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RESEARCH ARTICLE

Reactions of dimethoxycarbene with xanthates

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Dimethoxycarbene (DMC), generated by thermolysis of 2,2-dimethoxy-5,5-dimethyl–Δ^3-1,3,4-oxadiazoline at 110 °C, in benzene in a sealed tube, reacted with most xanthates by formal insertion of the carbene into the S=C−SR single bond. The reaction course is probably attack of the carbene at carbon of the C=S function, concomitant with (or followed by) migration of the SR group. The products, all new, are mixed orthoesters (two methoxy and one SR at the same carbon), a functional group that has been reported for one case only. In the case where the R group was CO_2Me, the reaction became complicated, probably from initial attack at the carbonyl group.

Keywords: Dimethoxycarbene; Oxadiazole; Thiocarbonyl compounds; Xanthate; Orthoester

1. Introduction

Reactions of dimethoxycarbene (DMC) with some thiocarbonyl compounds at 110 °C were reported recently [1–4]. DMC reacts with a variety of thiocarbonyl compounds to afford thiiranes and/or products of rearrangement. The latter include ring-expansion products and compounds in which DMC appears to have inserted into a bond alpha to the thiocarbonyl group. Dimethyl xanthate is in the latter category, and afforded the product of insertion of DMC into the S=C-SR single bond [2].

We now report reactions of a variety of additional xanthates with DMC at 110 °C to show that the reaction observed with MeOC(=S)SMe has some generality. The products may be of considerable interest in that an unusual functional group is generated; an orthoester with two methoxy and one SR group at the same carbon atom. Although 'xanthate' is the generic term for alkylated adducts of an alkoxide and CS_2, the IUPAC name of specific compounds is used in the Experimental section.

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2. Methods, results, and discussion

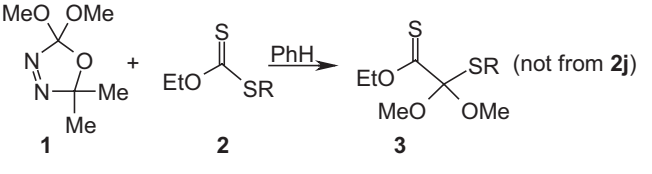
Xanthates (**2**) were readily prepared by reaction of potassium ethoxide with CS_2 and subsequent alkylation or acylation [5, 6]. Alkylating or acylating agents were chosen to produce the xanthates in scheme 1. DMC was generated by thermolysis of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**) (also known as 2,5-dihydro-2,2-dimethoxy-5,5-dimethyl-1,3,4-oxadiazole) in benzene, in a sealed tube, at 110 °C. One of the xanthates **2** (*ca.* 1.5 equivalents) was present also, scheme 1. Thermolysis of an oxadiazoline probably involves two steps, a cycloreversion to afford N_2 and a very short-lived carbonyl ylide (**4**), followed by fragmentation of the ylide to acetone and DMC (**5**) [7].

In general, the nucleophilic DMC reacted with a xanthate to afford the product of insertion (**3**) into the C(=S)−SR single bond, scheme 1. The mechanism by which insertion occurs is not known at this time. Electrophilic carbenes normally react with thiocarbonyl compounds to afford thiocarbonyl ylides, such as **6**, initially [8, 9]. Such an ylide should cyclize to the thiirane **7**, which was not found but which can be imagined to open homolytically to diradical **9**. Rearrangement of **9** would then afford **3**. The latter mechanism is currently considered to be unlikely because two dimethoxythiiranes, one from adamantanethione and DMC, have been reported. The one from adamantanethione appeared to be quite stable, even at 110 °C in benzene [4].

Insertion is most easily visualized in terms of a zwitterionic mechanism, *via* rearrangement of **8**. Nucleophilic additions and substitutions at carbonyl carbon are believed to occur by a stepwise mechanism, in general, with addition to form a tetrahedral intermediate as the first step [10]. Insertion in the case of xanthates and DMC could occur similarly, with initial addition to form **8** followed by migration of the singly-bonded sulfur substituent, scheme 2.

Although insertion is most easily visualized in terms of intermediate **8**, there are other possibilities because the erstwhile carbene carbon becomes a positive site as addition progresses. Migration could therefore occur late in the addition process, making the insertion concerted but asynchronous [4], avoiding an actual zwitterionic intermediate, such as **8**, but with charge separation like that in **8** (scheme 2).

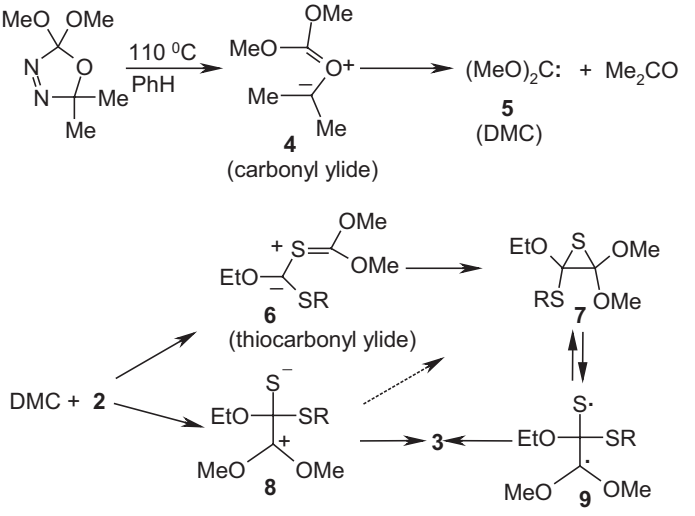
In the case of **2j**, initial attack appears to have occurred primarily at the carbonyl carbon instead of the thiocarbonyl carbon, in keeping with the finding by Hoffmann's group [11] that phenyl isocyanate is more reactive than phenyl isothiocyanate toward DMC. In the case of **2j** the methoxycarbonyl group was lost and the rest of the molecule was isolated as a solid that turned gradually to liquid on exposure to air. Those properties, and the spectra, are in keeping with initial formation of the xanthic acid (**10**), which oxidized slowly in air to afford diethyl dixanthogen (**11**), scheme 3 [12]. There is also a precedent for the greater reactivity of the carbonyl group in a compound containing both the carbonyl and the thiocarbonyl groups [3].



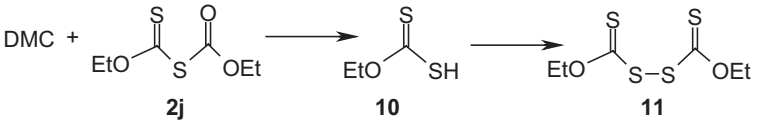
1 **2** **3**

2a: R= Me; **b**: R= Et; **c**: R= *n*-Pr; **d**: R= CH_2CN ;
e: R= CH_2CH_2CN; **f**: R= CH_2CO_2Et; **g**: R= $CH_2CH{=}CH_2$;
h: R= CH_2CH_2OMe; **i**: R= $CH_2C_6H_4Br(o)$; **j**: R= CO_2 Me

SCHEME 1



SCHEME 2



SCHEME 3

3. Summary

Most xanthates reacted with dimethoxycarbene, at 110 °C in benzene, by overall insertion of the carbene into the S=C−SR single bond. Although yields were not optimized, they were generally higher for xanthates with an electron-withdrawing group in R, suggesting that migration of the SR group involves some accumulation of negative charge in that group. A xanthate with a carbonyl group at the carbon atom bearing the dicoordinate sulfur gave products indicative of initial attack at the carbonyl group instead of the thiocarbonyl group.

4. Experimental

4.1 *General*

NMR spectra were recorded with Bruker DXR-500 or AC-200 spectrometers. Chemical shifts for ^{1}H NMR spectra were measured using C_6HD_5 in C_6D_6 ($\delta = 7.15$ ppm) or residual $CHCl_3$ in $CDCl_3$ ($\delta = 7.26$ ppm) as internal references. ^{13}C NMR spectra were referenced to the chloroform-*d* triplet ($\delta = 77.16$ ppm) or benzene-d_6 triplet ($\delta = 128.0$ ppm). Mass spectra were taken with a Micromass (Waters) GCT, TOF mass spectrometer, with ammonia for CI spectra. The FTIR spectrum of **3f** was obtained with a Bio-Rad, FTS-40 instrument. The C=S absorption band of xanthates [13], between 1020 and 1070 cm^{-1}, is not generally a useful criterion of structure because other bands appear in that frequency range. Benzene

was distilled from calcium hydride or benzophenone ketyl. Chromatography solvents (ethyl acetate and light petroleum, distillation range 30–60 °C) were distilled before use.

4.2 *Preparation of oxadiazoline (1) and xanthates (2)*

4.2.1 Preparation of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (1). Compound **1** was prepared by the oxidation of the (methoxycarbonyl)hydrazone of acetone with lead tetraacetate or iodobenzene diacetate in methanol according to previously published methods [14–16].

4.2.2 Preparation of dithiocarbonic acid O,S-diesters (xanthates). Dithiocarbonic acid, O,S-diesters were prepared according to standard literature procedures [5], in overall yields ranging from 44 to about 90%. Although most of them are known, NMR spectra are reported because they are not generally included in the references.

4.2.3 Dithiocarbonic acid *O*-methyl ester *S*-methyl ester. This xanthate, and the product of its reaction with DMC, have been described [2].

4.2.4 Dithiocarbonic acid *O*-ethyl ester *S*-methyl ester (2a). Yellow oil [17]. Yield 44%, bp 68–71 °C (14 Torr). ^{1}H NMR (200 MHz; C_6D_6) δ 0.92 (t, $J = 7.1$ Hz, 3H), 2.14 (s, 3H), 4.31 (q, $J = 7.1$ Hz, 2H); ^{1}H NMR (200 MHz; $CDCl_3$) δ1.41 (t, $J = 7.1$ Hz, 3H), 2.54 (s, 3H), 4.64 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; C_6D_6) δ 13.6, 18.8, 69.9, 216.1; ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.9, 19.0, 70.1, 215.9; GCMS (EI) m/z (rel. intensity) 138 $(M+2)^+$ (9), 137 $(M+1)^+$ (6), 136 (M^+, 97), 108 $(M - H_2C{=}CH_2)^+$ (6), 91 $(M - CH_3CH_2O)^+$ (45), 76 (45), 61 (42), 47 (63), 45 (100).

4.2.5 Dithiocarbonic acid *O*-ethyl ester *S*-ethyl ester (2b). Yellow oil [17]. Yield 51%, ^{1}H NMR (200 MHz; C_6D_6) δ 0.92 (t, $J = 7.1$ Hz, 3H), 1.02 (t, $J = 7.4$ Hz, 3H), 2.84 (q, $J = 7.4$ Hz, 2H), 4.31 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50 MHz; C_6D_6) δ 13.4, 13.6, 30.4, 69.7, 215.3; MS (EI) m/z 150 (M^+, 20); CI (NH_3) 151 [$(M + H)^+$, 100].

4.2.6 Dithiocarbonic acid *O*-ethyl ester *S*-propyl ester (2c). Yellow oil [18]. Yield 55%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.01 (t, $J = 7.3$ Hz, 3H), 1.41 (t, $J = 7.1$ Hz, 3H), 1.75 (sextet, $J = 7.3$ Hz, 2H), 3.09 (t, $J = 7.3$ Hz, 2H), 4.64 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; C_6D_6) δ 13.4, 13.6, 22.1, 38.1, 69.7, 215.5.

4.2.7 Dithiocarbonic acid *S*-cyanomethyl ester *O*-ethyl ester (2d). Yellow oil [19]. Yield 90%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.47 (t, $J = 7.1$ Hz, 3H), 3.89 (s, 2H), 4.71 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.7, 21.3, 72.0, 115.4, 209.0.

4.2.8 Dithiocarbonic acid *S*-(2-cyanoethyl) ester *O*-ethyl ester (2e). Yellow oil [20]. Yield 83%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.43 (t, $J = 7.1$ Hz, 3H), 2.82 (t, $J = 7.0$ Hz, 2H), 3.37 (t, $J = 7.0$ Hz, 2H), 4.65 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.8, 17.6, 31.1, 70.8, 117.9, 212.7.

4.2.9 Ethoxythiocarbonylsulfanylacetic acid ethyl ester (2f). Yellow oil [21]. Yield 49%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.28 (t, $J = 7.1$ Hz, 3H), 1.41 (t, $J = 7.1$ Hz, 3H), 3.90 (s, 2H), 4.21 (q, $J = 7.1$ Hz, 2H), 4.63 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.8, 14.2, 62.0, 70.7, 168.0, 212.7.

4.2.10 Dithiocarbonic acid *S*-allyl ester *O*-ethyl ester (2g). Yellow oil [22]. Yield 86%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.41 (t, $J = 7.1$ Hz, 3H), 3.77 (d, $J = 6.9$ Hz, 2H), 4.64 (q, $J = 7.1$ Hz, 2H), 5.14–5.32 (m, 2H), 5.77–5.95 (m, 1H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.9, 38.8, 70.1, 118.9, 131.9, 214.0.

4.2.11 Dithiocarbonic acid *O*-ethyl ester *S*-(2-methoxyethyl) ester (2h). Yellow oil. Yield 62%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.42 (t, $J = 7.1$ Hz, 3H), 3.35 (t, $J = 6.5$ Hz, superimposed on s at 3.38, 5H), 3.63 (t, $J = 6.5$ Hz, 2H), 4.65 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.9, 35.4, 58.8, 70.2, 214.7 (the $OCH_2{}^{13}C$ signals are coincident at 70.2 ppm); MS (CI, NH_3) m/z 181 $(M + H)^+$.

4.2.12 Dithiocarbonic acid *S*-(2-bromobenzyl) ester *O*-ethyl ester (2i). Yellow oil. Yield 55%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.42 (t, $J = 7.1$ Hz, 3H), 4.49 (s, 2H), 4.66 (q, $J = 7.1$ Hz, 2H), 7.10–7.29 (m, 2H), 7.47–7.58 (m, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.9, 40.8, 70.3, 124.9, 127.6, 129.4, 131.3, 133.0, 135.5, 213.7; MS (CI, NH_3) 294, 292 $(M + H)^+$.

4.2.13 Thiodicarbonic acid *O*-ethyl S-methyl ester (2j). The ^{1}H NMR spectrum of **2i** was in good agreement with that published [17].

4.3 *Reaction of DMC with xanthates*

In a typical procedure, a solution of oxadiazoline **1** (100 mg, 0.630 mmol) and a xanthate **2** (0.945 mmol) in dry benzene (6 mL) was sealed into a 25 mL thermolysis tube after freeze/pump/thaw degassing. The tube and its contents were heated in an oil-bath (110 $\pm$ 0.1 °C) for 20 h. The tube was then opened, the volatiles were removed with a rotary evaporator, and the residue was subjected to centrifugal chromatography (Chromatotron, 2 mm SiO_2 plate) with 30–60 °C light petroleum/ethyl acetate as eluent.

4.3.1 Dimethoxy(methylsulfanyl)thioacetic acid *O*-ethyl ester (3a). Pale yellow oil. Yield 26%, ^{1}H NMR (600 MHz; C_6D_6) δ 1.00 (t, $J = 7.1$ Hz, 3H), 1.91 (s, 3H), 3.17 (s, 6H), 4.30 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (150.9 MHz; $CDCl_3$) δ 13.6, 51.4, 69.1, 111.3, 210.7; a gradient HSQC spectrum showed that the signal at 13.6 ppm in the ^{13}C NMR spectrum is from coincident absorption by the CH_3CH_2 and SCH_3 groups. In C_6D_6 there were two signals, at 13.3 and 13.5 ppm; HRMS Calc'd for $C_7H_{15}O_3S_2$ $(M + H)^+$: 211.0463. Found: 211.0456.

4.3.2 Dimethoxy(ethylsulfanyl)thioacetic acid *O*-ethyl ester (3b). Pale yellow oil. Yield 35%, ^{1}H NMR (500 MHz; C_6D_6) δ 1.01 (t, $J = 7.1$ Hz, 3H), 1.04 (t, $J = 7.5$ Hz, 3H), 2.60 (q, $J = 7.5$ Hz, 2H), 3.20 (s, 6H), 4.32 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.9 MHz; C_6D_6) δ 13.3, 14.3, 25.0, 50.9, 68.6, 110.6, 211.6; HRMS (CI, NH_3) m/z Calc'd for $C_8H_{17}O_3S_2$ $(M + H)^+$: 225.0619. Found: 225.0614.

4.3.3 Dimethoxy(propylsulfanyl)thioacetic acid *O*-ethyl ester (3c). Yellow oil. Yield 35%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 0.94 (t, $J = 7.3$ Hz, 3H), 1.49 (m, 5H), 2.53 (t, $J = 7.3$ Hz, 2H), 3.39 (s, 6H), 4.65 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 13.8, 22.6, 32.6, 51.4, 69.1, 111.5, 211.6; MS (CI, NH_3) m/z 239 $(M + H)^+$; HRMS (CI, NH_3) m/z Calc'd for $C_9H_{19}O_3S_2$ $(M + H)^+$: 239.0776. Found: 239.0772.

4.3.4 Cyanomethylsulfanyl(dimethoxy)thioacetic acid *O*-ethyl ester (3d). Pale yellow oil. Yield 88%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.46 (t, $J = 7.1$ Hz, 3H), 3.84 (s, 2H), 3.44 (s, 6H), 4.65 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 15.7, 52.4, 69.9, 112.2, 117.0, 209.6; MS (CI, NH_3) m/z 236 $(M + H)^+$; HRMS Calc'd for $C_8H_{14}NO_3S_2$ $(M + H)^+$: 236.0415. Found: 236.0409.

4.3.5 (2-Cyanoethylsulfanyl)dimethoxythioacetic acid *O*-ethyl ester (3e). Pale yellow oil. Yield 87%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.46 (t, $J = 7.1$ Hz, 3H), 2.65 (t, $J = 7.2$ Hz, 2H), 2.88 (t, $J = 7.2$ Hz, 2H), 3.41 (s, 6H), 4.65 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 18.8, 26.6, 51.8, 69.5, 111.5, 118.4, 210.6; MS (CI, NH_3) m/z 250 $(M + H)^+$; HRMS Calc'd for $C_9H_{16}NO_3S_2$ $(M + H)^+$: 250.0572. Found: 250.0563.

4.3.6 [Ethoxythiocarbonyl(dimethoxy)methylsulfanyl]acetic acid ethyl ester (3f). Pale yellow oil. Yield 72%, IR (neat) ν 1736; ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.22 (t, $J = 7.1$ Hz, 3H), 1.45 (t, $J = 7.1$ Hz, 3H), 3.37(s) and 3.39 (s, total 8H), 4.14 (q, $J = 7.1$ Hz, 2H), 4.62 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 14.3, 33.1, 51.8, 61.6, 69.4, 111.5, 169.6, 210.0; HRMS Calc'd for $C_{10}H_{19}O_5S_2$ $(M + H)^+$: 283.0674. Found: 283.0669.

4.3.7 Allylsulfanyl(dimethoxy)thioacetic acid *O*-ethyl ester (3g). Pale yellow oil. Yield 88%, ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.45 (t, $J = 7.1$ Hz, 3H), 3.22 (d, $J = 6.9$ Hz, 2H), 3.39 (s, 6H), 4.64 (q, $J = 7.1$ Hz, 2H), 5.03 (d, $J = 9.9$ Hz, 1H), 5.17 (d, $J = 16.9$ Hz, 1H), 5.68–5.89 (m, 1H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 33.8, 51.5, 69.2, 111.4, 117.7, 133.4, 211.3. We were unable to get a high-resolution mass spectrum of **3g**.

4.3.8 Dimethoxy-(2-methoxyethylsulfanyl)thioacetic acid *O*-ethyl ester (3h). Yellow oil. Yield 15%, after repeated chromatography; ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.45 (t, $J = 7.1$ Hz, 3H), 2.78 (t, $J = 6.5$ Hz, 2H), 3.33 (s, 3H), 3.39 (s, 6H), 3.50 (t, $J = 6.5$ Hz, 2H), 4.64 (q, $J = 7.1$ Hz, 2H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 30.3, 51.5, 58.8, 69.2, 71.5, 111.4, 211.4; HRMS Calc'd for $C_9H_{19}O_4S_2$ $(M + H)^+$: 255.0725. Found: 255.0719.

4.3.9 (2-Bromobenzylsulfanyl)dimethoxythioacetic acid *O*-ethyl ester (3i). Pale yellow oil. Yield 80%; ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.43 (t, $J = 7.1$ Hz, 3H), 3.36 (s, 6H), 3.88 (s, 2H), 4.63 (q, $J = 7.1$ Hz, 2H), 7.05–7.54 (m, 4H); ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.6, 35.6, 51.6, 69.3, 111.9, 124.9, 127.5, 128.9, 131.4, 132.9, 136.9, 211.1; MS (CI, NH_3) m/z 335 and 333 [(M - OMe)$^+$ 1%)], 277 and 275 [(M-C(=S)OEt)$^+$, 3)], 171 and 169 ($C_7H_6Br^+$, 60), 163 [EtO(C=S)C(OMe)$_2^+$, 100]; HRMS Calc'd for $C_{13}H_{17}O_3S_2{}^{79}Br$: 363.9802. Found: 363.9790.

4.4 *Dithiocarbonic acid O-ethyl ester (9) and 3,8-dioxa-5,6-dithiadecane-4,7-dithione (10)*

Reaction of **2j** with DMC from **1** gave dithiocarbonic acid *O*-ethyl ester (also known as ethyl xanthic acid) (**9**) [23] (30%) as a colourless solid; ^{1}H NMR (200 MHz; $CDCl_3$) δ 1.47 (t, $J = 7.1$ Hz, 3H), 2.04 (s, 1H), 4.67 (q, $J = 7.1$ Hz, 2H). Upon storage in air for a few days the sample had oxidized and liquefied to 3,8-dioxa-5,6-dithiadecane-4,7-dithione [also known as *O*,*O*-diethyl dithiobis(thioformate) or diethyl dixanthogen] (**10**) [12], scheme 3; ^{13}C NMR (50.3 MHz; $CDCl_3$) δ 13.7, 71.2, 204.9; MS (CI, NH_3) m/z 242 (M^+, 1%), 210 [$(M\text{-}S)^+$, 35)].

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