Table V. Oxidation of Cyclohexane: Effect of Conversion on Selectivity[a]

	expt no.		
	28	29	30[b]
Product Yield, g (% Molar Selectivity)			
adipic acid	8.8 (92.5)	56.6 (89.4)	75.5 (70.7)
glutaric acid	0.5 (5.5)	3.6 (6.3)	14.7 (15.2)
succinic acid	0.15 (2.0)	2.2 (4.3)	11.8 (13.7)
Other Parameters			
molar ratio, adipic/(glutaric + succinic)	12.3	8.4	2.5
C_6H_{12} conversion, %	~8	~52	~88

[a] Reactants: 70 g of C_6H_{12}, 20 g of $Co(OAc)_2{\cdot}4H_2O$, 15 g of MEK, 420 g of HOAc; 20 atm of O_2 total pressure; 95 °C. [b] Average of experiments 1 and 2.

nism.[9] Other mechanisms involving direct attack on cyclohexyl intermediates are also expected to contribute.

Upon examination of the effect of cyclohexane conversion on adipic acid selectivity (Table V), the data clearly show that adipic acid degradation is linked to cyclohexane conversion, showing the importance of oxidative degradation. Ratios of adipic acid to glutaric acid formed at low or moderate conversion (16.8/1 and 14.2/1, respectively) are too high compared to a theoretical value of about 6/1.[1] Even with the assumption that all the succinic acid came from adipic acid degradation, the ratio of adipic acid to the sum of glutaric and succinic acids in expt 28 would still be excessive. Oxidation of cyclohexane in the "high cobalt system" must therefore be mechanistically different from classical autoxidations and involve other intermediates besides cyclohexanone.

The high activity retentions in Druliner's work on the oxidation of labeled cyclohexanone are most interesting.[3] His data eliminate a number of intermediates in the high-retention cobalt system but do not suggest a mechanism consistent with all the facts. We suggest that hydrogen atom abstraction at the α-, β-, and γ-positions of the ketone leads exclusively to labeled dicarboxylic acids with high retention. Agebekov et al.[10] reported the relative reactivity toward hydrogen atom abstraction by peroxy radicals in the α- and β-positions of cyclohexanone as (11 ± 3)/1, respectively. This implies that about 7-11% of abstraction occurs at the β-position, and, consequently, about half as much again occurs at the γ-position. This mechanism, while not previously reported for the high-retention cobalt system, is in complete agreement with Druliner's data as well as our own.

Experimental Section

General Methods. Oxidations were carried out in a 1-L, 316 stainless-steel, magnetically stirred autoclave which was equipped with a Dispersomax stirrer, a heating mantle, and cooling coils (Autoclave Engineers, Inc.). Molecular oxygen was used as the oxidant, introduced into the reactor through a medium-porosity, 2-in. o.d., stainless-steel sparger, and was supplied at the rate at which is was consumed. Carboxylic acids were analyzed by GLC as trimethylsilyl derivatives on a Varian 1520 chromatograph (thermal conductivity detector); 6 ft × 0.25 in., OV-1 column; programmed from 50 to 275 °C at 10 °C/min). The areas of peaks were measured by using a digital integrator connected to a computer and were corrected for the response of the detector by use of appropriate weighting factors: adipic acid, 1.00; glutaric acid, 0.85; succinic acid, 0.78; malonic acid, 1.02.

Oxidation of Cyclohexane. In a typical experiment, 20 g of $Co(OAc)_2{\cdot}4H_2O$, 15 g of methyl ethyl ketone, 70 g of cyclohexane, and 420 g of acetic acid were charged into the autoclave. The autoclave was heated to 95 °C and pressured with oxygen to 14 atm (total pressure). After an induction period of 1.5 h, the reaction was continued for 2 h. The autoclave was cooled and depressurized, and its contents were withdrawn. After evaporation of the reaction mixture to dryness in a rotary evaporator, the solids were extracted with acetone to afford, after evaporation of the extract, 83.2 g of product (82.1% adipic, 9.5% glutaric, 7.0%, succinic acids). The residual cobalt salts were boiled in 10% aqueous sodium hydroxide and filtered. The filtrate was sprung with concentrated hydrochloric acid, and the mixture again was evaporated to dryness. Extraction with acetone gave an additional 12.0 g of acids (56.1% adipic, 17.1% glutaric, and 26.2% succinic acids). Therefore, about 21% of the total amount of glutaric acid and 35% of the succinic acids appeared as cobalt salts. The conversion of cyclohexane, based on isolated dicarboxylic acids, was estimated at 80%. Oxidations of n-butane were carried out as reported.[8]

Registry No. Adipic acid, 124-04-9; glutaric acid, 110-94-1; succinic acid, 110-15-6; cyclohexane, 110-82-7; cyclopentane, 287-92-3; $Co(OAc)_2$, 71-48-7.

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Electron Delocalization in 2,4,6-Tris(1,3-dithiol-2-ylidene)-1,3,5-cyclohexanetrione and 2,4,6-Tris(1,3-dithiolan-2-ylidene)-1,3,5-cyclohexanetrione

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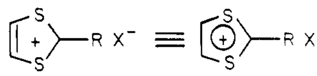
Tetrathiafulvene and its derivatives are of considerable interest because of the highly conducting charge-transfer complexes which they form with tetracyano-p-quinodimethane.[1] The metallic-like properties of these salts have been discussed in terms of ionization potentials and charge delocalization,[1-3] and a study of the electron delocalization in these compounds and other model systems is of continuing interest.

Proton and ^{13}C NMR investigations of the 1,3-dithiolium cation indicate the positive charge is delocalized to some extent over the entire ring system (1).[4-6] In 7,10-dithiasesquifulvalene-1,6-quinone (2) the carbonyl absorption frequency occurs at 1505 cm^{-1} while the dithiol proton resonance is found at δ 8.17.[7] Hydrogenation of the dithiol ring raises the carbonyl frequency to 1535 cm^{-1} which is taken as evidence for ground state contributing forms such



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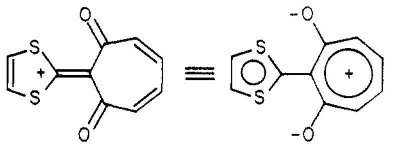

2a 2b

[‡] Saitama University.

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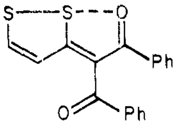
as **2b**; however, the low carbonyl absorption frequency cannot be explained entirely by delocalization. Comparison with a number of tropane derivatives indicates the carbonyl absorption frequency should be greater than 1600 cm^{-1}.[8] The additional lowering of the carbonyl frequency is indicative of a strong S··O interaction. The effects of delocalization and S··O interactions upon the carbonyl absorption frequencies are illustrated by derivatives **3**, **4**, **5**, and **6** of α-(1,2-dithiol-3-ylidene) β-diketones.[9]



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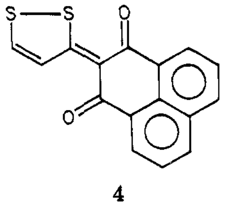

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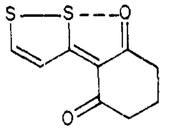

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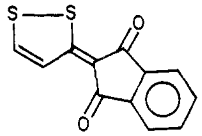

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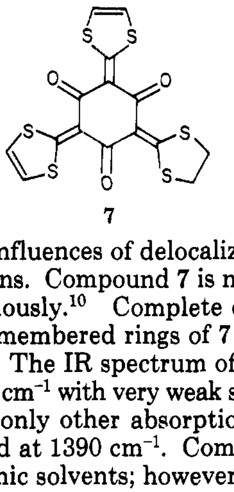
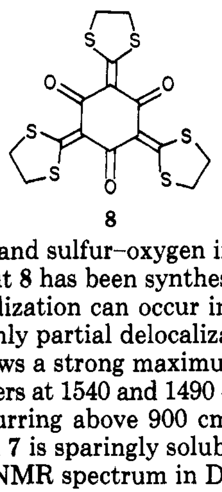
The frequencies of the trans ketones are in the range of 1630–1700 cm^{-1} while the cis ketones show absorptions in the range 1542–1554 cm^{-1} except for compound **6**. When the ketone function is part of a five-membered ring, the S··O distance is increased and the carbonyl frequency is raised to 1644 cm^{-1}. Antiaromatic resonance forms also make some contributions in this case.

2,4,6-Tris(1,3-dithiol-2-ylidene)-1,3,5-cyclohexanetrione (**7**) and 2,4,6-tris(1,3-dithiolan-2-ylidene)-1,3,5-cyclohexanetrione (**8**) were synthesized to investigate further the influences of delocalization and sulfur–oxygen interactions.



7



8

Compound **7** is new, but **8** has been synthesized previously.[10] Complete delocalization can occur in the five-membered rings of **7** but only partial delocalization in **8**. The IR spectrum of **7** shows a strong maximum at 1520 cm^{-1} with very weak shoulders at 1540 and 1490 cm^{-1}. The only other absorption occurring above 900 cm^{-1} is found at 1390 cm^{-1}. Compound **7** is sparingly soluble in organic solvents; however, the NMR spectrum in D_2SO_4 shows a single proton resonance at δ 9.50. Compound **8** exhibits a sharp IR maximum at 1565 cm^{-1} with weak shoulders at 1540 and 1520 cm^{-1}. The compound also exhibits a strong absorption at 1400 cm^{-1}. A few weak bands occur below 1400 cm^{-1} but none above 1565 cm^{-1}. The ^{1}H NMR spectrum in Me_2SO-d_6 shows a sharp singlet at δ 3.32 which indicates equivalency of the protons in solution. The resonance is shifted to δ 4.90 in D_2SO_4. Suitable single crystals of **7** could not be obtained; however, compound **8** provided adequate crystals for an X-ray structure analysis.

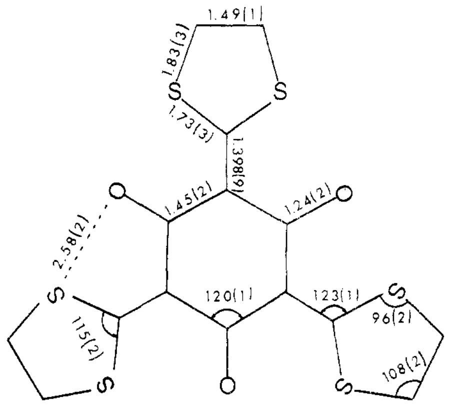


Figure 1. Average bond lengths (Å) and valence angles (deg) for 2,4,6-tris(1,3-dithiolan-2-ylidene)-1,3,5-cyclohexanetrione.

Figure 1 gives the average bond lengths and angles for **8**. There are two independent molecules per unit cell and the molecules are planar except for the methylene carbon atoms. The dithiane rings exhibit almost ideal twist (half-chair) conformations,[11] but the central carbon atom and sulfur atoms remain coplanar with the remainder of the molecule. The S··O separations average 2.59 (2) and 2.58 (2) Å for the two independent molecules, indicating a strong S··O interaction. The S–C–C–C–O system might be considered to be a planar five-membered ring with one elongated bond. The C–C distances between the six- and five-membered rings average 1.398 (9) Å, indicating a reduction in double bond character. The strengthening of the S··O interaction is consistent with a resonance form placing a positive charge on the sulfur atoms. The delocalization and possibly the short sulfur–oxygen interaction contribute to the lengthening of the connecting double bond.

Although the structure of **7** could not be determined, the entire molecule is probably planar with sulfur–oxygen interactions of the same order of magnitude as in **8**. The reduction of the carbonyl frequency to 1520 cm^{-1} in **7** can be attributed to a more extensive delocalization of the charge into the dithiole ring which reduces further the double bond character of the carbonyl.

Experimental Section

X-ray Analysis of 8. A crystal of dimensions 0.25 × 0.25 × 0.30 mm was used for all X-ray measurements. The unit cell was found to be monoclinic and the space group Pc with a = 11.853 (3), b = 7.998 (1), c = 21.569 (6) Å, β = 123.31 (2)°, V = 1710.8 (7) Å^3, and d_c = 1.681 mg/m^3 for Z = 4. The structure was refined by anisotropic least-squares refinement to a final R of 0.055. (Details of the data treatment, structure elucidation, and refinement are included in the supplementary material.)

2,4,4-Tris(1,3-dithiol-2-ylidene)-1,3,5-cyclohexanetrione (7). A mixture of 162 mg (1 mmol) of 1,3,5-trihydroxybenzene dihydrate, 828 mg (3 mmol) of 1,3-dithiolium iodide, and 0.5 mL of pyridine in 15 mL of acetonitrile was refluxed for 3 h and cooled to room temperature. The resulting crystalline precipitate was collected and washed with acetonitrile to give 264 mg (62%) of **7**. Recrystallization from Me_2SO yielded fine yellow-brown needles: mp >400 °C; IR (KBr) 1540 (sh), 1520 (s), 1490 (sh),

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1390 (s), 810, 740, 695, 630 cm^{-1}; NMR (D_2SO_4) δ 9.50 (s).

Anal. Calcd for $C_{15}H_6O_3S_6$: C, 42.23; H, 1.42; S, 45.09. Found: C, 42.23; H, 1.62; S, 45.20.

2,4,6-Tris(1,3-dithiolan-2-ylidene)-1,3,5-cyclohexanetrione (8). A mixture of 4.29 g (30 mmol) of ethylene trithiocarbonate and 3.0 mL of dimethyl sulfate was heated at 100 °C for 0.5 h and cooled to room temperature, and then 30 mL of acetic acid, 1.62 g (10 mmol) of 1,3,5-trihydroxybenzene dihyrate, and 3.0 mL of pyridine were added. The mixture was refluxed for 1 h and cooled. The resulting crystalline precipitate was collected and washed with acetic acid and then with benzene to give 1.83 g (42%) of 8. Recrystallization from Me_2SO yielded orange needles: mp >400 °C; IR (KBr) 1565 (s), 1540 (sh), 1400 (sh), 1275, 1150, 950, 890, 840, 815, 620 cm^{-1}; UV (CH_3CN) 4.04 (log ϵ, 4.65), 322 (4.67), 262 (4.21) nm; NMR (Me_2SO-d_6) δ 3.32; NMR (D_2SO_4) δ 4.90 (2).

Anal. Calcd for $C_{15}H_{12}O_3S_6$: C, 41.64; H, 2.80; S, 44.46. Found: C, 41.61; H, 2.76; S, 44.22.

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Registry No. 7, 74356-07-3; **8**, 2957-46-2; 1,3,5-trihydroxybenzene, 108-73-6; 1,3-dithiolium iodide, 1863-66-7; ethylene trithiocarbonate, 822-38-8.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bond lengths, valence angles, and torsion angles and ORTEP diagram of 8 (8 pages). Ordering information is given on any current masthead page.

Electroreduction of Allyl Quaternary Ammonium and Phosphonium Salts

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The electroreduction of quaternary ammonium and phosphonium salts containing the benzyl group has been the subject of a number of papers by Finkelstein et al.[1] The principal products of these electrolyses at an aluminum cathode in nonaqueous solvents have been shown to be bibenzyl and toluene.

Mechanistic studies by Finkelstein et al.[1] and by Mayell and Bard[2] indicate that bibenzyl is formed by the coupling of benzyl radicals and that toluene is formed by the reaction of the benzyl anion with the solvent.

$$PhCH_2NR_3 + e \rightarrow PhCH_2\cdot + R_3N$$

$$2PhCH_2\cdot \rightarrow PhCH_2CH_2Ph$$

$$PhCH_2\cdot + e \rightarrow PhCH_2^-$$

$$PhCH_2^- + SH \rightarrow PhCH_3$$

Recent evidence, however, suggests that in the electrochemical reduction of allylic and benzhydryl halides[3,4] dimer formation is more likely to be due to a nucleophilic attack of the carbanion intermediate on the starting halide rather than to radical coupling.

The electroreduction of allyl quaternary ammonium salts in aqueous solution at aluminum and platinum cathodes has been reported to give propene as the only hydrocarbon product,[5] and Finkelstein[6] found that no dimer was obtained from the electrolysis of allyltriphenylphosphonium nitrate 1 in dimethylformamide (DMF).

Our studies have shown that the electrolysis of allyltriethylammonium bromide (2) in nonaqueous solvents at an aluminum cathode gives appreciable yields of the coupled product, 1,5-hexadiene (3). Contrary to the report of Finkelstein,[6] coupling also occurs in the electrolysis of allyltriphenylphosphonium nitrate (1) under the above conditions.

$$\underset{\textbf{2}}{CH_2{=}CHCH_2N^+\,Et_3Br^-} \xrightarrow[\text{DMF, }NH_4NO_3]{\text{Al cathode}}$$
$$\underset{\textbf{3},\ 32\%}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + Et_3N + CH_3CH{=}CH_2$$

$$\underset{\textbf{1}}{CH_2{=}CHCH_2P^+\,Ph_3NO_3^-} \xrightarrow[\text{DMF, }NH_4NO_3]{\text{Al cathode,}}$$
$$\underset{\textbf{3},\ 24\%}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + Ph_3P + CH_3CH{=}CH_2$$

It is notable that anhydrous materials are necessary in order to achieve an appreciable yield of dimer in the electroreduction of these compounds. As in the electrolysis of benzyl quaternary ammonium salts,[1] it appears that in the presence of water rapid protonation of the intermediate radical or anion occurs, preventing the coupling reaction. The electrolysis of allyltriethylammonium nitrate failed to give any 1,5-hexadiene, but it was noted that this salt was very hygroscopic. Very low yields of the dimer were formed in the electrolysis of the phosphonium salt 1 unless it was carefully dried before use.

We have also investigated the effect of various factors, such as current, concentration of the quaternary salt, nature of the solvent and supporting electrolyte, and temperature, on the yield of 1,5-hexadiene in the electrolysis of these quaternary salts at constant current. The results of these electrolyses are summarized in Table I.

In their polarographic and coulometric studies on the electrolysis of benzyl quaternary ammonium salts, Mayell and Bard[2] suggested that radical coupling is favored by low temperatures, high concentration of quaternary salt, and relatively high current densities.

Our results show little evidence that changing the current over the range 0.25–1.0 A affects appreciably the yield of the coupled product. It was observed, however, that at the highest current used (1.0 A) the temperature rose considerably as the electrolysis proceeded, possibly causing some loss of the rather volatile product.

In agreement with Mayell and Bard,[2] it can be seen from Table I that there is a tendency for increased yields of 1,5-hexadiene when higher concentrations of the quaternary salt 2 were used.

The yields of dimer were compared with three different solvents: DMF, dimethyl sulfoxide (Me_2SO), and acetonitrile. Much lower yields were obtained in acetonitrile than in DMF and Me_2SO. It was notable that in acetonitrile, lower temperatures actually decreased the yield of 1,5-hexadiene.

Electrolyses of 2 were carried out in the presence of 0.1 M ammonium nitrate, tetraethylammonium nitrate, and

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