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Reaction of a β-Oxo-α-chlorosulfenyl Chloride with Nucleophiles. Formation and Reactions of Thione *S*-Dimethoxides and *S*-Imides

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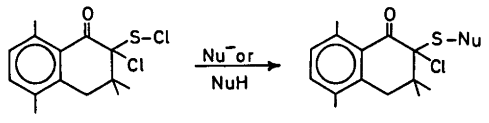
Dedicated to Professor K. A. Jensen on his 70th birthday

The α-chloro-β-oxosulfenyl chloride *1* reacts with methoxide, acetate, cyanide, aniline, trimethylaniline, and dimethylamine, to give the *S*-substituted compounds *2a–f*, respectively. Excess methoxide gives the *S*-dimethoxythione *5*, which rearranges in acids to the *S,C*-dimethoxy compound *6a*. Reaction of *1* with excess *tert*-butylamine gives the thione-*S*-imide *3*, which reacts with methanol or with acetic acid to give the α-methoxy- and the α-acetoxysulfenamides *4a* and *4b*, respectively. Reaction of *1* with dipivaloylmethane anion gives *7*, a dimer of the thioketone formed by reductive elimination of chlorine from *1*.

The reactions of α-chlorosulfenyl chlorides with nucleophiles have lately been studied in several laboratories and shown to involve substitution at sulfur.[1–3] These studies have here been extended to include the now readily available β-oxo-α-chlorosulfenyl chloride *1*.[4]



1 *2*

a Nu = OCH_3 *d* NuH = $C_6H_5NH_2$

b Nu = $OCOCH_3$ *e* NuH =

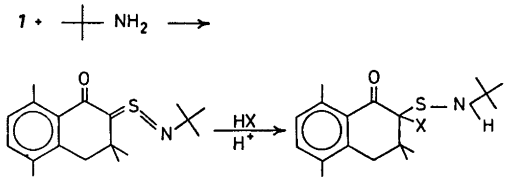
c Nu = CN *f* NuH = $(CH_3)_2NH$

Compound *1* gave the monosubstituted compounds *2a–f* when treated with molar amounts of the anions (*2a–c*) or with two equivalents of the amines (2d–f). Under these conditions no disubstitution was observed. The stability of the anilides was unexpected, partly on account of observations on similar compounds,[1] partly because of the reported ability of the amides from primary amines to eliminate HCl and give the colored thione *S*-imides.[1] The transient deep red color[5] observed when the anilides came in contact with, *e.g.*, aqueous sodium hydroxide might be due to this reaction. The trimethylanilide *2e* was prepared in a vain attempt to characterize the corresponding sterically hindered but apparently labile thione imide.

In contrast, the *tert*-butyl substituted thione imide *3* was stable.[1] The structure may be formulated as a carbonyl stabilized ylide:

$$\overline{O}-C=C-\overset{+}{S}=N- \longleftrightarrow O=C-C=S=N-$$

but the reactions of the imide with methanol (acid catalyzed) and with acetic acid to give the α-methoxy- and α-acetoxysulfenylamides *4a* and *4b*, respectively, bear witness to the thion character of *3*. Crystallographic data on *3* show the O–C–C–S–N system to be planar and form a CSN angle of 110° with the nitrogen *trans* to oxygen. The C–S and S–N bond

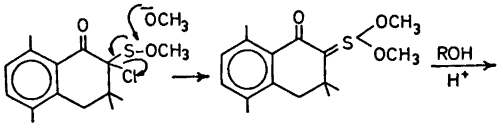


3 *a* X = OCH_3 *4*

b X = $OCOCH_3$

lengths are 1.65 and 1.56 Å, respectively. Details will be published elsewhere.[6]

The reaction of the α-chlorosulfenyl chloride *1* (or the sulfenic ester *2a*) with methanolic sodium methoxide in excess did not result in direct substitution of chlorine at the carbon atom. Rather, the methoxide attacked the dicoordinate sulfur in a conjugate, S_N2'-like manner to give the tricoordinate "sulfine ketal" *5*. As in the case of the thione imide *3*, the thione dimethoxide *5* may be formulated as an α-oxo ylide. Compounds exhibiting the structural feature of an *S*-dialkoxylated thione as in *5* have been described, but apparently in all cases the sulfur and the two oxygens form part of fused and aromatically resonance stabilized ring systems.[7–10] Compound *5* lacks this stabilizing effect, and slight decomposition takes place even at −19 °C *in vacuo*.



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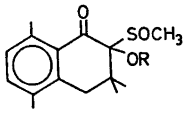


6a R = CH_3
6b R = CD_3

A solution of the *S,S*-dimethoxide in carbon tetrachloride rearranges to the *S,C*-dimethoxide *6a* in the presence of *p*-toluenesulfonic acid. If methanol-d_4 is present during the rearrangement $^2H_3$-methoxy is incorporated to give substantial amounts of *6b*. This suggests a monomethoxysulfonium intermediate:

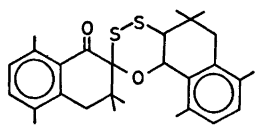
$$>C=\overset{+}{S}-OCH_3 + CD_3OD \rightarrow CD_3O-C-S-OCH_3 + D^+$$

again reflecting the thione character of the C–S bond as in the imide *3*.

Attempts to prepare ylides of the type >C=S=C<, in analogy with the preparation of thione imide *3* described above, by reacting sulfenyl chloride *1* with carbon nucleophiles such as the anion of dipivaloylmethane failed.[11] The attack apparently took place at the *S*-chlorine of *1* to give an α-oxothioketone, which subsequently dimerized to *7*:

$$Cl-C-S-Cl + \equiv\overline{C} \rightarrow \overline{Cl} + \equiv CCl + >C=S \rightarrow 7$$

A similar dimerization has been published.[12] A more recent and detailed work on dimerization of heterocyclic α-oxothioketones including theoretical considerations shows another (4+2)-cycloaddition type of this species. Under extrusion of sulfur 1,3-oxathiols are formed.[13]



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The structures proposed for the isolated compounds are in accordance with the ^{13}C NMR, ^1H NMR, and mass spectral data given in Experimental. However, spectral evidence as to which of the two chlorine atoms has been substituted is not conclusive. Thus, the loss of HSCl in the MS of the anilides *2e* and *2f* might even suggest substitution of Cl at C2 and not at S. This is not reasonable, however, considering the high reactivity of sulfenyl chlorides. The mass spectral decomposition pattern of the anilides may be rationalized by assuming loss of HCl to give the thione imide (*m/e* 323 in *2d*) and subsequent loss of S. The latter reaction must involve a rearrangement, and evidence is furnished from the MS of the *N-tert*-butyl thione imide *3* which exhibits loss of SH. A thiaziridine intermediate may explain the latter reaction.[1,2,14]

EXPERIMENTAL

Mass spectra were recorded on a Perkin-Elmer 270 instrument; IP 70 eV. ^1H NMR were recorded on a Varian 360 instrument at 60 MHz, and ^{13}C NMR on a Bruker WH-90 at 22.63 MHz with broad band noise ^1H-decoupling. Long relaxation times are indicated by a superscript a and the concentrations were *ca.* 20 % in deuteriochloroform.

2-Chloro-3,4-dihydro-2-methoxysulfenyl-3,3,5,-8-tetramethyl-1-(2H)-naphthalenone 2a. The sulfenyl chloride (*1*)[4] (606 mg) was suspended in ether (6 ml) and sodium methoxide in methanol (2 mmol in 2 ml) was added with stirring. After 2 min at 22 °C the reaction mixture was poured

onto ice, the aqueous phase extracted with ether, dried (K_2CO_3) and concentrated *in vacuo* to give colorless crystals. Yield 573 mg, 96 %, m.p. 58 – 61 °C. Recrystallization from hexane gave m.p. 64 – 65 °C. Anal. $C_{15}H_{19}ClO_2S$: C, H, Cl, S. MS [*m/e* (% rel. int.)]: 298 (33, M), 262 (16, M – HCl), 235 (44, M – $SOCH_3$), 231 (42, M – HCl – OCH_3), 199 (54), 177 (67), 146 (100). ^{1}H NMR: δ 1.18 and 1.35 (aliphatic methyl), 2.25 and 2.61 (aromatic methyl), 2.92 (broadened s, CH_2), 3.68 (methoxy), 7.04 and 7.18 (aromatic proton, *J* 8.0 Hz). ^{13}C NMR: δ 188.5[a] (C1), 98,2 (C2), 42.6[a] (C3), 41.6 (C4), 24.8 and 26.5 (aliphatic methyl), 19.4 and 22.9 (aromatic methyl), 129.0[a], 130.8, 133.9[a], 134.5, 138.9[a], 140.0[a] (aromatic carbon), 68.0 (methoxy).

2-Acetoxysulfenyl-2-chloro-3,4-dihydro-3,3,5,8-tetramethyl-1(2H)-naphthalenone 2b. The sulfenyl chloride (*1*, 303 mg) in chloroform (1 ml) and sodium acetate (1.15 mmol in 4 ml of methanol) was stirred for 2 min. Addition of CCl_4 and work-up as above gave the acetate *2b*. Yield 240 mg (73 %), m.p. 67 – 71 °C. Recrystallization from a mixture of hexane (1 ml) and toluene (0.2 ml) gave colorless crystals, m.p. 72 – 74 °C. Anal. $C_{16}H_{19}ClO_3S$: C, H, Cl, S. MS [*m/e* (% rel. int.)]: 326 (0.4, M), 286 (13), 284 (35, [M – $H_2C=C=O$]), 238 (30), 236 (92), 221 (100), 146 (38).

^{1}H NMR: δ 1.23, 1.45 (aliphatic methyl), 2.03 (acetoxy), 2.23, 2.56 (aromatic methyl), 2.93 (methylene), 7.08, 7.25 (2H, *J* 7.8 Hz). ^{13}C NMR: δ 188.4[a] (C1), 94.7[a] (C2), 42.7[a] (C3), 41.4 (C4), 25.0, 26.3 (aliphatic methyl), 19.4, 22.7 (aromatic methyl), 20.1, 168.9[a] (acetate), 128.4[a], 130.4, 133.9[a], 137.7, 138.8[a], 140.3[a] (aromatic).

2-Chloro-3,4-dihydro-3,3,5,8-tetramethyl-2-thiocyanato-1-(2H)-naphthalenone 2c. To a solution of the sulfenyl chloride (*1*, 606 mg) in chloroform (2 ml, 23 °C) was rapidly added first ethanol (8 ml) and then a solution of KCN (240 mg) in ethanol (2 ml) and water (2 ml). The mixture was stirred for 1 min, CCl_4 (10 ml) was added. Work-up as above and crystallization from hexane (5 ml) gave colorless crystals. Yield 434 mg (74 %), m.p. 82 – 84 °C. Anal. $C_{15}H_{16}ClNOS$: C, H, Cl, N, S. MS [*m/e* (% rel. int.)]: 293 (2, M), 235 (96, M – NCS), 199 (21), 146 (100). ^{1}H NMR: δ 1.30, 1.45 (aliphatic methyl), 2.25, 2.55 (aromatic methyl), 2.75, 3.07 (methylene, *J* 18.8 Hz), 7.05, 7.24 (2H, *J* 8 Hz). ^{13}C NMR: δ 187.6[a] (C1), 90.0[a] (C2), 44.0[a] (C3), 40.8 (C4), 24.4, 25.1 (aliphatic methyl), 19.3, 22.3 (aromatic methyl), 126.5[a], 130.6, 134.3[a], 135.6, 138.4[a], 140.7[a] (aromatic), 109.7[a] (thiocyanato).

Sulfenamides (2d, e, *and* f). A solution of the sulfenyl chloride (*1*, 2 mmol) and the amine (4.4 mmol) in ethanol (10 ml) was stirred for 3 min. CCl_4 and ice was added. Work-up as above gave the amides.

Anilide 2d, yield 611 mg (85 %), m.p. 115 – 116 °C. Recrystallization from hexane (5 ml) and toluene (1 ml), m.p. 115 – 116 °C. Anal. $C_{20}H_{22}ClNOS$: C, H, Cl, N, S. MS [*m/e* (% rel. int.)]: 359 (18, M), 323 (5, M – HCl), 291 (100, M – S – HCl). 248 (43). ^{1}H NMR: δ 1.10, 1.47 (aliphatic methyl), 2.06, 2.23 (aromatic methyl), 2.84, 3.16 (methylene, *J* 18 Hz), 4.90 (NH), 6.60 – 7.35 (7 H, m). ^{13}C NMR: δ 188.0[a] (C1), 97.3[a] (C2), 41.8[a] (C3), 40.9 (C4), 24.9, 26.1 (aliphatic methyl), 19.5, 22.8 (aromatic methyl), 115.1, 120.5, 128.7, 130.3, 133.6[a], 134.3, 138.4[a], 140.9[a], 145.8[a] (aromatic).

Trimethylanilide 2e, yield 245 mg from hexane (6 ml) (61 %), m.p. 135 – 137 °C. Recrystallization and treatment with carbon gave m.p. 138 – 140 °C. Anal. $C_{23}H_{28}ClNOS$: C, H, Cl, N. S. MS [*m/e* (% rel. int.)]: 401 (3, M), 365 (3, M – HCl), 333 (59, M – HCl – S), 290 (55), 146 (100). ^{1}H NMR: δ 1.04, 1.42 (aliphatic methyl), 1.70, 2.15, 2.20 (aromatic methyl), 2.06 (aromatic methyl, *ortho* to NH), 2.75, 3.04 (methylene, *J* 17 Hz), 4.73 (NH), 6.60 (mesityl), 6.87, 7.20 (2H, *J* 8 Hz). ^{13}C NMR: δ 188.6[a] (C1), 97.1[a] (C2), 41.6[a] (C3), 41.0 (C4), 24.7, 25.9 (aliphatic methyl), 19.3, 21.7, 20.4 (aromatic methyl), 18.9 (aromatic methyl, *ortho* to NH), 128.3[a], 129.3, 129.6, 129.9, 132.1[a], 133.0[a], 133.8, 138.0[a], 138.8[a], 140.7[a] (aromatic).

Dimethylamide 2f was prepared as above from aqueous dimethylamine (1 ml 40 %). The reaction time was *ca.* 30 s. Yield 507 mg (81 %), m.p. 105 – 107 °C. Recrystallization from light petroleum (4 ml) gave m.p. 106 – 107 °C. Anal. $C_{16}H_{22}ClNOS$: C, H, Cl, N. S. MS [*m/e* (% rel. int.)]: 311 (37, M), 276 (1, M – Cl), 268 (2), 235 [52, M – $SN(CH_3)_2$],[1] 199 (100). ^{1}H NMR: δ 1.05, 1.39 (aliphatic methyl), 2.23, 2.60 (aromatic methyl), 2.66 (dimethylamino), 2.76, 3.04 (methylene, *J* 8 Hz), 7.03, 7.19 (aromatic, *J* 17.6 Hz). ^{13}C NMR: δ 189.9[a] (C1), 98.9[a] (C2), 41.9[a] (C3), 41.2 (C4), 24.5, 26.1 (aliphatic methyl), 19.5, 23.1 (aromatic methyl), 129.3[a], 130.3, 133.8[a], 134.0, 138.7[a], 139.5[a] (aromatic), 49.1 (dimethylamino).

No homogeneous compounds were isolated by reaction of *1* with 1-butylamine or with ammonia.[1]

3,4-Dihydro-3,3,5,8-tetramethyl-2-thioxo-1(2H)-naphthalenone, S-tert-butylimide 3. The sulfenyl chloride (*1*, 606 mg) dissolved in chloroform (2 ml) and ethanol (10 ml) was cooled to 5 °C and *tert*-butylamine (0.8 ml) was added rapidly with stirring. The reaction time was 1 min. Work-up as above and crystallization from light petroleum (12 ml) at – 15 °C gave orange-crystals of *3*. Yield 442 mg (73 %), m.p. 119 – 122 °C. Recrystallizations from hexane gave m.p. 121 – 123 °C (dec.). Anal. $C_{18}H_{25}NOS$: C, H, N, S. MS [*m/e* (% rel. int.)]: 303 (11, M), 270 (8, M – SH), 247 (10, M – C_4H_8), 231 (13), 230 (14), 201 (100), 199 (20). ^{1}H NMR: δ 1.40 (*tert*-butyl), 1.50 (aliphatic methyl), 2.28, 2.53 (aromatic methyl), 2.70 (methylene), 6.98, 7.14 (aromatic, *J* 8 Hz). ^{13}C NMR: δ 187.2[a] (C1), 152.4[a] (C2), 40.5[a] (C3), 41.3 (C4), 23.7 (aliphatic methyl), 19.2, 22.6 (aromatic methyl), 31.5, 62.5[a] (*tert*-butyl), 129.7, 131.4[a] 132.6[a], 133.1, 136.4[a], 139.0[a] (aromatic).

2-tert-Butylamidosulfenyl-3,4-dihydro-2-methoxy-3,3,5,8-tetramethyl-1(2H)-naphthalenone 4a. A solution of ylide *3* (303 mg) in chloroform (1 ml) was allowed to react with methanol (5 ml) and *p*-toluenesulfonic acid (1.5 mg) at 22 °C for 30 s. Addition of carbon tetrachloride and work-up as above gave colorless crystals. Yield 334 mg, m.p. 97–103 °C. Recrystallizations from hexane gave m.p. 102–104 °C. Anal. $C_{19}H_{29}NO_2S$: C, H, N, S. MS [*m/e* (% rel. int.)]: 335 (2, M), 231 (41, M–$SNHC_4H_9$), 199 (100). ^{1}H NMR: δ 0.72 (*tert*-butyl), 1.03, 1.16 (aliphatic methyl), 2.23, 2.56 (aromatic methyl), 2.62, 3.32 (methylene, *J* 17.4 Hz), 3.78 (methoxy), 6.95, 7.12 (aromatic, *J* 7.6 Hz). ^{13}C NMR: δ 196.9[a] (C1), 100.4[a] (C2), 41.6[a] (C3), 42.7 (C4), 23.8, 24.7 (aliphatic methyl), 19.4, 22.3 (aromatic methyl), 28.7, 54.3[a] (*tert*-butyl), 54.8 (methoxy), 129.6, 131.8[a], 133.1[a], 133.7, 138.2[a], 139.4[a] (aromatic).

The same product is obtained by the slow addition of *tert*-butylamine to the sulfenyl chloride (*1*) in methanol.

2-tert-Butylamidosulfenyl-3,4-dihydro-2-acetoxy-3,3,5,8-tetramethyl-1(2H)-naphthalenone (4b) was prepared from the ylide *3* (303 mg) dissolved in chloroform (1 ml) and carbon tetrachloride (4 ml) by addition of acetic acid (0.2 ml) and immediate work-up as above. Crystallization from hexane (2 ml) gave colorless crystals. Yield 281 mg (77 %), m.p. 88–91 °C. Recrystallizations from hexane gave m.p. 92–94 °C (dec.). Anal. $C_{20}H_{29}NO_3S$: C, H, N, S. MS [*m/e* (% rel. int.)]: 363 (4, M), 303 (1, M–HOAc), 259 (6, M–$SNHC_4H_9$), 217 (100). ^{1}H NMR: δ 0.58 (*tert*-butyl), 1.07, 1.23 (aliphatic methyl), 2.23, 2.52 (aromatic methyl), 2.23 (acetyl; if the acetate is dissolved in carbon tetrachloride, the resonance is shifted 0.04 ppm upfield from the high field aromatic methyl group at δ 2.22), 2.71, 3.41 (methylene, *J* 17.4 Hz), 3.35 (NH, exchangeable), 6.99, 7.15 (aromatic, *J* 8.0 Hz). ^{13}C NMR: δ 192.0[a] (C1), 101.2[a] (C2), 41.4[a] (C3), 42.1 (C4), 23.9, 24.5 (aliphatic methyl), 19.3, 22.1 (aromatic methyl), 28.6, 52.9[a] (*tert*-butyl), 21.8, 169.8[a] (acetyl), 129.5, 131.3[a], 133.2, 133.7[a], 138.5[a], 138.8[a] (aromatic).

3,4-Dihydro-3,3,5,8-tetramethyl-2-thioxo-1(2H)-naphthalenone, S-*dimethoxide*, 5. The sulfenyl chloride (*1*, 606 mg) was stirred with methanolic sodium methoxide (from 400 mg of sodium and 20 ml of methanol) at 23 °C for 2 min. Addition of ice and work-up as above gave colorless crystals, which were washed with hexane at 0 °C. Yield 422 mg (71 %), m.p. 65–67 °C, gas evolution and smell of formaldehyde. Recrystallization from hexane (0.5 ml) and CCl_4 (0.5 ml) gave m.p. 66–68 °C, not stable at room temperature in the atmosphere, but only slightly decomposed (m.p. 60–68 °C) when kept for 9 months at –19 °C *in vacuo*. Anal. $C_{16}H_{22}O_3S$: C, H, S. MS [*m/e* (% rel. int.)]: 294 (15 M), 279 (25, M–CH_3), 264 (25, M–CH_3O), 231 (83), 201 (100), 146 (55). ^{1}H NMR: δ 1.29 (2 aliphatic methyl groups), 2.24, 2.60 (aromatic methyl), 2.66 (methylene), 3.71 (2 methoxy), 6.95, 7.07 (aromatic, *J* 8 Hz). ^{13}C NMR [CCl_4, 10 % C_6D_6]: δ 187.6[a] (C1), 93.4[a] (C2), 36.8[a] (C3), 43.2 (C4), 28,7 (aliphatic methyl), 19.4, 22.2 (aromatic methyl), 129.4, 131.6, 131.6[a], 132.8[a], 136.1[a], 138.1[a] (aromatic), 54.9 (methoxy, *J* 147 Hz).

2-Methoxy-2-methoxysulfenyl-3,3,5,8-tetramethyl-3,4-dihydro-1(2H)-naphthalenone 6a. A solution of the *S*-dimethoxy compound *5* (67 mg) in CCl_4 (0.4 ml) and methanol (0.1 ml) was mixed with *p*-toluenesulfonic acid (0.03 ml of a 0.1 M solution in $HCCl_3$). Addition of ice and work-up as above gave a yellow oil. Anal. $C_{16}H_{22}O_3S$: C, H, S. MS [*m/e* (% rel. int.)]: 294 (0.4, M), 264 (0.5, M–CH_2O), 231 (57, M–$SOCH_3$), 199 (100). ^{1}H NMR: δ 1.14, 1.20 (aliphatic methyl), 2.28, 2.53 (aromatic methyl), 2.28 (methylene), 3.36, 3.66 (methoxy), 7.05, 7.17 (aromatic, *J* 7.6 Hz). ^{13}C NMR [CCl_4, *ca.* 10 % C_6D_6]: δ 198.8[a] (C1), 102.7[a] (C2), 42.2[a] (C3), 42.0 (C4), 24.0, 24.8 (aliphatic methyl), 19.22, 22.0 (aromatic methyl), 129.5, 130.1[a], 133.5[a], 133.7, 140.0[a] (aromatic), 54.3 (*C*-methoxy), 65.4 (*S*-methoxy).

The corresponding 2-trideuteriomethoxy compound *6b* was prepared by using CD_3OD instead of methanol in the above experiment. MS [*m/e* (%rel. int.)]: 297 (0.6, M), 265 (5, M–CD_3O), 234 (48, M–$SOCH_3$), 199 (100). ^{1}H NMR: as for *6a*; the resonance at δ 3.66 was *ca.* 10 % of that of *6a*. Also ^{13}C NMR showed the same resonance for the two compounds. The peak at δ 54.4 of *6b* had only *ca.* 20 % of the intensity of that of *6a* and was broadened.

Dimer of 3,3,5,8-tetramethyl-2-thiono-1-(2H)-naphthalenone 7. A solution of dipivaloylmethane (180 mg) and sodium ethoxide (23 mg of sodium) in ethanol (3 ml) was added to the α-chlorosulfenyl chloride (*1*, 303 mg) in chloroform (1 ml) at room temperature. Sodium ethoxide (1 ml 1 M) was added dropwise. Work-up as above gave yellow crystals. Yield 183 mg (79 %), m.p. 180–184 °C. Two recrystallizations from toluene (1 ml) gave m.p. 189–190 °C. $C_{28}H_{32}O_2S_2$: C, H, S. MS [*m/e* (% rel. int.)]: 464 (0.3, M of dimer), 232 (100, M of monomer), 217 (50, monomer–CH_3), 199 (40), 146 (97). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.95, 1.21, 1.25, 1.48 (aliphatic methyl), 2.23, 2.24, 2.55, 2.58 (aromatic methyl), 2.59, 2.78 (methylene, *J* 15.0 Hz), 2.83, 3.11 (methylene, *J* 17.7 Hz), 7.07 (2 H, s), 7.15, 7.30 (2 H, *J* 8 Hz). ^{13}C NMR δ 19.3, 19.7, 21.1, 23.7, 24.5, 25.7, 26.2 (methyl), 36.7[a], 41.4[a] (tertiary carbon), 40.9, 42.5 (methylene), 128.9, 129.7, 130.7[a], 132.2[a], 133.4, 134.9[a], 138.0[a], 139.2[a] (aromatic), 95.8[a] (O–C–S), 115.1[a], 148.0[a] (vinylic), 188.4[a] (C=O).

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