Pergamon

Tetrahedron 54 (1998) 12609–12622

TETRAHEDRON

# Generation of Isoquinolino-*o*-quinodimethanes from Fused 3-Sulfolenes

Hong-Chuan Chen and Ta-shue Chou*

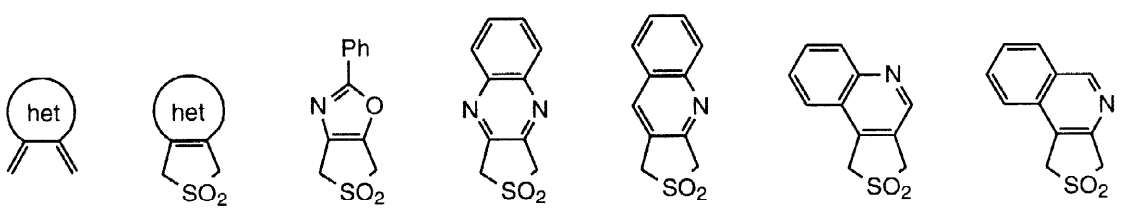
Institute of Chemistry, Academia Sinica, Taipei, Taiwan, and

Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C.

Received 13 February 1998; revised 24 April 1998; accepted 28 July 1998

***Abstract:*** Isoquinolino-3-sulfolene **7** has been prepared efficiently from 3,4-epoxysulfolene **8**. Deprotonation-alkylation reactions proceed smoothly but with low regioselectivity to give substituted isoquinolino-3-sulfolenes. The pyrolysis of these fused 3-sulfolenes at various temperatures provides an easy entry to the corresponding isoquinolino-*o*-quinodimethanes. © 1998 Elsevier Science Ltd. All rights reserved.

Heteroaromatic *o*-quinodimethanes **1** have now been established as useful synthetic intermediates for novel heterocyclic compounds.[1] These reactive species can be generated by several methods among which $SO_2$ extrusion of heteroaromatic-fused 3-sulfolenes **2** appears to be most attractive for synthetic purpose. Although the removal of $SO_2$ from **2** usually requires thermolysis at about 180 °C , there are exceptions. For example, 2-phenyloxazolo-3-sulfolene **3** loses $SO_2$ to give the corresponding *o*-quinodimethane at room temperature.[2] Whereas quinoxalino-3-sulfolene **4** does not lose $SO_2$ below 290 °C.[3] The difference in the thermal property of different systems may depend on the aromaticity of the heteroaromatic moiety, the bond order of the C3-C4 of the 3-sulfolene moiety, and the ring strain of the molecule.[4] Storr[5] recently reported the preparation of two types of quinolino-3-sulfolene **5** and **6** and discovered that they are different in thermal reactivity. Compound **6** loses $SO_2$ at 210 °C readily to give the corresponding *o*-quinodimethane. However, compound **5** fragments only above 240 °C. It is therefore necessary to examine how the very similar molecule, isoquinolino-3-sulfolene **7** behaves thermally. We now report the first preparation of compound **7** and the study of its thermal property and synthetic applications.



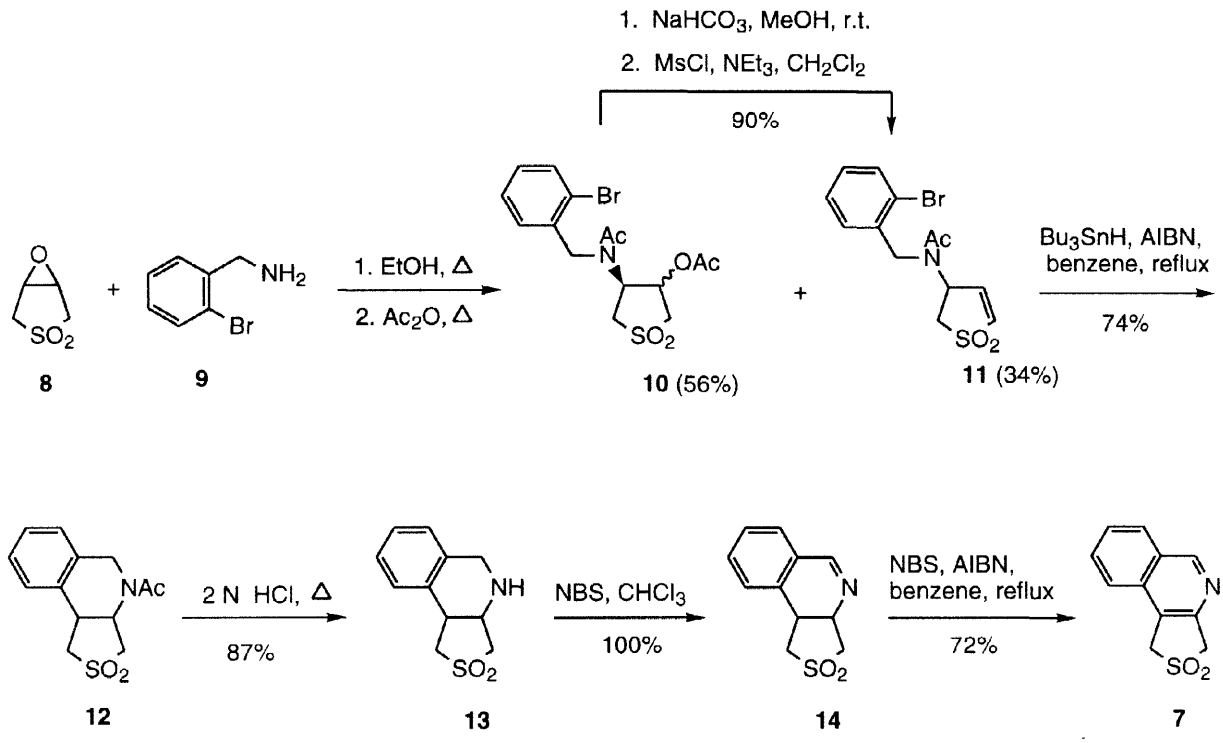

**1** **2** **3** **4** **5** **6** **7**

This paper is dedicated to the late Professor Yu Wang.


*PII:* S0040-4020(98)00739-X

The synthesis commenced with epoxysulfone **8** (scheme I).[6] Treatment of **8** with *o*-bromobenzylamine **9** in refluxing ethanol followed by acetylation gave a mixture of **10** and **11**. It was somewhat surprising that compound **11** could be obtained directly under the reaction conditions. Presumably benzylamine **9** induced compound **10** to undergo an elimination reaction to give **11**. Attempts were made to increase the yield of **11** by lengthening reaction time or by adding $Et_3N$ in the reaction mixture in a hope that the elimination reaction could be facilitated. However, all attempts were unsuccessful and unidentified side products were formed. Conversion of **10** to **11** could easily be achieved by a sequence of selective hydrolysis of the ester functionality and mesylation/elimination in good yield.

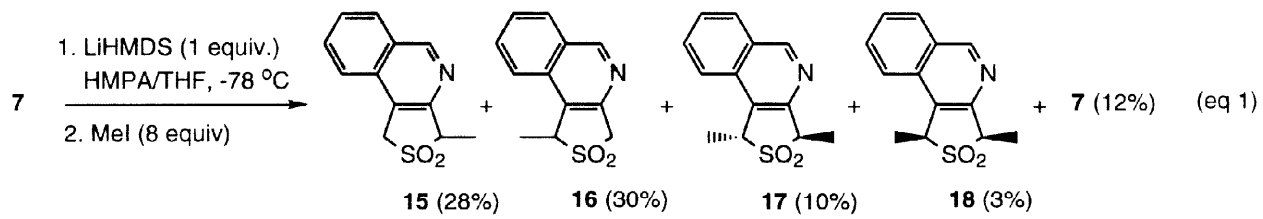
**Scheme I**




Free radical cyclization of **11** induced by $Bu_3SnH$ gave the tricyclic heterocycle **12** (74%)[7] from which the acetyl group was removed upon treatment with 2N HCl under reflux. The resulting tetrahydroisoquinoline **13** was aromatized by a two-step oxidation process. The first double bond was introduced by NBS in $CHCl_3$ in almost quantitative yield. Without purification, the dihydroisoquinoline **14** was treated with NBS and AIBN in refluxing benzene to give the target molecule **7** in 72% yield. Our attempts of one-step aromatization of **13** under various conditions, such as $MnO_2$, DDQ, or NBS/benzene, gave only poorer yield of **7**.

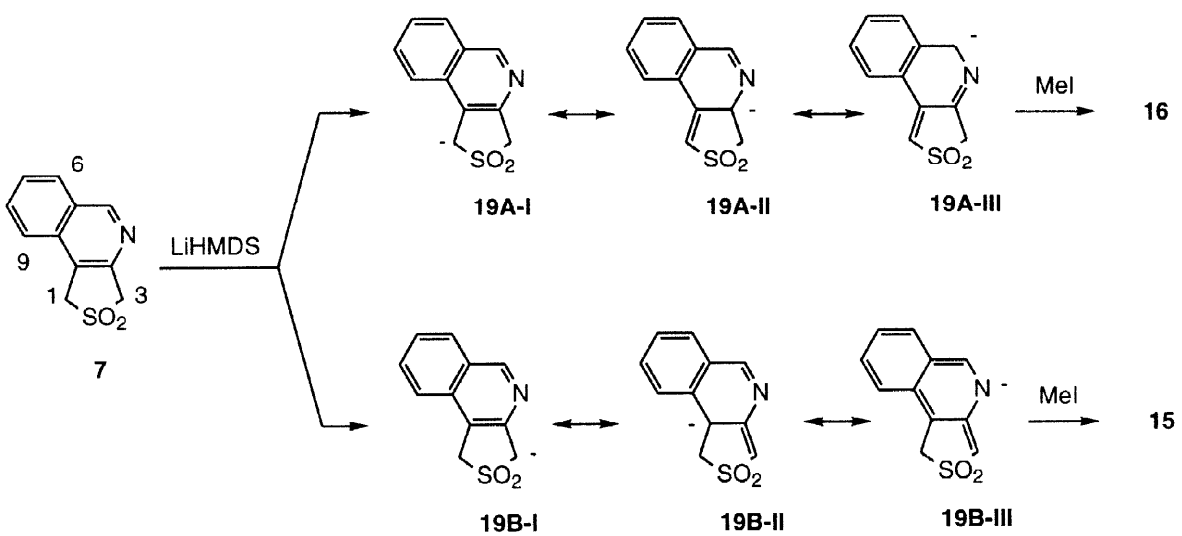
Contrary to the excellent regioselectivity of deprotonation/alkylation reactions of many other heteroaromatic-fused 3-sulfolenes,[8] compound **7** showed quite low regioselectivity upon deprotonation. When compound **7** was treated with one equiv. of LiHMDS at -78 °C followed by the addition of excess of MeI, a

mixture of products **15-18** was obtained along with recovered starting material (eq 1). If excess of LiHMDS (>1.5 equiv.) was used, the starting material was totally consumed but more dimethylated products **17** and **18** were obtained. On the other hand, dimethylation took place even if insufficient amount (0.6 equiv.) of LiHMDS was used. In all cases, the monomethylated products **15** and **16** were formed in approximately equal amount.




The poor regioselectivity of deprotonation/alkylation reactions of **7** and the unavoidable dimethylation indicate that anion exchange is fast as compared to methylation.[9] In other words, the acidities of the 1- and 3-positions of compound **7** are similar. The negative charge of both anions **19A** and **19B**, formed from **7** by deprotonation at 1- and 3-positions, respectively, can be delocalized at six atoms. Scheme II shows some of their resonance forms. Although anion **19B** seems to be more favored than **19A** because its negative charge can be delocalized on the more electronegative nitrogen atom (**19B-III**), the presentation of its benzene ring is not perfectly aromatic. Hence, **19B-III** should not have a significant contribution to the stability of the anion **19B**. On the other hand, **19A** is slightly more favored by the factor that three of the six possible resonance forms of **19A** (**19A-I** - **19A-III**), but only two for **19B** (**19B-I** and **19B-II**), have their benzene moiety presented as aromatic. This may explain why **19A** and **19B** were formed in about the same amount and why anion exchange takes place readily in this system.

**Scheme II**



The stereochemistry of the dimethylated products was unambiguously determined by the single crystal X-ray analysis of the *trans*-isomer **17** (Fig. 1). Whereas the regiochemistry of the monomethylation was determined by 2D-NMR NOESY experiments. It was found that the protons on the methyl group correlate with the C9 proton in molecule **16** but not in molecule **15**. In addition, NOE correlation was observed between the C1 protons and C9 proton in molecule **15**.

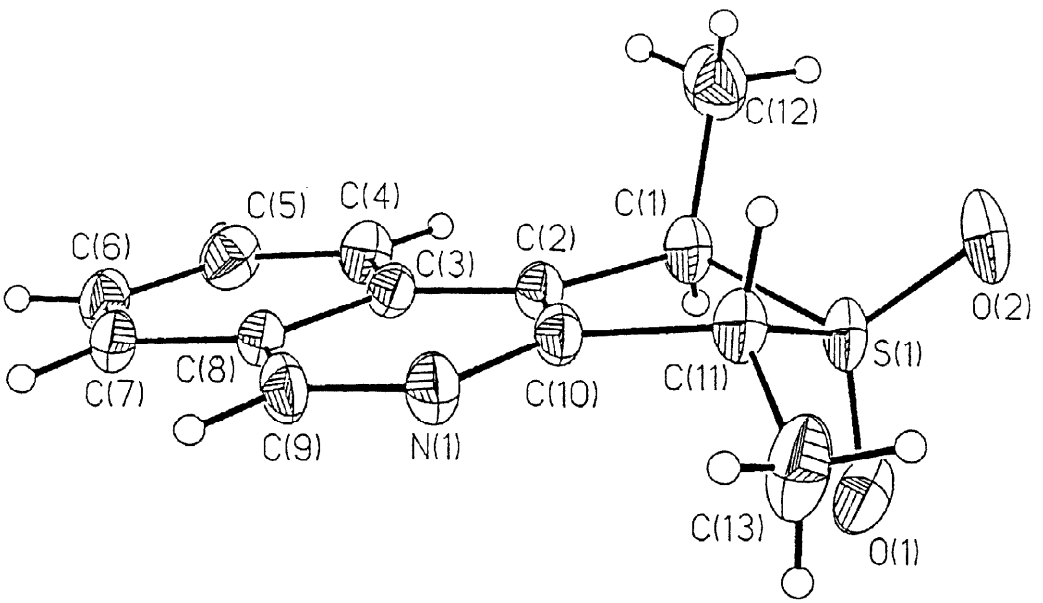
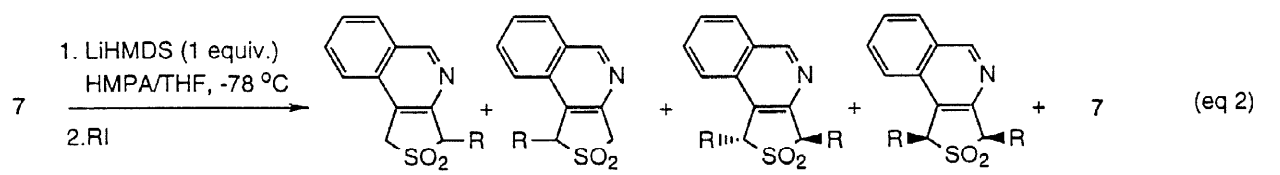



**Figure 1.** ORTEP of *trans*-1,3-Dimethyl-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide **17**.

Under the similar reaction conditions as deprotonation/methylation, pentenyl and hexenyl groups can be attached to compound **7** (eq 2). Again, low regioselectivity was observed and dialkylation was found unavoidable so that mixtures of products **20-23** and **24-27** were obtained. The stereochemistry of the dialkylation was again determined by NOESY experiments.

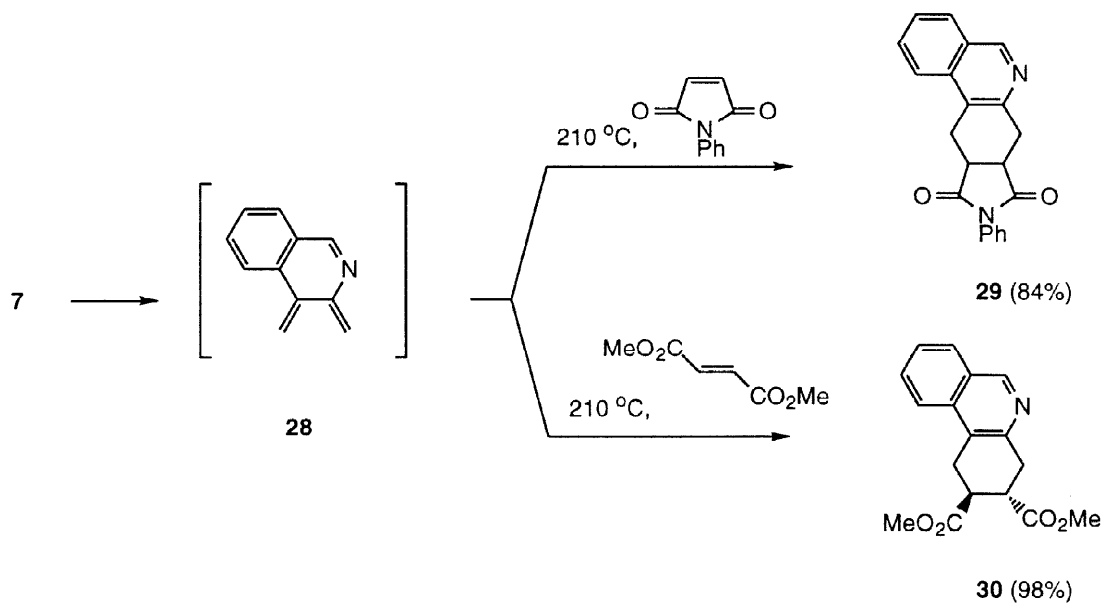



(eq 2)

| | | | | | |
|---|---|---|---|---|---|
| R= $CH_2$=CH$(CH_2)_3$- | **20** (20%) | **21** (24%) | **22** (13%) | **23** (4%) | 9% |
| R= $CH_2$=CH$(CH_2)_4$- | **24** (24%) | **25** (23%) | **26** (13%) | **27** (4%) | 3% |

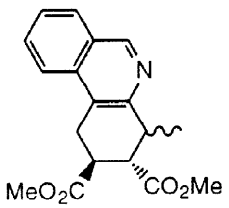
When compound **7** was thermolyzed at 210 °C in the presence of a dienophile, such as *N*-phenylmaleimide or dimethyl fumarate, the extrusion of $SO_2$ and the Diels-Alder reaction proceeded smoothly and the cycloadduct could be obtained in high yield (Scheme III). The isoquinolino-*o*-quinodimethane **28** should be the intermediate leading to products **29** and **30**. The thermal property of **7** is similar to that of the quinolino-3-sulfolene **6** but different from its isomer **5**.[5] Considering the most favorable canonical forms of molecules **5** - **7** where both the benzene ring and the pyridine ring are presented as aromatic, the C3-C4 of the 3-sulfolene moiety is a single bond on molecule **5**, but a double bond on compounds **6** and **7**. In other words, compounds **6** and **7** are more analogous to 3-sulfolene which decomposes thermally at relatively low temperatures.[9] Whereas compound **5** is more analogous to sulfolane which fragments only at very high temperatures.[10] Therefore, bond order is the key factor which influences the thermal property of this class of heteroaromatic-fused 3-sulfolenes.

**Scheme III**

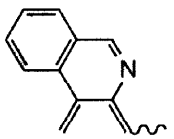



When compound **15** was heated to 210 °C in the presence of dimethyl fumarate for 6 h, a mixture of stereoisomeric cycloadducts **31** was obtained. The transient intermediacy of the *o*-quinodimethane **32** was thus evidenced. On the other hand, when compound **16** was subject to the same reaction conditions, the stereoisomeric mixture of cycloadducts **33** was formed only in 7% yield along with 44% of recovered starting material **16**. Apparently the thermal generation of the *o*-quinodimethane **34** from the corresponding 3-sulfolene is much more difficult than the isomer **32**. Raising the thermolysis temperature of **16** up to 240 °C for 6 h, the yield of **33** was increased to 54% and all the starting material was consumed. However, a side product **35**, derived from 1,5-hydrogen shift of the *o*-quinodimethane **34**, was detected in small quantity (4%). Steric effects must play an important role in the different thermal properties of the regioisomer **15** and **16**. Upon extrusion of $SO_2$, the methyl group of compound **16** unavoidably encounters repulsive interactions with the C9 hydrogen.

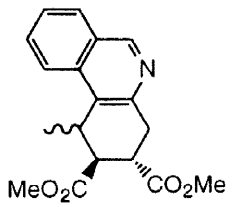
Whereas no such interactions exist in compound **15** so that $SO_2$ can be extruded more easily. This is the first example in which steric effects were found to influence the thermolysis temperatures of heteroaromatic-fused 3-sulfolenes.



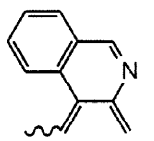

**31**



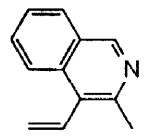

**32**




**33**

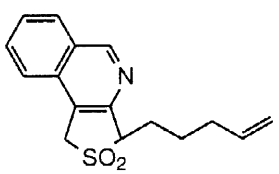



**34**



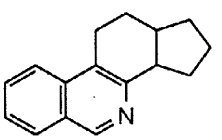

**35**

Thermal extrusion of $SO_2$ and subsequent intramolecular Diels-Alder reactions of compounds **20** and **24** proceeded readily at 210 °C to give **36** and **37**, respectively, in good yield. In each case, two stereoisomers were obtained of which the stereochemistry was not characterized (eq 3 and eq 4). Compounds **36** and **37**, bearing the tetracyclic skeleton, are aza analogues of steroids and tetracyclic triterpenes. Therefore, these reactions may be useful for the synthesis of analogues of natural products. As expected, thermolysis of compounds **21** and **25** did not take place at 210 °C due to steric reasons. They had to be heated at 240 °C for $SO_2$ extrusion to occur (eq 5 and eq 6). Although the intramolecular cycloadducts **38** and **40** could be obtained, the 1,5-hydrogen shift products **39** and **41** were produced in significant amount. In the case of the thermolysis of **25** (eq 6), compound **41** was the major product (48%) at 240 °C. When the thermolysis temperature was raised up to 270 °C, the same side products were obtained in a different ratio where the intramolecular Diels-Alder reaction predominated.



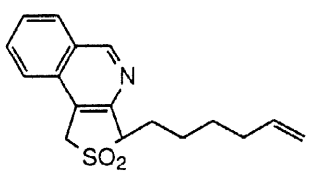

**20**

210 °C, 6h



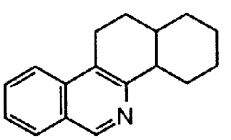

**36** (1:1.17, 91%, two isomers)

(eq 3)



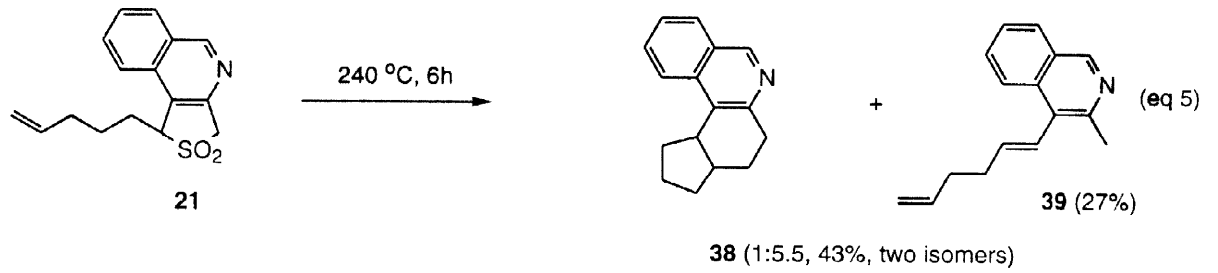

**24**

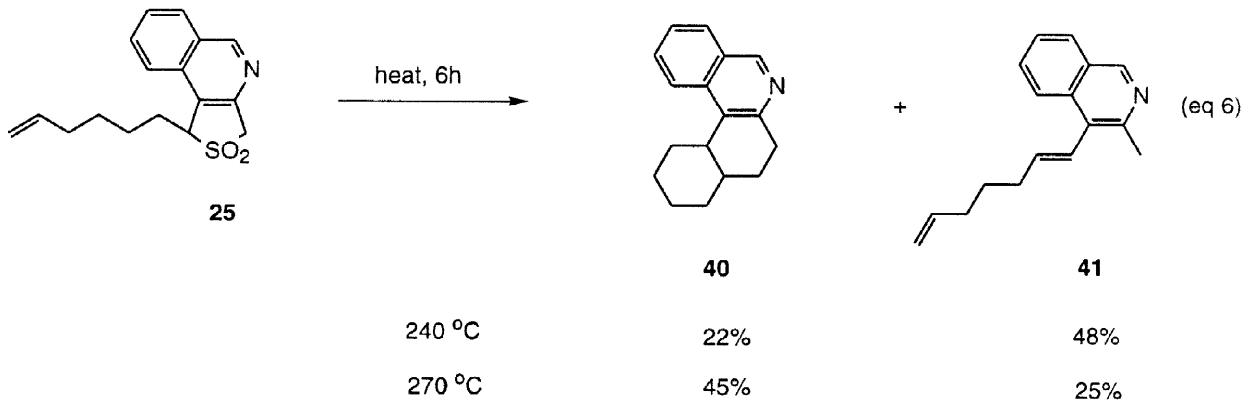
210 °C, 6h




**37** (1:6.8, 85%, two isomers)

(eq 4)




In summary, we have illustrated a facile synthesis of isoquinolino-3-sulfolene **7** and easy entries to its alkylated derivatives. We have also demonstrated that, depending on the structure of a heteroaromatic-fused 3-sulfolene, bond order and steric effects may influence the temperature required for thermal removal of $SO_2$. Isoquinolino-*o*-quinodimethanes have been generated for the first time.

## Experimental Section

The $^1H$ NMR spectra were measured as solutions in $CDCl_3$ with a Bruck AC 300 instrument and the 2 D NMR were measured with a Bruck AMX 500 NMR instrument, using tetramethylsilane as an internal standard. The IR spectra were measured with a Perkin-Elmer 882 or a Perkin-Elmer Paragon 1000 spectrometer. The mass spectra were measured with a VG 70-250s or a JOEL SX-102A mass spectrometer. Melting points (m.p.) were determined on a Yanaco apparatus and were uncorrected. Microanalyses were determined on a Perkin-Elmer 240C 2400 apparatus.

### 3-Acetoxy-4-[*N*-(*o*-bromobenzyl)acetamido]tetrahydrothiophene 1,1-Dioxide (10) and 3-[*N*-(*o*-Bromobenzyl)acetamido]-2,3-dihydrothiophene 1,1-Dioxide (11).

A mixture of 3,4-epoxysulfolane **8** (0.52 g, 3.87 mmol) , *o*-bromobenzylamine hydrochloride **9** (3.44 g, 15.48 mmol) and KOH (0.87 g, 15.5 mmol) in ethanol (90 mL) were heated at reflux for 7 h. The mixture was concerntrated under reduced pressure and acetic anhydride (30 mL) was added, and the resulting mixture was heated at reflux for 3 h. The solvent was removed under reduced pressure and the residue was purified by

column chromatography [silica gel, EtOAc/hexane (4:1)] to give **10** (0.83 g, 56%) and **11** (0.43 g, 34%). Compound **10** exists as an unseparable mixture of stereoisomers: white solid; mp 180-181 °C; $^1$H NMR δ 7.62 (d, *J* = 7.8 Hz, 1 H), 7.39-7.20 (m, 2 H), 7.10 (d, *J* = 7.1 Hz, 0.6 H), 7.02 (d, *J* = 7.6 Hz, 0.4 H), 5.69-5.56 (m, 1.3 H), 4.68-4.66 (m, 2 H), 4.01-3.91 (m, 1.3 H), 3.73-3.66 (m, 0.6 H), 3.50-3.29 (m, 1.3 H), 3.20-3.02 (m, 1.5 H), 2.21 (s, 1.8 H), 2.08 (s, 1.2 H), 2.04 (s, 1.8 H), 1.99 (s, 1.2 H); IR (KBr) 1744, 1650, 1312, 1211 cm$^{-1}$; MS (EI) *m/z* 391 ($M^+$+2), 389 ($M^+$), 307, 149 (100). Anal. Calcd for $C_{15}H_{18}BrNO_5S$: C, 44.49; H, 4.37; N, 3.49. Found: C, 44.56; H, 4.49; N 3.46. Compound **11**: white solid; mp 185-186 °C; $^1$H NMR δ 7.62 (d, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.26 (t, *J* = 7.5 Hz, 1 H), 7.16 (d, *J* = 7.5 Hz, 1 H), 6.74-6.71 (m, 1 H), 6.51-6.48 (m, 1 H), 5.90-5.87 (m, 1 H), 4.53 (s, 2 H), 3.60 (dd, *J* = 8.4, 14.4 Hz, 1 H), 3.14 (dd, *J* = 4.5, 14.4 Hz, 1 H), 2.10 (s, 3 H); IR (KBr) 3065, 2954, 1646, 1297, 1119 cm$^{-1}$; MS (EI) *m/z* 345 ($M^+$+2), 343 ($M^+$), 302, 300, 264 (100), 184, 186. Anal. Calcd for $C_{13}H_{14}BrNO_3S$: C, 45.35; H, 4.15; N, 3.94. Found: C, 45.36; H, 4.10; N, 4.07.

### *N*-Acetyl-1,3,3a,5,9b-pentahydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (12).

To a solution of **11** (0.069 g, 0.21 mmol) in benzene (20 mL) heated at reflux under a nitrogen atmosphere, was added a solution of AIBN (6.8 mg, 0.04 mmol) and $Bu_3SnH$ (0.07 mL, 0.26 mmol) in benzene (5 mL). After 3 h, the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel, EtOAc/hexane (4:1)] to give **12** (0.041 g, 74%): white solid; mp 202-203 °C; $^1$H NMR δ 7.32-7.20 (m, 4 H), 5.44 (bs, 1 H), 4.73-4.55 (m, 2 H), 4.01-3.99 (m, 1 H), 3.54-3.52 (m, 3 H), 3.12 (dd, *J* = 8.5, 13.5 Hz, 1 H), 2.23 (s, 3 H); IR (KBr) 2992, 1632, 1436, 1306, 1116 cm$^{-1}$; MS (EI) *m/z* 265 ($M^+$), 222 (100). Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.63; H, 5.67; N 5.14. Found: C, 58.84; H, 5.70; N 5.28.

### 1,3,3a,4,5,9b-Hexahydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (13).

A solution of **12** (0.22 g, 0.83 mmol) in 2 N HCl (20 mL) was heated at reflux for 48 h. The solvent was removed under reduced pressure and the residue was diluted with $CH_2Cl_2$ (100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL x 3). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give **13** (0.16 g, 87%): white solid; mp 147-148 °C; $^1$H NMR δ 7.26-7.09 (m, 4 H), 4.16 (d, *J* = 15.7 Hz, 1 H), 4.08 (d, *J* = 15.7 Hz, 1 H), 3.90-3.86 (m, 1 H), 3.68-3.48 (m, 2 H), 3.44-3.38 (m, 2 H), 3.17 (d, *J* = 14.0 Hz, 1 H); IR (KBr) 3328, 1288, 1122 cm$^{-1}$; MS (EI) *m/z* 223 ($M^+$), 206, 158, 130 (100). Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.10; H, 5.81; N, 6.10. Found: C, 59.17; H, 5.87; N, 6.27.

### 1,3,3a,9b-Tetrahydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (14).

A solution of **13** (14.2 mg, 0.06 mmol) and NBS (13 mg, 0.07 mmol) in $CHCl_3$ (10 mL) was stirred at room temperature for 1 h. The mixture was diluted with $CH_2Cl_2$ (100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL x 2). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give **14** (14.1 mg, 100%): white solid; mp 200-201 °C; $^1$H NMR δ 8.43 (bs, 1 H), 7.51-7.41 (m, 3 H), 7.24 (d, *J* = 6.3 Hz, 1 H), 4.49 (bs, 1 H), 3.91 (dd, *J* = 1.6, 13.8 Hz, 1 H), 3.78-3.66 (m, 2 H), 3.22 (dd, *J* = 7.4, 13.1 Hz, 1 H), 3.04 (t, *J* = 12.9 Hz, 1 H); IR (KBr) 2931, 1296, 1116 cm$^{-1}$; MS (EI) *m/z* 221 ($M^+$), 156 (100). Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.63; H, 4.94; N, 6.19. Found: C, 59.70; H, 5.01; N, 6.33.

**1,3-Dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (7).**

A solution of **14** (14.1 mg, 0.06 mmol), NBS (13.6 mg, 0.08 mmol) and AIBN (5.2 mg, 0.05 mmol) in benzene (10 mL) was heated at reflux under nitrogen for 3 h. The mixture was diluted with EtOAc (100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL x 2). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by HPLC [LiChrosorb column, EtOAc] to give **7** (10.1 mg, 71%): white solid; mp 210 °C (dec.); $^1$H NMR δ 9.25 (s, 1 H), 8.08 (d, $J$ = 7.1 Hz, 1 H), 7.86 (t, $J$ = 7.1 Hz, 1 H), 7.74 (d, $J$ = 7.1 Hz, 1 H), 7.69 (t, $J$ = 7.1 Hz, 1 H), 4.76 (s, 2 H), 4.72 (s, 2 H); IR (KBr) 1298, 1116 cm$^{-1}$; MS (EI) *m/z* 219 ($M^+$), 167, 155, 149 (100). Anal. Calcd for $C_{11}H_9NO_2S$: C, 60.00; H, 4.18; N, 6.21. Found: C, 60.25; H, 4.14; N, 6.39.

**Deprotonation/alkylation Reactions of 1,3-Dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (7).**

To a solution of **7** (0.1 g, 0.47 mmol) and HMPA (0.4 mL) in THF (15 mL) at -78 °C under nitrogen was added LiHMDS (2.0 M n-BuLi 0.23 mL, hexamethyldisilazane 0.18 mL) dropwise. After the mixture was stirred for 0.5 h, MeI (0.2 mL, 3.2 mmol) (or 5-iodo-pentene, 6-iodo-hexene) was added in one portion, and the resulting mixture was warmed to 0 °C. After 0.5 hour, EtOAc (5 mL) was added in one portion, and the resulting mixture was warmed to room temperature gradually. The mixture was concentrated under reduced pressure. The residue was eluted with EtOAc/hexane (1:1) through a silica gel column to remove HMPA and then purified by HPLC [LiChrosorb column, EtOAc/hexane (2:1) ] to give the mono- and dialkylated products of which the yields are shown in eq 1 and eq 2.

**3-Methyl-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (15).** White solid; mp 140-141 °C; $^1$H NMR δ 9.25 (s, 1 H), 8.07 (d, $J$ = 8.1 Hz, 1 H), 7.85 (t, $J$ = 6.2 Hz, 1 H), 7.74-7.66 (m, 2 H), 4.68 (s, 2 H), 4.57 (q, $J$ = 7.1 Hz, 1 H), 1.82 (d, $J$ = 7.1 Hz, 3 H); IR (KBr) 2928, 1303, 1128 cm$^{-1}$; MS (EI) *m/z* 233 ($M^+$), 168 (100). Anal. Calcd for $C_{12}H_{11}NO_2S$: C, 61.70; H, 4.70; N, 5.92. Found: C, 61.78; H, 4.75; N, 6.00.

**1-Methyl-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (16).** White solid; mp 214-215 °C; $^1$H NMR δ 9.22 (s, 1 H), 8.08 (d, $J$ = 8.2 Hz, 1 H), 7.86-7.71 (m, 3 H), 4.79 (q, $J$ = 7.3 Hz, 1 H), 4.66 (d, $J$ = 16.5 Hz, 1 H), 4.58 (d, $J$ = 16.5 Hz, 1 H), 1.79 (d, $J$ = 7.3 Hz, 3 H); IR (KBr) 2923, 1308, 1129 cm$^{-1}$; MS (EI) *m/z* 233 ($M^+$), 168 (100). HRMS Calcd for $C_{12}H_{11}NO_2S$ 233.0511, Found 233.0510.

***trans*-1,3-Dimethyl-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (17).** White solid; mp 170-171 °C; $^1$H NMR δ 9.24 (s, 1 H), 8.07 (d, $J$ = 6.7 Hz, 1 H), 7.84-7.00 (m, 3 H), 4.72 (q, $J$ = 7.4 Hz, 1 H), 4.53 (q, $J$ = 6.8 Hz, 1 H), 1.85 (d, $J$ = 6.8 Hz, 3 H), 1.78 (d, $J$ = 7.4 Hz, 3 H); IR (KBr) 2928, 1308, 1125 cm$^{-1}$; MS (EI) *m/z* 247 ($M^+$), 182 (100), 168. HRMS Calcd for $C_{13}H_{13}NO_2S$ 247.0663, Found 247.0667.

***cis*-1,3-Dimethyl-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (18).** White solid; mp 189-190 °C; $^1$H NMR δ 9.24 (s, 1 H), 8.07 (d, $J$ = 8.0 Hz, 1 H), 7.86 (t, $J$ = 8.0 Hz, 1 H), 7.79 (d, $J$ = 8.0 Hz, 1 H), 7.70 (t, $J$ = 8.0 Hz, 1 H), 4.78 (q, $J$ = 7.3 Hz, 1 H), 4.76 (q, $J$ = 7.5 Hz, 1 H), 1.81 (d, $J$ = 7.3 Hz, 3 H),

1.80 (d, $J$ = 7.5 Hz, 3 H); IR (KBr) 2921, 1308, 1125 $cm^{-1}$; MS (EI) $m/z$ 247 ($M^+$), 183, 168 (100), 156. HRMS Calcd for $C_{13}H_{13}NO_2S$ 247.0658, Found 247.0667.

**3-(4-Pentenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (20).** White solid; mp 103-104 °C; $^1H$ NMR δ 9.24 (s, 1 H), 8.06 (d, $J$ = 8.1 Hz, 1 H), 7.84 (t, $J$ = 8.6 Hz, 1 H), 7.73-7.65 (m, 2 H), 5.91-5.78 (m, 1 H), 5.10-4.97 (m, 2 H), 4.65 (s, 2 H), 4.50-4.45 (m, 1 H), 2.41-2.33 (m, 1 H), 2.28-2.16 (m, 3 H), 1.91-1.79 (m, 2 H); IR (KBr) 2920, 1621, 1575, 1303, 1126 $cm^{-1}$; MS (EI) $m/z$ 287 ($M^+$), 223, 168 (100). Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.62; H, 5.87; N, 4.71. Found: C, 66.87; H, 5.96; N, 4.87.

**1-(4-Pentenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (21).** White solid; mp 68-69 °C; $^1H$ NMR δ 9.22 (s, 1 H), 8.07 (d, $J$ = 8.2 Hz, 1 H), 7.88-7.69 (m, 3 H), 5.81-5.68 (m, 1 H), 5.04-4.95 (m, 2 H), 4.74-4.70 (m, 1 H), 4.66 (d, $J$ = 16.3 Hz, 1 H), 4.56 (d, $J$ = 16.3 Hz, 1 H), 2.27-2.05 (m, 4 H), 1.74-1.64 (m, 2 H); IR (KBr) 2926, 1623, 1575, 1306, 1119 $cm^{-1}$; MS (EI) $m/z$ 287 ($M^+$), 223, 180, 167 (100). Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.46; H, 5.86; N, 4.64. Found: C, 66.87; H, 5.96; N, 4.87.

***trans*-1,3-Bis(4-pentenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (22).** Colorless oil; $^1H$ NMR δ 9.22 (s, 1 H), 8.06 (d, $J$ = 8.2 Hz, 1 H), 7.83 (t, $J$ = 8.1 Hz, 1 H), 7.74-7.67 (m, 2 H), 5.93-5.69 (m, 2 H), 5.13-4.95 (m, 4 H), 4.66-4.61 (m, 1 H), 4.45-4.41 (m, 1 H), 2.64-2.56 (m, 1 H), 2.30-1.88 (m, 9 H), 1.74-1.63 (m, 2 H); IR ($CHCl_3$) 2931, 1575, 1308, 1121 $cm^{-1}$; MS (EI) $m/z$ 355 ($M^+$), 290, 236, 180, 149 (100). HRMS Calcd for $C_{21}H_{25}NO_2S$ 355.1605, Found 355.1606.

***cis*-1,3-Bis(4-pentenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (23).** Colorless oil; $^1H$ NMR δ 9.22 (s, 1 H), 8.05 (d, $J$ = 8.2 Hz, 1 H), 7.83 (t, $J$ = 8.4 Hz, 1 H), 7.74-7.67 (m, 2 H), 5.88-5.79 (m, 2 H), 5.09-4.97 (m, 4 H), 4.64 (dd, $J$ = 3.7, 9.0 Hz, 1 H), 4.30 (dd, $J$ = 5.9, 8.0 Hz, 1 H), 2.23-2.09 (m, 8 H), 1.94-1.86 (m, 4 H); IR ($CHCl_3$) 2902, 1794, 1462, 1380, 1304, 1105 $cm^{-1}$; MS (EI) $m/z$ 355($M^+$), 300, 291, 236(100), 223, 180, 168. HRMS Calcd for $C_{21}H_{25}NO_2S$ 355.1613, Found 355.1606.

**3-(5-Hexenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (24).** White solid; mp 68-69 °C; $^1H$ NMR δ 9.24 (s, 1 H), 8.06 (d, $J$ = 8.1 Hz, 1 H), 7.84 (t, $J$ = 7.5 Hz, 1 H), 7.73-7.65 (m, 2 H), 5.89-5.76 (m, 1 H), 5.05-4.94 (m, 2 H), 4.65 (s, 2 H), 4.49-4.44 (m, 1 H), 2.40-2.04 (m, 5 H), 1.82-1.72 (m, 2 H), 1.60-1.50 (m, 1 H); IR ($CHCl_3$) 2931, 1625, 1575, 1321, 1123 $cm^{-1}$; MS (EI) $m/z$ 301 ($M^+$), 260, 237, 196, 168 (100). HRMS Calcd for $C_{17}H_{19}NO_2S$ 301.1134, Found 301.1136.

**1-(5-Hexenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (25).** White solid; mp 93-94 °C; $^1H$ NMR δ 9.22 (s, 1 H), 8.07 (d, $J$ = 8.2 Hz, 1 H), 7.88-7.83 (m, 1 H), 7.75-7.69 (m, 2 H), 5.79-5.68 (m, 1 H), 4.99-4.91 (m, 2 H), 4.72-4.68 (m, 1 H), 4.64 (d, $J$ = 16.5 Hz, 1 H), 4.54 (d, $J$ = 16.5 Hz, 1 H), 2.30-2.01 (m, 4 H), 1.65-1.42 (m, 4 H); IR (KBr) 2931, 1622, 1574, 1306, 1120 $cm^{-1}$; MS (EI) $m/z$ 301 ($M^+$), 237, 180 (100). HRMS Calcd for $C_{17}H_{19}NO_2S$ 301.1126, Found 301.1136.

***trans*-1,3-Bis(5-hexenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (26).** White solid; mp 67-68 °C; $^1H$ NMR δ 9.21 (s, 1 H), 8.05 (d, $J$ = 8.2 Hz, 1 H), 7.83 (t, $J$ = 8.1 Hz, 1 H), 7.73-7.66 (m, 2 H), 5.92-5.70 (m, 2 H), 5.08-4.90 (m, 4 H), 4.61 (dd, $J$ = 4.0, 8.1 Hz, 1 H), 4.41 (dd, $J$ = 3.7, 10.4 Hz, 1 H), 2.62-2.50 (m, 1 H), 2.25-2.00 (m, 7 H), 1.97-1.75 (m, 2 H), 1.69-1.39 (m, 6 H); IR (KBr) 2923, 1623,

1571, 1298, 1120 $cm^{-1}$; MS (EI) *m/z* 383 ($M^+$), 342, 319, 278, 250 (100), 236, 180, 168. Anal. Calcd for $C_{23}H_{29}NO_2S$: C, 72.00; H, 7.56; N, 3.48. Found: C, 72.03; H, 7.62; N, 3.65.

***cis*-1,3-Bis(5-hexenyl)-1,3-dihydrothieno[3,4-*b*]isoquinoline 2,2-Dioxide (27).** Colorless oil; $^1H$ NMR δ 9.22 (s, 1 H), 8.06 (d, *J* = 8.1 Hz, 1 H), 7.86-7.81 (m, 1 H), 7.73-7.67 (m, 2 H), 5.87-5.76 (m, 2 H), 5.05-4.93 (m, 4 H), 4.62 (dd, *J* = 3.3, 9.2 Hz, 1 H), 4.28 (dd, *J* = 5.8, 8.2 Hz, 1 H), 2.21-2.04 (m, 10 H), 1.85-1.47 (m, 6 H); IR ($CHCl_3$) 2920, 1624, 1576, 1305, 1107 $cm^{-1}$; MS (EI) *m/z* 383 ($M^+$), 320, 278, 250, 180, 168 (100). HRMS Calcd for $C_{23}H_{29}NO_2S$: 383.1903, Found 383.1919.

**1,3-Dioxo-2-phenyl-1,3,3a,4,11,11a-hexahydropyrrolo[3,4-*d*]phenanthridine (29).**

A solution of **7** (6.6 mg, 0.03 mmol) and *N*-phenylmaleimide (31.9 mg, 0.076 mmol) in benzene (5 mL) was heated at 210 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc] to give **29** (8.3 mg, 84%): light yellow solid; mp 206-207 °C; $^1H$ NMR δ 9.12 (s, 1 H), 8.08 (d, *J* = 8.7 Hz, 1 H), 7.97 (d, *J* = 8.1 Hz, 1 H), 7.78-7.57 (m, 2 H), 7.34-7.24 (m, 3 H), 6.93-6.89 (m, 2 H), 3.93 (dd, *J* = 3.5, 15.2 Hz, 1 H), 3.69-3.61 (m, 3 H), 3.42-3.35 (m, 1 H), 3.18 (dd, *J* = 5.9, 15.2 Hz, 1 H); IR (KBr) 1707, 1388, 1182, 751 $cm^{-1}$; MS (EI) *m/z* 328 ($M^+$), 180 (100). HRMS Calcd for $C_{21}H_{16}N_2O_2$ 328.1219, Found 328.1212.

***trans*-2,3-Bis(methoxycarbonyl)-1,2,3,4-tetrahydrophenanthridine (30).**

A solution of **7** (3.6 mg, 0.016 mmol) and dimethyl fumarate (23.6 mg, 0.164 mmol) in benzene (4 mL) was heated at 210 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc] to give **30** (4.8 mg, 98%): mp 125-126 °C; $^1H$ NMR δ 9.10 (s, 1 H), 7.96 (d, *J* = 8.1 Hz, 1 H), 7.88 (d, *J* = 8.6 Hz, 1 H), 7.77-7.71 (m, 1 H), 7.62-7.56 (m, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.60-3.21 (m, 6 H); IR (KBr) 1729, 1438, 1199 $cm^{-1}$; MS (EI) *m/z* 299 ($M^+$), 240 (100), 180 (100). HRMS Calcd for $C_{17}H_{17}NO_4$ 299.1159, Found 299.1158.

***trans*-2,3-Bis(methoxycarbonyl)-4-methyl-1,2,3,4-tetrahydrophenanthridine (31).**

A solution of **15** (13.5 mg, 0.058 mmol) and dimethyl fumarate (90.0 mg, 0.624 mmol) in benzene (5 mL) was heated at 210 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **31** as a 1:1.25 mixture of stereoisomers (17.1 mg, 94%). The minor and more polar isomer: colorless oil; $^1H$ NMR δ 9.14 (s, 1 H), 7.97-7.56 (m, 4 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.65-3.40 (m, 2 H), 3.27-3.14 (m, 2 H), 2.89-2.82 (m, 1 H), 1.54 (d, *J* = 7.1 Hz, 3 H); IR ($CHCl_3$) 2950, 1729, 1437 $cm^{-1}$; MS (EI) *m/z* 313 ($M^+$), 282, 254 (100), 194. HRMS Calcd for $C_{18}H_{19}NO_4$ 313.1286, Found 313.1314. The major and less polar isomer: white solid; mp 145-146 °C; $^1H$ NMR δ 9.13 (s, 1 H), 7.95-7.59 (m, 4 H), 3.83 (s, 3 H), 3.79 (s, 3 H), 3.69-3.57 (m, 2 H), 3.40-3.23 (m, 2 H), 3.02 (dd, *J* = 11.5, 16.8 Hz, 1 H), 1.28 (d, *J* = 6.9 Hz, 3 H); IR (KBr) 2968, 1736, 1167 $cm^{-1}$; MS (EI) *m/z* 313 ($M^+$), 282, 254 (100), 194. HRMS Calcd for $C_{18}H_{19}NO_4$ 313.1309, Found 313.1314.

***trans*-2,3-Bis(methoxycarbonyl)-1-methyl-1,2,3,4-tetrahydrophenanthridine (33) and**

**3-Methyl-4-vinyl-isoquinoline (35).**

A solution of **16** (29.2 mg, 0.118 mmol) and dimethyl fumarate (170.0 mg, 1.18 mmol) in benzene (5 mL) was heated at 240 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:9)] to give **33** as a 1:1.75 mixture of unseparable stereoisomers (19.9 mg, 54%) and **35** (0.9 mg, 4%). Compound **33** (Although the stereoisomers could not be separated by HPLC, their NMR signals are well resolved): white solid; mp 110-115 °C; $^1$H NMR of the major isomer: δ 9.08 (s, 1 H), 7.98-7.53 (m, 4 H), 4.08-4.04 (m, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.59-3.08 (m, 5 H), 1.25 (d, *J* = 6.8 Hz, 3 H); the minor isomer: δ 9.06 (s, 1 H), 7.98-7.53 (m, 4 H), 4.08-4.04 (m, 1 H), 3.77 (s, 3 H), 3.76 (s, 3 H), 3.59-3.08 (m, 5 H), 1.46 (d, *J* = 7.2 Hz, 3 H); IR (KBr) 2950, 1735 cm$^{-1}$; MS (EI) *m/z* 313 ($M^+$), 282, 245 (100), 194. HRMS Calcd for $C_{18}H_{19}NO_4$ 313.1306, Found 313.1314. Compound **35**: colorless oil; $^1$H NMR δ 9.09 (s, 1 H), 8.07 (d, *J* = 8.5 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.65 (t, *J* = 8.5 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.00 (dd, *J* = 11.5, 17.8 Hz, 1 H), 5.81 (dd, *J* = 1.9, 11.5 Hz, 1 H), 5.52 (dd, *J* = 1.9, 17.8 Hz, 1 H), 2.71 (s, 3 H); IR ($CHCl_3$) 2960, 1622, 1573 cm$^{-1}$; MS (EI) *m/z* 169 ($M^+$), 145 (100), 91. HRMS Calcd for $C_{12}H_{11}N$ 169.0894, Found 169.0891.

**3,4-Cyclopentano-1,2,3,4-tetrahydrophenanthridine (36).**

A solution of **20** (20.1 mg, 0.07 mmol) in benzene (5 mL) was heated at 210 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **36** as a 1:1.17 mixture of stereoisomers (14.1 mg, 91%). The minor and less polar isomer: white solid; mp 76-77 °C; $^1$H NMR δ 9.09 (s, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.89 (d, *J* = 7.3 Hz, 1 H), 7.68 (dd, *J* = 7.6, 8.4 Hz, 1 H), 7.52 (dd, *J* = 7.3, 7.6 Hz, 1 H), 3.36 (dd, *J* = 6.2, 17.6 Hz, 1 H), 3.25-3.19 (m, 1 H), 2.74-2.71 (m, 1 H), 2.55-2.50 (m, 1 H), 2.36-2.30 (m, 1 H), 1.98-1.65 (m, 6 H), 1.44-1.34 (m, 1 H); IR (KBr) 2927,1569, 750 cm$^{-1}$; MS (M/Z) (EI) *m/z* 223 ($M^+$, 100), 208, 195. HRMS Calcd for $C_{16}H_{17}N$ 223.1353, Found 223.1361. The major and more polar isomer: colorless oil; $^1$H NMR δ 9.10 (s, 1 H), 7.94 (d, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.69 (dd, *J* = 7.6, 8.2 Hz, 1 H), 7.52 (dd, *J* = 7.6, 8.2 Hz, 1 H), 3.39 (dd, *J* = 7.7, 15.5 Hz, 1 H), 3.18 (td, *J* = 5.0, 16.7 Hz, 1 H), 2.99-2.89 (m, 1 H), 2.50-2.38 (m, 2 H), 2.08-1.83 (m, 2 H), 1.76-1.51 (m, 5 H); IR ($CHCl_3$) 2936, 1623, 1579 cm$^{-1}$; MS (EI) *m/z* 223 ($M^+$, 100), 208, 195. HRMS Calcd for $C_{16}H_{17}N$ 223.1356, Found 223.1361.

**5-Aza-1,2,3,4,4a,11,12,12a-octahydrochrysene (37).**

A solution of **24** (5.8 mg, 0.02 mmol) in benzene (5 mL) was heated at 210 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:2)] to give **37** as a 1:6.8 mixture of stereoisomers (3.9 mg, 85%). The minor and more polar isomer: white solid; mp 79-80 °C; $^1$H NMR δ 9.10 (s, 1 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.67 (t, *J* = 8.4 Hz, 1 H), 7.55 (t, *J* = 8.4 Hz, 1 H), 3.24 (dd, *J* = 5.8, 17.0 Hz, 1 H), 3.13-2.93 (m, 2 H), 2.04-1.94 (m, 2 H), 1.88-1.82 (m, 2 H), 1.69-1.09 (m, 6 H); IR (KBr) 2912, 753 cm$^{-1}$; MS (EI) *m/z* 237 ($M^+$, 100), 222, 208, 182. HRMS Calcd for $C_{17}H_{19}N$ 237.1519, Found 237.1517. The major and less polar isomer: white solid; mp 89-90 °C; $^1$H NMR δ 9.08 (s, 1 H), 7.94-7.90 (m, 2 H), 7.71-7.66 (m, 1 H), 7.56-

7.51 (m, 1 H), 3.32-3.24 (m, 1 H), 3.06-2.97 (m, 2 H), 2.19-2.08 (m, 3 H), 1.78-1.74 (m, 4 H), 1.70-1.48 (m, 4 H); IR (KBr) 2924 $cm^{-1}$; MS (EI) *m/z* 237 ($M^+$), 222, 208, 182(100). HRMS Calcd for $C_{17}H_{19}N$ 237.1517, Found 237.1517.

**1,2-Cyclopentano-1,2,3,4-tetrahydrophenanthridine (38) and 4-(1,5-Hexadienyl)-3-methylisoquinoline (39).**

A solution of **21** (10.3 mg, 0.04 mmol) in benzene (5 mL) was heated at 240 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **38** as a 1:5.5 mixture of unseparable stereoisomers (3.5 mg, 44%) and **39** (2.3 mg, 28%). Compound **38**: colorless oil; $^1H$ NMR δ 9.03 (s, 1 H), 8.13 (d, *J* = 8.5 Hz, 0.85 H), 8.0 (d, *J* = 9.0 Hz, 0.15 H), 7.90 (d, *J* = 8.1 Hz, 1 H), 7.67-7.47 (m, 2 H), 3.56-3.50 (m, 0.15 H), 3.32-3.07 (m, 2.15 H), 2.91-2.76 (m, 1.7 H), 2.54-2.45 (m, 0.3 H), 2.25-2.19 (m, 0.85 H), 2.02-1.37 (m, 5.85 H); IR ($CHCl_3$) 2950, 1695, 1622, 1579 $cm^{-1}$; MS (EI) *m/z* 223 ($M^+$, 100), 208, 194, 180. HRMS Calcd for $C_{16}H_{17}N$ 223.1353, Found 223.1361. Compound **39**: colorless oil; $^1H$ NMR δ 9.07 (s, 1 H), 8.05 (d, *J* = 8.6 Hz, 1 H), 7.91 (d, *J* = 8.0 Hz, 1 H), 7.67-7.61 (m, 1 H), 7.52 (dd, *J* = 7.4, 7.7 Hz, 1 H), 6.65 (d, *J* = 16.2 Hz, 1 H), 6.00-5.87 (m, 2 H), 5.16-5.04 (m, 2 H), 2.69 (s, 3 H), 2.49 (td, *J* = 7.0, 7.5 Hz, 2 H), 2.39-2.32 (m, 2 H); IR ($CHCl_3$) 2931, 1653, 1602 $cm^{-1}$; MS (EI) *m/z* 223 ($M^+$), 182 (100), 167. HRMS Calcd for $C_{16}H_{17}N$ 223.1364, Found 223.1361.

**1,2-Cyclohexano-1,2,3,4-tetrahydrophenanthridine (40) and 4-(1,6-Heptadienyl)-3-methylisoquinoline (41).**

A solution of **25** (16.9 mg, 0.06 mmol) in benzene (7 mL) was heated at 270 °C in a sealed tube under nitrogen for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by HPLC [LiChrosorb column, EtOAc/hexane (1:1)] to give **40** (6.0 mg, 45%) and **41** (3.3 mg, 25%). Compound **40**: white solid; mp 103-104 °C; $^1H$ NMR δ 9.01 (s, 1 H), 7.93-7.88 (m, 2 H), 7.66-7.60 (m, 1 H), 7.47 (t, *J* = 7.6 Hz, 1 H), 3.29-3.19 (m, 1 H), 2.96-2.87 (m, 2 H), 2.69-2.61 (m, 1 H), 1.93-1.82 (m, 4 H), 1.73-1.42 (m, 4 H), 1.16-1.04 (m, 2 H); IR (KBr) 2925, 1563, 753 $cm^{-1}$; MS (EI) *m/z* 237 ($M^+$, 100), 222, 208, 194, 180. HRMS Calcd for $C_{17}H_{19}N$ 237.1516, Found 237.1517. Compound **41**: colorless oil; $^1H$ NMR δ 9.06 (s, 1 H), 8.04 (d, *J* = 8.5 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.64 (dd, *J* = 8.1, 8.5 Hz, 1 H), 7.51 (dd, *J* = 8.1, 8.5 Hz, 1 H), 6.64 (d, *J* = 16.2 Hz, 1 H), 5.97-5.84 (m, 2 H), 5.12-5.00 (m, 2 H), 2.69 (s, 3 H), 2.40 (td, *J* = 6.3, 8.3 Hz, 2 H), 2.21 (td, *J* = 6.9, 7.5 Hz, 2 H), 1.74-1.64 (m, 2 H); IR ($CHCl_3$) 2932, 1640, 1620, 972, 917 $cm^{-1}$; MS (EI) *m/z* 237 ($M^+$), 222, 180 (100), 167. HRMS Calcd for $C_{17}H_{19}N$ 237.1517, Found 237.1517.

**Acknowledgement** We thank the National Science Council for financial supports. We also thank Dr. K. J. Lin for the X-ray analysis of compound **17** and Ms. S. C. Lin for the NOESY experiments.

## References


1. For a recent review on heteroaromatic-*o*-quinodimethanes, see: Chou, T. S. *Rev. Heteroatom Chem.* **1993**, *8*, 65.

2. Chou, T. S.; Chen, H. C.; Tsai, C. Y. *J. Org. Chem.* **1994**, *59*, 2241.

3. Chou, T. S.; Ko, C. W. *Tetrahedron* **1994**, *50*, 10721.

4. Chao, I.; Lu, H. F.; Chou, T. S. *J. Org. Chem.* **1997**, *62*, 7882.

5. White, L. A.; Storr, R. C. *Tetrahedron* **1996**, *52*, 3117.

6. Sorenson, W. R. *J. Org. Chem.* **1959**, *24*, 1796.

7. For a recent review, see: Aldabbagh, F.; Bowman, W. R. *Contemp. Org. Synth.* **1997**, *4*, 261.

8. (a) Chou, T. S.; Tsai, C. Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1287. (b) Chou, T. S.; Chang, R. C. *J. Chem. Soc., Chem. Commun.* **1992**, 549. (c) Chou, T. S.; Tsai, C. Y. *Tetrahedron Lett.* **1992**, *33*, 4201. (d) Chou, T. S.; Chang, R. C. *Tetrahedron Lett.* **1992**, *33*, 8121. (e) Chou, T. S.; Chang, R. C. *Heterocycles* **1993**, *36*, 2839. (f) Chou, T. S.; Chen, H. C. *Tetrahedron Lett.* **1996**, *37*, 7823.

9. For reviews see: (a) Chou, T. S.; Tso, H. H. *Org. Prep. Proc. Int.* **1989**, *21*, 257. (b) Chou, T. S.; Chou, S. S. P. *J. Chin. Chem. Soc.* **1992**, *39*, 625.

10. Mock, W. L.; Mehrotra, I.; Anderko, J. *J. Org. Chem.* **1975**, *40*, 1842.