major factor in determining relative reactivities. On the other hand, σ participation could occur in both the acid-catalyzed and spontaneous solvolyses of the *exo* isomers, although we would expect it to be less important in these systems where a secondary alkyl group would be interacting at a tertiary carbonium center than in systems in which both centers are secondary; initial state steric effects should affect both sets of solvolyses and are known to be small for these compounds.[8]

The similarity of the rates of ionization of camphene hydrate and methylisobornyl p-nitrobenzoates (III) and (VI), Table VI, shows that the rate enhancements due to relief of eclipsing strain and to secondary participation at a tertiary carbonium ion center in III approximately balance those due to relief of steric strains between the leaving group and the 1- and 7-methyl groups[9] and to tertiary participation at a tertiary carbonium ion center in VI. (Brown and his coworkers have presented rate data for solvolyses of 1,2-dimethylnorbornyl derivatives which show that participation must be less important in the ionization of 1,2-dimethylnorbornyl compounds than in the corresponding 1-methyl compounds, which they consider to exclude participation in the 1,2-dimethylnorbornyl system.[4a,20])

Recently it has been pointed out that torsional effects in bicyclo[2.2.1] compounds should favor *exo* over *endo* attack upon a carbonium ion and *exo* over *endo* departure, although the magnitude of these effects is not yet known. These torsional effects could be of major importance in determining *exo*/*endo* rate ratios and the stereochemistry of carbonium ion capture in these tertiary systems.[21]

If steric hindrance to ionization, or its equivalent, which is steric hindrance to solvation of the leaving group, is all important, we would expect to find systematic variations in the *exo*/*endo* rate ratios with changes in the nature of the leaving group and in the ability of the solvent to solvate it. Even though the solvents range from acetic acid to aqueous ethanol, and these ratios apply to both spontaneous and acid-catalyzed solvolyses, *exo*/*endo* rate ratios of 10^2 to 10^3 are generally observed.[7,8,18]

Our observation of similar *exo*/*endo* rate ratios irrespective of the formal charge upon the leaving group is consistent with all the other evidence. For example, similar *exo*/*endo* rate ratios are observed for the spontaneous acetolysis of the norbornyl tosylates and the acid-catalyzed acetate exchange.[22] Similarly borohydride ion and neutral molecules such as methanol and acetic acid behave similarly with respect to the preferred positions of attack upon 2-apobornyl,[23] 2-methoxynorbornyl, and 2-methoxybornyl[24] cations.[25] Despite large differences in the nature of the solvents and reagent, the general pattern of preferred loss and attack from the *exo* direction persists in these reactions involving norbornyl cations, even when the bulky 7-substituents are present.

Registry No.—III, R = p-$NO_2C_6H_4$, 13421-46-0; III, R = CH_3, 13389-75-8; IV, R = p-$NO_2C_6H_4$, 13389-76-9; IV, R = CH_3, 13389-77-0; V, R = p-$NO_2C_6H_4$, 13389-78-1; VI, R = p-$NO_2C_6H_4$, 13389-79-2.

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Homogeneous Oxidations of Alcohols with Palladium(II) Salts

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Primary and secondary alcohols are smoothly oxidized to the corresponding acetals and ketones by palladium(II) salts under mild conditions, typically 70–120°. This reaction, which becomes catalytic in the presence of oxygen and a reoxidant compound, is retarded by the chloride ion and by more than small amounts of water. Some oxidations are characterized by a secondary ester forming reaction. Tertiary alcohols do not react under these conditions.

The heterogeneous oxidation of alcohols to carbonyl compounds, catalyzed by noble metal compounds, has been known at least since Strecker's oxidation of cinnamyl alcohol to cinnamaldehyde with PtO and oxygen.[2] More recent heterogeneous alcohol oxidations with platinum and palladium are discussed by Ioffe[3] and by Heyns and Paulsen.[4] The capacity of dissolved palladium(II) salts to effect similar oxidations was strongly implied by Berzelius' observation that upon reflux of a wet ethanolic solution of potassium palladium chloride most of the palladium became reduced.[5] A recent short study by Moiseev's group indicates that these reactions, when carried out in mostly (95–98%) aqueous systems, are sluggish even at reflux.[6] The tendency of substantially anhydrous alcohols to reduce palladium(II) under much milder conditions has been noted as an undesired side reaction,[7] and the closely analogous reduction by alcohols of rhodium(III) to

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TABLE I

OXIDATION PRODUCTS OF 1-BUTANOL[a]

Catalyst	Temp, °C	Water[b]	Butyraldehyde free[c]	Butyraldehyde as acetal[c]	*n*-Butyl *n*-butyrate[c]	Aldehyde/ester ratio
d	100	0.4	0.01	<0.01	<0.005	...
e	100	2.4	0.09	0.06	0.04	4
f	60	1.5	0.07	<0.01	<0.005	...
f	80	1.8	0.08	<0.01	<0.005	...
f	100	4.0	0.11	0.05	0.075	2.1
f	120	7.0	0.14	0.05	0.10	1.9
g	60	2.7	0.12	0.16	<0.005	60
g	70	3.8	0.22	0.36	0.016	36
g	80	6.0	0.29	0.43	0.040	18
g	90	6.4	0.38	0.50	0.045	20
g	100	8.3	0.43	0.52	0.075	13
g	110	9.0	0.47	0.51	0.11	9
g	120	10	0.49	0.52	0.13	7.7
h	100	1.6	0.07	0.10	0.012	14
i	100	8.0	0.23	0.29	0.082	6.3

[a] All oxidations were carried out in a glass shaker-reactor under 3-atm oxygen pressure. [b] Water concentration in volume % at end of oxidation. [c] Product concentration in mole/kg after 120-min oxidation. [d] No catalyst, no reoxidant. [e] 0.040 *M* $PdCl_2$, no reoxidant. [f] 0.020 *M* $PdCl_2$, 0.100 *M* $CuCl_2 \cdot 2H_2O$. [g] 0.020 *M* $PdCl_2$, 0.100 *M* $Cu(NO_3)_2 \cdot 3H_2O$. [h] 0.020 *M* $PdCl_2$, 0.100 *M* 1,4-naphthoquinone. [i] 0.020 *M* $RhCl_3$, 0.100 *M* $Cu(NO_3)_2 \cdot 3H_2O$.

rhodium (I) has been shown to explain an anomalous "alcohol-catalyzed" ligand displacement reaction.[8] The present paper explores the homogeneous oxidation of simple alcohols by palladium(II) salts as a potentially useful synthetic reaction.

When undiluted 1-butanol was shaken for 2 hr under 3 atm of oxygen at 100° and in the presence of 0.040 *M* $PdCl_2$, the cooled mixture was found to contain *n*-butyraldehyde and its di-*n*-butyl acetal (0.15 mole/kg) as well as lesser amounts of *n*-butyl *n*-butyrate and water. In the absence of the palladous salt only a trace of oxidation products was found. The sluggish reoxidation of atomic palladium(0) by molecular oxygen is greatly facilitated by addition of a reoxidant, *e.g.*, a copper salt.[9] A parallel oxidation with 0.020 *M* $PdCl_2$ and 0.100 *M* $Cu(NO_3)_2 \cdot 3H_2O$ produced 0.95 mole/kg of *n*-butyraldehyde (mostly as the acetal) and 0.075 mole/kg of *n*-butyl *n*-butyrate. The formation of ester, recently claimed to be the principal reaction in alcohol–aldehyde–palladium(II) systems,[10] occurs here as a side reaction often of negligible importance. Typical results of oxidations of 1-butanol are shown in Table I.

The water content of these reaction mixtures, ranging as high as 10 vol. %, arises in part (<0.3%) from adventitious water contamination of the alcohol and palladium salt, and in part (0.4–0.6%) from the water of hydration of the copper salt, but it arises principally as water of reaction from the acetalation and reoxidant regeneration steps (eq 2 and 4). In eq 1–4, X represents chloride, nitrate, or other monovalent anion. When the main product is aldehyde, the over-all stoichiometry is the sum of eq 1, 3, and 4 (eq 5). When

$$RCH_2OH + PdX_2 \longrightarrow RCHO + Pd(0) + 2HX \qquad (1)$$

$$RCHO + 2RCH_2OH \rightleftarrows RCH(OCH_2R)_2 + H_2O \qquad (2)$$

$$Pd(0) + 2CuX_2 \longrightarrow PdX_2 + Cu_2X_2 \qquad (3)$$

$$Cu_2X_2 + 2HX + \tfrac{1}{2}O_2 \longrightarrow 2CuX_2 + H_2O \qquad (4)$$

$$RCH_2OH + \tfrac{1}{2}O_2 \longrightarrow RCHO + H_2O \qquad (5)$$

acetal is the main product, the stoichiometry is better indicated by the sum of eq 1–4 (eq 6).

$$3RCH_2OH + \tfrac{1}{2}O_2 \longrightarrow RCH(OCH_2R)_2 + 2H_2O \qquad (6)$$

The presence of a few per cent water exerts no first-order influence upon rate, although it obviously alters the aldehyde–acetal equilibrium. (For the system *n*-butyraldehyde–1-butanol the Table I data indicate $K_2 \cong 0.1\ M^{-1}$.) As the mole fraction of water exceeds about 0.2, however, the oxidation rate becomes sharply suppressed. Analyses of a group of three oxidations of 1-propanol (each for 2 hr at 90° under 3 atm of oxygen, with 0.020 *M* $PdCl_2$ and 0.100 *M* cupric nitrate) with 30% (v/v), 10%, and no initially added water revealed products totaling 0.01, 0.39, and 1.13 moles/kg, respectively.

The effect of varying the chloride–nitrate balance upon the oxidation of ethanol is shown in Table II. These data, like those in Table I, indicate greater selectivity and higher rates in chloride-poor systems.

TABLE II

OXIDATION PRODUCTS OF ETHANOL[a]

Anion concentrations, *M*		Acetaldehyde free[b]	Acetaldehyde as acetal[b]	Ethyl acetate[b]	Aldehyde/ester ratio
Chloride	Nitrate				
Nil	0.24	0.32	0.56	0.023	38
0.04	0.20	0.38	0.71	0.042	26
0.08	0.16	0.34	0.63	0.067	14
0.24	Nil	0.24	0.25	0.078	6.3

[a] All oxidations were carried out in a glass shaker-reactor under 3-atm oxygen pressure at 90° for 120 min. [b] Product concentration in mole/kg.

Among the primary 1-alkanols methanol is markedly stable (Table III). Methanol is also unique among the alcohols examined in this study, in that its major

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isolable product is the ester, methyl formate, rather than the acetal.

TABLE III

OXIDATION PRODUCTS OF METHANOL

Catalyst	Temp, °C (duration)	Water[a]	Methylal[b]	Methyl formate[b]	Aldehyde/ester ratio
c	90 (120 min)	1.1	<0.001	0.015	...
d	90 (120 min)	1.6	0.001	0.03	0.03
e	100 (40 min)	2.4	0.009	0.06	0.15
f	100 (40 min)	4.3	0.06	0.31	0.2
e	140–80 (100 min)	6.5	0.44	0.79	0.56

[a] Water concentration in volume % at end of oxidation. [b] Product concentration in mole/kg. [c] 0.02 *M* $PdCl_2$, 0.100 *M* $CuCl_2 \cdot 2H_2O$. [d] 0.020 *M* $PdCl_2$, 0.100 *M* $Cu(NO_3)_2 \cdot 3H_2O$. [e] 0.028 *M* $PdCl_2$, 0.29 *M* $CuCl_2 \cdot 2H_2O$. [f] 0.028 *M* $PdCl_2$, 0.21 *M* $Cu(NO_3)_2 \cdot 3H_2O$.

Oxidations of a number of other primary and secondary alcohols are shown in Table IV. Branched primary alcohols, as well as benzyl alcohol, are readily oxidized to the corresponding aldehydes in high yield. Secondary alcohols are oxidized to the corresponding ketones with no detectable side products. 2-Methyl-2-propanol under the same conditions does not react.

TABLE IV

OXIDATIONS OF ALCOHOLS[a]

Alcohol	Temp, °C	Product(s)	Conversion[b]
2-Butanol	70	Butanone	0.39
2-Butanol	90	Butanone	0.74
2-Butanol	110	Butanone	1.19
2-Methyl-1-propanol	90	Isobutyraldehyde,[c]	1.62
		isobutyl isobutyrate	0.10
2-Methyl-2-propanol	90	Nil	...
2,2-Dimethyl-1-propanol[d]	90	Pivalic aldehyde,[e]	1.66
		coproduct[f]	<0.02
Cyclohexanol	90	Cyclohexanone	0.23
1-Phenylethanol	90	Acetophenone	0.65
2-Phenylethanol	90	Phenylacetaldehyde	0.17
Benzyl alcohol	90	Benzaldehyde,	3.06
		benzyl benzoate	~0.01
Ethylene glycol	100	2-Methylol-1,3-dioxolane,	0.54[g]
		2-hydroxyethyl glycolate	0.032

[a] All oxidations were carried out in a glass shaker–reactor under 3-atm oxygen pressure, with 0.020 *M* $PdCl_2$ and 0.100 *M* $Cu(NO_3)_2 \cdot 3H_2O$. [b] Product concentration in moles/kg after 120-min oxidation. [c] Chiefly as the diisobutyl acetal. [d] "Neopentyl alcohol." [e] Including 0.28 mole/kg of the dineopentyl acetal. [f] Insufficient to identify; probably neopentyl pivalate. [g] Replacement of $Cu(NO_3)_2$ by $CuCl_2$ decreases dioxolane product while increasing ester formation; *cf.* Tables I and II.

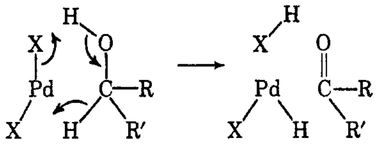
The expected principal product from ethylene glycol is glycolic aldehyde, and the product actually found is its cyclic acetal, 2-methylol-1,3-dioxolane. Under the same conditions 1,4-butanediol is oxidized to form 0.13 mole/kg of γ-butyrolactone and about 0.42 mole/kg of an acetal alcohol I, a stable, nonvolatile colorless liquid, $n^{25}D$ 1.4470, d^{25}_4 1.035, its infrared spectrum showing acetal and hydroxylic absorption but no unsaturation. Molar refraction calculations eliminate the hemiacetal 2-hydroxytetrahydrofuran, but are consistent (MR calcd 41.76, found 41.38) both with the normal cyclic acetal, 2-(ω-hydroxypropyl)-1,3-dioxepane, and with the more probable rearranged acetal, 2-(ω-hydroxybutoxy)tetrahydrofuran.

Oxidation of mixtures of methanol and 1-butanol affords the expected mixed acetals of *n*-butyraldehyde along with small amounts of methyl and *n*-butyl *n*-butyrates. With mixtures of methanol and ethylene glycol the favored cyclic acetal, 2-methylol-1,3-dioxolane, is the sole aldehydic product and the oxidation rate passes through a maximum under our experimental conditions at about a 1:1 mixture, suggesting that the oxidation of the viscous undiluted glycol is subject to diffusional control.

Discussion

These alcohol oxidations, carried out in alcoholic media, proceed much more readily than similar reactions in substantially aqueous media,[6] and indeed are sharply inhibited by about 10% or more water. The evident enhancement of reactivity of the palladium(II) species in alcohols may be contrasted with the rate enhancement of many anion-controlled reactions by media containing dipolar aprotic solvents such as dimethyl sulfoxide.[11,12] The latter effect is explained on the basis that the anionic reactants are relatively unsolvated or "bare," hence more reactive, in substantially aprotic media.[12] Alcohols, on the other hand, are excellent anion solvators but weak cation solvators. Thus, the ultraviolet–visible spectrum of dilute aqueous palladium(II) chloride displays three maxima, at 202, 303 and 418 mμ. As water is progressively replaced by methanol all three maxima undergo bathochromic shifts, appearing at 213, 323 and 434 mμ in dry methanol. These shifts suggest that alcohol-solvated palladium(II) is more "bare," hence more reactive, than the corresponding water-solvated species.

The facile reactions of alcohols possessing no β-hydrogen and the unreactivity of 2-methyl-2-propanol suggest a ligand dehydrogenation involving the alcoholic hydrogen and an α-hydrogen, *e.g.*, eq 7. Equation 7 indicates the coproduct to be hydridopalladium chloride, for which there is no present evidence. An intermediate of this type has been proposed, however, for a number of formally similar oxidation–reduction systems.[13]



(7)

The apparent utility of small amounts of chloride ion in predominantly nitrate systems may lie in its function as a bridging ligand in palladium(0) reoxidation. High chloride ion concentrations inhibit the

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over-all oxidation, probably by preempting ligand sites from the alcohol. The concurrent oxidation of acetal to ester,[10] a side reaction under our conditions, is only slightly retarded by hydroquinone but is almost eliminated by removal of the palladium salt; this side reaction is thus a true metal-catalyzed oxidation rather than a concurrent autoxidation.

Experimental Section

Oxidations were carried out in a standard, low-pressure catalytic apparatus (Parr Instrument Co., Model 3911), modified[14] to withstand the various organic media and the strongly oxidizing environment. In a typical run 50.0 ml of alcohol was charged to a 500-ml glass reactor vessel along with the desired amounts of catalyst and reoxidant, and the system was sealed, purged three times with oxygen, then pressured to 30-psig oxygen pressure and rapidly brought to the desired temperature by means of banked heat lamps. After 120 min of isothermal oxidation in this shaker-reactor, with repressuring as needed to maintain the oxygen pressure between 2.5 and 3.5 atm, the reactor was cooled and the contents were collected for analysis. Oxidations of methanol at higher temperatures and pressures (Table III) were conducted similarly, using a stainless steel, turbine-stirred autoclave.

Product identifications for commonly available aldehydes, acetals, ketones, and esters were made by matching gas chromatograph residence times with those of authentic samples on at least two stationary phases. Identifications were confirmed by one or more of the following measurements upon chromatographically isolated samples: infrared spectrum, refractive index, and density.

Pivalic aldehyde was identified by its sharp infrared spectrum, characterized by strong methyl absorption at 1485 and 2890 cm^{-1}, strong aldehyde absorption at 890, 1745 and 2710 cm^{-1}, and the absence of other functional group absorptions. Its dineopentyl acetal was characterized by its unusually simple spectrum, consisting of very strong methyl absorption along with four strong peaks in the 1000–1230-cm^{-1} range, characteristic of the acetal structure.[15] This acetal was further characterized: $n^{25}D$ 1.4092, d^{22}_4 0.8031, MR calcd 74.76, found 75.27 (error 0.68%).

2-Methylol-1,3-dioxolane, the major product from ethylene glycol oxidations, was identified by chromatographic matching with the glycolic aldehyde–ethylene glycol condensation product and its identity was confirmed by infrared spectrum, characterized by strong hydroxyl absorption near 3400 cm^{-1} and the four acetal peaks in the 1000–1230-cm^{-1} range.

Quantitative estimates of products are based upon signal strengths from thermal conductivity detectors, using integrated area measurements. For twelve different standard 10.00% solutions (*e.g.*, *n*-butyraldehyde in dioxane, *n*-butyl *n*-butyrate in 1-butanol), the average assay was 9.93%, standard deviation 0.73%.

Registry No.—Pivalic aldehyde, 630-19-3; pivalic aldehyde dineopentyl acetal, 13421-45-9; 2-methylol-1,3-dioxolane, 5694-68-8; 1-butanol, 71-36-3; ethanol, 64-17-5; methanol, 67-56-1.

Acknowledgment.—The writer gratefully acknowledges the valuable assistance of Mssrs. Paul T. Russotto and Joseph Kisutcza in obtaining much of the data.

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Sterically Crowded Amines. VIII. The Synthesis and Reactions of Some Polysubstituted 2-Imidazolidinones[1]

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1-Alkyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinones, $(CH_3)_2\overline{CN(R)CONHC}(CH_3)CONH_2$, were obtained in good yields from 3-alkylamino-3-methyl-2-butanones, $(CH_3)_2C(NHR)COCH_3$, by reaction with potassium cyanide and ammonium carbonate (the Bucherer-Bergs procedure). Hydrolysis with dilute hydrochloric acid led, with one exception, to the corresponding 4-carboxylic acids. When R was *t*-butyl, acid hydrolysis proceeded with facile loss of the *t*-butyl group as the initial reaction and thus gave either 4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (R = H) or the corresponding 4-carboxylic acid, depending on the acid concentration. Alkaline hydrolysis appeared to follow two competitive routes, one leading to the 4-carboxylic acids as obtained also from acid hydrolysis, the other to alanine, acetone, and primary amine by ring degradation. The 3 position of the ring was found to be nitrosated and acylated readily and to undergo condensation with acetone and benzaldehyde. However, alkylation at this position proved unsuccessful.

Motivated by the possibility that alkylamino ketones,[3-5] $(CH_3)_2C(NHR)COCH_3$, might be useful for the preparation of novel α-amino-β-alkylamino acids having both amino functions on tertiary carbon atoms, the reaction of the ketones with potassium cyanide and ammonium carbonate (Bucherer–Bergs reaction) was investigated. It is well known[6,7] that ordinary ketones react in this procedure to produce hydantoins which, by hydrolysis, lead to α-amino acids. Hence the alkylamino ketones, readily prepared from the appropriate acetylenes,[3-5] might well yield structures in which steric crowding would lead ultimately, *via* hydrolysis, not only to α-amino-β-alkylamino acids, but to the corresponding β-lactams as well.

Anomalous results have occasionally been observed, however, when certain ketones possessing an α-functional group are submitted to these reaction conditions. For example, Henze[8] reported that 4-carbamyl-4-phenyl-2-oxazolidinone was obtained using benzoylcarbinol acetate as the substrate in the Bucherer–Bergs procedure. Hennion and O'Shea[9] observed that the

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