

**Ethyl 9-Anthroate.** Recrystallization from ethanol yielded colorless crystals, mp 108–109 °C (lit.<sup>11</sup> mp 102 °C).

Anal. Calcd for C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>: C, 81.58; H, 5.64. Found: C, 81.52; H, 5.67.

This compound was also prepared by adding ethanolic KOH to a solution of **13** (0.78 mmol, 0.220 g) in hot ethanol (5 mL). The mixture was heated to boiling for 2 min and then cooled in ice. Addition of water gave crystals which were collected and recrystallized twice from ethanol to yield 0.150 g (77%).

**Isopropyl 9-Anthroate.** Recrystallization from ethanol/water yielded colorless crystals, mp 93–94 °C (lit.<sup>12</sup> mp 95 °C).

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.02.

**Propyl 9-Anthroate.** After cooling, the refluxed solution was taken to dryness by flash evaporation. The residue was dissolved in ethanol and 2 N NaOH added. The precipitated crystals were collected and recrystallized from ethanol to give pale yellow crystals, mp 68–69 °C.

Anal. Calcd for C<sub>18</sub>H<sub>16</sub>O<sub>2</sub>: C, 81.79; H, 6.10. Found: C, 81.99; H, 6.11.

**Dibenzo[e,h]-1-thiabicyclo[2.2.2]octan-2-one (12).** A mixture of **10** (0.002 mol, 0.716 g) in *tert*-butyl alcohol (10 mL) and 1 mL of 4 N HCl was refluxed for 1 h. After the mixture cooled the crystals were collected. Recrystallization from ethanol gave 0.370 g (78%) of colorless crystals which were recrystallized once more from benzene/petroleum ether, mp 135–137 °C; this

(11) Adams-Briers, M.; Fierens, P. J. C.; Martin, R. H. *Helv. Chim. Acta* 1955, 38, 2021.

(12) Heller, E.; Schmidt, G. M. *J. Isr. J. Chem.* 1971, 9, 449.

was followed by solidification and remelting at 210–214 °C (melting point of anthracene) in accordance with the literature.<sup>7</sup>

Anal. Calcd for C<sub>15</sub>H<sub>10</sub>OS: C, 75.60; H, 4.23. Found: C, 75.63; H, 4.42.

**Ethyl 4-Mercapto-2-cyclohexenecarboxylate (15).** The same procedure as above, using **9** (0.0038 mol, 1.0 g), yielded a light yellow liquid (0.68 g, 95%). Purification by TLC gave a colorless liquid with the same characteristics as those mentioned for **14**: *n*<sub>D</sub><sup>25</sup> 1.5080; <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.27 (t, 3 H, CH<sub>3</sub>), 1.60 (d, 1 H, SH), 1.96 (m, 4 H, CH<sub>2</sub>), 3.00 (m, 1 H, CH), 3.50 (m, 1 H, CH), 4.17 (q, 2 H, OCH<sub>2</sub>), and 5.83 (m, 2 H, CH=CH).

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**Registry No.** 1, 63976-76-1; 3, 6160-65-2; 5, 74346-63-7; 6, 74346-64-8; 7, 74356-05-1; 8, 74346-65-9; 9, 74346-66-0; 10, 74346-67-1; 11 (R = CH<sub>3</sub>), 1504-39-8; 11 (R = CH<sub>3</sub>CH<sub>2</sub>), 1754-54-7; 11 (R = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 71942-30-8; 11 (R = (CH<sub>3</sub>)<sub>2</sub>CH), 30536-62-0; 12, 59102-55-5; *cis*-**13**, 74356-06-2; *cis*-**14**, 74346-68-2; *cis*-**15**, 74346-69-3; 1,4-diphenyl-1,3-butadiene, 886-65-7; cyclopentadiene, 542-92-7; 1,1'-thiocarbonyldibenzotriazole, 4314-19-6; 1,3-cyclohexadiene, 592-57-4; anthracene, 120-12-7; methyl *cis*-4-mercapto-2-cyclopentenecarboxylate, 74346-70-6; methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; 2-propanol, 67-63-0.

## Notes

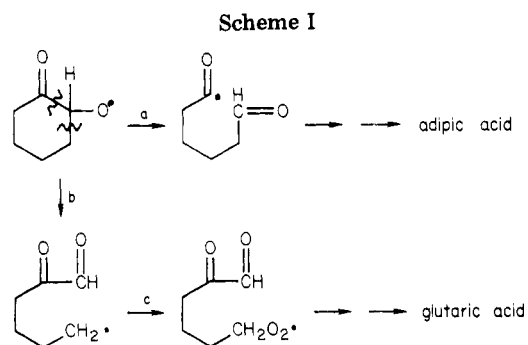
### Glutaric and Succinic Acids in the Cobalt Acetate Catalyzed Oxidation of Cyclohexane with Oxygen

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Radical-initiated autoxidation of cyclohexane was reported by Hendry et al.<sup>1</sup> to proceed predominantly over cyclohexanone as the intermediate which further reacted to form adipic and glutaric acids in a ratio of ~6:1. The same molar ratio was obtained in acetic acid in the presence of a catalytic amount of cobalt acetate. This suggests that (2-ketocyclohexyl)oxy radicals are involved in both cases, which in the latter are formed via ROOH + Co<sup>2+</sup> → RO· + Co<sup>3+</sup> + OH<sup>-</sup>. The two acids are formed as the result of competing cleavage at two possible locations (paths a and b, Scheme I). No succinic acid was reported at the low ketone conversions investigated. Kamiya and Kotake<sup>2</sup> employed substantial amounts of cobalt acetate to oxidize cyclohexanone in high conversion to adipic and glutaric acids (4.8:1 ratio), but no mention of succinic acid was made. More recently, Druliner<sup>3</sup> studied the cobalt acetate catalyzed oxidation of [1-<sup>14</sup>C]cyclohexanone in acetic acid



and produced a mixture of C<sub>4</sub>–C<sub>6</sub> dicarboxylic acids, with high retention of activity in glutaric and succinic acid. This work suggests little contribution of intermediates, including 1,2-cyclohexanedione<sup>4</sup> and 2,6-dihydroperoxycyclohexanone,<sup>5</sup> and no appreciable oxidative degradation of adipic acid as each of these events was expected to diminish the activity in the products by ~50%.

Earlier, we reported the oxidation of cyclohexane in the cobalt acetate system with high yields to C<sub>4</sub>–C<sub>6</sub> dicarboxylic acids.<sup>6</sup> The present work investigates the oxidative degradation of adipic acid to lower dibasics. Lande and Kochi reported on the thermolysis of cobaltic salts of monobasic acids in the absence of oxygen.<sup>7</sup> Reactions of

(1) D. G. Hendry, C. W. Gould, D. Schuetzle, M. G. Syz, and F. R. Mayo, *J. Org. Chem.*, 41, 1 (1976).

(2) Y. Kamiya and M. Kotake, *Bull. Chem. Soc. Jpn.*, 46, 2780 (1973).

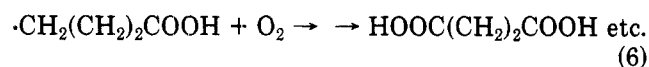
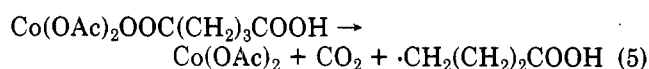
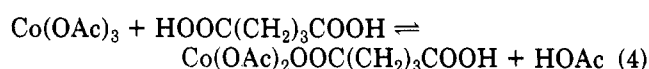
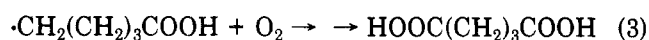
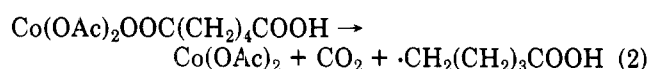
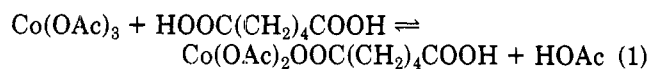
(3) J. D. Druliner, *J. Org. Chem.*, 43, 2069 (1978).

(4) I. I. Korsak and V. E. Agebekov, *Dokl. Akad. Nauk SSSR*, 19, 711 (1975).

(5) G. N. Koshel, M. I. Farberov, T. N. Anmonova, L. V. Bedareva, N. G. Vasil'ev, and L. V. Ob'edkova, *Neftekhimiya*, 14, 263 (1974).

(6) A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, 38, 3729 (1973).

this nature could equally occur with the dicarboxylic acids in our system, as 10–20% of the acids from cyclohexane oxidation appear in the product combined as cobalt salts. Of these, 30–60% is cobalt succinate, 20–35% glutarate, and 10–20% adipate, in line with decreasing acidity of the parent acids. Malonic and oxalic acids were also detected in trace amounts in some experiments, indicating that once the stable succinate ligand is formed there is little further degradation, unless more severe conditions are employed. Radicals generated via thermolysis, after reacting with oxygen, are expected to contribute toward propagation. A reasonable reaction sequence could include reactions 1–6, in addition to conventional hydrogen atom abstractions from adipic acid itself.



To determine the extent of its degradation, we subjected adipic acid to oxidizing conditions in the presence of *n*-butane as the cooxidant, which in this respect we consider to be equivalent to cyclohexane. *n*-Butane alone typically yields ~84% of acetic acid and some propionic and *n*-butyric acids but no dicarboxylic acids.<sup>8</sup> The fate of adipic acid in this case can therefore easily be followed.

### Discussion

Typical cyclohexane oxidation runs in our investigation afforded adipic acid (~70.7% selectivity), glutaric acid (~15.2%), and succinic acid (~13.6%) at ~88% conversion (Table I, average of expt 1 and 2). The ratio of adipic to glutaric acid of ~4.7:1 found by us is identical with that reported for cyclohexanone oxidation in the same system.<sup>2</sup> Adding water initially to the reaction mixture moderated the exothermicity and improved adipic acid selectivities. Experiments with optimum amounts of water produced adipic acid in ~80.1% selectivity, along with glutaric and (~10.8%) and succinic acid (~9.1%) (average of expt 7 and 8), corresponding to a 13% increase in adipic acid production over the base run. The mechanism of this phenomenon is not yet fully understood. It is also surprising that in cyclopentane oxidation under identical conditions the effect of added water is only minimal (Table II).

Oxidation of cyclohexane in the presence of a small amount of adipic acid (30 g) showed little increase in adipic acid degradation. Adding double this amount of adipic acid (60 g) to the initial cyclohexane charge led, however, to a significant increase in its degradation (Table III). Oxidations of adipic acid in the presence of *n*-butane are shown in Table IV. They more clearly show that adipic acid is indeed converted to lower acids in the presence of cobaltic ions and the hydrocarbon promoter. Under typical reaction conditions as much as 10–12 g of adipic acid was

Table I. Oxidation of Cyclohexane: Effect of Water on Selectivity to Adipic Acid<sup>a</sup>

	expt no.							
	1	2	3	4	5	6	7	8
adipic acid	77.2 (70.7)	73.8 (70.8)	85.5 (77.6)	85.8 (76.7)	91.9 (80.6)	84.2 (79.4)	84.0 (80.5)	78.5 (79.7)
glutaric acid	14.5 (14.7)	14.8 (15.7)	11.8 (11.8)	11.7 (11.6)	9.6 (9.3)	10.6 (11.0)	10.0 (10.6)	9.8 (11.0)
succinic acid	12.3 (13.9)	11.3 (13.4)	9.3 (10.4)	10.6 (11.7)	9.0 (9.8)	8.2 (9.6)	7.9 (9.4)	7.1 (8.9)
total diacids	104.0	99.9	106.6	108.1	110.5	103.0	101.9	95.4
adipic/(glutaric + succinic) adipic/glutaric	~2.5 ~4.8	~2.4 ~4.5	~3.5 ~6.6	~3.3 ~6.6	~4.2 ~8.7	~3.9 ~7.2	~4.0 ~7.6	~4.0 ~7.2
water added, g	none	none	15	15	30	30	45	45
induction time, h	1.3	1.3	2.3	3.5	3.0	3.0	4.3	4.0
rxn time, h	2	2	2.5	2.5	2.5	2.3	2	2
products, g (%)	62.8 (89.6)	60.6 (85.7)	63.4 (90.5)	64.4 (92.0)	65.6 (93.7)	61.0 (87.2)	60.3 (86.1)	56.5 (80.7)
conversion, %	~90	~86	~90	~92	~94	~87	~86	~81

<sup>a</sup> Reactants: 70.0 g of C<sub>6</sub>H<sub>12</sub>, 20 g of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, 15 g of MEK, 420 g of HOAc, 20 atm of O<sub>2</sub> (total pressure); 95 °C.

(7) S. S. Lande and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 5196 (1968).

(8) A. Onopchenko and J. G. D. Schulz, *J. Org. Chem.*, **38**, 909 (1973).

Table II. Oxidation of Cyclopentane: Effect of Water on Selectivity to Glutaric Acid<sup>a</sup>

	expt no.				
	9	10	11	12	13
Product Yield, g (% Molar Selectivity)					
glutaric acid	93.0 (80.7)	71.1 (78.7)	70.1 (80.0)	64.3 (81.8)	50.1 (82.9)
succinic acid	19.9 (19.3)	17.7 (20.3)	15.6 (20.0)	12.8 (18.2)	9.3 (17.1)
total diacids	112.9	90.8	85.7	77.1	59.4
Reaction Conditions					
water added, g	0	10	25	50	100
induction time, min	none	38	58	none	none
rxn time, h	2	2.3	3.5	3.0	3.5
Cyclopentane Material Balance					
products, g (%)	61.1 (87)	49.3 (85)	46.5 (80)	41.7 (60)	32.1 (46)
conversion, %	~87	~85	~80	~60	~46

<sup>a</sup> Reactants: 58 or 70 g of C<sub>5</sub>H<sub>10</sub>, 20 g of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O and 10 g of MEK or Co(acac)<sub>3</sub>, 400 g of HOAc, 20 atm of O<sub>2</sub> (total pressure); 110 °C.

Table III. Oxidation of Cyclohexane in the Presence of Additives

	expt no.				
	1	14	15	16	17
Amount of Reactant, g <sup>a</sup>					
C <sub>6</sub> H <sub>12</sub>	70	70	140	140	210
adipic acid		60			
water				30 <sup>b</sup>	
Product Yield, g (% Molar Selectivity)					
adipic acid	77.2 (70.7)	51.8 (61.4)	151.8 (78.8)	142.0 (77.9)	177.5 (79.6)
glutaric acid	14.5 (14.7)	15.5 (20.0)	20.7 (11.9)	21.5 (13.0)	24.4 (12.0)
succinic acid	12.3 (13.9)	12.7 (18.6)	14.5 (9.3)	13.4 (9.1)	15.1 (8.4)
total diacids	104.0	80.0	187.0	176.9	218.0
Molar Ratio					
adipic/(glutaric + succinic)	~2.5	~1.6	~3.7	~3.5	~3.9
adipic/glutaric	~4.8	~3.1	~6.6	~6.0	~6.6
Cyclohexane Material Balance					
products, g (%)	62.8 (89.7)	48.7 (75)	110.8 (79.1)	104.9 (74.9)	128.4 (61.0)
conversion, %	90	75	79	75	61

<sup>a</sup> 20 g of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, 15 g of MEK, 420 g of HOAc, 20 atm of O<sub>2</sub> (total pressure); 95 °C; 2–3 h. <sup>b</sup> Pumped in after initiation period of 1.5 h.

Table IV. Oxidation of *n*-Butane in the Presence of Dicarboxylic Acids

	expt no.									
	18	19	20	21	22	23	24	25	26	27
Amount of Reactant, g <sup>a</sup>										
Co(OAc) <sub>2</sub> ·4H <sub>2</sub> O	20	20	20	10	5	20	20	20	20	20
water						20	40			
adipic acid	30	30	30	30	30	30	30	90		
glutaric acid									40	
succinic acid										40
Product Yield, g										
adipic acid	22.2	15.2	11.6	13.3	14.3	13.6	14.0	67.2		
glutaric acid	2.1	2.9	3.1	3.4	3.3	3.3	3.1	8.1	25.0	
succinic acid	2.4	5.9	6.6	5.1	4.4	5.0	4.9	6.6	6.6	32 <sup>b</sup>
Other Parameters										
reaction temp, °C	95	105	115	115	115	115	115	115	130	130
adipic acid degraded, g <sup>d</sup>	5.8	10.5	11.6	10.1	9.1	9.8	8.2	17.3	7.4	8 <sup>c</sup>

<sup>a</sup> 20 g of MEK, 400 g of HOAc, ~50 g of *n*-C<sub>4</sub>H<sub>10</sub>, 20 atm of O<sub>2</sub> (total pressure); 1.7–3.5 h. <sup>b</sup> Malonic and oxalic acids were not detected. <sup>c</sup> Succinic acid, by difference. <sup>d</sup> Based on C<sub>4</sub> and C<sub>5</sub> acids. Blank run afforded a 90% adipic acid recovery.

degraded, which accounts for at least half of the lower acids formed during cyclohexane oxidation. Increasing the amount of adipic acid added to 90 g (expt 25) led to degradation of 17.3 g of adipic acid. The actual amount of adipic acid degraded in a typical cyclohexane run therefore lies between these values at about 10–17 g. Interaction of cobaltic ions with adipic acid, dependent in its magnitude

on adipic acid concentration, is believed to account for this degradation phenomenon.

The effects of cobalt concentration, adipic acid concentration, and temperature on adipic acid losses are consistent with the oxidative mode of degradation. The large amount of succinic acid produced, however, is inconsistent with oxidative degradation as the sole mecha-

Table V. Oxidation of Cyclohexane: Effect of Conversion on Selectivity<sup>a</sup>

	expt no.		
	28	29	30 <sup>b</sup>
Product Yield, g (% Molar Selectivity)			
adipic acid	8.3 (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 <sub>6</sub> H <sub>12</sub> conversion, %	~3	~52	~88

<sup>a</sup> Reactants: 70 g of C<sub>6</sub>H<sub>12</sub>, 20 g of Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, 15 g of MEK, 420 g of HOAc; 20 atm of O<sub>2</sub> total pressure; 95 °C. <sup>b</sup> Average of experiments 1 and 2.

nism.<sup>9</sup> 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.<sup>1</sup> 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.<sup>3</sup> 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  $\alpha$ -,  $\beta$ -, and  $\gamma$ -positions of the ketone leads exclusively to labeled dicarboxylic acids with high retention. Agebekov et al.<sup>10</sup> reported the relative reactivity toward hydrogen atom abstraction by peroxy radicals in the  $\alpha$ - and  $\beta$ -positions of cyclohexanone as (11  $\pm$  3)/1, respectively. This implies that about 7-11% of abstraction occurs at the  $\beta$ -position, and, consequently, about half as much again occurs at the  $\gamma$ -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 it was consumed. Carboxylic acids were analyzed by GLC as trimethylsilyl derivatives on a Varian 1520 chromatograph (thermal conductivity detector); 6 ft  $\times$  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)<sub>2</sub>·4H<sub>2</sub>O, 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.<sup>8</sup>

**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)<sub>2</sub>, 71-48-7.

### 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

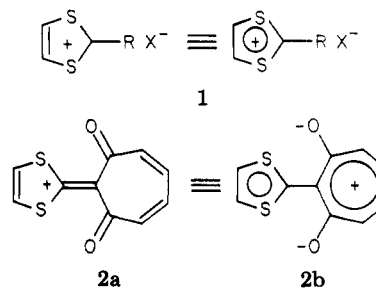
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Tetrathiafulvene and its derivatives are of considerable interest because of the highly conducting charge-transfer complexes which they form with tetracyano-*p*-quinodimethane.<sup>1</sup> The metallic-like properties of these salts have been discussed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

Proton and <sup>13</sup>C NMR investigations of the 1,3-dithiolium cation indicate the positive charge is delocalized to some extent over the entire ring system (1).<sup>4-6</sup> In 7,10-dithiasquifulvalene-1,6-quinone (2) the carbonyl absorption



frequency occurs at 1505 cm<sup>-1</sup> while the dithiol proton resonance is found at  $\delta$  8.17.<sup>7</sup> Hydrogenation of the dithiol ring raises the carbonyl frequency to 1535 cm<sup>-1</sup> which is taken as evidence for ground state contributing forms such

(9) We thank one of the referees for bringing this to our attention.

(10) V. E. Agebekov, E. T. Denisov, N. I. Mitzkevich, I. I. Korsak, and N. I. Golub, *Neftekhimiya*, 13, 846 (1973).

<sup>†</sup>Saitama University.