Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

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Zubaidha K. Pudukulathan [a] & Anjaneyulu Kasa [a]
[a] School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra, 431606, India

Version of record first published: 21 Mar 2012.

To cite this article: Zubaidha K. Pudukulathan & Anjaneyulu Kasa (2012): Iodine-catalyzed addition of aromatic mercaptans to indene, Journal of Sulfur Chemistry, 33:2, 187-195

To link to this article: http://dx.doi.org/10.1080/17415993.2012.660941

Journal of Sulfur Chemistry
Vol. 33, No. 2, April 2012, 187–195

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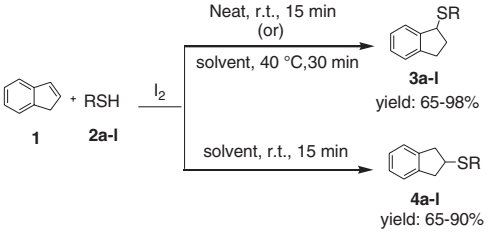
Iodine-catalyzed addition of aromatic mercaptans to indene

Zubaidha K. Pudukulathan* and Anjaneyulu Kasa

School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded, Maharashtra 431606, India

(*Received 20 December 2011; final version received 22 January 2012*)

Molecular iodine catalysis of additions of various substituted thiophenols to indene to afford the corresponding sulfides in good yields under mild conditions is reported. The regioselectivity of addition can be fine-tuned by modifying the reaction conditions, and the addition can also be effected under solvent-free conditions.



Keywords: substituted 1-indanyl and 2-indanyl thiols; addition; iodine; thiophenols; indene; solvent-free

1. Introduction

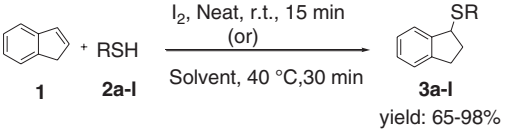
Over the past few years, molecular iodine (I_2) has emerged as a powerful catalyst, good mediator and reagent in organic synthesis (*1*, *2*). Iodine has several advantages over the vast majority of other Lewis acids in terms of tolerance for water, cost, simplicity of the reagent and its ability to effect reactions under dilute and solvent-free conditions (*3*, *4*). As part of our enduring effort to explore the catalytic activity of iodine, we had an opportunity to explore the addition of various substituted thiophenols to indene. Sulfoxides derived from indanyl sulfides find applications as additives in lubricating oil compositions, modifiers for synthetic rubber and petroleum resins, surface-active agents, constituents of fly repellents, insecticides and fungicides, as intermediates for agricultural and pharmaceutical chemicals and in numerous other areas. The addition of thiols to olefins, in general, is a known reaction usually proceeding concurrently by both ionic and radical chain mechanism. The nature of the catalyst has a profound effect on the mechanism of

*Corresponding author. Email: pzubaidha20001@yahoo.co.in

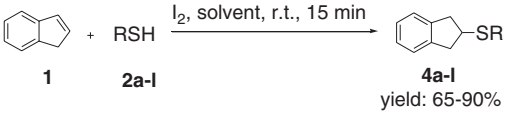
ISSN 1741-5993 print/ISSN 1741-6000 online

http://dx.doi.org/10.1080/17415993.2012.660941
http://www.tandfonline.com

addition, and the reported methods for addition of thienyl radicals to indene require the use of an initiator with heating, or the reaction at room temperature over a period of 96 h. Herein, we report the novel application of iodine as an efficient catalyst for addition of various aryl thiols to indene at room temperature in dichloromethane to afford the corresponding indanyl sulfides in good yields (Schemes 1 and 2).



Scheme 1. Addition of aryl thiols to indene under neat conditions.



Scheme 2. Addition of aryl thiols to indene at room temperature in solvent.

Cracked petroleum distillates contain indene and aromatic thiols (*5*, *6*) and it is possible that an addition reaction between these compounds can occur. In this context, addition of thiols to indene has been explored to study the properties of indanyl arylsulfides. Aromatic thiols add to indene in the presence or absence of peroxide catalyst to afford 2-indanyl derivatives and the reaction proceeds by a radical mechanism since ionic addition in the presence of acid affords 1-indanyl derivatives (*7*, *8*). The catalysts reported to effect addition of thiols to indene at room temperature and under heating require either prolonged reaction times or high temperature (*9–13*). Tosic acid is reported to effect addition of thiol to indene at the one and two positions in 2,2,4-trimethyl pentane under heating for 120 h (*14*). Herein we report iodine-catalyzed addition of aryl thiols to indene under mild conditions to afford either 1- or 2-indanyl sulfides depending on the reaction conditions.

2. Results and discussion

Aryl thiols undergo addition reactions to indene in the presence of catalytic amounts of iodine to afford 1- or 2-indanyl arylsulfides depending on the reaction conditions (Schemes 1 and 2). To study the effect of temperature and amount of iodine required for the addition, the reaction was performed under different conditions using 1 equiv. of indene and 1.5 equiv. of thiophenol (Table 1). Blank reaction carried out without catalyst under identical conditions led to recovery of starting material, and no trace of adducts **3a** and **4a** was detected by TLC even after 24 h of stirring (Table 1, entry 1). However, the product was formed after 216 h (*13*). Thus, it is apparent that iodine accelerates hydrothiolation of indene at room temperature within short duration in good yield. It is worth mentioning that increasing the catalyst concentration to 20 mol% had no dramatic effect on the yield, while an increase in temperature to 40 °C reverses the regioselectivity of addition to afford **3a** in 90% yield (Table 1).

Also the nature of the solvent influences the reaction considerably in terms of yield and regioselectivity of addition (Table 2). Among different solvents studied, the best results were obtained

Table 1. Reaction of **1** with **2a** under different conditions.[a]

Entry	I_2 (%)	Temperature (°C)	Time (h/min)	**3a**[b] (%)	**4a**[b] (%)	**1** (%)
1	0	rt	24 h[c]	0	0	98
2	10	rt	15 min	5	95	0
3	20	rt	15 min	7	93	0
4	10	40	30 min	90[d]	10	0

Notes: [a]Condition: 1 equiv. (2 mmol) of **1** was treated with 1.5 equiv. (3 mmol) of **2a** in acetonitrile.
[b]The yields were determined by analyzing the ^{1}H NMR spectra of the crude products.
[c]Product formed after 216 h at room temperature without using catalyst (*13*).
[d]Method B.

Table 2. Effect of solvent on the reaction of **1** with **2a** in the presence of 10 mol% of I_2 at room temperature and at 40 °C.[a]

		% yield at rt[b]			% yield at 40 °C[b]		
Entry	Solvent	**3a** (%)	**4a** (%)	Time	**3a** (%)	**4a** (%)	Time (min)
1	Neat	98	2	15 min	95	5	15
2	Hexane	10	50	18 h	15	30	30
3	C_6H_6	7	23	18 h	10	15	30
4	CH_2Cl_2	5	95	5 min	25	75	5
5	CH_3CN	10	90	15 min	90	10	30
6	DMF	0	0	15 min	0	0	15
7	DMSO	0	0	15 min	0	0	15

Notes: [a]Condition: 1 equiv. (2 mmol) of **1** was treated with 1.5 equiv. (3 mmol) of **2a** in the presence 10 mol% of I_2 at different temperatures.
[b]The yields were determined by analyzing the ^{1}H NMR spectra of the crude products.

in acetonitrile and dichloromethane, and no addition reaction was observed in DMF and DMSO. It is remarkable to note that the regioselectivity changes from **4a** in acetonitrile/dichloromethane to **3a** under solvent-free conditions, and yields of products were higher under neat conditions when compared to reactions carried out in the presence of solvents.

In order to evaluate the general applicability of the addition reaction and functional group tolerance, the reaction was carried out with various substituted thiophenols and the results are presented in Tables 3 and 4. The progress of the reaction was monitored by TLC, and adduct **3** was found to be less polar than **4** and was separated by column chromatography.

In most of the cases studied, the reaction went to completion in 15 min, whereas benzyl thiol required more time. Aromatic thiols bearing fluoro and pyridyl groups did not undergo any addition reaction to yield **3** under solvent-free conditions and instead the respective disulfides were formed (Table 3, entries 2 and 12). The addition reaction in solvents seem to be more prone to steric and electronic effects since hydrothiolation of indene was not observed with dichloro, dimethyl aryl mercaptans and 4-pyridyl mercaptan (Table 4, entries 3, 8–10 and 12). The reaction of alkyl thiols with indene did not yield the expected thiol adduct and led to formation of 2-indanyl indene **5** (*15*) in good yields (Scheme 3, Table 5) and this coupling reaction between indene molecules was not observed under identical conditions in the absence of mercaptan.

Formation of 1-indanyl sulfides at a higher temperature and under neat conditions implies that the addition of thiophenol to indene proceeds by an ionic mechanism, whereas the addition in the presence of solvents seems to favor a radical mechanism to afford the corresponding 2-indanyl sulfides. This is supported by the observation that the addition of thiophenol to indene carried out in acetonitrile or dichloromethane and under neat conditions in dark yields exclusively 1-indanyl sulfide **3a**. Further, the pure adducts **3a** and **4a** were subjected to the reaction conditions in dichloromethane, acetonitrile at room temperature, 40 °C and under neat conditions for 12 h

Table 3. Iodine-catalyzed addition of different thiols (**3a**–**3l**) to indene.[a]

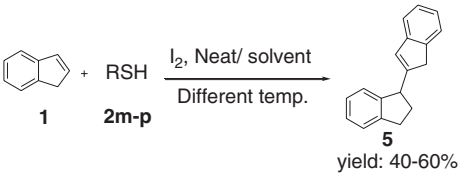
Entry	R	Product	Time (min)	Yield (%)[b]
1	C_6H_5	**3a**	15	98
2	4-FC_6H_4	**3b**	15	–
3	4-ClC_6H_4	**3c**	15	90
4	4-BrC_6H_4	**3d**	15	70[c]
5	4-MeC_6H_4	**3e**	15	65[c]
6	$C_6H_5CH_2$	**3f**	90	95[e]
7	2,4-$Cl_2C_6H_3$	**3g**	15	98[c]
8	3,5-$Cl_2C_6H_3$	**3h**	15	90
9	3,4-$Cl_2C_6H_3$	**3i**	15	87
10	2,4-$Me_2C_6H_3$	**3j**	15	91[c]
11	2-$C_{10}H_7$	**3k**	45	80[d]
12	4-Pyridyl	**3l**	15	–

Notes: [a]All reactions were performed by using 1 equiv. (2 mmol) of indene **1** and 1.5 equiv. (3 mmol) of thiols **2** (**3a**–**3l**) in the presence 10 mol% of I_2 under solvent-free conditions.
[b]Isolated yields.
[c]Reaction was carried out in acetonitrile at 40 °C.
[d]Reaction was carried out in dichloromethane at 40 °C.
[e]The reaction was carried out in the presence 20 mol% of I_2.

Table 4. Iodine-catalyzed addition of different thiols (**4a**–**4l**) to indene.[a]

Entry	R	Product	Time (min)	Yield (%)[b]
1	C_6H_5	**4a**	15	90
2	4-FC_6H_4	**4b**	15	85
3	4-ClC_6H_4	**4c**	15	70
4	4-BrC_6H_4	**4d**	15	70
5	4-MeC_6H_4	**4e**	15	65
6	$C_6H_5CH_2$	**4f**	90	–[d]
7	2,4-$Cl_2C_6H_3$	**4g**	15	89
8	3,5-$Cl_2C_6H_3$	**4h**	15	–
9	3,4-$Cl_2C_6H_3$	**4i**	15	–
10	2,4-$Me_2C_6H_3$	**4j**	15	–
11	2-$C_{10}H_7$	**4k**	45	80[c]
12	4-Pyridyl	**4l**	15	–

Notes: [a]All reactions were performed by using 1 equiv. (2 mmol) of indene **1** and 1.5 equiv. (3 mmol) of thiols **2** (**4a**–**4l**) in the presence 10 mol% of I_2 in acetonitrile at room temperature.
[b]Isolated yields.
[c]Reaction was carried out in dichloromethane at room temperature.
[d]**3f** was formed exclusively under different conditions studied using 20 mol% of I_2.



Scheme 3. Iodine catalyzed reaction of alkyl thiols with indene.

and were found to be stable. The regio-isomers were found to be noninterconvertible. Although the intimate mechanistic details of this reaction are not yet fully understood, a feasible pathway might involve the catalytic role of iodine as a Lewis acid in activating the double bond in the indene system. Solvent and temperature have a profound effect on the mechanism of addition. Further studies are in progress to understand the mechanism of iodine catalysis.

3. Conclusion

In conclusion, we have successfully developed an easy and efficient method for the addition of various thiophenols to indene. The advantages such as mild reaction conditions, simplicity of the reaction, excellent product yields and easy work-up procedure coupled with short reaction times make the present method an attractive alternative to synthesize indanyl arylsulfides of commercial significance.

4. Experimental

4.1. *Typical experimental procedure for addition of thiols to indene*

4.1.1. *Method A*

To a mixture of indene **1** (1.0 equiv.) and thiol **2** (1.5 equiv.), I_2 (0.1 equiv.) was added and the reaction mixture was stirred at room temperature for 15 min. After completion of the reaction (monitored by TLC), 5% sodium thiosulfate solution (5 mL) was added and extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine solution and dried over anhydrous sodium sulfate and evaporation of solvents under the reduced pressure afforded 90–98% yield of **3a**–**3l**. The pure product was obtained by passing through a 100–200-mesh silica gel column using petroleum ether as eluent.

4.1.2. *Method B*

To a mixture of indene **1** (1.0 equiv.) and thiol **2** (1.5 equiv.) in acetonitrile, 10 mol% I_2 in acetonitrile was added at 40 °C and the mixture was stirred at same temperature for 30 min. After completion of the reaction (monitored by TLC), 5% sodium thiosulfate solution (5 mL) was added and extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine solution and dried over anhydrous sodium sulfate, and evaporation of solvents under the reduced pressure afforded 70–98% yield of **3a**–**3l**. The pure product was obtained by passing through a 100–200-mesh silica gel column using petroleum ether as eluent.

4.1.3. *Method C*

To a mixture of indene **1** (1.0 equiv.) and thiol **2** (1.5 equiv.) in 5% *N*,*N*,-dimethylformamide in acetonitrile, 10 mol% I_2 in acetonitrile was added at room temperature and mixture was stirred for 15 min. After completion of reaction (monitored by TLC), 5% sodium thiosulfate solution (5 mL)

Table 5. Iodine-catalyzed reaction of **1** with alkyl thiols **2m**–**2p** under solvent-free and in solvent at different temperatures.[a]

Entry	Alkyl thiol (**2m**–**2p**)	Temperature (°C)	Time (min)	Adduct (3/4 (m–p)	Dimer **5** yield (%)[b]
1	Ethanethiol	−30, rt & 40 °C	15	–	60
2	Propanethiol	−30, rt & 40 °C	15	–	58
3	Cyclohexyl mercaptan	−30, rt & 40 °C	15	–	47
4	1-Propanethiol	−30, rt & 40 °C	15	–	40

Notes: [a]All reactions were performed with 1 equiv. (2 mmol) of indene **1** and 1.5 equiv. (3 mmol) of alkyl thiols **2m–2p** in the presence 10 mol% of I_2 in acetonitrile and dichloromethane at different temperatures.
[b]The yields were determined from ^{1}H NMR of crude reaction products.

was added and extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine solution and dried over anhydrous sodium sulfate, and evaporation of solvents under the reduced pressure afforded 50–70% yield of **3a**–**3l**. The pure product was obtained by passing through a 100–200-mesh silica gel column using petroleum ether as eluent.

4.1.4. *Method D*

To a mixture of indene **1** (1.0 equiv.) and iodine (0.1 equiv.) in dichloromethane/acetonitrile, thiol **2** (1.5 equiv.) in dichloromethane/acetonitrile was added at room temperature and the mixture was stirred for 15 min. After completion of the reaction (monitored by TLC), 5% sodium thiosulfate solution (5 mL) was added and extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine solution and dried over anhydrous sodium sulfate, and evaporation of solvents under the reduced pressure afforded 50–70% yield of **4a**–**4l**. The pure product was obtained by passing through a 100–200-mesh silica gel column using petroleum ether as eluent.

4.1.5. *Method E*

Under dark condition, to a mixture of indene **1** (1.0 equiv.) and thiol **2a** (1.5 equiv.), I_2 (0.1 equiv.) was added and the reaction mixture was stirred at room temperature for 15 min. After completion of the reaction (monitored by TLC), 5% sodium thiosulfate solution (5 mL) was added and extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine solution and dried over anhydrous sodium sulfate, and evaporation of solvents under reduced pressure afforded **3a** in 98% yield. The pure product was obtained by passing through a 100–200-mesh silica gel column using petroleum ether as eluent. Product **3a** was characterized by ^{1}H NMR.

4.1.6. *Method F*

Under dark condition, to a mixture of indene **1** (1.0 equiv.) and iodine (0.1 equiv.) in dichloromethane, thiol **2a** (1.5 equiv.) in dichloromethane was added at room temperature and the mixture was stirred for 15 min. After completion of the reaction (monitored by TLC), 5% sodium thiosulfate solution (5 mL) was added and extracted with dichloromethane (2 × 15 mL). The combined organic extracts were washed with brine solution and dried over anhydrous sodium sulfate, and evaporation of solvents under reduced pressure afforded **3a** in 95% yield. The pure product was obtained by passing through a 100–200-mesh silica gel column using petroleum ether as eluent. Product **3a** was characterized by ^{1}H NMR.

1-Indanyl-(phenyl)sulfane (**3a**): Colorless liquid (*10*, *11*); bp 127–128 °C (2 mm) (*9*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.17–2.25 (m, 1H), 2.48–2.57 (m, 1H), 2.82–2.84 (m, 1H), 2.98–3.06 (m, 1H), 4.75–4.76 (dd, 1H, J = 4.0, 7.2 Hz), 7.14–7.31 (m, 7H), 7.38–7.4 (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.76, 33.61, 51.85, 124.65, 124.90, 126.46, 126.66, 127.72, 128.78, 131.29, 136.01, 142.79, 143.73. EI MS: m/z (rel. abund. %) 227 [M^+, 100].

1-Indanyl-(4-chlorophenyl)sulfane (**3c**): Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13–2.20 (m, 1H), 2.46–2.55 (m, 1H), 2.80–2.87 (m, 1H), 2.94–3.02 (m, 1H), 4.69–4.72 (dd, 1H, J = 4.0, 7.6 Hz), 7.16–7.30 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.78, 33.65, 52.51, 124.62, 124.86, 126.49, 127.78, 128.85, 133.07, 133.17, 134.47, 142.67, 143.62. EI MS: m/z (rel. abund. %) 262.2 [M^+, 100]. Anal. Calcd. for $C_{15}H_{13}ClS$ (260.78): C, 69.08; H, 5.02; S, 12.30. Found: C, 69.14; H, 5.06; S, 12.17%.

1-Indanyl-(4-bromophenyl)sulfane (**3d**): Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14–2.21 (m, 1H), 2.47–2.57 (m, 1H), 2.81–2.87 (m, 1H), 2.96–3.04 (m, 1H), 4.71–4.73 (dd, 1H, $J = 4.0, 7.2$ Hz), 7.17–7.28 (m, 6H), 7.38–7.40 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.79, 33.60, 52.20, 120.92, 124.71, 124.88, 126.55, 127.86, 131.86, 133.15, 135.16, 142.54, 143.68. EI MS: m/z (rel. abund. %) 304 (M(79Br), 99), 306 (M(81Br), 100). Anal. Calcd. for $C_{15}H_{13}BrS$ (305.23): C, 59.02; H, 4.29; S, 10.51. Found: C, 58.97; H, 4.32; S, 10.45%.

1-Indanyl-(4-tolyl)sulfane (**3e**): Pale yellow liquid; bp 135–136 °C (2 mm) (*9*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15–2.22 (m, 1H), 2.33 (s, 3H), 2.44–2.53 (m, 1H), 2.79–2.86 (m, 1H), 2.96–3.04 (m, 1H), 4.67–4.70 (dd, 1H, $J = 4.2, 7.4$ Hz), 7.08–7.10 (d, 2H, $J = 8.0$ Hz), 7.17–7.21 (m, 3H), 7.26–7.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.82, 30.77, 33.73, 52.64, 124.48, 124.92, 126.34, 127.50, 129.45, 132.24, 132.42, 136.92, 143.25, 143.63. EI MS: m/z (rel. abund. %) 241.3 [M^+, 100].

1-Indanyl-(benzyl)sulfane (**3f**): Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.10–2.14 (m, 1H), 2.38–2.47 (m, 1H), 2.77–2.85 (m, 1H), 2.99–3.07 (m, 1H), 3.69–3.77 (dd, 2H, $J = 13.2$, 18.8 Hz), 4.20–4.23 (dd, 1H, $J = 4.8, 7.2$ Hz), 7.16–7.21 (m, 4H), 7.27–7.32 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.05, 34.10, 35.84, 49.10, 124.60, 124.82, 126.48, 126.86, 127.46, 128.43, 128.88, 138.73, 143.39, 143.61. EI MS: m/z (rel. abund. %) 241.3 [M^+, 100]. Anal. Calcd. for $C_{16}H_{16}S$ (240.36): C, 79.95; H, 6.74; S, 13.34. Found: C, 79.89; H, 6.75; S, 13.29%.

1-Indanyl-(2,4-dichlorophenyl)sulfane (**3g**): Colorless solid; mp 79–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15–2.22 (m, 1H), 2.49–2.58 (m, 1H), 2.87–2.94 (m, 1H), 3.09–3.17 (m, 1H), 4.83–4.85 (dd, 1H, $J = 3.2, 7.2$ Hz), 7.17–7.27 (m, 5H), 7.30–7.32 (d, 1H, $J = 8.4$ Hz), 7.41–7.42 (d, 1H, $J = 2.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.77, 33.50, 51.49, 124.69, 124.87, 126.56, 127.16, 128.00, 129.64, 132.93, 133.07, 134.41, 136.64, 142.00, 143.76. EI MS: m/z (rel. abund. %) 296.2 [M, 100], 298.2 [M^+, 66]. Anal. Calcd. for $C_{15}H_{12}Cl_2S$ (295.23): C, 61.02; H, 4.10; S, 10.86. Found: C, 61.11; H, 4.15; S, 10.69%.

1-Indanyl-(3,5-dichlorophenyl)sulfane (**3h**): White solid; mp 52–53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.18–2.25 (m, 1H), 2.55–2.65 (m, 1H), 2.88–2.95 (m, 1H), 3.03–3.11 (m, 1H),4.80–4.83 (dd, 1H, $J = 4.0, 7.2$ Hz), 7.20–7.26 (m, 6H), 7.30–7.32 (d, 1H, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.76, 33.75, 52.03, 124.72, 124.85, 126.55, 126.66, 128.10, 128.50, 135.09, 140.15, 141.80, 143.64. EI MS: m/z (rel. abund. %) 296.2 [M^+, 100], 298.2 [M^+, 66]. Anal. Calcd. for $C_{15}H_{12}Cl_2S$ (295.23): C, 61.02; H, 4.10; S, 10.86. Found: C, 61.10; H, 4.12; S, 10.81%.

1-Indanyl-(3,4-dichlorophenyl)sulfane (**3i**): White solid; mp 66–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.14–2.22 (m, 1H), 2.50–2.60 (m, 1H), 2.84–2.91 (m, 1H), 2.98–3.06 (m, 1H), 4.74–4.77 (dd, 1H, $J = 4.0$, 7.2 Hz), 7.16–7.29 (m, 5H), 7.32–7.34 (d, 1H, $J =$ 8.4 Hz), 7.43–7.44 (d, 1H, $J = 2.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.77, 33.60, 52.23, 124.79, 124.87, 126.64, 128.06, 130.42, 131.00, 132.67, 132.76, 136.38, 142.05, 143.70. EI MS: m/z (rel. abund. %) 296.2 [M, 100], 298.2 [M^+, 66]. Anal. Calcd. for $C_{15}H_{12}Cl_2S$ (295.23): C, 61.02; H, 4.10; S, 10.86. Found: C, 60.98; H, 4.08; S, 10.91%.

1-Indanyl-(2,4-dimethylphenyl)sulfane (**3j**): Pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.13–2.20 (m, 1H), 2.31 (s, 3H), 2.32 (s, 3H), 2.42–2.51 (m, 1H), 2.82–2.89 (m, 1H), 3.06–3.14 (m, 1H), 4.66–4.69 (dd, 1H, $J = 3.2, 7.2$ Hz), 6.95–6.98 (dd, 1H, $J = 0.8$, 8.0 Hz), 7.02 (s, 1H), 7.13–7.23 (m, 4H), 7.31–7.33 (d, 1H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.40, 20.74, 30.81, 33.67, 52.17, 124.50, 124.82, 126.29, 127.01, 127.52, 131.06, 131.79, 132.76, 136.95, 139.93, 143.35, 143.66. EI MS: m/z (rel. abund. %) 255.2 [M^+, 100]. Anal. Calcd. for $C_{17}H_{18}S$ (254.39): C, 80.26; H, 7.13; S, 12.60. Found: C, 80.31; H, 7.23; S, 12.51%.

1-Indanyl-(naphthalen-2-yl)sulfane (**3k**): Off white solid; mp 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21–2.83 (m, 1H), 2.51–2.60 (m, 1H), 2.82–2.89 (m, 1H), 2.99–3.07 (m, 1H), 4.86–4.89 (dd, 1H, $J = 4.0$, 7.2 Hz), 7.13–7.23 (m, 3H), 7.30–7.31 (d, 1H, $J = 7.2$ Hz), 7.41–7.48 (m, 3H), 7.71–7.79 (m, 3H), 7.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.90, 33.66, 51.82, 124.80, 125.02, 125.94, 126.53, 126.62, 127.35, 127.75, 127.88, 128.35, 128.96, 129.45, 132.12, 133.69, 133.76, 142.83, 143.87. EI MS: m/z (rel. abund. %) 277.2 [M^+, 100]. Anal. Calcd. for $C_{19}H_{16}S$ (276.40): C, 82.56; H, 5.83; S, 11.60. Found: C, 82.61; H, 5.81; S, 11.57%.

2-Indanyl-(phenyl)sulfane (**4a**): White solid (*9*, *12*, *16–18*); mp 46–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.97–3.03 (dd, 2H, $J = 6.0$, 16.0 Hz), 3.35–3.41 (dd, 2H, $J = 7.6$, 16.0 Hz), 4.08–4.15 (m, 1H), 7.15–7.25 (m, 5H), 7.28–7.32 (m, 2H), 7.37–7.42 (d, 2H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.18, 45.28, 124.46, 126.40, 126.63, 128.89, 130.56, 136.11, 141.52. EI MS: m/z (rel. abund. %) 227 [M^+, 100].

2-Indanyl-(4-fluorophenyl)sulfane (**4b**): White solid (*13*); mp 58–58.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.94–2.99 (dd, 2H, $J = 6.0$, 16.0 Hz), 2.28–2.34 (dd, 2H, $J = 7.2$, 16.0 Hz), 3.97–4.03 (m, 1H), 6.97–7.04 (m, 2H), 7.14–7.20 (m, 4H), 7.38–7.43(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.08, 46.54, 115.95, 116.17, 124.52, 126.73, 130.70, 130.74, 133.84, 133.92, 141.47, 160.93, 163.39. EI MS: m/z (rel. abund. %) 245 [M^+, 100].

2-Indanyl-(4-bromophenyl)sulfane (**4d**): White solid; mp 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95–3.00 (dd, 2H, $J = 5.8$, 16.0 Hz), 3.34–3.40 (dd, 2H, $J = 7.4$, 16.0 Hz), 4.04–4.11 (m, 1H), 7.15–7.20 (m, 4H), 7.24–7.26 (d, 2H $J = 8.4$ Hz), 7.41–7.43 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.09, 45.37, 120.38, 124.54, 126.79, 132.01, 132.02, 135.39, 141.31. EI MS: m/z (rel. abund. %) 304 [M, 99], 306 [M^+, 100]. Anal. Calcd. for $C_{15}H_{13}BrS$ (305.23): C, 59.02; H, 4.29; S, 10.51. Found: C, 58.93; H, 4.31; S, 10.58%.

2-Indanyl-(4-tolyl)sulfane (**4e**): White solid (*9*, *12*, *16*, *18*); mp 86–86.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 2.94–2.99 (dd, 2H, $J = 6.0$, 16.0 Hz), 3.28–3.34 (dd, 2H, $J = 7.2$, 16.0 Hz), 3.99–4.06 (m, 1H), 7.10–7.18 (m, 6H), 7.30–7.32 (d, 2H $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.10, 40.16, 45.98, 124.51, 126.64, 129.74, 131.61, 132.14, 136.80. 141.68. EI MS: m/z (rel. abund. %) 241.3 [M^+, 100].

2-Indanyl-(2,4-dichlorophenyl)sulfane (**4g**): Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.98–3.04 (dd, 2H, $J = 6.0$, 16.0 Hz), 3.40–3.46 (dd, 2H, $J = 7.6$, 16.0 Hz), 4.11–4.17 (m, 1H), 7.16–7.23 (m, 5H), 7.31–7.34 (d, 1H $J = 8.8$ Hz), 7.40–7.41 (d, 1H, $J = 1.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.00, 44.13, 124.54, 126.86, 127.41, 129.68, 130.85, 132.24, 134.50, 135.07, 141.11. EI MS: m/z (rel. abund. %) 296.2 [M, 100], 298.2 [M^+, 66]. Anal. Calcd. for $C_{15}H_{12}Cl_2S$ (295.23): C, 61.02; H, 4.10; S, 10.86. Found: C, 61.07; H, 4.08; S, 10.76%.

2-Indanyl-(naphthalen-2-yl)sulfane (**4k**): Off white solid (*9*, *12*, *16*); mp 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.02–3.07 (dd, 2H, $J = 5.6$, 16.0 Hz), 3.38–3.44 (dd, 2H, $J = 7.6$, 16.0 Hz), 4.20–4.26 (m, 1H), 7.15–7.22 (m, 4H), 7.42–7.49 (m, 3H), 7.74–7.80 (m, 3H), 7.83 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.22, 45.22, 124.58, 125.87, 126.60, 126.74, 127.23, 127.76, 128.38, 128.47, 128.57, 131.96, 133.73, 133.79, 141.56. EI MS: m/z (rel. abund. %) 277.2 [M^+, 100].

References

(1) (a) Ke, B.; Qin, Y.; He, Q.; Huang, Z.; Wang, F. *Tetrahedron Lett.* **2005,** *46,* 1751–1753; (b) Bandgar, B.P.; Shaikh, K.A. *Tetrahedron Lett.* **2003,** *44,* 1959–1961; (c) Ji, S.; Wang, S.; Zhang, Y.; Loh, T. *Tetrahedron* **2004,** *60,* 2051–2055.

(2) (a) Kim, K.M.; Ryu, E.K. *Tetrahedron Lett.* **1996,** *37,* 1441–1444; (b) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *J. Org. Chem.* **2001,** *66,* 7527–7529; (c) Ramalinga, K.; Vijayalakshmi, P.; Kaimal, T.N.B. *Tetrahedron Lett.* **2002,** *43,* 879–882; (d) Firouzabadi, H.; Iranpoor, N.; Sobhani, S. *Tetrahedron Lett.* **2002,** *43,* 3653–3655; (e) Yadav,

J.S.; Reddy, B.V.S.; Reddy, M.S.; Prasad, A.R. *Tetrahedron Lett.* **2002,** *43,* 9703–9706; (f) Das, B.; Banerjee, J.; Ramu, R.; Pal, R.; Ravindranath, N.; Ramesh, C. *Tetrahedron Lett.* **2003,** *44,* 5465–5468; (g) Saeeng, R.; Sirion, U.; Sahakitpichan, P.; Isobe, M. *Tetrahedron Lett.* **2003,** *44,* 6211–6215; (h) Yadav, J.S.; Reddy, B.V.S.; Shubashree, S.; Sadashiv, K. *Tetrahedron Lett.* **2004,** *45,* 2951–2954; (i) Phukan, P. *J. Org. Chem.* **2004,** *69,* 4005–4006; (j) Phukan, P. *Tetrahedron Lett.* **2004,** *45,* 4785–4787; (k) Sun, J.; Dong, Y.; Wang, X.; Wang, S.; Hu, Y. *J. Org. Chem.* **2004,** *69,* 8932–8934; (l) Bhosale, R.S.; Bhosale, S.V.; Wang, T.; Zubaidha, P.K. *Tetrahedron Lett.* **2004,** *45,* 9111–9113.

(3) (a) Chu, C.M.; Gao, S.J.; Sastry, M.N.V.; Yao, C.F. *Tetrahedron Lett.* **2005,** *46,* 4971–4974; (b) Banik, B.K.; Fernandez, M.; Alvarez, C. *Tetrahedron Lett.* **2005,** *46,* 2479–2482; (c) Banik, B.K.; Samajdar, S.; Banik, I. *J. Org. Chem.* **2004,** *69,* 213–216; (d) Basu, M.K.; Samajdar, S.; Frederick, F.; Banik, B.K. *Synlett* **2002,** 319–321; (e) Samajdar, S.; Basu, M.K.; Becker, F.F.; Banik, B.K. *Tetrahedron Lett.* **2001,** *42,* 4425–4427; (f) Mukhopadhyay, C.; Becker, F.F.; Banik, B.K. *J. Chem. Res.* **2001,** *108*, 28–31; (g) Banik, B.K.; Manhas, M.S.; Bose, A.K. *Tetrahedron Lett.* **1997,** *38,* 5077–5080; (h) Banik, B.K.; Zegrocka, O.; Manhas, M.S.; Bose, A.K. *Heterocycles* **1997,** *46,* 173–176; (i) Banik, B.K.; Manhas, M.S.; Bose, A.K. *J. Org. Chem.* **1994,** *59,* 4714–4716.

(4) (a) Ko, S.; Sastry, M.N.V.; Lin, C.; Yao, C.F. *Tetrahedron Lett.* **2005,** *46,* 5771–5774; (b) Shivaji, G.; Tingkai, T.; Sastry, M.N.V.; Chu, C.M.; Liu, J.T.; Lin, C.; Yao, C.F. *Tetrahedron Lett.* **2006,** *47,* 1889–1893.

(5) Sachaned, A.N. *The Chemical Constituents of Petroleum*; Reinhold Publishing Corp.: New York, NY, 1945, pp. 265–271.

(6) Windle, G.S. *Petroleum Refiner* **1944,** *23,* 83–87.

(7) Pope, W.J.; Read, J. *J. Chem. Soc.* **1912,** *101,* 758–780.

(8) Weissgerber, R. *Ber. Dtsch. Chem. Ges.* **1911**, 44, 1436–1448.

(9) Oswald, A. *J. Org. Chem.* **1960,** *25,* 467–469.

(10) Katritzky, A.R.; Yang, Z.; Lam, J.N.; Cundy, D.J. *Heterocycles* **1993,** *36,* 1367–1373.

(11) Brouwer, C.; Rahaman, R.O.; He, C. *Synlett* **2007,** *11,* 1785–1789.

(12) Esso Res. Engn. Co. US Patent 2968678, 1961.

(13) Szmant, H.H.; Baeza, H.J. *J. Org. Chem.* **1980,** *45,* 4902–4906.

(14) Baeza, J.; Freer, J.; Palma, G.; Szmant, H.H. *Phosphorus Sulfur Relat. Elem.* **1985,** *25,* 213–218.

(15) (a) Griffin, C.E.; Wells, H.J. *J. Org. Chem.* **1959,** *24,* 2049–2051; (b) Czogolla, C.; Boberg, F. *Phosphorus Sulfur Relat. Elem.* **1987,** *33,* 83–86; (c) Weissgerber. *Chemische Berichte* **1911,** *44,* 1446–1449; (d) Stobbe, H.; Faerber, E. *Chemische Berichte* **1924,** *57,* 1846–1851; (e) Courtot, C.; Dondelinger, A. *Compt. Rendus Hebdomadaires Seances l'Acad. Sci.* **1924,** *179,* 1168–1172; *Ann. Chim* **1925,** *10,* 349–354; (f) Whitby, G.S.; Katz, M. *Can. J. Res.* **1931,** *4,* 344–360; *Chem. Zentralb.* **1932,** *103,* 386–389; (g) Risi, J.; Gauvin, D. *Can. J. Res. Sect. B: Chem. Sci.* **1935,** *13,* 228–255; (h) Noland, W.E. *J. Org. Chem.* **1979,** *44,* 1358–1359; (i) Alesso, E.; Torviso, R.; Finkielsztein, L.; Lantano, B.; Moltrasio, G.; Aguirre, J.; Vazquez, P.; Pizzio, L.; Caceres, C.; Blanco, M.; Thomas, H. *J. Chem. Res.* **2001,** *12,* 1232–1245; (j) Moglioni, A.G.; Tombari, D.G.; Iglesias, G.Y.M. *J. Chem. Soc Perkin Trans. 1* **1998,** *20,* 3459–3462; (k) Pitchumani, K.; Ramamurthy, V. *J. Chem. Soc. Chem. Commun*. **1996,** *24,* 2763–2764.

(16) *Esso Res. Engn. Co. Chem. Abstr.* **1961,** *55,* 12378–12380.

(17) McCullough, K.J. *Tetrahedron Lett.* **1982,** *23,* 2223–2224.

(18) Ito, O.; Matsuda, M. *J. Org. Chem.* **1983,** *48,* 2748–2751.