic dyes in which the two heterocyclic nuclei are different, for it may be anticipated that the single hydrogen substituent on the conjugated chain of the dye will be adjacent to that nucleus that originally formed part of the 2-chloropropenyl salt. Accordingly, **4** and **5** were obtained from **6** and **11**, respectively. The isomeric pairs of dyes **19–30** (see Table I) were similarly obtained from the appropriate 2-chloropropenyl salts. Details of the preparations of the additional intermediates **31–38**, required for the synthesis of these dyes, are given in the Experimental Section.

Experimental Section

^{1}H NMR spectra were recorded using a Bruker HX-90 or Varian T-60 spectrophotometer. The spectra of the acetylenic dyes were obtained in Me_2SO-d_6 containing 3% pyridine-d_5 to inhibit isomerization.[8] Melting points were determined using a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded using a Perkin-Elmer Model 257 spectrophotometer. Electronic spectra of solutions of the dyes in the concentration range of $1–2 \times 10^{-5}$ M were recorded using a Perkin-Elmer Model 450 spectrophotometer. At these concentrations, Beer's law was obeyed. No detectable isomerization occurred during the recording of NMR, IR, or electronic spectra of the dyes, with one exception noted in Table I.

All the acetylenic dyes decomposed on heating without displaying any distinct melting point. All were isomerically pure, within the limits of detection, as judged by comparisons of electronic, NMR, and IR spectra. With the exception of dye **2**, the acetylenic dyes were not recrystallized, since in some cases this leads to partial isomerization.[8] Unless otherwise noted, the dyes were dried at 60 °C.

9-Chloro-3,3′-diethylthiacarbocyanine Chloride (1). To a mixture of the chloride salt of **6**[3] (1.37 g, 0.005 mol) and **7**[9] (1.22 g, 0.005 mol) in hot acetonitrile (50 ml) was added pyridine (2.5 ml). The

mixture was heated at reflux for 30 min, with constant stirring. The crystalline dye **1**, which separated during the reaction, was collected by filtration of the hot reaction mixture and washed with acetonitrile: yield 1.06 g (47%); mp 246–248 °C dec; λ_{max}(CH_3CN) 549 nm (ϵ 18.3 × 10^4). Anal. Calcd for $C_{21}H_{20}Cl_2N_2S_2 \cdot \frac{1}{2}H_2O$: C, 56.9; H, 4.8; Cl, 15.9; N, 6.3. Found: C, 56.7; H, 5.0; Cl, 15.9; N, 6.1.

11-Chloro-1,3'-diethylnaphtho[1,2-*d*]thiazolothiacarbocyanine Chloride (3). This dye was obtained from **7**[9] and the chloride salt of **11**[3] by the method described for the preparation of dye **1**: yield 22%; mp 214–216 °C dec; λ_{max} (CH_3CN) 567 nm (ϵ 18.0 × 10^4). Anal. Calcd for $C_{25}H_{22}Cl_2N_2S_2 \cdot 1.5H_2O$: C, 58.4; H, 4.9; N, 5.5. Found: C, 58.4; H, 4.8; N, 5.6.

Dehydrochlorination of Dye 3. A mixture of **3** (0.49 g, 0.001 mol), 50% aqueous acetonitrile (5 ml), and triethylamine (0.15 g, 0.0015 mol) was heated at reflux for 1 min. To the resulting solution was added sodium perchlorate (0.2 g) dissolved in a little water and the solution slowly diluted to 15 ml with water. The dye was collected and washed successively with water, methanol, and ether, yield 0.50 g (98%). The visible, NMR, and IR spectra of the product corresponded to a mixture of dyes **4** and **5** in a ratio of approximately 2:1.

3-Ethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl]-benzothiazolium Perchlorate (2) (Method A). A mixture of the perchlorate salt of **6**[3] (1.70 g, 0.005 mol) and **7**[9] (1.22 g, 0.005 mol) in acetonitrile (25 ml) was cooled at 0–5 °C and stirred as triethylamine (1.50 g, 0.015 mol) was added in one portion. After 1 min, the reaction mixture was filtered and the filtrate diluted with ether (175 ml). Decantation of the ethereal layer followed by trituration of the viscous residue with methanol (25 ml) yielded 0.85 g (37%) of crystalline dye, which was recrystallized from ethanol. The dye was identical with that reported previously:[1] NMR δ 1.3 (t, 3), 1.6 (t, 3), 4.3 (q, 2), 4.6 (q, 2), 5.8 (s, 1), 7.1–8.5 (m, 8).

3-Ethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl-*d*]benzothiazolium Perchlorate (17). This dye was prepared from **7**[9] and **14** by method A. The crude dye had λ_{max} (CH_3CN) 513 nm (ϵ 9.9 × 10^4). The proportion of undeuterated dye was estimated as <7% by comparison of the NMR spectra of dyes **17** and **2** (singlet at δ 5.8). Attempted recrystallization of the dye from ethanol resulted in replacement of most of the deuterium by hydrogen.

2-[(5,6-Dichloro-1,3-diethyl-2-benzimidazolinylidene)-1-propynyl]-1,3-diethylimidazo[4,5-*b*]quinoxalinium Perchlorate (20) (Method B). **35** (2.30 g, 0.0055 mol), **38** (1.85 g, 0.005 mol), and acetic anhydride (0.60 g, 0.006 mol) in acetonitrile (25 ml) were stirred at 0–5 °C as triethylamine (2.5 g, 0.025 mol) was added. The initially clear solution was stirred at 0–5 °C for 15 min as dye separated. The dye was collected, washed with acetonitrile, and dried at room temperature in vacuo, yield 0.54 g (18%).

1-Ethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl]-naphtho[1,2-*d*]thiazolium perchlorate (4) was prepared from the perchlorate salt of **6**[3] and *anhydro*-1-ethyl-2-sulfonaphtho[1,2-*d*]thiazolium hydroxide[9] by method A. The dye was isolated by dilution of the reaction mixture with methanol (4 volumes): yield 20%; NMR δ 1.3 (t, 3), 1.8 (t, 3), 4.1 (q, 2), 5.1 (q, 2), 5.7 (s, 1), 7.0–8.6 (m, 10).

3-Ethyl-2-[(1-ethylnaphtho[1,2-*d*]thiazolin-2-ylidene)-1-propynyl]benzothiazolium Perchlorate (5). A. The dye was prepared from **7**[9] and **11**[3] by the procedure described for the synthesis of dye **4**: yield 46%; NMR δ 1.6 (m, 6), 4.6 (m, 4), 5.9 (s, 1), 7.3–8.7 (m, 10).

B. The above procedure was repeated using an equimolar amount of **12** in place of **11**. On addition of aqueous sodium perchlorate solution, **5** separated, yield 50%.

C. **7** (0.17 g, 0.0007 mol) and **13** (0.32 g, 0.0007 mol) were stirred with a mixture of triethylamine (0.07 g, 0.0007 mol) and acetonitrile (3 ml) at room temperature. Solution was rapidly attained and the rate of appearance of dye color was slower than in the above reactions. After 5 min, the solid dye which had separated was collected and washed with acetonitrile, yield 0.20 g (56%).

5,6-Dichloro-1,3-diethyl-2-[(1,3-diethylimidazo[4,5-*b*]quinoxalinylidene)-1-propynyl]benzimidazolium perchlorate (19) was prepared from **34** and **37** by method B: yield 20%; NMR δ 1.5 (m, 12), 4.4 (m, 8), 5.5 (s, 1), 7.5–8.6 (m, 6).

5,6-Dichloro-1,3-diethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl]benzimidazolium perchlorate (21) was prepared from the perchlorate salt of **6**[3] and **37** by method B: yield 20%; NMR δ 1.3 (t, 3), 1.5 (t, 6), 4.2 (q, 2), 4.5 (q, 4), 5.7 (s, 1), 7.1–8.0 (m, 4), 8.4 (s, 2).

2-[(5,6-Dichloro-1,3-diethyl-2-benzimidazolinylidene)-1-propynyl]-3-ethylbenzothiazolium iodide (22) was prepared from **7**[9] and **35** by method A, except that the reaction was allowed to proceed for 5 min at 25 °C. Tetraethylammonium iodide (0.64 g, 0.0025 mol) was added to the filtered reaction mixture. The solution was chilled briefly and the dye that separated was collected and washed with a little acetonitrile, then with ether: yield 40%; NMR δ 1.4 (m, 9), 4.5 (m, 6), 5.6 (s, 1), 7.3–8.7 (m, 6).

3-Ethyl-2-[(3-ethyl-2,3-dihydrothiazolo[4,5-*b*]quinolin-2-ylidene)-1-propynyl]benzothiazolium perchlorate (23) was prepared by the acid-catalyzed isomerization[8] of **24**. Thus, dye **24** (0.40 g) was dissolved in acetonitrile (100 ml) and acetic acid (2 ml) was added. After 3 h the solution was concentrated to 15 ml and chilled to yield 0.14 g (35%) of **23**: NMR δ 1.4 (t, 3), 1.7 (t, 3), 4.4 (q, 2), 4.8 (q, 2), 6.1 (s, 1), 7.3–8.8 (m, 9).

3-Ethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl]-thiazolo[4,5-*b*]quinolinium perchlorate (24) was prepared from 3-ethyl-2-methylthiothiazolo[4,5-*b*]quinolinium *p*-toluenesulfonate[10] and the perchlorate salt of **6** by method A: yield 27%; NMR δ 1.4 (t, 3), 1.7 (t, 3), 4.6 (m, 4), 6.2 (s, 1), 7.3–9.2 (m, 9).

1-Ethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl]-quinolinium perchlorate (25) was prepared from *anhydro*-1-ethyl-2-sulfoquinolinium hydroxide[9] and the perchlorate salt **6**[3] by method A; yield 23%; NMR δ 1.3 (t, 3), 1.6 (t, 3), 4.3 (q, 2), 4.9 (q, 2), 5.8 (s, 1), 7.2–8.7 (m, 10).

3-Ethyl-2-[(1-ethyl-2,3-dihydro-2-quinolinylidene)-1-propynyl]benzothiazolium perchlorate (26) was prepared from **7**[9] and **36** by method A: yield 46%; NMR δ 1.4 (m, 6), 4.5 (m, 4), 5.6 (s, 1), 7.2–8.7 (m, 10).

1-Ethyl-2-[(1,3-diethyl-2,3-dihydroimidazo[4,5-*b*]quinoxalin-2-ylidene)-1-propynyl]naphtho[1,2-*d*]thiazolium perchlorate (27) was prepared from **8** and *anhydro*-2-sulfo-1-ethylnaphtho[1,2-*d*]thiazolium hydroxide[9] by method A. The dye separated spontaneously from the reaction mixture: yield 39%; NMR δ 1.6 (m, 9), 4.5 (q, 4), 5.1 (q, 2), 5.7 (s, 1), 7.3–8.8 (m, 10).

1,3-Diethyl-2-[(1-ethylnaphtho[1,2-*d*]thiazolin-2-ylidene)-1-propynyl]imidazo[4,5-*b*]quinoxalinium perchlorate (28) was prepared from **11**[3] and **38** by method B: yield 44%; NMR δ 1.6 (m, 9), 4.5 (m, 6), 6.2 (s, 1), 7.2–8.6 (m, 10).

3-Ethyl-2-[(1,3-diethyl-2,3-dihydroimidazo[4,5-*b*]quinoxalin-2-ylidene)-1-propynyl]benzothiazolium Perchlorate (29). A. **29** was prepared from **7**[9] and **8** by method A. The dye separated spontaneously from the reaction mixture: yield 48%; NMR δ 1.5 (m, 9), 4.5 (m, 6), 5.7 (s, 1), 7.3–8.6 (m, 8).

B. The above procedure was repeated using an equimolar amount of **10** in place of **8**. On addition of aqueous sodium perchlorate solution, **29** separated, yield 57%.

1,3-Diethyl-2-[(3-ethyl-2-benzothiazolinylidene)-1-propynyl]imidazo[4,5-*b*]quinoxalinium perchlorate (30) was prepared from the perchlorate salt of **6**[3] and **38** by method B: yield 27%; NMR δ 1.4 (t, 3), 1.6 (t, 6), 4.5 (m, 6), 6.1 (s, 1), 7.3–8.6 (m, 8).

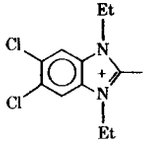
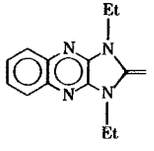
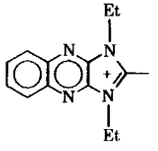
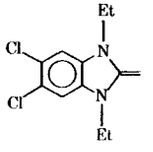
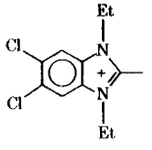
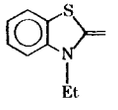
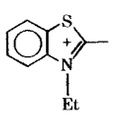
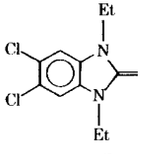
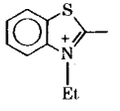
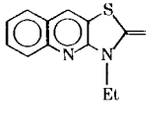
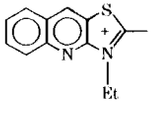
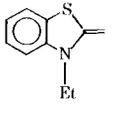
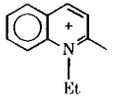
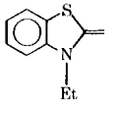
1,3-Diethyl-1,2-dihydro-2-(2-propynylidene)imidazo-[4,5-*b*]quinoxaline (10). Compound **8** (2.00 g, 0.005 mol) in acetonitrile (20 ml) was stirred as triethylamine (1.50 g, 0.015 mol) was added in one portion. After 1 min the solid that separated was collected and washed with a small volume of acetonitrile: yield 0.63 g (48%); mp (CH_3CN) ~135 °C dec; IR (KBr) 3260 (acetylenic H), 2081 cm^{-1} (C≡C); NMR (C_6D_6) δ 0.83 (t, 3), 1.32 (t, 3) 2.95 (d, 1), 3.36 (q, 2), 3.95 (d, 1), 4.36 (q, 2), 7.0–8.1 (m, 4). Anal. Calcd for $C_{16}H_{16}N_4$: C, 72.7; H, 6.1; N, 21.2. Found: C, 72.4; H, 6.2; N, 21.2.

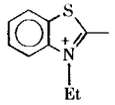
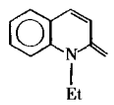
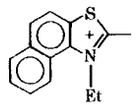
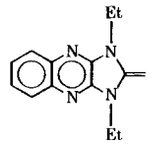
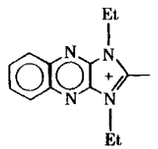
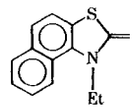
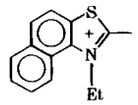
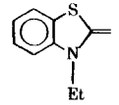
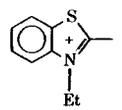
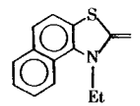
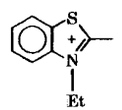
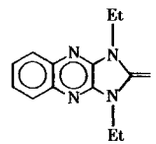
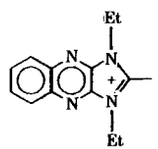
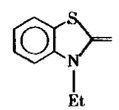
1-Ethyl-2-(2-propynylidene)naphtho[1,2-*d*]thiazoline (12). A mixture of **11**[3] (1.94 g, 0.005 mol), sodium hydride (0.6 g, 0.025 mol), and acetonitrile (25 ml) was stirred and cooled in an ice bath as diisopropylethylamine (2.5 g, 0.02 mol) was added dropwise. The mixture was filtered and solvent removed by evaporation at 30 °C, under reduced pressure. The residue was extracted with petroleum ether (bp 30–60 °C, 5 × 50 ml). The combined extracts were concentrated to 50 ml. Upon chilling, 0.28 g (22%) of **12** separated: mp (petroleum ether) ~100 °C dec; IR (KBr) 3281 (acetylenic H), 2035 cm^{-1} (C≡C); NMR (CD_3CN) δ 1.56 (t, 3), 3.61 (d, 1), 4.21 (q, 2), 4.78 (d, 1), 7.3–8.4 (m, 6). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.5; H, 5.2; N, 5.6; S, 12.8. Found: C, 76.6; H, 5.4; N, 5.2; S, 12.6.

Deuteration of 12. Compound **12** (0.03 g) was dissolved in CD_3CN (0.5 ml). D_2O (0.09 g) and triethylamine (0.05 g) were added and the rate of exchange of the acetylenic hydrogen was monitored by NMR (disappearance of doublet at δ 3.68). The half-life for this process was estimated as 6 min.

Reaction of 11 with Triethylamine. A suspension of **11**[3] (0.78 g, 0.002 mol) in acetonitrile (8 ml) was stirred as triethylamine (0.60 g, 0.006 mol) was added in one portion. The solid dissolved at once. From the resulting blue-colored solution, solid soon began to separate. After 1 min, the solid was collected and washed with acetonitrile, then with ether to yield 0.26 g (30%) of **13** as a colorless solid with no distinct melting point: NMR (CF_3CO_2H) δ 1.60 (t, 9), 2.02 (t, 3), 3.89 (q, 6).

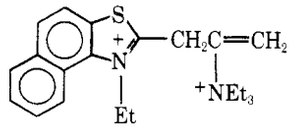
Table I. Visible Absorption Maxima of $R_1{}^+C{=}CCH{=}R_2\ ClO_4{}^-$

Registry no.	Dye[a]	R_1	R_2	λ_{max} (CH_3CN), nm	$\epsilon_{max} \times 10^{-4}$	Empirical formula	Calcd	Found
61268-47-1	**19**			488	13.0	$C_{27}H_{27}Cl_3N_6O_4$	C, 53.5; H, 4.5; N, 13.9	C, 53.1; H, 4.8; N, 13.7
61268-49-3	**20**			532	>12.7[b]			C, 53.4; H, 4.6; N, 13.8
56387-15-6	**21**			468	9.2	$C_{23}H_{22}Cl_3N_3O_4S$	C, 50.9; H, 4.1; N, 7.7	C, 50.7; H, 4.1; N, 8.0
61268-50-6	**22**[c]			510	12.2	$C_{23}H_{22}Cl_2IN_3S$	C, 48.4; H, 3.9; N, 7.4	C, 48.5; H, 3.8; N, 7.2
61268-52-8	**23**			508	9.8	$C_{24}H_{20}ClN_3O_4S_2$	C, 56.1; H, 3.9; N, 8.2	C, 56.1; H, 3.9; N, 8.3
61268-54-0	**24**			546	12.3			C, 56.4; H, 4.1; N, 8.4
56387-17-8	**25**			543	7.1	$C_{23}H_{21}ClN_2O_4S$	C, 60.5; H, 4.6; N, 6.1	C, 60.8; H, 4.8; N, 6.4

56387-19-0	**26**			543	12.1			C, 60.6; H, 4.7; N, 6.3
61268-56-2	**27**			537	14.1	$C_{29}H_{26}ClN_5O_4S$	C, 60.5; H, 4.6; N, 12.2	C, 60.3; H, 4.4; N, 11.8
61268-58-4	**28**			556	11.6			C, 60.3; H, 4.6; N, 11.8
61268-60-8	**4**			526	8.4	$C_{25}H_{21}ClN_2O_4S_2$	C, 58.5; H, 4.1; N, 5.5	C, 58.8; H, 4.2; N, 5.3
61268-62-0	**5**			535	8.4			C, 58.5; H, 4.1; N, 5.4
61268-64-2	**29**			523	16.3	$C_{25}H_{24}ClN_5O_4S$	C, 57.1; H, 4.6; N, 13.3	C, 57.0; H, 4.9; N, 13.6
61268-66-4	**30**			531	12.6			C, 56.8; H, 4.6; N, 13.3

[a] Satisfactory analytical data (±0.4%) for C, H, and N were obtained for all compounds listed in this table. [b] Isomerizes too rapidly in solution for accurate determination. [c] Iodide salt.

4.91 (s, 2), 6.03 (d, 1, J = 7 Hz), 6.32 (d, 1, J = 7 Hz), 7.9–8.9 (m, 6), consistent with a protonated structure



Anal. Calcd for $C_{22}H_{29}ClN_2O_4S$: C, 58.3; H, 6.5; Cl, 7.8; N, 6.2; S, 7.1. Found: C, 58.1; H, 6.4; Cl, 8.2; N, 6.2; S, 7.3.

2-Acetonylidene-1,3-diethyl-2,3-dihydroimidazo[4,5-*b*]quinoxaline (31). A mixture of 1,3-diethyl-2-methylimidazo[4,5-*b*]quinoxalinium *p*-toluenesulfonate (20.6 g, 0.05 mol), acetic anhydride (5.6 g, 0.06 mol), and pyridine (75 ml) was heated at reflux for 15 min, cooled, and diluted to 500 ml with water. The solid was collected and washed with water. The yield of crude product was 11.9 g (84%): mp (CH_3CN) 213–214 °C; NMR ($CDCl_3$) δ 1.33 (t, 6), 2.23 (s, 3) 4.40 (q, 4), 5.10 (s, 1), 7.3–7.9 (m, 4). Anal. Calcd for $C_{16}H_{18}N_4O$: C, 68.1; H, 6.4; N, 19.9. Found: C, 67.9; H, 6.2; N, 19.8.

2-Acetonylidene-5,6-dichloro-1,3-diethylbenzimidazoline (32). A mixture of 5,6-dichloro-1,3-diethyl-2-methylbenzimidazolium iodide (38.5 g, 0.11 mol), acetic anhydride (12.0 g, 0.12 mol), 1,5-diazabicyclo[4.3.0]non-5-ene (24.8 g, 0.2 mol), and pyridine (100 ml) was heated at reflux for 15 min. After cooling, the mixture was added to 1 N NaOH (1 l.) at <10 °C. The precipitated solid was collected and washed with water. The yield of crude material was 17.5 g (58%): mp (benzene–petroleum ether) 155 °C dec; NMR ($CDCl_3$) δ 1.30 (t, 6), 2.11 (s, 3), 4.17 (q, 4), 4.72 (s, 1), 7.09 (s, 2). Anal. Calcd for $C_{14}H_{16}Cl_2N_2O$: C, 56.2; H, 5.4; N, 9.1. Found: C, 55.8; H, 5.7; N, 9.1.

2-Acetonylidene-3-ethylbenzothiazoline was prepared according to the published procedure:[11] NMR ($CDCl_3$) δ 1.33 (t, 3), 4.01 (q, 2), 5.84 (s, 1), 7.0–7.6 (m, (m, 4).

2-(Acetonylidene-*1-d*)-3-ethylbenzothiazoline (33). A solution of 2-acetonylidene-3-ethylbenzothiazoline[11] (6.6 g, 0.03 mol) in chloroform (10 ml) was shaken with deuterium oxide (5 ml) containing 1 drop of DCl (20% in D_2O) and the chloroform layer was separated. After three such treatments, the chloroform was evaporated to yield **33**, 5.6 g (8.5%). The proportion of undeuterated product was estimated as <7% by comparison of NMR spectra (singlet at δ 5.84) of this and the preceding compound.

2-(2-Chloropropenyl)-3-ethylbenzothiazolium perchlorate (6) was prepared according to the published procedure:[3] NMR (CD_3CN) δ 1.58 (t, 3), 2.74 (s, 3), 4.82 (q, 2), 7.56 (d, 1), 7.7–8.4 (m, 4).

2-(2-Chloropropenyl-*1-d*)-3-ethylbenzothiazolium Perchlorate (14). Compound **33** (1.00 g, 0.0045 mol) was added to phosphoryl chloride (5 ml) with stirring, to give a clear solution from which solid soon began to separate. After 10 min, 20 ml of benzene was added. The solid was collected, washed with benzene, and dissolved in methanol (10 ml). Addition of a solution of sodium perchlorate (1 g) in water (2 ml) gave a precipitate which was collected and washed with methanol, yield 1.10 g (72%). The proportion of undeuterated product was estimated as <7% by comparison of the NMR spectra (doublet at δ 7.56) of this and the preceding compound.

2-(2-Chloropropenyl)-1,3-diethylimidazo[4,5-*b*]quinoxalinium Perchlorate (34). Compound **31** (5.64 g, 0.02 mol) was added to phosphoryl chloride (25 ml). The mixture was stirred for 30 min, then cautiously decomposed with 600 g of an ice–water mixture. Sodium perchlorate (4.9 g, 0.04 mol) dissolved in a little water was added. The resulting precipitate was collected and washed with water, then dried at room temperature in vacuo: yield 7.13 g (88%); mp (MeOH) 196–167 °C dec. Anal. Calcd for $C_{16}H_{18}Cl_2N_4O_4$: C, 47.9; H, 4.5; Cl, 17.7; N, 14.0. Found: C, 47.5; H, 4.8; Cl, 18.0; N, 13.9.

The following two compounds were prepared similarly.

2-(2-Chloropropenyl)-5,6-dichloro-1,3-diethylbenzimidazolium perchlorate (35) was prepared from compound **32:** yield 81%; mp (MeOH) 214–216 °C dec. Anal. Calcd for $C_{14}H_{16}Cl_4N_2O_4$: C, 40.2; H, 3.8; Cl, 33.9; N, 6.7. Found: C, 39.9; H, 3.6; Cl, 34.1; N, 6.6.

2-(2-Chloropropenyl)-1-ethylquinolinium perchlorate (36) was prepared from 2-acetonylidene-1-ethyl-1*H*-quinolone:[12] yield 80%; mp (MeOH) 158–160 °C dec. Anal. Calcd for $C_{14}H_{15}Cl_2NO_4$: C, 50.6; H, 4.6; N, 4.2. Found: C, 50.4; H, 4.7; N, 4.1.

5,6-Dichloro-1,3-diethyl-2-hydroxyiminomethylbenzimidazolium Iodide (37). 5,6-Dichloro-1,3-diethyl-2-methylbenzimidazolium iodide (30.8 g, 0.08 mol) was added to a suspension of sodium hydride (0.1 mol) in acetonitrile (150 ml). The mixture was stirred until hydrogen evolution ceased, then heated to boiling and filtered. Upon cooling, 9.1 g (44%) of 5,6-dichloro-1,3-diethyl-2-methylenebenzimidazoline separated, mp (CH_3CN) 121–122 °C. This material (4.0 g, 0.016 mol) was dissolved in benzene (80 ml) and nitrosyl chloride bubbled into the solution until no more solid separated. The solid was collected and washed with benzene. For purification, the crude product was dissolved in 2 N NaOH (80 ml) containing sodium iodide (20 g). After filtration of insoluble material, the filtrates were acidified with concentrated HCl, whereupon **38** separated: yield 2.6 g (40%); mp (CH_3CN) 240 °C dec. Anal. Calcd for $C_{12}H_{14}Cl_2IN_3O$: C, 34.8; H, 3.4; N, 10.1. Found: C, 34.6; H, 3.5; N, 10.0.

1,3-Diethyl-2-hydroxyiminomethylimidazo[4,5-*b*]quinoxalinium Perchlorate (38). A solution of 1,3-diethyl-2-methylimidazo[4,5-*b*]quinoxalinium *p*-toluenesulfonate (100 g, 0.24 mol) in acetic acid (625 ml) was cooled at 15 °C as sodium nitrite (34.5 g, 0.50 mol) in water (200 ml) was added slowly. The solution was allowed to stand at room temperature for 2.5 h, then sodium perchlorate (46 g) in water (400 ml) added. After cooling to 15 °C, the solid was collected and washed with water, then with acetone: yield 67.7 g (75%); mp (MeOH–CH_3CN) 280–282 °C dec. Anal. Calcd for $C_{14}H_{16}ClN_5O_5$: C, 45.5; H, 4.4; N, 18.9. Found: C, 45.8; H, 4.4; N, 19.3.

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Registry No.—**1,** 34256-42-3; **2,** 52846-53-4; **3,** 61268-75-5; **6** Cl^-, 4126-03-3; **6** ClO_4^-, 56387-12-3; **7,** 50818-84-3; **8,** 61268-68-6; **10,** 61268-76-6; **11,** 61268-78-8; **11** Cl, 41426-06-6; **12,** 61268-79-9; **13,** 61268-81-3; **31,** 61268-82-4; **32,** 61268-83-5; **34,** 61268-68-6; **35,** 61268-85-7; **36,** 61268-87-9; **37,** 61268-88-0; **38,** 61268-90-4; *anhydro*-1-ethyl-2-sulfonaphtho[1,2-*d*]thiazolium hydroxide, 61268-91-5; 3-ethyl-2-methylthiothiazolo[4,5-*b*]quinolinium *p*-toluenesulfonate, 61268-93-7; *anhydro*-1-ethyl-2-sulfoquinolinium hydroxide, 4329-91-3; triethylamine, 121-44-8; 1,3-diethyl-2-methylimidazo[4,5-*b*]quinoxalinium *p*-toluenesulfonate, 41450-78-6; pyridine, 110-86-1; 5,6-dichloro-1,3-diethyl-2-methylbenzimidazolium iodide, 24351-12-0; 1,5-diazabicyclo[4.3.0]non-5-ene, 3001-72-7; 2-acetonylidene-3-ethylbenzothiazoline, 13861-37-5; 2-acetonylidene-1-ethyl-1*H*-quinolone, 4589-41-7; 5,6-dichloro-1,3-diethyl-2-methylenebenzimidazoline, 61268-94-8.

References and Notes

(1) J. D. Mee, *J. Am. Chem. Soc.*, **96,** 4712 (1974). This paper constitutes part 1 of the series.
(2) F. M. Hamer in "The Chemistry of Heterocyclic Compounds", Vol. 18, "The Cyanine Dyes and Related Compounds", A. Weissberger, Ed., Interscience, New York, N.Y., 1964, Chapter 6.
(3) N. N. Sveshikov, I. I. Levkoev, N. I. Shirokova, and N. A. Damir, *Dokl. Akad. Nauk SSSR,* **148,** 1091 (1963).
(4) Leaving groups other than SO_3^- may be employed. Alkylthio or –CH=NOR[5] groups are suitable, but –SPh is not, since addition of benzenethiol to the acetylenic dye occurs.[1]
(5) See ref 2, Chapter 2.
(6) Reaction of **6, 7,** and triethylamine was earlier studied under different conditions: I. I. Levkoev, N. N. Sveshnikov, and N. I. Shirokova, *Dokl. Acad. Nauk SSSR,* **153,** 350 (1963). In this case a mixture of dyes, not including **2,** was obtained.
(7) Only a few, acyclic, ynenamines have been reported previously: (a) A. A. Petrov and I. A. Maretina, *Zh. Obshch. Khim.,* **29,** 2458 (1959); (b) A. A. Petrov, I. A. Maretina, and N. A. Pogorzhel'skaya, *Zh. Org. Khim.,* **2,** 1757 (1966).
(8) J. D. Mee and D. M. Sturmer, *J. Org. Chem.*, following paper in this issue.
(9) Obtained by the general method of H. Larivé and R. Baralle, U.S. Patent 3 437 659 (1969).
(10) L. G. S. Brooker, U.S. Patent 2 255 407 (1941).
(11) L. G. S. Brooker and F. L. White, U.S. Patent 2 112 139 (1938).
(12) L. G. S. Brooker and F. L. White, U.S. Patent 2 341 357 (1944).