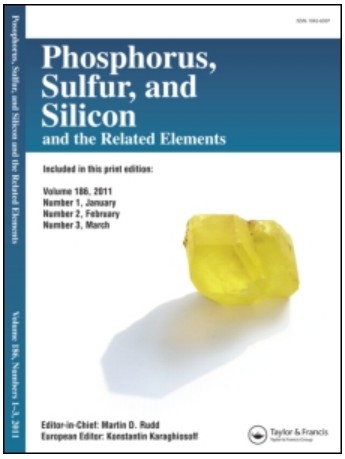

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DIMERIC AND MONOMERIC METHINE BASES IN THE 1,3,4-THIADIAZOLE SERIES

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DIMERIC AND MONOMERIC METHINE BASES IN THE 1,3,4-THIADIAZOLE SERIES

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Treatment of 2-alkyl-3,5-diaryl-1,3,4-thiadiazolium perchlorates **1** with triethylamine leads to monomeric or dimeric methine bases, **2** or **3**, depending on the extent of substitution (—CH_2R) within the alkyl group; 1,3,4-thiadiazolium salts **7** bearing a 2-isopropyl substitutent give monomeric methine bases **8**. Hydrolysis of methine bases **2** and **8** gives N′-alkanoyl-N′-arylbenzothiohydrazides **4** and **6** respectively. The first examples of isolation of monomeric methine bases **2** and their conversion to dimeric methine bases **3** in this series are provided where R = Cl.

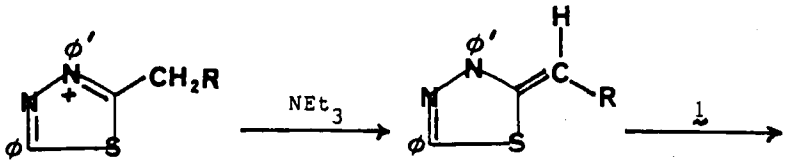
Key words: N′-Arylbenzothiohydrazides; methine bases; 1,3,4-thiadiazoles.

We have previously reported that treatment of the 1,3,4-thiadiazolium perchlorate **1a** with NEt_3 in dry MeCN at room temperature gives the dimeric compound **3a** and not the conjugate (methine) base **2a**.[1] This reaction, which parallels a case in benzothiazole chemistry[2] and which can be viewed formally as a conversion of an acetic acid unit to an acetoacetic acid unit under very mild conditions, is thought to involve addition of **2** to **1** *in situ*, followed by deprotonation to give **3** (Scheme I). The present work was undertaken to assess the scope and limitations of this reaction and to explore the feasibility of isolating monomeric methine bases under these conditions.

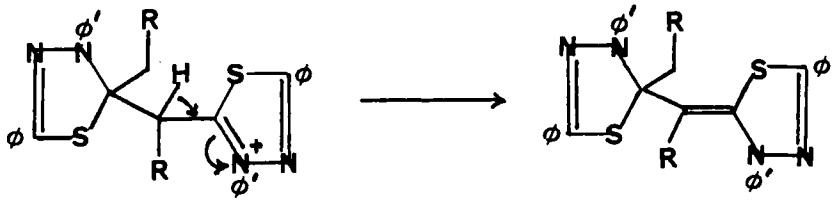
Thiadiazolium perchlorates **1** were prepared by established procedures[1,3] from N′-acyl-N′-arylbenzothiohydrazides **4** (ϕCSNHNϕ′$COCH_2R$) and from N′-arylbenzothiohydrazides **5** (ϕCSNHNHϕ′); the related hydrazides **6** (ϕCSNHNϕ′$COCHMe_2$) were used to prepare thiadiazolium perchlorates **7** (Scheme II).

Data for previously unreported N′-acyl-N′-arylbenzothiohydrazides are summarized in Table I, and for 1,3,4-thiadiazolium perchlorates in Table II. N′-Arylbenzothiohydrazides were normally acylated using the acyl chloride in pyridine (Table I),[4] but this method failed when chloroacetyl chloride or phenylacetyl chloride was used. Most of the thiadiazolium perchlorates were obtained in analytically pure condition, but two were deliquescent and their structures rest on spectroscopic data and subsequent transformation (Table II). The uv spectra (MeCN) of **1a–1k** and of **7a** and **7b** show maxima in the range 249–256 nm (log ε 4.09–4.35) and 279–290 nm (log ε 3.93–4.25); for **11** and **1m**, determined in presence of added $HClO_4$ to supress formation of **21** and **2m**, the spectra show one broad maximum at 256–258 nm (log ε 4.41).

After confirming the formation of **3a** from **1a** (81%), we extended the reaction to **1b**; this gave **3b** in 90% yield. Compounds **3a** and **3b** were obtained in pure condition starting from pure **1a** and **1b**, and reverted to **1a** and **1b** when treated with 70% $HClO_4$; on attempted crystallization, **3a** and **3b** became contaminated



1 2



3

1 - 5

ϕ' = 2,4-$Br_2C_6H_3$

a; R = H

c; R = Me

d; R = Et

f; R = Cl

h; R = ϕ

j; R = p-$MeOC_6H_4$

l; R = p-$NO_2C_6H_4$

ϕ' = ϕ (C_6H_5)

b; R = H

-

e; R = t-Bu

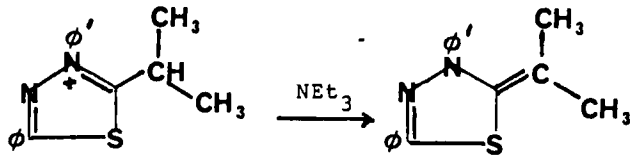
g; R = Cl

i; R = ϕ

k; R = p-$MeOC_6H_4$

m; R = p-$NO_2C_6H_4$

SCHEME 1



7 8

6 - 8

a; ϕ' = 2,4-$Br_2C_6H_3$ b; ϕ' = ϕ (C_6H_5)

SCHEME 2

TABLE I

N'-Acyl-N'-arylbenzothiohydrazides

Compound	Yield	Mp (°C)	Nmr ($CDCl_3$) ppm[a]	Formula	Found (%)/[Requires] (%)
4d	77%	160-162[b]	1.70 (3 H, m), 2.0 (2 H, m), 2.50 (2 H, t, J = 7 Hz), 9.30 and 9.63 (1 H, NH)	$C_{17}H_{16}Br_2N_2OS$	C, 44.86; H, 3.56; N, 5.98 [C, 44.74; H, 3.51; N, 6.14]
4e	86%	160-161[b]	1.08 (9 H, s), 2.30 (2 H, s), 9.96 (1 H, br s, NH)	$C_{19}H_{22}N_2OS$	C, 70.13; H, 6.87; N, 8.58 [C, 69.94; H, 6.75; N, 8.59]
6a	71%	130-132[c]	1.13 (6 H, m), 2.75 (1 H, m), 9.50 and 10.0 (1 H, NH)	$C_{17}H_{16}Br_2N_2OS$	C, 44.46; H, 3.60; N, 5.85 [C, 44.74; H, 3.51; N, 6.14]
6b	74%	167-169[d]	1.18 (6 H, d, J = 7 Hz,), 2.80 (1 H, m), 9.95 (1 H, br s, NH)	$C_{17}H_{18}N_2OS$	C, 68.43; H, 5.95; N, 9.58 [C, 68.45; H, 6.04; N, 9.40]

[a] Non-aromatic protons only; NH signals exchangeable with D_2O. [b] From benzene. [c] From benzene-hexane. [d] From 95% EtOH. All compounds show ir max (KBr) near 3180 (N-H) and 1660 (C=O) cm^{-1}.

TABLE II

2-Alkyl-3,5-diaryl-1,3,4-thiadiazolium Perchlorates

Salt	Method	Yield	Mp (°C)	Nmr ($CDCl_3$) ppm[a]	Formula	Found (%)/[Requires] (%)
1d	A, B	82%	161-163[b]	1.10 (3 H, t, J = 7 Hz), 2.05 (2 H, m), and 3.25 (2 H, t, J = 7 Hz)	$C_{17}H_{15}Br_2ClN_2O_4S$	C, 38.01; H, 2.57; N, 5.18 [C, 37.92; H, 2.79; N, 5.20]
1e	A	90%	165-167[b]	1.05 (9 H, s), 3.35 (2 H, s)	$C_{19}H_{21}ClN_2O_4S$	C, 55.89; H, 5.29; N, 6.92 [C, 55.88; H, 5.15; N, 6.85]
7a	A	88%	Oil[c]	1.45 (6 H, d, J = 7 Hz) and 3.37 (1 H, m)	$C_{17}H_{15}Br_2ClN_2O_4S$	
7b	A	92%	160-161[b]	1.45 (6 H, d, J = 7 Hz) and 3.50 (1 H, m)	$C_{17}H_{17}ClN_2O_4S$	C, 53.60; H, 4.50; N, 7.20 [C, 53.68; H, 4.47; N, 7.36]
1f	C	85%	179-180[b]	5.15 (2 H, s)	$C_{15}H_{10}Br_2Cl_2N_2O_4S$	C, 33.11; H, 1.82; N, 5.40 [C, 33.08; H 1.83; N, 5.15]

TABLE II (*Continued*)

Salt	Method	Yield	Mp (°C)	Nmr ($CDCl_3$) ppm[a]	Formula	Found (%)/[Requires] (%)
1h	C	80%	134-136[b]	4.48 (2 H, s)	$C_{21}H_{15}Br_2ClN_2O_4S$	C, 43.07; H, 2.65; N, 4.75
						[C, 43.00; H, 2.56; N, 4.78]
1i	C	78%	232-234[d]	4.54 (2 H, s)	$C_{21}H_{17}ClN_2O_4S$	C, 58.93; H, 4.00; N, 6.80
						[C, 58.88; H, 3.97; N, 6.54]
1j	C	78%	Oil[c]	3.80 (3 H, s),	$C_{22}H_{17}Br_2ClN_2O_5S$	
				4.38 (2 H, s)		
1k	C	74%	163-165[b]	3.75 (3 H, s),	$C_{22}H_{19}ClN_2O_5S$	C, 57.63; H, 4.13; N, 6.01
				4.43 (2 H, s)		[C, 57.64; H, 4.15; N, 6.11]
1l	C	80%	185-187[d]	4.73 (2 H, s)	$C_{21}H_{14}Br_2ClN_3O_6S$	C, 39.75; H, 2.33; N, 6.60
						[C, 39.94; H, 2.22; N, 6.66]
1m	C	76%	228-230[b]	4.75 (2 H, s)	$C_{21}H_{16}ClN_3O_6S$	C, 53.48; H, 3.28; N, 8.70
						[C, 53.28; H, 3.38; N, 8.88]

Methods:[1,3] A. 4 or 6 + acid anhydride = 70% $HClO_4$; B. 5 + acid anhydride + 70% $HClO_4$; C. 5 + nitrile + 70% $HClO_4$ in HOAc. [a] Non-aromatic protons only. [b] From HOAc. [c] Deliquescent; mass spectra show highest m/z values at $(M - HClO_4)^+$, as expected.[1] [d] From MeCN.

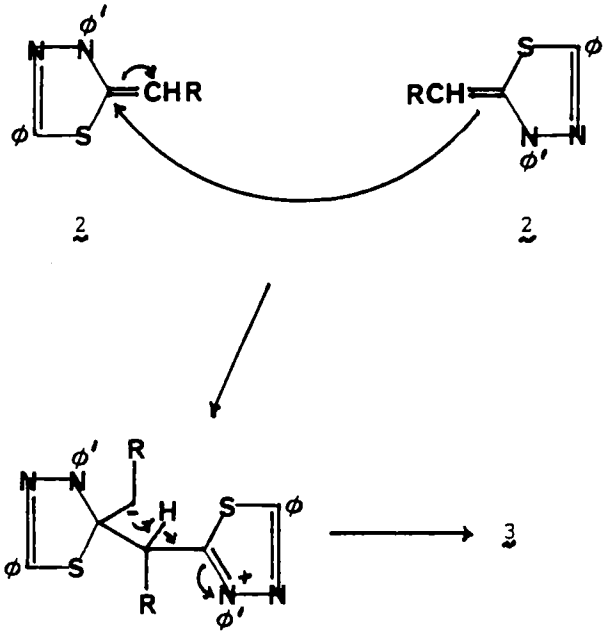
with decomposition products. Treatment of **1c** or **1d** with NEt_3 in MeCN or benzene gave viscous yellow oils (80–85% yield) which appeared, from thin layer chromatography (tlc) and ^1H nmr spectral data, to be mixtures of **3c** and **4c** or **3d** and **4d** respectively. Compositions were approximately 2:1 from **1c** (NH_2 and $=CCH_3$ integrations) and 3:2 from **1d** (NH_2 and ArH integrations). Treatment of either oil with $HClO_4$ gave **1c** or **1d**, while attempted crystallization led to recovery of **4c** or **4d**, with decomposition products of **3c** or **3d** concentrating in the mother liquors. Evidently hydrolysis of **2c** (or **d**), or of **1c** (or **d**) by hydroxide ion since these salts (unlike 1,3,4-oxadiazolium perchlorates[2b]) are stable in water, competes with the sequence **1** + **2** → **3**. Hydrolysis was not observed in the experiments with **1a** and **1b**, but the increased size of the alkyl group might well provide steric hindrance to dimer formation and so open the possibility of the alternative reaction. Such hydrolysis is consistent with the known ease of hydrolysis of 1,1-enediamines,[5] and the conversion of 3,5-di(ethoxycarbonyl)-1,2,4,6-tetramethylpyridinium iodide to 3-acetyl-5-ethoxycarbonyl-1,4,6-trimethyl-2-pyridinone by aqueous NaOH probably involves a similar hydrolysis, followed by ring closure to the pyridinone.[6]

We next examined the case of **1e**, reasoning that the increased size of the alkyl group should largely inhibit the formation of **3e**. Reaction gave **2e** as a viscous oil, slightly contaminated with **4e**. Relative to the two preceding cases, hydrolysis also seemed to be somewhat impeded. Compound **2e** underwent hydrolysis to **4e** on attempted crystallization or on standing in solution.

The sequence **1** + **2** → **3** would be blocked if **2** were modified to carry two alkyl groups at the methine carbon atom as in **7** → **8** (Scheme II), although hydrolysis would remain a possibility. In fact, treatment of **7a** and **7b** with NEt_3 gave **8a** and **8b** respectively, and these reverted to **7a** and **7b** when treated with $HClO_4$. Both **8a** and **8b** underwent hydrolysis in moist $CHCl_3$, giving **6a** and **6b** respectively.

We wished, if possible, to find an example of a thiadiazolium salt **1** which could be deprotonated to an isolable conjugate base **2** and its conversion to **3** demonstrated subsequently. Ideally, the nucleophilicity of the methine carbon should be lowered without creating significant steric hindrance to the reaction **1** + **2** → **3**. A chloro-substituent seemed a reasonable choice for this purpose. Attempts to acylate **5a** with chloroacetyl chloride did not yield **4f**; the actual product was **3f**. Probably the chloroacetyl derivative **4f** is formed, but undergoes reversible ring closure followed by dehydration to **2f**, which then proceeds further to **3f** (*cf.* Reference 4). Accordingly, **1f** was prepared directly by reaction of **5a** with chloroacetonitrile and $HClO_4$ in HOAc. Compound **1g** was prepared from **5b** and chloroacetic anhydride in the presence of $HClO_4$.

Compounds **1f** and **1g** proved to be good choices for the work in hand. Monitoring by ^1H nmr revealed immediate formation of **2f** from **1f**, and of **2g** from **1g** when either salt was treated with NEt_3. However, **2f** and **2g** decomposed in solution within thirty minutes, as shown by the disappearance of the methine proton signal. Treatment of **1f** with NaOH in aqueous MeCN gave **2f** and **3f**, which were separated and characterised; **1g** similarly gave **2g** and **3g** (not separated). Compounds **2f** and **2g** dimerized slowly in the solid state at room temperature to give **3f** and **3g** respectively, indicating the possibility of a second pathway for dimer formation (Scheme III); both **2f** and **2g** reverted to the corresponding perchlorate on treatment with $HClO_4$.



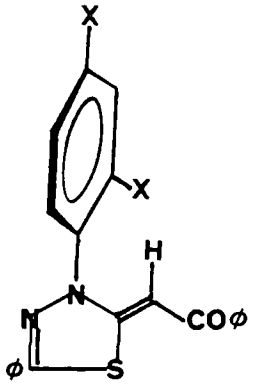
SCHEME 3

We finally examined the series **1h–1m**. Attempted acylation of **5a** with phenylacetyl chloride gave a mixture of unidentified products (tlc) similar to that produced from decomposition of **2h**. As in the case of chloroacetylation it seems likely that **2h** is produced, but decomposition then supervenes. Compounds **1h–1m** were therefore prepared by the nitrile route. The relatively acidic perchlorates **1l** and **1m** (effect of NO_2 group) equilibrate with their conjugate bases in aqueous or ethanolic solution. More generally, these salts were converted to the methine bases **2h–2m** by treatment with NaOH or NEt_3; there was no sign of accompanying dimers. Like **2f** and **2g**, **2h–2m** gave **1h–1m** when treated with $HClO_4$. In other respects they are more stable. They show no tendency to dimerize in the solid state, and **2l** and **2m** can be crystallized although the others decompose on attempted crystallization. The greater stability of **2h–2m**, and particularly of **2l** and **2m**, relative to the other methine bases is presumably due to conjugation[7] involving the aryl group (R), especially when this is *p*-nitrophenyl.

The nmr spectra of **2h–2m** show the methine proton signal at higher field for **2h**, **2j**, and **2l** than for **2i**, **2k**, and **2m**. Inspection of Dreiding models of the methine bases shows accommodation of the dibromophenyl ring twisted out of the plane of the thiadiazoline ring around the N – ϕ' axis as shown in **9**. The methine proton thus faces the plane of the dibromophenyl ring and so experiences aromatic ring current shielding. The non-coplanarity of these two rings also limits the extent of conjugation, and hypsochromic shifts (rather than bathochromic shifts of *ca.* 17 nm)[8] are observed in the uv spectra of **2h**, **2j**, and **2l** relative to **2i**, **2k**, and **2m**. The conclusions about molecular geometry would appear to be general for methine bases and dimers in this series.

We had earlier noted similar effects in the nmr spectra of a number of acyl[4] and thioacyl[9] derivatives in this series. For **2** (R = COMe, ϕ' as shown in parentheses),[4]

previously unreported chemical shift data ($CDCl_3$) are as follows: ppm 6.01 (1 H, s, ϕ' = 4-BrC_6H_4); 5.50 (1 H, s, ϕ' = 2,5-$Br_2C_6H_3$); 5.51 (1 H, s, ϕ' = 2,4,6-$Br_3C_6H_2$); 5.64 (1 H, br s, ϕ' = 2,4-$F_2C_6H_3$); 5.65 (1 H, d, J = 2 Hz, ϕ' = 2,4-FIC_6H_3); 5.46 (1 H, s, ϕ' = 2,4-$I_2C_6H_3$). These data are also compatible with (Z)-geometry and with a tilt conformation where the aryl group (ϕ') carries one (or two) *ortho*-substituent(s). The broadening or splitting of the methine proton signal accompanying fluoro-substitution in the aryl group is consistent with ^{19}F—^1H long range coupling through bonds (or possibly through space for the *ortho*-substituent).[10] Twist conformation and (Z)-geometry have been independently confirmed for **9** (X = Br) by X-ray crystallographic study.[11]



9

The present work shows that dimeric products **3** are likely from base treatment of salts **1** (R = H) under our conditions. Dimeric products are still noted where R = Me or Et, but not where R is a larger alkyl group or when salts such as **7** are used. Competing hydrolysis is observed in some cases. Monomeric methine bases **2** can be isolated where R = Cl, but they are accompanied by dimeric products **3**, and they show a definite tendency to dimerize. These compounds represent the first examples of simple monomeric methines in this series. Monomers **2** can be isolated where R = aryl, and these are reasonably stable. These results with 1,3,4-thiadiazoles confirm that caution should be exercised in formulating methine bases as monomeric unless there is adequate evidence on the point.

EXPERIMENTAL

The following instruments were used: FX-6220 FT IR for ir spectra; WP-60 FT and WP-80 CW spectrometers for ^1H nmr spectra (Me_4Si used as internal reference); DMS 100 UV-visible spectrophotometer for uv spectra (log ε values given in parentheses); AEI MS30 double beam instrument for mass spectra. Melting points are uncorrected.

Dimers **3a** *and* **3b**. Compound **3a** was prepared by the literature method[1]; uv (MeCN) 236 (4.62) and 346 (4.26) nm.

Similarly prepared, **3b** (90%) was obtained as a yellow solid, mp 131–135°C: nmr ($CDCl_3$) ppm 1.80 (3 H, s, Me), 5.08 (1 H, s, =CH), and 7.0–7.88 (20 H, m, ArH) (Note: methine proton signal at 4.3 for **3a**[1]); uv (MeCN) 246 (4.48) and 340 (4.15) nm. Even when a low probe temperature was used, the mass spectrum showed *m/z* 252 as the highest peak value, corresponding to the monomeric species **2b** (*cf.* Reference 1).

Anal. Calc'd for $C_{30}H_{24}N_2S_2$: C, 71.42, H, 4.76; N, 11.11.
Found: C, 71.34; H, 4.72; N, 11.09.

Similar treatment of the 1,3,4-oxadiazolium perchlorate corresponding to **1b** gave the rearranged dimer already described[2b]; no intermediates corresponding to **2b** or **3b** were detectable by nmr monitoring.

Methine base **2e**. Triethylamine (0.4 mL) was added to a stirred suspension of **1e** (0.5 g) in anhydrous benzene (5 mL). After 15 min, the yellow solution was quickly washed with water, and then dried (Na_2SO_4). Evaporation *in vacuo* gave **2e** as a viscous yellow oil (0.31 g, 82%): nmr ($CDCl_3$) ppm 1.12 (9 H, s, $-CMe_3$), 4.93 (1 H, s, =CH), and 7.13–7.75 (10 H, m, ArH); uv (MeCN) 248 (4.43) and 391 (3.79) nm. The sample contained traces of its hydrolysis product **4e** (tlc, ir spectrum), and satisfactory analytical data could not be obtained. Hydrolysis occurs at the methine base stage or perhaps from addition of hydroxide ion to **1e**, for solutions of **1e** in moist solvents are stable in the absence of added base.

Methine bases **8a** *and* **8b**. Treatment of **7a** (1.0 g) as in the foregoing experiment with **1e** gave **8a** as a viscous oil (0.70 g, 86%) which could not be induced to crystallize and which decomposed on attempted distillation *in vacuo*: nmr ($CDCl_3$) ppm 1.20 (3 H, s, Me), 1.75 (3 H, s, Me), and 7.07–7.85 (8 H, m, ArH); uv (EtOH) 248 (4.00) and 346 (3.40) nm; mass spectrum *m/z* 440/438/436 (M^+).

Anal. Calc'd for $C_{17}H_{14}Br_2N_2S$: C, 46.57; H, 3.19; N, 6.39.
Found: C, 46.69; H, 3.48; N, 5.94.

Triethylamine (0.25 mL) was added to a solution of **7b** (0.5 g) in dry MeCN (7 mL). On cooling, **8b** crystallized as a bright yellow solid (0.25 g, 68%), mp 87–88°C: nmr ($CDCl_3$) ppm 1.45 (3 H, s, Me), 1.85 (3 H, s, Me), and 7.13–7.75 (10 H, m, ArH); uv (EtOH) 249 (4.33) and 395 (3.62) nm; mass spectrum *m/z* 280 (M^+).

Anal. Calc'd for $C_{17}H_{16}N_2S$: C, 72.85; H, 5.71; N, 10.00.
Found: C, 72.67; H, 5.91; N, 10.02.

Conversion of **8b** *to* **7b**. A solution of **8b** (100 mg) in MeCN (2 mL) and 70% $HClO_4$ (0.2 mL) was stirred for 2 h. Addition of ether and trituration gave **7b** (130 mg, 95%), mp 159–161°C, identical with a reference sample. Compound **8a** behaved similarly.

Hydrolysis of **8b**. A solution of **8b** (0.4 g) in moist $CHCl_3$ (20 mL) was stirred for 4 days. The red solution was evaporated, and the residual oil was chromatographed on silica to yield **6b** (0.225 g, 53%, after crystallization), which was identical with a reference sample. Compound **8a** behaved similarly.

2-Chloromethyl-3,5-diphenyl-1,3,4-thiadiazolium perchlorate (**1g**). A solution of **5b** (2.3 g) and chloroacetic anhydride (3.4 g) in a mixture of MeCN (20 mL) and 70% $HClO_4$ (2 mL) was stirred overnight. Ether was added until the onset of turbidity. On trituration, a solid separated out. Crystallization from HOAc gave **1g** as white prisms (3.5 g, 90%), mp 193–195°C: nmr (CD_3CN) ppm 5.13 (2 H, s, CH_2) and 7.58–8.13 (10 H, m, ArH).

Anal. Calc'd for $C_{15}H_{12}Cl_2N_2O_4S$: C, 46.63; H, 3.10; N, 7.25.
Found: C, 46.77; H, 3.07; N, 7.22.

These conditions were unsuitable for the preparation of **1f**; reaction gave **1a** in moderate yield (*i.e.*, MeCN reacted preferentially).

Methine base **2f** *and its dimer* **3f**. 2M Sodium hydroxide solution (2 mL) was added to a stirred solution of **1f** (0.5 g) in MeCN (5 mL) at 0°C. After 20 min, water (15 mL) was added, resulting in formation of a light green solid in suspension together with a sticky red material which adhered to the wall of the vessel. The suspended solid was filtered off, washed with water, and dried to give **2f** (0.212 g, 52%), mp 53–56°C: nmr ($CDCl_3$) ppm 4.90 (1 H, s, =CH) and 7.25–8.0 (8 H, m, ArH). On standing at room temperature, **2f** dimerized to **3f** (for characterization, see below).

The sticky red material solidified when scratched, and was collected, washed with water, and dried to give **3f** (0.1 g, 25%), mp 126–130°C: nmr ($CDCl_3$) ppm 3.63 (2 H, s, CH_2) and 7.25–8.0 (16 H, m, ArH); the signal due to the methylene protons was also observed as a singlet in other solvents (benzene-d_6 and pyridine-d_5).

Anal. Calc'd for $C_{30}H_{18}Br_4Cl_2N_4S_2$: C, 40.54; H, 2.03; N, 6.30.
Found: C, 40.62; H, 2.07; N, 6.26.

Methine base **2g** *and its dimer* **3g**. Compound **1g** (2.0 g) was treated as was **1f** in the foregoing experiment. Addition of water (50 mL) precipitated **2g** as a light green solid (1.10 g, 74%), mp 60–

63°C: nmr ($CDCl_3$) ppm 5.75 (1 H, s, =CH) and 7.13–8.03 (10 H, m, ArH); mass spectrum *m/z* 288/286 (M^+). The nmr spectrum revealed the presence of **3g** in this sample.

Anal. Calc'd for $C_{15}H_{11}ClN_2S$: C, 62.94; H, 3.85; N, 9.79.
Found: C, 63.01; H, 3.86; N, 9.73.

Compound **2g** was stable at 0°C for 2 days, but dimerized at ambient temperature within 24 h to give **3g** as a red solid, mp 111–115°C: nmr ($CDCl_3$) ppm 3.63 (2 H, s, CH_2) and 7.25–8.0 (20 H, m, ArH).

Anal. Calc'd for $C_{30}H_{22}Cl_2N_4S_2$: C, 62.94; H, 3.85; Cl, 12.23; N, 9.79; S, 11.18.
Found: C, 62.90; H, 3.97; Cl, 12.00; N, 10.11; S, 10.98.

Methine bases **2h–2k**. The relevant perchlorate (1.0 g) in MeCN (10 mL) was treated with 2 M NaOH solution (3 mL). After stirring for 20–30 min, the precipitated methine base was filtered off, was washed with water and MeCN, and then dried. Base **2h** (90%) was obtained as a yellow solid, mp 119–121°C: nmr ($CDCl_3$) ppm 5.30 (1 H, s, =CH) and 7.0–7.95 (13 H, m, ArH); uv (MeCN) 244 (4.31), 326 (4.14), and 366 (4.02) nm; mass spectrum *m/z* 488/486/484 (M^+).

Anal. Calc'd for $C_{21}H_{14}Br_2N_2S$: C, 51.85; H, 2.88; N, 5.76.
Found: C, 51.76; H, 2.88; N, 5.41.

Base **2i** (91%), yellow, had mp 121–124°C: nmr ($CDCl_3$) ppm 6.0 (1 H, s, =CH) and 7.0–7.75 (15 H, m, ArH); uv (MeCN) 242 (4.10), 354 (4.08), and 404 (3.75) nm; mass spectrum *m/z* 328 (M^+).

Anal. Calc'd for $C_{21}H_{16}N_2S$: C, 76.83; H, 4.88; N, 8.53.
Found: C, 76.74; H, 4.91; N, 8.24.

Base **2j** (83%), yellow, had mp 137–140°C: nmr ($CDCl_3$) ppm 3.75 (3 H, s, OMe), 5.23 (1 H, s, =CH), and 6.75–7.88 (12 H, m, ArH); uv (MeCN) 242 (4.26), 305 (4.15), and 370 (3.93) nm; mass spectrum *m/z* 518/516/514 (M^+).

Anal. Calc'd for $C_{22}H_{16}Br_2N_2OS$: C, 51.16; H, 3.10; N, 5.43.
Found: C, 50.97; H, 3.07; N, 5.36.

Base **2k** (87%), yellow, had mp 91–93°C, 109–110°C (double mp; the nmr spectra indicated no change before/after the first mp and second mp): nmr ($CDCl_3$) ppm 3.73 (3 H, s, OMe), 5.96 (1 H, s, =CH), and 6.70–7.75 (14 H, m, ArH); uv (MeCN) 245 (4.21), 354 (4.09), and 409 (3.72) nm; mass spectrum *m/z* 358 (M^+).

Anal. Calc'd for $C_{22}H_{18}N_2OS$: C, 73.74; H, 5.03; N, 7.82.
Found: C, 73.53; H, 4.99; N, 7.72.

Methine bases **2l** *and* **2m**. Triethylamine (1.2 mL) was added to a stirred suspension of the relevant perchlorate (1.0 g) in dry benzene (15 mL), and the resulting red precipitate was filtered off. Base **2l** (80%) crystallized from pyridine as red prisms, mp 267–269°C (literature 4, mp 268–270°C): nmr ($CDCl_3$) ppm 5.36 (1 H, s, =CH) and 7.0–8.10 (12 H, m, ArH); uv (MeCN) 245 (4.08) and 465 (4.15) nm; mass spectrum *m/z* 533/531/529 (M^+).

Base **2m** (76%) crystallized from pyridine as red prisms, mp 221–223°C: nmr ($CDCl_3$) ppm 5.99 (1 H, s, =CH) and 7.10–8.23 (14 H, m, ArH); uv (MeCN) 250 (4.22) and 477 (4.37) nm; mass spectrum *m/z* 373 (M^+).

Anal. Calc'd for $C_{21}H_{15}N_3O_2S$: C, 67.56; H, 4.02; N, 11.26.
Found: C, 67.50; H, 4.33; N, 11.18.

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