

OXIDATION OF THIOACETALS WITH DDQ

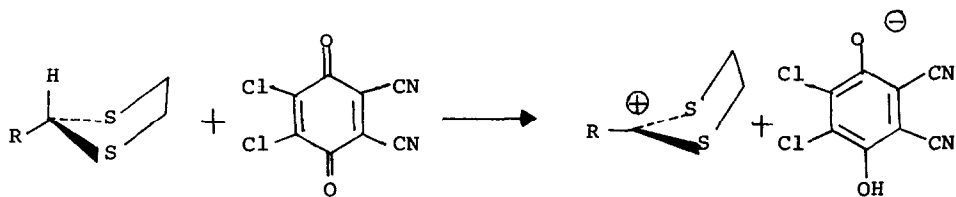
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(Received in USA 5 March 1969; received in UK for publication 29 April 1969)

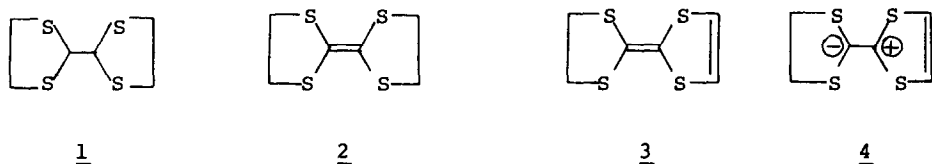
Oxidation with quinones of high reduction potential provides many molecular systems which are virtually inaccessible by other methods of synthesis. The efficacy of 2,3-dichloro-5,6-dicyano-quinone (DDQ) in effecting these hydride-abstraction oxidations generally makes it the reagent of choice (1).

We wish to report that on exposure to DDQ, certain thioacetals undergo oxidation according to the reaction:



The products derivable from this reaction depend on the nature of the substituent R. When possible, loss of a proton from the β -carbon atom occurs leading to ketene thioketals (2).

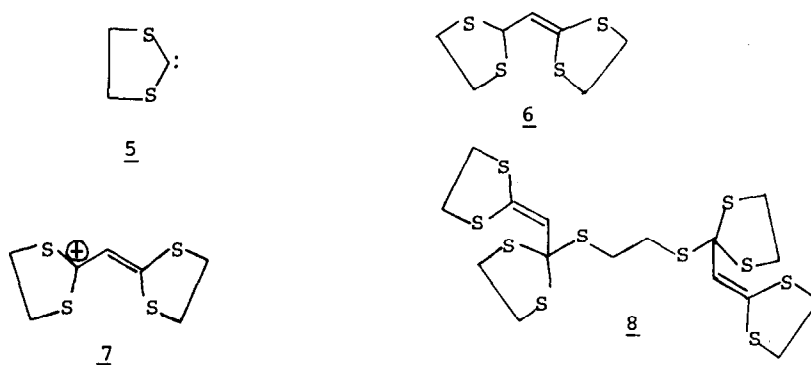
Oxidation of 2,2'-bi(1,3-dithiolanyl) (1) (3) afforded the tetrathioethylenes 2 and 3, the latter arising from further oxidation of 2.



Compound 2 crystallizes from ethanol as colorless plates, mp 200-2° nmr (CDCl_3) singlet at 3.49 ppm, and mol. wt. 208 (mass spectrum). Peaks at m/e 104 and 76 in the mass spectrum of this substance are consistent with the formation of

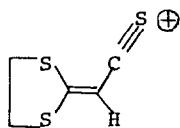
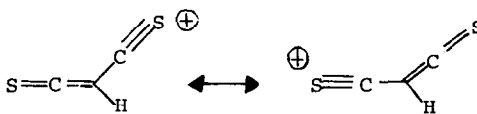
the carbene 5 (4) followed by decomposition to carbon disulfide and ethylene (2c). Compound 2 forms a green charge-transfer complex with tetracyanoethylene but, unlike tetramethoxyethylene (5), it does not form a cyclic adduct. Compound 3 sublimes to give yellow crystals, mp 115°; nmr (CDCl₃) singlets at 3.49 (4H) and 6.23 ppm (2H); and mol. wt. 206 (mass spectrum). This subsequent dehydrogenation of a 1,3-dithiolane ring is probably encouraged by the aromatic stabilization of the 1,3-dithiolenium ring shown in resonance structure 4. Oxidation of the second ring to yield a tetrathiafulvalene lacks this impetus. Tetrathiafulvalenes are known as carbene dimers (6).

Oxidation of 2,2'-bis(1,3-dithiolanyl)methane (7) proceeded through the ketene thioketal 6 to carbonium ion 7. We have not yet crystallized a pure salt of this cation but have characterized it by sodium borohydride reduction to compound 6 and by condensation with 1,2-ethanedithiol to provide compound 8. Compound 6 may be

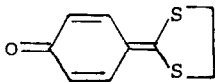
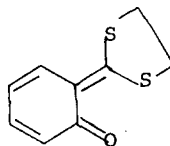


sublimed to give colorless crystals, mp 56-8°; infrared 1580 cm⁻¹; nmr (CDCl₃) 3.30, 3.38 (singlets, 8H), 5.29 and 5.66 ppm (doublets, J = 10 cps, 2H); and mol. wt. 222 (mass spectrum). Compound 8 crystallizes from methylene chloride /methanol in colorless crystals. Once purified it is highly insoluble but can be recrystallized (with substantial loss) from chlorobenzene. It turns yellow on standing, presumably due to formation of cation 7. The substance has mp 180-2°; infrared 1560 cm⁻¹; and gave the following analysis: Calcd. for C₁₆H₂₂S₁₀: C, 35.92; H, 4.14; S, 59.94. Found: C, 35.89; H, 4.26; S, 59.76. The mass spectrum of this compound shows no peak above m/e 221, the mass of

cation 7 (8). The spectrum is dominated by three intense peaks at m/e 221, 161, and 101. These are ascribed to resonance stabilized cations 7, 9, and 10.

9 m/e 16110 m/e 101

Systems which preclude the loss of a β -proton but which may yield neutral products by loss of a proton elsewhere have also been examined. Thus the thioacetals of ortho- and para-hydroxybenzaldehydes yielded the quinones 11 and 12 on DDQ oxidation in boiling dimethoxyethane.

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Compound 11 crystallizes out as it forms and is purified by recrystallization from dimethylformamide; yellow needles mp 208-12° (dec) (Lit. mp 196° dec). This substance has been prepared previously by sequential base-catalyzed condensation of phenol with carbon disulfide and ethylene bromide (9). Compound 12 was purified by chromatography on silica gel. Evaporation of a chloroform solution left a residue which crystallized to a red solid when chilled. It could not be readily recrystallized. This substance has infrared 1625, 1535, and 1505 cm^{-1} ; nmr (CDCl_3) 3.49 (singlet, 4H) 7.2 ppm (broad multiplet, 4H); and mol. wt. 196 (mass spectrum).

While the yields in the examples cited above are in the range of 50-70%, some of the thioacetals examined (e.g., 2-ethyl-1,3-dithiane, 2-benzyl-1,3-dithiolane, and the bis-thioacetal of terephthalaldehyde) gave none of the expected oxidation products. The factors governing the success or failure of the oxidation have yet to be elucidated.

References

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