SHORT PAPER

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Cathodic reduction of O-ethyl S-phenacyl dithiocarbonate

O. Picazo, B. Batanero and F. Barba*

Department of Organic Chemistry, University of Alcala, E- 28871 Madrid, Spain

The cathodic reduction of *O*-ethyl *S*-phenacyl dithiocarbonate (**1**) yields *O*-ethyl (benzoyl)-thioacetate (**2**) and *O*-ethyl *S*-[(ethoxythiocarbonyl)(phenacyl)]-dithiocarbonate (**3**) through an *Eschenmoser* process with an electrogenerated base (EGB).

In the literature there are several examples of the reduction of carbon–sulfur bonds.[1-6] A recent review by Simonet covers some new aspects of the electrochemistry of organic sulphur compounds.[7] The cathodic reduction of phenacyl xanthates, however, has not been studied. Xanthates are useful compounds in organic synthesis, the *Chugaev* reaction,[8] yielding alkenes, being a well known process. Lithium aluminium hydride reduction of β-carbonyl xanthates affords β-hydroxy mercaptans.[9] Their radical chemistry is used to promote interesting transformations.[10]

C–S bond cleavage is expected after the reduction step on *O*-ethyl *S*-phenacyl dithiocarbonate. However, bearing in mind that the enolate formed in the electrochemical step is an electrogenerated base (EGB), products due to the attack of this EGB on the acidic hydrogens on the substrate molecule and subsequent evolution of the generated anions can be expected.

The cathodic reduction of *O*-ethyl *S*-phenacyl dithiocarbonate in aprotic media (DMF) on a mercury pool cathode under a controlled potential of –1.5 V *vs* SCE was performed, yielding the following products: *O*-ethyl (benzoyl)thioacetate (**2**), (33% yield); *O*-ethyl S-[(ethoxythiocarbonyl)(phenacyl)]-dithiocarbonate (**3**), (12% yield); 1,4-diphenyl-1,4-butanedione (**4**), (18% yield) and acetophenone, (34% yield).

The first question which arises is whether *O*-ethyl–*S*-phenacyl dithiocarbonate suffers an electrochemical reduction over a carbon–sulfur bond or over a carbon-hydrogen bond given the acidic character of the hydrogens at an α position to a carbonyl group and a sulphur atom.

To answer this question, polarographic experiments were carried out on the starting material and the obtained β-oxo-thionester **2**; as the $–CH_2–$ hydrogens of the latter are more acidic than those in the former, those hydrogens should be reduced at a less negative potential than those in **1**. However, polarography showed the first reduction of **1** to occur at $E_{1/2}$ = -1.5V and the first polarographic wave of **2** at $E_{1/2}$ = –1.7V *vs* SCE. This result implies that there is no C–H bond reduction on the starting material, but a two-electron reduction of the C–S bond.

After the first electrochemical step, the lithium enolate of acetophenone is formed, which acts as an EGB, and takes a proton from another substrate molecule to give acetophenone and the anion (**a**). This anion **a** was proposed by Whitham *et al*.[11] when treating **1** with NaH in THF. Quenching with sodium dihydrogen phosphate buffer afforded **2**. They suggested a sulfide contraction process, as described and developed by *Eschenmoser.*[12]

Our electrochemical process is akin to *Eschenmoser* methodology in the use of $LiClO_4$, which acts as a complexing agent by Li^+ stabilisation of the anions evolved in the reaction.

The formation of **2** could also be explained by addition of the acetophenone enolate to the C=S bond of **1**, but in that case, phenacyl thiol, its oxidation product phenacyl disulfide or 2,5-diphenyl-1,4-dithiin (which is easily formed by reaction between two molecules of phenacyl thiol) should be formed as well. None of those compounds was detected.

The formation of the secondary product **3**, can be explained by addition of the anion **a**, to the C=S bond of **2**.

Furthermore, to confirm the *Eschenmoser* pathway, the following crossover experiment was performed: *p*-Cl-acetophenone sodium enolate (prepared by treatment of *p*-Cl-acetophenone with NaH in THF) was added to **1** in DMF. The product distribution from this reaction was the same as in the electrochemical one, and no chlorinated β-oxo-thionester was obtained. This result confirms that the *Eschenmoser* pathway occurs in the electrochemical reaction.

Additionally, acetophenone enolate acts as a nucleophile versus **1** in a nucleophilic substitution reaction, to give 1,4-diphenyl-1,4-butanedione.

Products **2** and **3** are formed by protonation of the corresponding anions when the crude reaction is poured onto ice water during work-up. In fact, the main amount of **3** is obtained in the ether extraction of the acidified aqueous phase.

The charge consumption in the reaction was slightly above 1 electron per substrate molecule.

The β-oxo-thionesters have been synthesised by several methods.[13] They are stable oils wich are extracted completely into aqueous sodium hydroxide but not into aqueous sodium carbonate. They are therefore quite acidic with pK_a values comparable with those of β-oxo-esters. Proton and ^{13}C NMR show compound **2** to be mainly in enolised form, while **3** is a mixture of enolised and non-enolised forms.

Experimental

Apparatus: Electrolyses were carried out using an Amel potentiostat Model 552 with an electronic integrator Amel Model 721. Mass spectra (EI, ionising voltage 70 eV) were determined using a Hewlett-Packard Model 5988A mass-selective detector equipped with a Hewlett-Packard MS Chem Station. I.R. spectra were obtained, as dispersions in KBr, on a Perkin-Elmer Model 583 spectrometer. ^1H NMR (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian Unity 300 apparatus with deuteriochloroform as internal standard. Chemical shifts are given in ppm. Polarography was carried out on a Metrohm apparatus Model 663 VA Stand and a Scanner 626 Polarecord. The potential values are given in volts. The products were purified on silica gel 60 (230–400 mesh) in a 5 cm diameter column, using several hexane/EtOAc mixtures as eluents.

Synthesis of the starting material: Potassium *O*-ethyl dithiocarbonate in water (3.2 g, 0.02 mol) was added slowly to 2-bromoacetophenone (4 g, 0.02 mol) in acetone yielding *O*-ethyl *S*-phenacyl dithiocarbonate in almost quantitative yield. Acetone was evaporated under reduced pressure, and the crude product was extracted with ether. The ethereal phase was dried over $MgSO_4$, filtered, and the solvent evacuated under reduced pressure yielding *O*-ethyl *S*-phenacyl dithiocarbonate as an amber solid m.p. 32 °C [Lit. [14]: 32ºC].

* To receive any correspondence.

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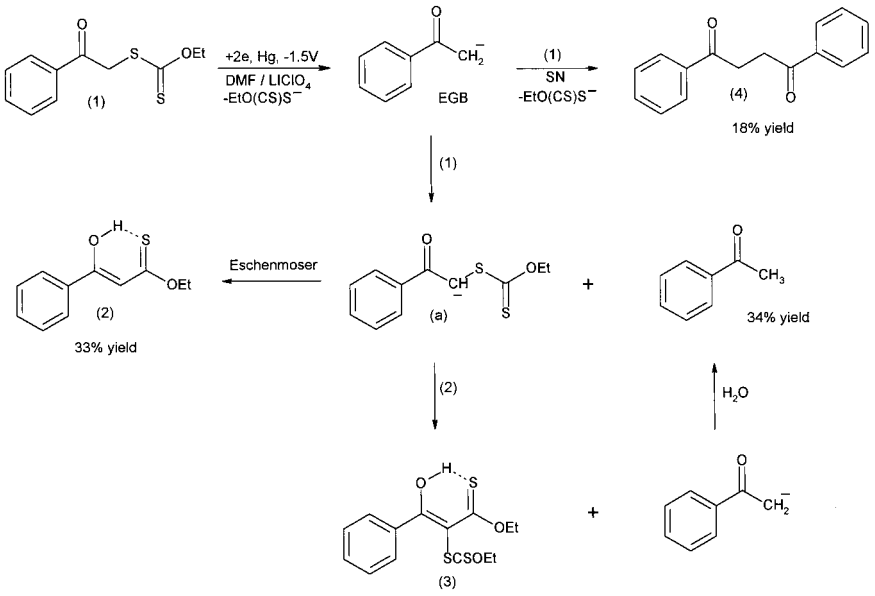

Scheme 1

General electrochemical procedure: The electrochemical reduction was carried out under the following conditions: Electrolysis cell: divided cell equipped with a magnetic stirrer containing a piece of glass tubing with a glass frit of medium porosity at one end (anodic compartment); Anode: platinum; cathode: mercury pool; reference electrode: SCE; Supporting solvent electrolyte (SSE): 1.596 g $LiClO_4$ (1.5×10^{-2} mol) in 50 cm^3 dry DMF of which 10 cm^3 were added to the anodic compartment and 40 ml to the cathodic compartment. Perchlorates are explosive compounds and appropriate caution should be taken including the avoidance of evaporation to dryness of perchlorate-containing residues. Solid sodium carbonate (2 g, 1.42 mmol) was added to the anodic compartment for *in situ* neutralisation of the generated perchloric acid. *O*-ethyl *S*-phenacyl dithiocarbonate (1.2 g , 5×10^{-3} mol) was added to the cathodic compartment. A constant cathodic potential of –1.50 V (*vs* SCE) was applied. The reaction time was about 2 h; during that time the evolution of the products in the reaction was monitored by TLC to confirm the complete consumption of the substrate.

Purification and isolation of the products: At the end of the electrolysis the DMF contained in the cathodic solution was evaporated under reduced pressure until 10–15 cm^3 of solvent were left, which were poured onto ice water. After 12h the precipitated solid was filtered, redissolved in ether and washed with water. After drying over sodium sulfate, filtering and evaporating the ether, a white solid was obtained, which was further purified by recrystallisation from ethanol yielding 1,4-diphenyl-1,4-butanedione.

The remaining cathodic solution was extracted with ether (2×100 cm^3) and chloroform (1×100 cm^3). The organic layers were combined and washed thoroughly with water in order to eliminate as much DMF as possible. After drying over sodium sulfate, the ether was stripped under vacuum and the residue purified by column chromatography. Compound **2** and acetophenone were the main products isolated from this phase.

Further treatment of the remaining aqueous layer with 50 cm^3 diluted hydrochloric acid (5% v/v) and subsequent extraction with ether yielded, after evaporation, another oily residue which was purified by column chromatography, **3** being the major product obtained.

The physical and spectroscopic data of the products obtained can be summarised as follows.

O-ethyl (benzoyl) thioacetate (**2**): (0.172 g, 33% yield). b.p. = 122–125 °C[11]. IR (KBr, cm^{-1}) : 3431, 1688, 1604, 1572, 1453, 1402, 1258, 1187, 764, 689. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) : 14.16 (s, 1H , OH), 7.43–7.49 (m, 3H, Ar), 7.82–7.86 (m, 2H, Ar), 6.37 (s, 1H, CH), 4.53–4.55 (q, 2H, –O–CH_2–), 1.44 (t, 3H, –CH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 212.9 (CS), 190.2 (CO), 134.1 (C_{ipso}), 131.2 (C_{para}), 128.2 (C_{meta}), 125.9 (C_{orto}), 100.4 (–CH–, enolised form), 65.2 (–O–CH_2), 13.7 (–CH_3). MS *m/e* (rel. inten.): 208 (M^++, 42), 207 (M^+-1, 4), 180 (10), 147 (43), 131 (76), 120 (4), 105 (100), 77 (71), 51 (22).

O-ethyl S-[(ethoxythiocarbonyl)(phenacyl)]-dithiocarbonate (**3**); (0.049 g, 12% yield). Oil. (Found: C, 51.42; H, 5.07; S, 29.29. $C_{14}H_{16}O_3S_3$ requires: C, 51–22; H, 4.88, 5, 29.27%) IR (KBr, cm^{-1}): 3434, 1691, 1599, 1574, 1447, 1367, 1299, 1234, 1187, 1047, 761, 691. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 15.32(s, 1H, –OH), 8.12–8.19 (d, 2H, Ar), 7.41–7.62 (m, 3H, Ar), 6.73 (s, 1H, CH), 4.50–4.63 (d of q, 4H, two -O-CH_2- groups), 1.32–1.43 (m, 6H, two –CH_3 groups). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 210.8 (CS, thioester group), 209.2 (CS, xanthate group), 189.2 (CO), 134.8 (C_{ipso}), 133.6 (C_{para}), 129.0 (C_{meta}), 128.4 (C_{orto}), 70.6 (–O–CH_2–), 69.4 (–O–CH_2), 68.6 (CH), 13.3 (–CH_3), 12.9 (–CH_3). MS *m/e* (rel. inten.): 328 (M^+, 0.6), 295 (4.5), 207 (27), 179 (7.6), 151 (4.2), 147 (3.4), 131 (1.9), 121 (2.4), 105 (100), 77 (44.3), 51 (9.8).

1,4-diphenyl-1,4-butanedione (**4**); (0.106 g, 18% yield). The physical and spectroscopic data were in accordance with those described in the literature.[15]

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References

1 H. Lund, *Acta Chem. Scand*., (1960), **14**, 1927.
2 T. Fuchigami, Z.E.S. Kandee and T. Nonaka, *Bull. Chem. Soc. Jap*., (1986), **59**, 338.
3 A. Kunugi, A. Muto and T. Hirai, *Bull. Chem. Soc. Jpn*., (1985), **58**, 1262.
4 B. Lamm and B. Samuelsson, *Acta Chem. Scand*. (1969), **23**, 691.
5 L. Horner and R.J. Singer, *Chem. Ber*., (1968), **101**, 3329.
6 K. Schwabe and J. Voigt, *Z. Elektrochem*., (1952), **56**, 44.
7 J. Simonet, *Supplement S: The Chemistry of sulphur-containing functional groups*, S.Patai and Z. Rappoport, (eds) John Wiley and Sons, Chichester, 1993, pp 439.
8 L.A. Chugaev, *Chem. Ber*., (1899), **32**, 3332.
9 (a) C.Djerassi, *J. Am. Chem. Soc*., (1955), **77**, 568; (b) K. Mori and Y. Nakamura, *J. Org. Chem*., 1969, **34**, 4170.
10 (a) P. Delduc, C. Tailhan and S. Z. Zard, *J. Chem. Soc. Chem. Commun*., (1988), 308; (b) D.H.R. Barton, S.I. Parekh and C. Tse, *Tetrahedran Lett*., (1993), **34**, 2733; (c) D. Crich and L. Quintero, *Chem. Rev*., (1989), **89**, 1413.
11 A.J. Bridges and G.H. Whitham, *J.C.S. Perkin I*, (1975), 1603.
12. M. Roth, P. Dubs, E. Götschi and A. Eschenmoser, *Helv. Chim. Acta*, (1971), **54**, 710.
13 G. Barnikov and G. Strickmann, *Chem. Ber*., (1967), **100**, 1428. Ref. 11; S. Scheithauer and H. Pech, Ger. (East) Pat., 94 361 (1972); *Chem. Abstr*., (1973), **79**, 5176.
14 B. Groth. *Arkiv Kemi*., (1924), 9, **63**.
15 *Dictionary of Organic Compounds*, 5th edn; Chapman and Hall: New York, 1982; Vol.2, p 2301 and references cited therein.