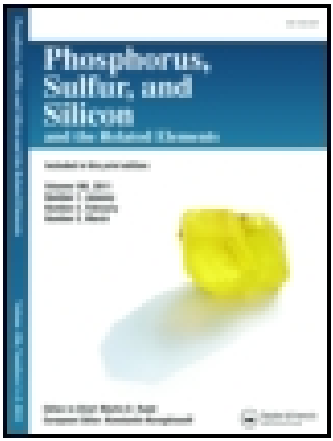

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Formation of 2-Methylene-1,3-oxathiole Derivatives in the Rhodium(II) Acetate-Catalyzed Reaction of α -Diazocarbonyl Compounds with Carbon Disulfide

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Published online: 28 Apr 2009.

To cite this article: Hirofumi Nakano & Toshikazu Ibata (2009) Formation of 2-Methylene-1,3-oxathiole Derivatives in the Rhodium(II) Acetate-Catalyzed Reaction of α -Diazocarbonyl Compounds with Carbon Disulfide, Phosphorus, Sulfur, and Silicon and the Related Elements, 184:5, 1224-1232, DOI: 10.1080/10426500902856313

To link to this article: http://dx.doi.org/10.1080/10426500902856313

Phosphorus, Sulfur, and Silicon, 184:1224–1232, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902856313

Formation of 2-Methylene-1,3-oxathiole Derivatives in the Rhodium(II) Acetate-Catalyzed Reaction of α-Diazocarbonyl Compounds with Carbon Disulfide

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The rhodium(II) acetate-catalyzed reaction of α-diazocarbonyl compound with carbon disulfide gave 1,3-oxathiole-2-thione, 2-methylene-1,3-oxathiole, and 2,2′-spirobis(1,3-oxathiole) derivatives depending on the substituent on the diazo compounds via 1,5- or 1,3-electrocyclization of thiocarbonyl ylide intermediate formed by the reaction of rhodium carbenoid with thiocarbonyl group.

Keywords Diazo compound; electrocyclization; oxathiole; rhodium(II); thiocarbonyl ylide

INTRODUCTION

1,3-Dipolar cycloaddition[1] is a useful reaction for the selective synthesis of heterocyclic frameworks. Carbonyl ylides[2] and thiocarbonyl ylides[3] have been extensively studied with respect to their formation, reaction, and synthetic applications. The chemistry of carbonyl ylides is very broad; especially, asymmetric 1,3-dipolar cycloaddition has been studied using chiral catalyst,[4–7] and intramolecular 1,3-dipolar cycloaddition has been used to synthesize complex natural products.[8–11] However, the chemistry of thiocarbonyl ylides is not as much investigated as that of carbonyl ylides, so we have been interested in the effective formation and reactions of thiocarbonyl ylides. Methods[3] for the formation of thiocarbonyl ylides have been developed, including thermolysis of 2,5-dihydro-1,3,4-thiadiazole or 2,4-dihydro-1,3-oxathiol-5-one,

Received 30 December 2007; accepted 15 February 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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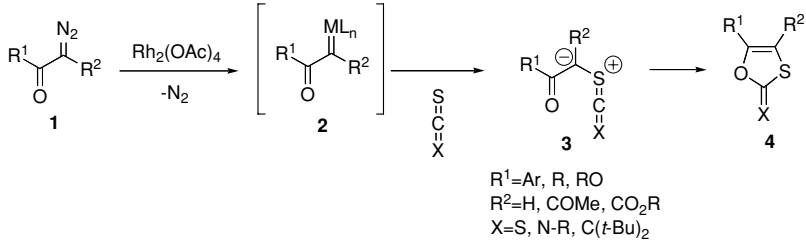
1,3-elimination of halomethyl trimethylsilylmethyl thioethers, deprotonation of thiooxonium salts, and reaction of carbene or carbenoid compounds with thiocarbonyl compounds.

We have described previously the formation of thiocarbonyl ylides **3** by the rhodium(II)-catalyzed reaction of diazo compounds **1** with thiocarbonyl compounds such as carbon disulfide,[12,13] isothiocyanate,[14,15] and thioketene[16] to give the corresponding 1,3-oxathiole derivatives **4**.[17]

In a previous paper,[12] we described the reaction of substituted α-diazoacetophenones (**1**: $R^1 = Ar$, $R^2 = H$) with carbon disulfide in the presence of rhodium(II) acetate to give the corresponding 5-aryl-1,3-oxathiole-2-thiones (**4**: $R^1 = Ar, R^2 = H, X = S$) through the thiocarbonyl ylide **3** (X = S), formed from the ketocarbenoid **2** and carbon disulfide (Scheme 1). In order to investigate the structural effect on the reaction, the reaction of diazoacetophenones having various substituents on α-position was studied.

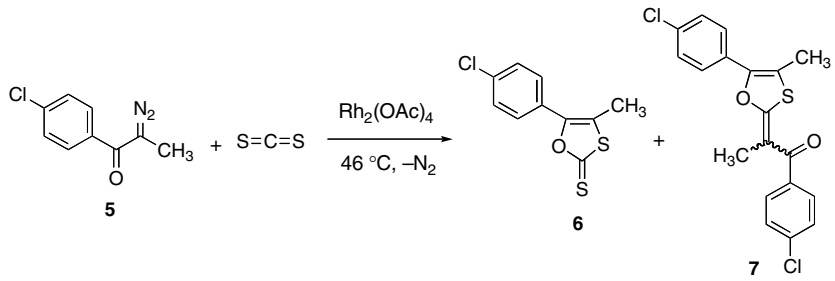


SCHEME 1

RESULTS AND DISCUSSION

The reaction of 1-(4-chlorophenyl)-2-diazopropan-1-one (**5**) with carbon disulfide in the presence of rhodium(II) acetate was carried out at 46°C. The reaction mixture was separated by medium pressure liquid chromatography to give 5-(4-chlorophenyl)-4-methyl-1,3-oxathiole-2-thione (**6**) in 27% yield together with product **7** (20%). The elemental analysis and mass spectrum measurement of **7** support the molecular formula $C_{19}H_{14}O_2SCl$, which corresponds to a 2:1 product of the ketocarbene with carbon disulfide, which has eliminated one sulfur atom (Scheme 2).

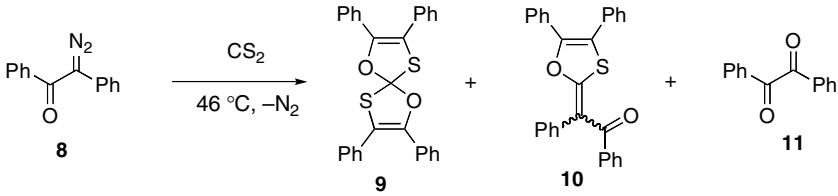
The structure of **7** was confirmed on the basis of its spectroscopic data. The ^{13}C NMR spectrum of **7** showed the signal of a carbonyl carbon at 190.9 ppm and that of 5-C of 1,3-oxathiole at 143.1 ppm, which is similar to that of 5-C of 1,3-oxathiole-2-thione (ca. 150 ppm).[12] The signal



SCHEME 2

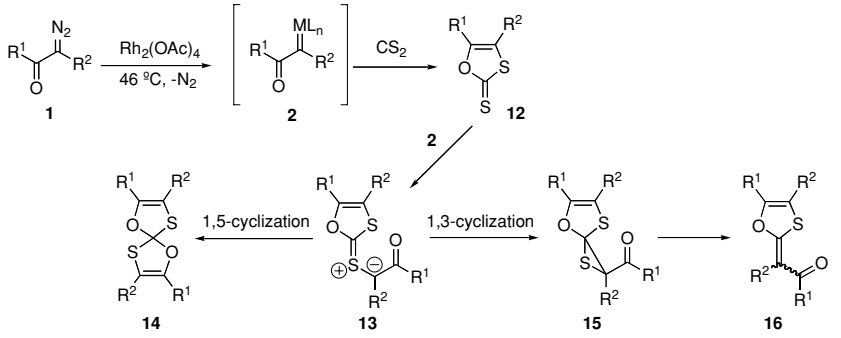
at 113.9 ppm is assigned to 4-C of 1,3-oxathiole on the basis of its chemical shift, multiplicity, and coupling constant ($^2J_{CH} = 7$ Hz) compared with those of 1,3-oxathiole-2-thione. These data suggest that product **7** is 1-(4-chlorophenyl)-2-[5-(4-chlorophenyl)-4-methyl-1,3-oxathiol-2-ylidene]-propan-1-one. There are two possible structures of oxathiole **7**: *E*- and *Z*-isomer. Determination of the geometrical structure based on the available spectroscopic data is not successful at this time. The formation of ethylenic compound by the elimination of sulfur atom in the reaction of carbene or carbenoid with thiocarbonyl compound was reviewed by Mloston and Heimgartner.[3]

The catalytic reaction of 2-diazo-1,2-diphenylethan-1-one (**8**) with carbon disulfide gave 2,2′-spirobis(1,3-oxathiole) **9**, 2-methylene-1,3-oxathiole **10**, and benzil **11** in 26, 4.0, and 40% yields, respectively, without affording 1,3-oxathiole-2-thione (Scheme 3).



SCHEME 3

Elemental analysis and mass spectrum data suggested that compound **9** was a 2:1 product of ketocarbene moiety and carbon disulfide. The ^{13}C NMR spectrum of **9** did not show signals of carbonyl and thiocarbonyl carbons, but showed a signal of quaternary carbon (127.9 ppm) originating from carbon disulfide. The carbon signals of two aromatic units originating from **8** are equivalent. So **9** was identified as 2,2′-spirobis(1,3-oxathiole) having symmetrical structure.

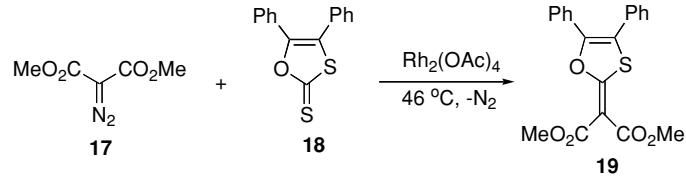


SCHEME 4

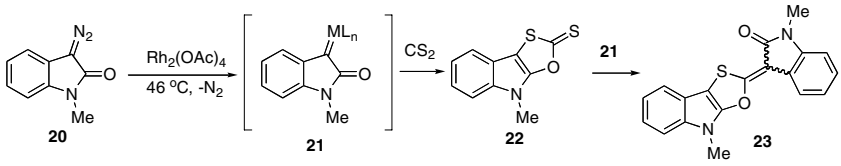
The reaction under the similar conditions using degassed solvents gave **9**, **10**, and **11** in 43%, 14%, and 6.6% yields, respectively, increasing the yield of **9** sacrificing the yield of **11**. The catalytic decomposition of **8** in benzene at 46°C under air gave **11** in 90% yield. These observations show that **11** is formed by the reaction of ketocarbenoid with oxygen. These results indicate that the substituent at the α-position of the diazoketone affects the distribution of the products.

1,3-Oxathiole-2-thione **12** was formed by cyclization of thiocarbonyl ylide **3** (X = S) generated by the reaction of ketocarbenoid **2** with carbon disulfide.[12] In the reaction of **8**, ketocarbenoid **2** attacks at the sulfur atom of oxathiole-2-thione **12** to generate thiocarbonyl ylide **13**, which undergoes 1,5-cyclization[18,19] to give spiro 1,3-oxathiole **14**. In the reaction of **5** or **8**, the 1,3-cyclization of thiocarbonyl ylide **13** to give thiirane **15** is followed by desulfurization to afford 2-methylene-1,3-oxathiole **16** (Scheme 4).

Trapping experiments for the thiocarbonyl ylide **13** by dipolarophiles were not successful. However, the formation of thiocarbonyl ylide **13** by the reaction of ketocarbenoid with 1,3-oxathiole-2-thione was confirmed by the following reaction. Rhodium(II) acetate-catalyzed reaction of dimethyl 2-diazomalonate (**17**) with 4,5-diphenyl-1,3-oxathiole-2-thione (**18**) gave the corresponding dimethyl 2-(4,5-diphenyl-1,3-oxathiol-2-ylidene)malonate **19** in 37% yield (Scheme 5).



SCHEME 5



SCHEME 6

Rhodium(II) acetate-catalyzed reaction of 3-diazo-1-methyl-1,3-dihydroindol-2-one (**20**) with carbon disulfide also gave 4-methyl-2-(1-methyl-2-oxo-2,3-dihydro-3-indoylidene)-4*H*[1,3]-oxathiolo[5,4-b]indole (**23**) in 21% yield. Several attempts to isolate the 1,3-oxathiole-2-thione using medium and high pressure liquid chromatography were unsuccessful (Scheme 6).

CONCLUSION

In conclusion, the rhodium(II) acetate catalyzed reaction of α-diazocarbonyl compounds with carbon disulfide gave 1,3-oxathiole-2-thione, 2-methylene-1,3-oxathiole, and 2,2′-spirobis(1,3-oxathiole) derivatives depending on the substituent on the diazo compounds via thiocarbonyl ylide intermediate formed by the reaction of rhodium carbenoid with thiocarbonyl group. The product distribution was determined by substituent at the diazo carbon atom: phenyl and methyl groups increased a second attack of the carbenoid on the thiocarbonyl sulfur atom of 1,3-oxathole-2-thione to form a thiocarbonyl ylide, phenyl group favored 1,5-cyclization of the thiocarbonyl ylide to give spirobis(1,3-oxathiole).

EXPERIMENTAL

Melting points were measured with a Yanagimoto melting point apparatus and were not corrected. IR spectra were recorded on a Perkin-Elmer model 983. ^{1}H NMR (399.65 MHz and 500 MHz) and ^{13}C NMR (100.40 MHz and 125.65 MHz) spectra were recorded with a JEOL GSX-400 and a JEOL GX-500 instrument in $CDCl_3$ solution, using TMS as internal standard. Mass spectra were obtained with a JEOL JMS-DX303 mass spectrometer.

Materials

1-(4-Chlorophenyl)-2-diazopropan-1-one (**5**) was prepared by the reaction of 4-chlorobenzoyl chloride with an excess of diazoethane in the presence of triethylamine according to the method of Newman and Beal.[20] 2-Diazo-1,2-diphenylethan-1-one (**8**) was prepared according to the reported methods.[21] Benzene was purified by distillation after reflux on CaH_2 and stored over molecular sieves 4 Å. Carbon disulfide was purified just before use by distillation after reflux over tetraphosphorus decaoxide.

Rhodium(II) Acetate-Catalyzed Decomposition of α-Diazocarbonyl Compounds: General Procedure

A solution of diazocarbonyl compound (3.00 mmol) in dry benzene (50 mL) was added over a period of ca. 4 h to a refluxing suspension of rhodium(II) acetate (4.3 mg, 9.7×10^{-3} mmol) in carbon disulfide (100 mL) under nitrogen atmosphere. The solution was heated at 46 °C until no more diazo compound was detected by TLC or IR spectroscopy. The resulting reaction mixture was concentrated under reduced pressure. The residue was separated by medium-pressure liquid chromatography (silica gel, eluted with ethyl acetate-hexane).

The rhodium(II) acetate-catalyzed reaction of 1-(4-chlorophenyl)-2-diazoethan-1-one (**5**) with carbon disulfide gave 1,3-oxathiole-2-thione **6** and 2-methylene-1,3-oxathiole **7** in 27% and 20% yields, respectively.

5-(4-Chlorophenyl)-4-methyl-1,3-oxathiole-2-thione (6)

Colorless prisms; mp 101.0–102.3°C (from benzene/hexane); ^{1}H NMR ($CDCl_3$): $\delta = 2.30$ (s, 3H, CH_3), 7.42–7.45 (m, 2H, arom-H), 7.50–7.53 (m, 2H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 11.7$ (q, CH_3), 117.6 (sq, $^2J_{CH} = 7.3$ Hz, S-C=), 125.9 (s, arom-C), 128.5 (d, arom-CH), 129.2 (d, arom-CH), 135.8 (s, arom-C), 149.3 (s, O-C=), 201.6 (s, C=S); IR (KBr): 1592, 1488, 1209, 1193, 1178, 1094, 1015, 996, 831, and 662 cm^{-1}; MS (EI, rel. intensity %, assignment) 244 (46, M^++2), 243 (14, M^++1), 242 (100, M^+), 226 (11), 182 (45), 155 (13), 149 (24), 138 (80), 111 (24), 103 (12), 75 (16), 59 (13). Calcd for $C_{10}H_7OS_2Cl$: C, 49.48; H, 2.91%. Found: C, 49.49; H, 2.91%.

1-(4-Chlorophenyl)-2-[5-(4-chlorophenyl)-4-methyl-1,3-oxathiol-2-ylidene]-propan-1-one (7)

Pale yellow crystals; mp 166.0–168.2°C (from benzene/hexane); ^{1}H NMR ($CDCl_3$): $\delta = 2.22$ (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 7.38–7.46 (m, 4H, arom-H), 7.52–7.56 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 11.5$

(q, CH_3), 13.7 (q, CH_3), 103.1 (sq, $^2J_{CH}$ = 5.9 Hz, Me-C=), 113.9 (sq, $^2J_{CH}$ = 7.3 Hz, Me-C=), 127.3 (s), 128.1 (s), 128.3 (d), 129.1 (d), 129.3 (d), 134.8 (s), 136.0 (s), 138.4 (s), 143.1 (s), 170.0 (s), 190.1 (s); IR (KBr): 2926, 1632, 1605, 1593, 1566, 1480, 1444, 1395, 1347, 1094, 1003, 988, 832, 753, 679 cm^{-1}; MS (EI, rel intensity %, assignment) 380 (18, M^++4), 379 (24, M^++3), 378 (76, M^++2), 377 (56, M^++1), 376 (100, M^+), 375 (48, M^+-1), 265 (11), 182 (42), 150 (11), 139 (64), 111 (25), 83 (12). Calcd for $C_{19}H_{14}O_2SCl_2$: C, 60.49; H, 3.74%. Found: C, 60.20; H, 3.90%.

The rhodium(II) acetate-catalyzed reaction of 2-diazo-1,2-diphenylethan-1-one (**8**) with carbon disulfide gave spirobis(oxathiole) **9**, 2-methylene-1,3-oxathiole **10**, and benzil **11** in 26%, 4%, and 40% yields, respectively.

2,2′-Spirobis(4,5-diphenyl-1,3-oxathiole) (9)

Colorless needles; mp 154.8–155.3°C (from acetone); ^{1}H NMR ($CDCl_3$): δ = 7.20–7.43 (m, 20H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 111.1 (s, =C-S), 127.8 (d, arom-C), 127.9 (s, spiro-C), 128.2 (d, arom-CH), 128.5 (d, arom-CH), 128.8 (d, arom-CH), 129.2 (d, arom-CH), 129.7 (s, arom-C), 130.8 (s, arom-C), 140.3 (s, arom-C); IR (KBr): 3045, 3022, 2918, 1633, 1598, 1571, 1494, 1443, 1222, 1157, 1085, 1065, 1028, 1012, 995, 963, 938, 916, 766, 753, 695 cm^{-1}; MS (EI, rel. intensity %, assignment): 466 (7, M^++2), 465 (15, M^++1), 464 (40, M^+), 432 (6, M^+-S), 359 (64, M^+-PhCO), 331 (23), 210 (36), 178 (19), 165 (16), 153 (36), 121 (100, $PhCS^+$), 105 (64, $PhCO^+$), 77 (79), 51 (14). Calcd for $C_{29}H_{20}O_2S_2$: C, 74.97; H, 4.30%. Found: C, 75.04; H, 4.53%.

2-(4,5-Diphenyl-1,3-oxathiol-2-ylidene)-1,2-diphenylethan-1-one (10)

Pale yellow crystals; mp 183.0–189.0°C (from benzene/hexane); ^{1}H NMR ($CDCl_3$): δ = 7.15–7.45 (m, 20H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 111.1 (d), 118.1 (s), 126.9 (d), 127.0 (d), 127.5 (d), 128.3 (d), 128.4 (d), 128.6 (d), 129.1 (d), 129.2 (d), 129.3 (d), 129.7 (d), 129.9 (s), 130.1 (d), 130.09 (d), 135.5 (s), 139.4 (s), 143.7 (s), 171.3 (s), 189.5 (s, C=O); IR (KBr): 1599, 1568, 1496, 1460, 1442, 1346, 1307, 1160, 1062, 1025, 960, 912, 867, 830, 751, 696, 691 cm^{-1}; MS (EI, rel. intensity %, assignment): 434 (12, M^++2), 433 (37, M^++1), 432 (100, M^+), 355 (5), 311 (2), 210 (35), 178 (11), 165 (14), 121 (10), 105 (49, $PhCO^+$), 77 (23). Calcd for $C_{29}H_{20}O_2S$: C, 80.33; H, 4.87%. Found: C, 80.53; H, 4.66%.

Rhodium(II) Acetate-Catalyzed Reaction of Dimethyl 2-Diazomalonate with 4,5-Diphenyl-1,3-oxathiole-2-thione

A solution of dimethyl 2-diazomalonate (**17**) (1 mmol) in dry benzene (10 mL) was added over a period of ca. 1 h to a solution of rhodium(II) acetate (9.1×10^{-3} mmol) and 4,5-diphenyl-1,3-oxathiole-2-thione (**18**)[22] (0.5 mmol) in benzene (10 mL) at 46°C under nitrogen atmosphere. The solution was heated at 46°C for 2 h. The resulting reaction mixture was concentrated under reduced pressure. The residue was separated by medium-pressure liquid chromatography (silica gel, eluted with ethyl acetate-hexane) to give dimethyl 2-(4,5-diphenyl-1,3-oxathiol-2-ylidene)malonate (**19**): yield 37%; colorless crystals; mp 140.0–143.0°C (from benzene/hexane); ^{1}H NMR ($CDCl_3$): $\delta = 3.87$ (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 7.28–7.49 (m, 10H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 51.9$ (q, OCH_3), 52.2 (q, OCH_3), 94.6 (s, =C(COOMe)$_2$), 118.1 (s, S-C=), 127.2 (d, arom-CH), 127.9 (s, arom-C), 128.6 (s, arom-C), 128.7 (d, arom-CH), 129.3 (d, arom-CH), 129.4 (d, arom-CH), 129.5 (d, arom-CH), 129.6 (d, arom-CH), 145.3 (st, $^3J_{CH} = 4.8$ Hz, O-C=), 164.2 (sq, $^3J_{CH} = 4.0$ Hz, ester C=O), 167.6 (sq, $^3J_{CH} = 4.0$ Hz, ester C=O), 178.3 (s, 2-C=); IR (KBr): 2924, 1713 (C=O), 1664, 1523, 1484, 1444, 1432, 1324, 1276, 1211, 1190, 1162, 1153, 1110, 1084, 1062, 1028, 1012, 811, 780, 755, 694, 665 cm^{-1}. Calcd for $C_{20}H_{16}O_5S$: C, 65.20; H, 4.38%. Found: C, 65.22; H, 4.49%.

The rhodium(II) acetate-catalyzed reaction of 3-diazo-1-methyl-1,3-dihydroindol-2-one (**20**)[23] with carbon disulfide gave 1-Methyl-3-(4-Methyl-4*H*-[1,3]oxathiolo-[5,4-b]-indole-2-ylidene)-1,3-dihydroindol-2-one (**20**): yield 21%; yellow crystals; mp 213.8–215.3°C (from benzene/hexane); ^{1}H NMR ($CDCl_3$): $\delta = 3.32$ (s, 3H, NCH_3), 3.89 (s, 3H, NCH_3), 6.86–7.73 (m, 8H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 26.0$ (q, NCH_3), 29.8 (q, NCH_3), 88.6 (s), 101.1 (s), 107.7 (s), 110.2 (s), 118.3 (d), 120.1 (s), 120.5 (d), 121.0 (s), 121.3 (d), 121.5 (d), 121.6 (d), 125.7 (d), 136.8 (s), 139.3 (s), 149.9 (s), 167.4 (s), 170.02 (s); IR (KBr): 1675 (C=O), 1626, 1598, 1559, 1514, 1483, 1468, 1449, 1374, 1344, 1318, 1263, 1220, 1116, 1076, 1020, 978, 813, 769, 740, 701, 685, 658 cm^{-1}; MS (EI, rel. intensity %, assignment): 336 (8, M^++2), 335 (25, M^++1), 334 (100, M^+), 333 (11, M^+-1), 319 (12, M^+-CH_3), 305 (28, M^+-NCH_3), 273 (14), 167 (16), 117 (14). Calcd for $C_{19}H_{14}N_2O_2S$: C, 68.24; H, 4.22; N, 8.38%. Found: C, 67.95; H, 4.38; N, 8.28%.

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