**Tetrahedron Letters No. 42, pp 3589 - 3590, 1975. Pergamon Press. Printed in Great Britain.**

# SYNTHESIS OF A SULFUR-BRIDGED BINUCLEAR OXOCARBON ACID

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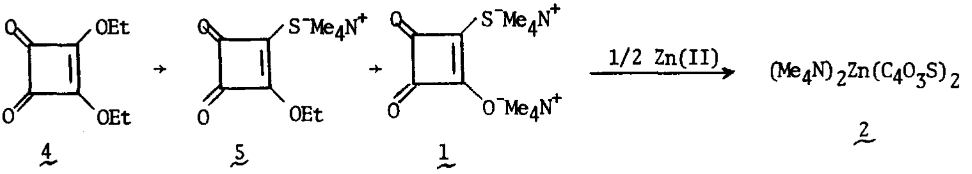
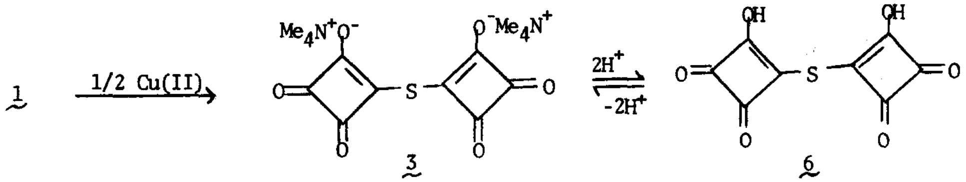
**(Received in USA 24th June 1975; received in UK for publication 9th September 1975)**

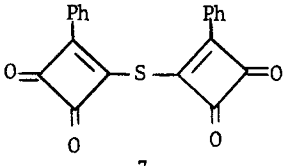
Earlier we reported the syntheses of the dithio- and monothiosquarate (1) dianions.[1] The dithiosquarate ion has been shown to form interesting coordination compounds with transition metal ions[1,2] and we find that an analogous ternary compound (2) is readily formed from 1 and zinc(II). In contrast, the reaction of 1 as its tetramethylammonium salt with copper(II) gives tetramethylammonium 2,2'-thiobis(3,4-dioxocyclobuten-1-olate) (3), a unique sulfur-bridged binuclear oxocarbon anion.

Compound 1 was prepared as previously reported from diethyl squarate (4) via tetramethylammonium 3-ethoxycyclobutenedione-4-thiolate (5).[1] An aqueous solution of 1 and copper(II) chloride (1/2 equiv) was heated at reflux for one hour. Evaporation of water left a black, CuS-containing residue from which 3 was extracted with methanol. Recrystallization from methanol gave yellow crystals of pure 3 in ca 80% yield,[3] mp 290° d. The ir spectrum of 3 (KBr) has bands at 1745(s), 1700(s) and 1590-1610 $cm^{-1}$(vs,br), and the uv-vis spectrum in water has $\lambda_{max}$ 413 nm (log $\varepsilon$ = 3.44), 340(4.25), 252(4.27) and 214(4.19).

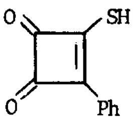




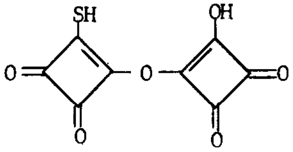
The structure of **3** is indicated by characterization of **6**, its conjugate acid. Treatment of a concentrated solution of **3** with cold 12 *N* aqueous hydrochloric acid yields 2,2'-thiobis-(3,4-dioxocyclobuten-1-ol) (**6**) which crystallizes as a dihydrate, dec 125°. Titration of **6** with aqueous base indicates an equivalent wt of 131.2 (calcd for loss of two protons from $C_8H_6O_8S$: 131.1). The uv-vis spectrum of **6** in water is identical to that of **3** when extinction coefficients are calculated from the dihydrate formula wt. High resolution mass spectroscopy shows a parent peak for unhydrated **6** at m/e 225.9572 (calcd for $C_8H_2O_6S$, 225.9572). The ir spectrum of **6** has bands at 1815, 1790 and 1735 $cm^{-1}$, consistent with the carbonyl frequencies at 1810, 1770 and 1750 $cm^{-1}$ reported for compound **7**.[4] Compound **8** is reported to have a strong S-H band at 2490 $cm^{-1}$.[5] Since **6** shows only a broad O-H band centered at *ca* 3000 $cm^{-1}$ and a sharper band at 3470 $cm^{-1}$, an oxygen-bridged structure such as **9** is ruled out.



**7**



**8**



**9**

The $pK_1$ of squaric acid has been found to be 0.5.[6] Compound **6** is also an extremely strong acid. The uv-vis spectrum of **6** in 0.1 *N* hydrochloric acid is nearly identical to that of **3** or **6** in water. In 2.0 *N* hydrochloric acid, the intensity of the band at 413 nm is reduced to about half the initial intensity, suggesting that **6** has a pK less than zero.

Acknowledgement. This work was supported by a grant from the National Science Foundation.

## References and Notes

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3. Satisfactory analytical data has been obtained for **3** and **6**.
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