conventional workup, the neutral products were column chromatographed on silica gel. The first fraction (elution with benzene–hexane, 7:3) contained a mixture of **2c** and **3c** (622 mg, 49%), the **2c**/**3c** ratio being 85:15. From the second fraction (elution with benzene), 1-methyl-3-phenyl-2-indanone[5] was obtained (30 mg, 3%). From the third fraction, 1-(2-benzoylphenyl)propionaldehyde[5] (40 mg, 3%) was obtained. The fourth fraction contained the unidentified polymeric products (150 mg). The ^{1}H NMR spectrum of the polymeric products indicated the absence of methoxy groups. The fifth fraction (elution with ether–benzene, 1:99) contained the partial-cleavaged product **11** (120 mg, 8%): an oil; ^{1}H NMR δ 1.41 (d, 3 H, J = 6.5 Hz), 2.81 (bs, 1 H, exchangeable with D_2O), 3.09 (s, 3 H), 3.15 (m, 1 H), 3.59 (d, 1 H, J = 8.0 Hz), 7.19–7.55 (m, 9 H); MS, m/e 254 (M^+); IR 3500, 1445, 1120, 1070 cm^{-1}. From the final fraction (elution with ether–benzene, 1:9), the hydroperoxide **10** (81 mg, 6%) was obtained: an oil; ^{1}H NMR δ 1.26 (d, 3 H, J = 8.0 Hz), 3.50 (m, 1 H), 3.52 (s, 3 H), 4.81 (d, 1 H, J = 6.5 Hz), 7.26–7.70 (m, 9 H), 9.62 (bs, 1 H, exchangeable with D_2O); IR 3300, 1660, 1450, 1320, 1300, 1195 cm^{-1}. Treatment of **10** with catalytic amounts of $ClSO_3H$ in methanol at 20 °C for 24 h gave quantitatively methyl 1-(2-benzoylphenyl)propinate.[5]

The ozonolysis of **1c** in a mixed solvent $MeOH–CH_2Cl_2$ (20 mL, 1:1 v/v) at −70 °C (1 molar equiv of ozone), followed by column chromatography on silica gel, afforded **2c** (542 mg, 42%), 1-(2-benzoylphenyl)propionaldehyde (29 mg, 2%), **11** (130 mg, 9%), and **10** (81 mg, 6%), along with the unidentified polymeric products (130 mg).

Ozonolysis of 1c in AcOH. Indene **1c** (1.034 g, 5 mmol) was ozonized in a mixed solvent $AcOH–CCl_4$ (20 mL, 7:3 v/v) by passing 1 equiv of ozone through the solution. The mixture was poured onto aqueous $NaHCO_3$ and extracted with ether. The products were separated by column chromatography on silica gel. Elution with benzene–hexane (1:1) gave a mixture of **2c** and **3c** (508 mg, 40%). From the second fraction (elution with benzene) was obtained 1-methyl-3-phenyl-2-indanone as an oil (37 mg, 3%). The third fraction contained 1-(2-benzoylphenyl)propionaldehyde (65 mg, 6%). From the fourth fraction were obtained the unidentified polymeric products, which did not contain acetoxy groups (180 mg). From the final fraction (elution with ether–benzene, 1:9) was obtained 1-acetoxy-1-phenyl-3-methylindan-2-ol as an oil (52 mg, 3%): ^{1}H NMR δ 1.34 (d, 3 H, J = 7.0 Hz), 2.02 (s, 3 H), 2.82 (bs, 1 H, exchangeable with D_2O), 3.42 (quintet, 1 H, J = 7.0 Hz), 5.38 (d, 1 H, J = 7.0 Hz), 7.10–7.90 (m, 9 H); IR 3400, 1740 cm^{-1}.

Ozonolysis of 1-Methyl-2,3-diphenylindene (7c) in MeOH at −70 °C. To a solution of indene **7c** (1.41 g, 5 mmol) in methanol (15 mL)–CH_2Cl_2 (15 mL) was added dry oxygen containing 2% ozone at a speed of 50 L/h for 30 min (2 equiv of ozone). The mixture was poured into ice-cold aqueous potassium dihydrogen phosphate, and the products were extracted with ether. The organic layer was spearated and dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum. The crude products were triturated with ether–hexane to give a white solid (**14**, 1.05 g, 58%): mp 155–157 °C (from ethyl acetate–hexane); IR (KBr) 3375 cm^{-1}; ^{1}H NMR δ 1.03 (d, 3 H, J = 7.5 Hz), 3.34 (q, 1 H, J = 7.5 Hz), 3.46 (s, 3 H), 7.00–7.80 (m, 14 H), 8.96 (s, 1 H, exchangeable with D_2O). Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12. Found: C, 76.19; H, 6.10. The ^{1}H NMR spectrum of the residue indicated the existence of considerable amounts of the isomeric ozonides **8c**/**9c**. The signals attributable to other methanol-participated products were not detected. The column chromatography on silica gel gave first a mixture of **8c** and **9c** in a yield of 30% (495 mg), followed by elution of 1-(2-benzoylphenyl)ethyl phenyl ketone[5] (80 mg, 5%).

Ozonolysis of 1,2-Dimethyl-3-phenylindene (4c) in MeOH at −70 °C. Indene **4c** (1.10 g, 5 mmol) was ozonized in a mixed solvent, $MeOH–CH_2Cl_2$ (20 mL, 1:1 v/v) at −70 °C for 20 min (1.3 equiv of ozone molecule). After workup, the crude products were triturated with ether–hexane to afford the hydroperoxide **13** (426 mg, 28%): mp 136–137 °C (from benzene–hexane); IR 3335 cm^{-1}; ^{1}H NMR δ 1.42 (d, 3 H, J = 7.5 Hz), 1.64 (s, 3 H), 3.16 (q, 1 H, J = 7.5 Hz), 3.43 (s, 3 H), 6.90–7.75 (m, 9 H), 9.08 (s, 1 H, exchangeable with D_2O). Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.68. Found: C, 71.98; H, 6.68.

The column chromatography of the mother liquor on silica gel gave 33% yield of a mixture of 52% **5c** and 48% **6c**, followed by elution of 1-(2-benzoylphenyl)ethyl methyl ketone (120 mg, 10%): an oil; IR 1720, 1660 cm^{-1}; ^{1}H NMR δ 1.30 (d, 3 H, J = 6.5 Hz), 1.96 (s, 3 H), 3.97 (q, 1 H, J = 6.5 Hz), 7.20–7.83 (m, 9 H).

Registry No. **1a**, 95532-75-5; **1b**, 81706-99-2; **1c**, 22360-62-9; **1d**, 95532-76-6; **1e**, 95532-77-7; **2a**, 95532-78-8; **2b**, 95532-79-9; **2c**, 84810-14-0; **2d**, 95532-80-2; **2e**, 95532-81-3; **3a**, 95588-49-1; **3b**, 95588-50-4; **3c**, 84847-60-9; **3d**, 95588-51-5; **3e**, 95588-52-6; **4a**, 95532-82-4; **4b**, 95532-83-5; **4c**, 42842-58-0; **4d**, 95532-84-6; **4e**, 95532-85-7; **5a**, 95532-86-8; **5b**, 95532-87-9; **5c**, 89619-58-9; **5d**, 95532-88-0; **5e**, 95532-89-1; **6a**, 95588-53-7; **6b**, 95588-54-8; **6c**, 89675-13-8; **6d**, 95588-55-9; **6e**, 95588-56-0; **7a**, 89619-42-1; **7a′**, 89619-43-2; **7b**, 95532-90-4; **7b′**, 95532-91-5; **7c**, 51310-25-9; **7d**, 89619-44-3; **7d′**, 89619-45-4; **7e**, 95532-92-6; **8a**, 89619-65-8; **8a′**, 89619-66-9; **8b**, 95532-93-7; **8b′**, 95532-94-8; **8c**, 84810-15-1; **8d**, 89619-67-0; **8d′**, 89619-68-1; **8e**, 95532-95-9; **9a**, 89707-69-7; **9a′**, 89675-20-7; **9b**, 95671-31-1; **9b′**, 95588-57-1; **9c**, 84847-61-0; **9d**, 89675-21-8; **9d′**, 89675-22-9; **9e**, 95588-58-2; **10**, 95532-96-0; **14**, 89619-71-6.

1,3-Oxathiole-2-thiones from the Reaction of Carbon Disulfide with Zwitterionic Iodonium Compounds

Maria Papadopoulou, Spyros Spyroudis, and Anastasios Varvoglis*

Laboratory of Organic Chemistry, University of Thessaloniki, GR 54006 Thessaloniki, Greece

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We have synthesized 1,3-oxathiole-2-thiones from the reaction of zwitterionic iodonium compounds with carbon disulfide. The reaction is shown to be photochemical and possible pathways are discussed.

Zwitterionic iodonium compounds (ZIC) are relatively unfamiliar polyvalent iodine compounds, the chemistry of which has recently been reviewed.[1] The majority of ZIC contain two C–I bonds and may be divided into (a) aryliodonium ylides of active methylene compounds[2] (**1**) where the negative charge is dispersed over a system of neighboring bonds usually belonging to keto groups or enolized 1,3-dicarbonyl heterocycles[3] and (b) aryl(oxidoaryl)-

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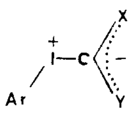
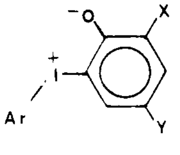


1

(X,Y = COR , NO$_2$, CO Het CO)



2

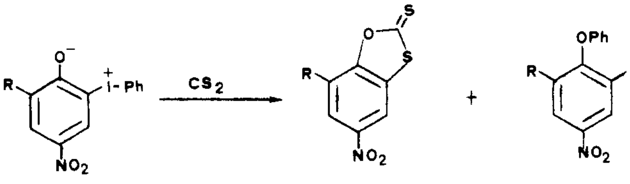
(X,Y = Cl , NO$_2$)

iodonium inner salts (2) in which the negative charge is largely localized on the oxygen atom.[4]

Among several interesting properties of ZIC, the ability of phenyliodonium dimedonate to give with a range of heterocumulenes various heterocycles[5,6] may be mentioned. The reaction of two ZIC of type 1 and two of type 2 with another heterocumulene, carbon disulfide, is presently reported. All four substrates give, exclusively or predominantly, 1,3-oxathiole-2-thiones, a class of compounds not easily accessible.

Results and Discussion

All reaction products were identified by elemental analysis and spectral data and in one case by X-ray analysis. The thermal reactions of 3 and 4 with an excess of CS$_2$ were conducted at room temperature since heating causes ylide rearrangement.[7] However, even after 60 days 4 gave 6 in only 5% yield in addition to a 10% yield of the rearranged iodo ether 8. A spectacular increase in yield and a drastic shortening of reaction time were observed when 4 was exposed to UV irradiation: after 9 h, 6 was obtained in 73% yield and 8 was not formed. Compound 3 reacted only photochemically to give in 9% yield 5 along with 7, whereas thermally 7 was the sole product. The low yield of 5 could be attributed to its limited stability and solubility problems. These results leave no doubt about the photochemical nature of the reactions. The competing isomerizations are typical examples of thermally allowed 1,4-sigmatropic shifts[4] and are suppressed photochemically. Few representatives of benzo-1,3-oxathiole-2-thiones are known; the unsubstituted benzo derivative[8] was obtained as a byproduct from *o*-hydroxybenzenediazonium chloride and potassium ethyl xanthate, and chlorinated benzo derivatives were formed from thermolysis or photolysis of 2-oxidobenzenediazonium inner salts.[9]



3, R=H

4, R=NO$_2$

5, R=H

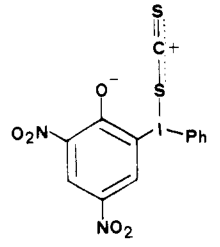
6, R=NO$_2$

7, R=H

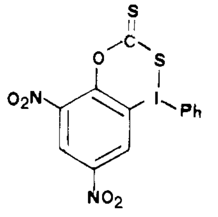
8, R=NO$_2$

A series of 4-hydroxybenzo derivatives was also obtained from substituted *p*-benzoquinones and potassium ethyl xanthate.[10]

It seems likely that compounds 5 and 6 are formed via trivalent iodine intermediates either of open-chain zwitterionic (A) or cyclic (B) structures.



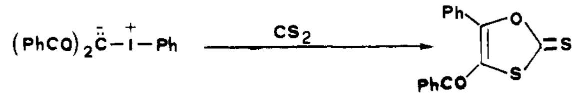
A



B

Iodonium salts are known to react with nucleophiles to give unstable trivalent iodine compounds, and stable compounds with an I–S bond have been isolated with 2-thionaphthol.[11] Compound 4 has also been found to react under photochemical conditions with thiourea[12] to afford a stable adduct believed to be analogous to A or B. The adducts of CS$_2$ are not stable; they eliminate iodobenzene and give oxathiole derivatives. Formation of carbenes as suggested[9] for the 2-oxidobenzenediazonium inner salts is not likely because irradiation of 4 in acetonitrile left it unchanged.

The iodonium ylide 9 gave only photochemically the oxathiole product 10 in very low yield, whereas in the dark it did not react.



9

10

The phenyliodonium ylide of dimedone 11 under photolytic conditions gives a very complex mixture of products, and in complete darkness it gave exclusively the rearranged ether 14. However, upon standing in diffuse daylight 11 produced after 2 weeks a 40% yield of the expected 1,3-oxathiole derivative 13 along with two other 1,3-oxathiole products, 20 and 21 (Scheme I). The spiro sulfide 20 is a known compound, having been produced from 11 with hydrogen sulfide[13] or phenyl isothiocyanate[6] and from dimedone with *N,N'*-bis(phenylsulfonyl)sulfur diimide.[14] The structure of 21 was corroborated by an X-ray analysis.[15]

Among the reaction pathways that might lead to 13, 20, and 21 we favor that shown in Scheme I. It accounts for the equal yields of 20 and 21 and is consistent with proposed mechanisms for related reactions.[6] The initially formed zwitterion 12 can either cyclize to 13 or react with 11 to afford ZIC 15. Elimination of iodobenzene from 15 would give the thioketone 16 and the thioketene 17. Both of these unstable intermediates could further react with 11, i.e., intermediate 16 to afford 20, as suggested by Koser, with the intermediacy of 18 and intermediate 17 through 19 to afford 21. It is noted that Wolff-type rearrangement products in Cu-catalyzed reactions of 11 have been formed[7] but no such products could be detected in our reactions,

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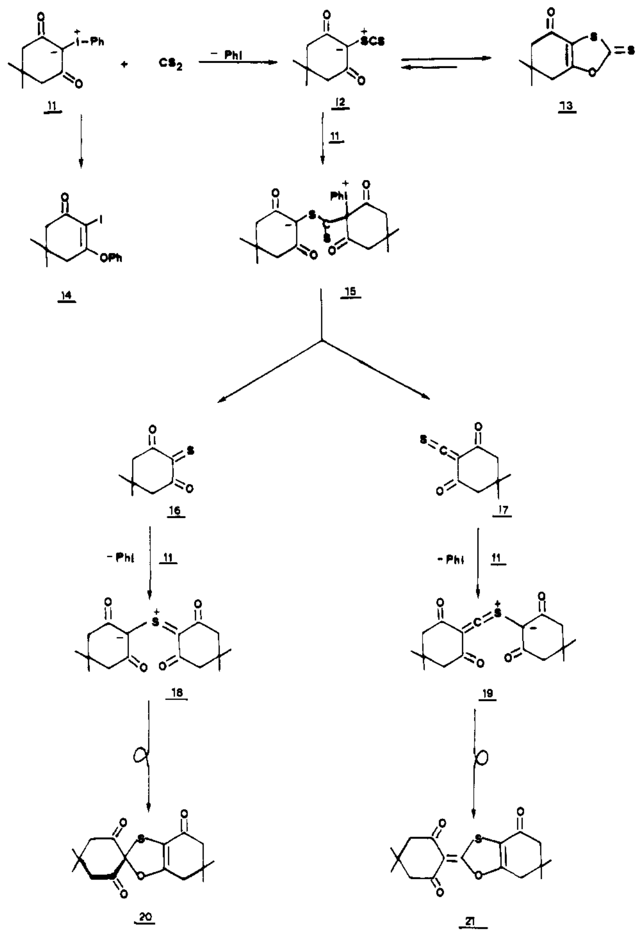

so that it seems unlikely that carbenes are formed.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian A-60A spectrometer. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer (Nujol mulls) and UV spectra with a Shimadzu UV 210A spectrophotometer. Mass spectra were obtained from a Hitachi Perkin-Elmer RMU-6L single-focusing spectrometer at 70 eV. Melting points are uncorrected. Chromatographic separations refer to column chromatography (silica gel; hexane–chloroform). The starting materials were known compounds.[4,16]

5,7-Dinitro-1,3-benzoxathiole-2-thione (6). A suspension of 4 (200 mg) in acetonitrile (20 mL), carbon disulfide (20 mL), and benzene (6 mL) was irradiated with a low-pressure Hg lamp (400 W, Pyrex vessel) for 9 h with occasional shaking. Partial removal of solvents led to the precipitation of some unreacted 4 (50 mg). The filtrate was chromatographed, and after iodobenzene, 6 was eluted: 73 mg (73% yield based on 4 consumed) of orange crystals; mp 158–159 °C (from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 8.85 (1 H, d, J = 2 Hz), 8.44 (1 H, d, J = 2 Hz); IR 3095, 1600, 1540, 1340, 1160, 1000 cm^{-1}; UV (EtOH) λ_{max} 237 nm (ϵ 14790), 265 (12880), 298 (14120), 355 (10710); MS, *m/e* 258 (M^+, 45), 168 (45), 124 (48), 93 (90), 82 (85), 62 (100).

Anal. Calcd for $C_7H_2N_2O_5S_2$: C, 32.55; H, 0.78; N, 10.85. Found: C, 32.15; H, 0.87; N, 10.64.

5-Nitro-1,3-benzoxathiole-2-thione (5). A suspension of 3 (600 mg) in carbon disulfide (14 mL), acetonitrile (16 mL), and benzene (6 mL) was irradiated as above for 1 h. After removal of unreacted 3 (200 mg), chromatographic separation afforded iodobenzene and then 2-iodo-4-nitrophenyl ether 7 (80 mg; mp 60–61 °C, lit.[17] mp 61 °C) and 5 (20 mg, 9% yield): mp 200–201 °C (light orange crystals from chloroform–hexane); ^{1}H NMR ($CDCl_3$) δ 8.25 (1 H, d, J = 2 Hz), 7.69 (1 H, two d, J = 2, 9 Hz), 6.51 (1 H, d, J = 9 Hz); IR 3100, 1535, 1520, 1350, 1340, 1200, 1020 cm^{-1}; UV (EtOH) λ_{max} 247 nm (ϵ 21380), 292 (16980), 330 (22910); MS, *m/e* 213 (M^+, 100), 197 (5), 95 (18), 91 (15), 69 (20), 63 (75).

Anal. Calcd for $C_7H_3NO_3S_2$: C, 39.43; H, 1.41; N, 6.57. Found: C, 39.66; H, 1.44; N, 6.70.

4-Benzoyl-5-phenyl-1,3-oxathiole-2-thione (10). A solution of 9 (800 mg) in carbon disulfide (30 mL) was irradiated for 3 h, after which time all 9 was consumed. Chromatographic separation gave iodobenzene, dibenzoylmethane (10 mg), and 20 mg (4% yield) of 10: mp 136–137 °C (off-white crystals from hexane); ^{1}H NMR ($CDCl_3$) δ 7.85–7.15 (m); IR 1640, 1610, 1470, 1330, 1180, 730, 715 cm^{-1}; UV (EtOH) λ_{max} 250 nm (ϵ 19050), 320 (19050); MS, *m/e* 298 (M^+, 85), 105 (100), 77 (50).

Anal. Calcd for $C_{16}H_{10}O_2S_2$: C, 64.40; H, 3.38. Found: C, 64.44; H, 3.49.

Reaction of 11 with Carbon Disulfide. A suspension of 11 (1 g) in carbon disulfide (20 mL) was stirred at room temperature for 2 days, until all solid dissolved. After standing for 2 weeks yellow crystals were deposited (250 mg, 40% yield) that proved to be **4-oxo-4,5,6,7-tetrahydro-6,6-dimethyl-1,3-benzoxathiole-2-thione (13)**: mp 190 °C (from methanol); ^{1}H NMR (Me_2SO-d_6) δ 0.8 (s), 2.4 (masked by the solvent); IR 2700–2500 (br), 1720, 1590, 1235, 1120, 715 cm^{-1}; UV (MeOH) λ_{max} 230 nm (ϵ 4700), 282 (2700), 410 (6310); MS, *m/e* 214 (M^+, 57), 83 (100), 55 (50).

Anal. Calcd for $C_9H_{10}O_2S_2$: C, 50.45; H, 4.70. Found: C, 50.47; H, 5.00.

The filtrate after removal of 13 was chromatographed, and besides iodobenzene the rearranged ether 14 and compounds 20 and 21 were eluted in that order (for the latter a 1:1 mixture of chloroform–ethyl acetate was used). Compound 20 was in all respects identical with that described in the literature:[6] 207 mg (23% yield); mp 178 °C (lit. mp 176–178 °C).

Compound 21 was obtained as off-white crystals: 215 mg (23% yield); mp 162 °C (from chloroform); ^{1}H NMR (C_6D_6) δ 2.24 (s, 4 H), 1.92 (s, 2 H), 1.80 (s, 2 H), 0.77 (s, 6 H), 0.57 (s, 6 H); IR 1675, 1640, 1610 cm^{-1}; MS, *m/e* 320 (M^+, 100), 223 (34), 208 (25), 83 (25), 55 (35).

Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.72; H, 6.30. Found: C, 63.20; H, 6.43.

Registry No. 3, 72212-81-8; 4, 95617-22-4; 5, 95617-24-6; 6, 95617-23-5; 9, 1292-43-9; 10, 95617-25-7; 11, 35024-12-5; 13, 95617-26-8; 14, 94569-94-5; 20, 56995-07-4; 21, 95617-27-9; carbon disulfide, 75-15-0; iodobenzene, 591-50-4; dibenzoylmethane, 120-46-7.

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