

*cis*-4-*tert*-butylcyclohexyl disulfide was prepared in the same fashion as the *trans* isomer in 85% yield, mp 116–117 °C after two recrystallizations from ethanol.

Anal. Calcd for C<sub>20</sub>H<sub>38</sub>S<sub>2</sub>: C, 70.11; H, 11.18. Found: C, 70.13; H, 11.14.

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**Registry No.**—1, 7133-37-1; 2, 56051-02-6; 3, 60260-74-4; 4, 60260-75-5; 5, 60260-76-6; 6, 60260-77-7; 7, 4934-66-1; 8, 60260-78-8; 9, 4943-25-3; 10, 5004-79-5; 10-*d*<sub>4</sub>, 60260-79-9; 11, 60260-80-2; 11-*d*<sub>4</sub>, 60260-81-3; 12, 4943-24-2; 12-*d*<sub>4</sub>, 60260-82-4; 13, 60260-83-5; 14, 60260-84-6; 15, 60260-85-7; 4-methylcyclohexanone, 589-92-4; hydrogen sulfide, 7783-06-4; 4-methylcyclohexyl-1,1-dithiol, 60260-86-8; 4-methylcyclohexyl mercaptan, 60260-87-9; *trans*-4-*tert*-butylcyclohexyl mercaptan, 60260-88-0; 4-*tert*-butylcyclohexyl disulfide, 60260-89-1; 2,2,6,6-tetradeuterio-*trans*-4-*tert*-butylcyclohexanol tosylate, 51933-09-6; *cis*-4-*tert*-butylcyclohexyl thiocyanate, 60260-90-4; *trans*-4-*tert*-butylcyclohexyl *p*-toluenesulfonate, 7453-05-6; *cis*-4-*tert*-butylcyclohexyl mercaptan, 53273-25-9; *cis*-4-*tert*-butylcyclohexyl disulfide, 60305-05-7.

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- In actual fact, since  $\Delta S \neq 0$  (see following discussion),  $-\Delta G$  should increase with temperature. The calculated increase for a 130 °C increase in temperature is, however, only 0.11 kcal/mol for the sulfide and sulfone and 0.18 kcal/mol for the sulfoxide, i.e., it may be hidden by the inherent imprecision of the data, which do, in fact, suggest some increase.
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## Synthesis of the Monothiosquarate and 1,2-Dithiosquarate Ions and Their Derivatives

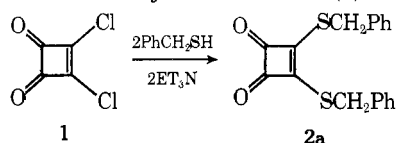
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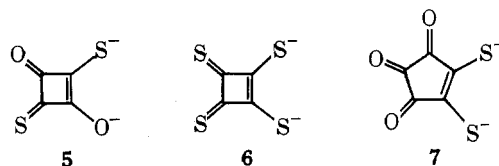
Reaction of diethyl squarate (diethoxycyclobutenedione) with 2 equiv of hydrosulfide ion gives the 1,2-dithiosquarate ion (DTS<sup>2-</sup>) and reaction with 1 equiv gives the 3-ethoxycyclobutenedione-4-thiolate ion (9), which can be hydrolyzed to the monothiosquarate ion (MTS<sup>2-</sup>). Thiosquarate ions are readily alkylated at sulfur to give alkylthio-substituted cyclobutenediones. For example, 3,4-bis(ethylthio)cyclobutenedione (2b) is prepared from DTS<sup>2-</sup> and 3-ethoxy-4-ethylthiocyclobutenedione (10b) is obtained from 9. Reaction of 10b with 1 equiv of dimethylamine selectively replaces the ethoxy group, and reaction of 2b with excess diethylamine gives a ring-opened product. The ir and <sup>1</sup>H NMR spectra of the compounds are discussed.

The monocyclic oxo carbon anions (C<sub>n</sub>O<sub>n</sub><sup>m-</sup>, n = 3–6), because of their unique electronic structures, have a number of unusual physical and chemical properties.<sup>1,2</sup> Several years ago we became interested in synthesizing sulfur analogues of oxo carbons and chose the four-membered ring series because of the chemistry already known for squaric acid (dihydroxycyclobutenedione) and its derivatives.<sup>3</sup> Addition–elimination reactions of oxygen and nitrogen nucleophiles were well known for cyclobutenediones with leaving groups on the vinyl carbons,<sup>3–6</sup> and some displacement reactions of sulfur nucleophiles have recently been reported.<sup>7–14</sup> For example,  $\alpha$ -toluenethiol and dichlorocyclobutenedione (1) in the presence



of base give 3,4-bis(benzylthio)cyclobutenedione (2a), a dithioester of squaric acid.<sup>7,15</sup>

Since our preliminary report of the monothiosquarate ion (3, MTS<sup>2-</sup>) and the 1,2-dithiosquarate ion (4, DTS<sup>2-</sup>),<sup>7</sup> others have reported the 1,3-dithiosquarate and tetrathiosquarate ions (5 and 6) and the 1,2-dithiocroconate ion (7).<sup>14,16</sup> In this



paper the chemistry of MTS<sup>2-</sup> and DTS<sup>2-</sup> and related compounds is described.

### Results and Discussion

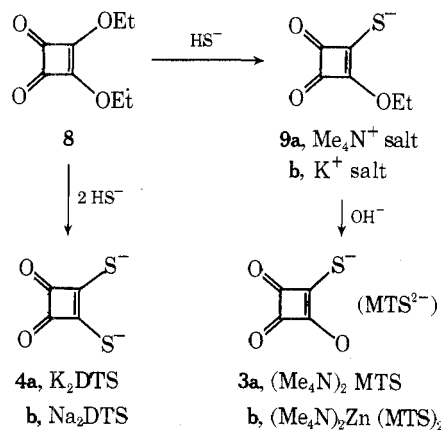
**Synthesis of Thiosquarates.** The thiosquarate anions

Table I.  $^1\text{H}$  NMR Chemical Shifts (ppm) of Cyclobutenediones and Acetates

Registry no.	Compd	R	R'	$\delta$ OCH <sub>2</sub> -	$\delta$ SCH <sub>2</sub> -	$\delta$ NCH <sub>3</sub>	
5231-87-8	8	OEt	OEt	4.71			
52427-65-3	9a	OEt	S <sup>-</sup> Me <sub>4</sub> N <sup>+</sup>	4.80			
60282-05-5	9b	OEt	S <sup>-</sup> K <sup>+</sup>	4.79			
52427-62-0	2b	SEt	SEt		3.46		
60282-06-6	10a	OEt	SMe	4.78	(2.85) <sup>a</sup>		
60282-07-7	10b	OEt	SEt	4.80	3.38		
60282-09-9	12	SMe	O <sup>-</sup> Me <sub>4</sub> N <sup>+</sup>		(2.73) <sup>a</sup>		
19230-33-2	13	OEt	NMe <sub>2</sub>	4.80		3.37, 3.23 <sup>b</sup>	
60282-10-2	11a	SMe	NMe <sub>2</sub>		(2.93) <sup>a</sup>	3.38, 3.23	
37669-71-9	11b	SEt	NMe <sub>2</sub>		3.53	3.40, 3.25	
		NMe <sub>2</sub>	NMe <sub>2</sub>			3.27 <sup>b</sup>	
		CH <sub>3</sub> C(=O)R					
141-78-6		OEt		4.05			
625-60-5		SEt			2.84 <sup>c</sup>		
127-19-5		NMe <sub>2</sub>				2.94, 3.02	

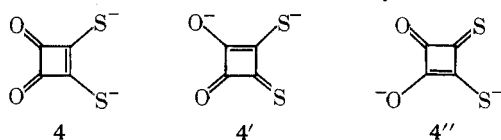
<sup>a</sup> S-Methyl groups. Add 0.6 ppm to compare to ethyl groups. <sup>b</sup> From ref 19. <sup>c</sup> R. Radeaglia, S. Scheithauer, and R. Mayer, *Z. Naturforsch. B*, 24, 283 (1969).

MTS<sup>2-</sup> and DTS<sup>2-</sup> are synthesized by reactions of hydrosulfide ion and diethyl squarate (diethoxycyclobutenedione, 8). Two equivalents of potassium or sodium hydrosulfide convert diethyl squarate to DTS<sup>2-</sup> in good yield.<sup>7</sup> With 1 equiv of potassium or tetramethylammonium hydrosulfide, displacement of one ethoxy group occurs, yielding the 3-ethoxycyclobutenedione-4-thiolate anion (9). Hydrolysis of 9 with



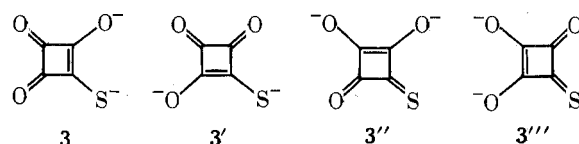
hydroxide is nearly quantitative, giving MTS<sup>2-</sup> which has been isolated and characterized as the hygroscopic tetramethylammonium salt (3a) and as the ternary zinc salt 3b.

The symmetrical delocalized structure of the squarate ion was originally proposed because no carbonyl band was observed in the ir.<sup>17</sup> The DTS<sup>2-</sup> ion has strong bands at 1705 and 1630 cm<sup>-1</sup>, suggesting that 4 is the major resonance contributor to the structure of DTS<sup>2-</sup>. However, the carbonyl stretching bands are shifted to higher frequency in the coordination complexes bonded through sulfur (1750–1655 cm<sup>-1</sup>) and in the S-alkylated compounds 2a,b (1770–1745 cm<sup>-1</sup>).<sup>7</sup> Therefore resonance forms 4' and 4'' may also contribute



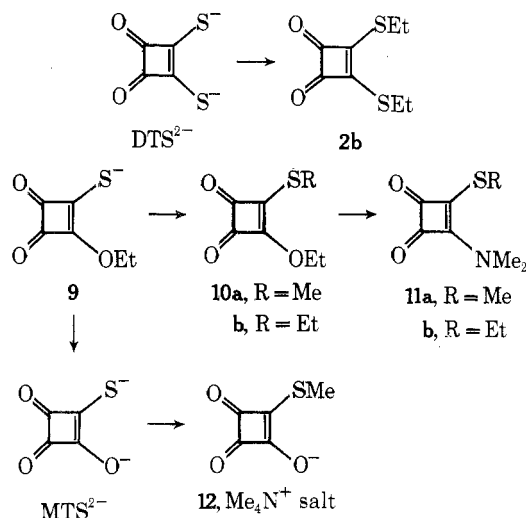
significantly to the structure of the free anion. The driving force for the incorporation of some carbon-sulfur double bond character may be the unfavorable  $\alpha$ -dicarbonyl dipole interaction in 4 which is reduced in 4' and 4''.

The MTS<sup>2-</sup> ion has a higher frequency carbonyl band than DTS<sup>2-</sup> (1735 vs. 1705 cm<sup>-1</sup>). In this ion, the equivalent canonical forms 3 and 3' can reduce the  $\alpha$ -dicarbonyl interaction,



and incorporation of carbon-sulfur double bond character (3'' and 3''') is not as important.

**Reactions of Thiosquarate Anions.** Alkylation of DTS<sup>2-</sup> with iodoethane occurs rapidly, yielding 3,4-bis(ethylthio)cyclobutenedione (2b) which has spectral properties similar



to those of 2a, the dibenzyl dithioester.<sup>7</sup> The 3-ethoxycyclobutenedione-4-thiolate ion (9) is also easily alkylated, forming 3-ethoxy-4-alkylthiocyclobutenediones 10a,b. Reaction of 10a,b with 1 equiv of dimethylamine gives only displacement of the ethoxy groups, yielding 3-dimethylamino-4-alkylthiocyclobutenediones 11a,b.<sup>18</sup> The MTS<sup>2-</sup> ion reacts only at sulfur with excess iodomethane to form the S-methylated ion 12.

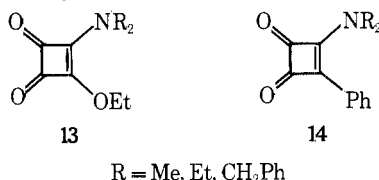
The structural assignments for compounds 2 and 9–12 are clear from the  $^1\text{H}$  NMR data summarized in Table I. The chemical shifts of the *O*-methylene and *S*-methylene protons are downfield from those of the corresponding acetates by

Table II. Infrared Spectra of Phosphorus- and Sulfur-Substituted Cyclobutenediones

	15	2a, R = PhCH <sub>2</sub>	2b, R = Et
$\nu_{C=O}$ , cm <sup>-1</sup>	1770	1765	1770
$\nu_{C4}$ , cm <sup>-1</sup>	1447	1453	1454
	1128	1124	1133

0.6–0.7 ppm, and dimethyl squaramides have *N*-methyls that appear 0.3–0.4 ppm downfield from dimethylacetamide.

Dialkylamino-substituted cyclobutenediones **13** and **14** undergo relatively slow rotation about the C–N bond, giving

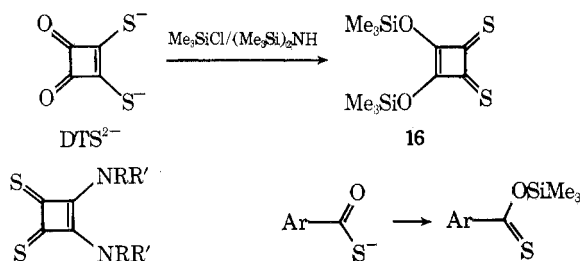


rise to nonequivalent alkyl groups in the <sup>1</sup>H NMR spectra.<sup>19</sup> Hindered rotation was also observed in the <sup>1</sup>H NMR spectra of **11a,b**, and a variable temperature study of **11b** showed coalescence of the *N*-methyls at 62.5 ± 1 °C, corresponding to an activation energy of 17.5 kcal/mol. Similar activation energies (15.7–17.3 kcal/mol) were found for the amides **13** and **14**.<sup>19</sup>

The ir spectra of cyclobutenediones with 2p-element substituents (CH<sub>3</sub>, NR<sub>2</sub>, OR) have two C=O stretching frequencies in the 1600–1900-cm<sup>-1</sup> region and a strong C=C band at 1500–1600 cm<sup>-1</sup>.<sup>20</sup> The ir spectra of 3-ethoxy-4-alkylthiocyclobutenediones **10a,b** and 3-dimethylamino-4-alkylthiocyclobutenediones **11a,b** are similar, having the expected C=O and C=C bands, but the spectra of 3,4-bis(alkylthio)cyclobutenediones **2a,b** lack the C=C band in the 1500–1600-cm<sup>-1</sup> range. Compounds **2a,b** have in common four especially strong bands at frequencies very near those previously assigned to C=O and cyclobutene stretching modes in 3,4-bis(diphenylphosphino)cyclobutenedione<sup>21</sup> (**15**, Table II).

Protonation of DTS<sup>2-</sup> gave a yellow solid with an S–H band in the ir, but rapid decomposition with loss of hydrogen sulfide discouraged further characterization.

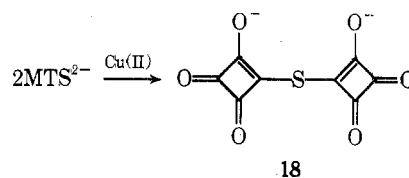
Silylation of DTS<sup>2-</sup> yielded an extremely moisture-sensitive red-orange compound (**16**) which readily dissolved in ether and carbon tetrachloride. Although **16** regenerated DTS<sup>2-</sup> on



**17a**, R = H; R' = cyclohexyl  
**b**, R = R' = Et

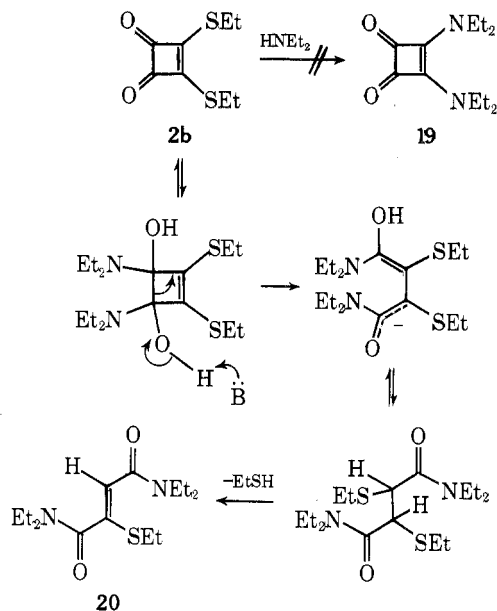
reaction with hydroxide, comparison of the ir spectrum with that of 3,4-bis(ethylthio)cyclobutenedione (**2b**) ruled out structural assignment as the *S,S'*-disilyl derivative. Comparison to the ir spectra of dithiosquaramides **17a,b**<sup>22</sup> and the report of O-silylation of potassium thiobenzoates<sup>23</sup> suggested that **16** was the O-silylated derivative of DTS<sup>2-</sup>.<sup>24</sup>

Reactions of DTS<sup>2-</sup> and transition metal ions have led to interesting coordination compounds,<sup>7,25</sup> and the reaction of MTS<sup>2-</sup> with aqueous copper(II) ion to give the bicyclic anion **18** has been reported.<sup>13</sup>



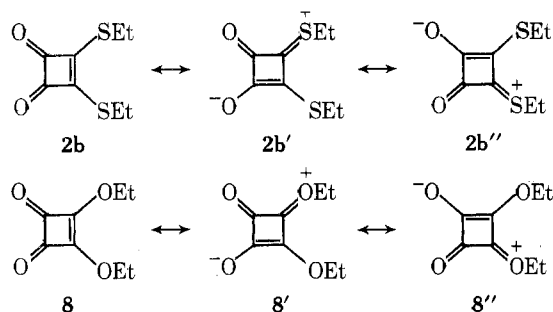
**Reaction of Thiosquarate Esters with Amines.** Reactions of dichlorocyclobutenedione (**1**) and diethyl squarate (**8**) resemble those of carboxylic acid chlorides and esters<sup>3a,6</sup> and carboxylic thioesters have long been known to react like esters.<sup>26</sup> To see if alkylthio groups could easily be removed from cyclobutenediones, several experiments were carried out. Reaction of 3-ethoxy-4-alkylthiocyclobutenediones **10a,b** with dimethylamine gave displacement of the ethoxy groups rather than the alkylthio groups (vide supra).

When 3,4-bis(ethylthio)cyclobutenedione (**2b**) was treated with an excess of diethylamine, formation of the expected squaramide **19** did not occur. The product in nearly quanti-



tative yield was identified from spectral data as fumaramide **20**. The *trans* geometry was established by comparison of the observed chemical shift of the vinyl proton ( $\delta$  7.65) with the chemical shifts calculated from substituent constants<sup>27</sup> for fumaramide **20** ( $\delta$  7.64) and the corresponding maleamide ( $\delta$  6.86). The reaction probably proceeds by addition of amine to the carbonyl groups followed by base-catalyzed ring opening to a sulfur-stabilized enolate ion which can go on to the observed product.<sup>28</sup> Diphenylcyclobutenedione undergoes similar ring-opening reactions with ethanol and aromatic or acetylenic Grignard reagents.<sup>29–31</sup>

Nucleophilic addition at the carbonyl groups of 3,4-bis(ethylthio)cyclobutenedione (**2b**) rather than at the vinyl carbons as seen in the reactions of diethyl squarate (**8**)<sup>3a,6</sup> is consistent with a smaller contribution of dipolar resonance forms. Contributions by canonical forms **2b'**, **2b''**, **8'**, and **8''** are expected to decrease electron deficiency at the carbonyl carbons and make the vinyl carbons more susceptible to nucleophilic attack. Because of the much greater bond energy of carbon–oxygen double bonds than carbon–sulfur double bonds,<sup>32</sup> the dipolar resonance forms **2b'** and **2b''** should be much less important than **8'** and **8''**.



It has been pointed out (vide supra) that the ir spectra of dithioesters **2a,b** differ from spectra of cyclobutenediones with 2p-element substituents, and the observed reactivity of **2b** is quite different from that of diethyl squarate (**8**). Dithioesters **2a,b**, as well as other alkylthiocyclobutenediones, obviously have unique chemical properties which cannot necessarily be predicted from those of the alkoxy-cyclobutenediones.

### Experimental Section

**General Methods.** The following instruments were used for spectral measurements:  $^1\text{H}$  NMR, Varian A-60A; ir, Perkin-Elmer 457; uv-visible, Cary 14; mass spectra, AEI-MS 902, ionization potential 70 eV. Gas-liquid chromatography was carried out on a Barber-Coleman 5340 with a thermal conductivity detector. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points and boiling points are uncorrected.

**Squaric acid** was obtained from Aldrich or Columbia Organic Chemicals.

**Diethyl squarate (8)** was prepared by reaction of squaric acid and ethanol<sup>3a,6</sup> and had the following spectral properties: ir ( $\text{CHCl}_3$ ) 1810 (m), 1735 (s), 1605 (s), 1480 (m), 1425 (m), 1380 (m), 1335 (m), 1080 (m), 1025  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  4.71 (q, 2 H), 1.50 (t, 3 H);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  4.68 (q, 2 H), 1.40 (t, 3 H).

**Dipotassium and Disodium 1,2-Dithiosquarate (4a,b).** A 130-ml portion of 0.47 M anhydrous potassium methoxide in methanol (0.61 mol) was cooled to 0 °C and saturated with hydrogen sulfide. Addition of 5.1 g (0.27 mol) of diethyl squarate (**8**) was carried out over 15 min while stirring at 0 °C and hydrogen sulfide addition were continued. The reaction mixture was then stirred at 0 °C for 1 h, allowed to warm, and stirred at room temperature for 1 h, and heated at reflux for 0.5 h. Evaporation of solvent gave 7.8 g of yellow solid which was recrystallized from 100 ml of 90% aqueous methanol and dried ( $\text{CaSO}_4$ ) to give 6.13 g (85%) of dipotassium 1,2-dithiosquarate monohydrate (**4a**): ir (KBr) 1705 (s), 1630 (s), 1340 (s), 1325 (s), 1205 (s), 920 (m), 565  $\text{cm}^{-1}$  (m); uv-visible (water)  $\lambda_{\text{max}}$  347 nm ( $\log \epsilon$  4.42), 322 sh (4.30), 250 (4.12), 231 (4.04). Anal. Calcd for  $\text{C}_4\text{O}_2\text{S}_2\text{K}_2 \cdot \text{H}_2\text{O}$ : C, 19.99; H, 0.84. Found: C, 19.89; H, 0.89.

Drying at 100 °C in vacuo removed ca. 0.33 mol of water. Anal. Calcd for  $\text{C}_4\text{O}_2\text{S}_2\text{K}_2 \cdot 0.67\text{H}_2\text{O}$ : C, 20.49; H, 0.60; S, 27.45. Found: C, 21.18; H, 0.58; S, 27.35.

Reaction of diethyl squarate with sodium hydrosulfide in ethanol under similar conditions, followed by recrystallization from aqueous ethanol and drying in vacuo at 100 °C, gave **4b** (80%) hydrated with ca. 2.67 mol of water. Anal. Calcd for  $\text{C}_4\text{O}_2\text{S}_2\text{Na}_2 \cdot 2.67\text{H}_2\text{O}$ : C, 20.16; H, 2.03; S, 26.92; O, 31.36. Found: C, 20.17; H, 2.25; S, 26.81; O, 31.33.

**Tetramethylammonium 3-Ethoxycyclobutenedione-4-thiolate (9a).** To a hydrogen sulfide saturated solution of 12 ml (0.033 mol) of 2.77 M tetramethylammonium hydroxide in methanol and 50 ml of absolute ethanol at 0 °C was added 5.1 g (0.033 mol) of diethyl squarate (**8**). The reaction mixture was then stirred at 0 °C for 1 h, allowed to warm to room temperature, and stirred for 1 h, and heated at reflux for 30 min. Evaporation of solvent gave a yellow solid which was recrystallized from 25 ml of absolute ethanol to give after drying ( $\text{CaSO}_4$ ) 5.1 g (74%) of **9a**: mp 151–154 °C; ir (KBr) 3020 (w), 2970 (w), 1755 (s), 1675 (s), 1500 (s), 1445 (s), 1360 (s), 1315 (s), 1295 (s), 1260 (s), 1045 (s), 955 (s), 940 (s), 770  $\text{cm}^{-1}$  (s);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  4.80 (q, 2 H), 3.15 (s, 12 H), 1.38 (t, 3 H); uv-visible (water)  $\lambda_{\text{max}}$  316 nm ( $\log \epsilon$  4.50). Anal. Calcd for  $\text{C}_{10}\text{H}_{17}\text{SNO}_3$ : C, 51.92; H, 7.41; N, 6.06; S, 13.86. Found: C, 52.03; H, 7.48; N, 6.11; S, 14.00.

**Potassium 3-Ethoxycyclobutenedione-4-thiolate (9b).** Under conditions similar to those used in the preparation of **9a**, 1.00 g (5.88 mmol) of diethyl squarate (**8**) was added to a solution of 6.00 ml (5.99 mmol) of 0.998 N methanolic potassium hydroxide and 20 ml of methanol saturated with hydrogen sulfide. Several recrystallizations

from ethanol gave 0.75 g (65%) of **9b**: ir (KBr) 1755 (s), 1650 (s), 1510 (s), 1390 (m), 1305 (s), 1040 (m), 995 (m), 975  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ )  $\delta$  4.79 (q), 1.38 (t). Anal. Calcd for  $\text{C}_6\text{H}_5\text{O}_3\text{SK}$ : C, 36.72; H, 2.57. Found: C, 36.62; H, 2.48.

**Bis(tetramethylammonium)zinc(II) Bis(monothiosquarate) (3b).** A solution of 6.1 g (0.0264 mol) of **9a** and 9.0 ml (0.0249 mol) of 2.77 N methanolic tetramethylammonium hydroxide in 10 ml of water was heated at reflux until the pH of the solution became neutral (90 min). A solution of 3.71 g (0.0125 mol) of zinc nitrate hexahydrate in 10 ml water was added and the solution was heated for 20 min longer. Evaporation of water and methanol, recrystallization from ethanol, and repeated recrystallization from methanol gave 0.9 g (14%) of light yellow  $(\text{Me}_4\text{N})_2\text{Zn}(\text{MTS})_2$  (**3b**): ir (KBr) 3010 (w), 1750 (s), 1650 (s), 1550 (s, br), 1480 (s), 1370 (s), 1280 (s), 1100 (m), 1040 (m), 950 (s), 800 (m), 680  $\text{cm}^{-1}$  (m); uv-visible (water)  $\lambda_{\text{max}}$  324 nm ( $\log \epsilon$  4.81), 269 (4.34). Anal. Calcd for  $\text{C}_{16}\text{H}_{24}\text{O}_6\text{S}_2\text{N}_2\text{Zn}$ : C, 40.88; H, 5.15. Found: C, 40.86; H, 5.02.

**Tetramethylammonium Monothiosquarate (3a).** A solution of 5.0 g (0.022 mol) of tetramethylammonium 3-ethoxycyclobutenedione-4-thiolate (**9a**) and 12 ml (0.033 mol) of 2.75 M methanolic tetramethylammonium hydroxide in 35 ml of methanol and 5 ml of water were heated at reflux for 1 h. Methanol and water were removed under vacuum and the solid residue was recrystallized from absolute ethanol to yield 4.7 g (71%) of highly hygroscopic **3a**: ir (KBr) 3005 (w), 2950 (w), 1735 (s), 1590 (s), 1540 (s), 1485 (s), 1400 (m), 1280 (s), 1130 (m), 955  $\text{cm}^{-1}$  (s).

When the uv-visible spectrum of a solution of **9a** and excess sodium hydroxide in water was monitored, nearly quantitative hydrolysis to the monothiosquarate ion was evidenced by the appearance in several hours of the following spectrum:  $\lambda_{\text{max}}$  324 nm ( $\log \epsilon$  4.49), 269 (3.99).

**3,4-Bis(ethylthio)cyclobutenedione (2b).** A solution of 31.0 g (0.129 mol) of dipotassium 1,2-dithiosquarate monohydrate (**4a**) in 200 ml of DMF and 20 ml of water was treated with 54.5 g (0.35 mol) of freshly distilled iodoethane. After stirring for 4.5 h at room temperature, the reaction mixture was added to 1 l of water and extracted with one 400-ml and four 200-ml portions of pentane. The combined organic extracts were washed with saturated aqueous sodium chloride, dried ( $\text{MgSO}_4$ ), and concentrated, and the yellow liquid was distilled (85–90 °C, 0.05 Torr) to give 23.6 g (91%) of **2b**. GLC analysis (20% QF-1, 202 °C) showed one peak with a retention time of 22 min. The following data were obtained: ir ( $\text{CCl}_4$ ) 1770 (s), 1747 (s), 1454 (s), 1421 (m), 1378 (m), 1265 (m), 1133 (s), 1078 (m), 1040 (m), 872  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{CCl}_4$ )  $\delta$  3.46 (q, 2 H), 1.48 (t, 3 H); mass spectrum (10 eV)  $m/e$  (rel intensity) 204 (11), 203 (12), 202 (100,  $\text{M}^+$ ), 174 (10), 148 (4), 147 (4), 146 (37); uv-visible (cyclohexane)  $\lambda_{\text{max}}$  321 nm sh ( $\log \epsilon$  4.22), 311 (4.36), 302 sh (4.29), 290 sh (4.17), 213 (4.07). Anal. Calcd for  $\text{C}_8\text{H}_{10}\text{S}_2\text{O}_2$ : C, 47.50; H, 4.98; S, 31.70. Found: C, 47.32; H, 4.88; S, 31.65.

**3,4-Bis(benzylthio)cyclobutenedione (2a).** A solution of 2.0 g (0.0171 mol) of  $\alpha$ -toluenethiol and 2.4 g (0.0170 mol) of triethylamine in 5 ml of chloroform was added dropwise in 1 h to a stirred solution of 1.28 g (0.0085 mol) of dichlorocyclobutenedione (**1**)<sup>33</sup> at 0 °C and stirred for an additional 1 h. The reaction mixture was washed twice with 25 ml of 2% aqueous hydrochloric acid and twice with water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to yield 2.8 g (103%) of a yellow oil, 75% **2a** by  $^1\text{H}$  NMR. Several recrystallizations from hexane and hexane-benzene yielded 1.0 g (36%) of yellow **2a**: mp 69–70 °C; ir ( $\text{CCl}_4$ ) 3060 (w), 3030 (w), 2915 (w), 2845 (w), 1765 (s), 1747 (s), 1495 (w), 1453 (s), 1415 (w), 1124 (s), 1070 (w), 690  $\text{cm}^{-1}$  (m);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.24 (s, 5 H), 4.75 (s, 2 H); mass spectrum  $m/e$  (rel intensity) 326 (12,  $\text{M}^+$ ), 235 (10,  $\text{M}^+ - \text{C}_7\text{H}_7$ ,  $\text{M}^*$  at 169.5), 207 (8), 123 (31), 91 (100), 65 (12).

**3-Ethoxy-4-methylthiocyclobutenedione (10a).** A solution of 2.31 g (0.0100 mol) of **9a** in 25 ml of acetonitrile was treated with 2.3 g (0.016 mol) of freshly distilled iodomethane. After the mixture had been stirred at room temperature for 20 min, solvent and excess iodomethane were evaporated. The residue was dissolved in 50 ml of water and extracted with one 75-ml and six 25-ml portions of hexane. The organic extracts were combined, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated, and the residue Kugelrohr distilled (80–100 °C, 0.15 Torr) to yield 1.22 g (71%) of **10a** as a light yellow liquid:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  4.80 (q, 2 H), 2.85 (s, 3 H), 1.48 (t, 3 H); ir ( $\text{CCl}_4$ ) 2980 (w), 2940 (w), 1790 (s), 1745 (s), 1565 (s), 1340 (m), 1315 (m), 1260 (m), 1035  $\text{cm}^{-1}$  (m); mass spectrum  $m/e$  (rel intensity) 172 (34,  $\text{M}^+$ ), 144 (24), 115 (84), 88 (45), 87 (100), 72 (10), 59 (22), 58 (23);  $m/e$  172.01945 (calcd for  $\text{C}_7\text{H}_8\text{O}_3\text{S}$ , 172.01941).

**3-Ethoxy-4-ethylthiocyclobutenedione (10b).** To a solution of 1.00 g (4.32 mmol) of **9a** in 10 ml of dimethylformamide was added 0.97 ml (12 mmol) of freshly distilled iodoethane. The mixture was

stirred for 15 min and then partitioned between 25 ml of hexane and 35 ml of water. The aqueous layer was washed with five 25-ml portions of hexane and the combined organic layers were washed with 25 ml of saturated aqueous sodium chloride, dried (MgSO<sub>4</sub>), concentrated, and Kugelrohr distilled (80–90 °C, 0.15 Torr) to give 0.63 g (78%) of **10b**. GLC (20% QF-1, 225 °C) showed one peak at 11.7 min. Analysis of samples purified by preparative GLC gave the following data: ir (CCl<sub>4</sub>) 1785 (s), 1740 (s), 1560 (s), 1315 (m), 1255 (m), 1030 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 4.78 (q, 2 H), 3.38 (q, 2 H), 1.50 (t, 3 H), 1.45 (t, 3 H); uv-visible (cyclohexane) λ<sub>max</sub> 285 nm (log ε 4.34), 258 (3.98); mass spectrum (10 eV) *m/e* (rel intensity) 188 (8), 187 (12), 186 (100, M<sup>+</sup>), 158 (62), 129 (20), 101 (9). Anal. Calcd for C<sub>8</sub>H<sub>10</sub>SO<sub>3</sub>: C, 51.59; H, 5.41; S, 17.22. Found: C, 51.39; H, 5.25; S, 17.45.

**3-Dimethylamino-4-methylthiocyclobutenedione (11a)**. A solution of 0.13 g (2.9 mmol) of dimethylamine in 10 ml of ether was added dropwise to a stirred solution of 0.50 g (2.9 mmol) of 3-ethoxy-4-methylthiocyclobutenedione (**10a**) in 10 ml of ether. After stirring at room temperature for 10 min, solvent was removed and the residue recrystallized from hexane/benzene to give 0.35 g (70%) of light yellow **11a**: mp 114–115 °C; ir (CHCl<sub>3</sub>) 1780 (s), 1725 (m), 1710 (m), 1610 (s), 1425 (m), 1350 (m), 1320 (m), 1180 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.38 (s, 3 H), 3.23 (s, 3 H), 2.93 (s, 3 H); mass spectrum *m/e* (rel intensity) 173 (3), 172 (5), 171 (50, M<sup>+</sup>), 143 (24), 115 (81), 100 (100), 95 (24), 85 (32), 81 (9), 70 (10); *m/e* 171.0353 (calcd for C<sub>7</sub>H<sub>9</sub>NO<sub>2</sub>S, 171.0354). Anal. Calcd for C<sub>7</sub>H<sub>9</sub>NO<sub>2</sub>S: C, 49.10; H, 5.30; N, 8.18; S, 18.73. Found: C, 49.12; H, 5.37; N, 8.09; S, 18.98.

**3-Dimethylamino-4-ethylthiocyclobutenedione (11b)**. A solution of 0.200 g (1.07 mmol) of 3-ethoxy-4-ethylthiocyclobutenedione (**10b**) in 10 ml of methylene chloride was cooled to -78 °C and treated with 0.080 ml (1.2 mmol) of dimethylamine. The solution was allowed to warm slowly to room temperature in 30 min. <sup>1</sup>H NMR analysis of the crude product showed only peaks for **11b** plus a trace of an impurity at δ 3.0 (integration ca. 5% of triplet at δ 1.43). Recrystallization of the crude yellow oil from ether gave 0.155 g (78%) of **11b**: mp 58–60 °C (lit.<sup>10</sup> 59 °C); ir (CHCl<sub>3</sub>) 1780 (s), 1715 (m), 1610 (s), 1425 (m), 1350 (m), 1175 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.53 (q, 2 H), 3.40 (s, 3 H), 3.25 (s, 3 H), 1.43 (t, 3 H); mass spectrum *m/e* (rel intensity) 185 (M<sup>+</sup>, 75), 157 (8), 129 (65), 101 (31), 100 (100), 96 (30), 85 (31), 70 (10); *m/e* 185.05112 (calcd for C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>S, 185.05105).

Variable temperature <sup>1</sup>H NMR measurements on **11b** in bromobenzene were carried out from room temperature to 100 °C. Temperatures were measured by thermocouple (±1 °C) before and after spectral determination. Coalescence of the *N*-methyls occurred at 62.5 °C, and, at 100 °C, a single sharp peak was observed for **11a,b** at δ 2.90.

**Tetramethylammonium 3-Methylthiocyclobutenedione-4-olate (12)**. A solution of 13.0 g (5.62 mmol) of tetramethylammonium 3-ethoxythiocyclobutenedione-4-thiolate (**9a**) and 2.0 ml (5.54 mmol) of 2.77 N methanolic tetramethylammonium hydroxide in 10 ml of methanol and 2.0 ml of water was heated at reflux in the dark for 3 h. Solvents were evaporated and the crude tetramethylammonium monothiosquarate (**3a**) obtained was dissolved in 10 ml of Me<sub>2</sub>SO and 2 ml of water and treated with 2.1 g (15 mmol) of freshly distilled iodomethane. After stirring at room temperature for 10 min, the mixture was filtered by suction. Water and Me<sub>2</sub>SO were removed by Kugelrohr distillation, leaving 1.09 g (89%) of crude **12**. Recrystallization from dichloromethane gave 0.89 g (73%) of **12** as a yellow solid: mp 112–116 °C; ir (KBr) 3020 (w), 2940 (w), 1760 (s), 1690 (s), 1670 (s), 1605 (sh), 1565 (s), 1490 (m), 1330 (m), 1270 (s), 1120 (m), 1055 (m), 960 (m), 950 (s), 930 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 3.31 (s, 12 H), 2.73 (s, 3 H); uv-visible (water) λ<sub>max</sub> 310 nm (log ε 4.30), 257 (4.11). Anal. Calcd for C<sub>9</sub>H<sub>15</sub>NO<sub>3</sub>S: C, 49.75; H, 6.96; N, 6.45; S, 14.76. Found: C, 49.67; H, 6.97; N, 6.43; S, 14.54.

**Silylation of DTS<sup>2-</sup>**. A 2.34-g (0.010 mol) sample of **4a** found to have the formula K<sub>2</sub>C<sub>4</sub>O<sub>2</sub>S<sub>2</sub>·0.67H<sub>2</sub>O was suspended in 50 ml of dry ether and stirred under dry nitrogen in the dark with 5.1 ml (0.040 mol) of trimethylchlorosilane and 1.0 ml (0.005 mol) of hexamethyldisilazane for 5 days. The resulting red-orange solution was filtered in a glove bag and a known fraction of the clear filtrate was added to excess aqueous potassium hydroxide. Measurement of the uv-visible spectrum and comparison to the spectrum of DTS<sup>2-</sup> indicated that the ethereal filtrate contained disilylated DTS<sup>2-</sup> in 82% yield. Evaporation of ether and excess silylating agent from the filtrate yielded a red-orange, highly moisture-sensitive oil: ir (CCl<sub>4</sub>) 2960 (m), 1665 (s), 1425 (s), 1335 (s), 1295 (s), 1255 (s), 1110 (m), 1100 (m), 980 (s), 940 cm<sup>-1</sup> (m).

**3,4-Bis(cyclohexylamino)cyclobutenedithione (17a) and 3,4-bis(diethylamino)cyclobutenedithione (17b)** were prepared by the reported method.<sup>3a,22</sup> Compound **17a** was prepared in 80% yield using hexamethylphosphoric triamide as solvent and recrystallized

from Me<sub>2</sub>SO: mp 348–350 °C (darkens at 290 °C); ir (Nujol) 3230 (m), 3170 (m), 3120 (m), 1705 (s), 1570 (s), 1330 (s), 1270 (s), 1250 (s), 1230 (s), 1140 (m), 1080 (m), 945 (m), 885 cm<sup>-1</sup> (m); mass spectrum *m/e* (rel intensity) 308 (M<sup>+</sup>, 53), 225 (23), 193 (15), 183 (11), 145 (14), 144 (26), 143 (32), 116 (18), 111 (14), 105 (13), 83 (38), 55 (100), 44 (58). Anal. Calcd for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>S<sub>2</sub>: C, 62.29; H, 7.84; N, 9.08; S, 20.79. Found: C, 62.25; H, 7.81; N, 8.97; S, 20.85.

Compound **17b** was prepared in 24% yield using THF as solvent and recrystallized from benzene: mp 160–162 °C; ir (Nujol) 1675 (s), 1550 (s), 1310 (s), 1270 (s), 1250 (s), 1205 (m), 1170 (s), 1100 (m), 1070 (m), 1055 (m), 1010 (m), 795 (m), 560 cm<sup>-1</sup> (m); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.89 (q, 2 H), 1.33 (t, 3 H); uv-visible (MeOH) λ<sub>max</sub> 403 nm (log ε 4.60), 371 sh (4.48), 283 (4.34); mass spectrum *m/e* (rel intensity) 258 (11), 257 (16), 256 (100, M<sup>+</sup>), 241 (5), 227 (36), 213 (16), 170 (18), 140 (17), 128 (11), 116 (14), 112 (11), 110 (11), 88 (16), 84 (30), 72 (45). Anal. Calcd for C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>S<sub>2</sub>: C, 56.20; H, 7.86; N, 10.92; S, 25.01. Found: C, 56.16; H, 7.82; N, 10.97; S, 25.01.

**N,N,N',N'-Tetraethyl-2-ethylthiofumaramide (20)**. A solution of 0.40 g (2.0 mmol) of 3,4-bis(ethylthio)cyclobutenedione (**2b**) and 0.58 g (8.0 mmol) of diethylamine in 10 ml of ether was stirred at room temperature for 2.5 h. Evaporation of solvent and Kugelrohr distillation of the residue (135–140 °C, 0.1 Torr) gave 0.55 g (95%) of **20**: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 7.65 (s, 1 H), 3.72 (q, broad, *J* = 7 Hz, 4 H), 3.39 (q, *J* = 7 Hz, 2 H), 3.17 (q, *J* = 7 Hz, 2 H), 2.64 (q, *J* = 8 Hz, 2 H), 1.0–1.5 (m, 15 H); ir (neat) 2980 (m), 1630 (s), 1580 (s), 1555 (s), 1450 (m), 1330 (m), 1220 (m), 1115 cm<sup>-1</sup> (m); mass spectrum *m/e* (rel intensity) 286 (13), 187 (13), 186 (100), 158 (61), 129 (15), 128 (15), 126 (15), 114 (35), 100 (10), 98 (27), 97 (14), 96 (19), 86 (11), 82 (10), 72 (22), 68 (10), 59 (11), 56 (38); *m/e* 286.1727 (calcd for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S, 286.1715). Anal. Calcd for C<sub>14</sub>H<sub>26</sub>N<sub>2</sub>O<sub>2</sub>S: C, 58.71; H, 9.15; N, 9.78; S, 11.19. Found: C, 58.57; H, 8.97; N, 9.76; S, 10.96.

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**Registry No.**—1, 2892-63-9; **2a**, 52427-63-1; **3a**, 52427-67-5; **3b**, 58288-49-6; **4a**, 52427-61-9; **4b**, 52427-60-8; **15**, 41006-27-3; **16**, 60282-11-3; **17a**, 60282-12-4; **17b**, 60282-13-5; **20**, 60282-14-6; squaric acid, 2892-51-5.

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## Crystal and Molecular Structure of *trans*-Biphtalyl, C<sub>16</sub>H<sub>8</sub>O<sub>4</sub>. Reaction of Substituted Phthalic Anhydrides with Trialkyl Phosphites

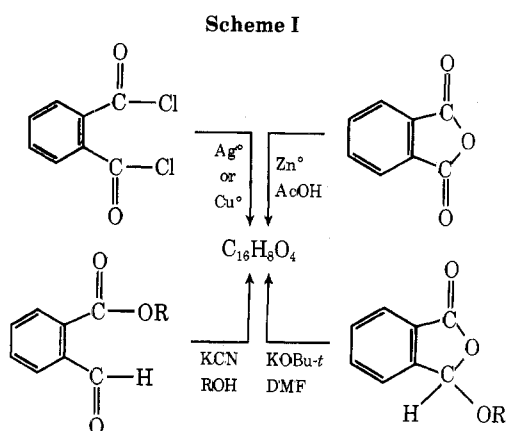
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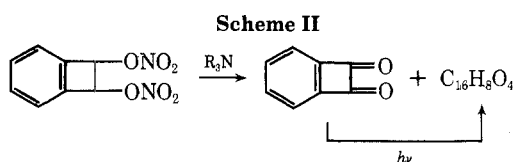
The crystal and molecular structure of *trans*-biphtalyl, the main product of the reaction of phthalic anhydride with triethyl phosphite, has been elucidated by x-ray crystallographic techniques. The yellow substance crystallizes in the monoclinic system, space group *P*2<sub>1</sub>/*c* with four asymmetric units per unit cell. The structure was refined by full-matrix least-squares techniques to a final *R* factor on *F* of 3.5% based on 571 observations above background. The molecule is planar, and some of the bond angles formed by the trigonal carbon atoms are significantly larger ( $\Delta \sim 12^\circ$ ) than the normal  $120^\circ$  value. It is suggested that the flexibility inherent in C-C-C, C-C-O, and C-O-C bond angles permits (a) the observed angle expansions which are required to allow for coplanarity of the chromophore O=C-C=C-C=C-C=C=O in the crowded molecule; and (b) the observed angle contractions, which are required to establish the five-membered rings. This effect accounts for the existence of octaphenyl-, octachloro-, and octabromo-*trans*-biphtalyl, although there is no assurance that the octahalo compounds have completely planar molecules.

The classical researches on the structure of phthalic anhydride, phthaloyl chloride, phthalaldehydic esters, and 3-alkoxyphthalides (Scheme I) led to a series of yellow and

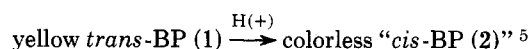


colorless isomers of the formula C<sub>16</sub>H<sub>8</sub>O<sub>4</sub>, known as "biphtalyls".<sup>2,3</sup> Some of those experiments were later repeated<sup>4</sup> and extended.<sup>5</sup>

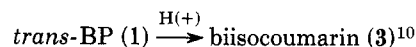
Structurally related C<sub>16</sub>H<sub>8</sub>O<sub>4</sub> compounds have been recently obtained from benzocyclobutene-1,2-diol dinitrate<sup>6</sup> (Scheme II), and from the photolysis<sup>7-9</sup> of benzocyclobutadienoquinone.<sup>6</sup>



The biphtalyls were initially formulated as the *trans* and *cis* isomers, 1 and 2, of the bis- $\gamma$ -lactone of *o,o'*-dicarboxybenzoin.<sup>2,3</sup> However, the work of Cava<sup>6</sup> and of Bird<sup>10</sup> suggests that, with one exception,<sup>7,8</sup> the colorless substance designated as *cis*-BP (2)<sup>11</sup> is identical with the biisocoumarin (3) that was obtained as a by-product of the benzocyclobutadienoquinone synthesis<sup>6</sup> (Scheme II). Thus, the *acid-catalyzed* isomerization



is actually



Scalar molecular models disclose an increasing degree of intramolecular crowding in the series: 3 < 1 << 2. Nevertheless (and this constitutes the exception mentioned above), Staab<sup>7,8</sup> has reported the isolation of authentic *cis*-BP (2, 5%), together with 1 (25%) and 3 (4%) from the photolysis of benzocyclo-

