Facile and Efficient Transformation of Xanthates into Thiocarbonates by Anodic Oxidation

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Xanthates are among the most widely used thiocarbonyl compounds in organic synthesis,[1] despite the fact that very little information is available about their oxidation.

In 1997, Metzner et al.[2] reported that sulfines are formed by reaction of xanthates with *m*-CPBA. These sulfines evolve at room temperature after 4 weeks to give dithioperoxycarbonates and thiocarbonates as main and secondary product, respectively. The syntheses of thiocarbonates are usually carried out by reaction of potassium phenoxide with carbonyl sulfide and subsequent alkylation using the corresponding alkyl halide[3] or by reaction of a sodium thiolate salt with alkyl chloroformates.[4] Thiocarbonates show many interesting properties. They have been used as pesticides,[5] insecticides, nematocides and acaricides,[6] antineoplastic[7] and antiulcer agents,[8] as well as in the preparation of antibiotics.[9]

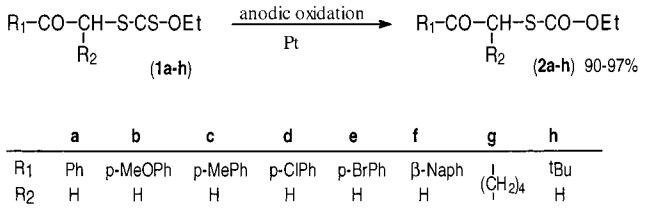
Results and Discussion

We have found that the electrochemical oxidation of *O*-ethyl xanthates (**1a**−**h**) leads to the formation of the corresponding *O*-ethyl thiocarbonates (**2a**−**h**) (90−97% yield) (Scheme 1).

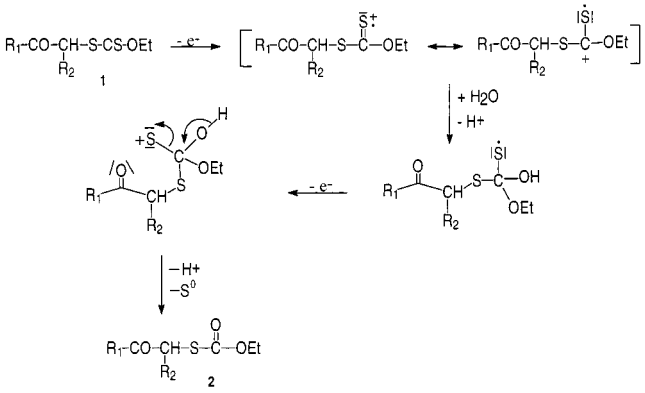
A logical mechanism to explain the electrochemical transformation is shown in Scheme 2.

In the anodic oxidation of 4-chlorophenacyl xanthate (**1d**), a small amount of dithioperoxycarbonate (**3d**) was isolated, and in the oxidation of 4-bromophenacyl xanthate (**1e**) traces of the corresponding dithioperoxycarbonate were also found. In both cases, the stabilization of the positive charge on the sulfur atom (by the free electron pairs of the oxygen atom of the carbonyl group) is lower than in the rest of xanthates due to the withdrawing effect of the halogen. Therefore, in **1d** and **1e** there is some stabilization coming from the free electron pairs of the sulfur atom, to afford the small amount of **3**, as is indicated in Scheme 3.

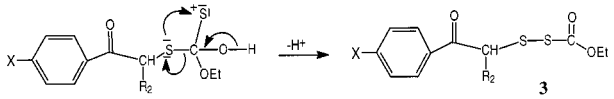
Scheme 1



Scheme 2



Scheme 3



The cyclic species proposed by Metzner[2] in the sulfine decomposition (Figure 1) cannot be assumed in our main pathway because experimentally it has never been detected and the dithioperoxycarbonate is not obtained as the major product. However, it could be implicated in the formation of **3** as a parallel minor pathway.

The electrochemical process was carried out under argon atmosphere, and the consumed charge was 2 F/mol. However, when the reaction was performed in an open air cell the electricity consumption was lower than this value. To demonstrate the participation of the oxygen (atmospheric and dissolved) in the process, electrolyses were carried out bubbling an oxygen flow through the anodic compartment. In this case, only 1 F/mol was consumed in the reaction. The easy oxidation of the sulfur radical can be explained having in mind that the oxidation potential of a radical is controlled largely by the ability of a group to stabilize the developing of positive charge. This suggests that there is considerable development of cation character in the transition state in the electron-transfer oxidation of radicals.[10] In our case, the free electron pairs in the oxygen atom stabilize the sulfur cation.

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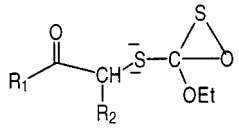

Figure 1.

When the oxidation of the xanthate **1** was performed using *m*-CPBA, no sulfines were detected but again thiocarbonate was obtained in lower yield.

Our electrochemical process can only be compared (ratio thiocarbonate/dithioperoxycarbonate) with the oxidation of **1** using *trans*-2-(phenylsulfonyl)-3-phenyloxaziridine[2] as oxidant agent. Nevertheless, our electrochemical process is cheaper, cleaner, more efficient and it does not need sophisticated reagents.

Experimental Section

β-Haloketones are commercially available and have been used without purification. Dithiocarbonates (**1a**−**h**) were prepared in almost quantitative yield according to Whitham.[11]

***O*-Ethyl *S*-phenacyl dithiocarbonate (1a):** mp 31−32 °C (lit.[12] mp 32 °C); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.7, 43.5, 70.7, 128.4, 128.8, 133.7, 135.8, 192, 213.8; MS *m/e* (relative intensity) EI 240 (M^+, 5), 207 (22), 180 (20), 151 (11), 105 (100), 91 (8), 77 (40), 51 (10).

***O*-Ethyl *S*-(4-methoxyphenacyl) dithiocarbonate (1b):** mp 68−69 °C; IR (KBr) ν 2909, 1665, 1600, 1575, 1256, 1216, 1109, 1056, 832; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (t, 3H, J = 5 Hz), 3.88 (s, 3H), 4.62 (q, 2H, J = 5 Hz), 4.62 (s, 2H), 6.96 (d, 2Har, J = 5.8 Hz), 8.0 (d, 2Har, J = 5.8 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ: 13.4, 43.0, 55.2, 70.3, 113.6, 128.5, 130.5, 163.7, 190.4, 213.1; MS *m/e* (relative intensity) EI 270 (M^+, 3), 237 (5), 210 (3), 181 (5), 135 (100), 121 (8), 107 (8), 92 (10), 77 (16), 64 (6), 51 (2). Anal. Calcd for $C_{12}H_{14}O_3S_2$: C, 53.33; H, 5.18; S, 23.7. Found: C, 53.3; H, 5.08; S, 23.9.

***O*-Ethyl *S*-(4-methylphenacyl) dithiocarbonate (1c):** mp 88−89 °C; IR (KBr) ν 2971, 1690, 1604, 1226, 1051, 811; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (t, 3H, J = 7 Hz), 2.43 (s, 3H), 4.62 (q, 2H, J = 7 Hz), 4.64 (s, 2H), 7.3 (d, 2Har, J = 8 Hz), 7.9 (d, 2Har, J = 8 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.4, 21.4, 43.2, 70.3, 128.2, 129.2, 133, 144.4, 191.5, 213.0; MS *m/e* (relative intensity) EI 254 (M^+, 4), 237 (5), 221 (11), 194 (9), 165 (7), 119 (100), 105 (6), 91 (30), 65 (14), 51 (3). Anal. Calcd for $C_{12}H_{14}O_2S_2$: C, 56.69; H, 5.51; S, 25.2. Found: C, 56.59; H, 5.7; S, 25.5.

***O*-Ethyl *S*-(4-chlorophenacyl) dithiocarbonate (1d):** mp 63−65 °C; IR (KBr) ν 2979, 1696, 1589, 1256, 1112, 1052, 990, 814; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 3H, J = 7.3 Hz), 4.53 (q, 2H, J = 7.3 Hz), 4.57 (s, 2H), 7.39 (d, 2Har, J = 8.4 Hz), 7.9 (d, 2Har, J = 8.4 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.4, 43.0, 70.5, 128.7, 129.5, 133.8, 139.8, 190.8, 212.6; MS *m/e* (relative intensity) EI 276 (M^+ + 2, 2), 274 (M^+, 4), 243 (4), 241 (12), 216 (6), 214 (16), 185 (10), 141 (32), 139 (100), 111 (27), 75 (16). Anal. Calcd for $C_{11}H_{11}O_2S_2Cl$: C, 48.09; H, 4.01; S, 23.32. Found: C, 48.27; H, 3.92; S, 23.11.

***O*-Ethyl *S*-(4-bromophenacyl) dithiocarbonate (1e):** mp 81−83 °C; IR (KBr) ν 2979, 1694, 1584, 1256, 1113, 1052, 988, 810; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.4 (t, 3H, J = 7 Hz), 4.61 (s, 2H), 4.63 (q, 2H, J = 7 Hz), 7.64 (d, 2Har, J = 8.4 Hz), 7.87 (d, 2Har, J = 8.4 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.4, 43.0, 70.5, 128.7, 129.6, 131.8, 134.2, 191.2, 212.8; MS *m/e* (relative intensity) EI 320 (M^+ + 2, 3), 318 (M^+, 3), 287 (10), 285 (10), 260 (13), 258 (13), 232 (6), 230 (6), 185 (100), 183 (100), 157 (32), 155 (32), 89 (17), 76 (32). Anal. Calcd for $C_{11}H_{11}O_2S_2Br$: C, 41.38; H, 3.45; S, 20.06. Found: C, 41.37; H, 3.65; S, 20.17.

***O*-Ethyl *S*-(2-naphthalen-2-yl-2-oxoethyl) dithiocarbonate (1f):** mp 93−94 °C; IR (KBr) ν 3051, 2981, 1691, 1624, 1591, 1347, 1212, 1054, 823; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.38 (t, 3H, J = 7 Hz), 4.63 (q, 2H, J = 7 Hz), 4.8 (s, 2H), 7.52−7.66 (m, 2Har), 7.84−8.06 (m, 4Har), 8.54 (s, 1Har); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.4, 43.3, 70.4, 123.5, 126.7, 127.5, 128.4, 128.6, 129.4, 130, 132.1, 132.8, 135.5, 191.9, 213; MS *m/e* (relative intensity) EI 290 (M^+, 3), 258 (6), 201 (4), 155 (100), 150 (18), 127 (65), 60 (19). Anal. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.07; H, 4.83; S, 22.07. Found: C, 62.11; H, 4.8; S, 21.91.

***O*-Ethyl *S*-(2-oxo-cyclohexyl) dithiocarbonate (1g):** mp 10−11 °C; IR(KBr) ν 2940, 1715, 1219, 1112, 1051; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.3(t, 3H, J = 7 Hz), 1.6−2.6(m, 8H), 4.42(m, 1H), 4.5(q, 2H, J = 7 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.3, 24.8, 27.1, 33.9, 41.4, 59.2, 69.8, 204.4, 212.5; MS *m/e* (relative intensity) EI 218 (M^+, 4), 185 (100), 157 (30), 129 (20), 97 (57), 86 (21), 67 (71), 55 (39). Anal. Calcd for $C_9H_{14}O_2S_2$: C, 49.54; H, 6.42; S, 29.36. Found: C, 49.44; H, 6.21; S, 29.52.

***O*-Ethyl *S*-(3,3-dimethyl-2-oxo-butyl) dithiocarbonate (1h):** mp 24−25 °C; IR(KBr) ν 2969, 1716, 1366, 1221, 1113, 1047, 1001; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (s, 9H), 1.29 (t, 3H, J = 7 Hz), 4.16 (s, 2H), 4.5 (q, 2H, J = 7 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.4, 26.3, 42.1, 43.9, 70.0, 206.7, 213.2; MS *m/e* (relative intensity) EI 220 (M^+,4), 187 (18), 163 (18), 135 (13), 107 (8), 85 (7), 57 (100). Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.09; H, 7.27; S, 29.09. Found: C, 48.86; H, 7.09; S, 29.39.

Despite the fact that the obtained voltammetric E_{pa} values are around +2.0 V (vs SCE), the electrochemical oxidations were carried out at +1.8 V (vs SCE) (the initial current intensity was not over 150 mA to avoid danger due to the use of $LiClO_4$ as electrolyte) using a concentric cell with two compartments separated by a porous (D3) glass tubing diaphragm and equipped with a magnetic stirrer. The solvent supporting electrolyte (SSE) was CH_3CN-H_2O (1%)/$LiClO_4$ (0.1 M). Other details: Anode: platinum; anolyte: *O*-ethyl dithiocarbonate **1** (2.0 mmol) in SSE (40 mL). Cathode: platinum; catholyte: SSE (15 mL). At the end of the electrolysis the solvent in the anodic solution was removed under reduced pressure. The residue was extracted with ether/water and the organic phase was dried over $MgSO_4$ and concentrated by evaporation. The resulting solid or oil was chromatographed on a silica gel (18 × 3 cm) column, using hexane/EtOAc (6/1) as eluent. Boiling points are given at atmospheric pressure.

***O*-Ethyl *S*-phenacyl thiocarbonate (2a):** 94% yield; bp 171−173 °C; IR (KBr) ν 3060, 2981, 1718, 1697, 1597, 1148, 750, 689; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.1 Hz), 4.21 (q, 2H, J = 7.1 Hz), 4.31 (s, 2H), 7.3−7.6 (m, 3Har), 7.8−8.0 (m, 2Har); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 14.2, 38.5, 64.1, 128.4, 128.7, 133.7, 135.5, 169.8, 193.0; MS *m/e* (relative intensity) EI 224 (M^+, 1), 105 (100), 77 (38), 51 (13). Anal. Calcd for $C_{11}H_{12}O_3S$: C, 58.93; H, 5.36; S, 14.28. Found: C, 59.11; H, 5.44; S, 14.01.

***O*-Ethyl *S*-(4-methoxyphenacyl) thiocarbonate (2b):** 95% yield; mp 40−41 °C; IR (KBr) ν 2979, 1704, 1670, 1599, 1261, 1146, 826; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, 3H, J = 7 Hz), 3.85 (s, 3H), 4.26 (q, 2H, J = 7 Hz), 4.32 (s, 2H), 6.93 (d, 2Har, J = 8.8 Hz), 7.96 (d, 2Har, J = 8.8 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 37.9, 55.2, 63.7, 113.6, 128.2, 130.5, 163.6, 169.7, 191.2; MS *m/e* (relative intensity) EI 254 (M^+, 2), 136 (9), 135 (100), 107 (6), 92 (7), 77 (9). Anal. Calcd for $C_{12}H_{14}O_4S$: C, 56.69; H, 5.51; S, 12.60. Found: C, 56.61; H, 5.72; S, 12.41.

***O*-Ethyl *S*-(4-methylphenacyl) thiocarbonate (2c):** 97% yield; mp 20−21 °C; IR (KBr) ν 2982, 1714, 1692, 1604, 1146, 806; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, 3H, J = 7 Hz), 2.37 (s, 3H), 4.24 (q, 2H, J = 7 Hz), 4.32 (s, 2H), 7.23 (d, 2Har, J = 8.1 Hz), 7.85 (d, 2Har, J = 8.1 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 21.4, 38.1, 63.8, 128.2, 129.1, 132.6, 144.4, 169.6, 192.4; MS *m/e* (relative intensity) EI 238 (M^+, 2), 193 (1), 165 (2), 120 (9), 119 (100), 105 (4), 91 (26), 77 (3), 65 (11). Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.50; H, 5.88; S, 13.45. Found: C, 60.60; H, 5.99; S, 13.23.

***O*-Ethyl *S*-(4-chlorophenacyl) thiocarbonate (2d):** 90% yield; mp 68−69 °C; IR (KBr) ν 3091, 2973, 1699, 1674, 1586, 1402, 1143, 831; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 3H, J = 7 Hz), 4.27 (q, 2H, J = 7 Hz), 4.32 (s, 2H), 7.4 (d, 2Har, J = 8.4 Hz), 7.9 (d, 2Har, J = 8.4 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 37.9, 63.9, 128.8, 129.5, 133.5, 139.9, 169.4, 191.7; MS *m/e* (relative intensity) EI 260 (M^+ + 2, 3), 258 (M^+, 2), 213 (1), 185 (3), 141 (31), 139 (100), 113 (6), 111 (18), 75 (10), 50 (3). Anal. Calcd for $C_{11}H_{11}O_3SCl$: C, 51.06; H, 4.26; S, 12.38. Found: C, 50.89; H, 4.37; S, 12.42.

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***O*-Ethyl *S*-(4-bromophenacyl) thiocarbonate (2e):** 92% yield; mp 79−80 °C; IR (KBr) ν 3091, 2973, 1699, 1677, 1580, 1174, 1142, 814; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 3H, J = 7 Hz), 4.25 (q, 2H, J = 7 Hz), 4.3 (s, 2H), 7.58 (d, 2Har, J = 8.1 Hz), 7.82 (d, 2Har, J = 8.1 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 37.9, 64, 128.6, 129.6, 131.7, 133.9, 169.4, 191.9, 212.8; MS *m/e* (relative intensity) EI 304 (M^+ + 2, 3), 302 (M^+, 3), 259 (1), 257 (1), 231 (3), 229 (3), 200 (2), 198 (2), 185 (100), 183 (100), 157 (22), 155 (22), 104 (5), 90 (7), 76 (18), 50 (12). Anal. Calcd for $C_{11}H_{11}O_3SBr$: C, 43.56; H, 3.63; S, 10.56. Found: C, 43.26; H, 3.81; S, 10.37.

***O*-Ethyl *S*-(2-naphthalen-2-yl-2-oxoethyl) thiocarbonate (2f):** 95% yield; mp 50−52 °C; IR (KBr) ν 3062, 2976, 1708, 1690, 1623, 1358, 1174, 1152, 1020, 816, 746; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, 3H, J = 7 Hz), 4.28 (q, 2H, J = 7 Hz), 4.3 (s, 2H), 7.5−7.64 (m, 2Har), 7.82−8.2 (m, 4Har), 8.5 (s, 1Har); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 38.3, 63.9, 123.5, 126.7, 127.5, 128.4, 128.6, 129.3, 130.2, 132.0, 132.4, 135.5, 169.7, 193; MS *m/e* (relative intensity) EI 274 (M^+, 7), 173 (3), 156 (12), 155 (100), 127 (47), 101 (4), 77 (6). Anal. Calcd for $C_{15}H_{14}O_3S$: C, 65.69; H, 5.11; S, 11.68. Found: C, 65.49; H, 5.16; S, 11.88.

***O*-Ethyl *S*-(2-oxocyclohexyl) thiocarbonate (2g):** 97% yield; bp 150−151 °C; IR(KBr) ν 2928, 1720, 1702, 1147, 848; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.28 (t, 3H, J = 7 Hz), 1.6−2.7 (m, 8H), 4.1−4.2 (m, 1H), 4.24 (q, 2H, J = 7 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 24.8, 27.0, 34.8, 41.2, 54.8, 63.5, 169.3, 205.1; MS *m/e* (relative intensity) EI 202 (M^+, 22), 171 (33), 130 (72), 97 (82), 83 (66), 67 (100), 55 (71). Anal. Calcd for $C_9H_{14}O_3S$: C, 53.47; H, 6.93; S, 15.85. Found: C, 53.67; H, 7.11; S, 16.07.

***O*-Ethyl *S*-(3,3-dimethyl-2-oxobutyl) thiocarbonate (2h):** 92% yield; bp 133−135 °C; IR (KBr) ν 2972, 1728, 1705, 1367, 1149, 847, 675; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (s, 9H), 1.25 (t, 3H, J = 7 Hz), 3.91 (s, 2H), 4.2 (q, 2H, J = 7 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.8, 26.1, 36.9, 43.9, 63.4, 169.5, 207.6; MS *m/e* (relative intensity) EI 204 (M^+, 3), 187 (18), 164 (1), 147 (19), 119 (8), 85 (23), 57 (100). Anal. Calcd for $C_9H_{16}O_3S$: C, 52.94; H, 7.84; S, 15.69. Found: C, 53.03; H, 8.01; S, 15.47.

***O*-Ethyl *S*-(4-chlorophenacyl) dithioperoxycarbonate (3d):** 5% yield; mp 47−49 °C; IR (KBr) ν 2956, 1730, 1673, 1587, 1147, 1091, 999, 813; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 3H, J = 7 Hz), 4.17 (s, 2H), 4.31 (q, 2H, J = 7 Hz), 7.4 (d, 2Har, J = 8.4 Hz), 7.9 (d, 2Har, J = 8.4 Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 13.9, 44.2, 65.2, 128.8, 129.7, 133.2, 139.9,168.1, 191.6; MS *m/e* (relative intensity) EI 220 (4-$ClC_6H_4COCH_2SSH$, 3), 218 (7), 186 (3), 154 (27), 141 (32), 139 (100), 113 (11), 111 (35), 75 (22), 61 (14), 50 (8). Anal. Calcd for $C_{11}H_{11}O_3S_2Cl$: C, 45.44; H, 3.79; S, 22.03. Found: C, 45.75; H, 4.01; S, 21.83.

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