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# Solvent effects in the reaction between (anthracen-9-yl)methyl sulfides and electron-deficient acetylenes

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**Solvent-dependent diverse reactivity of (anthracen-9-yl)methyl sulfides with a few electron-deficient acetylenes is described. Diversity in reactivity is attributed to competition between one electron transfer, two electron transfer and Diels–Alder reaction of these sulfides with electron-deficient acetylenes. We have proposed plausible mechanisms to account for various reactions observed by us. Copyright © 2015 John Wiley & Sons, Ltd.**

**Keywords:** competing reactions; electron transfer; Diels–Alder reaction; Michael addition; electron-deficient acetylenes

## INTRODUCTION

Competing reactions[1–6] are those in which a substance reacts or decomposes in more than one pathway to give different products. Recently we observed multiple pathways operating concurrently in the reaction between (anthracen-9-yl)methanamines with reactive acetylenes.[7–9] Depending on the nature of solvent, major pathway changes from single electron transfer to nucleophilic addition. In nonpolar and polar aprotic media, depending on substrate concentration, competition between one electron transfer and Diels–Alder reaction pathways was observed. In polar protic solvents, Michael type addition was the major pathway. With increasing concentration of reactants, cycloaddition pathway gained prominence in all solvents examined by us. These results prompted us to investigate similar competing reaction sequences with other suitable substrates. Since tertiary amines and organic sulfides have comparable ionization potential (~8.2 eV),[10] we reasoned that (anthracen-9-yl)methyl sulfides also should give similar reactions with electron-deficient acetylenes. In support of our assumption, it has already been reported that organic sulfides efficiently undergo fast one[11,12] and two electron[13,14] oxidation reactions, owing to their relatively low ionization potentials. Thus, suitable oxidants can produce sulfur centred radical cations from organic sulfides. Sulfur-centred radical cations are important intermediates in a wide variety of chemical processes, extending from those of industrial importance to biological processes.[15–18] Organic sulfides are excellent nucleophiles capable of undergoing substitution and addition reactions.[19] (Anthracen-9-yl)methyl sulfides by virtue of being 9-substituted anthracenes are reactive dienes capable of undergoing Diels–Alder reaction with a variety of dienophiles.[20,21] Hence it is reasonable to assume that anthracenemethyl sulfides also should undergo competing one electron transfer (*path* ***a***), two electron transfer (Michael type addition, *path* ***b***) and [4 + 2] cycloaddition reaction (Diels–Alder reaction, *path* ***c***) with electron-deficient acetylenes such as dimethyl acetylenedicarboxylate (DMAD) and dibenzoylacetylene (DBA) in different solvents (Scheme 1). In the present study, we examined competing reactions of (anthracen-9-yl)methyl sulfides with electron-deficient acetylenes as a function of variables including solvent polarity and substrate concentration.

## EXPERIMENTAL

### General method

All reactions were carried out in oven dried glass wares. 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. All the reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. 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. Melting points are uncorrected and were determined on a Neolab melting point apparatus. Infra-red spectra were recorded using Jasco 4100 and ABB Bomem (MB Series) FT-IR spectrometers. The $^{1}H$ and $^{13}C$ NMR spectra were recorded at 400 MHz on a Bruker Avance III FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts ($\delta$) 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 electrospray ionization (ESI) method using GC-MS (Agilent GC-7890A, Mass-5975C) and fast atom bombardment (FAB) using JMS 600 JEOL mass spectrometers. All new compounds were identified on the basis of spectral and analytical data. Relevant references are cited for known compounds.

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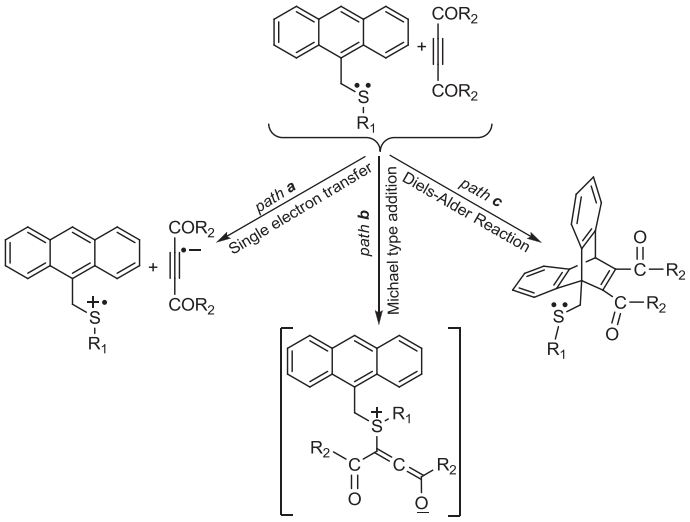



**Scheme 1**. Possible competing reactions between (anthracen-9-yl)methyl sulfides and electron-deficient acetylenes

### Synthesis of (anthracen-9-yl)methyl sulfides

Anthracenemethyl sulfides, **1**, **26**, **27**, **28** and **29** were prepared by adaptation of known procedures.[22,23]

## GENERAL EXPERIMENTAL PROCEDURE FOR THE REACTIONS OF (ANTHRACEN-9-YL) METHYL METHYL SULFIDE (1) WITH ELECTRON-DEFICIENT ACETYLENES

### In xylene, DMF and glacial acetic acid

To a solution (0.42 M) of (anthracen-9-yl)methyl methyl sulfide (**1**) in corresponding solvent, acetylene (**2**/**3**, 2 equivalents) was added, and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was cooled and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel using hexane and dichloromethane. Details of reaction time and product yield are presented in Tables 1, 2 and 4. In order to examine the effect of substrate concentration, experiments were repeated at 0.042 M concentration in all the three solvents.

Similar reaction conditions were employed for the reaction of acetylenes **2** and **3** with anthracenemethyl sulfides **26–29** in xylene.

### In methanol: with DMAD

To a solution (0.11 M) of **1** in methanol, dimethyl acetylenedicarboxylate (**2**, 2 equivalents) were added, and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was cooled, and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel using mixtures of hexane and dichloromethane. Details of reaction time and product yield are presented in Table 3.

### In methanol: with DBA

To a solution (0.11 M) of (anthracen-9-yl)methyl methyl sulfide (**1**) in methanol, dibenzoylacetylene (**3**, 2 equivalents) was added, and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was cooled, and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel using hexane and dichloromethane. Details of reaction time and product yield are presented in Table 3.

### Characterization data

**Compound 1**[69]: Yellow solid; Yield: 74%; mp: 72–74 °C; IR $\nu_{max}$ (KBr): 3055, 2958, 2846, 1619, 1598, 1392, 719 $cm^{-1}$; $^1H$ NMR

**Table 1.** Yield (%) of different products and time taken for the reaction of **1** with **2** and **3** in xylene (0.42 M)

| Electron-deficient acetylene | Reaction time | 4 | 5 | 6 | 7 | 8 | 9 | 10a/10b | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 10 h | 2% | <1% | <1% | 9% | 10% | 1% | 44% | — | — | <1% |
| **3** | 15 h | <1% | <1% | <1% | 5% | — | <1% | 56% | <1% | <1% | — |

**Table 2.** Yield (%) of different products and time taken for the reaction of **1** with **2** and **3** in DMF (0.42 M)

| Electron-deficient acetylene | Reaction time | 4 | 5 | 6 | 7 | 8 | 9 | 10a/10b | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 15 h | <1% | <1% | <1% | 10% | 8% | 3% | 50% | — | — | <1% |
| **3** | 15 h | <1% | <1% | <1% | 10% | — | 2% | 76% | <1% | <1% | — |

**Table 3.** Yield (%) of different products obtained in the reaction of **1** with **2** and **3** in methanol

| Electron-deficient acetylene | Reaction time | 4 | 5 | 6 | 8 | 9 | 10a/10b | 21a | 22 | 23a |
|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 15 h | <1% | <1% | 3% | 8% | 2% | <1% | 41% | 38% | 6% |
| **3** | 30 h | <1% | <1% | <1% | — | <1% | 61% | — | — | — |

($CDCl_3$): δ 8.31–7.38 (m, 9H), 4.65 (s, 2H), 2.06 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 130.60, 128.94, 128.34, 128.17, 126.19, 125.07, 123.99, 123.23, 37.54, 17.23; MS: *m/z* 238 ($M^+$), 191; Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45; Found: C, 80.58; H, 5.85; S, 13.39.

**Compound 8**: Yellow puffy solid; mp: 166 °C; IR $\nu_{max}$ (KBr): 3016, 2955, 2925, 2853, 1732, 1713, 1665, 1437, 1273, 768 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 8.87–7.52 (m, 8H), 4.05 (s, 3H), 3.98 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 182.08, 167.71, 164.69, 134.77, 133.87, 132.79, 132.16, 130.91, 130.06, 128.37, 128.22, 127.61, 127.53, 127.25, 127.22, 126.20, 124.70, 122.60, 122.08, 52.15, 52.04; MS: *m/z* 347 $(M+1)^+$; Anal. Calcd for $C_{21}H_{14}O_5$: C, 72.83; H, 4.07; Found: C, 72.75; H, 3.98.

**Compound 10a**: White crystalline solid; mp: 172 °C; IR $\nu_{max}$ (KBr): 3066, 2968, 2947, 2912, 1728, 1715, 1628, 1433, 1328, 1264, 754 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.52–6.99 (m, 8H), 5.56 (s, 1H), 3.95 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.35 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 167.36, 164.17, 152.06, 145.76, 143.83, 143.05, 125.19, 125.13, 123.54, 122.37, 72.71, 64.21, 56.05, 52.30, 51.46, 50.73, 21.93; MS: *m/z* 380 ($M^+$); Anal. Calcd for $C_{22}H_{20}O_4S$: C, 69.45; H, 5.30; S, 8.43; Found: C, 69.36; H, 5.25; S, 8.38.

**Compound 10b**: Off-white crystalline solid; mp: 178 °C; IR $\nu_{max}$ (KBr): 3061, 3029, 2983, 2911, 2853, 1660, 1645, 1598, 1448, 1385, 1276, 1069, 690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.55–7.02 (m, 18H), 5.47 (s, 1H), 4.02 (s, 2H), 1.95 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 194.50, 193.69, 151.88, 145.86, 138.28, 137.23, 132.89, 132.35, 128.95, 128.12, 127.81, 125.44, 125.21, 123.61, 53.44, 33.22, 18.09; MS: *m/z* 473 $(M+1)^+$, 105; Anal. Calcd for $C_{32}H_{24}O_2S$: C, 81.33; H, 5.12; S, 6.78; Found: C, 81.23; H, 5.06; S, 6.71.

**Compound 11**[66]: White crystalline solid; mp: 284 °C; IR $\nu_{max}$ (KBr): 3057, 2922, 1667, 1595, 1449, 1229, 729 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.44–7.16 (m, 30H); $^{13}C$ NMR ($CDCl_3$): δ 195.06, 141.26, 136.51, 133.80, 129.83, 128.16; MS: *m/z* 702 ($M^+$); Anal. Calcd for $C_{48}H_{30}O_6$: C, 82.04; H, 4.30; Found: C, 81.91; H, 4.19.

**Compound 12**: Yellow solid; mp: 232 °C; IR $\nu_{max}$ (KBr): 3056, 2926, 1682, 1663, 1599, 1447, 1245, 694 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.83 (s, 2H), 7.77–7.39 (m, 20H); $^{13}C$ NMR ($CDCl_3$): δ 195.05, 141.51, 136.28, 133.72, 130.20, 129.93, 128.64; MS: *m/z* 494 ($M^+$); Anal. Calcd for $C_{34}H_{22}O_4$: C, 82.58; H, 4.48; Found: C, 82.45; H, 4.39.

**Compound 13**: Off-white crystalline solid; mp: 116 °C; IR $\nu_{max}$ (KBr): 2956, 1753, 1727, 1253 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 8.65 (s, 2H), 3.96 & 3.94 (two singlets, 30H), 3.89 (s, 6H); MS: *m/z* 854 ($M^+$); Anal. Calcd for $C_{36}H_{38}O_{24}$: C, 50.59; H, 4.48; Found: C, 50.38; H, 4.36.

**Compound 21a**: Yellow waxy material; IR $\nu_{max}$ (KBr): 3005, 2952, 2926, 2854, 1737, 1715, 1591, 1437, 1259, 1202, 1167 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 6.28 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 2.34 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 164.93, 163.05, 150.39, 110.83, 52.12, 50.80, 13.62; MS: *m/z* 190 ($M^+$); Anal. Calcd for $C_7H_{10}O_4S$: C, 44.20; H, 5.30; S, 16.86; Found: C, 44.13; H, 5.22; S, 16.78.

**Compound 21b**: Off-white crystalline solid; mp: 60 °C; IR $\nu_{max}$ (KBr): 3066, 2998, 2941, 2915, 1671, 1634, 1598, 1540, 1359, 1219, 1038, 783, 695 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 8.01–7.41 (m, 10H), 7.04 (s, 1H), 2.45 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 193.72, 185.14, 160.79, 137.26, 134.88, 133.60, 132.98, 128.74, 128.63, 128.47, 115.88, 14.93; MS: *m/z* 282 ($M^+$); Anal. Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00; S, 11.36; Found: C, 72.25; H, 4.91; S, 11.27.

**Compound 23a**: White crystalline solid; mp: 132 °C; IR $\nu_{max}$ (KBr): 3056, 2968, 2947, 2912, 1717, 1623, 1430, 1332, 1261, 754 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.37–6.98 (m, 8H), 5.59 (s, 1H), 4.71 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.59 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 167.57, 164.07, 152.01, 145.65, 143.57, 142.79, 125.27, 125.19, 123.62, 122.16, 68.75, 59.35, 56.36, 52.33, 52.08, 50.61; MS: *m/z* 364 ($M^+$); Anal. Calcd for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53; Found: C, 72.35; H, 5.44.

**Compound 25a:** White crystalline solid; mp: 163 °C; IR $\nu_{max}$ (KBr $cm^{-1}$): 1715 (C=O stretch), 1231 (C-O stretch); $^1H$ NMR ($CDCl_3$): δ 7.41-7.03 (m, 8H), 5.62 (s, 1H), 5.44 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.13 (s, 3H); $^{13}C$ NMR ($CDCl_3$): δ 170.62, 166.89, 163.91, 150.95, 145.42, 143.82, 142.84, 125.60, 125.30, 123.91, 121.73, 60.92, 54.84, 52.46, 52.22, 50.71, 20.62; MS: *m/z* 392 ($M^+$); Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.13. Found: C, 70.12; H, 4.95.

**Compound 26:** Yellow solid, Yield: 59%; mp: 62-64 °C; IR $\nu_{max}$ (KBr): 3053, 2957, 2858, 1620, 1597, 1384, 722 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 8.31-7.37 (m, 9H), 4.68 (s, 2H), 3.19- 3.09 (m, 1H), 1.38-1.36 (d, 6H, *J*= 6.8 Hz); $^{13}C$ 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 $C_{18}H_{18}S$: C, 81.15; H, 6.81; S, 12.04; Found: C, 81.07; H, 6.76; S, 11.99.

**Compound 27:** Yellow solid, Yield: 74%; mp: 66-68 °C; IR $\nu_{max}$ (KBr): 3084, 2952, 2857, 1619, 1598, 1399, 723 $cm^{-1}$; $^1H$ 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); $^{13}C$ 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 $C_{20}H_{20}S$: C, 82.14; H, 6.89; S, 10.96; Found: C, 82.08; H, 6.81; S, 10.89.

**Compound 28:** Yellow solid, Yield: 61%; mp: 74-76 °C; IR $\nu_{max}$ (KBr): 3061, 2911, 1599, 1384, 735, 697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 8.36-7.32 (m, 14H), 4.60 (s, 2H), 3.89 (s, 2H); $^{13}C$ 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 $C_{22}H_{18}S$: C, 84.03; H, 5.77; S, 10.20; Found: C, 83.92; H, 5.73; S, 10.12.

**Compound 29:** Yellow solid, Yield: 52%; mp: 94-96 °C; IR $\nu_{max}$ (KBr): 3080, 3046, 2931, 2860, 1598, 1380, 779, 716 $cm^{-1}$; $^1H$ NMR: ($CDCl_3$): δ 8.35-7.32 (m, 16H), 4.65 (s, 2H), 4.33 (s, 2H); $^{13}C$ 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 $C_{26}H_{20}S$: C, 85.67; H, 5.53; S, 8.80; Found: C, 85.58; H, 5.46; S, 8.76.

**Compound 30a:** White crystalline solid; mp: 130°C; IR $\nu_{max}$ (KBr): 3024, 2998, 2957, 2915, 2858, 1712, 1697, 1592, 1380, 1328, 1297, 618 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.54-6.98 (m, 8H), 5.55 (s, 1H), 3.96 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.15-3.05 (m, 1H), 1.43-1.41 (d, 6H, *J*=6.4 Hz); $^{13}C$ NMR ($CDCl_3$): δ 167.43, 164.32, 145.67, 144.60, 143.99, 125.38, 125.05, 123.61, 122.49, 56.89, 52.34, 51.97, 51.05, 38.39, 29.99, 23.46; MS: *m/z* 408 ($M^+$); Anal. Calcd for $C_{24}H_{24}O_4S$: C, 70.56; H, 5.92; S, 7.85; Found: C, 70.43; H, 5.47; S, 7.74.

**Compound 30b:** Off-White crystalline solid; mp: 150°C; IR $\nu_{max}$ (KBr): 3061, 3035, 2952, 2911, 2863, 1660, 1600, 1592, 1453, 1396, 1318, 1256, 1240, 705, 612 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): δ 7.48-

6.94 (m, 18H), 5.39 (s, 1H), 3.93 (s, 2H), 2.55-2.49 (m, 1H), 1.12-0.86 (br, 6H); $^{13}$C NMR ($CDCl_3$): δ 194.44, 193.87, 151.39, 145.93, 138.24, 137.24, 132.89, 132.31, 129.02, 128.12, 127.73, 125.41, 125.20, 123.58, 60.61, 53.37, 38.94, 29.87; MS: *m/z* 500 ($M^+$), 105; Anal. Calcd for $C_{34}H_{28}O_2S$: C, 81.57; H, 5.64; S, 6.40; Found: C, 81.49; H, 5.52; S, 6.35.

**Compound 31a**: White crystalline solid; mp: 176°C; IR $\nu_{max}$ (KBr): 3066, 3009, 2946, 2869, 1712, 1623, 1598, 1431, 1328, 1276, 1209, 1074, 768, 618 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 7.54-6.98 (m, 8H), 5.55 (s, 1H), 3.96 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.31-3.26 (m, 1H), 2.16-1.72 (m, 8H); $^{13}$C NMR ($CDCl_3$): δ 167.46, 164.29, 145.66, 143.79, 125.36, 125.03, 123.60, 122.49, 56.98, 52.33, 52.02, 50.98, 47.14, 33.72, 30.82, 24.85; MS: *m/z* 434 ($M^+$); Anal. Calcd for $C_{26}H_{26}O_4S$: C, 71.86; H, 6.03; S, 7.38; Found: C, 71.76; H, 5.96; S, 7.32.

**Compound 31b:** Off-White crystalline solid; mp: 182°C; IR $\nu_{max}$ (KBr): 3061, 3035, 2946, 2905, 2869, 1660, 1608, 1588, 1448, 1396, 1261, 1110, 705, 685, 602 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 7.56-7.01 (m, 18H), 5.46 (s, 1H), 4.02 (s, 2H), 2.86-2.79 (m, 1H), 1.59-1.46 (m, 8H); $^{13}$C NMR ($CDCl_3$): δ 194.47, 193.87, 151.35, 145.92, 138.25, 137.25, 132.87, 132.28, 129.03, 128.11, 127.71, 125.39, 125.18, 123.57, 60.56, 53.36, 47.45, 30.55, 24.58; MS: *m/z* 526 ($M^+$), 105; Anal. Calcd for $C_{36}H_{30}O_2S$: C, 82.10; H, 5.74; S, 6.09; Found: C, 81.99; H, 5.69; S, 6.02.

**Compound 32a:** White crystalline solid; mp: 162°C; IR $\nu_{max}$ (KBr): 3058, 3023, 2938, 2839, 1717, 1619, 1598, 1447, 1425, 1332, 1280, 1210, 774, 705 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 7.49-6.98 (m, 13H), 5.54 (s, 1H), 3.94 (s, 2H), 3.86 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H); $^{13}$C NMR ($CDCl_3$): δ 167.42, 164.27, 145.53, 144.04, 137.99, 129.01, 128.69, 127.29, 125.39, 125.02, 123.64, 122.43, 56.75, 52.38, 52.17, 50.96, 39.38, 30.98; MS: *m/z* 456 ($M^+$); Anal. Calcd for $C_{28}H_{24}O_4S$: C, 73.66; H, 5.30; S, 7.02; Found: C, 73.58; H, 5.23; S, 6.94.

**Compound 32b:** Off-White crystalline solid; mp: 170°C; IR $\nu_{max}$ (KBr): 3066, 3029, 2983, 2920, 2837, 1640, 1592, 1572, 1448, 1318, 1276, 1069, 690, 596 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 7.39-6.89 (m, 23H), 5.39 (s, 1H), 3.93 (s, 2H), 3.46 (s, 2H); $^{13}$C NMR ($CDCl_3$): δ 194.53, 194.03, 151.92, 145.82, 138.39, 137.53, 137.29, 132.94, 132.46, 128.98, 128.39, 128.17, 127.91, 126.98, 125.46, 125.23, 123.61, 60.49, 53.44, 39.33, 30.64; MS: *m/z* 548 ($M^+$), 105; Anal. Calcd for $C_{38}H_{28}O_2S$: C, 83.18; H, 5.14; S, 5.84; Found: C, 83.09; H, 5.08; S, 5.78.

**Compound 33a:** White crystalline solid; mp: 164°C; IR $\nu_{max}$ (KBr): 3061, 3035, 2946, 2843, 1727, 1707, 1618, 1598, 1457, 1427, 1333, 1281, 1213, 779, 705 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 8.31-6.89 (m, 15H), 5.52 (s, 1H), 4.39 (s, 2H), 3.89 (s, 2H), 3.74 (s, 3H), 3.69 (s, 3H); $^{13}$C NMR ($CDCl_3$): δ 162.15, 159.02, 140.24, 138.83, 128.95, 128.10, 126.32, 123.62, 123.19, 122.15, 120.99, 120.73, 120.09, 119.96, 119.73, 118.91, 118.31, 117.24, 51.40, 47.10, 46.90, 45.71, 31.67, 25.91; MS: *m/z* 506 ($M^+$); Anal. Calcd for $C_{32}H_{26}O_4S$: C, 75.87; H, 5.17; S, 6.33; Found: C, 75.79; H, 5.10; S, 6.27.

**Compound 33b:** Off-White crystalline solid; mp: 166°C; IR $\nu_{max}$ (KBr): 3061, 2972, 2926, 2858, 1644, 1590, 1540, 1448, 1396, 1266, 779, 690 cm$^{-1}$; $^1$H NMR ($CDCl_3$): δ 7.83-7.05 (m, 25H), 5.46 (s, 1H), 4.08 (s, 2H), 3.99 (s, 2H); $^{13}$C NMR ($CDCl_3$): δ 194.55, 194.21, 152.21, 145.78, 138.51, 137.29, 133.90, 133.35, 132.95, 132.50, 131.50, 128.95, 128.18, 128.09, 127.96, 127.44, 125.98, 125.68, 125.44, 125.23, 123.94, 123.59, 60.32, 53.50, 53.40, 37.02, 30.98; MS: *m/z* 598 ($M^+$), 105; Anal. Calcd for $C_{42}H_{30}O_2S$: C, 84.25; H, 5.05; S, 5.36; Found: C, 84.18; H, 4.97; S, 5.29.

## RESULTS AND DISCUSSION

Anthracenemethyl sulfides are conveniently synthesized via a one-pot reaction of (anthracen-9-yl)methyl alcohol, thiourea and the corresponding alkyl halide and also by base promoted one-pot reductive coupling of tosylhydrazones with thiols.[22,23] We selected (anthracen-9-yl)methyl methyl sulfide (**1**) to demonstrate solvent and concentration dependency in their reactions with electron-deficient acetylenes such as DMAD (**2**) and DBA (**3**) (Chart 1).

Reaction between (anthracen-9-yl)methyl methyl sulfide (**1**) and acetylenes **2** and **3** was examined in different solvents. As expected, product distribution changed under different conditions. However, a few products arising through (*i*) single electron transfer mediated transformations such as 9-methylanthracene[24] (**4**), 1,2-bis(9-anthracenyl)ethane[25–28] (**5**), lepidopterene[25,29–33] (**6**) 9-anthraldehyde[34] (**7**) and dimethyl 1-oxo-1*H*-benzo[*de*]anthracene-2,3-dicarboxylate (**8**), (*ii*) reaction with adventitious oxygen[35] such as 9,10-anthraquinone (**9**) and (*iii*) Diels–Alder reaction (**10a** or **10b**) were common in all reactions (Chart 2). In most cases, DBA underwent cyclotrimerization to yield hexabenzoylbenzene (**11**) and 1,2,4,5-tetrabenzoylbenzene (**12**).[36]a DMAD underwent oligomerization, and in a few cases the corresponding hexamer **13** could be isolated in very low yields[36]b,c (Chart 3).

## EFFECT OF SOLVENT ON THE REACTION OF (ANTHRACEN-9-YL)METHYL METHYL SULFIDE WITH SUITABLE ELECTRON-DEFICIENT ACETYLENES

### Reactions in nonpolar medium: xylene

A 0.42 M solution of (anthracen-9-yl)methyl methyl sulfide (**1**) was refluxed with 2 equivalents of DMAD (**2**) in xylene. Diels–Alder adduct[20,37] **10a** was obtained in major amounts along with a variety of products including 9-methylanthracene (**4**), 1,2-bis(9-anthracenyl)ethane (**5**), lepidopterene (**6**) 9-anthraldehyde (**7**), dimethyl 1-oxo-1*H*-benzo[*de*]anthracene-2,3-dicarboxylate (**8**) and 9,10-anthraquinone (**9**) in minor amounts. The reaction was accompanied by high degree of DMAD oligomerization to give highly polar, intractable residue. However, hexamer **13** could be isolated in trace amounts. Similar results were obtained when the reaction was repeated with **3** as the electron-deficient acetylene. But product analogous to **8** was not formed when DBA (**3**)

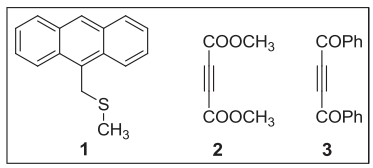



**Chart 1**. Selected (anthracen-9-yl)methyl methyl sulfide and electron-deficient acetylenes

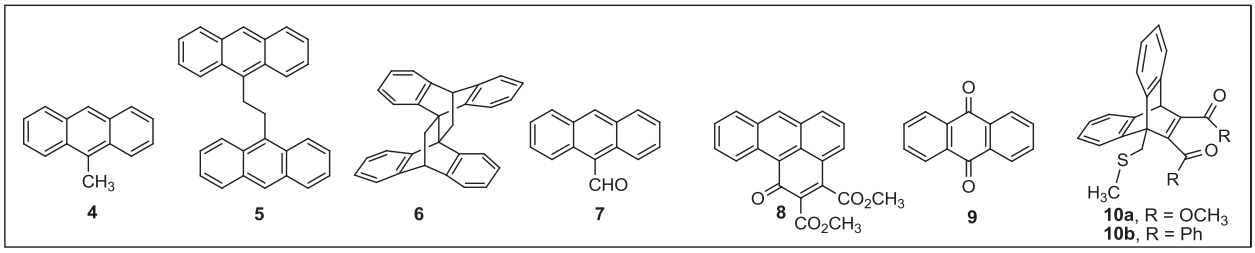



**Chart 2**. Common products formed in the reaction between **1** and electron-deficient acetylenes

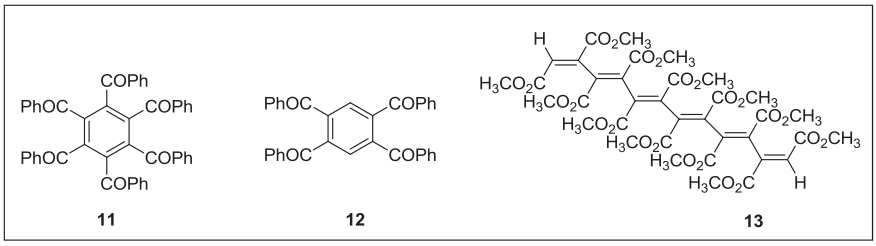
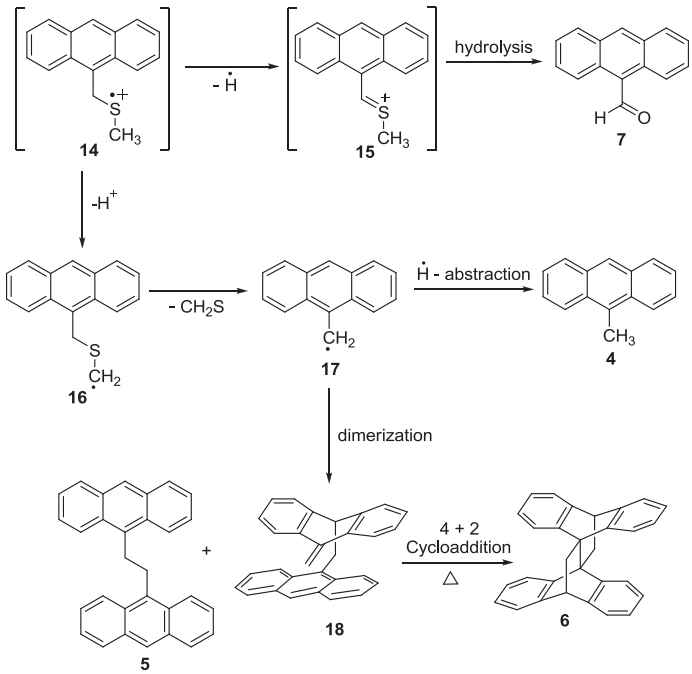



**Chart 3**. Oligomerization products of electron-deficient acetylenes

was used as the electron-deficient acetylene. In this case, cyclotrimerization products such as **11** and **12** were isolated in trace amounts. We repeated the reaction of (anthracen-9-yl) methyl methyl sulfide (**1**) with electron-deficient acetylenes **2** and **3** at 0.042 M substrate concentration in xylene. In contrast to dramatic concentration dependence observed in the reaction between anthracenemethanamines and acetylenes,[7] anthracenemethyl sulfide-acetylene reactions were unaffected by change in concentration with Diels–Alder pathway predominating at both lower and higher concentrations examined by us. However, at lower concentration, reaction took much longer times to reach completion. Because of solubility constraints, we could not examine reactions at concentrations exceeding 0.42 M. Details of yield of different products and time taken for the reaction are depicted in Table 1.

Similarities and subtle differences exist in the reaction of electron-deficient acetylenes with anthracenemethanamines[7] and anthracenemethyl sulfides. Though similar products are generated in both the cases, mass balance is much better, and reactions are cleaner in the case of sulfides. Irrespective of substrate concentration, Diels–Alder reaction predominates in the case of sulfides. Products such as lepidopterene, 1,2-bis(9-anthracenyl)ethane and 9-methylanthracene are formed in negligible amounts, and their presence was ascertained by GC-MS and/or LC-MS analysis. As with amines, anthraquinone (**9**) is probably generated through the involvement of adventitious oxygen.[38–40] Mechanism for the generation of products **4–7** from **1** is briefly indicated in Scheme 2. Products such as 9-methylanthracene (**4**), 1,2-bis(9-anthracenyl)ethane (**5**), lepidopterene (**6**) and 9-anthraldehyde (**7**) were formed from a common intermediate: sulfide radical cation[41] **14** generated through single electron transfer to the electron-deficient acetylene **2** or **3** (*path* ***a***, Scheme 1). Degradation of **14** initiated by either hydrogen atom or proton loss may be understood in terms of pathways indicated in Scheme 2. Hydrogen atom loss from the methylene carbon leads to (anthracen-9-yl)(methylene)sulfonium ion precursor (**15**) of 9-anthraldehyde (**7**). On the other hand, proton loss from the methyl group followed by carbon–sulfur bond cleavage with loss of elements of thioformaldehyde leads to 9-anthracenemethyl radical (**17**). Homolytic cleavage of C—S bond in sulfides and aldehyde formation from organic sulfides has literature precedence.[42–45] Hydrogen radical abstraction by **17** leads to the formation of 9-methylanthracene (**4**). Isomers **5** and **6** are formed by the dimerization of 9-anthracenemethyl radical[25,31,46] which in turn is a clear indicator to involvement of radical pathway in the reaction (Scheme 2). DMAD radical anion formed via single electron transfer mediated pathway undergoes oligomerization to form the DMAD hexamer **13** along with other unidentified oligomeric materials. Similarly, DBA (**3**) underwent cyclotrimerization to give **11** and **12** in minor amounts.




**Scheme 2**. Mechanism of the formation of single electron transfer mediated products of **1** with **2**/**3**

### Reactions in polar aprotic medium: dimethylformamide

We explored the outcome of the reaction in a non-nucleophilic polar aprotic solvent such as dimethylformamide

(DMF). A 0.42 M solution of (anthracen-9-yl)methyl methyl sulfide (**1**) in DMF was refluxed with acetylenes **2** and **3**. Products obtained were identical to those in the reactions in nonpolar medium. Depending on the acetylene employed, Diels–Alder adduct **10a** or **10b** was the major product. Electron transfer mediated products and oxidation product were also formed in low yields. Yield of different products obtained and the time taken for the reaction are depicted in the Table 2. As with the reactions in xylene, even at a substrate concentration of 0.042 M, product ratio remained unchanged.

### Reactions in polar protic media: a) alcohols

As stated earlier, we reasoned that reactions involving polar transition states (*path* ***b***) should be more competitive in polar protic solvents. With a view to test this hypothesis, we examined the reactions of **1** with acetylenes **2** and **3** in polar protic solvents. We selected methanol (highly polar, but low boiling) and acetic acid (intermediate polarity and boiling point) for this investigation. Compound **1** exhibited only limited solubility in methanol. Hence reactions in methanol were carried out at a lower concentration. When a 0.11 M solution of (anthracen-9-yl)methyl methyl sulfide (**1**) was refluxed with 2 equivalents of DMAD (**2**) in methanol, we observed the formation of 9-(methoxymethyl)anthracene[47–50] (**22**) and dimethyl (2-methylthio)maleate/fumarate[51–53] (**21a**) in good yields along with products **4–6**, **8**, **9** (Chart 2) and Diels–Alder adduct **10a** in minor amounts. Diels–Alder adduct of 9-(methoxymethyl)anthracene[47,54] **23a** was also obtained in low yields (Table 3, Scheme 3).

To study the effect of acetylenes in methanol reaction, we repeated the reaction of **1** with **3**. A 0.11 M solution of **1** was refluxed with 2 equivalents of **3** in methanol; Diels–Alder adduct **10b** was obtained in major amount. Single electron transfer mediated products **4–6** and oxidation product **9** were obtained in negligible amounts (Chart 2). Yield of different products obtained is collected in Table 3.

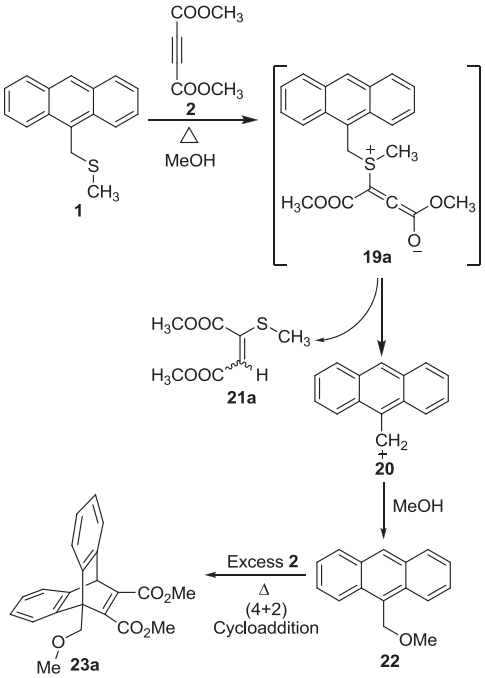
We propose that nucleophilic attack of (anthracen-9-yl)methyl methyl sulfide (**1**) on DMAD in a Michael type addition pathway generates Michael adduct/zwitterion[53,55,56] **19a** (Scheme 3). This leads to the weakening and eventual cleavage of C—S bond giving rise to 9-anthracenemethyl cation[30] (**20**) and **21a**. Cation **20** is captured by the solvent to give 9-(methoxymethyl)anthracene (**22**).

Minor products are formed through single electron transfer pathways and oxidation reaction of (anthracen-9-yl)methyl methyl sulfide (**1**) (Chart 2). In reactions done in alcohol solvents, when DMAD (**2**) is taken as the electron-deficient acetylene, we observed competition between one electron transfer (*path* ***a***), two electron transfer (*path* ***b***) and Diels–Alder reactions (*path* ***c***). From experimental results, we conclude that Michael type addition (*path* ***b***) is the major pathway. But when DBA (**3**) was used as the reactive acetylene, nucleophilic addition was not observed. In this case, Diels–Alder reaction (*path* ***c***) was the major pathway.

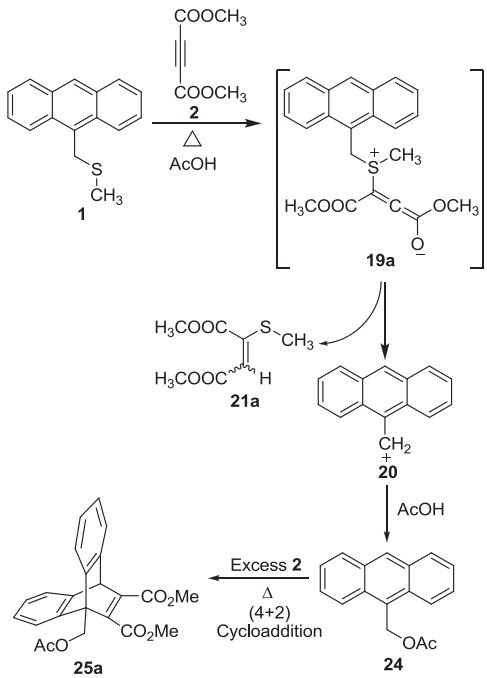
### Reactions in polar protic media: b) acids

We refluxed a 0.42 M solution of **1** with 2 equivalents of DMAD (**2**) in glacial acetic acid. After the completion of reaction, (anthracen-9-yl)methyl acetate[57–60] (**24**) and dimethyl (2-methylthio)maleate/fumarate **21a** were obtained in major yields along with single electron transfer mediated products **4–7**, oxidation product **9**, Diels–Alder adduct **10a** and Diels–Alder adduct of (anthracen-9-yl)methyl acetate[7,61] **25a** in minor yields (Scheme 4).

In continuation, we examined the reaction of **1** with **3** in glacial acetic acid. When a 0.42 M solution of **1** was refluxed with **3**, Diels–Alder adduct **10b** was obtained in major yields along




**Scheme 3**. Mechanism of the reaction of **1** with **2** in polar protic media, methanol




**Scheme 4**. Mechanism of the reaction of **1** with **2** in polar protic media, acetic acid

**Table 4.** Yield (%) of products obtained in the reaction of **1** with **2** and **3** in acetic acid (0.42 M)

| Electron-deficient acetylene | Reaction time | **4** | **5** | **6** | **7** | **9** | **10a/10b** | **11** | **12** | **21a/21b** | **24** | **25a** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2** | 3 h | <1% | <1% | <1% | 6% | <1% | <1% | — | — | 18% | 63% | <1% |
| **3** | 13 h | <1% | <1% | 6% | 19% | <1% | 42% | 2% | <1% | 10% | 14% | — |

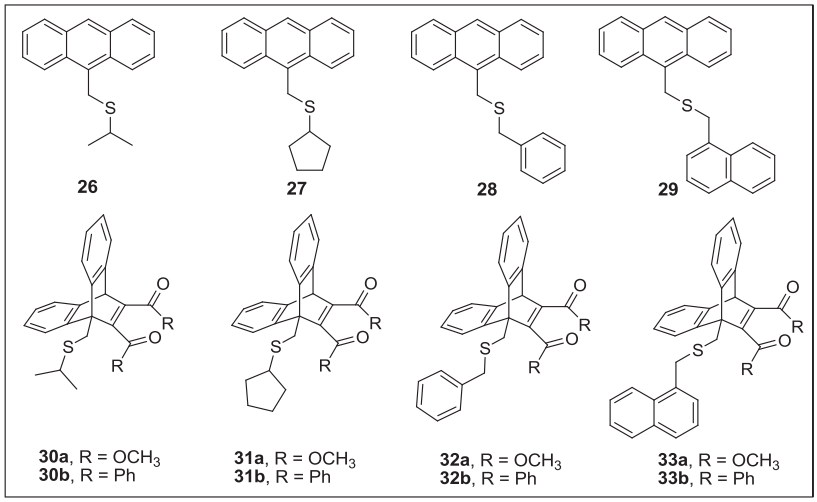



**Chart 4**. Different (anthracen-9-yl)methyl sulfides and the corresponding Diels–Alder adducts obtained in the reaction of sulfides with reactive acetylenes **2** and **3**

with (anthracen-9-yl)methyl acetate (**24**) and (2-methylthio)1,2-dibenzoylethylene[62–65] (**21b**) in moderate yields. Products **4–7** and **9**, hexabenzoylbenzene[66] (**11**) and tetrabenzoylbenzene[67,68] (**12**) were obtained in minor yields. Diels–Alder reaction (*path* **c**) was the major pathway in the reaction of **1** with **3**. Generation of solvolysis product **24** suggests mechanism similar to that observed in methanol.

For reactions carried out in acetic acid, percentage yield of different products obtained and the reaction time is depicted in the Table 4. No change in product distribution was observed when the reaction was repeated at 0.042 M substrate concentration.

In order to verify the generality of the sulfide-activated acetylene reaction observed by us, we repeated the experiments with other anthracenemethyl sulfides such as (anthracen-9-yl)methyl isopropyl sulfide (**26**), (anthracen-9-yl)methyl cyclopentyl sulfide (**27**), (anthracen-9-yl)methyl benzyl sulfide (**28**) and (anthracen-9-yl)methyl naphthylmethyl sulfide (**29**) (Chart 4) with DMAD (**2**) and DBA (**3**) in xylene (0.42 M sulfide concentration). Products such as **4–8** along with the corresponding Diels–Alder adducts **30a/b**, **31a/b**, **32a/b** and **33a/b** (Chart 4) and oligomerization products **11**, **12** (or **13**) were formed in yields comparable to those reported for **1**.

**Table 5.** Major reaction pathway followed by (anthracen-9-yl)methyl sulfides with reactive acetylenes **2** and **3**

| Solvent | Acetylene | Major reaction pathway (Scheme 1) |
|---|---|---|
| Xylene | **2** | *Path* ***c*** |
| | **3** | *Path* ***c*** |
| DMF | **2** | *Path* ***c*** |
| | **3** | *Path* ***c*** |
| Methanol | **2** | *Path* ***b*** |
| | **3** | *Path* ***c*** |
| Acetic acid | **2** | *Path* ***b*** |
| | **3** | *Path* ***c*** |

## CONCLUSION

We have illustrated interesting solvent-dependent reactions of (anthracen-9-yl) methyl sulfides with electron-deficient acetylenes and explored the mechanistic pathways of these reactions under different conditions. As with anthracenemethanamines, products arising through single electron transfer, nucleophilic addition and cycloaddition pathways could be isolated. However, unlike anthracenemethanamines, substrate concentration is not a major factor in controlling selectivity for anthracenemethyl sulfides. Single electron transfer reaction (*path* ***a***) was not favoured under any of the conditions examined by us. Major reaction pathway observed with anthracenemethyl sulfides are controlled by the nature of solvent and substituents on acetylene (Table 5).

## Acknowledgements

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