New Entries to 2(1*H*)-Quinolinones and 2*H*-1-Benzazepin-2-ones by Acid-Catalyzed Olefin Cyclization of *N*-[*o*-(Alk-1-enyl)phenyl]-2-(methylsulfinyl)acetamides

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Treatment of *N*-[*o*-(alk-1-enyl)phenyl]-2-(methylsulfinyl)acetamides with trifluoroacetic anhydride gave 2(1*H*)-quinolinones or 2*H*-1-benzazepin-2-ones, depending upon the position of the substituents on the alkene double bond.

Keywords cationic cyclization; sulfoxide; 2(1*H*)-quinolinone; carbostyril; 2*H*-1-benzazepin-2-one; Pummerer rearrangement; α-thiocarbocation

Previously we reported the synthesis of oxindoles,[1,2] tetrahydroisoquinolin-3-ones,[1] and tetrahydro-2*H*-3-benzazepin-2-ones[3] by means of acid-catalyzed aromatic cyclization of α-sulfinylacetamides. We also demonstrated efficient routes to various types of five- and six-membered lactams by acid-catalyzed olefin cyclization of *N*-(prop-2-enyl)-2-sulfinylacetamides.[4] These reactions can be formulated as proceeding *via* α-thiocarbocations, which undergo cyclization with a phenyl ring or an olefinic double bond. As a logical extension of these studies, we examined the behavior of the α-thiocarbocations generated from *N*-[*o*-(alk-1-enyl)phenyl]-2-(methylsulfinyl)acetamides **3** under the Pummerer reaction conditions, with the hope of developing new routes to the pharmacologically important 2(1*H*)-quinolinone(carbostyril) and 2*H*-1-benzazepin-2-one systems.

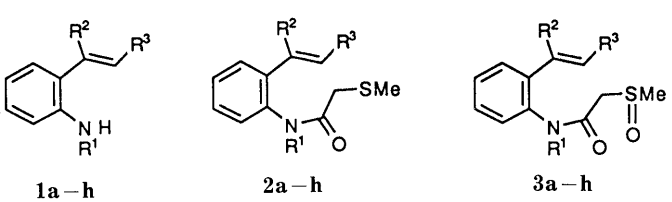
The 2-(methylsulfinyl)acetamides **3a**—**h** employed in this study were synthesized from the corresponding anilines or tosylanilides by standard methods (see Experimental).

When the sulfoxide **3a** was treated with a stoichiometric amount of trifluoroacetic anhydride (TFAA) in dichloromethane at 0 °C (method A), 4-ethenyl-3,4-dihydro-1-methyl-3-methylthio-2(1*H*)-quinolinone (**7a**) was obtained as an inseparable diastereomeric mixture (26 : 74) in 80% combined yield. The infrared (IR) spectrum of the mixture showed bands at 1675 (a lactam carbonyl), and the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum revealed a multiplet due to three vinylic protons between δ 4.65 and 6.3. The *trans*-stereochemistry was assigned to the major product on the basis of the fact that the diastereomeric mixture was transformed into the 4-ethenyl-2(1*H*)-quinolinone **8a** in 38% yield by oxidation with $NaIO_4$ followed by heating of the resulting sulfoxide in toluene.[5]

A similar treatment of the *N*-tosylsulfoxide **3b** yielded only a Pummerer reaction product **5** [IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790 ($OCOCF_3$)]. However, after evaporation of the solvent (dichloromethane), the trifluoroacetate **5** was dissolved in trifluoroacetic acid (TFA) and the mixture was stirred at room temperature to yield the 3,4-dihydro-2(1*H*)-quinolinone **7b** as an inseparable diastereomeric mixture (28 : 72) in 97% combined yield (method B). In practice, the reaction was carried out in TFA as a solvent instead of dichloromethane (method C) to give directly **7b** in 94% yield. The stereochemistry of the major product of **7b** was assigned as *trans* again by oxidative desulfurization of the diastereomeric mixture to give the 4-ethenyl-2(1*H*)-quinolinone **8b** (59% yield).

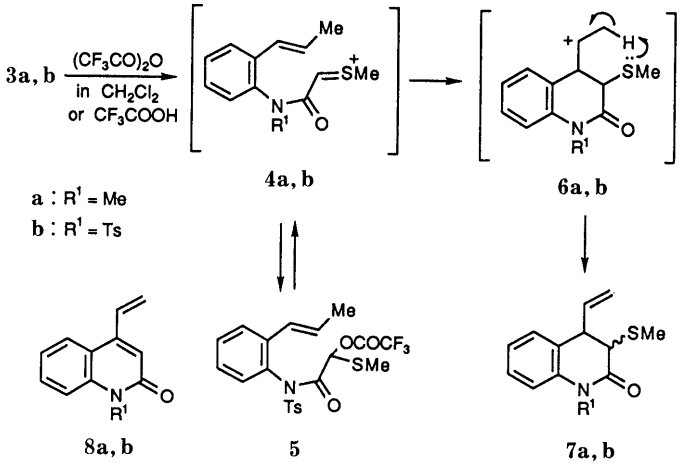
The formation of **7a, b** can be rationalized in terms of an intramolecular polar "ene" reaction[6] as shown in Chart 1. The sulfoxides **3a, b** are initially converted into the α-thiocarbocations **4a, b**. The trifluoroacetate **5** once formed is also labile in TFA to yield **4b**. These intermediates **4a, b** then undergo a 6-*exo* closure followed by regioselective proton abstraction from the newly formed carbocations **6a, b** with the aid of the sulfur atom through six-membered transition states, giving **7a, b**.

In contrast, cyclization of the *N*-[*o*-(1-methylethenyl)-phenyl]acetamide **3c** (method A) gave the 7-*endo* products, 2*H*-1-benzazepin-2-one **9c** (74%) and trifluoroacetate **10** (24%). Cyclization of the *N*-tosylsulfoxide **3d** (method C) gave exclusively **9d** in quantitative yield. The structures of the products **9c, d** were determined on the basis of spectroscopic and chemical evidence. For example, the ^{1}H-NMR spectrum of **9c** showed a 5-methyl signal at δ



1a—h **2a—h** **3a—h**

a : $R^1 = R^3 = Me$, $R^2 = H$
b : $R^1 = Ts$, $R^3 = Me$, $R^2 = H$
c : $R^1 = R^2 = Me$, $R^3 = H$
d : $R^1 = Ts$, $R^2 = Me$, $R^3 = H$
e : $R^1 = Me$, $R^2 = Ph$, $R^3 = H$
f : $R^1 = Ts$, $R^2 = Ph$, $R^3 = H$
g : $R^1 = Me$, $R^2 = R^3 = H$
h : $R^1 = Ts$, $R^2 = R^3 = H$



3a, b $\xrightarrow[\text{in } CH_2Cl_2 \text{ or } CF_3COOH]{(CF_3CO)_2O}$ **4a, b** → **6a, b**

a : $R^1 = Me$
b : $R^1 = Ts$

8a, b **5** **7a, b**

Chart 1

2.20 (d, $J=1.5$ Hz), and two broad signals due to 3-H and an olefinic proton in the regions of δ 3.0—4.0 (1H) and 5.6—5.95 (1H), respectively. Reduction of **9c** with Raney nickel gave 1,3,4,5-tetrahydro-1,5-dimethyl-2*H*-1-benzazepin-2-one (**11**). The trifluoroacetate **10** showed a band at 1780 cm^{-1} ($OCOCF_3$) in the IR spectrum, and lacked an olefinic proton signal but, instead, showed a methyl singlet at δ 2.03 and a multiplet due to methylene and methine protons between δ 2.3 and 3.7 (3H) in the ^{1}H-NMR spectrum. Hydrolysis of **10** with potassium carbonate in aqueous methanol gave the alcohol **12**.

Treatment of the 1-phenyl congeners **3e** and **3f** with TFAA gave only the 2*H*-1-benzazepin-2-ones **13e, f** (7-*endo* products) in 100 and 60% yields, respectively. Reduction of **13e** with Raney nickel gave the known 2*H*-1-benzazepin-2-one **14**.[7]

The cyclization of **3c—f** involves tertiary cationic intermediates **15**, which are then deprotonated to give the benzazepinones **9** and **13**. The isolation of the trifluoroacetate **10** provides clear evidence for involvement of the carbocation **15**.

An attempted cyclization of the *N*-(*o*-ethenylphenyl)acetamide **3g**, however, produced only the bis(methylthio)acetal **16** in 34% yield: cyclized products could not be detected. Treatment of the *N*-tosylsulfoxide **3h** with TFAA resulted in the formation of the hydrolysis product **1h** in 81% yield. Failure of the cyclization of **3g** and **3h** may be attributed to the low nucleophilicity of the ethenyl group.

For the *N*-[*o*-(alk-1-enyl)phenyl]acetamide substrates, ring-closures to both six- (6-*exo*) and seven-membered (7-*endo*) rings are recognized as "favored" processes.[8] Our results suggest that the 6-*exo* closure is favored over the 7-*endo* closure in the cyclization of the *N*-[*o*-(alk-1-enyl)phenyl]acetamide derivatives **3**, unless very stable carbocation intermediates such as tertiary carbocations are involved. The presence of methyl substitution at the 2-position of the alkene leads exclusively to the six-membered rings (6-*exo* products). At first glance, the 7-*endo* closure appears to be preferred to the 6-*exo* closure, since the former would involve a benzylic cation and the latter, a secondary cationic intermediate. Models indicate, however, that there is decreased interaction between the *p*-orbital of the benzylic cationic center and the π-system of the benzene ring due to steric interference with the *o*-acylamino group, so that the phenyl ring cannot help stabilize the developing carbocation at the benzylic position. Consequently, there is no particular preference for 7-*endo* closure. On the other hand, methyl or phenyl substitution at C-1 leads exclusively to the seven-membered rings (7-*endo* products), because the formation involves the more stable tertiary carbocation intermediates (in the case of the 1-phenyl derivative, the transition state is further stabilized by the 1-phenyl group).

In summary, our study has provided novel approaches to the 2(1*H*)-quinolinones and 2*H*-1-benzazepin-2-ones. The size of the ring formed is greatly influenced by the position of the substituent on the alkene double bond, but is usually predictable.

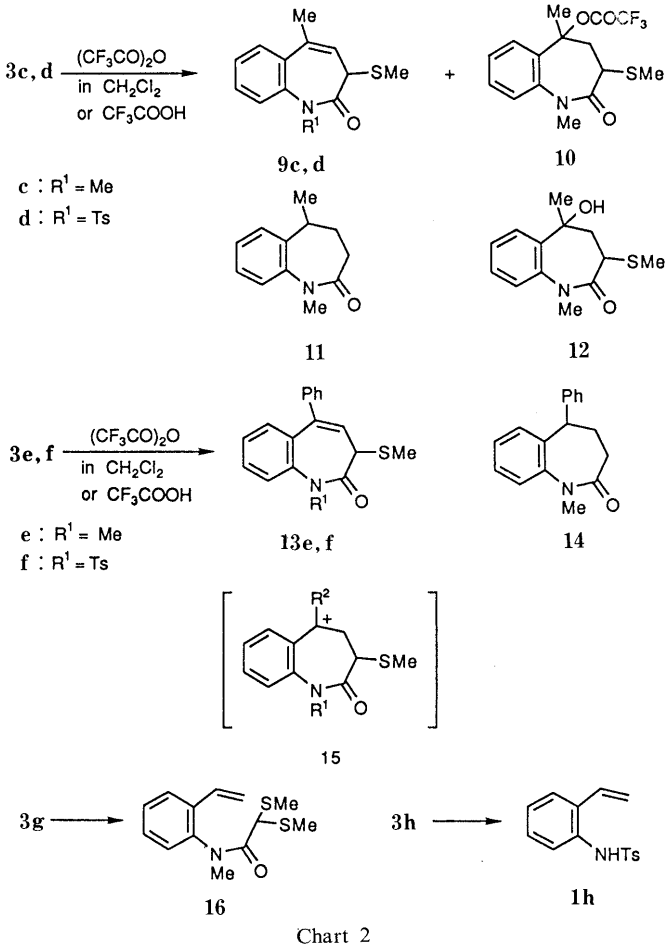


Chart 2

Experimental

IR spectra were recorded with a JASCO IRA-100 spectrophotometer. ^{1}H-NMR spectra were determined with a JEOL JNM-PMX 60 (60 MHz) or a Varian XL-300 (300 MHz) spectrometer in $CDCl_3$, and δ values are given relative to tetramethylsilane. Exact mass spectra (MS) were obtained on a Hitachi M-80 instrument operating at 20 eV. Chromatographic separation was performed with Silica gel 60 PF_{254} (Merck) under pressure.

Materials *o*-Ethenylaniline,[9] *o*-ethenyl-*N*-methylaniline (**1g**),[10] *o*-(prop-1-enyl)aniline,[11] *N*-methyl-*o*-(prop-1-enyl)aniline (**1a**),[12] *o*-(1-methylethenyl)aniline,[13] *N*-methyl-*o*-(1-methylethenyl)aniline (**1c**),[14] and *o*-(1-phenylethenyl)aniline[15] were prepared according to the reported procedures.

***N*-Methyl-*o*-(1-phenylethenyl)aniline (1e)** Dicyclohexylcarbodiimide (DCC) (7.26 g, 35.2 mmol) was added to a solution of *o*-(1-phenylethenyl)aniline (4.30 g, 23.5 mmol),[15] formic acid (1.28 g, 27.9 mmol), and 4-(dimethylamino)pyridine (DMAP) (0.144 g, 1.17 mmol) in AcOEt (50 ml) and the solution was stirred at room temperature for 16 h. The precipitated dicyclohexylurea was filtered off, then the filtrate was washed with 5% HCl, brine, and saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 9 : 2) to give crystalline *o*-(1-phenylethenyl)formanilide (4.6 g, 93%), which was immediately used for the next stage.

A solution of the formanilide (2.55 g, 12.1 mmol) in tetrahydrofuran (THF) (10 ml) was added dropwise to a suspension of lithium aluminum hydride (595 mg, 15.7 mmol) in dry ether (60 ml) at 0 °C and the mixture was stirred at room temperature for 16 h. Usual work-up gave a crude oily material which was purified by chromatography on silica gel (hexane–AcOEt, 20 : 1) to give **1e** (1.20 g, 51%) as an oil. ^{1}H-NMR ($CDCl_3$) δ: 2.64 (3H, s, NMe), 3.4—3.9 (1H, br, NH), 5.27, 5.74 (1H each, ABq, $J=2$ Hz, $C=CH_2$), 6.5—7.4 (9H, m, aromatic H). *Anal.* Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.88; H, 7.05; N, 6.65.

General Procedure for the Preparation of *N*-[*o*-(Alk-1-enyl)phenyl]-*N*-methyl-2-(methylthio)acetamides (2a, c, e, g) A solution of DCC (795 mg, 3.85 mmol) in AcOEt (3 ml) was added dropwise to a solution of an appropriate *N*-methylaniline derivative (2.57 mmol), (methylthio)acetic acid (324 mg, 3.06 mmol), and DMAP (31 mg, 0.27 mmol) in AcOEt (3 ml) at 0 °C and the mixture was stirred at room temperature for 16 h. The precipitated dicyclohexylurea was filtered off, and the filtrate was washed

with 10% HCl, brine, and saturated $NaHCO_3$ solution, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 4:1) to give the acetamide. The following compounds were thus obtained. *cis*- and *trans*-*N*-Methyl-2-(methylthio)-*N*-[*o*-(prop-1-enyl)phenyl]acetamide (**2a**, 24%), an oil. Exact MS *m/z*: Calcd for $C_{13}H_{17}NOS$: 235.1029. Found: 235.1015. *N*-Methyl-*N*-[*o*-(1-methylethenyl)phenyl]-2-(methylthio)acetamide (**2c**, 51%), mp 54.5—56 °C (from hexane). *Anal.* Calcd for $C_{13}H_{17}NOS$: C, 66.35; H, 7.28; N, 5.95. Found: C, 66.04; H, 7.54; N, 5.53. *N*-Methyl-2-(methylthio)-*N*-[*o*-(1-phenylethenyl)phenyl]acetamide (**2e**, quant.), an oil, which was used for the next stage without further purification. *N*-(*o*-Ethenylphenyl)-*N*-methyl-2-(methylthio)acetamide (**2g**, 93%), an oil. Exact MS *m/z*: Calcd for $C_{12}H_{15}NOS$: 221.0873. Found: 221.0896.

Preparation and Cationic Cyclization of *cis*- and *trans*-*N*-Methyl-2-(methylsulfinyl)-*N*-[*o*-(prop-1-enyl)phenyl]acetamide (3a) A solution of $NaIO_4$ (280 mg, 1.31 mmol) in water (3 ml) was added dropwise to a solution of the sulfide **2a** (280 mg, 1.19 mmol) in acetone (8 ml) at 0 °C and the mixture was stirred at room temperature for 16 h. The precipitate was filtered off and the filtrate was concentrated. The residue was dissolved in chloroform and the solution was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (AcOEt) to give the sulfoxide **3a** (267 mg, 89%), which was used for the next stage without further purification.

Method A: TFAA (167 mg, 0.88 mmol) was added dropwise to a solution of the sulfoxide **3a** (200 mg, 0.80 mmol) in dry dichloromethane (4 ml) at 0 °C and the mixture was stirred at room temperature for 30 min. The solvent was evaporated off and the residue was chromatographed on silica gel (hexane–AcOEt, 7:1) to give a mixture of *cis*- and *trans*-4-ethenyl-3,4-dihydro-1-methyl-3-(methylthio)-2(1*H*)-quinolinone (**7a**, 150 mg, 80%) [26:74, determined from the ^{1}H-NMR spectrum (300 MHz)] as an oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1675. ^{1}H-NMR ($CDCl_3$) δ: 2.22 (3H, s, SMe), 3.36 (3H, s, NMe), 3.45—3.71 (2H, m, 3- and 4-H), 4.65—6.3 (3H, m, CH=CH_2), 6.8—7.45 (4H, m, aromatic H). Exact MS *m/z*: Calcd for $C_{13}H_{15}NOS$: 233.0873. Found: 233.0894.

4-Ethenyl-1-methyl-2(1*H*)-quinolinone (8a) Using a procedure similar to that described for the preparation of **3a**, the sulfide **7a** (150 mg, 0.64 mmol) was oxidized with $NaIO_4$ (152 mg, 0.71 mmol) to give the crude sulfoxide, which was dissolved in toluene (5 ml). $NaHCO_3$ (134 mg, 1.6 mmol) was added and the whole was refluxed for 2 h. After cooling, the insoluble material was filtered off and the filtrate was concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 9:2) to give **8a** (45 mg, 38%), which appeared to be oxidized upon exposure to air, thus precluding elemental analysis. ^{1}H-NMR ($CDCl_3$) δ: 3.70 (3H, s, NMe), 5.58 (1H, dd, J=11.0, 2.0 Hz, one of CH=C$\underline{H}_2$), 5.82 (1H, dd, J=17.5, 2.0 Hz, one of CH=C$\underline{H}_2$), 6.7—7.9 (6H, m, aromatic and olefinic H).

Preparation and Cationic Cyclization of *N*-Methyl-2-(methylsulfinyl)-*N*-[*o*-(1-methylethenyl)phenyl]acetamide (3c) Using a procedure similar to that described for the preparation of **3a**, the sulfide **2c** (500 mg, 2.12 mmol) was oxidized with $NaIO_4$ (500 mg, 2.34 mmol) to give **3c** (450 mg, 84%), mp 124—125 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 62.06; H, 6.85; N, 5.53.

Following method A, the sulfoxide **3c** (300 mg, 1.19 mmol) was treated with TFAA (276 mg, 1.31 mmol) in dichloromethane (5 ml) and the crude material was chromatographed on silica gel (hexane–AcOEt, 7:1). The first fraction gave 1,3-dihydro-1,5-dimethyl-3-methylthio-2*H*-1-benzazepin-2-one (**9c**, 205 mg, 74%), mp 67—68.5 °C (from hexane–AcOEt). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1680. ^{1}H-NMR ($CDCl_3$) δ: 2.10 (3H, s, SMe), 2.20 (3H, d, J=1.5 Hz, 5-Me), 3.0—4.0 (1H, br, 3-H), 3.38 (3H, s, NMe), 5.6—5.95 (1H, br, 4-H), 7.0—7.6 (4H, m, aromatic H). *Anal.* Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.48; N, 6.00. Found: C, 66.79; H, 6.76; N, 5.97. The second fraction gave the trifluoroacetate **10** (98 mg, 24%) as an oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1780 (OCOCF$_3$), 1685 (lactam carbonyl). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, 5-Me), 2.07 (3H, s, SMe), 2.3—3.7 (3H, m, 3-H, 4-H_2), 3.27 (3H, s, NMe), 7.1—7.6 (4H, m, aromatic H). Since the trifluoroacetate **10** was labile, the structure was confirmed after conversion into the corresponding alcohol.

Hydrolysis of the Trifluoroacetate 10 A solution of **10** (70 mg, 0.20 mmol) and potassium carbonate (70 mg, 0.50 mmol) in methanol (4 ml) and water (3 ml) was stirred at room temperature for 1 h. Methanol wasevaporated off and the aqueous layer was extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 9:2) to give 1,3,4,5-tetrahydro-5-hydroxy-1,5-dimethyl-3-methylthio-2*H*-1-benzazepin-2-one (**12**, 36 mg, 72%), mp 164—166 °C (from hexane–AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.76 (3H, s, 5-Me), 2.02 (3H, s, SMe), 2.46 (2H, d, J=9 Hz, 4-H_2), 3.03 (1H, br s, OH), 3.31 (3H, s, NMe), 3.54 (1H, d, J=9 Hz, 3-H), 7.1—7.6 (4H, m, aromatic H). *Anal.* Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.57. Found: C, 61.82; H, 7.00; N, 5.46.

1,3,4,5-Tetrahydro-1,5-dimethyl-2*H*-1-benzazepin-2-one (11) A suspension of **9c** (100 mg, 0.42 mmol) and Raney Ni (*ca.* 1 g) in ethanol (5 ml) was refluxed for 3 h. The catalyst was filtered off, and the filtrate was concentrated to give **11** (72 mg, 91%) as an oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1665. ^{1}H-NMR ($CDCl_3$) δ: 1.25—3.4 (5H, m), 1.34 (3H, d, J=6.5 Hz, 5-Me), 3.33 (3H, s, NMe), 7.21 (4H, br s, aromatic H). Exact MS *m/z*: Calcd for $C_{12}H_{15}NO$: 189.1152. Found: 189.1126.

Preparation and Cyclization of *N*-Methyl-*N*-[*o*-(1-phenylethenyl)phenyl]-2-(methylsulfinyl)acetamide (3e) Using a procedure similar to that described for the preparation of **3a**, the sulfide **2e** (360 mg, 1.21 mmol) was oxidized with $NaIO_4$ (285 mg, 1.33 mmol) in aqueous acetone to give a crude material, which was chromatographed on silica gel (AcOEt) to give **3e** (360 mg, 95%) as an oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1655, 1060. ^{1}H-NMR ($CDCl_3$) δ: 2.5—3.75 (2H, m, $COCH_2S$), 2.57, 2.76 (total 3H, 2×s, SOMe), 2.70 (3H, s, NMe), 5.3—5.45 (1H, m, one of C=CH_2), 5.6—5.7 (1H, m, one of C=CH_2), 7.0—7.65 (9H, m, aromatic H).

Following method A, the sulfoxide **3e** (360 mg, 1.15 mmol) was treated with TFAA (265 mg, 1.26 mmol) in dichloromethane (5 ml) and work-up gave a crude material, which was chromatographed on silica gel (hexane–AcOEt, 9:2) to give 1,3-dihydro-1-methyl-3-methylthio-5-phenyl-2*H*-1-benzazepin-2-one (**13e**, 345 mg, quant.), mp 112—114 °C (from hexane–AcOEt). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1680. ^{1}H-NMR ($CDCl_3$) δ: 2.18 (3H, s, SMe), 3.47 (3H, s, NMe), 3.67 (1H, br d, J=6.5 Hz, 3-H), 6.10 (1H, br d, J=6.5 Hz, 4-H), 7.05—7.5 (9H, m, aromatic H). *Anal.* Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.11; H, 5.98; N, 4.69.

1,3,4,5-Tetrahydro-1-methyl-5-phenyl-2*H*-1-benzazepin-2-one (14) A suspension of **13e** (86 mg, 0.29 mmol) and Raney Ni (*ca.* 1 g) in ethanol (5 ml) was refluxed for 3 h. Usual work-up gave **14** (74 mg, quant.), mp 102—103.5 °C (from hexane) (lit.[7] mp 102—104 °C).

Preparation and Attempted Cyclization of *N*-(*o*-Ethenylphenyl)-*N*-methyl-2-(methylsulfinyl)acetamide (3g) Using a procedure similar to that described for the preparation of **3a**, the sulfide **2g** (100 mg, 0.45 mmol) was oxidized with $NaIO_4$ (212 mg, 1.00 mmol) to give **3g** (90 mg, 84%) as an oil, which was used for the next stage without further purification.

Following method C, the sulfoxide **3g** (90 mg, 0.38 mmol) was treated with TFAA (88 mg, 0.41 mmol) to give *N*-(*o*-ethenylphenyl)-*N*-methyl-2,2-bis(methylthio)acetamide (**16**) (34 mg, 34%) as an oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1665. ^{1}H-NMR ($CDCl_3$) δ: 2.07, 2.10 (3H each, 2×s, 2×SMe), 3.20 (3H, s, NMe), 4.05 (1H, s, CHCO), 5.39 (1H, dd, J=10.5, 2.0 Hz), 5.75 (1H, dd, J=17.5, 2.0 Hz), 6.80 (1H, dd, J=17.5, 10.5 Hz), 6.9—7.8 (4H, m, aromatic H). Exact MS *m/z*: Calcd for $C_{13}H_{17}NOS_2$: 267.0751. Found: 267.0761.

General Procedure for the Preparation of *p*-Toluenesulfonamides (1b, d, f, h) *p*-Toluenesulfonyl chloride (677 mg, 3.55 mmol) was added portionwise to a solution of an appropriate aniline derivative (2.37 mmol) in pyridine (2 ml) and the mixture was stirred at room temperature for 16 h. Dichloromethane (10 ml) was added and the whole was washed with 10% HCl and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 3:1) to give the sulfonamide. The following compounds were thus prepared. *N*-[*o*-(Prop-1-enyl)phenyl]-*p*-toluensulfonamide (**1b**, 82% from *o*-(prop-1-enyl)aniline), mp 129—132 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.70; H, 5.98; N, 4.73. *N*-[*o*-(1-Methylethenyl)phenyl]-*p*-toluenesulfonamide (**1d**, 97% from *o*-(1-methylethenyl)aniline], mp 76—78 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.70; H, 6.17; N, 5.08. *N*-[*o*-(1-Phenylethenyl)phenyl]-*p*-toluenesulfonamide (**1f**, 70% from *o*-(1-phenylethenyl)aniline), mp 89—91 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.00. Found: C, 72.00; H, 5.48; N, 3.92. *N*-(*o*-Ethenylphenyl)-*p*-toluenesulfonamide (**1h**, 87% from *o*-ethenylaniline), mp 120—122 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{15}H_{15}NO_2S$: C, 65.91; H, 5.53; N, 5.12. Found: C, 66.02; H, 5.63; N, 5.25.

General Procedure for the Preparation of *N*-[*o*-(Alk-1-enyl)phenyl]-*N*-[2-(methylthio)acetyl]-*p*-toluenesulfonamides (2b, d, f, h) An appropriate *p*-toluenesulfonamide (1.40 mmol) was added to a suspension of NaH (60% in oil, 278 mg, 6.96 mmol; washed with dry hexane before use) in dry benzene (15 ml) and the mixture was stirred at room temperature for 30 min. A solution of (methylthio)acetyl chloride (346 mg, 2.78 mmol) in benzene (5 ml) was added to the above solution and the whole was refluxed for 2 h, then allowed to cool. Water was added, and the organic layer was

separated. The aqueous layer was extracted with dichloromethane. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 7:1) to give the sulfide. The following compounds were thus obtained. *cis*- and *trans*-*N*-[2-(Methylthio)acetyl]-*N*-[*o*-(prop-1-enyl)phenyl]-*p*-toluenesulfonamide (**2b**, quant. from **1b**), mp 138—140 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{19}H_{21}NO_3S_2$: C, 60.77; H, 5.64; N, 3.73. Found: C, 60.77; H, 5.73; N, 3.54. *N*-[*o*-(1-Methylethenyl)phenyl]-*N*-[2-(methylthio)acetyl]-*p*-toluenesulfonamide (**2d**, 97% from **1d**), mp 109.5—111 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{19}H_{21}NO_3S_2$: C, 60.77; H, 5.64; N, 3.73. Found: C, 60.68; H, 5.61; N, 3.70. *N*-[2-(Methylthio)acetyl]-*o*-(1-phenylethenyl)phenyl-*p*-toluenesulfonamide (**2f**, 72% from **1f**), mp 136—138 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{24}H_{23}NO_3S_2$: C, 65.89; H, 5.30; N, 3.20. Found: C, 65.87; H, 5.34; N, 2.99. *N*-(*o*-Ethenylphenyl)-*N*-[2-(methylthio)acetyl]-*p*-toluenesulfonamide (**2h**, 86% from **1h**), mp 108—110 °C (from hexane–benzene). *Anal.* Calcd for $C_{18}H_{19}NO_3S_2$: C, 59.81; H, 5.30; N, 3.87. Found: C, 60.26; H, 5.42; N, 4.27.

General Procedure for the Preparation of *N*-[*o*-(Alk-1-enyl)phenyl]-*N*-[2-(methylsulfinyl)acetyl]-*p*-toluenesulfonamides (3b, d, f, h) A solution of *m*-chloroperoxybenzoic acid (MCPBA) (80%, 241 mg, 1.12 mmol) in dichloromethane (3 ml) was added to a solution of an appropriate sulfide (1.12 mmol) in dichloromethane (5 ml) at 0 °C and the mixture was stirred at room temperature for 10 min. The reaction mixture was washed with saturated $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (AcOEt) to give the sulfoxide. The following compounds were thus prepared. *cis*- and *trans*-*N*-[2-(Methylsulfinyl)acetyl]-*N*-[*o*-(prop-1-enyl)phenyl]-*p*-toluenesulfonamide (**3b**, 87% from **2b**), mp 151.5—153.5 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{19}H_{21}NO_4S_2$: C, 58.29; H, 5.41; N, 3.58. Found: C, 58.03; H, 5.54; N, 3.52. *N*-[*o*-(1-Methylethenyl)phenyl]-*N*-[2-(methylsulfinyl)acetyl]-*p*-toluenesulfonamide (**3d**, quant. from **2d**), mp 138—140 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{19}H_{21}NO_4S_2$: C, 58.29; H, 5.41; N, 3.58. Found: C, 58.07; H, 5.39; N, 3.67. *N*-[2-(Methylsulfinyl)acetyl]-*N*-[*o*-(1-phenylethenyl)phenyl]-*p*-toluenesulfonamide (**3f**, 94% from **2f**), mp 172—174 °C (from benzene–AcOEt). *Anal.* Calcd for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.09. Found: C, 63.81; H, 5.49; N, 3.12. *N*-(*o*-Ethenylphenyl)-*N*-[2-(methylsulfinyl)acetyl]-*p*-toluenesulfonamide (**3h**, 89% from **2h**), mp 142—144 °C (from hexane–AcOEt). *Anal.* Calcd for $C_{18}H_{19}NO_4S_2$: C, 57.28; H, 5.07; N, 3.71. Found: C, 57.14; H, 5.18; N, 3.62.

Cyclization of the *N*-Tosylsulfoxide 3b Method B: TFAA (144 mg, 0.69 mmol) was added dropwise to a solution of the sulfoxide **3b** (256 mg, 0.65 mmol) in dichloromethane (5 ml) at 0 °C and the mixture was stirred at room temperature for 30 min. The solvent was evaporated off to give the Pummerer rearrangement product **5** (345 mg) as an oil. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1790, 1715. ^{1}H-NMR ($CDCl_3$) δ: 1.65—2.3 (3H, m, CH=CHMe), 1.98, 2.10 (total 3H, 2×s, SMe), 2.44 (3H, s, Ar-Me), 5.61, 5.73 (total 1H, 2×s, COCH), 5.9—7.1 (10H, m).

Compound **5** was dissolved in TFA (1 ml) and the solution was allowed to stand at room temperature for 1.5 h. Dichloromethane (10 ml) was added and the solution was washed with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane–AcOEt, 9:2) to give a mixture of *cis*- and *trans*-4-ethenyl-3,4-dihydro-3-(methylthio)-1-(*p*-toluenesulfonyl)-2(1*H*)-quinolinones (**7b**, 236 mg, 97%) [28:72, determined from the ^{1}H-NMR spectrum (300 MHz)], mp 149 °C (from hexane–AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1705, 1366, 1170. ^{1}H-NMR ($CDCl_3$) δ: 2.08 (3H, s, SMe), 2.40 (3H, s, aromatic Me), 3.1—3.85 (2H, m, 3- and 4-H), 4.65—6.1 (3H, m, CH=CH_2), 7.0—8.0 (8H, m, aromatic H). *Anal.* Calcd for $C_{19}H_{19}NO_3S_2$: C, 61.10; H, 5.13; N, 3.75. Found: C, 61.06; H, 5.32; N, 3.64.

Method C: TFAA (104 mg, 0.49 mmol) was added dropwise to a solution of the sulfoxide **3b** (184 mg, 0.47 mmol) in TFA (1 ml) at 0 °C and the mixture was stirred at the same temperature for 1.5 h. Work-up as described for method B gave **7b** (165 mg, 94%).

4-Ethenyl-1-(*p*-toluenesulfonyl)-1(2*H*)-quinolinone (8b) Using a procedure similar to that described for the preparation of **3b**, the sulfide **7b** (270 mg, 0.72 mmol) was oxidized with MCPBA (80%, 156 mg, 0.72 mmol) to give the sulfoxide, which was dissolved in toluene (5 ml). $NaHCO_3$ (151 mg, 1.8 mmol) was added and the whole was refluxed for 4.5 h. Work-up gave **8b** (139 mg, 59%), mp 115.5—117 °C (from hexane–AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1585, 1375, 1160. ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s, aromatic Me), 5.65 (1H, d, J=11.5 Hz, one of CH=CH_2), 5.89 (1H, d, J=18.0 Hz, one of CH=CH_2), 7.0—8.1 (10H, m, aromatic and olefinic H). *Anal.* Calcd for $C_{18}H_{15}NO_3S$: C, 66.44; H, 4.65; N, 4.30. Found: C, 66.49; H, 4.80; N, 4.38.

Cyclization of the *N*-Tosylsulfoxide 3d Following method C, the sulfoxide **3d** (50 mg, 0.12 mmol) was treated with TFAA (29 mg, 0.14 mmol) to give 1,3-dihydro-5-methyl-3-methylthio-1-(*p*-toluenesulfonyl)-2*H*-1-benzazepin-2-one (**9d**, 49 mg, quant.), mp 193.5—195 °C (from benzene–AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1360, 1175. ^{1}H-NMR ($CDCl_3$) δ: 2.04 (3H, s, SMe), 2.15 (3H, d, J=1.5 Hz, 5-Me), 2.41 (3H, s, aromatic Me), 3.55—3.8 (1H, m, 3-H), 5.2—5.4 (1H, m, 4-H), 7.0—8.0 (8H, m, aromatic H). *Anal.* Calcd for $C_{19}H_{19}NO_3S_2$: C, 61.10; H, 5.13; N, 3.75. Found: C, 61.11; H, 5.12; N, 3.61.

Cyclization of the *N*-Tosylsulfoxide 3f Following method C, the sulfoxide **3f** (150 mg, 0.33 mmol) was treated with TFAA (76 mg, 0.36 mmol) to give 1,3-dihydro-3-methylthio-5-phenyl-1-(*p*-toluenesulfonyl)-2*H*-1-benzazepin-2-one (**13f**, 86 mg, 60%), mp 195—197 °C (from hexane–AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1365, 1175. ^{1}H-NMR ($CDCl_3$) δ: 2.10 (3H, s, SMe), 2.26 (3H, s, aromatic Me), 3.81 (1H, d, J=6.5 Hz, 3-H), 5.71 (1H, d, J=6.5 Hz, 4-H), 6.9—7.8 (13H, m, aromatic H). *Anal.* Calcd for $C_{24}H_{21}NO_3S_2$: C, 66.18; H, 4.86; N, 3.22. Found: C, 66.18; H, 4.96; N, 3.32.

Attempted Cyclization of the *N*-Tosylsulfoxide 3h Following method C, the sulfoxide **3h** (140 mg, 0.38 mmol) was treated with TFAA (89 mg, 0.43 mmol) to give **1h** (86 mg, 81%), mp 120—121 °C (from hexane–AcOEt).

References and Notes

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