mmol) was refluxed in $SOCl_2$ (40 mL) for 2 h. The solvent was removed by distillation (80 °C (760 mmHg)), and the resulting solid was treated with ether and filtered. Recrystallization from $EtOH/H_2O$ (8:2) yielded the chloro compound **22** (11.2 g, 80%) as colorless needles: mp 294–297 °C; ^1H NMR (Me_2SO-d_6) 8.37 (4 H, d, 7 Hz), 7.20 (4 H, d, 7 Hz), 5.1–4.2 (5 H, m), 3.25 (12 H, s). Anal. Calcd for $C_{17}H_{25}Cl_3N_4O_8$: C, 39.28; H, 4.85; N, 10.78; Found: C, 39.16; H, 4.93; N, 10.71.

1,1′-(1-Propene-1,3-diyl)bis[4-(dimethylamino)pyridinium] Diperchlorate (21). A suspension of finely powdered chloro compound **22** (4 g, 8.16 mmol) in ethanol (50 mL) was treated with aqueous NaOH (2.5 N, 3.9 mL, 9.8 mmol) and stirred for 24 h. The reaction mixture was acidified with $HClO_4$ (70%) and concentrated to a third of its volume, yielding **21** as colorless crystals, recrystallized from $EtOH/H_2O$ (8:2) (2.5 g, 76%, needles): mp 274–275 °C; ^1H NMR ($CDCl_3$/TFA) 8.35 (2 H, d, 8 Hz), 8.25 (2 H, d, 8 Hz), 7.45 (1 H, d, 14 Hz), 7.10 (2 H, d, 8 Hz), 7.05 (2 H, d, 8 Hz), 6.55 (1 H, dt, 14 Hz, 7 Hz), 5.05 (2 H, d, 7 Hz), 3.40 (6 H, s), 3.35 (6 H, s). Anal. Calcd for $C_{17}H_{24}Cl_2N_4O_8$: C, 42.25; H, 5.01; N, 11.59. Found: C, 42.08; H, 5.07; N, 11.49.

Hydrogen–Deuterium Exchange. Due to the low solubility of pyridinium perchlorates in D_2O, it took us several attempts to develop working conditions for the H–D exchange. The exchange experiments were conducted at 25 °C in Me_2SO-d_6–D_2O (v/v 3:2) saturated with dry K_2CO_3; substrate concentration 0.075 mmol in 0.4 mL solvent. In all cases the H_2O concentration was below 5%. Rates were calculated from five to eight points by applying first-order kinetics, after following at least 1.5 half-lives.

Acknowledgment. We thank the "Minna-James-Heinemann-Stiftung, Hannover" for grants to W.H.R and A.O.

Registry No. **1a**, 94821-09-7; **1b**, 94821-11-1; **1c**, 94821-13-3; **2a**, 94821-15-5; **2b**, 94821-17-7; **2c**, 94821-19-9; **3a**, 94821-21-3; **3b**, 94821-23-5; **4a**, 94821-25-7; **5b**, 94821-27-9; **6b**, 94821-29-1; **7a**, 93288-50-7; **7b**, 93288-56-3; **7c**, 94821-31-5; **8a**, 93288-65-4; **8b**, 93288-69-8; **8c**, 93288-67-6; **9a**, 93288-58-5; **9b**, 94821-33-7; **9c**, 94821-35-9; **10b**, 94821-37-1; **11**, 94843-11-5; **12**, 94821-39-3; **13**, 94843-13-7; **14**, 94821-40-6; **15a**, 94821-42-8; **15b**, 94821-44-0; **15d**, 94821-46-2; **16** (X = Cl), 106-89-8; **16** (X = Br), 3132-64-7; **17a**, 94821-48-4; **17b**, 94821-50-8; **18**, 94821-52-0; **19a**, 94821-54-2; **19b**, 94821-56-4; **19d**, 94843-15-9; **21**, 94821-58-6; **22**, 94821-60-0; DMAP, 1122-58-3; DMAP·HCl, 71561-71-2; thiophenol, 108-98-5; 4-phenylpyridine hydrochloride, 16663-69-7; 4-picoline, 1333-41-1; 4-phenylpyridine hydroperchlorate, 94821-61-1; 4-pyrrolidinopyridine, 2456-81-7; 4-pyrrolidinopyridine hydrochloride, 94821-62-2; 4-(dimethylamino)-1-(oxiranylmethyl)pyridinium bromide, 94821-63-3; benzyl mercaptan, 100-53-8; 4-phenylpyridine, 939-23-1.

Heterocyclic Ynammonium Salts

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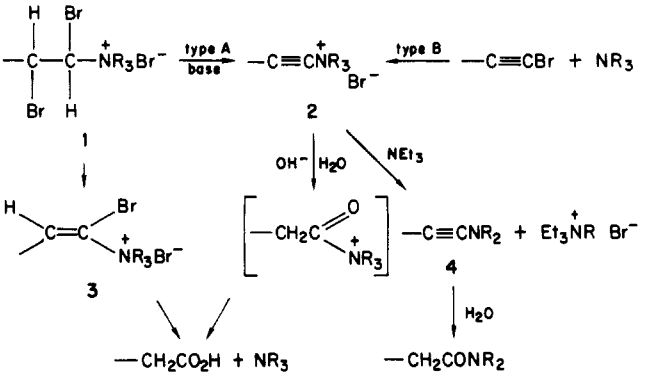
9(10*H*)-Acridinone anion reacts with ethynyl bromides to give 10-ethynyl-9(10*H*)-acridinones which are converted by phenyllithium to the corresponding 9-phenyl-9-hydroxy-10-ethynylacridinanes. The latter are converted by acid into 10-ethynylacridinium salts. ^{13}C NMR spectra are obtained, assigned, and discussed for all compounds mentioned.

Ynamines **4**, first described some 20 years ago,[1] are now familiar and versatile synthons. Their chemistry has been reviewed recently.[2,3] By contrast, there are few reports of ynammonium salts **2**. The first synthesis, claimed[4] in 1892, was disproved by Klages[5] in 1940. Ynammonium intermediates **2** have been postulated[6,7] in reactions of type A and B (Scheme I). Babayan et al.[6] studied the elimination of HBr from the dibromide **1** and suggested that intermediate **2** underwent addition of a hydroxide ion to form the acid and tertiary amine which were isolated. However, reaction of hydroxide ion with a vinyl bromide intermediate (**3**) would lead to the same products.

In reactions of the type B (Scheme I) Viehe[8] and Miller[7] also postulated the same unstable intermediates **2** which, by a transalkylation similar to a von Braun degradation, gave the ynamines **4** (or amide hydrolysis products) that were actually isolated.

Dumont[9] reported some diynammonium salts, but without physical data. The only ynammonium salt **2** that

Scheme I



has been isolated and adequately characterized is *N,N,N*-triethylethynylammonium bromide (**5**) by Miller.[10] Under

$$HC{\equiv}CBr + NEt_3 \rightarrow HC{\equiv}C^+NEt_3Br^-$$

analogous conditions but using pyridine, quinoline, or acridine (in place of NEt_3) and (bromoethynyl)benzene, Miller[10] observed only tar formation. Thus, as far as we are aware, no heterocyclic ynammonium salts have previously been reported.

However, heterocyclic ynammonium salts should be considerably more stable than aliphatic analogues, as transalkylation is precluded. We attempted their prepa-

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(4) Bode, A. *Liebigs Ann. Chem.* **1892**, *267*, 286.
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(10) Tanaka, R.; Miller, S. I. *J. Org. Chem.* **1971**, *36*, 3856.

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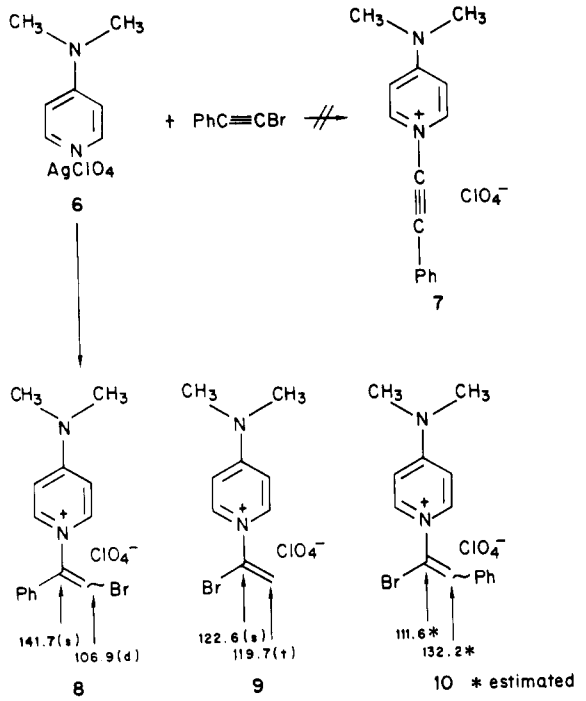
Scheme II



ration to allow more detailed studies of reactivity and spectroscopic properties and followed a similar approach to that taken by Miller[10] in his successful preparations of the aliphatic ynammonium salt **5** via nucleophilic substitution at an acetylenic carbon atom.

Attempted Preparation of 1-Ethynyl-4-(dimethylamino)pyridinium Salts. The highly nucleophilic 4-(dimethylamino)pyridine (DMAP) (**6**) (p*K*a 9.7, pyridine p*K*a 5.2, triethylamine p*K*a 10.9)[11] was used in an attempted nucleophilic substitution at the acetylenic carbon of (bromoethynyl)benzene. As in the preparation of 1-cyano-4-(dimethylamino)pyridinium perchlorate by Wakselman,[12] the silver perchlorate–DMAP complex was generated in acetonitrile and used as an activated pyridine derivative (Scheme II). However, in place of the expected **7**, we isolated only the addition product **8**. The ^{13}C NMR of compound **8** exhibits a singlet at 145.1 ppm (C-1) and a doublet at 106.9 ppm (C-2). Comparison with the ^{13}C NMR of compound **9**[13] ruled out structure **10** which would result from α-attack (relative to bromine in (bromoethynyl)benzene) of DMAP according to a type B mechanism (Scheme I) as suggested by Miller.[14] The formation of compound **8** can be explained by β-attack similar to a mechanism described by Viehe[3,15] for nucleophilic substitution at acetylenic carbons. In all previous cases, β-attack was followed by rearrangement (of the Fritsch–Buttenberg–Wiechell type). Experiments with dried starting materials and at raised reaction temperatures still gave only **8**. With the more hindered (bromoethynyl)-mesitylene, no reaction was observed.

10-Ethynylacridinones. We chose the acridine systems for further studies for two reasons: (i) Commencing with 9(10*H*)-acridinone (**11**) allows a two-step sequence, separating the alkylation from the quarternization step. (ii) Some protection of the triple bond against addition reactions is provided by the peri hydrogens 4-CH and 5-CH.

1-Propynyl-9(10*H*)-acridinone (**12a**) was recently synthesized by a one-pot phase-transfer-catalyzed alkylation and subsequent propargyl rearrangement.[16] This procedure in our hands gave mixtures of the 1-propynyl and propadienyl products; pure **12a** resulted from a two-step procedure in which the intermediate 10-propargyl derivative **15** was isolated and rearranged by KOH–Me_2SO.

Nucleophilic substitution of phenyl- and mesitylethynyl bromides with the acridinone anion led to the analogous products **12b** and **12c** (Scheme III). Better results were obtained in DMF at 70 °C than at lower temperatures or with THF or DME as solvents. The yields in acridinone alkylations are sensitive to the steric demand of the alkylating agent;[17] e.g., isopropyl bromide gives the *N*-isopropyl derivative in only 4% yield. Whereas (bromoethynyl)mesitylene always formed mainly **12c**, (bromoethynyl)benzene invariably gave mixtures of **12b** and the addition product **16b**, and 1-bromo-3,3-dimethylbutyne gave mainly only **16d** with traces of **12d**. Some 9(10*H*)-acridinone was recovered from all the reactions. Structures **16b** and **16d** are supported by the ^{13}C spectra analogous to our results with DMAP.

We believe that the different orientations found for the principal product of the reaction with different bromoethynes reflects the considerable steric hinderance in the mesityl compound toward attack to the β-bromine atom, together with the tendency of α-bromine to stabilize developing negative charge.

The intermediate 10-alkynyl-9(10*H*)-acridinones **12** are "vinylogous" *N*-alkynylamides[15] in which the nitrogen electron pair is shared between the triple bond and the 9(10*H*)-acridinone system. Thus, the triple bond in **12** is neither as electron rich as in ynamines nor as electron deficient as in ynammonium salts. The vinylogous ynamides **12a–c** displayed their expected properties: compound **12a** can be recrystallized from ethanol but adds CF_3CO_2H to form an ester (**17a**).

10-Alkynylacridinium Salts. Two methods were applied to quaternize the 10-alkynylacridinones **12a–c**. Alkylation at the acridinone oxygen with strong alkylating agents should lead to the desired salts **18a–c**. Attempted reactions with Meerwein salts in CH_2Cl_2 gave complex mixtures. However, treatment with trimethylacetyl chloride and $AgClO_4$ in Et_2O or $CHCl_3$ yielded deep red, moisture-sensitive, and highly insoluble crystals, which probably possess the expected structure (**18a–c**, R′ = $(CH_3)_3CC{=}O$).

Nucleophilic addition of phenyllithium (*tert*-butyllithium failed) to the C=O moiety in **12a–c** gave the pseudobases **13a–c** which were converted by trifluormethanesulfonic acid into the highly colored heterocyclic ynammonium salts **14a–c**. These ynammonium salts are stable crystalline solids with absorption maxima around 250, 350, and 450 nm (see Experimental Section). Comparison of the long wavelength maximum of the *N*-methylacridinium cation **21** at 405 nm with the long wavelength maxima of the ynammonium salts **14a–c** ranging from 445 to 470 nm demonstrates the bathochromic shift caused by the triple bond and reflects the different colors of the products.

As described below, the 10-alkynylacridinium salts undergo reversible reactions with nucleophiles at the 9-pos-

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(12) Wakselman, M.; Guibe-Jampel, E.; Raoult, A.; Busse, W. D. *J. Chem. Soc., Chem. Commun.* **1976**, 21.
(13) Katritzky, A. R.; Markees, D., unpublished results.
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(15) Goffin, E.; Legrand, Y.; Viehe, H. G. *J. Chem. Res., Miniprint* **1977**, 1168; *J. Chem. Res., Synap.* **1977**, 105.
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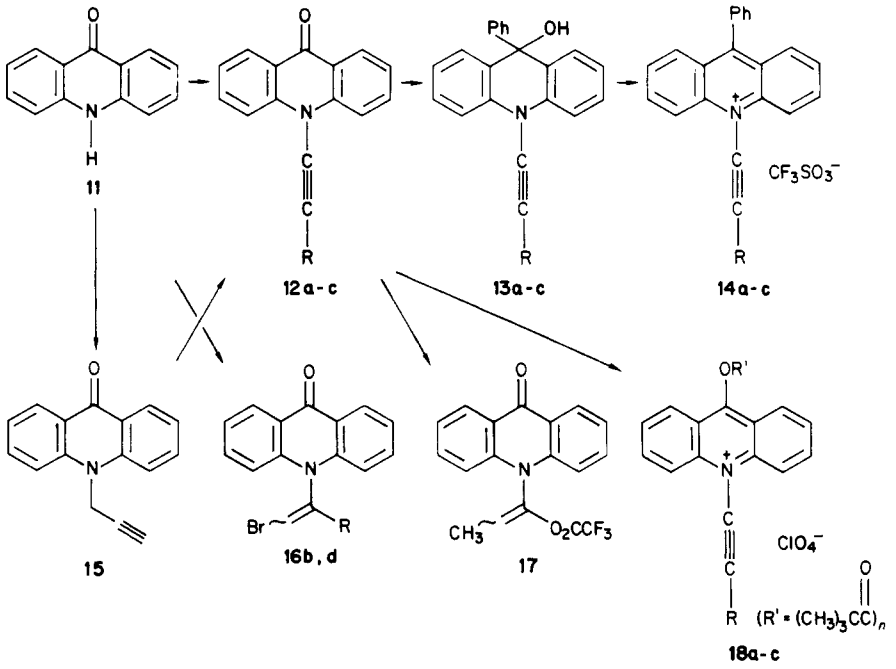
Scheme III[a]



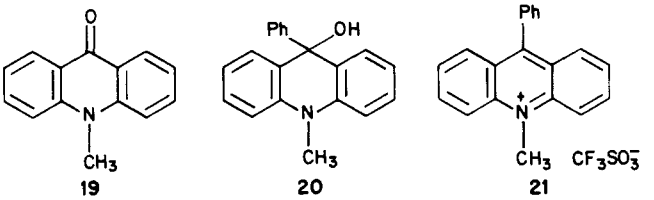
[a] Series a, R = CH_3; b, R = Ph; c, R = 2,4,6-$(CH_3)_3C_6H_2$; d, R = *t*-Bu.

ition: this could be observed qualitatively by absorption spectroscopy in solutions of different pH.

The pseudobase–salt equilibria of N-heterocycles have been reviewed by Bunting et al.[18] The loss of resonance energy upon pseudobase formation in the acridinium cation to 9-hydroxyacridane equilibrium is small compared to the loss for other N-heterocyclic systems. This is reflected in the relatively high pK_{R^+} for *N*-methyl-9-phenylacridinium salts of ca. 11.0.[19] Hence, for the 10-alkynylacridinium salts **14a–c** there is an intrinsic "protection" of the triple bond. The first nucleophilic attack takes place in the 9-position of the acridinium system, and the electrophilic ynammonium salt is converted to a nucleophilic ynamine, relatively stable under basic conditions. Small-scale reactions were followed by ^1H NMR: acridinium salt **14a** gave with NaOH, EtONa, NaCN, and $NaBH_4$ colorless solutions and high-field shifts of 1-CH and 8-CH (e.g., $NaBH_4$, 7.72 (1-CH + 8-CH); 5.30 (9-CH).

NMR Spectroscopy. ^1H NMR spectroscopy (see Experimental Section) generally adequately characterized the heterocyclic acridine ring system but not the acetylenic moiety. To obtain insight into charge changes in the triple bond, ^{13}C NMR spectroscopy was the method of choice.

Comparison across the three series, acridinane (ynamine), acridinone ("vinylogous" ynamide), and acridinium (ynammonium salt), allows an instructive study of the ^{13}C NMR shifts without major changes in the geometry of the heterocyclic part. The acridine carbon signals were assigned according to their chemical shifts and their off-resonance multiplicity and by comparison with reported data.[20-22] The acetylene carbons of the 1-propynyl series (**12a**, **13a**, **14a**) were distinguished by their C,H-coupling [**13a**, $^2J_{CH}$ = 10.5 Hz, $^3J_{CH} \simeq$ 4 Hz; **12a** and **14a**, $^2J_{CH}$ = 9.8 Hz, $^3J_{CH}$ = 6.1 Hz] obtained from their undecoupled spectra. For comparison, 10-methyl-9(10*H*)-acridinone (**19**), 9-hydroxy-10-methyl-9-phenylacridinane (**20**), and



10-methyl-9-phenylacridinium trifluoromethanesulfonate (**21**) were prepared by literature methods and their ^{13}C NMR spectra recorded. The relevant data are compiled in Table I.

For related chemical structures, the effects of substituents on ^{13}C chemical shifts are usually largely additive.[23] Table I gives the ^{13}C shifts C_α and C_β of the acetylene carbons and also selected ^{13}C shifts of the acridine moiety. The parameters A_α and A_β measure the effect of the heterocyclic ring on the ^{13}C shift for the acetylenic carbons. They were calculated from C_α and C_β shifts by using the equations $C_\alpha = 71.9 + A_\alpha + B_\beta$ and $C_\beta = 71.9 + A_\beta + B_\alpha$, respectively. Here, B_α and B_β are parameters for the substituent R and are calculated from spectra of the appropriate acetylenes $RC_\alpha{\equiv}C_\beta H$ rerecorded to avoid solvent effects. For R = Me, B_α = 7.3, B_β = −5.0; for R = Ph, B_α = 11.7, B_β = 5.3; for R = MeS, B_α = 9.4, B_β = 12.5.

Deviations from the average values ($\bar{A}_\alpha$ and $\bar{A}_\beta$) are small: for acridinones $\bar{A}_\alpha = 1.5 \pm 0.5$, $\bar{A}_\beta = -5.1 \pm 0.1$; for acridinanes $\bar{A}_\alpha = 4.1 \pm 0.1$, $\bar{A}_\beta = -7.3 \pm 0.6$; for acridiniums $\bar{A}_\alpha = 0.3 \pm 1.4$, $\bar{A}_\beta = 7.7 \pm 1.7$.

The difference between the shift values ($\Delta = A_\beta - A_\alpha$) was used previously[24] as a measure of the polarization of the charge in the triple bond. The present values of Δ fit well with our conceptions of the polarization of the triple bond: of opposite sign for ynamines **13** (Δ −11.4) and

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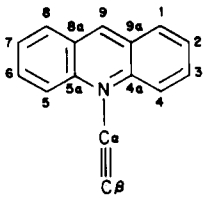
(23) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 390.
(24) Rosenberg, D.; Drenth, W. *Tetrahedron* **1971**, *27*, 3893.

Table I. Selected ^{13}C NMR Shifts of 10-Alkynyl-9-hydroxy-9-phenyl-9,10-dihydroxyacridines 13c, 10-Alkynyl-9(10*H*)-acridinones 12a–c, and 10-Alkynyl-9-phenylacridinium Trifluoromethanesulfonates 14a–c



	^{13}C chemical shifts					substituent parameters[d]	
	C-9	C-8a, C-9a	C-4a, C-5a	C_α	C_β	A_α	A_β
acridinones							
19[a]	177.9	121.1	142.4				
12a[a]	177.4	122.1	140.9	68.9	74.0	+2.0	−5.2
12b[a,c]	177.3	122.3	140.5	78.6	78.5	+1.4	−5.1
12c[a]	177.1	123.2	140.6	85.6	76.2	+1.2	−5.1
acridinanes							
20[a]	73.3	128.3	139.9				
13a[a,c]	71.9	129.3	135.9	71.1	71.3	+4.2	−7.9
13b[a]	72.0	128.5	135.4	81.3	76.7	+4.1	−6.9
13c[a]	72.1	128.6	135.7	88.4	74.3	+4.0	−7.0
acridiniums							
21[b]	159.4	126.1	141.5				
14a[b,c]	164.7	125.7	141.8	67.3	88.6	+0.4	+9.4
14b[b,c]	165.5	125.7	141.3	75.6	90.2	+1.6	+6.6
14c[b,c]	164.5	125.9	141.7	82.3	88.3	−1.1	+7.0

[a] Recorded in $CDCl_3$, chemical shifts δ in ppm, referrenced to $CDCl_3$ (77.00 ppm). [b] Recorded in $CDCl_3$/TFA; chemical shifts δ in ppm, referenced to $CDCl_3$ (77.00 ppm). [c] Recorded at 7 tesla (Nicolet NT 300). [d] For definition see discussion.

ynammonium salts **14** (Δ +7.4), with an intermediate value for the ynamides **12** (Δ −6.6).

The biggest effect of the acetylene moiety on the acridine ring chemical shifts was observed in the acridinium cations **14a–c**. We found a deshielding of carbon C-9 at 5.2 ppm compared to that of the *N*-methyl analogue, probably due to an electron-withdrawing effect of the triple bond. A shielding of some −4.2 ppm of the carbons C-4a and C-5a in the acridinane series **13a–c** probably reflects an anisotropic effect.

Mass Spectra. The hydroxyacridinane **13c** and the corresponding acridinium salt **14c** exhibited almost identical mass spectra. In both, the acridinium ion *m/e* 398 (M^+) was the most intense peak (loss of OH from **13c**). Further strong peaks were detected at *m/e* 323 ($M^+ - 76$), *m/e* 255 ($M^+ - 143$), *m/e* 254 ($M^+ - 144$), *m/e* 143 ($M^+ - 255$), and *m/e* 128 ($M^+ - 270$).

Experimental Section

Melting points were determined with a Kofler hot stage microscope and are uncorrected. ^1H NMR spectra were run on a Varian Model EM 360 L; the chemical shifts were reported in δ downfield of Me_4Si as internal standard. ^{13}C NMR spectra were run on either a JEOL Model JNM-FX 100 or a Nicolet NT-300 spectrometer in $CDCl_3$ or Me_2SO-d_6 referenced to 77.00 or 39.5 ppm, respectively. For IR spectra a Perkin-Elmer Model 283 grating spectrometer (solutions in tetrachloroethane) was used. Mass spectra were recorded on a AEI MS 30 spectrometer. Elemental analyses were carried out by Dr. R. W. King at our department and provided C, H, N analysis within 0.4% for all new compounds.

Ether and THF were dried over Na and benzophenone. Acetonitrile was refluxed over P_2O_5, distilled (50-cm column), and stored over 3-Å molecular sieves. DMF was dried by azeotropic distillation with benzene and stored over 4-Å molecular sieves. $AgClO_4$ was dried as previously reported.[25] The following compounds were prepared by the literature methods quoted: 9-(10*H*)-acridinone, mp 350 °C (lit.[26] mp 354 °C); 10-methyl-9-(10*H*)-acridinone mp 198 °C (lit.[27] mp 198–199 °C); 9-hydroxy-10-methyl-9-phenylacridinane, mp 149–150 °C (lit.[28] mp 139 °C); (bromoethynyl)benzene $bp_{1.0}$ 60 °C (lit.[29] $bp_{0.1}$ 40–41 °C); 1-bromo-3,3-dimethylbutyne, bp_{130} 60 °C (lit.[30] bp_{150} 70 °C); 1-(bromoethynyl)-2,4,6-trimethylbenzene, bp_{12} 90 °C (lit.[31] bp_{10} 88–90 °C).

1-(2-Bromo-1-phenylethynyl)-4-(dimethylamino)-pyridinium Perchlorate (8). To $AgClO_4$ (1.03 g, 5.0 mmol) dissolved in dry CH_3CN (5 mL) was added 4-(dimethylamino)-pyridine (DMAP) (0.61 g, 5.0 mmol). A white precipitate formed after 5 min of stirring. 1-Bromo-2-phenylethyne (0.65 g, 5.5 mmol) in dry CH_3CN (5 mL) was added, and the mixture was heated to 60 °C for 2 h. The solid was filtered off and ether added to give a precipitate of product and DMAP. Repeated recrystallization from EtOH (discarding always the first crop) gave a 9:91 mixture of DMAP and perchlorate 8 (0.35 g, 18%): IR 1650, 1570, 1450, 1400; ^1H NMR ($CDCl_3$/TFA) 7.90 (d, J = 8 Hz, 2 H), 7.6–7.1 (m, 5 H), 7.24 (s, 1 H), 7.05 (d, J = 8 Hz, 2 H), 3.40 (s, 6 H); ^{13}C NMR ($CDCl_3$/TFA) 156.9 (s, DMAP C-γ), 145.1 (s, C-1), 141.7 (d, DMAP C-α), 132.7 (s, Ph), 131.2 (d, Ph), 129.7 (d, Ph), 125.9 (d, Ph), 108.0 (d, DMAP C-β), 106.9 (d, C-2), 40.3 (q, NCH_3). Anal. Calcd for 91% $C_{15}H_{16}Br_2ClN_2O_4$ + 9% $C_7H_{10}N_2$: C, 45.33; H, 4.12; N, 7.40. Found: C, 45.19; H, 4.13; N, 7.56.

Preparation of 10-(1-Alkynyl)-9(10*H*)-acridinones 12a–c. To a suspension of 9(10*H*)-acridinone (1.0 g, 5.1 mmol) in dry DMF (25 mL) was added NaH (0.13 g, 5.4 mmol) in portions at ca. 25 °C. After stirring for 30 min at ca. 50 °C, the suspension became a yellow greenish fluorescent solution which was used in the following alkylations.

10-(2-Propynyl)-9(10*H*)-acridinone (15). To the solution described above was added 3-bromopropyne (0.9 g, 80 wt % in toluene, 6.0 mmol) at ca. 25 °C with stirring. Stirring was continued for 6 h more; after cooling, the mixture was poured into water (80 mL) and the precipitate filtered off and washed with water. Recrystallization from EtOH yielded the acridinone (0.75 g, 66%) as fine yellow needles: mp 219 °C; ^1H NMR ($CDCl_3$/TFA)

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9.2–8.9 (m, 2 H), 8.6–7.8 (m, 6 H), 5.75 (d, J = 3 Hz, 2 H), 2.70 (t, J = 3 Hz, 1 H). Anal. Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.61; H, 4.83; N, 5.93.

10-(1-Propynyl)-9(10*H*)-acridinone (12a). A mixture of **11** (0.75 g, 3.3 mmol), powdered KOH (35 mg, 0.6 mmol), and Me_2SO (5 mL) was stirred for 16 h at ca. 25 °C. The mixture was poured into water (40 mL) and the precipitate filtered off. Crystallization from EtOH yielded the acridinone (0.55 g, 73%) as fine yellow needles: mp 213 °C (lit.[16] mp 211 °C); ^1H NMR ($CDCl_3$) 8.8–8.6 (m, 2 H), 8.3–7.4 (m, 6 H), 2.30 (s, 3 H).

Reaction of 1-Bromo-2-phenylethyne with 9(10*H*)-Acridinone. To the solution described above was added (bromoethynyl)benzene (1.3 g, 7.1 mmol), and the mixture was held at 60 °C for 10 h. After cooling, the mixture was poured into water (80 mL) and the product was filtered off. The crude dried material was separated by chromatography on silica gel (toluene) to give 10-(phenylethynyl)-9(10*H*)-acridinone (**12b**) [0.15 g, 10%, R_f 0.20, as pale yellow needles from EtOH; mp 221–222 °C; IR ($C_2H_2Cl_4$) 2240, 1635, 1480, 1460; ^1H NMR ($CDCl_3$) 8.7–8.5 (m, 2 H), 8.3–7.9 (m, 2 H), 7.9–7.3 (m, 9 H). Anal. Calcd for $C_{21}H_{13}NO$: C, 85.40; H, 4.43; N, 4.74. Found: C, 85.35; H, 4.58; N, 4.46] and 10-(2-bromo-1-phenylethenyl)-9(10*H*)-acridinone (**16b**) [0.53 g, 28%, R_f 0.15, as yellow plates from EtOH; mp 209–210 °C; IR ($C_2H_2Cl_4$) 1620, 1595, 1475, 1455; ^1H NMR ($CDCl_3$) 8.8–8.5 (m, 2 H), 8.38 (s, 1 H), 8.0–7.3 (m, 11 H); ^{13}C NMR ($CDCl_3$) 178.0 (s, C-9), 140.9 (s, olefin C-1), 140.3 (s, C-4a + C-5a), 134.0 (d, C-3 + C-6), 133.3 (s, Ph), 130.0 (d, Ph), 129.4 (d, Ph), 127.6 (d, C-1 + C-8), 125.4 (d, Ph), 122.1 (d, C-2 + C-7), 122.1 (s, C-8a + C-9a), 115.7 (d, C-4 + C-5), 111.6 (d, olefin C-2). Anal. Calcd for $C_{21}H_{14}BrNO$: C, 67.04; H, 3.75; N, 3.72. Found: C, 67.33; H, 3.61; N, 3.64.

Reaction of 1-Bromo-3,3-dimethylbutyne with 9(10*H*)-Acridinone. The above procedure was followed, except with 1-bromo-3,3-dimethylbutyne (1.15 g, 7.1 mmol) instead of 1-bromo-2-phenylethyne. The crude material was purified by chromatography on silica gel (toluene) to give 10-(1-bromo-3,3-dimethyl-1-buten-2-yl)-9(10*H*)-acridinone (**16d**): 0.03 g, 12%, R_f 0.16, yellow plates from EtOH/EtOAc; mp 215–217 °C; IR ($C_2H_2Cl_4$) 1630, 1595, 1475, 1455; ^1H NMR ($CDCl_3$) 8.9–8.7 (m, 2 H), 8.0–7.3 (m, 7 H), 2.3 (s, 0.6 H, H_2O), 1.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) 177.8 (s, C-9), 148.9 (s, olefin C-1), 140.4 (s, C-4a + C-5a), 133.1 (d, C-3 + C-6), 127.5 (d, C-1 + C-8), 122.0 (s, C-9a), 121.8 (d, C-2 + C-7), 116.6 (d, C-4 + C-5), 113.1 (d, olefine C-2), 40.4 (s, *t*-Bu), 30.8 (q, *t*-Bu). Anal. Calcd for $C_{19}H_{18}BrNO \cdot {}^1/_3H_2O$: C, 63.00; H, 5.19; N, 3.87. Found: C, 62.99; H, 5.12; N, 3.75.

10-[(2,4,6-Trimethylphenyl)ethynyl]-9(10*H*)-acridinone (12c). To the solution described above was added 1-bromo-2-(2,4,6-trimethylphenyl)ethyne (1.6 g, 7.1 mmol), and the mixture was held at 80 °C for 14 h. After cooling, the reaction mixture was poured into water (80 mL) and filtered with suction. The crude material gave after several recrystallizations from EtOH (0.38 g, 22%) fine pale yellow needles: mp 199 °C, ^1H NMR ($CDCl_3$) 8.8–8.6 (m, 2 H), 8.5–7.4 (m, 6 H), 7.10 (s, 2 H), 2.60 (s, 6 H), 2.35 (s, 3 H). Anal. Calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.14. Found: C, 85.18; H, 5.57; N, 4.00.

10-[1-[(Trifluoroacetyl)oxy]-1-propenyl]-9(10*H*)-acridinone (17a). Addition of TFA to a solution of **12a** in $CDCl_3$ changed the ^1H NMR, consistent with formation of **17a**: ^1H NMR ($CDCl_3$/TFA) 8.85–8.55 (m, 2 H), 8.15–7.40 (m, 6 H), 6.45 (q, J = 7 Hz, 1 H), 1.65 (d, J = 7 Hz, 3 H).

Reaction of 10-Alkynyl-9(10*H*)-acridinones with Phenyllithium. Formation of Pseudobases 13a–c. General Procedure. To a suspension of 1.0 mmol of 10-alkynyl-9-(10*H*)-acridinone **12a–c** in dry THF (20 mL) under N_2 and stirring at −78 °C was added dropwise 1.1 mmol of phenyllithium. The reaction mixture was kept at the same temperature for 30 min and then warmed to −20 °C, quenched with saturated aqueous $NaHCO_3$ solution, and extracted with $CHCl_3$ (3 × 30 mL). The combined organic layers were washed with water (10 mL) and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo to dryness (60 °C (50 mmHg)) to yield the 10-alkynyl-9-hydroxy-9-phenylacridinones **13a–c**. The crude materials were recrystallized from Et_2O/*n*-pentane to give colorless microcrystals.

13a: 76%; mp 179–180 °C; ^1H NMR ($CDCl_3$) 7.9–7.6 (m, 2 H), 7.6–6.8 (m, 11 H), 2.20 (s, 3 H), 1.45 (bs, 1 H). Anal. Calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.61; H, 5.67; N, 4.36.

13b: 85%; mp 165–167 °C; ^1H NMR ($CDCl_3$) 8.0–7.8 (m, 2 H), 7.7–7.1 (m, 16 H), 1.65 (bs, 1 H). Anal. Calcd for $C_{27}H_{19}NO$: C, 86.84; H, 5.13; N, 3.75. Found: C, 86.09; H, 5.31; N, 3.56.

13c: 80%; mp 180–182 °C; ^1H NMR ($CDCl_3$) 8.1–7.8 (m, 2 H), 7.6–7.0 (m, 11 H), 7.02 (s, 2 H), 2.60 (s, 6 H), 2.35 (s, 3 H), 1.52 (s, 1 H). Anal. Calcd for $C_{30}H_{23}NO$: C, 86.71; H, 6.06; N, 3.37. Found: C, 86.60; H, 6.07; N, 3.25.

Formation of 10-Alkynyl-9-phenylacridinium Trifluoromethanesulfonates 14a–c. General Procedure. Pseudobase **13a–c** (1.0 mmol) dissolved in dry Et_2O (5 mL) was treated with a solution of trifluoromethanesulfonic acid (0.18 g, 1.2 mmol) in dry Et_2O (5 mL). The highly colored precipitate was filtered with suction and washed several times with dry Et_2O. The yields were almost quantitative. The products were purified for analysis by recrystallization from CH_3CN/Et_2O.

14a: orange prisms; mp 242–243 °C, ^1H NMR ($CDCl_3$/TFA) 9.3–8.9 (m, 2 H), 8.8–7.5 (m, 11 H), 2.62 (s, 3 H); UV (CH_3CN, λ_{max} (log ϵ)): 207 (4.2), 252 (4.7), 352 (4.3), 445 (3.9). Anal. Calcd for $C_{23}H_{16}F_3NO_3S$: C, 62.30; H, 3.64; N, 3.16. Found: C, 62.46; H, 3.71; N, 3.11.

14b: bright red needles; mp 240–241 °C; ^1H NMR ($CDCl_3$/TFA) 9.3–9.0 (m, 2 H), 8.9–7.5 (m, 16 H); UV (CH_3CN) 207 (4.4), 253 (4.3), 353 (4.3), 460 (4.0). Anal. Calcd for $C_{28}H_{18}F_3NO_3S$: C, 66.53; H, 3.59; N, 2.77. Found: C, 66.64; H, 3.62; N, 2.73.

14c: dark red needles; 232–233 °C; ^1H NMR ($CDCl_3$) 9.3–9.0 (m, 2 H), 8.8–7.6 (m, 11 H), 7.2 (s, 2 H), 2.75 (s, 6 H), 2.45 (s, 3 H); UV (CH_3CN) 207 (4.4), 254 (4.7), 352 (4.3), 470 (4.1). Anal. Calcd for $C_{31}H_{24}F_3NO_3S$: C, 68.00; H, 4.42; N, 2.56. Found: C, 68.02; H, 4.48; N, 2.44.

UV for compound **21** under analogous conditions: 207 (4.2), 244 (4.6), 342 (4.3), 406 (3.8).

10-Methyl-9-phenylacridinium trifluoromethanesulfonate (21) was prepared from **20** in a method similar to that used for **14a–c**: green-yellow needles from CH_3CN/Et_2O; mp 200 – 201 °C. Anal. Calcd for $C_{21}H_{16}F_3NOS$: C, 60.14; H, 3.85; N, 3.34. Found: C, 60.31; H, 3.77; N, 3.56.

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