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A Convenient Synthesis of 2H-3,4-Dihydro-1,4-Benzothiazines

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Abstract: Aminothioalkenols react with paratoluenesulfonic acid in benzene or with phosphoric acid in toluene, and provide mainly heterocyclization in 2H-3,4-dihydro-1,4- benzothiazines; formation of some indenes and diene (in one case) was observed too.

Introduction

Dihydro-1,4-benzothiazines are compounds of pharmacological interest[1]. In the last two decades, steady progress in their chemistry has been made along with the discovery of this structural unit in pheomelanins and trichochromes (characteristic pigments of red human hair)[2].

These compounds are usually prepared from acyclic precursors[1-3] or by ring expansion of benzothiazoles and benzothiazolines[4]. One drawback of such

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a synthetic strategy is that, each time, different precursors are required for the construction of the thiazine ring (yields are seldom high).

A more convenient method involves the functionalisation of simple and easily available precursors containing the thiazine ring[5].

The literature provides only scanty information on 2H-3,4-dihydro-1,4-benzothiazines; it has been proposed that benzothiazinones could partake, to some extent, in the building up of the 1,4- benzothiazines units[1,6].

In connection with our studies on the chemistry of arylsulfides[7], we wish to report a direct new route to produce various 3- alkylidene-2H-3,4-dihydro-1,4- benzothiazines **2**. The method illustrates the successful utilization of aminothioalkenols **1** and represents a novel intramolecular approach to substituted benzothiazines.

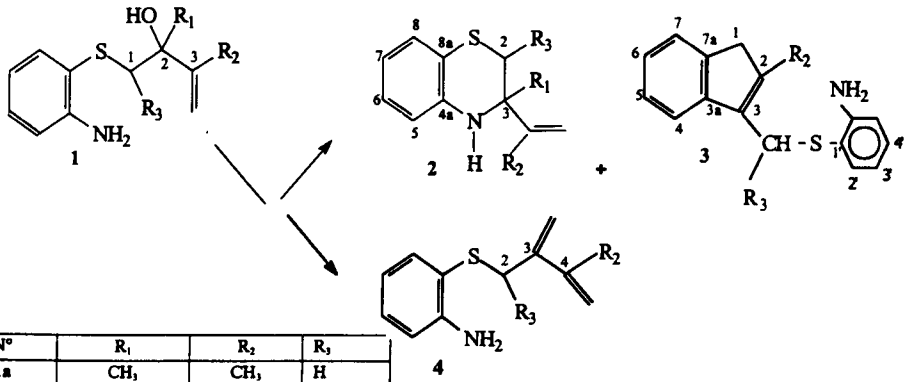
Moreover, the reaction used permitted the introduction of various substituents in the 2 and 3 positions without requiring construction of the benzothiazine ring from acyclic precursors each time a different substituent was desired.

As far as we know, there have been no previous reports on the generation of compounds **2** with an alkene substituent in the 3 position.

Results and discussion

The synthetic steps leading to the formation of compounds **2a-h** are outlined in Scheme 1.

Scheme 1



N°	R_1	R_2	R_3
1a	CH_3	CH_3	H
1b	C_6H_5	CH_3	H
1c	C_6H_5	H	H
1d	CH_3	H	H
1e R*S*	C_6H_5	CH_3	CH_3
1f R*R*	C_6H_5	CH_3	CH_3
1g R*S*	CH_3	CH_3	CH_3
1h R*R*	CH_3	CH_3	CH_3

The desired aminothioalkenols **1a-h** required for the present study were readily prepared from the corresponding ethylenic epoxides by nucleophilic attack of 2-amino thiophenol in basic medium with satisfactory yields[7,8]. Synthesis of the new compounds **1e, 1g R*S*** and **1f, 1h R*R*** was achieved from the corresponding diastereoisomeric vinyloxiranes; the stereochemical assignments for **2e - h** were derived from their ^1H , ^{13}C NMR spectra and from our own findings on aminoalcohols[9]. In a typical experiment, when **1** was heated in the presence of paratoluenesulfonic acid (TsOH) in benzene (method A) or with phosphoric acid in xylene (method B), the reaction mixture after work-up afforded predominantly benzothiazines **2** and sometimes a mixture of

Table 1: reaction of Aminothioalkenols **1** with TsOH (method A) or H_3PO_4 (method B)

Substrate	Method	Total % yield	Time (h)	Products % (ratio) **2**	**3**
1a	A	77	2.5	87[1]	-
	B	75	0.5	80[1]	-
1b	A	55	5	55	45
	B	53	1.5	66	34
1c	A	45	2	86	14
	B	65	0.75	80	20
1d	A	70	10.5	100	-
	B	60	1	100	-
1e R*S*	A	50	10	87	13
	B	70	1	50	50
1f R*R*	A	73	10	82	18
	B	60	1	87	13
1g R*S*	A	70	8	100	-
	B	65	1.5	100	
1h R*R*	A	60	7	100	-
	B	50	1.5	100	

[1] Compound **4** was obtained only with **1a**. Product **4a**,yield%, A/B: 13/20.

2 with indenes **3** and diene **4a** (Table 1). The products **2**, **3**, **4a** were purified by column chromatography on silica gel and identified through their analytical and spectral data. All compounds were investigated by ^1H, ^{13}C NMR and IRFT spectra.

The high resolution IR spectrum showed for **2**, a peak about 3390 cm^{-1} (NH stretching vibrations of non-associated species) and absence of hydroxyl (3300 cm^{-1}) absorption. For the conjugated system **4a** two absorption bands were observed at 1650 cm^{-1} and 1600 cm^{-1}, vinylidene groups were noted at 890 cm^{-1}. The ^{13}C NMR data (experimental part) provided support for the structural assignments of **2** and **3**:

➢ in **2**, substantial evidence for the intramolecular cyclization of **1**:

- an upfield shift of about 19 ppm (C_3) and 14 ppm (C_2) in **2a** (compared with **1a**: C_1: 46.77 ppm, C_2: 74.87 ppm)[7].

- the ^{1}JCH coupling constants for carbons of the Ar-S-CH_2 moiety in **2a** ^{1}J=142 Hz (in **1a**:145.2 Hz)[7] were similar to methylene coupling constants (about140 Hz) in benzothiazines ring systems[10,11].

➢ in **3b** for example the absence of the vinylic carbons (C=CH_2), while two sp^2 quaternary carbon pairs at C_2/C_3 appear at about 145 / 132 ppm and two methylene sp^3 CH_2-S and CH_2-1 absorbed respectively at 29.54 ppm (^{1}J=132 Hz) and 42.59 ppm (^{1}J=127 Hz).

We found that arylaminothioalcenols **1e R*S*** and **1h R*R*** underwent cyclization to give in each case two diastereoisomers : **2e** (60%/40%) and **2h** (55%/45%). In contrast, the reaction of **1f R*R*** and **1g R*S*** provided only *one* diastereoisomer, **2f** (identical with **2e** 60%), and **2g** (identical with **2h** 55%) respectively.

Apparently, if we take into consideration structures **2-4**, they testify the involvement of a delocalized carbocation developed on C_2 in the presence of acids, which is significantly stabilized along the side chain of reactants **1**; the presence of an aryl group in compounds **1** (R_1=C_6H_5) - a good stabilizing substituent- which increases the delocalization in the benzylic- allylic cationic

system, permits cyclization with ortho-aryl position (indenes **3b**, **3c**, **3e** and **3f**).

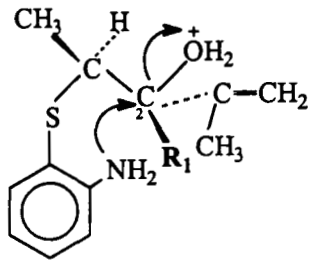
On the other hand, the existence of a carbocationic species allows us to understand the formation of a diene **4a** which was isolated only in the case of **1a** (not with **1d**, **1g** and **1h**).

In the light of the results obtained with arylaminothioalkenols **1e R*S***, **1h R*R*** we think that the cyclization into benzothiazines **2e**, **2h** is not only subject to charge control but also affected principally by steric hindrance. The selection observed, that is to say the formation of one diastereoisomer **2f** or **2g** (**from 1f** or **1g**) , and of two diastereoisomers **2e** or **2h** (from **1e or 1h**), could be rationalized by assuming that carbon-2 undergoes the nucleophilic attack of the nitrogen lone pair from the less sterically hindered site of the *incipient* carbocation. If we suppose that a phenyl group (R_1) cause less steric hindrance than an isopropenyl group, scheme 2A can depict the main conformation of **1g R*S*** and **1f R*R***; in such a conformation the lone pair of the nitrogen atom might be able to attack rapidly the *incipient* carbocation.

The cis geometry of the CH_3 group attached at C_2 and C_3 of benzothiazine **2g** based upon NMR ^{13}C spectral evidence (gamma gauche effect) is consistent with this mechanism.

In contrast, scheme 2B represents the main conformation of **1e R*S*** and **1h R*R*** and shows steric hindrance between NH_2-Ar-S and the isopropenyl

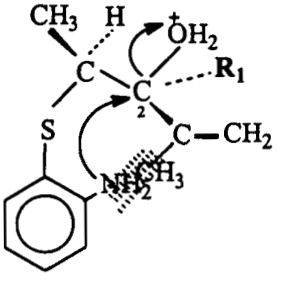
Scheme 2



A

1g R*S* $R_1=CH_3$

1f R*R* $R_1=C_6H_5$



B

1h R*R* $R_1=CH_3$

1e R*S* $R_1=C_6H_5$

group. Thus the isolation of two diastereoisomers in each case, supports the total development of the carbocation intermediate at C_2. Then the lone pair of the nitrogen atom is able to approach either side of the positive carbon to give a mixture of diastereoisomers : **2e** 60/40 (or **2h**: 55/45).

Conclusion.

In conclusion all arylaminothioalkenols are readily heterocyclized and the reaction used permits the introduction of various susbtituents in the 2 and 3 positions without requiring construction of the benzothiazine ring from acyclic precursors each time a different substituent is desired.

It is worth noting that the outcome of the reaction depends on the degree of substitution of the NH_2 moiety in compounds **1**. We have reported earlier[7] that if a tosyl moiety (NH-Ts) is substituted to the NH_2 group in

compounds **1**, heterocyclization at C_1 is predominant and the balance is tipped in favor of benzothiazoles.

Experimental

IR spectra were recorded on a 16 PC FTIR Perkin-Elmer Spectrometer. Solids were examined with a diffuse reflectance accessory. For liquids, a horizontal attenuated total reflectance (HATR) accessory with a ZnSe crystal was used.^{1}H NMR and ^{13}C NMR spectra were recorded using a Brucker DMX (at 500 MHz and 125 MHz respectively). $CDCl_3$ was used as solvent with TMS as the internal standard; chemical shifts (δ) were in ppm. Mass spectrometric analyses were performed using a Varian MAT 311 instrument. All compounds were purified by column chromatography with silica gel 60 (70-230 mesh) purchased from Merck.Arylaminothioalkenols **1a-d** are described by us in[7].

Synthesis of new arylaminothioalkenols 1e-h

To a solution of KOH (0.05M) in absolute ethanol was added freshly distilled orthoaminothiophenol (0.05M). After cooling at room temperature, 0.05M of each diastereoisomer of the corresponding epoxide was added. The reaction occurred at room temperature (16 h) when R_3=CH_3 but was heated at 80°C for 15 h when R_3=C_6H_5. Water was added to the mixture and after extraction with ether, the organic layer was dried with sodium sulfate and evaporated. Each product was purified by chromatography on a silica gel column.

2-hydroxy-2-phenyl-1,3-dimethyl-1-(2-aminophenylthio)-3 butene R*S*:1e

Yield 50% (chromatography in $CH_2Cl_2/CH_3COOC_2H_5$ 90/10);mp 86-88°C. IR:υ cm^{-1}:NH2 3409-3340, C=CH2: 902. ^1H NMR δ ppm: CH_3-1(d: 1.23); CH_3-3(m:1.60); CH-1. (m: 4.0-4.05); C=CH2(m: 4.84-5.30) ; Ar (m: 6.63-7.53). ^{13}C NMR δ ppm:CH_3-1 (15.88^{1}J= 128.37); CH_3-3 (19.35 ^{1}J=127.15); C_1 (49.51 ^{1}J=139.26); C_2 (81.17 ^{1}J=161.07); C_4 (111.15 ^{1}J=157.43) C3' (115.32 ^{1}J= 157.43); $C_{1'}$ (116.41); $C_{5'}$ (118.98); $C_{2''}$(126.08 ^{1}J=156.22); $C_{4''}$ (126.86 ^{1}J=159.85); $C_{3''}$ (127.78 ^{1}J=159.85); $C_{4'}$ (130.40 ^{1}J=157.43); $C_{6'}$ (138.41 ^{1}J=161.07);$C_{1''}$ (144.71); $C_{2'}$(147.11) C_3 (149.05).HR-SM for $C_{18}H_{21}NO$,cal.267.3396,found267.3399

2-hydroxy-2-phenyl-1,3-dimethyl-1-(2-aminophenylthio)-3 buteneR*R*:1f

Yield 56% (chromatography with CH_2Cl_2). IR υcm^{-1}:NH2: 3409-3340, C=CH_2: 900. ^1H NMR δ ppm:CH_3-1(d: 0.95); CH_3-3(m:1.69); CH-1. (m: 4.0-4.07); C=CH2 (m: 4.90-5.37) ; Ar (m: 6.63-7.53). ^{13}C NMR δ ppm:CH_3-1 (15.89^{1}J= 129.58); CH_3-3 (19.44 ^{1}J=127.16); C_1 (49.15 ^{1}J=139.27); C_2 (81.00); C_4 (111.34 1J=156.22);C3' (115.37 ^{1}J= 157.43);$C_{1'}$ (115.96); $C_{5'}$ (118.99); $C_{2''}$(125.60 ^{1}J=157.43); $C_{4''}$ (126.68 ^{1}J=159.86); $C_{3''}$ (127.86 ^{1}J=158.65); $C_{4'}$ (130.54 ^{1}J=158.65); $C_{6'}$ (138.64 ^{1}J=161.06); $C_{1''}$ (143.03); $C_{2'}$(149.30); C_3 (149.40). Anal. Calcd. for $C_{18}H_{21}NOS$: C, 74.24; H,7.02; N,4.68. Found: C, 75.0; H,6.80; N,4.70.

2-hydroxy-1,2,3-trimethyl-1-(2-aminophenylthio)-3 butene R*S*:1g

50% (chromatography with CH_2Cl_2); mp 55-57°C. IR υcm^{-1}: NH2: 3459-3354, C=CH_2: 902. ^{1}H NMR:CH_3-2(s: 1.27); CH_3-1(d: 1.29); CH_3-3 (m: 2.04); CH-1. (q: 3.89); C=CH_2 (m: 4.92-5.12) ; Ar (m: 6.65-7.25). ^{13}C NMR δ ppm: CH_3-1 (13.20 ^{1}J= 125.50); CH_3-3 (21.10 ^{1}J=128.20);CH_3-2 (22.78 ^{1}J=126.0); C_1 (50.47 ^{1}J= 139.43); C_2 (80.10); C_4 (110.53 ^{1}J= 158.20); $C_{3'}$ (114.55 ^{1}J= 156.0); $C_{1'}$ (116.42); $C_{5'}$ (119.99);$C_{4'}$ (132.20 ^{1}J=157.20); $C_{6'}$ (139.0 ^{1}J=163.06); $C_{2'}$(149.10); C_3 (150.0).

2-hydroxy-1,2,3-trimethyl-1-(2-aminophenylthio)-3 butene R*R*:1h

70% (chromatography with CH_2Cl_2/$CH_3COOC_2H_5$: 80/20). IR υcm^{-1} :NH2: 3459-3354, C=CH_2: 900. ^{1}H NMR δ ppm:CH_3-1 (d: 1.21); CH_3-2 (s: 1.36); CH_3-3(m: 1.76); CH-1. (q: 3.33); C=CH_2(m: 4.92-5.12) ; Ar (m: 6.65-7.25). ^{13}C NMR δ ppm:CH_3-1 (15.26^{1}J= 124.50); CH_3-3 (19.10 ^{1}J=127.16);CH_3-2 (23.78 ^{1}J=126.82);C_1 (52.47 ^{1}J=140.43); C_2 (77.11); C_4 (111.531J=157.20); $C_{3'}$(115.55 ^{1}J= 156.45);$C_{1'}$ (117.42); $C_{5'}$ (118.99);$C_{4'}$ (130.25 ^{1}J=157.65); $C_{6'}$ (137.67 ^{1}J=163.06);$C_{2'}$(148.39); C_3 (149.45).Anal. Calcd. for $C_{13}H_{19}NOS$: C, 65.82; H,8.01; N,5.91. Found: C, 66.10; H,7.90; N,5.90.

Synthesis of 2*H*-3,4- dihydro-1,4-benzothiazines 2a-h: general procedure

Method A (Method B): To a solution of the appropriate aminothioalkenol **1** (0.01 mol) in 50 mL of anhydrous benzene (anhydrous xylene),was added 0.001 mol of TsOH (H_3PO_4 85%). The reaction mixture was stirred at reflux for

the time determined in Table 1. After added water (20 mL) the solution was extracted with $(C_2H_5)_2O$. The extracts were dried (sodium sulfate), evaporated and purified by column chromatography (solvent for **2a-c**: $CH_2Cl_2/C_6H_5CH_3$:50/50, for **2d-f**: toluene and **2g-h**: CH_2Cl_2)

(3-propenyl-3-methyl)-2H-3,4-dihydro-1,4-benzothiazine: 2a

IR:υNH: 3390, CH=CH2: 1640. ^{1}H NMR δ ppm:CH_3-3 (s: 1.42); CH_3-$C_{(1')}$ (s:1.83); CH_2-2 (2.7- 3.03 J_{AB}= 12.8);CH_2-2'(m:4.88 à 5.13) ; Ar (m:7.14-7.46). ^{13}C NMR δ ppm: CH_3-1' (18.0 ^{1}J=127); CH_3-3 (27.4 ^{1}J=127.8); CH_2-2 (33.9 ^{1}J=142.0 Hz); C_3 (55.2);$C_{2'}$ (112.5 ^{1}J=156.1); C_{8a} (114.7) C_5 (115.0 ^{1}J=155.2); C_7 (117.5 ^{1}J=161.7); C_6 (125.6 ^{1}J=158.7); C_8 (127.3 ^{1}J=158.0; C4a (140. 9); $C_{1'}$ (148.0). HR-SM for $C_{12}H_{15}SN$, cal. 205.09226, found 205.09252. Anal. Calcd. for $C_{12}H_{15}SN$:C, 70.24; H,7.32; N,6.83. Found: C, 70.14; H,7.30; N,6.80.

(3-propenyl-3-phenyl)-2H-3,4-dihydro-1,4-benzothiazine: 2b

IR:υcm^{-1} : NH: 3418. ^{1}H NMR δ ppm:CH_3-1' (s: 1.71); CH_3-$C_{(1')}$ (s:1.83); CH_2-2 (3.28-3.37 J_{AB}= 12.6); CH_2-2'(m :4.97-5.28) ; Ar (m:6.64- 7.43).^{13}C NMR δ ppm:CH_3-1'(17.2 ^{1}J=126.0); CH_2-2 (31.9 ^{1}J=144.1); C_3 (60.74); $C_{2'}$ (114.9 ^{1}J=157.2);C_5 (115.3 ^{1}J=155); C_{8a} (114.7); C_7 (117.9 ^{1}J=161.0); C_6 (125.5 J^1=158.7);$C_{3''}$ (125.7); $C_{2''}$ (126.4); $C_{4''}$ (127.6); C_8 (128.6); $C_{1''}$ (140.8); $C_{1'}$ (148); C_{4a} (144.6). Anal. Calcd. for $C_{17}H_{17}NS$: C, 76.4; H,6.38; N,5.24. Found: C, 76.30; H,6.20; N,5.40.

(3-vinyl-3-phenyl)-2H-3,4-dihydro-1,4-benzothiazine: 2c

IR:υcm^{-1}: NH: 3396. ^{1}H NMR δ ppm: CH_2-2 (2.90-3.20 J_{AB}= 12.8); CH=CH_2-2'(m: 5.14-5.29); Ar (m: 6.57-7.41). ^{13}C NMR δ ppm:CH_2-2 (36.1 ^{1}J= 144.0); C_3 (58.8); $C_{2'}$ (114.5 ^{1}J=157.2); C_5 (115.2 ^{1}J=155.0); C_{8a} (116.0); C_7 (117.8 ^{1}J=161.0); C_6 (125.5 ^{1}J=158.8);$C_{3''}$ (125.7);$C_{2''}$ (126.5);$C_{4''}$ (127.5); C_8 (128.5 ^{1}J=159.7); $C_{1''}$ (140.9); $C_{1'}$ (141.4 1J=155); C_{4a} (144.6).HR-SM for $C_{16}H_{15}NS$, cal. 253.0932, found 253.09252. Anal. Calcd. for $C_{16}H_{15}SN$:C, 75.89; H,5.93 N,5.53. Found: C, 76.10; H,5.90; N,5.50.

(3-vinyl-3-methyl)-2H-3,4-dihydro-1,4-benzothiazine: 2d

IR:υ cm^{-1}:NH: 3376. ^{1}H NMR δ ppm:CH_2-2 (2.69-2.79 J_{AB}= 12.5);CH_3-3 (s:1.36); CH=CH_2-2'(m: 5.20- 5.39); Ar (m:6.59-6.99). ^{13}C NMR δ ppm: CH_3-3 (27.92 ^{1}J= 127.6); CH_2-2 (35.76 ^{1}J=1 43.0); C_3 (52. 39); $C_{2'}$ (112.0 ^{1}J=156.1); C_{8a} (114.0); C_5 (115.0 ^{1}J=155.0); C_7 (117.0 ^{1}J=161.0); C_6 (125. 6 ^{1}J=159.7); C_8 (127.3 ^{1}J=158.0); C_{4a} (140.9); $C_{1'}$ (142.0). Anal. Calcd. for $C_{11}H_{13}SN$: C, 69.10; H,7.02; N,7.32. Found: C, 70.10; H,6.90; N,7.30.

(2-methyl-3-propenyl-3-phenyl)-2H-3,4-dihydro-1,4-benzothiazine: 2e

(60/40)

IR:υcm^{-1}:NH: 3458. ^{1}H NMR δ ppm:CH_3-2 (d:1.23; 1.39); CH_3-1' (s:1.60-1.63); CH-2 (q: 3.70; 3.80);CH2-2'(m: 4.97-5.28; 5.03-5.23); Ar (m: 6.57- 7.48). ^{13}C NMR δ ppm:CH_3-2 (19.01;19.27 ^{1}J=128.37); CH_3-1' (19.73 ^{1}J=125.95); C_2 (37.36;38.15 ^{1}J=139.27); C_3 (63.92;65.02); $C_{2'}$ (111.94;113.32

^{1}J=157.43); C_{8a} (115.24;115.77); C_5 (115.90;116.04 ^{1}J=161.07); C_7 (118.57;118.64 ^{1}J=162.27); C_6 (124.99;125.13 ^{1}J=157.43); $C_{2''}$ (126.48;126.24 ^{1}J=157.43); $C_{4''}$ (126.75;127.75 ^{1}J=161.07); $C_{3''}$ (127.51;127.69 ^{1}J=158.65);C (128.04;128.27 ^{1}J=159.85); $C_{1''}$ (139.92;140.09); C_{4a} (144.82); $C_{1'}$ (145.94; 147.46). Anal. Calcd. for $C_{18}H_{19}SN$ (mixture **2e,2f**): C, 76.87; H,6.76; N,4.98. Found: C, 76.90; H,6.63; N,5.03.

(2-methyl-3-propenyl-3-phenyl)-2H-3,4-dihydro-1,4-benzothiazine: 2f

IR:υcm^{-1}: NH: 3458. ^{1}H NMR δ ppm:CH_3-2 (d:1.39); CH_3-1' (s:1.63); CH-2 (q: 3.80); CH_2-2'(m: 5.03-5.23); Ar (m: 6.58-7.48). ^{13}C NMR δ ppm:CH_3-2 (19.27^{1}J=128.37); CH_3-1' (19.73 ^{1}J=125.95); C_2 (38.15 ^{1}J=139.27); C_3 (63.92); $C_{2'}$ (111.94 ^{1}J=157.43); C_{8a} (115.24); C_5 (115.90 ^{1}J=155.01); C_7 (118.57 ^{1}J=162.27); C_6 (124.99 ^{1}J=157.43); $C_{2''}$ (126.48 ^{1}J=157.43); $C_{4''}$ (126.75 ^{1}J=161.07); $C_{3''}$ (127.51 ^{1}J=158.65); C_8 (128.04 ^{1}J=159.85); $C_{1''}$ (139.92); C_{4a} (144.82); $C_{1'}$ (145.94).

(2-methyl-3-propenyl-3-methyl)-2H-3,4-dihydro-1,4-benzothiazine: 2g

IR:υcm^{-1}: NH: 3380. ^{1}H NMR δ ppm:CH_3-2 (d:1.26, J=6.70); CH_3-3 (s:1.41); CH_3-$C_{1'}$ (s: 1.82);CH-2 (q:3.23 J=6.84); CH_2-2'(m: 5.0-5.02); Ar (m: 7.14-7.46). ^{13}C NMR δ ppm:CH_3-2 (19.66 ^{1}J=128.0); CH_3-1' (27.8 ^{1}J=126.0); CH_3-3 (19.4 ^{1}J=127.15); C_2 (40.1 ^{1}J=138.06); C_3 (56.7); $C_{2'}$ (112.5 ^{1}J=162.2); C_{8a} (113.9); C_5 (114.75 ^{1}J=154.0); C_7 (118.0); C_6 (125.18 ^{1}J=158.7); C_8

(127.48); C_{4a} (140.24); $C_{1'}$ (147.95). Anal. Calcd. for $C_{13}H_{17}SN$ (mixture of **2g, 2h**)C, 71.23; H,7.76; N,6.39. Found: C, 72.10; H,7.75; N,6.45.

(2-methyl-3-propenyl-3-methyl)-2H-3,4-dihydro-1,4-benzothiazine:2h

(55/45)

IR:υcm^{-1}:NH:3390. ^{1}H NMR δ ppm:CH_3-2 (d:1.20;1.26 J=6.90); CH_3-3 (s: 1.34;1.41); CH_3-$C_{(1')}$ (s:1.82) CH-2 (q: 2.97;3.23 J=6.87) CH_2-2'(m: 4.88-4.97; 5.0-5.02); Ar (m:7.14-7.46; 7.17- 7.48). ^{13}C NMR δ ppm:CH_3-1' (18.0; 27.8 ^{1}J= 126.5); CH $_3$-2 (17.05;19.66 ^{1}J=127.16); CH_3-3 (19.4;23.6); C_2 (38.2;40.1^{1}J=141.6); C_3 (56.7;58.1); $C_{2'}$ (111.0;112.5 ^{1}J=156.2); C_{8a} (114.7;113.9); C_5 (113.92; 114.75 ^{1}J=155.0); C_7 (117.58;118.0); C_6 (125.18;125.30 ^{1}J=160.0); C_8 (127.48;127.55); C_{4a} (140.24;140.44); $C_{1'}$ (147.95;148.78).

[2-methyl-3-(phenylamino) thiomethylene]-1H-indene: 3b

IR: υcm^{-1}: NH_2:3458-3360. ^{1}H NMR δ ppm:CH_3-2 (s: 1.62);CH_2-3 (s: 3.20); CH_2-1 (s: 3.81); NH_2 (s: 4.26); Ar (m: 6.57-7.39). ^{13}C NMR δ ppm:CH_3-2 (13.28 ^{1}J=125.94); CH_2-S (29.54, ^{1}J=132); CH_2-1 (42.59 1J=127); $C_{1'}$ (117.3); C_3 (132.23)); C_{3a} (142.12); C_{7a} (142.52); C_2 (145.13); $C_{2'}$ (149.18); (114.47); (118.11); (118.54); .18);(123.88); (126.12); (130.18); (137.45).HR-SM for C_{17} $H_{17}NS$, cal. 267.0332, found, 267.0335. Anal. Calcd. for $C_{17}H_{17}SN$: C, 76.40; H,6.38; N,11.98. Found: C, 76.80; H,6.10; N,12.10.

[3-(phenylamino) thiomethylene]-1H-indene: 3c

IR: υcm^{-1}: NH_2:3455-3360. ^{1}H NMR δ ppm:CH_2-3 (s: 3.10); CH_2-1 (s: 3.90); NH_2 (s: 4.0); CH-2(d: 5.2); Ar (m: 6.57-7.50). ^{13}C NMR δ ppm: CH_2-S (28.0, ^{1}J=135); CH_2-1 (42.50 ^{1}J=127); C_2 (111,15); $C_{1'}$ (117.2); C_3 (132.50); C_{3a} (142.20); C_{7a} (142.52); $C_{2'}$ (149.18); Ar: (114.54); (118.10); (118.54); (123.20); (123.80); (126.24); (131.18); (138.45). Anal. Calcd. for $C_{16}H_{15}SN$: C, 75.89; H,5.93; N,5.53. Found: C, 76.15; H,5.85; N,5.56.

[2-methyl-3-(phenylamino) thiomethyl]-1H-indene: 3e or 3f

IR: υcm^{-1}: NH_2:3460-3360. ^{1}H NMR δ ppm:CH_3-2 (s: 1.69); CH_3(CH-S) (d: 1.70); CH_2-1 (3.09-3.22 J_{AB}=22.57); NH_2 (s: 4.27); CH-S (q: 4.36-4.40); Ar (m: 6.51-7.54). ^{13}C NMR δ ppm:CH_3-2 (13.73 ^{1}J=125.95); CH_3(CH-S) (19.39, ^{1}J=128.37); CH-S (40.64 ^{1}J=141.69); CH_2-1 (42.71 ^{1}J=128.37); $C_{1'}$ (117.70); C_3 (136.84); C_{3a} (140.62); C_{7a} (142.53); C_2 (144.13); $C_{2'}$ (149.14); Ar: (114.42); (117.92); (120.48); (123.29);(123.55); (125.75); (130.08); (137.56). Anal. Calcd. for $C_{18}H_{19}SN$:C, 76.87; H,6.76; N,4.98. Found: C, 76.90; H,6.70; N,5.10.

4-(amino phenylthio)-2-methylbutane-1,3-diene: 4a

IR: υcm^{-1}: C=CH_2: 1650,1600,890. ^{1}H NMR δ ppm:CH_3-2 (s: 1.84); CH_2-4 (s: 3.50); NH_2 (s: 4.20); CH_2-1, CH_2-3(dxd: 4.70-5.20); Ar (m: 6.51-7.30). ^{13}C NMR δppm:CH_3-2 (21.06 ^{1}J=126.80); CH_2-4 (38.56 ^{1}J=141.50);CH_2-1 (113.39 ^{1}J=157); $C_{5'}$ (114.72); CH_2- C_3 (txt: 115.53 ^{1}J=158); $C_{1'}$ (118.09); $C_{5'}$(118.35

^1J=161); $C_{4'}$ (136.54 ^1J=161); $C_{2'}$ (140.87); C_3 (143.31); C_2 (148.63). Anal. Calcd. for $C_{12}H_{15}SN$: C, 70.24; H,7.32; N,15.61. Found: C, 71.10; H,7.14; N,15.60.

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