

with 2 mol of $\text{NaC}\equiv\text{CH}$ as previously described; after the NH_3 had evaporated, the mixture was decomposed with 800 ml of water; and solid CO_2 was added until the pH of the solution was approximately 8. The ether layer was separated and dried (MgSO_4), and the solvent was removed. Distillation of the residue gave two fractions. The first fraction, bp 64–66° (4 mm), weight 7.5 g (10%), was cyclohexyl ethynyl ketone (28): nmr (CDCl_3) τ 6.65 (1 H, s, $\equiv\text{C-H}$), 8.42 (11 H, broad m, cyclohexyl); ir (CHCl_3) 3.02 ($\equiv\text{C-H}$), 4.76 ($\text{C}\equiv\text{C}$), 6.0 μ (CO). *Anal.* Calcd for $\text{C}_9\text{H}_{12}\text{O}$: C, 79.37; H, 8.88. Found: C, 79.21; H, 8.86.

The higher boiling fraction crystallized from petroleum ether (bp 35–60°) to give 3.5 g of solid with ir and nmr spectra identical with those of 22.

Treatment of 3 with H_2SO_4 . A.—A solution of 10 g (0.064 mol) of 3 in 250 ml of EtOH was cooled with an ice-water bath, and 25 ml of concentrated H_2SO_4 in 100 ml of water was added slowly. The mixture was allowed to stir for 5 days at room temperature. After being diluted with water, the mixture was extracted with ether. The ether solution was washed several times with water and dried (MgSO_4); distillation gave 8 g of oil, bp 60–65° (0.05 mm).

An analysis of the nmr spectrum of this oil indicated 72% 3-ethoxy-3-phenyl-1,4-pentadiyne (29), 16% *cis*- β -ethynylcin-namaldehyde (30), and 12% *trans* isomer (31).¹¹

The ether 29 was purified by column chromatography (Florasil, benzene) and distillation: bp 54° (0.01 mm); nmr (CDCl_3) τ 8.75 (3 H, t, methyl), 6.20 (2 H, q, methylene), 8.96 (2 H, s, $\text{C}\equiv\text{CH}$), and 2.56 and 2.28 (5 H, 2 m, phenyl); ir (CHCl_3) 3.06 μ ($\text{C}\equiv\text{CH}$). *Anal.* Calcd for $\text{C}_{13}\text{H}_{12}\text{O}$: C, 84.75; H, 6.57. Found: C, 84.47; H, 6.47.

B.—To 10 g (0.064 mol) of 3 in 150 ml of EtOH was added 25 ml of H_2SO_4 in 100 ml of H_2O ; the resulting mixture was heated to reflux temperature. A vigorous reaction ensued, and after 5 min, the mixture was worked up as above. The crude oil was distilled, bp 74–84° (0.03 mm). The distillate (31) which solidified was crystallized twice from petroleum ether (bp 60–71°): weight 3.5 g; mp 64–66°; nmr (CDCl_3) τ 6.21 (1 H, s, $\text{C}\equiv\text{CH}$), 3.85 (1 H, d, $J = 8$ Hz, vinyl), -0.33 (1 H, d, $J = 8$ Hz, aldehyde), and 2.53 and 2.30 (5 H, 2 m, phenyl); ir (CHCl_3) 3.05 ($\text{C}\equiv\text{CH}$), 4.75 ($\text{C}\equiv\text{C}$), 6.0 μ (CO). *Anal.* Calcd for $\text{C}_{11}\text{H}_8\text{O}$: C, 84.59; H, 5.16. Found: C, 84.86; H, 5.45.

Triethynylmethanol (32).—Ethylene carbonate (0.4 mol) dissolved in 300 ml of CH_2Cl_2 was treated with 2 mol of sodium acetylide in 2.5 l. of liquid NH_3 as before, and, after evaporating

(11) The nmr spectra of pure samples of 29 and 31 are described below. The assignment of the *cis* compound 30 was based on the presence of two additional doublets centered at τ 4.52 and 0.03 ($J = 8$ Hz). Isolation of this compound was not attempted.

the NH_3 , dry NH_4Cl (150 g), followed by ice and water (2 l.), was added. The mixture was allowed to stand for 30 min, and the aqueous layer was separated. The ether layer was washed with water (difficult emulsion) and dried (MgSO_4), and the ether was removed at reduced pressure. The residue was passed over a Florasil column with 9:1 $\text{C}_6\text{H}_5\text{-EtOAc}$, and the eluate was distilled, bp 50–55° (4 mm). This distillate solidified on cooling, mp 28–30°. Yields of 1–8% were obtained. Elemental analysis was not possible on this compound because of its explosive nature when combustion is attempted.

The nmr spectrum showed two peaks, 7.25 (3 H, s, acetylenic protons) and 6.70 (1 H, s, OH, D_2O exchangeable).

The ir spectrum had peaks at 3.05 μ for the acetylenic CH, 4.7 μ for the triple bond, and 2.84 μ for the OH (no peaks in the carbonyl region).

Triethynylmethyl Acetate (33).—An ethereal solution of 32 (0.05 mol) was added to a suspension of 30 g of powdered KOH in 500 ml of ether, cooling with an ice-ethanol bath and vigorously stirring. At -5° 20.2 g (0.2 mol) of acetic anhydride in an equal volume of ether was added dropwise over 20 min. Stirring and cooling were maintained for 45 min, and 500 ml of water was added. The ether solution was separated, washed twice with water, and dried (MgSO_4), and the ether was removed at reduced pressure. The residue was recrystallized from benzene-petroleum ether (bp 35–60°) to give 1.6 g (23%) of product, mp 88–89°. *Anal.* Calcd for $\text{C}_8\text{H}_6\text{O}_2$: C, 73.96; H, 4.14. Found: C, 73.93; H, 4.33.

Registry No.—3, 27410-03-3; 4, 27410-04-4; 5, 27410-05-5; 6, 27410-06-6; 7, 27410-07-7; 8, 27410-08-8; 9, 27410-09-9; 10, 27410-10-2; 11, 27410-11-3; 12, 27410-12-4; 13, 27410-13-5; 14, 27410-14-6; 15, 27410-15-7; 16, 27410-16-8; 17, 27410-17-9; 18, 27410-18-0; 19, 27410-19-1; 20, 27410-20-4; 21, 27410-21-5; 22, 27410-22-6; 23, 27410-23-7; 24, 27410-24-8; 25, 27410-25-9; 26, 27410-26-0; 27, 27410-27-1; 28, 7560-69-2; 29, 27410-29-3; 31, 27390-88-1; 32, 27410-30-6; 33, 27410-31-7.

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A New Method for the Preparation of α,β -Unsaturated Carbonyl Compounds

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A unique preparation of α,β -unsaturated aldehydes and ketones from the corresponding saturated analogs is reported. The procedure involves a homogeneous liquid-phase oxidative dehydrogenation by air or oxygen in the presence of a group VIII metal [preferably Pd(II)] catalyst and a cocatalyst. Particular attention is given to the synthesis of 2-cyclohexen-1-one (2). The scope and limitations of this reaction are discussed. In addition, probable and alternative mechanisms of this selective dehydrogenation technique are examined.

The preparation of α,β -unsaturated ketones and aldehydes customarily involves allylic oxidation of olefins,¹ elimination reactions on α substituted carbonyl compounds,² or dehydration of aldols.³ Most methods either involve several steps or are often complicated by

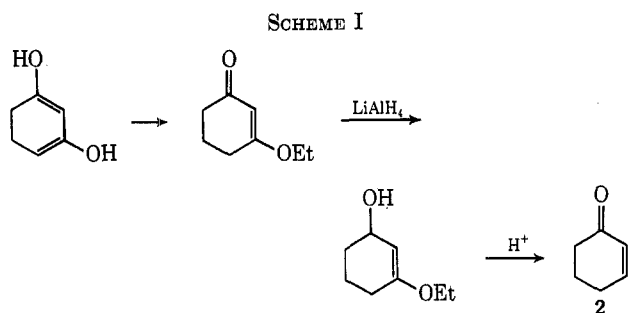
low yields and unwanted by-products. Typical of an excellent, but several-step synthesis of an α,β -unsaturated ketone is that pictured in Scheme I for 2-cyclohexen-1-one (2) from dihydroresorcinol.⁴ Since no short and easy synthetic scheme was available for the preparation of a highly versatile compound such as 2, it was advantageous to develop a one-step dehydrogenation of the corresponding saturated ketone or aldehyde. In contrast to the present liquid-phase reaction, only

(1) N. Rabjohn, *Org. React.*, **5**, 339 (1949); A. Robertson and W. A. Waters, *Trans. Faraday Soc.*, **42**, 201 (1946); F. E. Mertz and L. D. Dermer, *Proc. Okla. Acad. Sci.*, **30**, 134 (1949); E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 149 (1953).

(2) E. A. Braude and E. A. Evans, *ibid.*, 607 (1954); W. S. Johnson, *et al.*, *J. Org. Chem.*, **27**, 1612 (1962).

(3) A. T. Neilsen and W. J. Houlihan, *Org. React.*, **16**, 1 (1968).

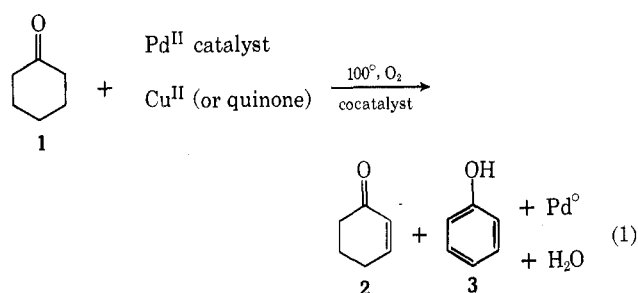
(4) W. F. Gannon and H. O. House, *Org. Syn.*, **40**, 14 (1960).



vapor phase procedures for the preparation of olefinically unsaturated ketones from the corresponding saturated carbonyl compounds or alcohols have been reported.⁵

Results

A study of group VIII [particularly Pd(II)] metal complex catalysis has revealed a unique liquid-phase oxidative dehydrogenation of ketones and aldehydes. As illustrated (eq 1) for cyclohexanone (1), the oxidation is effected by air or oxygen in the presence of a catalyst and a cocatalyst.



Usual conversions of 1 in the range of 15–30% and at selectivities to 2 of 95–80% were obtained in the presence of a Pd(II) catalyst and either a Cu(II) or a quinone cocatalyst.⁶ By comparison, a combination of Cu(II) and quinone cocatalysts gave 43–48% conversions of 1 with selectivities to 2 of 88–83%. However, synthesis of unsaturated ketone 1, as with all other substrates, is limited by (1) catalyst deactivation, (2) aldol condensation reactions, and (3) secondary oxidations, *e.g.*, 1 to adipic acid. The latter two reactions, although minimal at lower conversions, become significant at higher ones. Thus, total estimated conversions and selectivities were 50–53% and 73–66%, respectively. Table I lists typical results in reactions with 1.

This unique oxidative dehydrogenation technique has modest general applicability for the preparation of α,β -unsaturated materials. Except for 1, the reaction conditions generally were not optimized. Thus, in several cases only preliminary screening runs are listed which employ no cocatalyst or solvent. Usually, however, the Pd(II) catalyst was about 0.2–0.4 molar % of sub-

(5) H. F. Hardman and R. K. Grasselli, U. S. Patent 3,364,264 (1968); R. W. Etherington and K. L. Liauw, U. S. Patent 3,476,808 (1969).

(6) Conversion and selectivity are defined as

$$\% \text{ convn} = \frac{\text{moles (2 + 3)}}{\text{moles (1) charged}} \times 100$$

$$\% \text{ select} = \frac{\text{moles (2)}}{\text{moles (2 + 3)}} \times 100$$

References to total conversion and total selectivity are based upon all products observed by vpc analysis.

TABLE I
CONVERSION AND SELECTIVITY IN REACTIONS
OF CYCLOHEXANONE (1)

	% convn of 1	% select to 2	Pd(II) ^a activity
Usual range ^b	15–30	95–80	50–1000
Highest range ^c (based on vpc)	43–48	88–83	1300–2700
Highest actual range (based on isolation)	50–53	73–66	1300–2700

^a The catalyst activity is defined as cat. act. = moles of desired product/moles of Pd(II) catalyst. ^b Conversions depend on the choice of solvent as well as the concentration and type of catalyst and cocatalyst used. ^c The best results were obtained from a combination of Cu(II) and quinone cocatalysts.

strate. The cocatalyst, except where noted, was *p*-benzoquinone (*p*-BQ), and the solvent was neat substrate, HOAc, or HOBz. The reactions were run for 1–24 hr at 90–110° bubbling oxygen or air into the solution at 10–15 cc/min.

Analyses of reaction products were carried out by vpc. In general, all significant products were separated by preparative vpc and their structures confirmed by infrared and nmr spectra. Tables II–V list the results

TABLE II
REACTIONS OF CYCLIC KETONES^a

Substrate	% convn	Theor % convn ^b	% select	Product
Cyclopentanone	17	18	97	Cyclopentenone
Cyclopentanone ^c	22	1	91	Cyclopentenone
Cyclohexanone	15–30	15–30	98–90	Cyclohexenone
Cyclohexanone ^c	15–30	2	95–90	Cyclohexenone
Cycloheptanone ^d	2	0.3	38	Cycloheptenone
Cyclooctanone ^d	0.7	0.4	30	Cyclooctenone

^a Except where noted, *p*-benzoquinone (*p*-BQ) was employed in all reactions as "cocatalyst." ^b Theoretical per cent conversion is equivalent to the stoichiometric amount of cocatalyst or to the Pd(II) catalyst in systems containing no cocatalyst. Thus, since *p*-BQ is a stoichiometric reagent, the theoretical per cent conversion is equivalent to the amount present, whereas reoxidation of copper or palladium complexes may yield actual conversions greater than the theoretical (stoichiometric) conversion. ^c Cu(acac)₂ was used as cocatalyst, time 15–25 hr. ^d Preliminary screening runs; no cocatalyst or solvent was used.

and products obtained from cyclic ketones, substituted cyclic ketones, acyclic ketones, and aldehydes.

In attempting to optimize reaction conditions, especially for those employing 1 as substrate, several variables were studied. These included (1) catalyst, (2) cocatalyst, (3) temperature, (4) oxygen and pressure dependence, and (5) solvent.

Over 45 catalysts, primarily the group VIII metal salts and complexes, were investigated. Palladium compounds are the most active and selective with rhodium, osmium, iridium, and platinum showing decreasing catalytic activity. The best complexes are soluble ones such as dichlorobis(triphenylphosphine)palladium(II) and palladium(II) acetylacetonate. Palladium(II) chloride itself has modest catalytic activity and an initial selectivity of >90% to 2. However, the Lewis acid character of this simple salt readily promotes aldol condensations which are minimized in the case of the complexes.

In all cases, conversion of 1 to 2 and 3 stops (see Figures 1 and 2) when a mirror and/or Pd⁰ (black) are observed. Continued contact with metallic Pd slowly

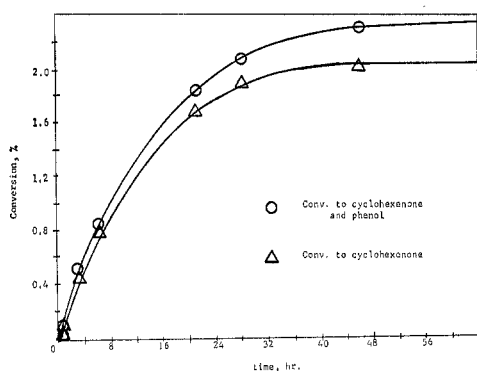


Figure 1.—Conversion of cyclohexanone (0.5 mol) to cyclohexenone and phenol at 110° and 10 cc of O₂/min catalyzed by [Pd(PPh₃)₂Cl₂] (7 × 10⁻⁴ mol).

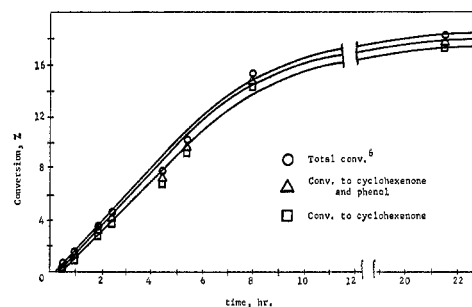


Figure 2.—Conversion of cyclohexanone (1.0 mol) to cyclohexenone and phenol at 100° and 10 cc of O₂/min catalyzed by [Pd(PPh₃)₂Cl₂] (3 × 10⁻³ mol) and [Cu(PPh₃)₂Cl₂] (1.5 × 10⁻² mol).

TABLE III
REACTIONS OF SUBSTITUTED CYCLIC KETONES^a

Substrate	% convn	Theor % convn ^b	% select	Product
α -Decalone ^c (t/c = 19/1)	32	100	36	
β -Decalone ^c (t/c = 2/1)	20	100	1.5	
			43	
2-Methylcyclohexanone	47	37	80	
3-Methylcyclohexanone	36	100	58	
			23	
3-Cholestanone	82	64	>95	Δ^1 -Cholesten-3-one

^a See footnote a, Table II. ^b See footnote b, Table II. ^c See footnote d, Table II.

TABLE IV
REACTIONS OF ACYCLIC KETONES^a

Substrate	% convn	Theor % convn ^b	% select	Product
2-Butanone ^c	4	18	100	1-Buten-3-one
3-Pentanone ^c	6	18	94	1-Penten-3-one
			6	1,4-Pentadien-3-one
3-Methyl-2-butanone ^c	4	18	100	2-Methyl-1-buten-3-one
Propiophenone	3	36	100	3-Phenyl-1-propen-3-one
4-Heptanone	7	18	83	<i>trans</i> -2-Hepten-4-one
			17	<i>trans,trans</i> -2,5-Heptadien-4-one
2-Octanone	5-7	18	100	<i>trans</i> -3-Octen-2-one

^a See footnote a, Table II. ^b See footnote b, Table II. ^c Reaction carried out in pressure bottle.

converts 2 to 3. In the presence of only a Pd catalyst and at low levels of conversion (<2%), *i.e.*, before Pd⁰ deposition, it is possible to recover the catalyst which can be recycled.

TABLE V
REACTIONS OF ALDEHYDES^a

Substrate	Theor			Product
	% convn	% convn ^b	% select	
Propanal ^c	6	18	100	Propenal
Butanal	15-18	18	80	<i>trans</i> -2-Butenal
2-Methylpropanal ^c	4	18	100	2-Methylpropenal
<i>n</i> -Heptanal	20	18	>90	<i>trans</i> -2-Heptenal
<i>n</i> -Nonanal	26	27	91	<i>trans</i> -2-Nonenal

^a See footnote a, Table II. ^b See footnote b, Table II. ^c See footnote c, Table IV.

Catalyst activity is extended by the use of both inorganic and organic cocatalysts. These materials do not produce the desired compound by themselves but substantially increase both the rate and conversion when combined with the primary catalyst.

Of most of the 1st row transition metal salts and complexes (V through Cu) studied, copper compounds are superior for reoxidation of the palladium catalysts.⁷ In practice, a 5-500 molar excess of Cu(II) is used. Reoxidation of Cu(I) is achieved by air or oxygen. Cupric acetylacetonate or dichlorobis(triphenylphosphine)copper(II) are preferred. Cupric acetate may also be used, but hydrolysis of cuprous acetate to insoluble cuprous oxide is competitive with reoxidation.

The organic cocatalysts, quinones, theoretically function as redox systems, but their main role is to act as hydrogen acceptors.⁸ *p*-Benzoquinone is the most effective cocatalyst for regeneration of Pd(II); however, it is consumed and must be used as a stoichiometric reagent.

The temperature dependence of this reaction with 1 as substrate is illustrated in Figure 3. The rate of reaction progressively increases from 50-140°, but the activity of the catalyst⁹ is a maximum at *ca.* 110°. The higher temperature favors the formation of phenol and aldol condensation products, in addition to numerous other unknown by-products.

Some oxygen is required for the reaction, although, except for reoxidation of Cu(I) and of a possible palladium hydride intermediate (see discussion of mechanism), its role is uncertain. However, in analogous systems the reaction appears to be more complex than a

(7) G. Szonyi, *Advan. Chem. Ser.*, **70**, 53 (1968); R. G. Schultz and D. E. Gross, *ibid.*, **97** (1968).

(8) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Acad. Nauk SSSR*, **133**, 377 (1969); Rhone-Poulenc, British Patent 990,447 (1965); D. Clark, P. Hayden, W. D. Walsh, and W. D. Jones, British Patent 964,001 (1964); D. Clark, W. D. Walsh, W. D. Jones, and C. B. Cotterill, British Patent 975,709 (1964).

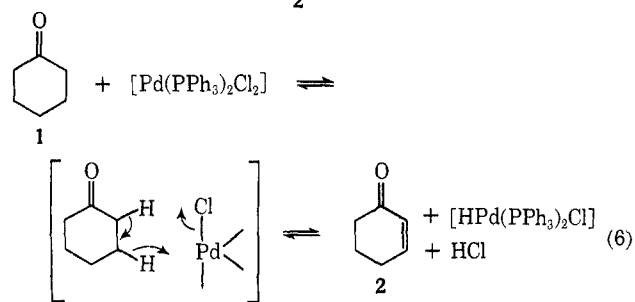
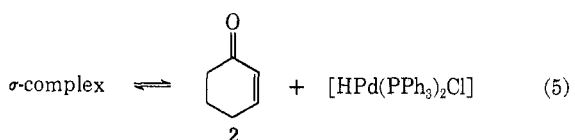
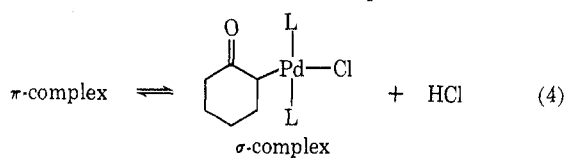
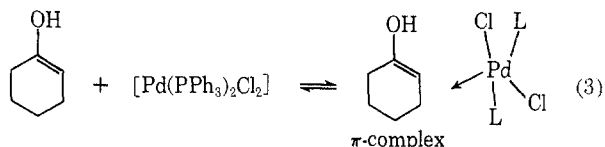
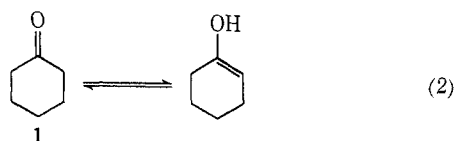
(9) See footnote a, Table I.

simple series of redox steps.¹⁰ Systems which contain only catalyst and catalyst-Cu(II) cocatalyst show little or no formation of 2 in the absence of air or oxygen. However, they function normally when open to an air atmosphere or when air or oxygen is bubbled into the solution. There is no readily apparent advantage of oxygen over air. High pressures or flow rates of oxygen rapidly convert 1 to adipic acid. As might be expected, reactions employing *p*-BQ as a cocatalyst proceed even in a nitrogen atmosphere. However, for uniform reaction conditions, an air or oxygen atmosphere was used in *p*-BQ experiments the same as in Cu(II) systems.

The oxidative dehydrogenation of 1 to 2 can be carried out in a variety of solvents, whose utility depends upon the choice of Pd(II) catalyst and inorganic or organic cocatalyst. A completely homogeneous solution is favored both from the standpoint of reaction rate and catalyst activity. Neat substrate, *e.g.*, 1, is the best reaction medium with a Cu(II) cocatalyst. On the other hand, a protonic acid solvent, such as acetic or benzoic acid, is best when using *p*-BQ.

Discussion

The exact reaction mechanism is uncertain and the following explanation, illustrated by the reaction of 1 with [Pd(PPh₃)₂Cl₂], is highly speculative. However, reports in the literature^{10,11} seem to indicate an initial enolization (eq 2), followed by a π complex (eq 3) which



(10) E. Stern, *Catal. Rev.*, **1**, 73 (1967).

(11) (a) J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. Ind. (London)*; 859 (1959); (b) E. H. Brooks and F. Gloeckling, *J. Chem. Soc.*, 1030 (1967); (c) W. G. Lloyd, *J. Org. Chem.*, **32**, 2816 (1967), and references cited therein.

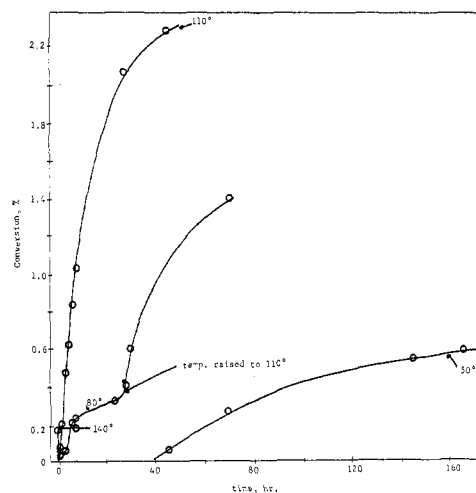


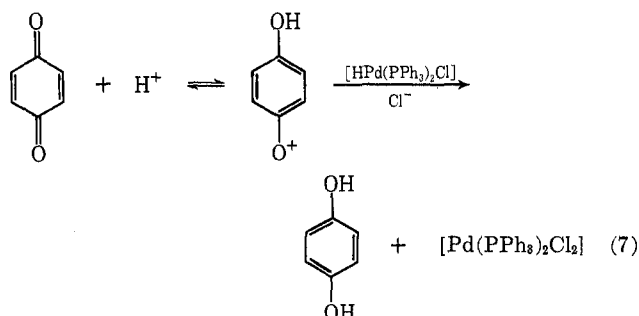
Figure 3.—Temperature dependence on conversion of cyclohexanone (0.5 mol) to cyclohexenone and phenol with 10 cc of O₂/min catalyzed by [Pd(PPh₃)₂Cl₂] (7 × 10⁻⁴ mol).

rearranges to a σ complex (eq 4). Ultimate decomposition of the σ complex yields the desired product (eq 5), but, without any real proof for a stepwise sequence, a fully concerted one-step reaction (eq 6) is entirely possible.

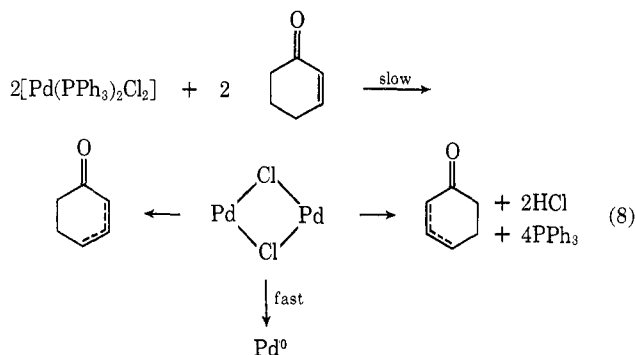
The catalyst and/or metallic palladium, from catalyst decomposition, may subsequently convert 1 to 3. Whether this reaction occurs by dehydrogenation or oxidative dehydrogenation of 1 is unknown. Separate experiments under identical conditions ([Pd(PPh₃)₂Cl₂] catalyst) were compared for the conversion of 1 to 2 and for the conversion of 2 to 3. The relative rate of the latter reaction was 3–5 times faster than the former. This result would indicate that the maximum conversion to 2 is about 16–25% based only on a mass law effect. However, other pertinent factors must be involved since conversions to 2 twice as large have been obtained, without an appreciable amount of 3 being formed. The above proposed palladium hydride is very unstable,^{11a} but a number of hydride complexes do exist^{11b} and such intermediates have been proposed for a number of formally similar oxidation-reduction systems.^{10,11c}

Subsequent catalyst regeneration in Cu-Pd redox reactions is well documented.^{7,10} In addition, alternate modes of catalyst regeneration and destruction are known for analogous group VIII metal complexes.^{12a}

Based upon a proposed palladium hydride intermediate, the function of *p*-benzoquinone as cocatalyst in the absence of oxygen is readily explained. A protonated species (eq 7) would be a more likely cocatalyst.



(12) (a) H. B. Charman, *Nature*, **212**, 278 (1966); (b) J. Tsuji and S. Imamura, *Bull. Chem. Soc. Jap.*, **40**, 197 (1967).



π -Allylic palladium complexes with α,β -unsaturated compounds are well known.^{12b} The present system may also be complicated by the possible formation of a cyclohexenone-palladium complex (eq 8). This complex is known to decompose in solution to give a palladium mirror.¹³ This cyclohexenonyl-palladium complex probably formed slowly (if at all) under normal reaction conditions, since the catalyst promoted the equivalent of up to 1000–2000 dehydrogenation reactions. This proposal is also supported by the observation that the concentration of 2 could be raised to 26% by oxidation of 1 initially containing 17.5% 2. However, deposition of a palladium mirror did occur more readily.

Further catalyst decomposition can result from oxidation of triphenylphosphine, which, although it is not oxidized by air, can be oxidized to triphenylphosphine oxide in the presence of Pd⁰, Pt⁰, and Ni⁰.¹⁴

Several observations are readily apparent from a consideration of the list of substrates and products listed in Tables II–V. The first is that most cyclic ketones and aldehydes are more reactive and give higher conversions to α,β -unsaturated products than do acyclic ketones. As indicated, the proposed first step in the reaction mechanism is an enolization which is known to be favored in cyclic ketones.¹⁵

A second finding is that the aldehydes giving the lowest conversions, namely propanal and 2-methylpropanal, have a common feature with the first four acyclic ketones in Table IV. The products all possess a terminal vinyl grouping, CH₂=C. Possible explanations for this result may include the thermodynamic stability of the terminal vinylic compounds as well as a mechanistic hypothesis on the stability of possible π - and σ -palladium complex intermediates. Most of these substrates are low boiling and could be dehydrogenated only by use of a pressure bottle apparatus in order to attain the optimum temperature of 100–110°.

A third and unexpected observation is seen in reactions of substrates yielding internally unsaturated olefins. The α,β -unsaturated products all have a trans orientation around the carbon-carbon double bond. No cis products have been observed. In addition, when there is a possibility of forming an $\alpha,\beta,\alpha',\beta'$ -unsaturated product, as is the case with 4-heptanone, the diolefin produced has complete trans geometry.

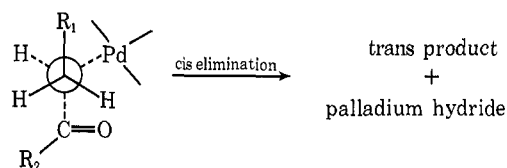
According to the proposed mechanism, the staggered conformation of the intermediate palladium σ complex,

(13) A. Kashara, K. Tanaka, and K. Asamiya, *Bull. Chem. Soc. Jap.*, **40**, 351 (1967).

(14) G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem., Int. Ed. Engl.*, **6**, 92 (1967); S. Takahashi, K. Sonogashira, and N. Hagihara, *Nippon Kagaku Zasshi*, **87**, 610 (1966).

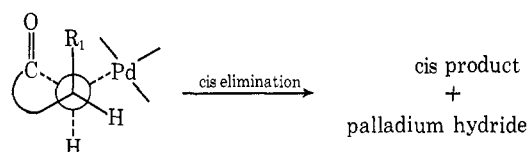
(15) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold, New York, N. Y., 1963, p 409.

SCHEME II
ELIMINATION FROM A STAGGERED ACYCLIC INTERMEDIATE



pictured in Scheme II, is expected to be the most stable.¹⁶ The formation of trans product and the subsequent palladium hydride intermediate can arise by a cis-elimination pathway.¹⁸ On the other hand, the most favorable conformation for an intermediate of a cyclic substrate is illustrated in Scheme III. Here cis

SCHEME III
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elimination yields only a cis product. Cyclooctanone is the lowest cyclic ketone homolog in which twisting is sufficiently unrestricted to give either the cis or trans isomer.^{19a} However, only *cis*-cyclooctenone was formed and its spectral properties are in complete agreement with published data.¹⁹ The trans isomer, even if formed initially, would undoubtedly isomerize at the required reaction temperature and is known to readily convert to the cis isomer in the presence of mineral acid.^{19a}

Finally, attempted extension of this oxidative technique to the preparation of other α,β -unsaturated compounds was unsuccessful. Acids, esters, and nitriles are almost totally unreactive. The homogeneous liquid-phase dehydrogenation of alcohols in the presence of group VIII metal catalysts, *e.g.*, Rh²⁰ and Pd^{11c} complexes, is well known, but, in the present endeavor, alcohols gave only modest amounts (1–5% conversion) of α,β -unsaturated products. In contrast to the present study, the oxidation of cyclohexanol in the presence of a PdCl₂-Cu(NO₃)₂ system is reported^{11c} to give low conversions, *ca.* 2%, to 1 only. Conversions for a number of other primary and secondary alcohols vary from 1–30%. No α,β -unsaturated ketones or aldehydes were observed.

The method of synthesis described by this study lends itself to the preparation of small to medium-sized quantities of material. Since it is applicable to a number of aldehydes and ketones, the primary disadvantages can often be minimized. It thus may offer a new and at-

(16) As seen by Dreiding models of compounds depicted in Scheme II, steric repulsions are significantly minimized by a trans orientation of R₁ and COR₂. Interaction of R₁ with the Pd complex is significantly less severe due to a C-Pd bond distance of *ca.* 2.05–2.2 Å.¹⁷

(17) M. R. Churchill and R. M. Mason, *Advan. Organometal. Chem.*, **5**, 93 (1967).

(18) A counterclockwise rotation of the group CH₂R₁ by 120° would have PdL₂X flanked by two H atoms. A nonselective elimination of a palladium-hydrido complex would be expected to yield a mixture of cis and trans products.

(19) (a) P. E. Eaton and K. Lin, *J. Amer. Chem. Soc.*, **86**, 2087 (1964);

(b) O. L. Chapman, *ibid.*, **85**, 2014 (1963).

(20) H. B. Charman, *J. Chem. Soc.*, 629 (1967); *Nature*, **212**, 278 (1966).

tractive route to certain olefinically unsaturated carbonyl compounds.

Experimental Section

Analyses of reaction products were done by vpc on an Aerograph Model A-90-P gas chromatograph, using one of the three following columns: (1) 10% neopentylglycol succinate on 60-80 mesh Chromosorb W, 10 ft \times $\frac{3}{8}$ in.; (2) 10% free fatty acid phthalate on 60-80 mesh Chromosorb W, 10 ft \times $\frac{3}{8}$ in.; and (3) 20% free fatty acid phthalate on 60-80 mesh Chromosorb W, 10 ft \times $\frac{1}{4}$ in. In general, all significant products were preparatively separated. Infrared spectra were obtained on a Beckman IR-5 spectrometer and nmr spectra were obtained with a Varian A-60 spectrometer in CDCl_3 solution with TMS as an internal standard.

The usual technique for work-up and isolation was as follows. First all organic volatiles were distilled from the catalyst-cocatalyst system under reduced pressure. Then, depending upon the boiling point and solubility of the product and the starting material, either fractional distillation, preparative vpc, or liquid column chromatography was used for separation.

Alternatively, in some instances, the reaction could be diluted with hexane to precipitate most of the catalyst. Then, after distillation of solvent one of the above three methods was used for separation.

Cyclohexenone (2). **Procedure A.**—A stirred mixture of cupric acetate monohydrate (8.5 g, 0.0425 mol) and dichlorobis(triphenylphosphine)palladium(II) (1.5 g, 0.00214 mol) in cyclohexanone (100 g, 1.02 mol) and acetic acid (50 g, 0.84 mol) was warmed to 77° while an oxygen bubble (15 cc/min) was maintained below the surface. The blue-green solution slowly changed to brown and a red-brown precipitate (cuprous oxide) formed. The progress of the reaction was monitored by vpc; after 10.5 hr the conversion was 8.0% with selectivities to cyclohexenone and phenol of 95 and 5%, respectively. Total conversion as indicated by vpc was 8.3% with a total selectivity to cyclohexenone of 92%. After distillation of all volatiles, the residue was extracted with base, which upon acidification gave a crude acid, whose infrared spectrum was very similar to that of adipic acid.

Procedure B.—A stirred mixture of dichlorobis(triphenylphosphine)copper(II) (10.0 g, 0.0151 mol) and dichlorobis(triphenylphosphine)palladium(II) (2.0 g, 0.00286 mol) in cyclohexanone (100 g, 1.02 mol) was warmed to 100° with 15 cc of O_2 /min bubbling into the solution. A mirror and a gray-black haze formed slowly on the flask. After a 6-hr reaction time, the conversion was 17% (98% cyclohexenone and 2% phenol) while the total conversion was 17.6% with a 94% selectivity to cyclohexenone. A vacuum distillation gave 97.5 g of volatile organic materials, the vpc analysis of which closely corresponded to that of the reaction mixture.

Procedure C.—A stirred mixture of cupric acetylacetonate (5.5 g, 0.021 mol) and palladium acetylacetonate (0.05 g, 0.000164 mol) in cyclohexanone (98.0 g, 1.00 mol) and acetic acid (52.0 g, 0.87 mol) was heated to 105° with 150 cc of O_2 /min bubbling into the green-blue solution. A gray-black film slowly formed on the flask and a brown precipitate formed. Analysis of the reaction mixture after 24 hr showed a 19.7% conversion (95% cyclohexenone and 5% phenol). The total conversion based on vpc was 21.5% with an 85% selectivity to cyclohexenone. It was evident, however, that upward of 20% of the cyclohexanone had been oxidized to higher boiling materials (likely adipic acid). As a result the estimated total conversion is 36% with cyclohexenone selectivity about 39%.

Procedure D.—A stirred solution of *p*-benzoquinone (20.0 g, 0.185 mol) and palladium acetylacetonate (0.5 g, 0.00164 mol) in cyclohexanone (100 g, 1.02 mol) and acetic acid (52 g, 0.87

mol) was heated to 110° with 10 cc of O_2 /min bubbling into the solution. After 15 min the solution had turned a dark brown and a heavy palladium mirror was on the flask. Analysis after 1 hr showed 15.3% conversion (98% cyclohexenone and 2% phenol). The total conversion was 15.5% with a cyclohexenone selectivity of 96%. No further increase in conversion was observed with continued heating.

Procedure E.—A stirred mixture of *p*-benzoquinone (20.0 g, 0.185 mol), palladium acetylacetonate (0.1 g, 0.00033 mol), cupric acetylacetonate (2.6 g, 0.01 mol), and benzoic acid (50.0 g, 0.41 mol) in cyclohexanone (98.0 g, 1.0 mol) was heated to 110° while 15 cc of O_2 /min was bubbled into the solution. The initial green slurry turned brown-green with heating and some gray-black haze as well as a green precipitate was formed on the flask. After 3.5 hr the total conversion was 18.6% (94% cyclohexenone). This after 23 hr had increased to 43.0% (88% selectivity to cyclohexenone). At this point, it was estimated that about 13% of the cyclohexanone had been oxidized to higher boiling materials not observed by vpc so that the estimated actual total conversion and selectivity were 50 and 73%, respectively.

Propenal.—Into a pressure bottle equipped with a release valve was placed *p*-benzoquinone (20.0 g, 0.185 mol), palladium acetylacetonate (0.5 g, 0.00164 mol), and benzoic acid (25.0 g, 0.205 mol) in propanal (58.0 g, 1.0 mol). The bottle was sealed and the stirred solution heated to 110° at which temperature a palladium mirror formed rapidly. After 4 hr of heating, the conversion was 6.3% with an approximate 100% selectivity to propanal.

Butenal.—Butenal (72.0 g, 1.0 mol) in a similar reaction to that for propanal, but under atmospheric pressure at 90° with an O_2 bubble of about 10 cc/min gave a 14.6% conversion after 5 hr to *trans*-2-butenal (79%) and the aldol condensation product from 2 mol of butenal (21%).

1-Penten-3-one.—In a pressure-bottle reaction identical with that for propanal but with 3-pentanone (86.0 g, 1.0 mol), the conversion was 6.0% after 2.5 hr with selectivities to 1-penten-3-one and 1,4-pentadien-3-one of 94 and 6%, respectively.

Cyclopentenone.—A stirred mixture of cupric acetylacetonate (5.5 g, 0.021 mol) and palladium acetylacetonate (0.5 g, 0.00164 mol) in acetic acid (52 g, 0.87 mol) and cyclopentanone (84.0 g, 1.0 mol) was heated to 105° while 15 cc of O_2 /min flowed into the blue-green solution. The solution slowly turned a dark brown color and a palladium mirror formed. The conversion after a 25-hr reaction time was 21.8% with a 91% selectivity to cyclopentenone.

Δ^7 -Cholesten-3-one.—A stirred solution of cholestan-3-one (0.2 g, 0.00052 mol) and palladium acetylacetonate (0.16 g, 0.00052 mol) in acetic acid (8.0 g, 0.13 mol) was heated at 110° for 18 hr while 1-2 cc of O_2 /min was bubbled into the solution. A palladium mirror had formed and the reaction was a green-yellow at the end of the reaction. The solution was filtered free of precipitated Pd^0 (black) and the acetic acid solution diluted with water (50 ml) to give a tan-brown precipitate (270 mg). Unused catalyst (120 mg) was recovered from this brown solid by dissolving the organic material in the minimum amount of hexane and filtering. The crude reaction product (150 mg) was freed of residual catalyst by chromatography on alumina with diethyl ether as eluent. Infrared and nmr spectra confirmed an 82% conversion with the primary product being Δ^7 -cholesten-3-one.

Registry No.—1, 108-94-1; 2, 930-68-7; 3, 108-95-2; dichlorobis(triphenylphosphine)palladium(II), 13965-03-2; dichlorobis(triphenylphosphine)copper(II), 27396-56-1; cupric acetylacetonate, 13395-16-9; palladium(II) acetylacetonate, 14024-61-4; *p*-benzoquinone, 106-51-4.