

pressure. Alternatively, the gas mixture was circulated internally through the solution. At the conclusion, gas and solution samples were analyzed chromatographically, and the metal complex was recovered and identified. At 20–30°, only negligible conversions were observed within several hours; at 40°, 12 mole %<sup>14</sup> of ethane was produced from C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> catalyzed by [IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>] (24 hr.); at 60°, the yield of C<sub>2</sub>H<sub>6</sub> was 40% (18 hr.). At the latter conditions, 10% propane was obtained from propylene, and 10 and 5% of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were obtained, respectively, from acetylene. With [RhCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>], lower conversions were observed (e.g., 24% of C<sub>2</sub>H<sub>6</sub> from C<sub>2</sub>H<sub>4</sub> at 60°, 22 hr.).<sup>15</sup> The homogeneous hydrogenation of acetylene and ethylene has also been reported for the related rhodium complex [RhCl(Ph<sub>3</sub>P)<sub>3</sub>],<sup>4a,16</sup> as well as the platinum–tin system.<sup>4d</sup>

The possible mechanisms of these reactions and some factors determining catalytic hydrogenations with metal complexes will be discussed in a subsequent communication.

(14) The per cent yield refers to the mole per cent of the product in the final gas mixture (consisting of excess reactants, products, and solvent vapor) above the solution in the closed reactor.

(15) At higher temperatures, > 80°, gas circulation over extended periods caused slow reduction of the complexes to metals which rapidly catalyzed hydrogenation of the aromatic solvent. Thus, the absence of these hydrogenated species (e.g., cyclohexane) among the products served as an evidence for the homogeneity of the catalyses reported in this note.

(16) This compound, discovered by us independently several years ago, is highly dissociated in solution, and its composition and structure in solution are unknown at present (cf. (a) in text).

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## Cyclohex-2-ene-1,4-dione

Sir:

Although a considerable number of isolable diketo tautomers of di- and higher-substituted hydroquinones are known,<sup>1</sup> the parent compound, cyclohex-2-ene-1,4-dione (1), is unreported. Our curiosity about the conformation and tautomeric stability of 1 prompted its attempted synthesis. In this report, we wish to describe briefly this synthesis and relate some information regarding the stability of 1.

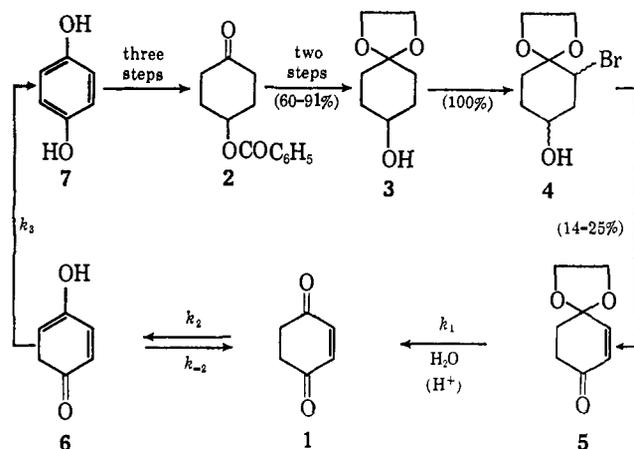
The starting material was hydroquinone (7) which was converted to 4-benzoyloxycyclohexanone (2) in three steps according to a reported procedure.<sup>2</sup> Transformation of 2 to 3 was effected by ketalization followed by saponification. Monobromination of 3 proceeded quantitatively at 40–45° in ethylene glycol containing 25 mole % sulfuric acid to give 4.<sup>3</sup> During

(1) See, for example: G. R. Yoke and co-workers, *J. Org. Chem.*, **24**, 1251 (1959); W. Mayer and R. Weiss, *Angew. Chem.*, **68**, 680 (1956); A. P. Ter Borg, *Rec. trav. chim.*, **73**, 5 (1954); M. Orchin and L. W. Butz, *J. Org. Chem.*, **8**, 509 (1943).

(2) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

(3) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965). Excess bromine (10%) was used for the bromination of 3. Brominations in ether led to considerable oxidation of the hydroxyl.

2–3 days at 30°, chromium trioxide–pyridine<sup>4</sup> converted crude 4 to 5, b.p. 77–80° (0.4 mm.), m.p. 39–41°; n.m.r. (in CCl<sub>4</sub>)  $\tau$  5.86 ( $\alpha$ -vinyl) and 3.50 ( $\beta$ -vinyl),  $J_{\alpha,\beta}$  = 10.4 c.p.s. *Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>: C, 62.33; H, 6.54. Found: C, 62.10; H, 6.34.



A mixture of one part of 5 and three parts of 0.5 M sulfuric acid (w./v.) was stirred at room temperature until a homogeneous solution resulted; this was left for approximately 30 min. (the reaction may be monitored conveniently by n.m.r.). Extraction of this solution with methylene chloride yielded, after drying the extract and evaporation of the solvent at 1 mm. and 0°, crude 1. Sublimation of the crude product at 0.1 mm. and 25° afforded 20–30% of 1, m.p. 54°; n.m.r.<sup>6</sup> (in CCl<sub>4</sub>)  $\tau$  3.30 (vinyl) and 7.12 (aliphatic) (relative areas 1:2),  $J_{\text{vinyl}}$  = 10.2 c.p.s. (<sup>13</sup>C satellite); infrared (in CCl<sub>4</sub>)  $\nu$  1690 (C=O) and 1600 cm.<sup>-1</sup> (C=C); ultraviolet (in ethanol)<sup>7</sup>  $\lambda$  233 ( $\epsilon$  15,100,  $\pi \rightarrow \pi^*$ ) and 352 m $\mu$  ( $\epsilon$  64,  $n \rightarrow \pi^*$ ), (in isooctane)  $\lambda$  219 ( $\epsilon$  15,700,  $\pi \rightarrow \pi^*$ ) and 365 m $\mu$  ( $\epsilon$  58,  $n \rightarrow \pi^*$ ). *Anal.* Calcd. for C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>: C, 65.45; H, 5.49. Found: C, 65.67; H, 5.49.

Crystalline 1 is stable over prolonged periods at 10°. In nonpolar aprotic solvents, tautomerization to 7 is slow, but in aqueous and alcoholic solutions this reaction proceeds rapidly (see below).<sup>7</sup> In trifluoroacetic acid-*d*-deuterium oxide, 5 is converted to 7 with no detectable (<5% by n.m.r.) incorporation of deuterium and no spectroscopic (ultraviolet and n.m.r.) evidence for the intermediacy of 6. Consequently,  $k_3 \gg k_{-2}$  and  $k_2$  in the above reaction sequence. First-order rate constants,  $k_1$  and  $k_2$ , for the consecutive reactions 5 to 1 and 1 to 6 may be obtained conveniently by n.m.r. ( $k_1$  by following the appearance of ethylene glycol and  $k_2$  by following the appearance of 7 or disappearance of 1). Some results over various sulfuric acid concentrations are given in Table I.

The significant aspects of the data in Table I are the large value of  $k_1/k_2$  which allows the described synthesis and the high rate of enolization of 1 ( $k_2$ ) in

(4) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(5) The freshly distilled 5 freezes at 20–25°. Many recrystallizations from ether–pentane with concomitant loss of material are required to raise the melting point to that reported. There appears to be no disadvantage in using crude 5 in the reaction sequence.

(6) Two per cent solution (w./w.).  $\tau$  values decrease upon increasing concentration.

(7) Approximately 6% of 7 was formed during the time required to prepare the ultraviolet solution and determine the spectrum. The value of  $\epsilon$  is corrected for this extent of tautomerization.

**Table I.** Rate Constants  $k_1$  and  $k_2$  for Conversion of **5** to **7** at 40°<sup>a</sup>

Acid concn. <sup>b</sup>	$k_1 \times 10^2$ , min. <sup>-1 c</sup>	$k_2 \times 10^2$ , min. <sup>-1 c</sup>	$k_1/k_2$
0.303	27	1.31	21
0.152	13	0.58	22
0.0303	2.9	0.139	21
0.000 <sup>d</sup>		3	

<sup>a</sup> 0.4 M **5** and 0.15 M methanol (used for internal reference) in aqueous solution. <sup>b</sup> Molarity of sulfuric acid. <sup>c</sup>  $\pm 15\%$ . <sup>d</sup> Neutral unbuffered aqueous solution of **1**.

neutral aqueous solution relative to the rates in moderately acidic solutions. This latter result demonstrates a small and probably negligible contribution to  $k_2$  from catalysis by water ( $k_0$ ) and suggests a large specific hydroxide ion catalytic constant ( $k_{OH^-}$ ).<sup>8</sup>

**Acknowledgment.** The author is appreciative of support of this work by the National Science Foundation (Grant No. GP 3589).

(8) R. P. Bell, "The Proton in Chemistry," Methuen & Co., Ltd., London, 1959, Chapter IX.

(9) A. P. Sloan Foundation Research Fellow.

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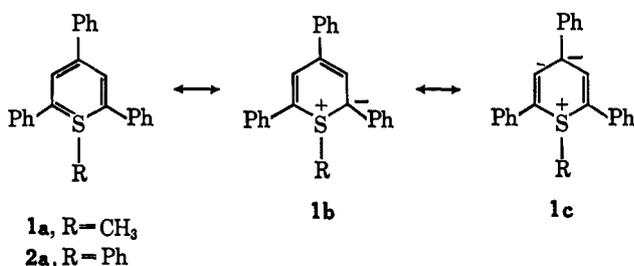
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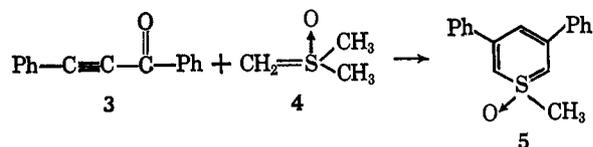
## Thiabenzenes. A Stable Thiabenzene 1-Oxide

Sir:

Several thiabenzene derivatives (**1a**, **2a**) have been reported recently<sup>1</sup>; of current interest is the question of



whether these structures are ylene-like and possess appreciable cyclic aromatic conjugation or whether they are more accurately represented as hybrid structures principally composed of ylide-like contributing structures such as **1b** and **1c**. In this communication the novel synthesis of a related heterocycle, 1-methyl-3,5-diphenylthiabenzene 1-oxide, is reported.



In a typical preparation a solution of 3-phenylpropiolophenone (**3**, 8.0 g., 0.039 mole) in 20 ml. of dry dimethyl sulfoxide was added rapidly under nitrogen to a solution of dimethyloxosulfonium methylide (**4**,<sup>2</sup> 0.082

(1) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962); C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963).

mole) in 80 ml. of dimethyl sulfoxide at 20°. After 20 hr. at room temperature the resulting red-orange solution was poured into water; the precipitated solid was crystallized from ethyl acetate-petroleum ether (b.p. 63–69°) to yield 6.75 g. (62%) of 1-methyl-3,5-diphenylthiabenzene 1-oxide (**5**) as yellow needles, m.p. 147–148.5°. A purified sample of **5** (sublimed at 140° (0.05 mm.)) melted at 148–148.5°; ultraviolet<sup>3</sup>  $\lambda_{max}^{MeOH}$  240 m $\mu$  ( $\epsilon$  26,200), 364 m $\mu$  ( $\epsilon$  10,000); infrared  $\nu_{max}^{CHCl_3}$  1527, 1490, 1385, 1371, 1130, and 697 cm.<sup>-1</sup>; n.m.r. (CDCl<sub>3</sub>) signals at  $\delta$  7.15–7.65 (10 H, multiplet), 6.19 (1 H, triplet,  $J = 1.1$  c.p.s.), 5.75 (2 H, doublet,  $J = 1.1$  c.p.s.), and 3.50 (3 H, singlet). *Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>SO: C, 77.12; H, 5.75; S, 11.42; mol. wt., 280.4. Found: C, 77.15; H, 5.76; S, 11.60; mol. wt., 276 (osmometer), 323 (Rast).<sup>4</sup>

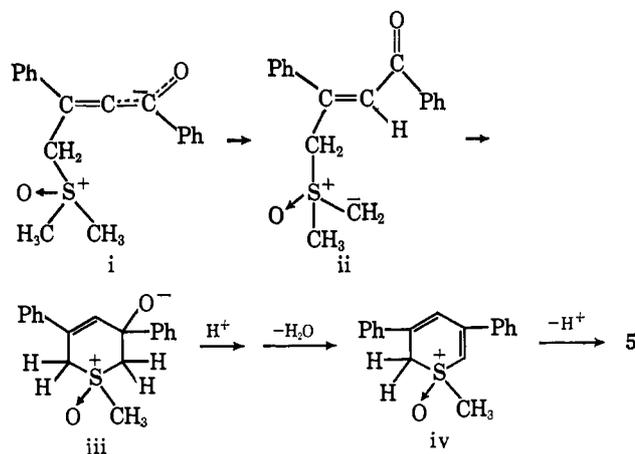
Refluxing **5** with D<sub>2</sub>O–CH<sub>3</sub>OD–NaOD (21 hr.) followed by aqueous workup gave **5-d<sub>3</sub>** in which the methyl hydrogens were exchanged (absence of 3 H singlet at  $\delta$  3.50); a solution of **5** in deuterioacetic acid (containing a trace of D<sub>2</sub>O) showed disappearance of the signals at  $\delta$  5.75 and 6.19 and appearance of a broad singlet (ca. 3 H) at  $\delta$  8.0 due to rapid exchange of the S-ring protons.<sup>5</sup>

The remarkable stability of **5** when compared with that of **1a** and **2a** is particularly noteworthy.<sup>6</sup> A similar relationship has been observed between dimethyloxosulfonium methylide and dimethylsulfonium methylide.<sup>2</sup> The behavior of **5** in acidic media taken with the n.m.r. peak positions (in CDCl<sub>3</sub>) for the S-ring protons suggests ylide-like character for **5**. However, the possibility of some cyclic aromatic conjugation involving the use of 3d orbitals by sulfur<sup>7</sup> cannot be discounted on this basis alone; further work leading

(2) E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965); **84**, 867 (1962).

(3) The ultraviolet spectrum was unchanged when measured in dilute methanolic sodium hydroxide; addition of hydrochloric acid to a neutral solution of **5** effected appearance of a new band at 313 m $\mu$ . No pK values have been obtained as yet.

(4) A reasonable route for the formation of **5** might involve initial Michael addition of **4** to **3** to give **i**, proton exchange to yield **ii**, followed by the transformations **ii** → **iii** → **iv** → **5**.



(5) Facile protonation has been reported for the somewhat similar 1,1-diphenylphosphabenzene system: G. Märkl, *Angew. Chem.*, **75**, 669 (1963).

(6) Whereas **1a** and **2a** rearrange readily at 25° to yield thiapyrans, **5** can be evaporatively distilled at 160° (0.05 mm.) without decomposition; compound **5** is stable to air whereas **2a** reacts rapidly with oxygen to yield a "peroxide" (see ref. 1).

(7) See, however, R. Breslow and E. Mohacsy, *J. Am. Chem. Soc.*, **84**, 684 (1962), and references cited therein.