the value of 0.62 found above. Extrapolation of the Brφnsted correlation (with statistical corrections) to the pK'_a of H_3PO_4, determined as discussed in the Results section, gives an expected value for $k_{H_3PO_4}$ of $1.07 \times 10^3\ M^{-1}\ min^{-1}$; the observed value (Table II, eq 9) is $6.25 \times 10^3\ M^{-1}\ min^{-1}$, a factor of 5.8 larger than predicted. Since it has been shown by direct measurement of $k_{H_3PO_4}$ for ethyl vinyl ether that this catalytic constant lies about 0.5 log unit (a factor of 3) above the Brφnsted prediction *based on carboxylate buffers,* our observed $k_{H_3PO_4}$ is thus within a factor of 2 of the expected value. The significance of the remaining difference is questionable in view of the assumptions and approximations made in this and other[3] work. The calculated values of $k_{H_3PO_4}$ for **1, 2,** and **4** show similar agreement with observed values when we assume that the pK'_a of H_3PO_4 in the 5% ethanol, $\mu = 1.0\ M$ (KCl) system is the same as that in the dioxane system. This last assumption is quite reasonable, since a number of acids of diverse types show such an identity in pK'_a in the two solvents.

Several conclusions result from this work. (1) Kresge's caution,[3,6] that one should construct Brφnsted plots from the same type of catalysts, is further underscored. (2) H_3PO_4 is confirmed to be an unusually active catalyst in vinyl ether hydrolysis, and probably in similar reactions as well. (3) Catalytic constants determined for components of polyprotic acids should be based on an exploration of the full range of pH covered by the buffer, because (4) strong acids, even if present in miniscule amounts, may have detectable catalytic activity. (5) In favorable cases such as this, catalytic constants for the stronger acids in a polyprotic array may be evaluated without direct measurement at pH values at which the strong acid dominates, at which the reaction under consideration may be too fast to measure, and at which buffer failure leads to troublesome complications in measuring buffer catalysis. (6) Finally, effects similar to those observed here might be anticipated for polybasic amines in reactions during which negative charge is present in the rate-determining step.

Experimental Section

The synthesis of all compounds, product analyses, and kinetic methods have been previously described.[1,4]

To determine the pK'_a of H_3PO_4, standard 0.1 M phosphoric acid was established by potentiometric titration with standard KOH. Known molarities, M_0, of H_3PO_4 were formulated in the 5% dioxane, $\mu = 1.0\ M$ (KCl) solvent system, and the pH was determined on a Radiometer Model 26 instrument using a combination electrode standardized at several pH values. The hydrogen ion concentration was determined from the pH meter reading (see Results section for a justification of this procedure) and a dilution plot, Figure 2, constructed according to eq 7. A weighted, linear least-squares analysis[7] was carried out to obtain the parameters of fit.

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Registry No.—**1**, 56650-73-8; **2**, 56650-74-9; **3**, 4747-13-1; **4**, 51440-56-3.

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The Oxidation of Terminal Olefins to Methyl Ketones by Jones Reagent Is Catalyzed by Mercury(II)[1]

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The oxidation of terminal olefins by Jones reagent in the presence of a catalytic quantity of mercury(II) affords good yields (>70%) of the corresponding methyl ketones. Similar oxidations of 1,2-disubstituted olefins gives fair (20–70%) yields; in the case of unsymmetrically substituted olefins, mixtures of ketones are produced.

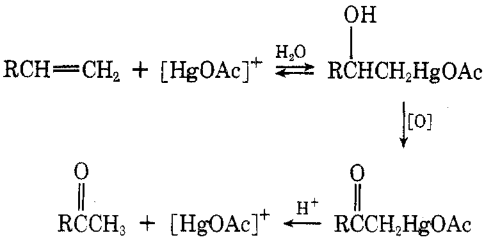
The Wacker process for oxidation of olefins to ketones has three mechanistically distinct parts:[3] first, activation of the olefinic double bond toward nucleophilic attack by coordination with Pd(II) and addition of a hydroxide moiety to this electrophilic double bond; second, conversion of the resulting 2-hydroxyethylpalladium(II) compound to ketone and a (formally) Pd(0) atom by a series of palladium(II) hydride addition–eliminations involving vinylic alcohol intermediates; third, reoxidation of the palladium(0) to palladium(II) by copper(II). Wacker oxidation is an extremely useful and general reaction. It is, nonetheless, worthwhile to try to develop procedures for oxidizing olefins that use as catalysts metals less expensive than palladium, and which involve reactions (and possibly generate products) different from those of the Wacker oxidation. Mercury(II) is an obvious candidate for the catalyst for new oxidation reactions: it resembles palladium(II) in its ability to activate olefins for nucleophilic attack,[4] but differs in that decomposition of the oxymercuration products normally generates cations by loss of mercury(0) rather than olefins by loss of mercury hydride.[5] Unfortunately, neither we nor others[6] have been able to discover a satisfactory solution to the principal problem in developing a mercury(II)-catalyzed analog of the Wacker oxidation: viz., an efficient regeneration of mercury(II) from mercury(0). In the absence of a solution to this problem, there are, however, ways of involving mercury(II) in catalytic oxidation of olefins other than in a direct analog of a Wacker oxidation.

Table I
Oxidation of Terminal Olefins by Jones Reagent Catalyzed by Mercury(II)

Olefin	Registry no.	Product	Registry no.	Isolated yield, %
1-Octene	111-66-0	2-Octanone	111-13-7	82
Undecylenic acid	112-38-9	10-Oxoundecanoic acid	676-00-6	83
3,3-Dimethyl-1-butene	558-37-2	3,3-Dimethyl-2-butanone	75-97-8	86
2-Allylcyclododecanone	32539-89-2	β-Oxo-2-propylcyclododecanone[a]	56666-10-5	70
Styrene	100-42-5	Acetophenone[b]	98-86-2	26
1,3-Hexadiene	592-48-3	Polymer		

[a] In addition, a 7% yield of 2-allyl-2-hydroxycyclododecanone was obtained. [b] Benzoic acid (16%) was also isolated, together with polymer.

One, explored in this paper, utilizes mercury(II) in oxymercuration of an olefin, oxidizes the hydroxyl moiety of the resulting 2-hydroxyalkylmercury(II) compound to an acid-labile 2-ketoalkylmercury(II) derivative, and regenerates mercury(II) by proteolysis of the carbon–mercury bond of this substance (eq 1). Thus, the mercury(II) performs the



$$\mathrm{RCH{=}CH_2 + [HgOAc]^+ \overset{H_2O}{\rightleftharpoons} R\overset{OH}{\overset{|}{C}}HCH_2HgOAc}$$

$$\downarrow [O] \qquad (1)$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}CH_3 + [HgOAc]^+ \xleftarrow{H^+} R\overset{O}{\overset{\|}{C}}CH_2HgOAc}$$

essential function of olefin activation, but is regenerated without leaving the mercury(II) oxidation level. This cycle is, in a sense, one in which mercury(II) catalyzes the hydration of the double bond, and in which the reaction is driven in the direction of the thermodynamically less stable hydrated form by trapping this form by oxidation to ketone.

Results and Discussion

Jones reagent (CrO_3–H_2SO_4–H_2O) oxidizes alcohols to ketones efficiently, and is relatively unreactive toward olefins.[7] When Jones reagent is added to an acetone solution of an olefin at 20°, a slow, nonselective oxidation takes place. Addition of mercuric acetate or mercuric propionate (20 mol % based on olefin) to the solution results in a rapid consumption of the oxidant. Terminal olefins are converted to methyl ketones in yields of 80–90% (Table I); 1,2-disubstituted olefins react readily, but give low yields of ketones under these conditions. The yield of methyl ketones resulting from the catalyzed Jones oxidation of terminal olefins is relatively insensitive to the amount of mercuric salt added (Figure 1). The catalyzed oxidation of terminal olefins by sodium dichromate–trifluoroacetic acid solution showed similar insensitivity to the amount of mercuric salt added; the yields were, however, substantially lower than those obtained using Jones reagent (Figure 1). Note that the plots in Figure 1 are based on data collected under roughly comparable conditions, but that these conditions are not necessarily those that generated the highest yield of product. In particular, in plot A of Figure 1, the maximum detected yield of 2-octanone was approximately 50%, while the best yield isolated under optimized synthetic conditions was 82% (see the Experimental Section for details). The major function of the plots in Figure 1 is to establish the relative sensitivities of primary and secondary olefins to catalysis by mercury(II) and to provide a qualitative estimation of the absolute activity of mercury(II) as a catalyst in reactions based on Jones reagent and dichromate ion as oxidants.

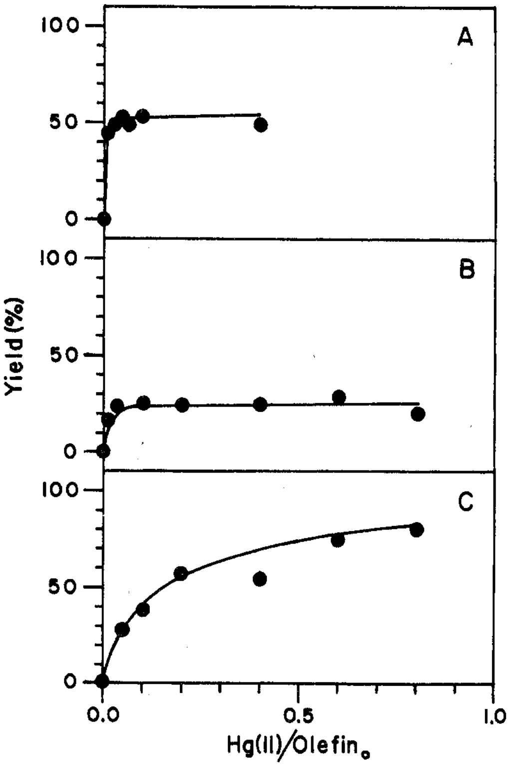


Figure 1. The yield of ketone depends on the ratio of equivalents of mercury(II) to olefin present at the start of the reaction: A, $(EtCO_2)_2Hg$-catalyzed oxidation of 1-octene to 2-octanone (25°, acetone, Jones reagent, 18 hr); B, $(EtCO_2)_2Hg$-catalyzed oxidation of 1-octene to 2-octanone (25°, dioxane, $Na_2Cr_2O_7 \cdot 2H_2O$–CF_3CO_2H, 18 hr); C, $(EtCO_2)_2Hg$-catalyzed oxidation of a mixture of *cis*- and *trans*-2-octene to a mixture of 2- and 3-octanone (25°, dioxane, $Na_2Cr_2O_7 \cdot 2H_2O$–CF_3CO_2H, 18 hr). Note that the maximum yield shown in A does not correspond to an optimized yield (see the text for a discussion of this point).

The yield of ketones from 1,2-disubstituted olefins can be improved using different reaction conditions (Table II); however, each 1,2-disubstituted olefin required different optimum conditions. Mercuric acetate oxymercurates olefins efficiently in aqueous tetrahydrofuran or dioxane[4,8] and these solvents also proved useful as oxidation media. Experiments in these solvents were carried out using sodium dichromate as oxidant, and making the solution acidic with trifluoroacetic acid. The yields of ketones from the oxidation of 1,2-disubstituted olefins were significantly poorer when other chromate salts, Jones reagent, hydrogen peroxide, or hypochlorite ion were used as oxidants. Yields were also poorer when mercury(II) chloride, nitrate, and tosylate were used in place of mercury(II) propionate.

Several metal ions other than mercury(II) were explored briefly, and found to be unsatisfactory as catalysts. No reaction took place on treating 2-octene with sodium dichromate–trifluoroacetic acid solution in the presence of thalli-

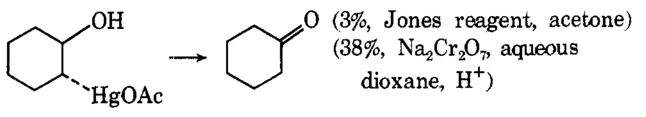
Table II
Oxidation of 1,2-Disubstituted Olefins by Sodium Dichromate–Trifluoroacetic Acid Solution Catalyzed by Mercury(II)

Olefin	Registry no.	Product	Registry no.	Isolated yield, %
cis-2-Octene	7642-04-8	2-Octanone (64%) +		56[a]
		3-octanone (36%)	106-68-3	
trans-2-Octene	13389-42-9	2-Octanone (63%) +		54[a]
		3-octanone (37%)		
Cyclohexene	110-83-8	Cyclohexanone	108-94-1	41[b]
Cyclododecene[c]	1501-82-2	Cyclododecanone	830-13-7	36[b]
Norbornene	498-66-8	Norcamphor[d]	497-38-1	20[a]
$\Delta^{2,3}$-Cholestene	15910-23-3	No reaction		

[a] Oxidation was carried out in the presence of 0.2 equiv of mercuric propionate. [b] Oxidation was carried out in the presence of 0.5 equiv of mercuric propionate. [c] A mixture of cis and trans isomers. [d] The product was isolated as the 2,4-dinitrophenylhydrazone.

um(I), suggesting that olefin activation was slow. Similar treatment of 2-octene in the presence of gold(III), palladium(II), and rhodium(III) afforded mixtures of 2- and 3-octanone in yields of 30, 10, and 2%, respectively. Gold(0) and palladium(0) deposited on the walls of the reaction vessel in substantial amounts during the oxidation.

Evidence for the mechanism of the mercury(II)-catalyzed oxidations (eq 1) is inferential. Treatment of cyclohexene with aqueous mercury(II) acetate gives *trans*-2-hydroxycyclohexylmercuric acetate[9] (**1**), which is oxidized to cyclohexanone in yields very similar to those obtained from cyclohexene under the same reaction conditions. Similarly, 2-(chloromercuri)cyclohexanone (**2**) is converted rapidly and in high yield to cyclohexanone by aqueous sulfuric or trifluoroacetic acid. Compound **1** is itself relatively stable toward the acid conditions encountered in the oxidation. Oxidation products arising directly from the β-hydroxyalkylmercury(II) cation therefore seem unlikely. Mercury(0) has been observed to form in small amounts only at elevated temperatures; no Hg(0) was observed under the conditions described. The β-hydroxymercury(II) cations have previously been shown to be stable in acid solution.[10] The difference in the yields of ketones from 1- and 1,2-disubstituted olefins under strongly acidic (Jones reagent) or weakly acidic ($Na_2Cr_2O_7$–CF_3CO_2H) conditions is reasonably attributed to differences in the oxidative and/or solvolytic[11] stabilities of primary and secondary carbon–mercury bonds. We have tested these stabilities under the conditions of these reactions by examining the behavior of cyclohexylmercuric acetate (**3**) and *n*-hexylmercuric acetate (**4**) toward Jones reagent in acetone. Compound **3** reacts rapidly; oxidation is complete in 30 min at 20°, yielding cyclohexanone in 65% yield. Under the same conditions, the carbon–mercury bond of **4** does not react appreciably: *n*-hexylmercuric sulfate can be recovered in good yield. Compound **1** does not solvolyze appreciably when treated with the components of the Jones reagent *without* the chromium trioxide (that is, acetone, water, and sulfuric acid): a small quantity of 2-hydroxycyclohexylmercuric sulfate precipitates, but no metallic mercury is formed and no organic solvolysis products can be detected. Thus, it appears that the rapid disappearance of **1** when treated with Jones reagent may be an oxidative reaction (eq 2). Cyclohexanol can be detected in ca. 5% yield after 5 min reaction time.



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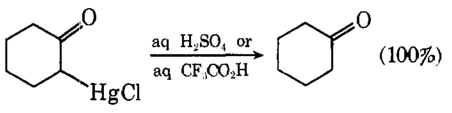

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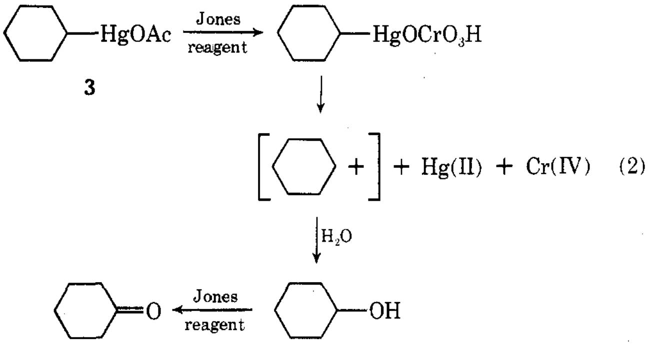

Conclusions

Jones reagent or trifluoroacetic acid–sodium dichromate solution oxidizes olefins to ketones in the presence of catalytic quantities of mercury(II); of the various metals tried as catalysts for the oxidation—thallium(I), gold(III), palladium(II), rhodium(III), and mercury(II)—mercury(II) gives the best yields. Qualitative evidence described above suggests that these transformations occur by the sequence of reactions outlined in eq 1. This oxidation provides a useful alternative to several of the procedures presently used to convert olefins to ketones. It is less complex than Wacker oxidation: the problems that arise in applying Wacker oxidation to high molecular weight, water-insoluble substances do not seem to be important, and it is unnecessary to have present the large excess of copper salts normally used to make the Wacker oxidation catalytic. It can be applied to unprotected olefinic carboxylic acids, where diborane–chromic acid results in destruction of the carboxylic acid moiety. It is more direct and more economical than the several procedures (oxymercuration–reduction, epoxidation–reduction) that generate an alcohol preliminary to a Jones oxidation.

Experimental Section

General. Melting points, determined on a Thomas-Hoover capillary melting point apparatus, are not corrected. GLC analysis was performed using a 10 ft × 0.125 in. 15% Carbowax 20M column on a F & M Model 810 gas chromatograph equipped with a hydrogen flame detector and a Hewlett-Packard Model 3373B electronic integrator. All solvents were reagent grade and were used without further purification. 1-Octene, 2-octene (a mixture of cis and trans isomers), *cis*-2-octene, and *trans*-2-octene (Chemical Samples Co.) were used as supplied. Norbornene, cyclohexene, styrene, cyclododecene (a mixture of cis and trans isomers), 3,3-dimethyl-1-butene, and undecylenic acid (Aldrich) were used as supplied. Mercuric acetate and sodium dichromate dihydrate (Mallinckrodt), trifluoroacetic acid (Matheson Coleman and Bell), gold(III) chloride, palladium(II) chloride, and thallium(I) acetate (Fisher Scientific), and rhodium(III) chloride (Alfa) were used without further purification. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J.

Mercuric Propionate. Red mercuric oxide (108 g) was added in 10-g portions to 100 ml of hot propionic acid. The oxide dissolved, giving a slightly yellowish solution which was filtered and allowed to cool to room temperature. The resulting crystals were recrystallized from propionic acid, washed with cold, dry acetone, and dried under vacuum (0.04 mm) at room temperature for 24 hr. The yield of product was 168.7 g (97%) as white needles having mp 114–116°.

General Procedure for the Mercury(II)-Catalyzed Oxidation of Olefins. Method A. To a 500-ml erlenmeyer flask was added 22.0 g (74 mmol) of sodium dichromate dihydrate, 50 ml of water, and 300 ml of dioxane. With stirring, 6.8 g (20 mmol) of mercuric propionate and 35 ml of trifluoroacetic acid were added. The dark orange-red solution was stirred until the salts had dissolved (ca 10 min), and the flask was placed in a water bath. With continued stirring, 100 mmol of olefin was added. The solution became dark and warm; ice was added as necessary to maintain the temperature at 25 ± 5°. The solution was stirred for 18 hr, poured into water (300 ml), and extracted with hexane (3 × 75 ml). The combined extracts were washed with water (3 × 50 ml), saturated sodium chloride solution (1 × 50 ml), and water (1 × 50 ml) and dried ($MgSO_4$).

General Procedure for the Mercury(II)-Catalyzed Oxidation of Olefins. Method B. To a 500-ml erlenmeyer flask was added 200 ml of acetone, 5 ml of water, and 6.8 g (20 mmol) of mercuric propionate. The flask was placed in a water bath and, with stirring, 100 mmol of olefin was added to the bright yellow solution. Jones reagent[7] (2*M*, 75 ml) was added dropwise during 4 hr. Ice was added as necessary to maintain the temperature at 25 ± 5°. The dark greenish-brown solution was stirred for an additional 4 hr and then poured into water (200 ml) and extracted with diethyl ether (3 × 75 ml). The combined extracts were washed with water (3 × 50 ml), saturated sodium chloride solution (1 × 50 ml), and water (1 × 50 ml) and dried ($MgSO_4$).

References and Notes

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(2) John M. Lyons Fellow, 1972–1974.

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Intramolecular van der Waals–London Cohesions and Chemical Properties. Acid Weakening by Halogens and Related Effects.

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Substituent effects arising from intramolecular van der Waals–London attractions are examined. For substituents adjacent to reaction centers at which a single bond is converted into a double bond, or close to a site acquiring a charge, order-of-magnitude calculations (using London's formula) show appreciable stabilization of the new unsaturated species, or the species that has gained a negative charge, or lost a positive one, and increasing in the sequence $F < Cl < Br \simeq H < I < Me$.

Stabilization of anions, and destabilization of cations, by halogen substituents bound to sp^2-hybridized C atoms, which increases in the order $F < H < Cl < Br < I$ (or roughly this order), has long been known for aromatic compounds in aqueous media.[1–3] This order is prominent in the acidities, in water, of some α-halogeno nitroalkanes[4–6] forming anions $X–C(Y){=}NO_2^-$ (see Table I); i.e., effects opposing the normal inductive effect (acid strengthening by X: $H \ll I < Br < Cl < F$) are important here. The (exceptionally) large anion destabilization by F (relative to H) in $F–C(Y){=}NO_2^{-}$[4,5] has been attributed[4] to (a) an increase in the order $I < Br < Cl < F$ in the sum of mesomeric electron donation by Hal and Hal p-electron–π-electron repulsions (both are zero for H), (b) a weakening of the C–F bond on changing from sp^3 to sp^2 hybridization, (c) double bond–no bond resonance effects. However, much evidence militates, in turn, against each of these explanations: (a)[7] e.g.[2a,d] the ionization potentials[8] of compounds $Hal–CH{=}CH_2$ and $Hal–C_6H_5$ [IP lowest for iodides; i.e. electron donation plus repulsion greatest with I; $ICH(NO_2)_2$ should be the weakest $HalCH(NO_2)_2$ acid]; (b) C–F bond lengths,[2a,d] $r(F–C_{sp^2}) < r(F–C_{sp^3})$; (c) numerous instances where F is greatly acid strengthening despite[2a,d] similar possibilities of double bond–no bond resonance.

In addition, in compounds $Me–CHYNO_2$, Me is acid *weakening*[9] unless Y is strongly electron withdrawing—a very rare situation for Me attached to an sp^2-hybridized atom.

This article deals with a relevant and neglected nonpolar substituent effect, viz., intramolecular van der Waals–Lon-