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Tetrahedron Letters 46 (2005) 1395-1397

Tetrahedron Letters

## Tetracyanoethylene oxide not only oxidizes sulfides to sulfoxides but also reduces sulfoxides to sulfides

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Received 21 December 2004; revised 7 January 2005; accepted 13 January 2005 Available online 25 January 2005

Abstract—It was found that tetracyanoethylene oxide not only oxidizes sulfides to sulfoxides but also reduces sulfoxides to sulfides with generation of two molecules of carbonyl cyanide. The reaction thus also functions as a new method for generation of carbonyl cyanide.

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Here we report that tetracyanoethylene oxide (TCNEO) reduces sulfoxides to sulfides with liberation of two molecules of carbonyl cyanide (COCN) (Scheme 1). Previously, the following have been reported on the reactions of TCNEO with sulfides.<sup>1,2</sup> TCNEO reacts with sulfides, with liberation of COCN, to furnish the corresponding sulfur ylides in 36–80% yields.<sup>2b</sup> In addition, the reaction gives rise to the corresponding sulfoxides as by-product in less than 40% yield with liberation of tetracy-anoethylene (TCNE),<sup>2b</sup> that is, TCNEO also acts as an oxidizing agent toward sulfides (Scheme 2). Therefore the present findings meet with an interesting paradox that TCNEO not only oxidizes sulfides.

It is known that TCNEO thermally equilibrates with the carbonyl ylide 4 that functions as a typical 1,3-dipole.<sup>3</sup> For our interest in 3,4-di-*tert*-butylthiophene 1-oxide (1) as a 1,3-dipolarophile,<sup>4</sup> we have examined the reaction of 1 with TCNEO in refluxing toluene. The reaction failed to give the expected 1,3-dipolar cycloadduct of 1



Scheme 1.

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with 4, but instead gave 3,<sup>5</sup> the Diels–Alder adduct of 1 with COCN, in 52% yield.<sup>4</sup> Thiophene 2, reduction product of 1, was also formed in 27% yield. These results can be explained by assuming that TCNEO reduced 1 to give 2 and COCN, and then the resulting COCN underwent the Diels–Alder reaction with 1 to furnish 3 (Scheme 3). We therefore investigated the reaction of TCNEO with sulfoxides in more detail.

The reaction of TCNEO with the simplest sulfoxide DMSO was investigated initially. Reportedly, TCNEO reacts with dimethyl sulfide in ether to give ylide **5** in better than 80% yield.<sup>2a</sup> Re-examination of the reaction in CDCl<sub>3</sub> at room temperature revealed that the reaction is completed within 5 h to give DMSO in 3% yield as a by-product together with **5** in 84% yield.<sup>6</sup> On the other hand, the reaction of TCNEO with DMSO was sluggish. The reaction in CDCl<sub>3</sub> at room temperature for 8 h gave **5** in 8% yield and a trace amount of dimethyl sulfide, and for 6 days gave **5** in 47% yield and a trace amount of dimethyl sulfide.<sup>6</sup> Therefore TCNEO reduces DMSO, though slowly, to dimethyl sulfide, which is quickly





*Keywords*: Oxidation and reduction; Sulfur ylide; Carbonyl cyanide; Sulfide; Sulfoxide.

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converted to **5** by TCNEO. Thus the whole results would be depicted as shown in Scheme 4. The COCN, produced by the two reactions shown in Scheme 4, was trapped by [2+4] cycloaddition with a diene. Thus when TCNEO (0.28 mmol) and DMSO (0.12 mmol) was heated in the presence of excess 2,3-diphenyl-1,3-butadiene,<sup>7</sup> the adduct **6**<sup>5</sup> was obtained in good isolated yield (0.19 mmol)<sup>8</sup> (Scheme 5). The reaction thus provides a new method for generation of COCN.<sup>9</sup>

The reaction of TCNEO with thioanisole in  $\text{CDCl}_3$  at room temperature for 6.5 h produced methyl phenyl sulfoxide and ylide 7 in 6% and 73% yields, respectively, with 21% recovered starting sulfide (Scheme 5). Meanwhile the reaction of TCNEO with methyl phenyl sulfoxide under the same conditions for 6 days gave 7 in 38% yield and a trace amount of methyl phenyl sulfide with 61% recovered starting sulfoxide. When the reaction of TCNEO with the sulfoxide was carried out in the presence of the diene, the adduct **6** was obtained in good yield.<sup>7</sup>

For diaryl sulfides, oxidation (sulfoxide formation) predominates over ylide formation. Thus heating an equimolar mixture of di-p-tolyl sulfide and TCNEO in refluxing benzene for 0.5 h produced di-p-tolyl sulfoxide and ylide 8 in 54% and 18% yield, respectively, with 28% recovered starting sulfide, while an equimolar mixture of di-p-tolyl sulfoxide and TCNEO under the same conditions gave di-*p*-tolyl sulfide and **8** in 44% and 8% yields, respectively, with 48% recovered sulfoxide (Scheme 6). These tell us that the use of excess TCNEO for the reaction with the sulfide would increase the yield of 8 since the resulting sulfoxide is re-converted to the sulfide and then converted to 8 by TCNEO. The same will be true for the reaction of TCNEO with the sulfoxide. Thus, heating di-p-tolyl sulfide with 5 M amounts of TCNEO gave 8 and di-p-tolyl sulfoxide in 59% and 25% yields, respectively, with 16% recovered sulfide, and heating di-p-tolyl sulfoxide with 5 M amounts of TCNEO gave 8 and di-p-tolyl sulfide in 55% and 18% vields with 26% recovered sulfoxide (Scheme 6). Accordingly, similar-ratio mixtures of di-p-tolyl sulfide, di-p-tolyl sulfoxide, and 8 become obtainable, when TCNEO was used in excess, whether the starting material is the sulfide or the sulfoxide. Similar results were also obtained for the reaction of TCNEO with diphenyl sulfide or diphenyl sulfoxide; also for this case, the adduct 6 was obtained in good yield in the presence of the diene. Heating a 2:1 mixture of TCNEO and dibenzothiophene S-oxide gave dibenzothiophene in 74% yield with recovery of a small amount of the S-oxide,<sup>10</sup> thereby giving 6 in good yield in the presence of the diene.















## Scheme 7.

For the reduction, we propose a mechanism that involves a zwitterion intermediate A, which produces sulfide and two molecules of COCN by a simultaneous cleavage of the C-C and O-S bonds (Scheme 7).<sup>11</sup> On the other hand, a mechanism that involves a zwitterion **B** as a common intermediate is proposed for the formation of ylide and sulfoxide, where we assume that **B** is in equilibrium with sulfurane C. Thus, ylide and COCN are produced by C–C bond cleavage of **B**, while sulfoxide and TCNE are given by a simultaneous C–O and C– S bond cleavage of C (path a) or through C-C bond cleavage of zwitterion **D** (path b). The zwitterions **A** and **B** would be formed by electrophilic attack of TCNEO on the sulfoxide oxygen and the sulfide sulfur, respectively, and not by electrophilic attack of the thermally-formed ylide 4, because both sulfides and sulfoxides react with TCNEO even at room temperature, though slowly for sulfoxides, and seemingly TCNEO equilibrates with 4 only when heated.<sup>3</sup>

## **References and notes**

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- 4. For cycloaddition chemistry of 1, see: Nakayama, J. J. Synth. Org. Chem. Jpn. 2003, 61, 1106, and references cited therein.
- 5. Compound **3**: mp 184 °C (dec); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  1.33 (s, 9H), 1.37 (s, 9H), 5.03 (d, J = 1.9 Hz, 1H); 5.93 (d, J = 1.9 Hz, 1H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  31.4, 32.1, 34.5, 35.1, 64.5, 75.1, 102.0, 109.8, 112.8, 144.5, 147.2; IR (KBr) 2248, 1110, 1089 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S: C, 61.61; H, 6.89; N, 9.58. Found: C, 61.48; H, 6.93; N, 9.53. Compound **6**: mp 99–101 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  3.24 (t, J = 2.3 Hz, 2H), 4.71 (t, J = 2.3 Hz, 2H), 6.99–7.04 (m, 4H), 7.12–7.20 (m, 6H); <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  39.1, 63.3, 67.3, 112.7, 127.0, 127.7, 128.0, 128.3, 128.4, 128.5, 128.8, 133.2, 135.6, 138.1; IR (KBr) 2248 (C=N) cm<sup>-1</sup>. HRMS (EI, 70 eV) calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O: 286.1106. Found: 286.1106.
- Progress of the reactions was monitored by <sup>1</sup>H NMR and the yields were determined by <sup>1</sup>H NMR analysis.
- 7. The reaction was carried out in refluxing acetonitrile, where the reduction of DMSO to dimethyl sulfide took place in a practical rate.
- Note that COCN is produced by both reduction of DMSO to dimethyl sulfide and ylide formation from the resulting sulfide; theoretically, three molecules of COCN are produced from two molecules of TCNEO.
- 9. Carbonyl cyanide is most conveniently prepared by reaction of TCNEO with dibutyl sulfide; Martin, E. L. *Org. Synth. Coll. Vol.* **1988**, *6*, 268, see also Ref. 2a.
- 10. The corresponding ylide might be seemingly formed, but could not be isolated.
- 11. Proposed intermediates such as **A–D** would be short-lived; any intermediates could not be detected by <sup>1</sup>H NMR.