2% methanol in methylene chloride) and various fractions were removed from the plate and extracted with chloroform in a Soxhlet extractor. One of these fractions gave pale yellow crystals of 4-ethyl-2-phenyloxazolo[4,5-c]pyridine (**3**, 192 mg, 17%). Recrystallization from hexane gave colorless crystals: mp 89–90°; ir (KBr) 2980–2850 cm^{-1} (aliphatic CH); uv max (95% EtOH) 282 nm (ϵ 3000); nmr ($CDCl_3$) τ 1.50 (d, J = 8 Hz, 1 H, H_6), 1.6–1.9 (m, 2 H, ortho H's of phenyl), 2.3–2.8 (m, 4 H, meta and para H's of phenyl and H_7), 6.75 (q, 2 H, CH_2), 8.53 (t, 3 H, CH_3); the nmr spectrum lacks the characteristic singlet at τ 0.87 due to H_4 in the starting material.[13]

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 74.73; H, 5.68; N, 11.84.

Another fraction from the plc separation yielded 79 mg of a brown nonhomogeneous oil (at least three spots by tlc) which we believe contains the dihydropyridine derivative **2**: ir (film) 3300 (broad, OH and NH), 2980–2850 cm^{-1} (aliphatic CH); nmr ($CDCl_3$) τ 6.47 (q, 2 H, CH_2CH_3), 8.47 (d, 3 H, CH_3CH), 8.77 (t, 3 H, CH_2CH_3) (although quite complex the above features could be discerned).

3-Benzamido-4-pyridone (5).—A sample of the oxazolopyridine **1** (110 mg, 0.56 mmol) was dissolved in 10 ml of dilute hydrochloric acid and allowed to stand at room temperature for 72 hr. At this stage, colorless needles had formed and they were removed by filtration, washed with water, and air dried. These crystals were shown to be the hydrochloride salt of the pyridinol tautomer of **5** (140 mg, 93%): mp 219–222°; ir (KBr) 3300 (broad, OH), 2800–2300 (broad, NH^+), 1635 cm^{-1} (amide C=O).

Anal. Calcd for $C_{12}H_{13}N_2O_3Cl$ (monohydrate of hydrochloride salt): C, 53.64; H, 4.88; N, 10.42. Found: C, 53.53; H, 4.80; N, 10.49.

The product from above was dissolved in 20 ml of water containing 1 ml of dilute sodium hydroxide, stirred for 10 min, and then acidified with glacial acetic acid; the resulting colorless solid was filtered, washed with water, and air dried. Elution of this material through a short column of alumina with 2% methanol in chloroform (to remove contaminating sodium acetate) resulted in formation of 3-benzamido-4-pyridone (**5**) which was recrystallized from acetone–hexane to give colorless needles: mp 255–256°; ir (KBr) 3360 (NH), 1670 (pyridone C=O), 1635 cm^{-1} (amide C=O); uv max (95% EtOH) 292 nm (sh, ϵ 7340), 275 (8560), 225 (10,700).

Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.20; H, 4.78; N, 12.92.

2-Ethyl-3-benzamido-4-pyridone (4).—A sample of the oxazolopyridine **3** (54 mg, 0.24 mmol) was dissolved in 20 ml of 3 *N* hydrochloric acid and allowed to stand at room temperature for 48 hr. To this solution was added 3 g of alumina and the resultant mixture was evaporated to dryness at reduced pressure. The resultant powder was packed on the top of an 8-in. alumina column and the column was eluted with 2% methanol in chloroform. Evaporation of the eluate and recrystallization from ethanol–hexane gave the pyridone **4** as colorless needles (28 mg, 48%): mp 148–149°, 178–180° (resolidifies above 148° and then melts at 178–180°); ir (KBr) 3340 (NH), 1660 (pyridone C=O), 1624 cm^{-1} (amide C=O); uv max (95% EtOH) 260 nm (ϵ 11,800), 226 (sh, 14,000); high resolution mass spectrum,[14] calcd mol wt 242.1055, found 242.1054.

Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.72; H, 5.71; N, 11.74.

Detection of Ethanol.—The irradiation of **1** was monitored directly by vpc by withdrawing aliquots from the reaction mixture and analyzing on a 30% FFAP column (3/8 in., 20 ft, on 50–60 Chromosorb W) at 105°. With a helium flow rate of ~100 ml/min the approximate retention times for various components were the following: air, 3 min; ether, 4 min; ethanol, 21 min. By analyzing standard solutions of ethanol in ether (1.0, 0.1, 0.01, and 0.001% v/v) the lower limits of detectability were determined; it was shown that 0.001% ethanol could easily be detected. At the start of the irradiation the ethanol concentration in the ether used as solvent was less than 0.001%. As the photolysis progressed the buildup of ethanol could easily be observed and at completion of the irradiation (41 hr) the ethanol concentration was 0.002%.

(13) The nmr spectrum of **1** shows the following features: τ 0.87 (slightly broadened singlet, 1 H, H_4), 1.42 (d, J = 5.5 Hz, 1 H, H_5), 1.6–1.9 (m, 2 H, ortho H's of phenyl), 2.3–2.8 (m, 4 H, meta and para H's of phenyl and H_7).

(14) We thank Dr. Ted R. Evans, Eastman Kodak Laboratories, for this measurement.

Registry No.—**1**, 34297-84-2; **3**, 34282-21-8; **4**, 34282-22-9; **5**, 34282-23-0; **5** HCl, 34282-24-1; diethyl ether, 60-29-7.

The Catalytic Oxidation of Vicinal Diols to α Diketones[1]

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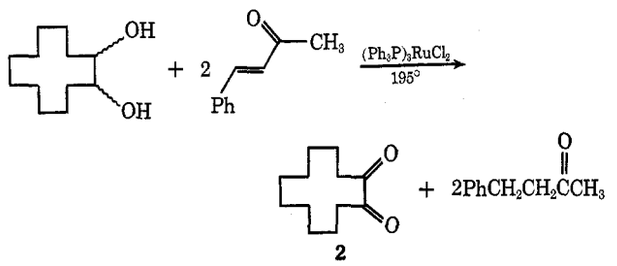
We wish to describe a convenient method for the oxidation of certain vicinal diols to α diketones, based on the ruthenium-catalyzed transfer–hydrogenation reaction reported by Sasson and Blum.[3] α diketones are of value as precursors of acetylenes and dioximes. However, despite interest in substances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

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-cyclododecanedione (**2**), an appreciable quantity of α-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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(2) A. D. Little Fellow, 1969–1970; A. P. Sloan Graduate Trainee, 1971–1972.

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TABLE I

OXIDATION OF VICINAL DIOLS TO α DIKETONES[a]

Diol	Diketone	Catalyst	Hydrogen acceptor	Time, hr	Yield, %
cis-1	2	$(Ph_3P)_3RuCl_2$	Benzalacetone	6	53
		$(Ph_3P)_3RhCl$			20
		$(PhCN)_2PdCl_2$			14
		$(Ph_3P)_2IrCOCl$			7
		Pd/C			4
		$(Ph_3P)_3RuCl_2$	Chalcone		48
			Mesityl Oxide		34
			1-Docosene		20
cis-1			Benzalacetone	10	78 (50)[b]
trans-1				10	100
2,3-Norbornanediol	2,3-Norbornanedione			1	74
trans-1,2-Cyclohexanediol	1,2-Cyclohexanedione			1	85
2,3-Butanediol	2,3-Butanedione			4	70 (40)[b]
1,2-Diphenyl-1,2-dihydroxyethane	Benzil			2	63
9,10-Dihydroxystearic acid	9,10-Diketostearic acid			4	22
α-Hydroxycyclododecanone	2			10	84

[a] 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. [b] 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 α 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 α 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.[7]

Experimental Section[9]

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: $(Ph_3P)_3RuCl_2$ and $(Ph_3P)_2IrCOCl$ (Strem Chemical Co); $(Ph_3P)_3RhCl$ (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.[10] bp 100° (1.5 mm)] and an ir and a mass spectrum indistinguishable from those of an authentic sample.[11,12]

(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.

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

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

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A Convenient Synthesis of 1,2,3,4,6,7,12,12b-Octahydroindolo[2,3-*a*]quinolizine

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The indole alkaloid 1,2,3,4,6,7,12,12b-octahydroindolo[2,3-*a*]quinolizine (**1**) was first synthesized 20 years ago[2] and in 1966 it was found to occur in nature,

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