

ORGANIC CHEMISTRY | RESEARCH ARTICLE

Efficient one-pot synthesis of (anthracen-9-yl) methyl sulfane derivatives

Reshma Gopalakrishnan, Jomon P. Jacob, Ranjith Chirakandathil, Perupparampil A. Unnikrishnan and Sreedharan Prathapan

Cogent Chemistry (2015), 1: 1033820



Received: 02 December 2014
Accepted: 18 March 2015
Published: 28 April 2015

*Corresponding author: Sreedharan Prathapan, Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682 022, Kerala, India
E-mail: prathapans@gmail.com

Reviewing editor:
George Weaver, University of Loughborough, UK

Additional information is available at the end of the article

ORGANIC CHEMISTRY | RESEARCH ARTICLE

Efficient one-pot synthesis of (anthracen-9-yl) methyl sulfane derivatives

Reshma Gopalakrishnan¹, Jomon P. Jacob¹, Ranjith Chirakandathil¹, Perupparampil A. Unnikrishnan¹ and Sreedharan Prathapan^{1*}

Abstract: A series of unsymmetrical (anthracen-9-yl)methyl sulfanes have been synthesized using a one-pot reaction from (anthracen-9-yl)methyl alcohol, thiourea, and the corresponding alkyl halide and also by a base-promoted one-pot reductive coupling of tosylhydrazones with thiols.

Subjects: Applied & Industrial Chemistry; Chemistry; Organic Chemistry

Keywords: (anthracen-9-yl)methyl sulfanes; thiourea; tosylhydrazones; reductive coupling

1. Introduction

Organosulfur compounds are important intermediates for specialized organic synthesis (Bauld, Aplin, Yueh, & Loinaz, 1997; Chatgililoglu, Bertrand, Ferreri, & Alfassi, 1999; Wrzyszczyński, Scigalski, & Paczkowski, 2000). These compounds are well known for their radical chemistry under thermal and photochemical conditions (Andrzejewska, Hug, Andrzejewski, & Marciniak, 1999; Bobrowski, Marciniak, & Hug, 1996; Kang & Friend, 2004; Kretschmar, Friend, & Sigman, 2002; Marciniak, Andrzejewska, & Huc, 1998; Steffen et al., 1991; Wiegand & Friend, 1992; Wiegand, Napier, Friend, & Uvdal, 1996; Wrzyszczyński, Scigalski, et al., 2000). Sulfur-centered radicals and radical ions play unique roles in diverse areas of chemistry. Thanks to their low ionization potentials, organic sulfides undergo fast one-electron oxidation reactions to give the corresponding radical cations. It is reported that organic sulfides are ideal precursors for sulfur-centered radical cations that can be used for probing mechanisms of electron transfer quenching of excited states as well as for monitoring the fate of the sulfur radicals (Bauld et al., 1997; Bisby, Cundall, Redpath, & Adams, 1976; Chatgililoglu & Asmus, 1990a; Chatgililoglu et al., 1999; Kosower, Kosower, & Pryor, 1976; Lalitha & Mittal, 1971; Thompson, Carroll, Watson, O'Donnell, & McGlynn, 1966; Wolff, Aldrich, Penner, &

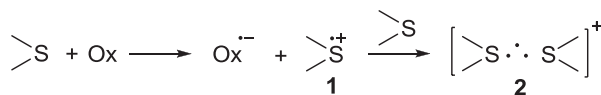
ABOUT THE AUTHORS

We are currently interested in unraveling reaction mechanisms of photochemical and electron transfer reactions, developing novel applications of well-known reagents such as Burgess reagent and synthesis of fluorescent thiophene-based oligomers. Examination of multiple reactivity and identification of minor reaction pathways are of primary interest to us. Synthesis of complementary substrate pairs that can exhibit multiple reaction modes is thus an integral part of our research effort. Anthracenemethyl sulfides that can differentially react as a single electron donor, Michael donor and a diene, and reactive acetylenes that are single electron acceptors, Michael acceptors and dienophiles constitute a prototypical pair that will satisfy our concerns.

PUBLIC INTEREST STATEMENT

In this article, we describe the generation of sulfides employing thiourea as the sulfur source. The advantage here include: (i) avoidance of malodorous thiols, (ii) faster reaction time, (iii) relatively high yields, and (iv) excellent product selectivity to name a few. Several new sulfides were synthesized and all new compounds were characterized on the basis of spectral and analytical data.

Scheme 1. Mechanism of one-electron oxidation of aliphatic sulfides.



Hunt, 1975; Wrzyszczyński, Filipiak, Hug, Marciniak, & Pączkowski, 2000). Photoexcited organic sulfides produce different responses which can lead to bond scissions or ionization channels (Anastasi, Broomfield, Nielsen, & Pagsberg, 1991; Callear & Dickson, 1970; Ohbayashi, Akimoto, & Tanaka, 1977). These sulfur radical cations are important intermediates in a variety of chemical processes (Baclocchi, Lanzalunga, & Pirozzi, 1997; Chatgililoglu & Asmus, 1990b). Aliphatic sulfide radical cation **1** and radical cation complex **2** can form sulfoxide in oxygen-containing aqueous solution (Miller, Williams, & Schöneich, 1996; Scheme 1).

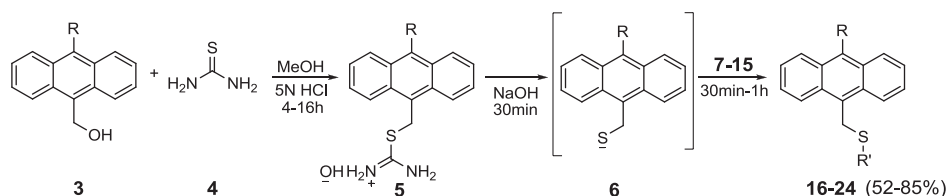
Conventional method used for the synthesis of organic sulfides involves the reaction of a thiol (or disulfide) with a halide in the presence of a strong base (Smith & March, 2001). This method is robust but requires handling of malodorous thiols and reactive halides that are difficult to handle. Moreover, not many thiols are commercially available. Reported method for the synthesis of (anthracen-9-yl)methyl methyl sulfane involves reaction of methyl iodide with sodium salt of (anthracen-9-yl)methyl thiol. The reaction condition is somewhat tedious because of the use of malodorous thiol, reactive sodium metal, and inert atmosphere in the procedure (Stein & Gellman, 1992). Recently, a one-pot synthesis of symmetrical and unsymmetrical benzyl sulfanes from benzyl halides using thiourea has been developed. The synthetic scope of this reaction is limited by its use of highly reactive benzyl halides (Eccles, Ecloate, Lawrence, & Maguire, 2010). There are many reports on the formation of aryl and alkyl sulfanes (Dunn et al., 2012; Gundermann & Röker, 1976) using cross-coupling reactions of aryl or alkyl halides with various nucleophilic compounds, but these reactions require more forcing conditions such as use of transition metal catalyst (Ham, Yang, & Kang, 2004; Huang et al., 2013; Jammi, Barua, Rout, Saha, & Punniyamurthy, 2008; Prasad & Sekar, 2011; Takagi, 1986) or photochemical activation (Argüello, Schmidt, & Peñeñory, 2003). High cost and toxicity of some transition metal catalysts and ligands restrict their applications in large-scale processes. Recent modifications such as metal free reactions have shown the same levels of efficiency as metal-catalyzed reactions (Borisova, Reshetova, & Ustynyuk, 2007). Ding et al. reported the synthesis of substituted benzyl phenyl sulfides via the metal-free reductive coupling of tosyl hydrazones with substituted benzene thiols (Ding, Cao, Yuan, Liu, & Peng, 2011). Since none of the reported methods satisfied our requirements to generate anthracenemethyl sulfanes in sufficient quantities, we explored the possibility of adopting a new strategy.

Herein, we describe a robust and convenient procedure for the synthesis of (anthracen-9-yl)methyl alkyl sulfanes or substituted (anthracen-9-yl)methyl alkyl sulfane **16–24** by a one-pot reaction using readily accessible (anthracen-9-yl)methyl alcohol or substituted (anthracen-9-yl)methyl alcohol **3**, thiourea (**4**), and the corresponding alkyl halide **7–15** adapting a reported procedure for the synthesis of thiols (Vetter, 1998). Conspicuous advantage of this procedure is avoidance of direct use of thiols. (Anthracen-9-yl)methyl phenyl sulfane (**31**) and (anthracen-9-yl)methyl *p*-tolyl sulfane (**32**) were prepared by the reductive coupling between 9-anthraldehyde tosylhydrazones (**27**) and benzene thiol (**29**) or *p*-tolyl thiol (**30**) following the protocol developed by Ding et al. (2011). Though, we synthesized a handful of naphthylmethyl and benzyl sulfanes (Ding et al., 2011; Eccles et al., 2010; Santoni et al., 2010) using these procedures, in this article, we restrict our discussion to the synthesis of a few anthracenemethyl sulfane derivatives.

2. Results and discussions

Anthracenemethyl thiol is conveniently prepared by the reaction between (anthracen-9-yl)methyl alcohol and thiourea (Miller, Amidon, & Tawney, 1955). We reasoned that the thiolate ion generated as an intermediate can be intercepted by a suitable alkyl halide to give the corresponding sulfane in a one-pot reaction. Applying this strategy, we synthesized (anthracen-9-yl)methyl alkyl sulfanes **16–24** by the one-pot reaction of (anthracen-9-yl)methyl alcohol **3**, thiourea (**4**), and the

Scheme 2. Synthesis of (anthracen-9-yl)methyl alkyl sulfane.



corresponding alkyl halide. Reaction of **3** with **4** under acidic conditions affords the isothiuronium salt **5** which upon treatment with a strong base generates the thiolate **6**. This intermediate is further reacted *in situ* with a series of alkyl halides **7-15** to generate the (anthracen-9-yl)methyl alkyl sulfanes **16-24** (Scheme 2). Here the isolation of intermediate thiol or isothiuronium salt is not required, thereby significantly simplifying this synthetic method. The reaction took place in good yields (Table 1). Steps involved in the synthesis of (anthracen-9-yl)methyl alkyl sulfanes **16-24** are presented in Scheme 2. A notable feature of this strategy is the flexibility available here: we could select the alcohol and halide substrates based on their availability and ease of handling. This procedure is compatible with several organic halides and substituted anthracenes.


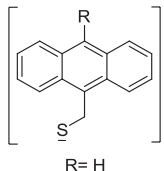
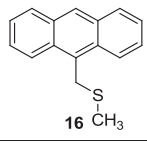

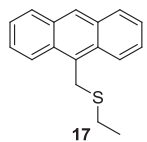

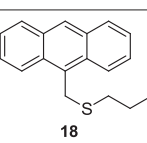

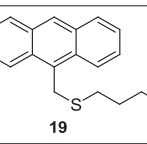
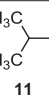
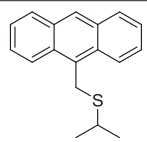
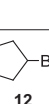
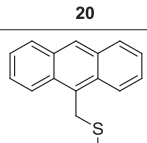

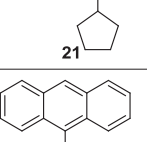

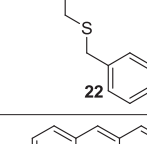
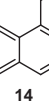
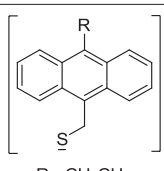
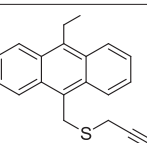
As can be inferred from the mechanism presented in Scheme 2, phenols cannot react with thiourea to generate isothiuronium salts analogous to **5**. Additionally, the reaction fails with halobenzenes. Thus, a major limitation of the procedure shown in Scheme 2 is that this method is not suitable for the preparation of aryl sulfanes such as **31** and **32**. Hence, we adopted the metal-free reductive coupling reaction reported by Ding et al. (2011) for the generation of aryl sulfanes. Reaction of benzene thiol (**29**) and *p*-tolyl thiol (**30**) with tosylhydrazone **27** derived from 9-anthraldehyde (**25**) proceeded smoothly to give (anthracen-9-yl)methyl phenyl sulfane (**31**) and (anthracen-9-yl)methyl *p*-tolyl sulfane (**32**) in high yields (Scheme 3). The proposed reductive coupling mechanism involves the initial generation of an intermediate carbene **28** via the base-promoted thermal decomposition of the tosylhydrazone (Barluenga, Tomás-Gamasa, Aznar, & Valdés, 2010; Liu, Yan, & Lu, 2013) **27**. Insertion of incipient carbene **28** into the S-H bond of the benzene thiol (**29**) and *p*-tolyl thiol (**30**), giving rise to (anthracen-9-yl)methyl phenyl sulfane (**31**) and (anthracen-9-yl)methyl *p*-tolyl sulfane (**32**). Structure of **16-24**, **31**, and **32** was established on the basis of analytical and spectral data. ¹H and ¹³C NMR spectra of these compounds were in agreement with the expected structure and they exhibited acceptable elemental analysis and mass spectral data.

3. Experimental section

3.1. General techniques

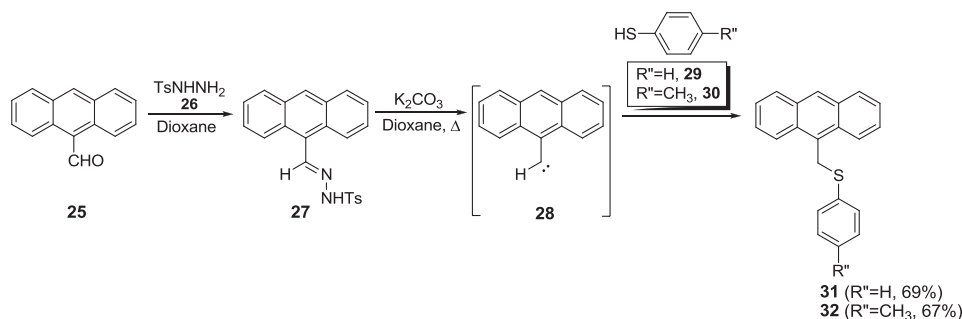
All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried and activated silica gel TLC plates (aluminum sheets coated with silica gel, *E. Merck*). Visualization of TLC plates was acquired by exposure to iodine vapors or UV lamp. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60-120 mesh). The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph* rotary evaporator. Melting points were determined on a *Neolab* melting point apparatus. Infrared spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ¹H and ¹³C NMR spectra were recorded at 400 MHz on a *Bruker Advance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment using *JMS 600 JEOL* mass spectrometer. All the required starting materials are commercially available and were used as received.

Table 1. List of (anthracen-9-yl)methyl sulfanes synthesized using a one-pot reaction from (anthracen-9-yl)methyl alcohol, thiourea, and alkyl halide*

Entry	Alkyl Halide R'-X	Thiolate intermediate, 6	Product	Yield (%)	Time
1	 7	 R= H	 16	74	30 min
2	 8		 17	78	30 min
3	 9		 18	78	1 h
4	 10		 19	72	1 h
5	 11		 20	59	30 min
6	 12		 21	74	1 h
7	 13		 22	61	30 min
8	 14		 23	52	1 h
9	 15		 R=-CH ₂ CH ₃	 24	85

*Note: Only a few typical examples are listed herein.

Scheme 3. Base-promoted one-pot reductive coupling mechanism for the synthesis of (anthracen-9-yl)methyl aryl sulfane.



3.2. General procedure for the synthesis of (anthracen-9-yl)methyl alkyl sulfanes 16–24

To a solution of (anthracen-9-yl)methyl alcohol (2 g, 9.6 mmol, 1 equiv.) or (10-ethylanthracen-9-yl)methyl alcohol (2 g, 8.5 mmol, 1 equiv.) in 15 mL of methanol, thiourea (**4**) (2 equiv.) and 10 mL of 5 N HCl were added and the mixture was stirred at RT for 10 h. To this mixture, NaOH pellets (3 equiv.) were added and the mixture was stirred vigorously for 30 min. On addition of NaOH, yellow color of the solution turned into gray. At this point, 1.1 equiv. of alkyl halide was added and the mixture was stirred for one hour. After the completion of the reaction, the reaction mixture was poured into water and extracted with dichloromethane. Organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4 . Solvent was removed under reduced pressure and the product obtained was passed through a silica gel column to purify (anthracen-9-yl)methyl alkyl sulfanes **16–23** and (10-ethylanthracen-9-yl)methyl prop-2-ynyl sulfane (**24**). The solid obtained upon removal of solvent was purified by recrystallization from a mixture (1:3) of hexane and dichloromethane.

3.3. General procedure for the synthesis of (anthracen-9-yl)methyl aryl sulfanes, **31** & **32**

To a solution of 9-anthraldehyde (**25**) (1.0 g, 4.8 mmol) in 5 mL of dioxane, tosyl hydrazide (**26**) (1.8 g, 9.6 mmol) was added and the mixture was stirred for 1 h. To this mixture, benzene thiol (**29**) (0.98 mL, 9.6 mmol) or *p*-tolyl thiol (**30**) (1.19 g, 9.6 mmol) and K_2CO_3 (2 g, 14.4 mmol) were added and the mixture was stirred at 100°C for 2 h. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature. Ethyl acetate (25 mL) was added and the organic phase was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The product obtained was purified by column chromatography on silica gel.

4. Characterization data

(anthracen-9-yl)methyl methyl sulfane (16) (Stein & Gellman, 1992): Yellow solid, Yield: 1.70 g, 74%; mp: 72–74°C; IR ν_{max} (KBr): 3055, 2958, 2846, 1619, 1598, 1392, 719 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.31–7.38 (m, 9H), 4.65 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (CDCl_3): δ 130.6, 128.9, 128.3, 128.2, 126.2, 125.1, 124.0, 123.2, 37.5, 17.2; MS: m/z 238 (M^+), 191; Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{S}$: C, 80.63; H, 5.92; S, 13.45; Found: C, 80.58; H, 5.85; S, 13.39.

(anthracen-9-yl)methyl ethyl sulfane (17) (Stein & Gellman, 1992): Yellow solid, Yield: 1.88 g, 78%; mp: 68–70°C; IR ν_{max} (KBr): 2965, 1443, 1218, 885, 840, 791, 772, 602, 524 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.39–7.43 (m, 9H), 4.76 (s, 2H), 2.70 (q, 2H, $J = 7.4$ Hz), 1.36 (t, 3H, $J = 7.4$ Hz); MS: m/z 252 (M^+), 191; Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{S}$: C, 80.90; H, 6.39; S, 12.71; Found: C, 80.81; H, 6.32; S, 12.65.

(anthracen-9-yl)methyl propyl sulfane (18): Yellow solid, Yield: 1.99 g, 78%; mp: 92–94°C; IR ν_{max} (KBr): 3058, 2961, 2856, 1620, 1596, 1388, 1221, 716 cm^{-1} ; ^1H NMR (CDCl_3): δ 8.41–7.46 (m, 9H), 4.75 (s, 2H), 2.80 (t, $J = 7.3$ Hz, 2H), 1.82–1.70 (m, 2H), 1.00 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (CDCl_3): δ 131.44, 131.40, 129.01, 127.62, 125.69, 125.03, 124.89, 67.15, 54.59, 53.70; MS: m/z 266 (M^+), 191; Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{S}$: C, 81.15; H, 6.81; S, 12.04; Found: C, 81.19; H, 6.78; S, 12.03.

(anthracen-9-yl)methyl butyl sulfane (19) (Stein & Gellman, 1992): Yellow solid, Yield: 1.94 g, 72%; mp: 52–54°C; IR ν_{\max} (KBr): 2960, 1446, 1217, 888, 842, 727 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.29–7.40 (m, 9H), 4.74 (s, 2H), 2.67 (t, 2H, $J = 7.2$ Hz), 1.69 (m, 2H), 1.44 (m, 2H), 0.91 (t, 3H, $J = 7.3$ Hz); MS: m/z 280 (M^+), 191; Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{S}$: C, 81.38; H, 7.19; S, 11.43; Found: C, 81.32; H, 7.14; S, 11.32.

(anthracen-9-yl)methyl isopropyl sulfane (20): Yellow solid, Yield: 1.52 g, 59%; mp: 62–64°C; IR ν_{\max} (KBr): 3053, 2957, 2858, 1620, 1597, 1384, 722 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.31–7.37 (m, 9H), 4.68 (s, 2H), 3.19–3.09 (m, 1H), 1.37 (d, 6H, $J = 6.8$ Hz); $^{13}\text{C NMR}$ (CDCl_3): δ 130.6, 128.9, 128.3, 128.2, 126.2, 125.1, 124.0, 123.2, 35.7, 26.9, 22.6; MS: m/z 266 (M^+), 191; Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{S}$: C, 81.15; H, 6.81; S, 12.04; Found: C, 81.07; H, 6.76; S, 11.99.

(anthracen-9-yl)methyl cyclopentyl sulfane (21): Yellow solid, Yield: 2.08 g, 74%; mp: 66–68°C; IR ν_{\max} (KBr): 3084, 2952, 2857, 1619, 1598, 1399, 723 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.30–7.36 (m, 9H), 4.68 (s, 2H), 3.29–3.22 (m, 1H), 2.05–1.98 (m, 2H), 1.73–1.69 (m, 2H), 1.63–1.51 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3): δ 130.6, 128.9, 128.6, 128.1, 126.1, 125.0, 123.9, 123.2, 44.1, 33.2, 33.0, 28.1, 24.0, 23.8; MS: m/z 292 (M^+), 191; Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{S}$: C, 82.14; H, 6.89; S, 10.96; Found: C, 82.08; H, 6.81; S, 10.89.

(anthracen-9-yl)methyl benzyl sulfane (22): Yellow solid, Yield: 1.85 g, 61%; mp: 74–76°C; IR ν_{\max} (KBr): 3061, 2911, 1599, 1384, 735, 697 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.36–7.32 (m, 14H), 4.60 (s, 2H), 3.89 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3): δ 136.4, 130.5, 129.1, 128.5, 128.1, 127.5, 127.1, 126.8, 126.5, 125.1, 124.1, 123.4, 42.8, 35.9; MS: m/z 314 (M^+), 191, 91; Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{S}$: C, 84.03; H, 5.77; S, 10.20; Found: C, 83.92; H, 5.73; S, 10.12.

(anthracen-9-yl)methyl naphthylmethyl sulfane (23): Yellow solid, Yield: 1.82 g, 52%; mp: 94–96°C; IR ν_{\max} (KBr): 3080, 3046, 2931, 2860, 1598, 1380, 779, 716 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.35–7.32 (m, 16H), 4.65 (s, 2H), 4.33 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3): δ 134.2, 133.5, 131.6, 131.5, 130.1, 129.1, 128.8, 128.3, 127.4, 127.3, 126.1, 126.0, 125.9, 125.1, 125.0, 124.1, 35.3, 29.0; MS: m/z 364 (M^+), 191, 141; Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{S}$: C, 85.67; H, 5.53; S, 8.80; Found: C, 85.58; H, 5.46; S, 8.76.

(10-ethylanthracen-9-yl)methyl prop-2-ynyl sulfane (24): Yellow solid, Yield: 2.09 g, 85%; mp: 103–105°C; IR ν_{\max} (KBr): 3299, 3119, 3090, 2953, 2860, 2127, 1597, 1382, 1272, 1024, 890, 728, 686, 632 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.45–7.49 (m, 9H), 4.92 (s, 2H), 3.65 (q, $J = 7.6$ Hz & 15.2 Hz, 2H), 3.37 (d, $J = 2.8$ Hz, 2H), 2.44 (t, $J = 2.4$ Hz & 4.8 Hz, 1H), 1.46 (t, $J = 7.6$ Hz & 15.2 Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3): δ 137.63, 130.17, 129.08, 126.68, 125.71, 125.14, 125.10, 124.95, 80.56, 71.35, 28.98, 21.39, 20.56, 15.52; MS: m/z 290 (M^+), 191; Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{S}$: C, 82.71; H, 6.25; S, 11.04; Found: C, 82.64; H, 6.21; S, 10.92.

(anthracen-9-yl)methyl phenyl sulfane (31): Yellow solid, Yield: 1.01 g, 69%; mp: 100–102°C; IR ν_{\max} (KBr): 3061, 2951, 2859, 1597, 1384, 729, 686 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.42–7.22 (m, 14H), 5.12 (s, 2H); $^{13}\text{C NMR}$ (CDCl_3): δ 137.4, 131.5, 130.1, 129.9, 129.2, 129.0, 127.6, 126.5, 126.2, 125.1, 124.1, 32.1; MS: m/z 300 (M^+), 191; Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{S}$: C, 83.96; H, 5.37; S, 10.67; Found: C, 83.91; H, 5.33; S, 10.58.

(anthracen-9-yl)methyl p-tolyl sulfane (32) (Santoni et al., 2010): Yellow solid, Yield: 1.02 g, 67%; mp: 124–126°C; IR ν_{\max} (KBr): 3069, 3059, 2948, 2859, 1599, 1470, 1379, 733, 691 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3): δ 8.30–7.08 (m, 13H), 4.95 (s, 2H), 2.30 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3): δ 136.49, 133.55, 131.35, 130.29, 129.92, 129.65, 129.02, 127.78, 127.50, 126.05, 124.90, 124.03, 32.51, 21.01; MS: m/z 314 (M^+), 191; Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{S}$: C, 84.03; H, 5.77; S, 10.20; Found: C, 83.96; H, 5.73; S, 10.13.

5. Conclusion

We have developed an efficient, inexpensive, and operationally simple procedure for the synthesis of (anthracen-9-yl)methyl alkyl sulfanes using commercially available compounds. This method is superior to other reported procedures due to its inherent flexibility, simplicity, and avoidance of less accessible and malodorous thiols.

Supplementary material

Supplementary material for this article can be accessed here <http://dx.doi.org/10.1080/23312009.2015.1033820>.

Acknowledgments

The authors acknowledge STIC, Kochi for NMR and elemental analysis.

Funding

Reshma Gopalakrishnan and Jomon P. Jacob gratefully acknowledge UGC, CUSAT, and Kerala Government for financial support in the form of Research Fellowships. Additional funding for this work was provided by DST (PURSE and FIST schemes).

Author details

Reshma Gopalakrishnan¹
E-mail: reshmag21@gmail.com
Jomon P. Jacob¹
E-mail: jacobpjomon@yahoo.com
Ranjith Chirakandathil¹
E-mail: cranjith85@gmail.com
Perupparampil A. Unnikrishnan¹
E-mail: paunni@gmail.com
Sreedharan Prathapan¹
E-mail: prathapans@gmail.com

¹ Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682 022, Kerala, India.

Citation information

Cite this article as: Efficient one-pot synthesis of (anthracen-9-yl)methyl sulfane derivatives, Reshma Gopalakrishnan, Jomon P. Jacob, Ranjith Chirakandathil, Perupparampil A. Unnikrishnan & Sreedharan Prathapan, *Cogent Chemistry* (2015), 1: 1033820.

Cover image

Source: Authors.

References

- Anastasi, C., Broomfield, M., Nielsen, O. J., & Pagsberg, P. (1991). Ultraviolet absorption spectra and kinetics of CH₂S and CH₂SH radicals. *Chemical Physics Letters*, 182, 643–648. [http://dx.doi.org/10.1016/0009-2614\(91\)90139-Z](http://dx.doi.org/10.1016/0009-2614(91)90139-Z)
- Andrzejewska, E., Hug, G. L., Andrzejewski, M., & Marciniak, B. (1999). Trithianes as coinitiators in benzophenone-induced photopolymerizations. *Macromolecules*, 32, 2173–2179. <http://dx.doi.org/10.1021/ma9815408>
- Argüello, J. E., Schmidt, L. C., & Peññory, A. B. (2003). “One-pot” two-step synthesis of aryl sulfur compounds by photoinduced reactions of thiourea anion with aryl halides. *Organic Letters*, 5, 4133–4136. <http://dx.doi.org/10.1021/ol035545n>
- Baciocchi, E., Lanzalunga, O., & Pirozzi, B. (1997). Oxidations of benzyl and phenethyl phenyl sulfides. Implications for the mechanism of the microsomal and biomimetic oxidation of sulfides. *Tetrahedron*, 53, 12287–12298. [http://dx.doi.org/10.1016/S0040-4020\(97\)00560-7](http://dx.doi.org/10.1016/S0040-4020(97)00560-7)
- Bartuenga, J., Tomás-Gamasa, M., Aznar, F., & Valdés, C. (2010). Straightforward synthesis of ethers: Metal-free reductive coupling of tosylhydrazones with alcohols or phenols. *Angewandte Chemie International Edition*, 49, 4993–4996. <http://dx.doi.org/10.1002/anie.v49:29>
- Bauld, N. L., Aplin, J. T., Yueh, W., & Loinaz, A. (1997). A non-outer sphere mechanism for the ionization of aryl vinyl sulfides by triarylaminium salts. *Journal of the American Chemical Society*, 119, 11381–11389. <http://dx.doi.org/10.1021/ja9706965>
- Bisby, R. H., Cundall, R. B., Redpath, J. L., & Adams, G. E. (1976). One-electron reduction reactions with enzymes in solution. A pulse radiolysis study. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 72, 51–63. <http://dx.doi.org/10.1039/f19767200051>
- Bobrowski, K., Marciniak, B., & Hug, G. L. (1996). Sensitized photo-oxidation of sulfur-containing amino acids and peptides in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry*, 95, 81–88.
- Borisova, N. E., Reshetova, M. D., & Ustynuk, Y. A. (2007). Metal-free methods in the synthesis of macrocyclic schiff bases. *Chemical Reviews*, 107, 46–79. <http://dx.doi.org/10.1021/cr0683616>
- Callear, A. B., & Dickson, D. R. (1970). Transient spectra and primary processes in the flash photolysis of CH₃SCH₃, CH₃SCH₂, CH₃SH and C₂H₅SH. *Transactions of the Faraday Society*, 66, 1987–1995. <http://dx.doi.org/10.1039/tf9706601987>
- Chatgililoglu, C., & Asmus, K. D. (Eds.). (1990a). *Sulfur-centered reactive intermediates in chemistry and biology* (p. 116). New York, NY: Plenum Press.
- Chatgililoglu, C., & Asmus, K. D. (Eds.). (1990b). *Sulfur-centered reactive intermediates in chemistry and biology* (Vol. 197, NATO ASI Series, p. 155). New York, NY: Plenum Press. <http://dx.doi.org/10.1007/978-1-4684-5874-9>
- Chatgililoglu, C., Bertrand, M. P., Ferreri, C., & Alfassi, Z. B. (Eds.). (1999). *Sulfur-centred radicals in organic synthesis* (p. 311). Chichester: Wiley.
- Ding, Q., Cao, B., Yuan, J., Liu, X., & Peng, Y. (2011). Synthesis of thioethers via metal-free reductive coupling of tosylhydrazones with thiols. *Organic & Biomolecular Chemistry*, 9, 748–751. <http://dx.doi.org/10.1039/C0OB00639D>
- Dunn, D., Hostetler, G., Iqbal, M., Messina-McLaughlin, P., Reiboldt, A., Lin, Y. G., ... Gruner, J. (2012). Wake-promoting agents: Search for next generation modafinil: Part I. *Bioorganic & Medicinal Chemistry Letters*, 22, 2312–2314. <http://dx.doi.org/10.1016/j.bmcl.2011.12.099>
- Eccles, K. S., Ecloate, C. J., Lawrence, S. E., & Maguire, A. R. (2010). Convenient and robust one-pot synthesis of symmetrical and unsymmetrical benzyl thioethers from benzyl halides using thiourea. *Arkivoc*, 2010, 216–228. <http://dx.doi.org/10.3998/ark.5550190.0011.921>
- Gundermann, K.-D., & Röker, K.-D. (1976). Konstitution und chemilumineszenz, VII. Chemilumineszierende paracyclophane, II: Intramolekular sensibilisierte chemilumineszenz. *Justus Liebigs Annalen der Chemie*, 1976, 140–152. [http://dx.doi.org/10.1002/\(ISSN\)1099-0690](http://dx.doi.org/10.1002/(ISSN)1099-0690)
- Ham, J., Yang, I., & Kang, H. (2004). A facile one-pot synthesis of alkyl aryl sulfides from aryl bromides. *The Journal of Organic Chemistry*, 69, 3236–3239. <http://dx.doi.org/10.1021/jo049758h>
- Huang, L. Z., Han, P., Li, Y. Q., Xu, Y. M., Zhang, T., & Du, Z. T. (2013). A facile and efficient synthesis of diaryl amines or ethers under microwave irradiation at presence of KF/Al₂O₃ without solvent and their anti-fungal biological activities against six phytopathogens. *International Journal of Molecular Sciences*, 14, 18850–18860. <http://dx.doi.org/10.3390/ijms140918850>
- Jammi, S., Barua, P., Rout, L., Saha, P., & Punniyamurthy, T. (2008). Efficient ligand-free nickel-catalyzed C–S cross-coupling of thiols with aryl iodides. *Tetrahedron Letters*, 49, 1484–1487. <http://dx.doi.org/10.1016/j.tetlet.2007.12.118>
- Kang, D. H., & Friend, C. M. (2004). Sensitivity of methyl thiolate desulfurization selectivity to reaction temperature and hydroxyl coverage. *Langmuir*, 20, 11443–11449. <http://dx.doi.org/10.1021/la04882n>
- Kosower, N. S., Kosower, E. M., & Pryor, W. A. (Eds.). (1976). *Free radicals in biology* (Vol. II, p. 55). New York, NY: Academic Press.

- Kretzschmar, I., Friend, C. M., & Sigman, M. E. (2002). Effect of coadsorbed species and temperature on competitive reaction channels for nascent radicals: $c\text{-C}_3\text{H}_7\text{CH}_2\text{SH}$ on $\text{Mo}(110)\text{-(}6 \times 1\text{)-O}$. *The Journal of Physical Chemistry B*, 106, 663–672. <http://dx.doi.org/10.1021/jp013238y>
- Lalitha, B., & Mittal, J. P. (1971). Electron transfer reaction in the radiation chemistry of some biologically important disulphide compounds. *Radiation Effects*, 7, 159–162. <http://dx.doi.org/10.1080/00337577108230982>
- Liu, J.-B., Yan, H., & Lu, G. (2013). N-Alkylation of tosylhydrazones via a metal-free reductive coupling procedure. *Tetrahedron Letters*, 54, 891–895. <http://dx.doi.org/10.1016/j.tetlet.2012.11.124>
- Marciniak, B., Andrzejewska, E., & Hugc, G. L. (1998). Photoreduction of benzophenone by 2,4,6-trimethyl-1,3,5-trithiane in solution. Laser flash photolysis study. *Journal of Photochemistry and Photobiology A: Chemistry*, 112, 21–28. [http://dx.doi.org/10.1016/S1010-6030\(97\)00253-0](http://dx.doi.org/10.1016/S1010-6030(97)00253-0)
- Miller, B. L., Williams, T. D., & Schöneich, C. (1996). Mechanism of sulfoxide formation through reaction of sulfur radical cation complexes with superoxide or hydroxide ion in oxygenated aqueous solution. *Journal of the American Chemical Society*, 118, 11014–11025. <http://dx.doi.org/10.1021/ja962032l>
- Miller, M. W., Amidon, R. W., & Tawney, P. O. (1955). Some meso-substituted anthracenes. I. 9,10-Bis-(chloromethyl)-anthracene as a synthetic intermediate. *Journal of the American Chemical Society*, 77, 2845–2848. <http://dx.doi.org/10.1021/ja01615a053>
- Ohbayashi, K., Akimoto, H., & Tanaka, I. (1977). Emission spectra of methoxyl, ethoxyl, and isopropoxyl radicals. *The Journal of Physical Chemistry*, 81, 798–802. <http://dx.doi.org/10.1021/j100523a023>
- Prasad, D. J. C., & Sekar, G. (2011). Cu-catalyzed one-pot synthesis of unsymmetrical diaryl thioethers by coupling of aryl halides using a thiol precursor. *Organic Letters*, 13, 1008–1011. <http://dx.doi.org/10.1021/ol103041s>
- Santoni, G., Mba, M., Bonchio, M., Nugent, W. A., Zonta, C., & Licini, G. (2010). Stereoselective control by face-to-face versus edge-to-face aromatic interactions: The case of $\text{C}_3\text{-Ti}^{\text{IV}}$ amino trialkolate sulfoxidation catalysts. *Chemistry—A European Journal*, 16, 645–654. <http://dx.doi.org/10.1002/chem.v16:2>
- Smith, M. B., & March, J. (2001). *Advanced organic chemistry: Reaction, mechanism, and structure* (5th ed.). New York, NY: Wiley.
- Steffen, L. K., Glass, R. S., Sabahi, M., Wilson, G. S., Schoeneich, C., Mahling, S., & Asmus, K.-D. (1991). Hydroxyl radical induced decarboxylation of amino acids. Decarboxylation vs bond formation in radical intermediates. *Journal of the American Chemical Society*, 113, 2141–2145. <http://dx.doi.org/10.1021/ja00006a035>
- Stein, T. M., & Gellman, S. H. (1992). Synthesis and aggregation properties of a new family of amphiphiles with an unusual headgroup topology. *Journal of the American Chemical Society*, 114, 3943–3950. <http://dx.doi.org/10.1021/ja00036a048>
- Takagi, K. (1986). A facile synthesis of sulfides using S-aryl-isothiuronium intermediates. *Chemistry Letters*, 15, 1379–1380. <http://dx.doi.org/10.1246/cl.1986.1379>
- Thompson, S. D., Carroll, D. G., Watson, F., O'Donnell, M., & McGlynn, S. P. (1966). Electronic spectra and structure of sulfur compounds. *The Journal of Chemical Physics*, 45, 1367–1379. <http://dx.doi.org/10.1063/1.1727769>
- Vetter, S. (1998). Direct synthesis of di- and trimethoxybenzyl thiols from the corresponding alcohol. *Synthetic Communications*, 28, 3219–3223. <http://dx.doi.org/10.1080/00397919808004425>
- Wiegand, B. C., & Friend, C. M. (1992). Model studies of the desulfurization reactions on metal surfaces and in organometallic complexes. *Chemical Reviews*, 92, 491–504. <http://dx.doi.org/10.1021/cr00012a001>
- Wiegand, B. C., Napier, M. E., Friend, C. M., & Uvdal, P. (1996). Ion and radical rearrangements as a probe of the mechanism of a surface reaction: The desulfurization of cyclopropylmethanethiol and 3-butene-1-thiol on $\text{Mo}(110)$. *Journal of the American Chemical Society*, 118, 2962–2968. <http://dx.doi.org/10.1021/ja951966r>
- Wolff, R. K., Aldrich, J. E., Penner, T. L., & Hunt, J. W. (1975). Picosecond pulse radiolysis. V. Yield of electrons in irradiated aqueous solution with high concentrations of scavenger. *The Journal of Physical Chemistry*, 79, 210–219. <http://dx.doi.org/10.1021/j100570a005>
- Wrzyszczyński, A., Filipiak, P., Hug, G. L., Marciniak, B., & Pączkowski, J. (2000). Photoinduced electron transfer polymerization. 4. 4-carboxybenzophenone-sulfur-containing carboxylic acids photoredox pairs as a photoinitiating system for free-radical polymerization. *Macromolecules*, 33, 1577–1582. <http://dx.doi.org/10.1021/ma991242q>
- Wrzyszczyński, A., Scigalski, F., & Pączkowski, J. (2000). Sulfur-containing initiator and coinitiators of free radical polymerization. *Nukleonika*, 45, 73–81.



© 2015 The Author(s). This open access article is distributed under a Creative Commons Attribution (CC-BY) 4.0 license.

You are free to:

Share — copy and redistribute the material in any medium or format

Adapt — remix, transform, and build upon the material for any purpose, even commercially.

The licensor cannot revoke these freedoms as long as you follow the license terms.

Under the following terms:

Attribution — You must give appropriate credit, provide a link to the license, and indicate if changes were made.

You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use.

No additional restrictions

You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits.

