234. Preparation and Some Reactions of 1*H*-1,4-Benzothiazine Ylides (= 1*H*-1,4-Benzothioniaazin-4-ide)

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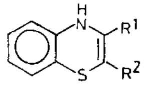
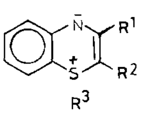
A series of fifteen 1*H*-1,4-benzothiazine ylides were obtained by alkylation of the corresponding 4*H*-1,4-benzothiazines **1**. Ylides of type **2g–r** showed slight [1, 2] rearrangements upon thermolysis besides main dealkylation to **1** and olefin production. The ylides of this type underwent redox reactions when treated with hydrazine hydrate alone, giving 3,4-dihydro-2*H*-1,4-benzothiazines mainly, while ylides of type **2a–f** failed to react.

Syntheses. – Recently, we have investigated possible routes to the formation of some 1*H*-1,4-benzothiazines ylides **2** [1]. Two routes were established: the cyclodehydration of the precursor sulfoxides **3** and direct alkylation of 4*H*-1,4-benzothiazines **1**. We now have explored the second as a general route to an easy synthesis of these cyclic ylides. Fifteen new ylides **2** were prepared and their physical data recorded (*Tables 1* and *2*). The ylides **2** were isolated as crystalline solids except for a few, obtained as oils and characterised as



1a R^1 = Me, R^2 = COMe
b R^1 = Me, R^2COPh
c R^1, R^2 = $CH_2CMe_2CH_2C(O)$
d R^1, R^2 = $(CH_2)_3C(O)$



2a R^1 = Me, R^2 = COMe, R^3 = Me
b R^1 = Me, R^2 = COMe, R^3 = Et
c R^1 = Me, R^2 = COMe, R^3 = Pr
d R^1 = Me, R^2 = COPh, R^3 = Me
e R^1 = Me, R^2 = COPh, R^3 = Et
f R^1 = Me, R^2 = COPh, R^3 = Pr
g R^1, R^2 = $CH_2CMe_2CH_2C(O)$, R^3 = Me
h R^1, R^2 = $CH_2CMe_2CH_2C(O)$, R^3 = Et
i R^1, R^2 = $CH_2CMe_2CH_2C(O)$, R^3 = Pr
j R^1, R^2 = $CH_2CMe_2CH_2C(O)$, R^3 = i-Pr
k R^1, R^2 = $CH_2CMe_2CH_2C(O)$, R^3 = Bu
l R^1, R^2 = $CH_2CMe_2CH_2C(O)$, R^3 = Pentyl
m R^1, R^2 = $(CH_2)_3C(O)$, R^3 = Et
n R^1, R^2 = $(CH_2)_3C(O)$, R^3 = Pr
o R^1, R^2 = $(CH_2)_3C(O)$, R^3 = i-Pr
p R^1, R^2 = $(CH_2)_3C(O)$, R^3 = Bu
q R^1, R^2 = $(CH_2)_3C(O)$, R^3 = i-Bu
r R^1, R^2 = $(CH_2)_3C(O)$, R^3 = Pentyl

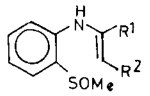


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Table 1. *Spectral Data and Analysis of* **2a–f**

No.	R^3	Yield [%]	M.p. [°C]	$\tilde{\nu}_{max}$ (Nujol) [cm^{-1}]	$\lambda_{max}^{(CHCl_3)}$ (ε) [nm]		Analysis [%][c] C	H	N
2a[a])[b])	Me	50	93–95	770, 790, 1050, 1270, 1570, 1590, 1710	289 (5300), 306 (4910), 387 (10570)	$C_{18}H_{16}N_4O_8S$	48.20 (48.21)	3.6 (3.67)	12.4 (12.5)
b[a])	Et	90	158–160	770, 785, 1061, 1270, 1570, 1590, 1710	287 (5315), 307 (5120), 388 (10595)	$C_{19}H_{18}N_4O_8S$	49.4 (49.35)	4.0 (3.9)	12.1 (12.1)
c	Pr	75	133–135	770, 781, 1065, 1272, 1575, 1585, 1710	287 (6220), 307 (5115), 388 (11620)	$C_{14}H_{17}NOS$	67.6 (68.0)	7.0 (6.9)	5.6 (5.7)
d	Me	94.3	128–129	720, 790, 1030, 1160, 1180, 1230, 1270, 1290, 1560, 1590	243 (20300), 285 (5350), 305 (4910), 382 (10480)	$C_{17}H_{15}NOS$	72.4 (72.6)	5.5 (5.3)	4.9 (5.0)
e	Et	83	96–97	720, 780, 1040, 1090, 1160, 1190, 1240, 1280, 1590, 1600	243 (21240), 285 (5190), 305 (4250), 382 (7790)	$C_{18}H_{17}NOS$	73.3 (73.2)	5.9 (5.8)	4.7 (4.75)
f	Pr	72.3	110–112	710, 770, 780, 1030, 1150, 1190, 1230, 1270, 1570, 1580	243 (22630), 285 (5600), 305 (5100), 382 (8720)	$C_{19}H_{19}NOS$	73.7 (73.8)	6.2 (6.15)	4.5 (4.5)

[a]) Analytical data for picrates.

[b]) Systematic name of **2a**: 2-acetyl-1,3-dimethyl-1*H*-1,4-benzothioniaazin-4-ide.

[c]) Calculated values in parentheses.

Table 2. *Spectral Data and Analysis of* **2g–r**

No.	R^3	Yield [%]	M.p. [°C]	$\tilde{\nu}_{max}$ (Nujol) [cm^{-1}]	$\lambda_{max}^{(MeOH)}$ (ε) [nm]		Analysis [%][a]) C	H	N
2g[b])	Me	90.4	180–181 (179–181)[c])						
h	Et	96.4	110–112	740, 770, 870, 890, 900, 1050, 1070, 1130, 1150, 1230, 1280, 1290, 1570, 1590	238 (25620), 265 (6300), 293 (3780), 339 (2100)	$C_{16}H_{19}NOS$	70.8 (70.3)	7.4 (7.0)	4.8 (5.1)
i	Pr	78.7	135–136	740, 770, 810, 860, 880, 890, 1040, 1050, 1070, 1130, 1150, 1230, 1280, 1560, 1580, 1600	242 (20440), 264 (5560), 293 (3190), 338 (2170)	$C_{17}H_{21}NOS$	71.7 (71.7)	7.4 (7.3)	4.8 (4.9)
j	i-Pr	61.0	125–126	740, 770, 810, 880, 890, 1050, 1070, 1130, 1160, 1230, 1280, 1560, 1600	242 (16270), 267 (5424), 287 (4520), 345 (1455)	$C_{17}H_{21}NOS$	71.1 (71.1)	7.6 (7.3)	4.7 (4.9)
k	Bu	89.35	75–77	740, 770, 810, 880, 890, 1040, 1050, 1070, 1130, 1150, 1230, 1280, 1560, 1580, 1600	233 (36150), 266 (8380), 305 (3530), 338 (2200)	$C_{18}H_{23}NOS$	71.5 (71.8)	7.7 (7.6)	4.7 (4.65)
l	Pentyl	98.4	93–94	740, 770, 810, 860, 880, 1040, 1050, 1070, 1130, 1150, 1230, 1280, 1560, 1580, 1600	242 (20330), 262 (5300), 293 (3980), 338 (2650)	$C_{19}H_{25}NOS$	72.5 (72.4)	8.0 (8.0)	4.4 (4.4)
m[d])	Et	81.6	135–136	740, 1000, 1015, 1050, 1140, 1170, 1190, 1220, 1270, 1560, 1590	239 (18090), 263 (4150), 305 (2640), 358 (1880)	$C_{14}H_{15}NOS$	68.4 (68.6)	6.2 (6.1)	5.6 (5.7)
n	Pr	86.65	114–115	740, 1010, 1080, 1130, 1170, 1180, 1230, 1270, 1565, 1590	240 (18840), 265 (3920), 305 (2390), 358 (1960)	$C_{15}H_{17}NOS$	69.6 (69.5)	6.7 (6.6)	5.2 (5.4)
o	i-Pr	67.6	122–123	710, 770, 1010, 1040, 1170, 1200, 1240, 1280, 1540, 1570	247 (15750), 267 (4970), 288 (3315), 340 (1660)	$C_{15}H_{17}NOS$	69.5 (69.5)	6.7 (6.6)	5.2 (5.4)
p	Bu	72.7	108–109	740, 1140, 1190, 1230, 1280, 1560, 1590	239 (18480), 263 (4200), 305 (2520), 358 (1260)	$C_{16}H_{19}NOS$	70.3 (70.3)	7.1 (7.0)	5.2 (5.1)
q	i-Bu	64	116–117	740, 770, 1030, 1120, 1180, 1210, 1260, 1280, 1560, 1580	247 (15470), 267 (7735), 340 (1820)	$C_{16}H_{19}NOS$	69.7 (70.3)	7.1 (7.0)	5.0 (5.1)
r	Pentyl	65–66	102–104	700, 770, 1010, 1140, 1170, 1230, 1270, 1360, 1560, 1590	239 (17220), 263 (3530), 305 (3750), 350 (2870)	$C_{17}H_{21}NOS$	71.0 (71.1)	7.4 (7.3)	4.8 (4.9)

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[a]) Calculated values in parentheses.

[b]) Systematic name of **2g**: 2,3,4,5-tetrahydro-2,2,5-trimethyl-4-oxo-1*H*-phenothioniaazin-10-ide.

[c]) M.p. in literature in parentheses.

[d]) Systematic name of **2m**: 5-ethyl-2,3,4,5-tetrahydro-4-oxo-1*H*-phenothioniaazin-10-ide.

Table 3. *^{1}H-NMR Spectra of Ylides* **2a–d**, **2j**, *and* **2p**

No.	Arom. H-atoms	R^1	R^2	R^3
2a	7.27–7.42 (*m*, 3H); 7.08–7.04 (*m*, 1H)	2.18 (*s*, Me)	2.52 (*s*, COMe)	2.31 (*s*, MeS^+)
b	8.05 (*m*, 1H); 7.0–7.5 (*m*, 3H)	2.95 (*s*, COMe)	2.85 (*s*, Me)	3.35 (*q*, J = 6, $MeCH_2$); 2.25 ('*t*', J = 6, 12, *Me*CH_2)
c	7.37–7.41 ('*quint.*', J = 7, 1.5, 1H); 7.23–7.25 ('*q*', J = 7, 1.5, 1H); 7.03–7.05 ('*sext.*', J = 7, 1.5, 1H)	2.30 (*s*, Me)	2.52 (*s*, COMe)	2.37–2.54 (*m*, $CH_2S^+ <$); 1.28–1.38 (*m*, 2H); 0.83 (*t*, J = 7.5, 3H); 2.38 (*s*, Me)
d	7.58–7.61 (*m*, 3H); 7.38–7.58 (*m*, 4H); 7.20–7.41 (*m*, 2H)		2.07 (*s*, Me)	2.38 (*s*, Me)
h	7.4–7.5 (*m*, 2H); 7.35 ('*q*', J = 1.2, 7.5, 1H); 7.15 ('*t*', J = 1.2, 7.5, 1H)	2.87–2.97 (*m*, 2H); 1.08 (*s*, 3H)	1.8–2.5 (*m*, 2H); 1.15 (*s*, 3H)	2.42 ('*t*', J = 7.8, 6.7, 2H); 2.50–2.78 (*m*, 3H)
j	7.55–7.63 (*m*, 1H); 7.50 (*m*, 1H); 7.40 (*m*, 1H); 7.23 ('*sext.*', J = 3, 8, 1H)	2.78–2.9 (*m*, 2H); 2.5–2.7 (*m*, 2H); 1.13 (*s*, 3H); 1.10 (*s*, 3H)		2.44 ('*t*', J = 6.0, 7.0, $CH_2S^+ <$); 1.3–1.5 (*m*, 5H)
p	7.42–7.58 (*m*, 2H); 7.35 ('*q*', J = 2.4, 7.0, 1H); 7.15 ('*t*', J = 2.4, 7.0, 1H)	2.60–3.0 (*m*, 6H); 2.0–2.1 (*m*, 2H)		2.55 ('*t*', J = 6.0, 7.0, 3H); 1.28–1.5 (*m*, 4H); 0.8–0.90 (*m*, 3H)

their picrates. ^{1}H-NMR spectra for some of the ylides (*Table 3*) show an upfield shift for R^3-S (MeS, CH_2S, or CHS) (2.3–2.5 ppm) as compared to the reported R^3-S signals of the precursor sulfoxides, *e.g.* **3**, with R^1, R^2 = $CH_2CMe_2CH_2C(O)$ and R^1, R^2 = $(CH_2)_3C(O)$ [1]. Tentative assignments of the ^{13}C-NMR spectra for the ylides **2d** and **2j** are shown in *Fig. 1*, and offer close analogy to the Me-S compound [1], *e.g.* the C(4a) signal is consistent with the data observed for other sulfonium ylides [2], the MeS, CH$_2$S and CHS signal is also within the average limits (±0.7 ppm) from the mean value of 31.2 ppm. High-resolution ^{1}H-NMR in $CDCl_3$ solution revealed the presence of conformational isomers where closely spaced signals of the R^3-S alkyl chains are observed for some of these compounds. The H-atoms geminal to the S-atom other than the Me-S ones are presumably diastereotopic.

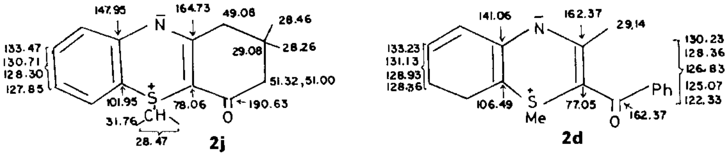


Fig. 1. *^{13}C-NMR spectra of* **2j** *and* **2d**

X-Ray Crystal Data. – Crystals for X-ray analysis of the ylides **2g** and **2m** were slowly grown from AcOEt. Compound **2g** had the following crystal data: $C_{15}H_{17}NOS$, monoclinic, mol.wt. 259.37, a = 11.987(1), b = 9.919(1), c = 12.099(1) Å, β = 110.03(2)°, U = 1351.15(2) Å^3; D_c = 1.276 g cm^{-3} for Z = 4, F(000) = 276, MoKα radiation, (MoKα) = 0.71 cm^{-1}. Space group $P2_1/n$, total independent reflections = 1630, R = 0.050.

Ylide **2m** had the following crystal data: $C_{14}H_{15}NOS$, monoclinic, mol.wt. 245.35; a = 13.690(2), b = 7.469(3), c = 13.748(4) Å, β = 119.37(2)°, U = 1225.0(2) Å^3; D_c = 1.33 g cm^{-3} for Z = 4, F(000) = 260, MoKα radiation, (MoKα) = 0.91 cm^{-1}. Space group $P2_1/n$, total independent reflections = 2015, R = 0.045.

Intensity data were collected to a maximum θ = 25° on an *Enraf-Nonius-CAD-4* diffractometer. The structure was solved using MULTAN [3] and refined by anisotropic (isotropic only for H-atoms) least squares [4]. The

Table 4. *Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses for* **2g**

Atom	*x*	*y*	*z*	*B(A2)*
C(1)	0.7776(2)	0.8078(3)	0.3747(2)	3.31(6)
C(2)	0.6621(3)	0.7338(4)	0.3262(3)	4.38(8)
C(3)	0.6609(2)	0.6145(3)	0.2463(2)	3.25(6)
C(4)	0.7691(3)	0.5267(3)	0.3078(3)	3.53(7)
C(5)	0.8861(2)	0.6002(3)	0.3483(2)	2.68(6)
C(6)	0.8819(2)	0.7367(3)	0.3817(2)	2.79(6)
C(7)	1.1166(2)	0.7243(3)	0.4242(2)	2.77(6)
C(8)	1.2295(3)	0.7758(3)	0.4499(3)	4.08(7)
C(9)	1.3176(3)	0.6999(4)	0.4337(3)	5.10(9)
C(10)	1.2928(3)	0.5695(4)	0.3918(3)	4.78(8)
C(11)	1.1810(3)	0.5171(3)	0.3657(2)	3.75(7)
C(12)	1.0883(2)	0.5920(3)	0.3807(2)	2.78(6)
C(13)	1.0399(3)	0.8064(3)	0.6049(2)	3.62(7)
C(14)	0.6655(3)	0.6648(4)	0.1291(3)	4.60(8)
C(15)	0.5477(3)	0.5332(4)	0.2245(3)	5.38(9)
S	1.00972(6)	0.82968(7)	0.44956(6)	2.89(1)
O	0.7810(2)	0.9258(2)	0.4402(2)	4.47(5)
N	0.9777(2)	0.5313(2)	0.3473(2)	3.07(5)

Table 4, cont.

Atom	x	y	z	$B(A2)$
*H*1C(2)	0.600(2)	0.798(3)	0.277(2)	4.8(7)
*H*2C(2)	0.639(2)	0.695(3)	0.394(3)	6.2(8)
*H*1C(4)	0.774(2)	0.455(3)	0.253(2)	4.6(7)
*H*2C(4)	0.760(2)	0.490(3)	0.380(2)	5.0(7)
*H*C(8)	1.244(2)	0.865(3)	0.481(2)	5.2(7)
*H*C(9)	1.392(3)	0.735(4)	0.453(3)	6.5(8)
*H*C(10)	1.355(2)	0.516(3)	0.387(3)	5.8(8)
*H*C(11)	1.162(2)	0.426(3)	0.335(2)	3.9(6)
*H*1C(13)	1.034(2)	0.714(3)	0.620(2)	3.9(6)
*H*2C(13)	0.971(2)	0.857(3)	0.616(2)	4.3(7)
*H*3C(13)	1.118(2)	0.845(3)	0.645(2)	5.0(7)
*H*1C(14)	0.592(3)	0.724(4)	0.090(3)	6.5(8)
*H*2C(14)	0.740(2)	0.709(3)	0.138(2)	3.9(6)
*H*3C(14)	0.656(3)	0.589(4)	0.075(3)	8.0(1)
*H*1C(15)	0.553(2)	0.457(3)	0.179(2)	5.1(7)
*H*2C(15)	0.479(3)	0.588(3)	0.189(3)	6.4(9)
*H*3C(15)	0.555(3)	0.497(4)	0.306(3)	9.0(1)

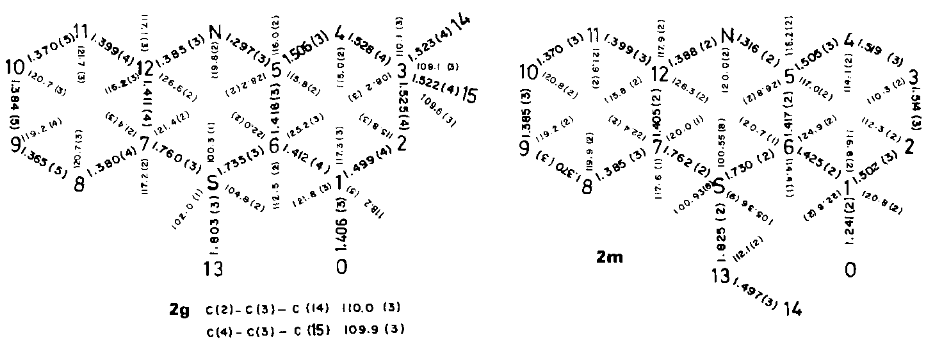


Fig. 2. *Bond lengths (Å) and angles (°) of* **2g** *and* **2m**

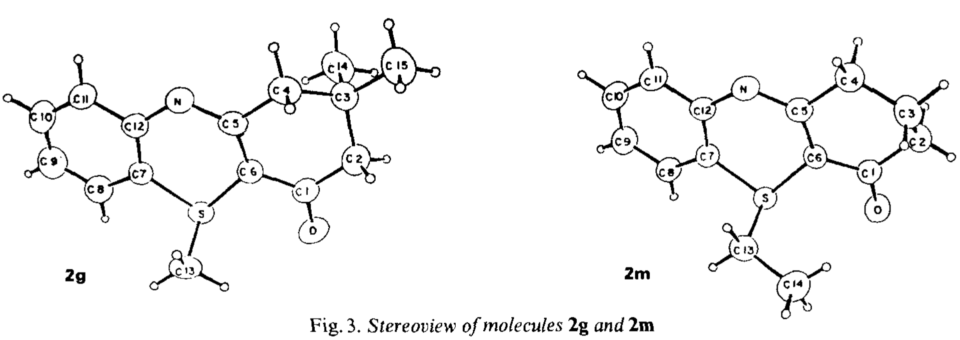


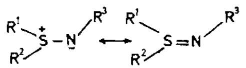
Fig. 3. *Stereoview of molecules* **2g** *and* **2m**

Table 5. *Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses for* **2m**

Atom	x	y	z	B(A2)
C(1)	–0.4774(1)	0.2581(3)	–0.1752(1)	2.92(4)
C(2)	–0.4782(2)	0.1237(3)	–0.2569(2)	3.82(5)
C(3)	–0.3659(2)	0.0319(3)	–0.2144(2)	4.14(5)
C(4)	–0.2741(2)	0.1700(3)	–0.1848(2)	4.11(5)
C(5)	–0.2734(1)	0.3178(3)	–0.1100(1)	2.87(4)
C(6)	–0.3734(1)	0.3446(3)	–0.1051(1)	2.69(4)
C(7)	–0.2609(1)	0.6254(3)	0.0231(1)	2.59(4)
C(8)	–0.2531(2)	0.7856(3)	0.0772(2)	3.30(4)
C(9)	–0.1632(2)	0.8963(3)	0.1059(2)	3.97(5)
C(10)	–0.0821(2)	0.8471(3)	0.0786(2)	3.92(5)
C(11)	–0.0903(1)	0.6891(3)	0.0245(1)	3.41(4)
C(12)	–0.1799(1)	0.5711(1)	–0.0054(1)	2.72(4)
C(13)	–0.3164(2)	0.3510(3)	0.1224(1)	3.18(4)
C(14)	–0.3880(2)	0.1924(3)	0.112(2)	4.06(5)
S	–0.37489(3)	0.48402(3)	–	
	0.00534(3)	2.448(9)		
O	–0.5632(1)	0.2870(2)	–0.1685(1)	3.82(3)
N	–0.1812(1)	0.4140(2)	–0.0599(1)	3.18(4)
*H*1C(2)	–0.498(2)	0.188(3)	–0.330(1)	4.6(5)
*H*2C(2)	–0.535(2)	0.046(3)	–0.278(2)	4.3(5)
*H*1C(3)	–0.370(2)	–0.043(3)	–0.275(2)	4.4(5)
*H*2C(3)	–0.350(2)	–0.037(4)	–0.146(2)	6.36(6)
*H*1C(4)	–0.284(2)	0.228(3)	–0.257(2)	5.6(6)
*H*2C(4)	–0.202(2)	0.115(3)	–0.150(2)	5.6(6)
*H*C(8)	–0.308(2)	0.813(3)	0.093(1)	4.0(5)
*H*C(9)	–0.156(2)	1.005(3)	0.143(2)	4.9(5)
*H*C(10)	–0.017(1)	0.930(3)	0.102(1)	3.7(5)
*H*C(11)	–0.038(2)	0.659(3)	0.008(2)	4.6(5)
*H*1C(13)	–0.314(2)	0.440(4)	0.176(2)	5.7(6)
*H*2C(13)	–0.242(2)	0.314(3)	0.138(1)	4.1(5)
*H*1C(14)	–0.355(2)	0.116(3)	0.172(1)	4.7(5)
*H*2C(14)	–0.404(2)	0.126(4)	0.050(2)	6.4(6)
*H*3C(14)	–0.460(2)	0.221(3)	0.101(2)	6.2(6)

H-atoms were found from an electron density difference *Fourier* synthesis. Atom coordinates of **2g** and **2m** are given in *Tables 4* and *5*, bond lengths and angles in *Fig. 2*, and stereoviews in *Fig. 3*.

For both **2g** and **2m**, the molecule is non-planar having a boat-like conformation with its prow-S higher than its stern-N (0.46 *vs.* 0.11 Å) above the plane defined by C(5), C(6), C(7), and C(12), and the S-alkyl bond is almost orthogonal to this plane (87°, slight lean to N). The S-atom is pyramidal with the C–S–C angles less than tetrahedral. The smallest angle is C(6)–S–C(7) (100.3 and 100.55° for **2g** and **2m**, respectively), because of the constraints imposed on the ring by the long C(7)–S bonds (1.760 and 1.762 Å). Also, S–C(6) bonds are slightly shorter (1.735 and 1.73 Å) suggesting cross allylic overlap between the N–S dipoles and substantial delocalisation in the nearly planar thiazine



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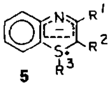
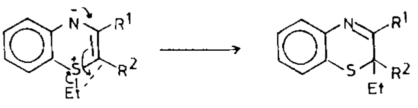


5

central ring. The possibility of electron-density transfer from an ionic centre to a vacant 3d orbital of a second-row element in acyclic ylides is described [5] in which case sulfimides **4** are properly represented as resonance hybrids. It is unlikely, however, that for **2** much overlap is present to induce a homoaromatic structure of type **5**. Thus **2g** and **2m** are best represented as stabilised sulfonium ylides [6] [7] with much of the negative charge divided between C(5) and the N-atom.

Thermolysis of the Ylides 2g–r. – The ylides **2g–r** underwent facile dealkylations when heated neat in aprotic solvents (*e.g.* toluene or xylene), and in slightly polar media (DMF or MeCN) or highly polar media (HCl) [1], the 4*H*-1,4-benzothiazines **1** were obtained in quantitative yield. Attempted thermolysis of **2h** and **2m** in DMSO in an NMR tube rising the temperature to 125 °C (^{1}H-NMR monitoring) revealed the formation of ethylene, a trace of the 4a-ethyl derivative **6** (complex pattern at 1.05–1.85 ppm for Et) and the corresponding 4*H*-1,4-benzothiazines (*ca.* 95%). From **2m**, 4a-ethyl-3,4a-dihydro-2*H*-phenothiazin-4(1*H*)-one (**6**; R^1, R^2 = $(CH_2)_3CO$; *Scheme 1*) was isolated and characterised.

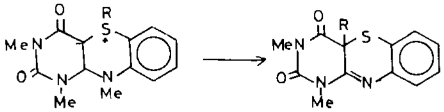
Scheme 1



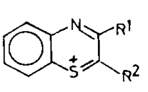
2h, 2m **6**

The rearrangement of **2** and **6** *(Scheme 1)* may involve a radical process, similar to the anionic [1] [2] (*Stevens*-type) rearrangement observed for the ylides **7** to **8** [8] *(Scheme 2)*. An S_Ni process *(Scheme 1)* may be feasible, though it would probably be of relatively high activation energy [8]. Contrary to previous observation [8] for ylides of type **7**, no competing [1,4] rearrangement product is detected in this case.

Scheme 2



7 **8**

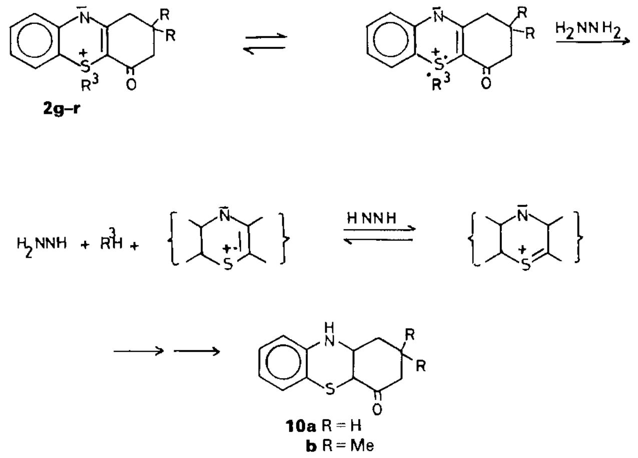


9

The ease of dealkylation at the S-atom of the ylides studied is demonstrated by their mass spectra where the ion corresponding to $M^+ - R$ is invariably the base peak. Other relevant fragmentations for **2g–r** are those of the thiazinyl cation **9**.

Redox Reactions of Ylides 2g–r. – The ylides **2g–r** reacted smoothly with hydrazine hydrate in the absence of H_2O_2 and at room temperature. N_2 gas was evolved, and the 3,4-dihydro-2*H*-1,4-benzothiazines **10** were isolated quantitatively *(Scheme 3)*. Reduc-

Scheme 3



tion was envisaged by initial radical formation of di-imide which effectively reduced the 2,3-double bond. No redox reactions were observed for **1** and hydrazine.

The homolytic cleavage of the C–S bond to give a radical-pair intermediate is conceivable where the alkyl radical can either eliminate a H-atom to give an alkene (as for the thermolytic reaction) or else initiate the following chain process *(Scheme 3)*. Failure of the other ylides (**2a–f**) to undergo similar reactions is rather puzzling, but can best be explained, at present, by the assumption that the radical pair, if initially formed, recombines rapidly to give back the parent ylide.

The photo-induced transformations of these ylides are under current study and will be reported later.

We thank Dr. *T. L. Gilchrist*, University of Liverpool, for helpful discussion.

Experimental Part

General. M.p.: *Kofler* block hot stage apparatus; uncorrected. UV spectra: *Pye-Unicam-SP-800* instrument. IR spectra: *Nujol* mulls on *Unicam SP 1000* spectrophotometer. ^{1}H-NMR spectra (220 MHz): in $CDCl_3$ on a *Perkin-Elmer-R-34-B* instrument. Mass spectra: *AEI MS 12* spectrometer with a direct insertion probe at 70 eV.

*Ylides by Alkylation of the 4*H*-1,4-Benzothiazines* **1**. A slurry of the 4*H*-1,4-benzothiazin **1** (2 mmol) in dry DMF (10 ml) was stirred magnetically at (*ca.* 20°) and NaH (0.25 g of 50% dispersion in oil) was added portionwise. To the bright red soln. the alkyl halide (2.5 mmol) was added dropwise, and the red mixture faded to yellow. For **1a** and **1b**, the colour often darkened further. After stirring for ¾ h, the mixture was poured into ice/H_2O and the product extracted with CH_2Cl_2 (2 × 25 ml), the extract washed with H_2O, dried, and the solvent evaporated. The residue was crystallised from EtOAc/hexane to give **2**. Spectral data and analyses are given in *Tables 1, 2,* and *3.*

Thermolysis of Ylides **2h** *and* **2m**. The ylide **2h** or **2m** (0.05 g) in (D_6)DMSO (0.5 ml) was heated in a sealed NMR tube at *ca.* 125° and the reaction monitored by ^{1}H-NMR. After 2 h, a complex *m* at 1.05–1.85 ppm for the

4a-ethyl derivative **6** appeared. Signals for the parent **1c** and **1d** (95%), resp., and for ethylene (5.35 ppm) were also observed.

The ylide **2m** (1 g) in DMSO (10 ml) was heated as before. After cooling, the mixture was poured into H_2O (10 ml), and the major product **1d** was isolated as a yellow precipitate and identified by comparison of IR and m.p. with an authentic sample. The aq. phase was extracted with $CHCl_3$ (2 × 30 ml), the extract dried (Na_2SO_4), and then evaporated *in vacuo*. Chromatography of the residue on silica gel (EtOAc/hexane 1:4) gave **6** (R^1, $R^2 = (CH_2)_3C(O)$) as orange flakes (5 mg), m.p. 150° (from hexane). UV (EtOH): 282 (5000), 307 (4100), 390 (10115). IR: 740, 810, 1000, 1105, 1225, 1560, 1590. ^{1}H-NMR: 1.05 (*t*, *J* = 7, CH_2Me); 1.60–1.85 (*m*, CH_2Me); 2.45–2.65 (*m*, 2H); 2.72–2.80 (*m*, 2H); 2.87–2.95 (*m*, 2H); 7.42–7.73 (*m*, 2H); 7.85–7.90 (*m*, 2H). Anal. calc. for $C_{14}H_{15}NOS$ (245): C 68.57, H 6.11, N 5.71; found: C 68.52, H 6.11, N 5.58.

Redox Reactions of Ylides **2g–r**. The ylide **2** (0.15 g) in MeOH (1 ml) was stirred at r.t., and the hydrazine hydrate (2 ml) was added portionwise. A crystal of $CuSO_4$ was also added to catalyse the reaction. N_2 gas evolved immediately, and the reaction was complete in *ca.* 20–30 min as shown by TLC (Kieselgel *60 pF_{254}*, EtOAc/hexane 1:1). The product **10** often separated as orange flakes. It was filtered, washed with H_2O and dried (90%).

*2,3-Dihydrophenothiazin-4(1*H*)-one* (**10a**): Orange flakes (from MeOH/EtOAc), m.p. 236–240° (dec.). UV (EtOH): 285 (5250), 302 (4200), 382 (10020). IR: 740, 825, 1000, 1110, 1230, 1560, 1590, 3260 (NH). ^{1}H-NMR: 1.85–2.05 (*m*, 2H); 2.42–2.50 (*m*, 4H); 2.58–2.90 (*m*, 2H); 3.40 (*s*, 1H); 3.62 (*s*, NH); 7.40–7.70 (*m*, 2H); 7.75–7.90 (*m*, 2H).

*2,3-Dihydro-2,2-dimethylphenothiazin-4(1*H*)-one* (**10b**): Orange flakes (from MeOH/EtOAc), m.p. 242–245° (dec.). UV (EtOH): 287 (5100), 301 (4000), 383 (10025). IR: 740, 750, 880, 1015, 1120, 1140, 1260, 1570, 1580, 1610, 3240 (NH). ^{1}H-NMR: 1.60 (*s*, 6H); 1.83–2.00 (*m*, 2H); 2.40–2.61 (*m*, 4H); 3.47 (*s*, 1H); 3.60 (*s*, NH); 7.56–7.71 (*m*, 2H); 7.70–7.87 (*m*, 2H). Anal. calc. for $C_{12}H_{13}NOS$ (219): C 65.75, H 5.94, N 6.39; found: C 66.00, H 5.65, N 6.50.

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