

## The Catalytic Oxidation of Vicinal Diols to $\alpha$ Diketones<sup>1</sup>

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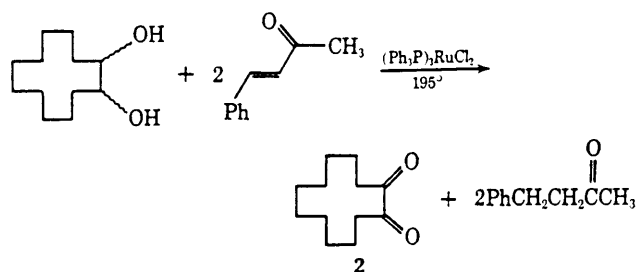
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We wish to describe a convenient method for the oxidation of certain vicinal diols to  $\alpha$  diketones, based on the ruthenium-catalyzed transfer-hydrogenation reaction reported by Sasson and Blum.<sup>3</sup>  $\alpha$  diketones are of value as precursors of acetylenes and dioximes. However, despite interest in substances containing the  $\alpha$ -diketone moiety, practical synthetic entries into this class of compounds are restricted to the oxidation of acyloins<sup>4</sup> and  $\alpha$ -halo ketones<sup>5</sup> using metal salts or dimethyl sulfoxide, oxidation of ketones with selenium dioxide,<sup>6</sup> and oxidation of olefins with potassium permanganate.<sup>7</sup> Although in principle vicinal diols would appear to be attractive as precursors of  $\alpha$  diketones, in practice the direct oxidation of vicinal diols produces  $\alpha$  diketones only in erratic yields.<sup>8</sup>

The procedure described here involves the transition metal catalyzed transfer of hydrogen from the diol to a suitable olefinic hydrogen acceptor. Exploration of several metallic catalysts and hydrogen acceptors (Table I) suggests that the combination described by

Sasson and Blum, tris(triphenylphosphine)ruthenium dichloride and benzalacetone, is the most effective, although the reaction appears less sensitive to the hydrogen acceptor than to the catalyst. At low conversion of 1,2-cyclododecanediol (1) to 1,2-cyclododecane-



dione (2), an appreciable quantity of  $\alpha$ -hydroxycyclododecanone (3) can be detected in the reaction mixture; 3 is itself smoothly oxidized to 2 under the reaction conditions. Thus, we presume that the overall con-

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- (3) Y. Sasson and J. Blum, *Tetrahedron Lett.*, 2167 (1971).
- (4) A. T. Blomquist and A. Goldstein, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 838.
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TABLE I  
 OXIDATION OF VICINAL DIOLS TO  $\alpha$  DIKETONES<sup>a</sup>

Diol	Diketone	Catalyst	Hydrogen acceptor	Time, hr	Yield, %		
<i>cis</i> -1,2-cyclododecanediol	2	(Ph <sub>3</sub> P) <sub>3</sub> RuCl <sub>2</sub>	Benzalacetone	6	53		
		(Ph <sub>3</sub> P) <sub>3</sub> RhCl			20		
		(PhCN) <sub>2</sub> PdCl <sub>2</sub>			14		
		(Ph <sub>3</sub> P) <sub>2</sub> IrCOCl			7		
		Pd/C			4		
				Chalcone		10	48
			Mesityl Oxide				34
			1-Docosene				20
			Benzalacetone				78 (50) <sup>b</sup>
							100
<i>trans</i> -1,2-cyclododecanediol	2,3-Norbornanediol			1	74		
<i>trans</i> -1,2-Cyclohexanediol	1,2-Cyclohexanedione			1	85		
2,3-Butanediol	2,3-Butanedione			4	70 (40) <sup>b</sup>		
1,2-Diphenyl-1,2-dihydroxyethane	Benzil			2	63		
9,10-Dihydroxystearic acid	9,10-Diketostearic acid			4	22		
$\alpha$ -Hydroxycyclododecanone	2			10	84		

<sup>a</sup> Unless noted otherwise, reactions were carried out using the following starting concentrations: [diol], 0.2 M; [hydrogen acceptor], 1.0 M; [catalyst], 0.0025 M. Tetrahydrofuran was used as solvent; the reaction temperature was 195°. Yields were obtained by glpc. <sup>b</sup> Isolated yield; 1,2-bis(2-methoxyethoxy)ethane was used as solvent.

version of 1 to 2 proceeds in an unexceptional two-stage oxidation through intermediate 3.

The advantage of this procedure for the preparation of  $\alpha$  diketones lies in its simplicity and in its avoidance of the reactive oxidants and strong Lewis acids employed in certain of the other syntheses of these compounds; its principal disadvantage is the high temperature at which the reaction is carried out. However, perhaps because the reactions are carried out under neutral conditions, it has proved possible to obtain good yields of certain  $\alpha$  diketones (in particular 2,3-butanedione and 1,2-cyclohexanedione) that cannot be obtained in satisfactory yields by the most convenient of these alternative procedures.<sup>7</sup>

### Experimental Section<sup>9</sup>

**General Methods.**—Unless otherwise specified, all reagents were obtained commercially and were used without further purification. Tetrahydrofuran was dried by distillation from sodium benzophenone ketyl under a nitrogen atmosphere. The 1,2-bis(2-methoxyethoxy)ethane used was purified by distillation from calcium hydride under a nitrogen atmosphere. The following commercial catalysts (sources) were used: (Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub> and (Ph<sub>3</sub>P)<sub>2</sub>IrCOCl (Strem Chemical Co); (Ph<sub>3</sub>P)<sub>3</sub>RhCl (Alpha Inorganics); Pd/C (Engelhard).

**General Procedure for Small-Scale Reactions.**—Procedures similar to that described for the conversion of *cis*-1,2-cyclododecanediol to 1,2-cyclododecanedione were followed for all of the small scale oxidations described in Table I. A mixture of 16 mg

(0.08 mmol) of *cis*-1,2-cyclododecanediol, 35 mg (0.24 mmol) of benzalacetone, 1 mg (0.001 mmol) of tris(triphenylphosphine)ruthenium dichloride, and 0.4 ml of tetrahydrofuran was sealed under a nitrogen atmosphere in a 4-in., 5-mm Pyrex tube. The tube was placed in an oil bath, maintained at 195° for 10 hr, withdrawn, and cooled. An internal standard was then added to the reaction mixture, and the mixture was analyzed by glpc using a UC-W98 on Chromosorb W column.

**Oxidation of *cis*-1,2-Cyclododecanediol.**—To a mixture of 10 g (0.05 mol) of *cis*-1,2-cyclododecanediol, 14.6 g (0.1 mol) of benzalacetone, and 0.2 g (0.0002 mol) of tris(triphenylphosphine)ruthenium dichloride was added 55 ml of freshly distilled 1,2-bis(2-methoxyethoxy)ethane, and the resulting solution was heated under nitrogen at 195°. The course of the reaction was monitored by glpc (the end of the reaction was indicated by the disappearance of benzalacetone from the reaction mixture). After 10 hr, the reaction mixture was cooled, poured into 300 ml of water, and extracted with 100 ml of ether. The ether solution was dried and concentrated, and the residue was distilled through a 10-cm vacuum-jacketed stainless steel spinning-band column to yield 5 g (50%) of 1,2-cyclododecanedione having bp 98–100° (1.5 mm) [lit.<sup>10</sup> bp 100° (1.5 mm)] and an ir and a mass spectrum indistinguishable from those of an authentic sample.<sup>11,12</sup>

**Registry No.**—*cis*-1, 4422-05-3; 2, 3008-41-1.

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(10) C. W. Cumper, G. B. Leton, and A. I. Vogel, *J. Chem. Soc.*, 2067 (1965).

(11) An authentic sample of 1,2-cyclododecanedione was prepared by the procedure described by Sharpless, *et al.*<sup>7</sup>

(12) S. Cenini, A. Fusi, and G. Capparella [*Inorg. Nucl. Chem. Lett.*, 127 (1972)] have reported the rapid reaction of (Ph<sub>3</sub>P)<sub>3</sub>RuCl<sub>2</sub> with molecular oxygen. Thus, these oxidations should be carried out with careful exclusion of oxygen.

(9) Boiling points are uncorrected. Ir spectra were taken in sodium chloride cells using a Perkin-Elmer Model 237-B spectrophotometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Product mixtures were analyzed by glpc on an F & M Model 810 flame ionization instrument.