SYNTHESIS OF TETRAHYDRO-1-BENZAZOCIN-2(1*H*)-ONES USING 8-*ENDO-TRIG* RADICAL CYCLIZATION OF 2,2-BIS-(PHENYLTHIO)-*N*-[*o*-(PROP-2-ENYL)-PHENYL]ACETAMIDES†

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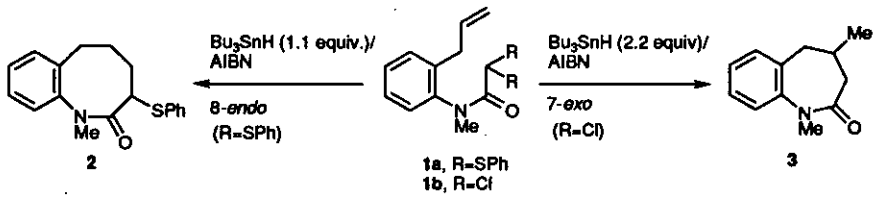
Abstract—The effects of *N*-substituents upon the 8-*endo-trig* radical cyclization of 2,2-bis(phenylthio)-*N*-[*o*-(prop-2-enyl)phenyl]acetamides (**4**) were examined. The *N*-(*p*-methoxybenzyl) (**4a**) and *N*-tosyl derivatives (**4b**), when treated with tributyltin hydride in the presence of a small amount of azoisobutyronitrile, gave regioselectively the corresponding 3,4,5,6-tetrahydro-3-phenylthio-1-benzazocin-2(1*H*)-ones (**5a,b**) (8-*endo* cyclization products) in 40 and 47% yields, respectively, while the *N*-unsubstituted derivative (**4c**) afforded the reduction products (**6c**) and (**8**) as the major products. Some chemical transformation reactions of **5a** are also described.

N-Alkenylcarbamoylmethyl radicals undergo cyclization to give four- to eight-membered lactams.[1,2] During the course of our own studies in this area, we found that *N*-methyl-*N*-[*o*-(prop-2-enyl)phenyl]-2,2-bis(phenylthio)acetamide (**1a**), upon treatment with tributyltin hydride (Bu_3SnH) in the presence of a small amount of azoisobutyronitrile (AIBN), gave regioselectively the 1-benzazocin-2-one (**2**) (an 8-*endo* cyclization product), while the 2,2-dichloroacetamide (**1b**) yielded exclusively the 1-benzazepin-2-one (**3**) (a 7-*exo* cyclization product).[1d] From the synthetic point of view, it seems to be of interest to explore a

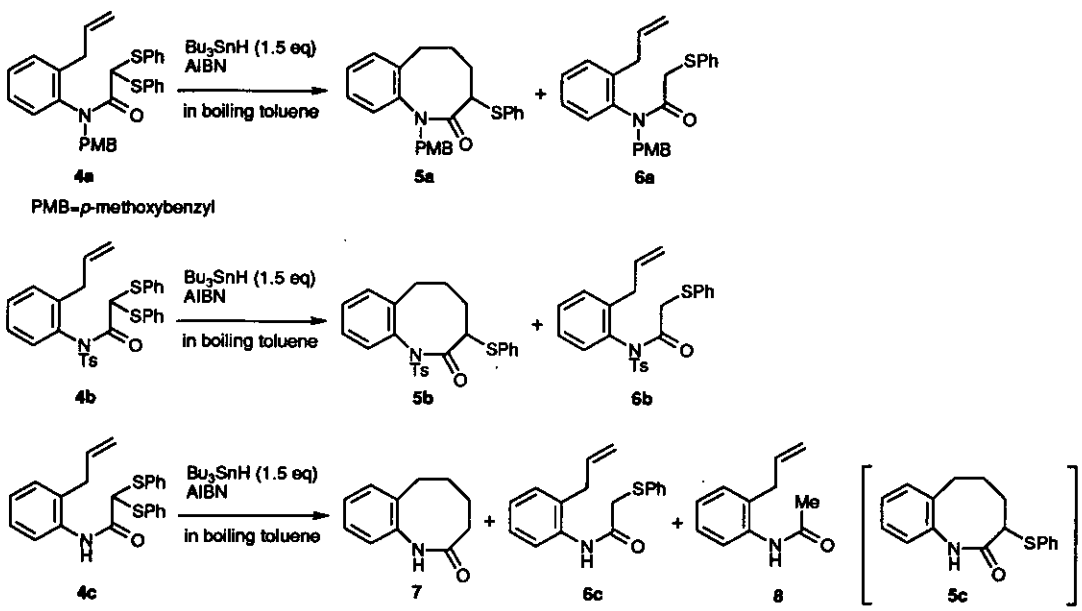
†This paper is dedicated to Dr. Shigeru Oae, Professor Emeritus of Tsukuba University, on the occasion of his 77th birthday.

general route to the 1-benzazocines, because this ring system has sometimes been used as synthetic intermediates of natural products[3] or pharmaceuticals.[4] We now report the effects of *N*-substituents upon the 8-*endo-trig* radical cyclization of 2,2-bis(phenylthio)-*N*-[*o*-(prop-2-enyl)phenyl]acetamides (**4**). In this paper some chemical transformation reactions of the tetrahydro-3-phenylthio-1-benzazocin-2(1*H*)-one (**5a**) are also described.



The radical precursors (**4a-c**) were prepared from *o*-(prop-2-enyl)aniline[5] by standard procedures (see Experimental section).

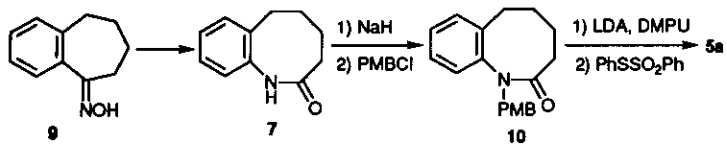
In general, a mixture of Bu3SnH (1.5 mol equiv.) and a small amount of AIBN in toluene was added to a boiling solution of the 2,2-bis(phenylthio)acetamide (**4**) in toluene during 1 h, and the resulting mixture was further refluxed for several hours. After work-up, the crude material was chromatographed on silica gel. In this manner, the *N*-(*p*-methoxybenzyl) (**4a**) and *N*-tosyl derivatives (**4b**) gave the 1-benzazocin-2-ones (**5a**) (40%) and (**5b**) (47%) along with the reduction products (**6a**) (18%) and (**6b**) (23%), respectively. In contrast, the *N*-unsubstituted derivative (**4c**) gave the (monophenylthio)acetamide (**6c**) as



Scheme 1

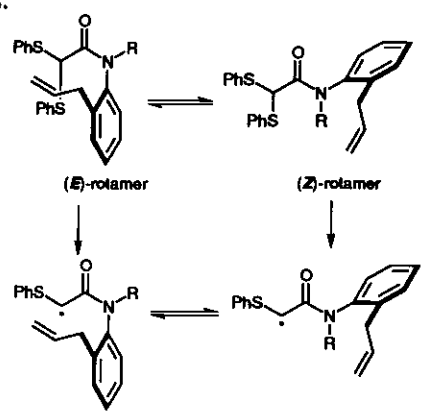
the major product (63%), together with the 1-benzazocin-2-one (**7**)[6] (14%) and the acetamide (**8**) (10%). The expected 3-phenylthio-1-benzazocin-2-one (**5c**) was not obtained.

The structure of **5a** was confirmed by an alternative synthesis. Thus, *N*-alkylation of **7**, prepared by Beckmann rearrangement of benzosuberone oxime (**9**),[6] with *p*-methoxybenzyl chloride gave *N*-(*p*-methoxybenzyl) derivative (**10**) in 98% yield, which was treated with *S*-phenyl benzenethiosulfonate and lithium diisopropylamide (LDA) in tetrahydrofuran in the presence of *N*,*N*-dimethylpropyleneurea (DMPU) to afford **5a** in 36% yield together with the unchanged starting material (**10**) (40%).

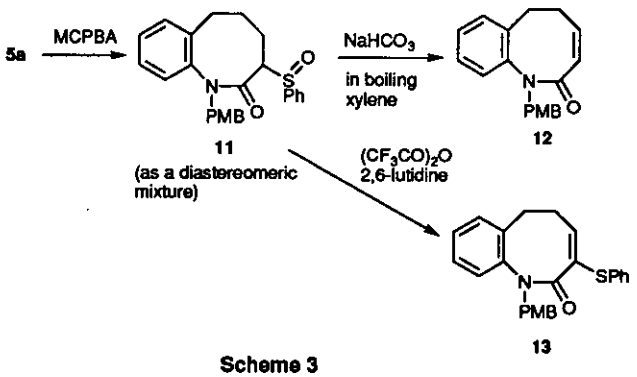


Scheme 2

Considering the fact that the radical cyclization of the *N*-(*o*-ethenylphenyl)-2,2-dichloroacetamides gives the quinolin-2(1*H*)-ones (the 6-*exo* cyclization products) in high yields regardless of the nature of the *N*-substituents,[1d] it is somewhat surprising that a significant quantity of **7** (or **5c**) is not produced from **4c**. It is known that acetanilide exists exclusively in the (*Z*)-rotamer (Ph and O are *syn*),[7] while *N*-alkylation reverses the structure of the preferred conformer and the *N*-alkylacetanilides exist predominantly in the (*E*)-rotamer (Ph and O are *anti*), in which the plane of the aryl ring is twisted with respect to the plane of the amide.[8] We therefore expected that the *N*-substituted *N*-[*o*-(prop-2-enyl)phenyl]acetamides (**1a**, **4a,b**) and the derived radicals would be present mainly in the (*E*)-rotamer, a suitable conformation for the cyclization. However, in the *N*-unsubstituted congener (**4c**) and the derived radical, the (*Z*)-rotamer would be favored over the (*E*)-rotamer. The radical must rotate its amide C-N bond prior to cyclization. Apparently, in the 8-*endo* cyclization of **4c**, the simple reduction process seems to compete well with the rotation/cyclization processes.



Finally, some chemical transformation reactions of **5a** were examined. Thus, oxidation of **5a** with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane gave the sulfoxide (**11**) as a diastereomeric mixture in 77% yield. Refluxing **11** in xylene in the presence of sodium bicarbonate for 16 h gave the 5,6-dihydro-1-benzazocin-2(1*H*)-one (**12**) in 78% yield. Pummerer reaction of the sulfoxide (**11**) with trifluoroacetic anhydride in dichloromethane in the presence of 2,6-lutidine gave the 5,6-dihydro-3-phenylthio-1-benzazocin-2(1*H*)-one (**13**) in 70% yield.



Scheme 3

EXPERIMETNAL

Melting points are uncorrected. Ir spectra were recorded with a JASCO IR A-100 spectrophotometer. ^{1}H-Nmr spectra were determined with a JEOL JNM-PMX 60 or a Varian XL-300 spectrometer, using tetramethylsilane as an internal standard. High-resolution mass spectra were obtained with a JEOL JMS-SX 102A spectrometer. Column chromatography was performed on Silica gel 60 PF_{254} (Nacalai Tesque, Inc.) under pressure.

***N*-(*p*-Methoxybenzyl)-*o*-(prop-2-enyl)aniline** A solution of *o*-(prop-2-enyl)aniline (500 mg, 3.75 mmol), *p*-methoxybenzaldehyde (510 mg, 3.75 mmol), and *p*-toluenesulfonic acid (10 mg) in benzene (50 ml) was heated under reflux with azeotropic removal of water for 2 h. The solvent was evaporated off and the residue was dissolved in methanol (20 ml). To this solution was added sodium borohydride (0.16 g, 4.13 mmol) and the mixture was refluxed for 1 h. After removal of the solvent, water (10 ml) was added to the residue and the whole was extracted with dichloromethane. The extract was dried (K_2CO_3) and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 10:1) to give the title compound (740 mg, 78%) as an oil. ^{1}H-Nmr (60 MHz, $CDCl_3$) δ: 3.1-3.4 (2 H, m, ArCH_2CH=CH_2), 3.70 (3 H, s, OCH_3), 3.5-4.1 (1 H, m, NH), 4.0-4.4 (2 H, m, NCH_2Ar), 4.8-5.2 (2 H, m, CH=CH_2),

5.6-6.2 (1 H, m, C*H*=CH_2), 6.45-7.4 (8 H, m, ArH). Exact MS *m/z*: Calcd for $C_{17}H_{19}NO$: 253.1467. Found: 253.1451.

***N*-(*p*-Methoxybenzyl)-2,2-bis(phenylthio)-*N*-[*o*-(prop-2-enyl)phenyl]acetamide (4a)** A solution of bis(phenylthio)acetyl chloride (1.05 g, 3.55 mmol) in toluene (10 ml) was added to a solution of *N*-(*p*-methoxybenzyl)-*o*-(prop-2-enyl)aniline (600 mg, 2.37 mmol) and triethylamine (360 mg, 3.55 mmol) in toluene (20 ml) at 0 °C and the mixture was stirred for 2 days. The mixture was diluted with water (10 ml) and the organic layer was separated and the aqueous layer was extracted with toluene. The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 20:1) to give **4a** (670 mg, 55 %) as an oil. Ir ν_{max} (CCl_4) cm^{-1}: 1660; ^{1}H-nmr (60 MHz, $CDCl_3$) δ: 3.0-3.3 (2 H, m, ArC*H*$_2$), 3.76 (3 H, s, OCH_3), 4.05, 5.36 (1 H each, ABq, *J*=14 Hz, NC*H*$_2$Ar), 4.59 [1 H, s, C*H*(SPh)$_2$], 4.7-5.2 (2 H, m, CH=C*H*$_2$), 5.4-6.2 (1 H, m, C*H*=CH_2), 6.6-7.5 (18 H, m, ArH). *Anal.* Calcd for $C_{31}H_{29}NO_2S_2$: C, 72.77; H, 5.71; N, 2.74. Found: C, 72.43; H, 5.59; N, 2.97.

***N*-[*o*-(Prop-2-enyl)phenyl]-*p*-toluenesulfonamide** *p*-Toluenesulfonyl chloride (1.07 g, 5.36 mmol) was added to a solution of *o*-(prop-2-enyl)aniline (475 mg, 3.57 mmol) in pyridine (2 ml) and the mixture was stirred at room temperature overnight. The reaction mixture was diluted with dichloromethane (10 ml) and the solution was washed with 10% HCl and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 5:1) to give the title compound (940 mg, 92%), mp 65-69 °C (from hexane-AcOEt); ^{1}H-nmr (60 MHz, $CDCl_3$) δ: 2.35 (3 H, s, $ArCH_3$), 3.0-3.5 (2 H, m, $ArCH_2$), 4.7-5.2 (2 H, m, CH=C*H*$_2$), 5.4-6.1 (1 H, m, C*H*=CH_2), 6.88 (1 H, br s, NH), 6.8-7.9 (8 H, m, ArH). *Anal.* Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.55; H, 5.96; N, 4.87.

2,2-Bis(phenylthio)-*N*-[*o*-(prop-2-enyl)phenyl]-*N*-(*p*-toluenesulfonyl)acetamide (4b) Thus obtained *p*-toluenesulfonamide (1.0 g, 3.48 mmol) was added a suspension of sodium hydride (60% in oil, 0.70 g, 17.5 mmol, washed with dry hexane) in benzene (40 ml) and the whole was stirred at room temperature for 30 min. To this mixture was added a solution of bis(phenylthio)acetyl chloride (1.54 g, 5.22 mmol) in benzene (20 ml) and the whole was refluxed for 2 h and then diluted with water (10 ml). The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 20:1) to give **4b** (877 mg, 46%) as an oil. ^{1}H-Nmr (60 MHz, $CDCl_3$) δ: 2.42

(3 H, s, CH_3), 3.3-3.5 (2 H, m, ArCH_2), 4.42 [1 H, s, $CH(SPh)_2$], 4.9-5.3 (2 H, m, CH=CH_2), 5.5-6.1 (1 H, m, CH=CH_2), 6.6-7.45 (16 H, m, ArH), 7.94 (2 H, one part of ABq, J=8 Hz, ArH). Exact MS *m/z*: Calcd for $C_{30}H_{27}NO_3S_3$: 545.1153. Found: 545.1150.

2,2-Bis(phenylthio)-*N*-[*o*-(prop-2-enyl)phenyl]acetamide (4c) A solution of 1,3-dicyclohexylcarbodiimide (1.63 g, 7.88 mmol) in dichloromethane (20 ml) was added dropwise to a solution of *o*-(prop-2-enyl)aniline (1.0 g, 7.5 mmol), bis(phenylthio)acetic acid (2.18 g, 7.88 mmol), and 4-dimethylaminopyridine (0.09 g, 0.7 mmol) in dichloromethane (40 ml) at 0°C and the whole was stirred at room temperature overnight. Precipitated *N,N*-dicyclohexylurea was filtered off and the filtrate was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 10:1) to give **4c** (720 mg, 37%), mp 94.5-96 °C (from AcOEt-hexane); ir ν_{max} (CCl_4) cm^{-1}: 3360, 1690; ^{1}H-Nmr (60 MHz, $CDCl_3$) δ: 2.9-3.6 (2 H, m, ArCH_2), 4.90 [1 H, s, $CH(SPh)_2$], 4.7-5.2 (2 H, m, CH=CH_2), 5.4-6.3 (1 H, m, CH=CH_2), 6.5-7.9 (4 H, m, ArH). *Anal.* Calcd for $C_{23}H_{21}NOS_2$: C, 70.55; H, 5.41; N, 3.58. Found: C, 70.32, H, 5.42; N, 3.42.

Radical Cyclization of 4a A solution of Bu_3SnH (626 mg, 2.15 mmol) and AIBN (32 mg, 0.20 mmol) in toluene (60 ml) was added dropwise to a solution of **4a** (1.0 g, 1.95 mmol) in boiling toluene (90 ml) over 1 h, and the mixture was refluxed for 2 h. After evaporation of the solvent, ether (60 ml) and an 8% aqueous solution of KF (60 ml) were added and the whole was vigorously stirred for 1 h. The ethereal layer was separated and the aqueous layer was extracted with ether. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 20:1). The first fraction gave *N*-(*p*-methoxybenzyl)-2-phenylthio-*N*-[*o*-(prop-2-enyl)phenyl]acetamide (**6a**) (144 mg, 18%) as an oil. ^{1}H-Nmr (60 MHz, $CDCl_3$) δ: 3.0-3.3 (2 H, m, ArCH_2), 3.35 (2 H, s, CH_2SPh), 3.70 (3 H, s, OCH_3), 4.26, 5.36 (1 H each, ABq, J=14 Hz, NCH_2Ar), 4.8-5.2 (2 H, m, CH=CH_2), 5.4-6.15 (1 H, m, CH=CH_2), 6.5-7.5 (13 H, m, ArH), 7.94 (2 H, ArH). The second fraction gave 3,4,5,6-tetrahydro-1-(*p*-methoxybenzyl)-3-phenylthio-1-benzazocin-2(1*H*)-one (**5a**) (190 mg, 40%), mp 100-102.5 °C (from hexane-AcOEt); ir ν_{max} (CCl_4) cm^{-1}: 1660; ^{1}H-nmr (60 MHz, $CDCl_3$) δ: 0.9-2.8 (6 H, m), 3.73 (3 H, s, OCH_3), 3.5-3.95 (1 H, m, 3-H), 4.66, 4.99 (1 H each, ABq, J=14 Hz, NCH_2Ar), 6.5-7.5 (13 H, m, ArH). *Anal.* Calcd for $C_{25}H_{25}NO_2S$: C, 74.41; H, 6.24; N, 3.47. Found: C, 74.44; H, 6.32; N, 3.59.

Radical Cyclization of 4b Following a procedure similar to that described for the cyclization of **4a**, **4b** (500 mg, 0.92 mmol) was treated with Bu_3SnH (400 mg, 1.38 mmol) and AIBN (15 mg, 0.09 mmol) and workup gave the crude material, which was chromatographed on silica gel (hexane-AcOEt, 10:1). The first fraction gave 2-phenylthio-*N*-[*o*-(prop-2-enyl)phenyl]-*N*-(*p*-toluenesulfonyl)acetamide (**6b**) (93 mg, 23%), mp 94-96.5 °C (from AcOEt-hexane); ir ν_{max} (CCl_4) cm^{-1}: 1700; ^{1}H-nmr (60 MHz, $CDCl_3$) δ: 2.44 (3 H, s, CH_3), 3.25 (2 H, m, CH_2SPh), 3.35-3.6 (2 H, m, $ArCH_2$), 4.9-5.3 (2 H, m, $CH=CH_2$), 5.5-6.1 (1 H, m, $CH=CH_2$), 6.8-7.5 (11 H, m, ArH), 7.88 (2 H, one of ABq, *J*=8 Hz, ArH). *Anal.* Calcd for $C_{24}H_{23}NO_3S_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 65.96; H, 5.32; N, 3.22. The second fraction gave 3,4,5,6-tetrahydro-3-phenylthio-1-(*p*-toluenesulfonyl)-1-benzazocin-2(1*H*)-one (**5b**) (190 mg, 47%), mp 122-124 °C (from hexane-AcOEt); ir ν_{max} (CCl_4) cm^{-1}: 1705; ^{1}H-nmr (60 MHz, $CDCl_3$) δ: 1.2-2.9 (6 H, m), 2.39 (3 H, s, CH_3), 3.64 (1 H, dd, *J*=7, 5.5 Hz, 3-H), 6.8-7.5 (11 H, m, ArH), 7.80 (2 H, one part of ABq, *J*=8 Hz, ArH). *Anal.* Calcd for $C_{24}H_{23}NO_3S_2$: C, 65.88; H, 5.30; N, 3.20. Found: C, 66.01; H, 5.32; N, 3.25.

Radical Cyclization of 4c Following a procedure similar to that described for the cyclization of **4a**, **4c** (500 mg, 1.28 mmol) was treated with Bu_3SnH (559 mg, 1.92 mmol) and AIBN (21 mg, 0.13 mmol) and workup gave the crude material, which was chromatographed on silica gel (hexane-AcOEt, 7:1). The first fraction gave 2-phenylthio-*N*-[*o*-(prop-2-enyl)phenyl]acetamide (**6c**) (230 mg, 63%), mp 82.5-83.5 °C (from AcOEt-hexane); ir ν_{max} (CCl_4) cm^{-1}: 3360, 1690. *Anal.* Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94. Found: C, 72.32, H, 6.05; N, 4.93. The second fraction gave *N*-[*o*-(prop-2-enyl)phenyl]acetamide (**8**) (22 mg, 10%), mp 94-95.5 °C (from AcOEt-hexane); ir ν_{max} (CCl_4) cm^{-1}: 3420, 1700. *Anal.* Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.07; H, 7.26; N, 7.67. The third fraction gave 3,4,5,6-tetrahydro-1-benzazocin-2(1*H*)-one (**7**) (31 mg, 14%), mp 151-155 °C (from AcOEt-hexane) (lit.,[6] mp 151-153 °C).

3,4,5,6-Tetrahydro-1-(*p*-methoxybenzyl)-1-benzazocin-2(1*H*)-one (10) A solution of **7**[6] (1.00 g, 5.7 mmol) in benzene (5 ml) was added a suspension of sodium hydride (60% in oil, 343 mg, 8.6 mmol, washed with dry hexane) in benzene (30 ml) and the whole was stirred at room temperature for 30 min. To this mixture was added *p*-methoxybenzyl chloride (1.35 g, 8.6 mmol) and the whole was refluxed for 1 h and then diluted with water (10 ml). The organic layer was separated and the aqueous layer was extracted with benzene. The combined extracts were washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 5:1) to give **10** (1.65 g,

98%), mp 104-106 °C (from hexane-AcOEt); ir ν_{max} (CCl_4) cm^{-1}: 1645; ^{1}H-nmr (60 MHz, $CDCl_3$) δ: 0.9-2.6 (8 H, m), 3.72 (3 H, s, OCH_3), 4.50, 5.20 (1 H each, ABq, *J*=14 Hz, NCH_2Ar), 6.6-7.8 (8 H, m, ArH). *Anal.* Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.07; H, 7.25; N, 4.76.

3,4,5,6-Tetrahydro-1-(*p*-methoxybenzyl)-3-phenylthio-1-benzazocin-2(1*H*)-one (5a) To a solution of LDA [prepared from diisopropylamine (446 mg, 4.41 mmol) and butyllithium (2.75 ml, as a 1.6 mol/l hexane solution)] was added successively DMPU (565 mg, 4.41 mmol) and a solution of **10** (1.0 g, 3.39 mmol) in THF (5 ml) and the whole was stirred at -78 °C for 20 min. To the reaction mixture was added a solution of *S*-phenyl benzenethiosulfonate (1.27 g, 5.08 mmol) in THF (5 ml) at -78 °C and the whole was stirred at room temperature overnight. Saturated NH_4Cl solution was added and the organic layer was separated and the aqueous layer was extracted with ether. The combined extracts were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 10:1). The first fraction gave **5a** (496 mg, 36%) and the second fraction gave the unchanged **10** (404 mg, 40%).

5,6-Dihydro-1-(*p*-methoxybenzyl)-1-benzazocin-2(1*H*)-one (12) MCPBA (80%) (160 mg, 0.74 mmol) was added dropwise to an ice-cooled solution of **5a** (300 mg, 0.74 mmol) in dichloromethane (30 ml) over a period of 30 min and the mixture was stirred at room temperature for 10 min. The reaction mixture was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to give a crude diastereomeric mixture of the sulfoxide (**11**). The sulfoxide (**11**) (308 mg, 0.74 mmol) was dissolved in xylene (5 ml) and $NaHCO_3$ (120 mg, 1.43 mmol) was added. The whole was heated under reflux for 16 h. After removal of the inorganic materials and the solvent, the residue was chromatographed on silica gel (hexane-AcOEt, 5:1) to give **12** (131 mg, 78%), mp 78.5-79 °C (from hexane-AcOEt); ir ν_{max} (CCl_4) cm^{-1}: 1655, 1620; ^{1}H-nmr (300 MHz, $CDCl_3$) δ: 2.00-2.60 (4 H, m), 3.73 (3 H, s, OCH_3), 4.48, 5.31 (1 H each, ABq, *J*=13.9 Hz, NCH_2Ar), 5.47 (1 H, ddd, *J*=2.2, 5.9, 13.0 Hz, 4-H), 5.82 (1 H, br d, *J*=13.0 Hz, 3-H), 6.70-7.28 (8 H, m, ArH). *Anal.* Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 78.22; H, 6.67; N, 4.81.

5,6-Dihydro-1-(*p*-methoxybenzyl)-3-phenylthio-1-benzazocin-2(1*H*)-one (13) The sulfide (**5a**) (243 mg, 0.6 mmol) was oxidized with MCPBA (80%) (130 mg, 0.6 mmol) using a procedure similar to that described above for the preparation of **12**. To a solution of the resulting sulfoxide (**11**) (257 mg, 0.6 mmol) in dichloromethane (5 ml) was added trifluoroacetic anhydride (252 mg, 1.2 mmol) and 2,6-lutidine (193 mg, 1.8 mmol) and the whole was stirred at room temperature overnight. The reaction

mixture was washed with saturated $NaHCO_3$ solution, 10% HCl, and brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (hexane-AcOEt, 5:1) to give **13** (166 mg, 70%), mp 125-126 °C (from hexane-AcOEt); ir ν_{max} (CCl_4) cm^{-1}: 1640; ^{1}H-nmr (300 MHz, $CDCl_3$) δ: 2.14-2.71 (4 H, m), 3.75 (3 H, s, OCH_3), 4.51, 4.83 (1 H each, ABq, *J*=14.0 Hz, NCH_2Ar), 5.93 (1 H, dd, *J*=2.5, 6.9 Hz, 4-H), 6.5-7.4 (13 H, m, ArH). *Anal.* Calcd for $C_{25}H_{23}NO_2S$: C, 74.78; H, 5.77; N, 3.49. Found: C, 74.53; H, 5.85; N, 3.44.

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