Tetrahedron Vol. 47, No. 42, pp. 8855-8862, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

THE CONVERSION OF BENZOTHIAZINES TO 2-ALKENYL ANILINES

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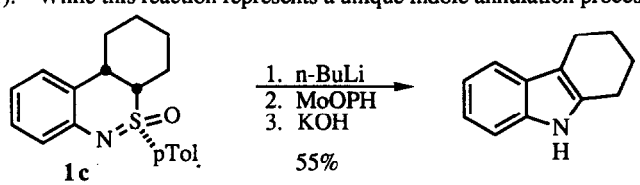
(Received in USA 5 September 1991)

Key Words: Benzothiazine; Vinyl Aniline; Alkenyl Aniline; Sulfoximine; Elimination

Abstract: *Upon treatment with excess potassium dimsylate in DMSO benzothiazines* ***1a-1j*** *undergo an elimination of the sulfoximine functional group to give 2-alkenylsulfinanilides nonstereoselectively in good to excellent yield. These are easily converted to the corresponding anilines with ethanolic potassium hydroxide. Mechanistic studies indicate that the elimination reaction takes place via an E1cb mechanism.*

We recently reported the synthesis of a variety of 2,1-benzothiazines by the Lewis acid mediated reaction of N-phenyl-S-(4-methylphenyl)sulfoximidoyl chloride with alkenes.[1] We reasoned that the adducts from this reaction could have utility in the synthesis of other heterocyclic systems by virtue of the rich synthetic chemistry associated with the sulfoximine functional group.[2] For example, treatment of **1c** with n-BuLi followed by oxidation of the resulting carbanion with MoOPH[3] and hydrolytic work-up gave tetrahydrocarbazole in 55% isolated yield (equation 1).[4] While this reaction represents a unique indole annulation process, it has not yet



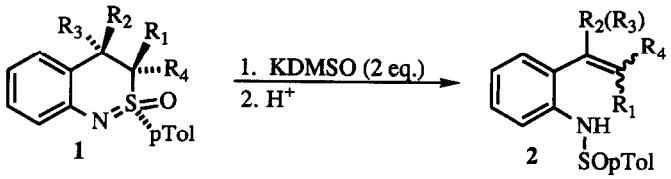
1c (1)

been made general.[5] During the course of this investigation, we discovered an interesting, general reaction which resulted in the formation of 2-alkenyl anilines in high yield.

It should be noted that 2-alkenyl anilines are versatile starting materials for the synthesis of a number of heterocyclic systems including indoles, quinolines and cinnolines.[6] They have been used as key intermediates in several total syntheses.[7] Syntheses of 2-alkenyl anilines have included protocols[6,8] but none, to the best of our knowledge, comparable to that described herein.

The results of our study are shown in Table 1. In general, the benzothiazines **1a-1j** were treated with 2 equivalents of potassium dimsylate in DMSO for 5 to 75 minutes at the temperatures shown. The product sulfinamides were obtained in good yield after chromatographic purification. Since these compounds appeared to be somewhat unstable, they were characterized only by ^{1}H NMR spectroscopy and quickly converted to the

Table 1. Reaction of benzothiazines **1a-lj** with potassium dimsylate.



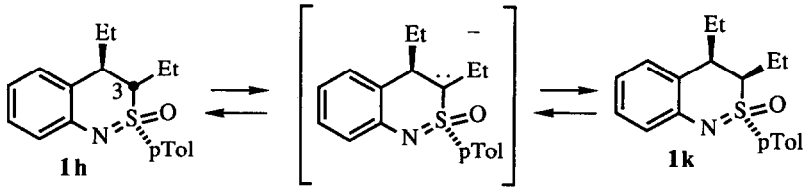
Entry[a]	Benzothiazine	Sulfinamide	R_1	R_2	R_3	R_4	T° C	Time (min.)	Yield(%)
1	**1a**	**2a**	$-(CH_2)_3-$		H	H	45	15	73
2	**1b**	**2a**	H	H	$-(CH_2)_3-$		69	17	85
3	**1c**	**2b**	H	H	$-(CH_2)_4-$		67	5	90
4	**1d**	**2c**	$-(CH_2)_5-$		H	H	65-70	75	94
5	**1e**	**2c**	H	H	$-(CH_2)_5-$		65-70	8	82
6	**1f**	**2d**	$-(CH_2)_6-$		H	H	45	23	89
7	**1g**	**2d**	H	H	$-(CH_2)_6-$		45	22	71
8	**1h**	**2e**	H	Et	H	Et	77	20	95[b]
9	**1i**	**2f**	Me	H	Et	Et	79	22	65[c]
10	**1j**	**2g**	Me	H	$-(CH_2)_4-$		78	35	59

[a]All reactions were conducted using 2 equivalents of potassium dimsylate at a concentration of 0.2 M. [b]A ca. 1:1 mixture of E and Z alkene isomers was obtained. [c]A ca. 1:2 mixture of E and Z alkene isomers was obtained.

corresponding anilines via base catalyzed hydrolysis (Table 2). The hydrolysis proceeded in good yield in most cases, but some sulfinamides presented problems and considerable experimentation was required to obtain reasonable yields.

Notably, there were essentially no consistent differences in the yields of sulfinamides derived from diastereomeric benzothiazines (compare entries 1 and 2, 4 and 5 and 6 and 7, Table 1). The loss of stereochemistry observed with benzothiazine **1h** was also interesting. We thus undertook a study to elucidate the mechanism of the reaction.

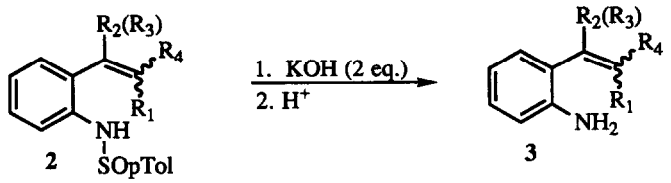
The loss of stereochemistry in the reaction of benzothiazine **1h** could be easily understood in terms of a rapid equilibrium which epimerized the benzothiazine at carbon 3 (equation 2). Indeed, in reactions of **1h** in



(2)

which starting material was recovered, it could be unequivocally shown that a mixture of **1h** and **1k** was present. The other two possible diastereomers in this series could not be detected.[9]

Table 2. Reaction of sulfinamides **2a-2g** with potassium hydroxide.

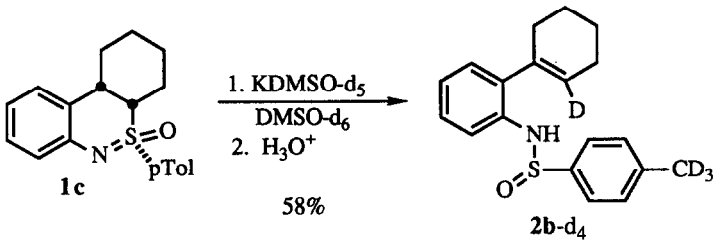


2 3

Entry[a]	Sulfinamide	Aniline	T° C (bath)	Time (hr.)	Yield(%)
1	**2a**	**3a**	87	1.5	67
2	**2b**	**3b**	47/55	1/3.75	77
3	**2c**	**3c**	69	1.5	71
4	**2d**	**3d**	40-50	4	67
5	**2e**	**3e**	79	3	78
6	**2f**	**3f**	79	.75	92
7	**2g**	**3g**	78	.75	89

[a]All reactions were conducted using 2 equivalents of potassium hydroxide. The concentration of sulfinamide was 0.2 M.

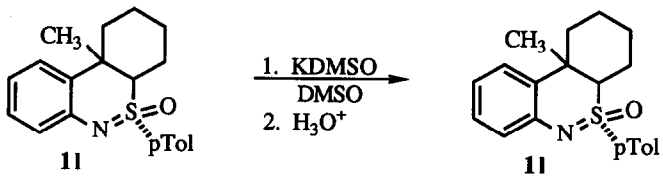
The rapidity of this exchange was demonstrated by conducting an elimination reaction in DMSO-d_6. Thus treatment of benzothiazine **1c** with potassium dimsylate-d_5 in DMSO-d_6 for 25 minutes gave **2b**-d_4 in 58% yield (equation 3). A control experiment demonstrated that under the reaction conditions no deteurium was incorporated into **2b**.



1c **2b**-d_4 (3)

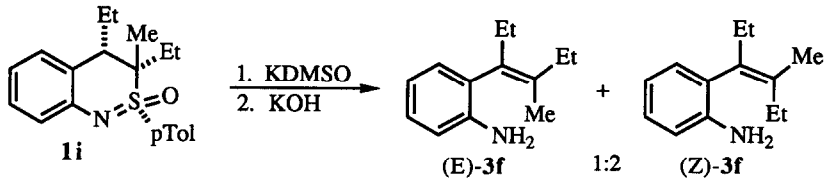
One might conclude the loss of stereochemistry at carbon 3 due to epimerization to be the sole source of the low stereoselectivity in the elimination reaction. Another possibility would include an alpha elimination process in which carbene formation and carbon-carbon bond rotation preceded a hydrogen migration. This unlikely possibility was definitively eliminated by treatment of **1l** with potassium dimsylate under our standard reaction conditions. With no hydrogen available for abstraction on carbon 4, no elimination product was observed (equation 4).[10]

Would high stereoselectivity be observed if the possibility of epimerization at carbon 3 were eliminated? To answer this question, we prepared benzothiazine **1i** by a stereoselective alkylation and subjected it to the elimination reaction (Table 1, entry 9). Elimination products were formed in a ratio of 1:2 (equation 5). The



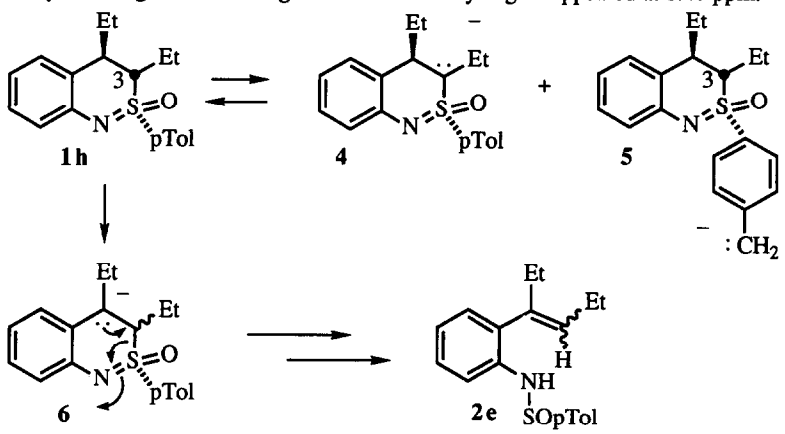
(4)

major isomer was assigned as (Z)-**3f** on the basis of a difference nOe experiment on a mixture of (E) and (Z)-**3f**. Two methyl signals appear in the ^{1}H NMR spectrum of this mixture at 1.48 and 1.81 ppm, respectively. The upfield signal was assigned to (E)-**3f** by virtue of the anticipated shielding effect of the proximal phenyl



(5)

ring.[11] Irradiation of this signal resulted in a 4.3% enhancement of the broad signal at 3.60 ppm, assigned to the amino protons of (E) and (Z)-**3f**. Further support for this assignment came from the ^{1}H NMR spectrum of the stereochemically unambiguous aniline **3g** in which the methyl signal appeared at 1.47 ppm.



Scheme 1

In summary, we have discovered a general route to 2-alkenyl anilines which is regioselective but not stereoselective. The high regioselectivity is associated with the cycloaddition reaction leading to the benzothiazines which are starting materials for this process.[1] The lack of stereoselectivity arises from the mechanism of the reaction as shown in Scheme 1 using **1h** as a model substrate. A rapid equilibrium is established (if possible) between the benzothiazine and carbanions **4** and **5** resulting in epimerization at carbon 3. Irreversible deprotonation of carbon 4 and subsequent rotation of the carbanion and elimination exhibit low stereoselectivity in absence of large steric constraints (e.g. rings). This elimination can thus be characterized as Elcb.[12]

Experimental Section

General Methods

Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl and dichloromethane was freshly distilled from calcium hydride prior to use. Dimethyl sulfoxide was distilled under reduced pressure from calcium hydride and stored over molecular sieves. Ethanol was 200 proof. Reactions were performed in oven (120°C) or flame dried glassware under an inert atmosphere of nitrogen. Flash chromatography was performed on 230-400 mesh silica gel (Merck) with technical grade solvents which were distilled prior to use with exception of diethyl ether which was ACS reagent grade and was used without purification. TLC was performed on silica gel plates (Merck), .25 mm Hg, with F_{254} fluorophore. Visualization of compound on silica gel plates was accomplished with UV light, iodine, and phosphomolybdic acid. ^{1}H NMR spectra were obtained on a Nicolet NT-300 or a JEOL FX-90Q spectrometer (300 MHz and 90 MHz respectively). ^{13}C spectra were obtained on a Nicolet NT-300 or a JEOL FX-90Q spectrometer (75 MHz and 22.5 MHz respectively). All NMR spectra were obtained as $CDCl_3$ solutions with TMS (0 ppm or 77 ppm) as the internal standard. Chemical shifts are reported in ppm (δ) with multiplicities reported as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multuplet), br (broadened). IR spectra were obtained on a Nicolet 20 DXB FTIR spectrometer in CCl_4 solution. Intensities are reported as: s (strong 67-100%), m (medium 34-66%), w (weak 0-33%) with the following abbreviations: br (broadened) and sh (shoulder). Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Low resolution mass spectral data was obtained on a Hewlett Packard 5890 B gas ghromatograph with a HP 5790 B mass-selective detector. Exact mass spectra were obtained on a Kratos MS 25 spectrometer.

General procedure for preparation of sulfinamides 2a-2g.

A three-necked flask was charged with a mineral oil suspension of potassium hydride. The addition of the emulsion was under a nitrogen flow. Removal of the mineral oil was accomplished by three washing with 1.5 mL of dry THF. DMSO was slowly added to the potassium hydride and the ca. 0.2 M solution was allowed to stir until the evolution of hydrogen ceased. The flask was then placed in an oil bath to warm the solution to the desired temperature. A solid sample of benzothiazine (**1a-1j**) was then added to the dimsylate ion solution. The reaction was monitored by TLC. Upon completion the reaction was quenched with a saturated sodium sulfite solution and then extracted with ethyl acetate. The organic phase was washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The product was purified by flash chromatography; hexane:ethyl acetate, 10:1. These products were characterized immediately by ^{1}H NMR and carried to the next step.

General procedure for preparation of 2-alkenyl anilines 3a-3g.

A flask equipped with a stirring bar and septum was charged with N-phenyl-2-(-1-alkenyl)-p-toluene sulfinamide (1 eq) which was then dissolved in ethanol to give ca. 0.2 M solution. Potassium hydroxide (2 eq) was then added as a solid. The flask was then placed in an oil bath to equilibrate the solution to the desired temperature. The reaction was monitored by TLC. Upon completion the reaction was diluted with ether. The organic phase was washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. Purification by flash chromatography, solvent system that was hexane/dichloromethane, 3/1 respectively.

4-Methyl-N-(2-(cyclopent-1-enyl)-phenyl)benzenesulfinamide (2a)

Benzothiazines **1a** and **1b** gave **2a** under the conditions shown in Table 1 (entries 1 and 2) in 73% and 85% yield, respectively. ^{1}H NMR (90 MHz) δ 7.58 (d, 2H, J=8.1), 6.80-7.40 (m, 6H), 6.42 (s, 1H), 5.72-5.87 (m, 1H), 2.32 (s, 3H), 2.20-2.67 (m, 4H), 1.64-2.02 (m, 2H).

2-(Cyclopent-1-enyl)aniline (3a)

Treatment of **2a** under the reaction conditions shown in Table 2 (entry 1) gave **3a** in 67% yield. bp 95-100°C at 0.15-0.2 mm Hg; ^{1}H NMR (90 MHz) δ 6.55-7.25 (m, 4H), 5.98 (t, 1H, J=2.1), 3.71 (s, 2H, br), 2.40-2.90 (m, 4H), 1.80-2.2 (m, 2H); ^{13}C NMR (22.5 MHz) δ 143.86, 141.18, 128.31, 128.13, 127.53, 123.72, 118.24, 115.73, 36.30, 33.86, 23.12; IR(CCl_4) 3458m (br), 3368w(br), 3075w, 3051m, 3024m, 2953s, 2932m, 2892m, 2866m, 2846s, 1923w, 1893w, 1852w, 1810w, 1762, 1694, 1678, 1649w (sh),

1613s, 1575m, 1547w, 1495s, 1451s, 1410w, 1319m, 1289s, 1260m, 1237w, 1202w, 1159m, 1146w, 1053w, 975w, 957w, 930w; MS (70eV) *m/z* 160 (M+1, 12),159 (M+, 100), 158(55), 144(51), 143(38), 142(14), 141(17), 131(14), 130(72), 128(10), 118(13), 117(18), 115(16), 103(10), 77(14). Exact mass calcd. for $C_{11}H_{13}N$: 159.1048. Found: 159.1048.

4-Methyl-N-(2-(cyclohex-1-enyl)-phenyl)benzenesulfinamide (2b)

Benzothiazine **1c** gave **2b** under the conditions shown in Table 1 (entry 3) in 90% yield. ^{1}H NMR (90 MHz) δ 7.65 (d, 2H, J=8.1), 7.25-7.45 (m, 4H), 6.98-7.20 (m, 2H), 6.38 (s,br, 1H), 5.62-5.75 (m, 1H), 2.42 (s, 3H), 2.00-2.28 (m, 4H), 1.55-1.70 (m, 4H).

2-(Cyclohex-1-enyl)aniline (3b)

Treatment of **2b** under the reaction conditions shown in Table 2 (entry 2) gave **3b** in 77% yield. ^{1}H NMR (90MHz) δ 6.83-7.00(m, 2H), 6.52-6.70(m, 2H), 5.64(m, 1H, br), 3.65(s, 2H, br), 2.05-2.25(m, 4H), 1.61-1.78(m, 4H); IR (CCl_4) 3464w, 3384w, 3063w, 3014w, 2929s, 2852m, 2837m, 1612s, 1492s, 1453s, 1437m, 1346w, 1289s, 1258w, 1156w, 1143w, 1050w, 1005w, 916w, 850w.

4-Methyl-N-(2-(cyclohept-1-enyl)-phenyl)benzenesulfinamide (2c)

Benzothiazines **1d** and **1e** gave **2c** under the conditions shown in Table 1 (entries 4 and 5) in 94% and 82% yield, respectively. ^{1}H NMR (90 MHz) δ 7.58 (d, 2H, J=8.1), 7.19-7.34 (m, 4H), 6.86-7.08 (m, 2H), 6.23(s,br, 1H), 5.68-5.83 (m, 1H), 2.33 (s, 3H), 2.02-2.18 (m, 4H), 1.39-1.68 (m, 6H).

2-(Cyclohept-1-enyl)aniline (3c)

Treatment of **2c** under the reaction conditions shown in Table 2 (entry 3) gave **3c** in 71% yield. bp 110-120°C at 0.3 mm Hg. ^{1}H NMR (90MHz) δ 6.50-7.40 (m, 4H), 5.79-6.05 (t, 1H, J=6.4), 3.59 (s, 2H, br), 2.08-2.58 (m, 4H), 1.30-1.94 (m, 6H); ^{13}C NMR (75MHz) δ 143.33, 142.75, 132.44, 132.21, 128.71, 127.34, 118.26, 115.29, 34.27, 33.32, 29.82, 27.82, 27.27; IR (CCl_4) 3474w, 3385w, 3374w, 3356w, 3023m, 2963w, 2922s, 2850s, 1612s, 1577w, 1491s, 1453s, 1447s, 1315w, 1291s, 1262w, 1156w, 1130w, 965w; MS (70eV) *m/z* 187(M+, 31), 186(10), 185(15), 184(10), 158(12), 156(15), 144(52), 143(29), 132(11), 131(28), 130(100), 128(12), 118(16), 117(23), 115(21), 106(33), 103(12), 102(10), 93(13), 91(20), 90(14), 89(13), 77(11), 77(31), 69(10), 65(15), 63(14), 51(19), 42(15), 41(33), 39(46). Exact mass calcd for $C_{13}H_{17}N$: 187.1361. Found: 187.1353.

4-Methyl-N-(2-(cycloocten-1-enyl)-phenyl)benzenesulfinamide (2d)

Benzothiazines **1f** and **1g** gave **2d** under the conditions shown in Table 1 (entries 6 and 7) in 89% and 71% yield, respectively. ^{1}H NMR (90MHz) δ 7.66 (d, 2H, J=8.1), 7.20-7.44 (m, 4H), 6.95-7.10 (m, 2H), 6.29 (s,br, 1H), 5.53-5.71 (m, 1H), 2.42 (s, 3H), 2.02-2.40 (m, 4H), 1.5 (s,br, 8H).

2-(Cyclooct-1-enyl)aniline (3d)

Treatment of **2d** under the reaction conditions shown in Table 2 (entry 3) gave **3d** in 71% yield. bp 100-120°C at 0.25 mm Hg. ^{1}H NMR (90MHz) δ 6.88-7.10 (m, 2H), 6.58-6.80 (m, 2H), 5.70 (t, 1H, J=8.2), 3.42 (s, 1H, br), 2.50-2.60 (m, 4H), 1.40-1.70 (s, 8H, br); ^{13}C NMR (22.5MHz) δ 143.09, 139.39, 130.57, 130.10, 129.14, 127.47, 117.14, 115.14, 29.86, 29.27, 28.55, 26.76, 26.64, 26.47; IR (CCl_4) 3476w, 3385w, 3023w, 2926s, 2852m, 1613s, 1492m, 1467w, 1453m, 1291w; MS (70eV) *m/z* 201(M+,54), 173(25), 158(19), 146(12), 145(12), 144(50), 143(23), 133(14), 132(38), 131(30), 130(100), 119(14), 118(19), 117(23), 115(14), 106(23), 91(16), 77(13), 39(17). Exact mass calcd for $C_{14}H_{19}N$: 201.1517. Found: 201.1518.

4-Methyl-N-(2-(1-ethylbut-1-enyl)-phenyl)benzenesulfinamide (2e)

Benzothiazine **1h** gave **2e** as a mixture of isomers under the conditions shown in Table 1 (entry 8) in 95% yield. ^{1}H NMR (90 MHz) δ 7.66 (d, 4H, J=8.1), 6.97-7.55 (m, 12H), 6.36 (s,br, 1H), 6.18 (s,br, 1H), 5.25-5.51 (m, 2H), 2.42 (s, 6H), 2.03-2.55 (m, 6H), 1.63-1.79 (m, 2H), 0.711-1.17 (m, 12H).

2-(1-Ethylbut-1-enyl)aniline (3e)

Treatment of **2e** under the reaction conditions shown in Table 2 (entry 5) gave **3e** in 78% yield. bp 60-65°C at 0.2 mm Hg. ^{1}H NMR (90 MHz) δ 6.68-7.07 (m, 4H), 5.55 (t, 1/2H, J=2.1), 5.41 (t, 1/2H, J=2.1), 3.68 (s, 2H, br), 2.39 (q, 1H, J=7.5), 2.31-2.16(m, 2H), 1.85-1.81 (m, 1H), 1.08-0.89 (m, 6H); ^{13}C NMR (22.5MHz) δ 143.53, 143.20, 139.30, 138.92, 131.77, 130.20, 129.60, 129.39, 129.22, 127.49, 127.38,

127.17, 118.01, 115.19, 114.81, 31.17, 24.23, 22.28, 21.25, 14.54, 14.27, 13.24, 12.86; IR (CCl_4) 3479w, 3389w, 3064w, 3022w, 2966s, 2932m, 2873m, 1649w, 1612s, 1493s, 1452s, 1293m, 1258w; MS (70eV) *m/z* 175(M+, 53), 150(18), 147(12), 146(100), 145(12), 144(10), 132(14), 131(27), 130.00(26), 118(23), 117(18), 77(10). Exact mass calcd for $C_{12}H_{17}N$: 175.1361. Found: 175.1348.

(+/-)-(2S*,3S*,4S*)-3,4-Diethyl-3,4-dihydro-3-methyl-2-(4-methylphenyl)-2λ^4-2,1-benzothiazine-2-oxide (1i)

A flame-dried, roundbottomed flask equipped with a stir bar, septum and N_2 balloon was charged with (+/-)-(2S*,3S*,4S*)-3,4-diethyl-3,4-dihydro-2-(4-methylphenyl)-2λ4-2,1-benzothiazine-2-oxide[1] and sufficient dry THF and HMPA (20% by volume) were added to give a 0.2 M solution. The flask was placed in a dry ice/isopropanol bath and allowed to cool. n-BuLi (1.2 equiv.) was added followed after 5 min. by MeI (1.2 equiv.). Upon completion (TLC) the reaction was quenched with sat'd Na_2SO_3 and extracted with ethyl acetate. Purification by flash chromatography (hexanes/ethyl acetate, 7:1) gave **1i** in 95% yield. An analytical sample was obtained by recrystallization from hexanes/dichloromethane. mp 111°C; ^{1}H NMR (90MHz) 7.90 (d, 2H, J=8.3), 7.32 (d, 2H, J=8.3), 6.78-7.21 (m, 4H), 2.77-2.91 (m, 1H), 2.43 (s, 3H), 1.25-1.73 (m, 4H), 1.40 (s, 3H), 0.97 (t, 3H, J=7.1), 0.73 (t, 3H, J=7.3); ^{13}C NMR (22.5MHz) 144.52, 144.40, 133.14, 131.29, 129.32, 128.31, 127.77, 125.81, 123.18, 120.08, 63.77, 47.80, 26.05, 21.46, 21.10, 19.20, 14.07, 7.94; IR (CCl_4) 3066w, 3030w, 3013w, 2976m, 2935w, 2882w, 1598m, 1570w, 1479s, 1449s, 1402w, 1384w, 1378w, 1345w, 1325w, 1306s, 1297m, 1279s, 1228w, 1213m, 1204s, 1192m, 1180m, 1163w, 1154w, 1133w, 1123w, 1104w, 1094s, 1042w, 1024w, 1008s, 909s. Anal. Calcd for $C_{20}H_{25}NSO$: C, 73.35; H, 7.69. Found: C, 73.33; H, 7.81.

4-Methyl-N-(2-(1-ethyl-2-methylbut-1-enyl)-phenyl)benzenesulfinamide (2f)

Benzothiazine **1i** gave **2i** as a mixture of isomers under the conditions shown in Table 1 (entry 9) in 65% yield.. ^{1}H NMR (90MHz) 7.64 (d, 2H, J=8.1), 6.95-7.37 (m, 6H), 6.16 (s,br, 1H), 2.42 (s, 3H), 2.02-2.28 (m, 3H),1.62-1.94 (m, 3H), 1.28-1.47 (m, 1H), 0.72-1.08 (m, 7H).

2-(1-Ethyl-2-methylbut-1-enyl)aniline (3f)

Treatment of **2f** under the reaction conditions shown in Table 2 (entry 6) gave **3f** as a inseparable 1:2 mixture of isomers. bp 95-100°C at 0.15 mm Hg. ^{1}H NMR (300 MHz) δ 7.02-7.07 (m, 1H), 6.85-6.89 (m, 1H), 6.67-6.75 (m, 2H), 3.60 (s, 2H, br), 2.18-2.34 (m, 2xCH_2, major isomer) and 1xCH_2,minor isomer), 1.78-1.85 (m, 1xCH_2, minor), 1.81 (s, 3H, major), 1.48 (s, 3H, minor), 1.09 (t, 1xCH_3, minor), J=7.45), 0.99-0.84 (m, 1xCH_3, minor) and 1xCH_3, major); ^{13}C NMR (22.5MHz) δ 143.39, 134.98, 134.69, 132.78, 129.86, 129.56, 129.20, 127.12, 118.06, 117.94, 114.72, 28.49, 26.47, 26.11, 18.90, 16.40, 13.48, 13.30, 12.88, 12.70; IR (CCl_4) 3481m, 3478m, 3388m, 3074w, 3064w, 3051w, 3021m, 2966s, 2933s, 2892m, 2873s, 1611s, 1597m, 1577w, 1492s, 1461m, 1451s, 1372m, 1312w, 1293m, 1275w, 1258w, 1182w, 1156m, 1142w, 1131w, 1088w, 1071w, 1063w, 1052w, 1037w, 920w, 856w; MS (70 eV) *m/z* 189(M+,58), 174(25), 161(13), 160(100), 145(24), 144(22), 143(12), 132(30),131(21), 130(25), 118(12), 117(10), 77(10). Exact mass calcd for $C_{13}H_{19}N$: 189.1517. Found: 189.1498.

(+/-)-(5S*,4aS*,10bS*)-1,2,3,4,4a,10b-Hexahydro-4a-methyl-5-(4-methylphenyl)-5λ^4-dibenzo[c,e]-1,2-thiazine-5-oxide (1j)

The procedure was essentially identical as that for the preparation **1i**. Chromatographic purification (hexanes/ethyl acetate, 4:1) gave **1j** as a single isomer in 92 % yield. An analytical sample was obtained by recrystallization from hexanes/dichloromethane. mp 148-152°C; ^{1}H NMR (300MHz) δ 7.96 (d, 2H, J=8.0), 7.37 (d, 2H, J=8.1), 7.30 (d, 1H, J=7.8), 7.17 (t, 1H, J=7.3), 7.05 (d, 1H, J-7.9), 6.91 (d, 1H, J=7.5), 3.54 (s, 1H, br), 2.40-2.57 (m, 1H), 2.46 (s, 3H), 1.7-1.93 (m,2H), 1.49(s, 3H), 1.46-1.31(m, 4H), 1.01-1.06(m, 1H); ^{13}C NMR (22.5MHz) δ 144.88; 144.46, 131.53, 129.38, 128.84, 127.59, 126.58, 124.49, 122.95, 120.56, 55.61, 38.68, 28.20, 23.67, 21.58, 21.34, 19.55, 18.18; IR (CCl_4) 3065w, 3033w, 3028w, 3023w, 2978w, 2948m, 2892w, 2889w, 2866w, 1598w, 1483m, 1474w, 1470w, 1446s, 1317m, 1304m, 1297m, 1283s, 1275s, 1264w, 1246s, 1214m, 1203s, 1181m, 1158w, 1132m, 1116m, 1105s, 1095w, 1050m, 1028w, 1013s, 909s; MS (70eV) *m/z* 326(M+1, 15), 325(M+, 73), 187.15(17),

186.10(100), 184.10(10), 171.10(23), 170.10(25), 156.10(11), 145.10(12), 143(21), 131(13), 130(48), 91(13), 77(12). Exact mass calcd for $C_{20}H_{23}NOS$: 325.1500. Found: 325.1506.

4-Methyl-N-(2-(2-methylcyclohex-1-enyl)-phenyl)benzenesulfinamide (2g)

Benzothiazine **1j** gave **2g** under the conditions shown in Table 1 (entry 10) in 59% yield. ^1H NMR (90 MHz) δ 6.92-7.78 (m, 8H), 6.06-6.25 (m, 1H), 2.49 (s, 3H), 0.72-2.28 (m, 11H).

2-(2-Methyl-cyclohex-1-enyl)aniline (3g)

Treatment of **2g** under the reaction conditions shown in Table 2 (entry 7) gave **3g** in 89% yield. bp 100-105°C at 0.15 mm Hg. ^1H NMR (300 MHz) δ 7.09-7.03 (m, 1H), 6.91-6.88 (dd, 1H, J=1.6, J=7.5), 6.67-6.77 (m, 2H), 3.62 (s, 2H, br), 2.15-2.08 (m, 4H), 1.67-1.76 (m, 4H), 1.47 (s, 3H); ^{13}C NMR (22.5MHz) δ 142.87, 131.17, 129.80, 128.96, 127.20, 118.29, 114.78, 31.09, 30.77, 23.48, 23.16, 20.23; IR (CCl_4) 3477m, 3385m, 3073w, 3065w, 3052m, 3021m, 2980m, 2928s, 2887s, 2873s, 2857s, 2833s, 1610s, 1576m, 1493s, 1453s, 1447s, 1378m, 1315w, 1292s, 1276m, 1264m, 1244w, 1198w, 1156m, 1144m, 1110w, 1050w, 1036w, 1014w, 1005w, 934w, 909s, 893w, 872w, 840w; MS (70eV) *m/z* 187(M+, 70), 172(47), 158(19), 145(18), 144(100), 143(23), 131(12), 130(39), 119(27), 117(11), 115(12), 106(19), 77(15), 65(10), 39(11). Exact mass calcd for $C_{13}H_{17}N$: 187.1361. Found: 187.1356.

References and Notes

1. Harmata, M.; Claassen II, R.J.; Barnes, C.L. *J. Org. Chem.* **1991**, *56*, 0000.
2. (a) Johnson, C.R. *Aldrichimica Acta* **1985**, *18*, 3-10. (b) Johnson, C.R. In *Comprehensive Organic Chemistry* Jones, N.D. Ed.; Pergamon Press: Oxford, 1979; Vol. 3, Chapter 11. (c) Kennewell, P.E.; Taylor, J.B. *Chem Soc. Rev.* **1975**, *4*, 189-209.
3. Little, R.D.; Myong, S.O. *Tetrahedron Lett.* **1980**, *21*, 3339-3342.
4. Harmata, M.; Herron, B.F. Unpublished results from these laboratories.
5. For example, using the procedure depicted in equation 1, **1a**, **1d**, and **1h** gave the corresponding indoles in 35%, 10% and 0% yields, respectively.
6. (a) Harrington, P.J.; Hegedus, L.S. *J. Org. Chem.* **1984**, *49*, 2657-2662. (b) Harrington, P.J.; Hegedus, L.S. McDaniel, K.F. *J. Am. Chem. Soc.* **1987**, *109*, 4335-4338. (c) Kametani, T.; Kasai, H. In *Studies in Natural Product Chemistry* Rahman, A.-ur-, Ed.; Elsevier: Amsterdam, 1989; Vol. 3 Part B pp. 395-396. (d) Qiang, L.G.; Baine, N.H. *Tetrahedron Lett.* **1988**, *29*, 3517-3520. (e) Qiang, L.G.; Baine, N.H. *J. Org. Chem.* **1988**, *53*, 4218-4222. (f) Singermann, G.M. In *The Chemistry of Heterocyclic Compounds* Castle, R.N., Ed.; John Wiley and Sons: New York, Vol. 27, Chapter 1, pp. 19-20. (g) Padwa, A.; Nahm, S. *J. Org. Chem.* **1981**, *46*, 1402-1409.
7. (a) Magnus, P.D.; Sear, N.L. *Tetrahedron* **1984**, *40*, 2795-2797. (b) Jiang, J.B.; Hesson, D.P.; Dusak, B.A.; Dexter, D.L.; Kang, G.J.; Hamel, E. *J. Med. Chem.* **1990**, *33*, 1721-1728. (c) Subramanyam, C.; Noguchi, M.; Weinreb, S.M. *J. Org. Chem.* **1989**, *54*, 5580-5585.
8. (a) Gassman, P.G.; Drewes, H.R. *J. Am. Chem. Soc.* **1978**, *100*, 7600-7610. (b) Horino, H.; Inoue, W. *Tetrahedron Lett.* **1979**, *20*, 2403-2406. (c) Fleming, I.; Loreto, J.A.; Wallace, I.H.M. *J. Chem. Soc. Perkin Trans. I* **1986**, 349-359. (d) Pleuyak, J.E.; Heck, R.F. J. Org. Chem. 1978, 43, 2454-2456.
9. The product mixture was compared with authentic samples of each possible stereoisomer using HPLC.
10. NMR and HPLC analysis suggested that epimerization at carbon 3 occurred during this reaction.
11. The chemical shift of substituents on styrenes and stilbenes are well known to be subject to conformational effects. The methyl shifts for (Z) and (E) isomer of 1-methyl-2-(1-propenyl)-benzene are 1.75 ppm and 1.90 ppm, respectively. See: Tiecco, M.; Tingoli, M.; Wenkert, E. *J. Org. Chem.* **1985**, *50*, 3828-3831.
12. Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also supported in part by a Weldon Spring Award (880WS-051) from the University of Missouri-Columbia. We are grateful to the National Science Foundation for partial support of the NMR (PCM-8115599) and MS (PCM-8117116) at the University of Missouri-Columbia.