

1,2-Bis(phenylsulfonyl)-1*H*-indole as an acceptor of organocuprate nucleophiles

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Dedicated to Professor James M. Cook on the occasion of his 65th birthday

DOI: <http://dx.doi.org/10.3998/ark.5550190.0011.406>

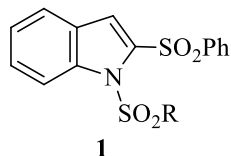
Abstract

1,2-Bis(phenylsulfonyl)-1*H*-indole is a novel example of an electron-deficient indole that undergoes nucleophilic attack at C-3. Though a variety of other organometallic nucleophiles fail to engender nucleophilic substitution, organocuprates produce 3-substituted 2-(phenylsulfonyl)-1*H*-indoles. These reactions contribute to the growing number of examples of nucleophilic addition to the indole core.

Keywords: Electron-deficient indole, nucleophilic addition, arylsulfonyl

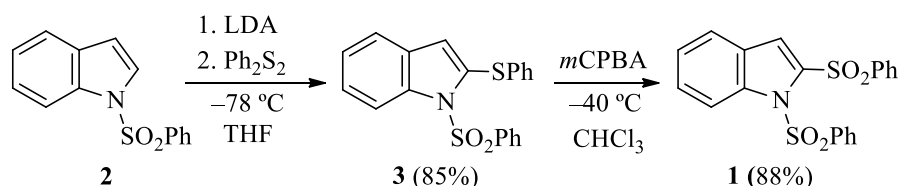
Introduction

While the electron-rich indole is typically reactive towards electrophilic reagents, electron-deficient indoles allow access to the divergent utility of nucleophiles.¹ Indeed, several electron-withdrawing functionalities permit nucleophilic addition to the indole nucleus, with recent examples favoring the use of nitro groups.² In most cases, the presence of a leaving group is necessary for this reactivity, resulting in a formal S_N2' or addition-elimination mechanism to give the substituted indole. Nucleophilic substitution at C-3 is especially appealing because these transformations are almost entirely contrary to the traditional reactivity of indole. To effect C–H substitution, leaving groups may be placed at N-1 as discussed in the review by Joule.³ Early examples employed 1-hydroxy- and 1-methoxy-substituted indoles to enable substitution, while more recent techniques have favored the phenylsulfonyl group.^{2,4} The phenylsulfonyl group is a versatile moiety capable of acting as a powerful electron-withdrawing group, direct-metalation group, and leaving group.⁵ Noting these advantages, we investigated 1,2-bis(phenylsulfonyl)-1*H*-indole **1** as an electron-deficient indole capable of undergoing nucleophilic substitution at C-3.



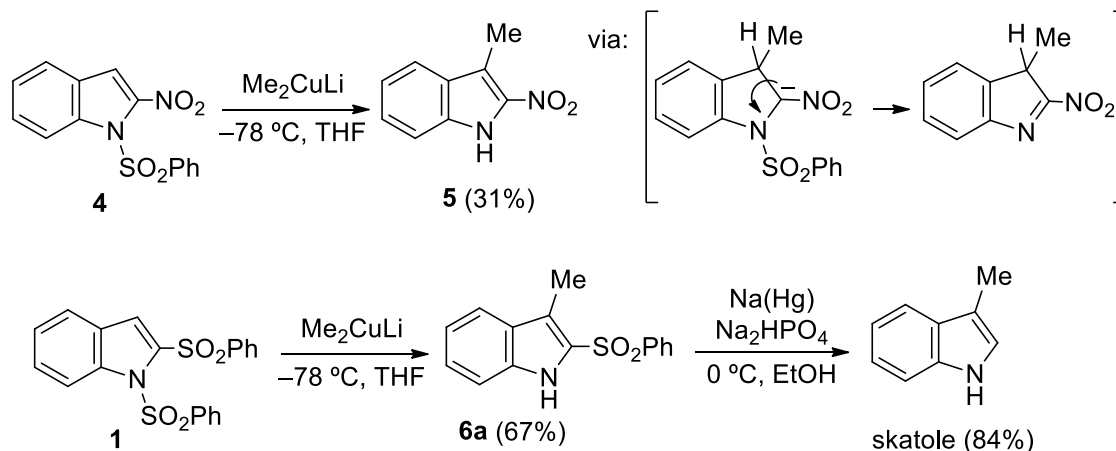
Results and Discussion

1,2-Bis(phenylsulfonyl)-1*H*-indole **1** is readily produced from indole in three steps in high overall yield (75%). Thus, direct lithiation of 1-(phenylsulfonyl)-1*H*-indole **2** and a subsequent quench with diphenyldisulfide produced 2-thiophenylindole **3** in excellent yields. It should be noted that quenching the 2-lithio-1-(phenylsulfonyl)-1*H*-indole with benzenesulfonyl chloride does not produce **3**, but surprisingly produces 2-chloro-1-(phenylsulfonyl)-1*H*-indole. Oxidation of **3** with *m*-CPBA cleanly provides **1** in high yield.



Scheme 1. Synthesis of 1,2-bis(phenylsulfonyl)-1*H*-indole **1**.

Our initial work with electron-deficient indoles involved nucleophilic addition to 2-nitro-1-(phenylsulfonyl)indole **4**.^{2a} Through a formal $\text{S}_{\text{N}}2'$ mechanism, 2-nitroindole **4** demonstrated reactivity with a variety of nucleophiles including the first example of cuprate addition to an indole (Scheme 2). Unfortunately, syntheses of **4** suffer from low yields and difficult reaction conditions.⁶ In contrast, 1,2-bis(phenylsulfonyl)-1*H*-indole **1** provides a readily accessible 2-substituted electron-deficient indole that may demonstrate reactivity similar to the corresponding 2-nitroindole **4**.



Scheme 2. Addition of lithium dimethyl cuprate to **4** and **1**.

As an initial comparison, the addition of lithium dimethylcuprate to **1** produced favorable yields (67% vs. 31%) of 3-methylated product. To verify the structure of **6a**, Na(Hg) was employed to reductively cleave the sulfonyl moiety, producing skatole; this transformation highlights an additional advantage of the C-2 phenylsulfonyl group.

With preliminary results in hand, we screened various sources of organometallic methyl nucleophiles. Grignard and organozinc reagents offered no reaction and allowed clean recovery of starting material. Methyllithium showed a slight inclination towards C-3 nucleophilic attack, but produced a mixture of other products as well as starting material. Gilman reagents were generated from methyllithium and copper bromide dimethylsulfide complex.⁷ While these cuprates readily produced **6a** as the major product at $-78\text{ }^{\circ}\text{C}$, reactions at higher temperatures were less consistent and favored sulfone **7a**. Formation of **7a** is presumed to result from attack on the *N*-protecting phenylsulfonyl group. However, the corresponding unprotected 3-methyl-2-(phenylsulfonyl)-1*H*-indole was never isolated under these reaction conditions. Reaction time beyond 2 hours did not significantly increase yields of either product.

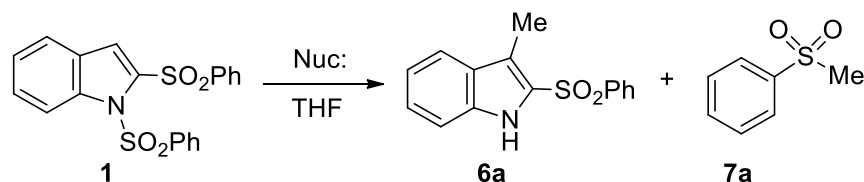
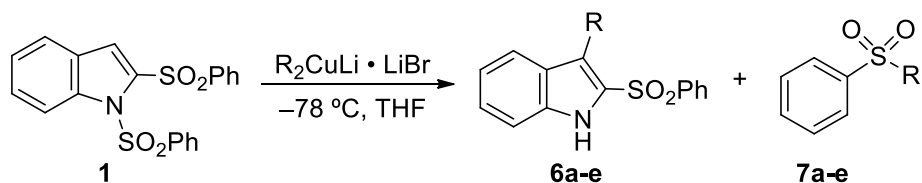


Table 1. Addition of organometallic methyl nucleophiles to **1**

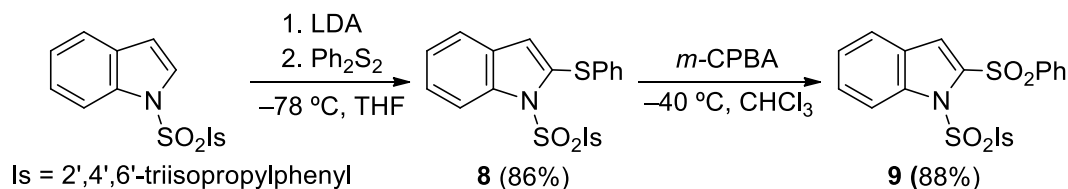
Nucleophile	Solvent	Time	Temp. ($^{\circ}\text{C}$)	Yield 6a (%)	Yield 7a (%)	Recovery 1 (%)
MeMgBr	THF	2 h	-78 to rt	0	0	>95
Me ₂ Zn	THF	2 h	-78 to rt	0	0	>95
MeLi	THF	2 h	-78 to rt	4	3	79
Me ₂ CuLi	THF	2 h	-78 to rt	67	12	5
Me ₂ CuLi	THF	12 h	-78 to rt	68	12	3
Me ₂ CuLi	THF	2 h	0 to rt	trace	26	45
Me ₂ CuLi	THF	12 h	0 to rt	trace	30	32
Me ₂ CuLi	Et ₂ O	2 h	-78 to rt	47	10	12
Me ₂ CuMgBr	Et ₂ O	4 h	-78 to rt	0	0	>95

Following the success of lithium dimethylcuprate, we examined a series of Gilman reagents to determine the generality of this reaction. While the *n*-butyl derivative gave results in line with our previous reactions, the other cuprates showed varied selectivity. The structure, reactivity, and stability of organocuprates can be expected to vary as a function of solvent, temperature, counter ion, as well as alkyl ligand.⁸ In this case, the results from Table 2 suggest a sensitivity to the structure or dynamics of the copper complex, rather than a steric effect.

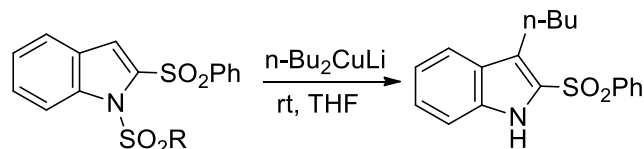
**Table 2.** Nucleophilic addition of lithium dialkyl cuprates to **1**

Entry	R	Yield 6 (%)	Yield 7 (%)	Recovery 1 (%)
a	Me	67	12	5
b	<i>n</i> -C ₄ H ₉	77	5	9
c	<i>s</i> -C ₄ H ₉	0	36	21
d	<i>t</i> -C ₄ H ₉	40	0	28
e	Ph	43	20	15

As sulfone formation presumably cannibalizes the yield of these processes, the more hindered and less labile 'isitylsulfonyl' protecting group was examined (isityl = 2',4',6'-triisopropylphenyl). 1-(Isitylsulfonyl)-2-(phenylsulfonyl)-1*H*-indole **9** was produced in the same manner as **1** (Scheme 3).

**Scheme 3.** Preparation of 1-(isitylsulfonyl)-2-(phenylsulfonyl)-1*H*-indole **9**.

In comparison to the room temperature addition of Bu₂CuLi to **1**, which favors formation of the undesired sulfone **7b**, reaction with isitylsulfonyl-protected **9** showed no sign of sulfone formation and produced the 3-substituted product **6b** in 43% yield.



R	Yield 6b (%)	Yield 7b (%)
Is	43	0
Ph	Trace	60

Scheme 4. Comparison of phenylsulfonyl and isitylsulfonyl protecting groups.

Conclusions

1,2-Bis(phenylsulfonyl)-1*H*-indole **1** has provided new examples of nucleophilic attack on the indole nucleus. Organocuprates effect C–H substitution at C-3 by an addition-elimination mechanism via expulsion of phenylsulfinate. Though the selectivity of cuprate addition varies by alkyl ligand, side product formation can be blocked by the use of a highly hindered isitylsulfonyl protecting group.

Experimental Section

General. A Varian XL-300 Fourier transform NMR spectrometer was used to record ^1H and ^{13}C NMR spectra. Chemical shifts (δ) are reported using the solvent's residual proton or carbon signal (CDCl_3 : δ_{H} 7.27, δ_{C} 77.23) as an internal reference. Melting points were determined using open capillary tubes with a Laboratory Devices Mel Temp. High-resolution mass spectrometry (HRMS) was performed at the University of Illinois (Urbana-Champaign) mass spectrometry laboratory. Tetrahydrofuran (THF) and diethyl ether were dried over alumina columns as described by Grubbs.⁹ All alkyllithium reagents were purchased from either Aldrich or Acros, and were titrated with 3,5-dimethoxybenzyl alcohol in dilute THF prior to use.

1-Phenylsulfonyl-2-(phenylthio)-1*H*-indole (3). To a stirred solution of 1.03 M lithium diisopropylamide from Acros (42 mL, 43.3 mmol) in THF (100 mL) at $-78\text{ }^\circ\text{C}$ was added solid 1-(phenylsulfonyl)-1*H*-indole **2** (10.00 g, 38.9 mmol). This reaction mixture was stirred for 1.5 h before being quenched with diphenyldisulfide (10.2 g, 46.7 mmol) in THF (50 mL). The solution was warmed to room temperature overnight and was poured onto 5% NaHCO_3 (aq, 100 mL). It was then extracted with methylene chloride (4 x 50 mL). The organic layers were combined, washed with saturated NaHCO_3 (aq, 3 x 100 mL) and brine (100 mL), and dried using MgSO_4 . After rotary evaporation, the resulting yellow oil was placed under vacuum to give a brown solid, which was recrystallized from CH_2Cl_2 :hexanes (1:1) to yield orange crystals **3** (12.15 g, 33.2 mmol, 85%); mp $115\text{--}116\text{ }^\circ\text{C}$ (lit.¹⁰ mp $118.5\text{--}119\text{ }^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3): δ 8.01 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 6.9$ Hz, 2H), 7.57 (d, $J = 3.6$ Hz, 1H), 7.53 (m, 2H), 7.43 (m, 2H), 7.52 (m, 1H), 7.23 (m, 1H) 6.67 (d, $J = 3.9$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): δ 138.9, 138.5, 134.4, 134.3, 133.8, 131.8, 129.4, 129.8, 129.5, 128.5, 127.6, 125.2, 124.2, 120.6, 115.9, 115.2. Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}_2\text{S}_2$: C, 65.73; H, 4.14; N, 3.83; S, 17.55. Found: C, 65.77; H, 4.14; N, 3.83; S, 17.55.

1,2-Bis(phenylsulfonyl)-1*H*-indole (1). To a stirred solution of 1-(phenylsulfonyl)-2-(phenylthio)-1*H*-indole **3** (6.00 g, 16.4 mmol) in CHCl_3 (40 mL) at $-40\text{ }^\circ\text{C}$ was added 70–75% *m*-chloroperoxybenzoic acid (*m*-CPBA, 12.00 g, 50.0 mmol) in CHCl_3 (60 mL) in 3 batches. This solution was stirred for 10 h at $-40\text{ }^\circ\text{C}$ and then allowed to warm to $0\text{ }^\circ\text{C}$. Excess *m*-CPBA was removed by vacuum filtration. The filtrate was washed with 5% NaHCO_3 (aq, 2 x 60 mL)

and brine (60 mL), and dried with MgSO₄. Rotary evaporation resulted in a dark orange oil. Addition of methanol induced the precipitation of tan crystals **1** (5.74 g, 14.4 mmol, 88%); mp 177–177.5 °C (lit.^{2a} mp 177.5–178.5 °C). ¹H NMR (300 MHz, CDCl₃): δ 8.17 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.82 (s, 1H), 7.65 (m, 2H), 7.55 (m, 4H), 7.44 (m, 2H), (7.34, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 140.8, 139.1, 137.9, 134.6, 133.7, 129.4, 128.8, 128.8, 128.6, 127.9, 126.7, 124.8, 123.4, 123.2, 123.1, 115.5. Anal. Calcd for C₂₀H₁₅NO₄S₂: C, 60.44; H, 3.80; N, 3.52; S, 16.13. Found: C, 60.49; H, 3.82; N, 3.49; S, 16.14.

General procedure for 1-alkyl-2-(phenylsulfonyl)-1*H*-indoles (**6a,b,d,e**) from 1,2-bis-(phenylsulfonyl)-1*H*-indole (**1**)

To a stirred suspension of CuBr·Me₂S (62 mg, 0.30 mmol) in THF (10 mL) at –78 °C was added alkyllithium solution (2 equiv.). This was followed by 1,2-bis(phenylsulfonyl)-1*H*-indole **1** (100 mg, 0.25 mmol) in THF (10 mL) via cannula. After stirring for 2 h, the reaction mixture was poured onto 10% NH₄Cl (aq, 50 mL). It was then extracted with methylene chloride (3 x 40 mL). The organic layers were combined, washed with brine (30 mL), dried (MgSO₄), and concentrated to a brown oil which was purified by column chromatography (silica gel, hexanes:ethyl acetate 12:1).

3-Methyl-2-(phenylsulfonyl)-1*H*-indole (6a**).** White solid (46 mg, 0.17 mmol, 67%); mp 168.5–169.5 °C (lit.¹¹ mp 167–168 °C). ¹H NMR (300 MHz, CDCl₃): δ 8.80 (br s, 1H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.53 (m, 3H), 7.36 (m, 2H), 7.17 (m, 1H), 2.53 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 141.7, 135.9, 133.1, 129.1, 128.8, 128.0, 126.7, 126.0, 120.5, 118.7, 112.2, 8.8. MS: *m/z* 271 (M⁺), 236, 206, 146, 129, 100, 85, 77. Anal. Calcd for C₁₅H₁₃NO₂S: C, 66.40; H, 4.83; N, 5.16; S, 11.82. Found: C, 66.40; H, 4.86; N, 5.16; S, 11.78.

3-*n*-Butyl-2-(phenylsulfonyl)-1*H*-indole (6b**).** White solid (60 mg, 0.19 mmol, 77%); mp 126–127 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.70 (br s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.53 (m, 3H), 7.38 (m, 2H), 7.16 (m, 1H), 2.96 (t, *J* = 7.7 Hz, 2H) 1.50 (m, 2H), 1.37 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 142.4, 136.3, 133.5, 129.5, 129.1, 127.3, 126.3, 124.2, 121.4, 120.9, 112.5, 33.1, 23.2, 23.2, 14.2. MS: *m/z* 313 (M⁺), 270, 172, 130, 77. Anal. Calcd for C₁₈H₁₉NO₂S: C, 68.99; H, 6.11; N, 4.47; S, 10.21. Found: C, 68.90; H, 6.34; N, 4.47; S, 10.36.

3-*t*-Butyl-2-(phenylsulfonyl)-1*H*-indole (6d**).** Faint pink solid (27 mg, 0.088 mmol, 35%); mp 120–122 °C. ¹H NMR (300 MHz, CDCl₃): δ 9.42 (br s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.56 (m, 1H), 7.47 (m, 3H), 7.35 (m, 1H), 7.15 (m, 1H), 1.44 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ 143.6, 135.5, 133.3, 129.2, 126.6, 125.6, 124.6, 120.5, 112.6, 109.9, 34.3, 32.2, 29.9. HRMS: *m/z* calcd for C₁₈H₁₉NO₂S: 313.1137, found: 313.1124.

3-Phenyl-2-(phenylsulfonyl)-1*H*-indole (6e**).** Amorphous brown solid (36 mg, 0.11 mmol, 43%). ¹H NMR (300 MHz, CDCl₃): δ 8.26 (br s, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.51–7.40 (m, 5H), 7.40–7.25 (m, 6H), 7.17 (m, 1H). ¹³C NMR (75 MHz, CDCl₃): δ 130.4, 130.1, 129.6, 128.9, 128.4, 128.2, 127.9, 126.5, 123.0, 122.3, 121.4, 120.7, 119.9, 111.1, 29.9. HRMS: *m/z* calcd for C₂₀H₁₅NO₂S: 333.0824, found: 333.0805.

Methylphenylsulfone (7a). White solid; mp 84–85 °C (lit.¹² mp 85–87 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, *J* = 9.5 Hz, 2H), 7.65 (t, *J* = 8.8 Hz, 1H), 7.56 (m, 2H), 3.05 (s, 3H).

***n*-Butylphenylsulfone (7b).** Viscous oil; bp 117 °C (lit.¹³ b.p. 117 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, *J* = 4.2 Hz, 2H), 7.64 (t, *J* = 3.0 Hz, 1H), 7.58 (m, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 1.61 (m, 2H), 1.35 (m, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

***s*-Butylphenylsulfone (7c).** Viscous oil; bp 113 °C (lit.¹³ bp 113.5 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.92 (d, *J* = 3.8 Hz, 2H), 7.64 (t, *J* = 3.5 Hz, 1H), 7.57 (t, *J* = 3.5 Hz, 2H), 4.60 (m, 1H), 1.59 (m, 2H), 1.26 (d, *J* = 3.2 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H).

Diphenylsulfone (7e). Light yellow solid; mp 123–124 °C (lit.¹² mp 123–124 °C). ¹H NMR (300 MHz, CDCl₃): δ 7.60 (d, 4H, *J* = 3.5 Hz), 7.44 (m, 4H), 7.35 (t, 2H, *J* = 2.1 Hz).

1-(2',4',6'-Triisopropylphenylsulfonyl)-2-(phenylthio)-1*H*-indole (8). Diisopropylamine (0.40 mL, 2.8 mmol) was dissolved in THF (3 mL) and was cooled to 0 °C. A solution of 2.5 M *n*-butyllithium in hexanes (1.2 mL, 3.0 mmol) was added dropwise to the amine. After 1 h, the solution was cooled to –78 °C, and 1-(2',4',6'-triisopropylphenylsulfonyl)-1*H*-indole (1.07 g, 2.79 mmol) in THF (10 mL) was added dropwise to the LDA. After 3 h, diphenyl disulfide (608 mg, 2.73 mmol) in THF (10 mL) was added dropwise to the anion. The solution was allowed to warm to r.t. overnight and was poured onto satd. NaHCO₃ (aq., 50 mL). It was extracted with methylene chloride (3 x 25 mL). The organic layers were combined, washed with 2 M NaOH (aq., 20 mL), 5% NaHCO₃ (aq., 20 mL), and brine (20 mL), were dried (MgSO₄), and were concentrated to yield an oil, which was triturated with methanol to yield a white solid **8** (1.18 g, 2.40 mmol, 86%); mp 126–127 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.35 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.48 (m, 1H), 7.37 (m, 1H), 7.27–7.29 (m, 5H), 7.11–7.14 (m, 2H), 6.81 (s, 1H), 4.37 (septet, *J* = 6.8 Hz, 2H), 3.00 (septet, *J* = 6.9 Hz, 1H), 1.37 (d, *J* = 6.9 Hz, 6H), 1.18 (d, *J* = 6.6 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 154.4, 151.5, 138.6, 135.9, 134.2, 130.8, 129.23, 129.19, 128.7, 127.2, 125.4, 124.0, 123.1, 120.9, 117.7, 114.9, 34.5, 29.5, 24.6, 23.9. Anal. Calcd for C₂₉H₃₃NO₂S₂: C, 70.84; H, 6.76; N, 2.85; S, 13.04. Found: C, 70.45; H, 6.76; N, 2.82; S, 12.64.

1-(2',4',6'-Triisopropylphenylsulfonyl)-2-(phenylsulfonyl)-1*H*-indole (9). To a stirred solution of 1-(2',4',6'-triisopropylphenylsulfonyl)-2-(phenylthio)-1*H*-indole **8** (0.35 g, 0.71 mmol) in CHCl₃ (10 mL) at –40 °C was added 50–60% *m*-CPBA (0.61 g, 1.8 mmol) in CHCl₃ (7 mL) dropwise via addition funnel. This solution was stirred at –40 °C for 10 h and then was allowed to warm to 0 °C in the refrigerator overnight. Then, the solution was cooled to –40 °C over 1 h and was filtered to remove any excess *m*-CPBA. The filtrate was washed with 2 M NaOH (2 x 30 mL), brine (30 mL), and was dried (MgSO₄). Upon rotary evaporation, the yellow oil was triturated with methanol to yield a white powder **9** (33 mg, 0.63 mmol, 88%); mp 157–158 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.96–7.99 (m, 2H), 7.85 (s, 1H), 7.67–7.70 (m, 1H), 7.50–7.60 (m, 3H), 7.22–7.25 (m, 2H), 7.12 (s, 2H), 7.03–7.05 (m, 1H), 3.93 (septet, 6.8 Hz, 2H), 2.89 (septet, *J* = 7 Hz, 1H), 1.23 (d, *J* = 7 Hz, 6H), 0.96 (d, *J* = 6.8 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 155.1, 151.4, 141.4, 138.9, 137.9, 133.4, 132.7, 128.9, 128.4, 128.0, 126.1,

124.3, 123.8, 123.3, 121.3, 113.8, 34.4, 29.5, 24.3, 23.7. Anal. Calcd for C₂₉H₃₃NO₄S₂: C, 66.51; H, 6.35; N, 2.67; S, 12.25. Found: C, 66.33; H, 6.23; N, 2.59; S, 11.95.

Acknowledgements

This work was supported by the Donors of the Petroleum Research Fund (PRF), administered by the American Chemical Society, and by Wyeth.

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