nitrobenzene, 3% 4,4′-dinitrobiphenyl, and recovered starting material. An advantage of these activated copper Ullmann coupling reactions is the ease of separation and the lack of tarry residues so often found under the standard conditions.[17]

Cross coupling of aryl groups with other aryl groups is fairly common for the Ullmann reaction. Utilizing activated copper, pentafluorophenyl iodide was cross-coupled with allyl bromide at room temperature to yield 34% 1-(pentafluorophenyl)-2-propene. Side reactions of the aryl iodide did not occur and the only other product observed was 1,5-hexadiene. The cross coupling in this instance is believed to result from the trapping of the pentafluorophenylcopper intermediate, vide supra.

Reactions of activated copper with other organic substrates have been observed. Allyl bromide is quantitatively converted to 1,5-hexadiene within 5 min of reflux temperature of dimethoxyethane.

Several methods have been published for the preparation of a form of uranium metal which will react with organic compounds: these methods include thermal decomposition of uranium amalgam,[18] thermal decomposition of uranium hydride,[19] and reductive cleavage of tetrakis(cyclopentadienyl)uranium.[20] None of these methods is suitable for cleanly providing reactive uranium under ordinary laboratory conditions. Recent attempts by Evans to apply the standard Rieke recipe to the preparation of activated uranium had failed due to incomplete reduction.[21] In the case of praseodymium, the residual potassium metal caused unique chemistry to occur effecting a conversion of 1,5-cyclooctadiene (1,5-COD) to cyclooctatetraene (COT).[22]

Activated uranium has been made by a variation of the recently published method of Rieke et al.[9] Reduction of uranium tetrachloride in dimethoxyethane by sodium–potassium alloy and 5–10% naphthalene (based on NaK) under an argon atmosphere produces in 24 h a black slurry of activated uranium in a clear colorless solution. This activated uranium has exhibited approximately the same reactivity as the pyrophoric uranium produced from uranium hydride. The added advantages of this activated uranium are the ease of preparation and the nonpyrophoric nature of the metal slurry.

The activated uranium slurry obtained by the NaK reduction does not contain excess alkali metal. The naphthalide radical anion is an effective indicator as to when the reduction is complete. If the slurry is syringed onto water, indications of residual alkali metal are totally lacking. Unlike the results reported for praseodymium, this activated uranium slurry does not react with 1,5-COD. Our results match those of Evans when the reduction is attempted using sodium or potassium with or without naphthalene; the alkali metal becomes covered with an extremely hard coating resulting in incomplete reduction. In contrast the surface of the NaK alloy remains shiny throughout the reduction. No attempt has been made to optimize the conditions for the production of even more reactive uranium by variations in the reductive procedure.

Several reactions of this activated uranium with organic compounds have been investigated. A very vigorous and exothermic reaction occurs upon the addition of allyl iodide to this slurry at room temperature. The product of the reaction is an almost quantitative yield of 1,5-hexadiene. If an intermediate allyl complex of the uranium is formed during this reaction, it is most probable that it is not thermally stable at room temperature.[25] Activated uranium reacts with benzophenone in refluxing dimethoxyethane to yield up to 50% tetraphenylethylene. This reaction is very clean, allowing almost total recovery of the unreacted starting material.

Uranocene has been prepared from activated uranium. A 1:1 ratio of cyclooctatetraene and activated uranium was refluxed in dimethoxyethane (85 °C) for 24 h, evaporated to dryness in vacuo, and Soxhlet extracted with xylene for 36 h. All manipulations were performed with strict exclusion of air. Lustrous green crystals of uranocene were isolated in >35% yield. Streitweiser obtained a 57% yield of uranocene in a sealed tube reaction at 150 °C using pyrophoric uranium obtained from the thermal decomposition or uranium hydride.[23] This reaction of COT with activated uranium has particular significance as it is the first example of a metal produced by the Rieke procedure reacting by coordination to an unsaturated hydrocarbon to yield an isolatable organometallic complex.

In summary, both activated copper and activated uranium have been prepared via the Rieke procedure. Activated copper reacts with aryl halides to yield organocopper compounds and/or Ullmann coupled biaryls. Cross coupling of organic halides has also been effected in good yields. Activated copper has shown reactivity toward other organic compounds. Activated uranium has been prepared, although certain variations must be used to effect complete reduction. Activated uranium reacts rapidly with allyl iodide to give 1,5-hexadiene. Uranocene can be prepared in good yield and is the first olefin coordination reaction of a metal produced by the Rieke method. We are continuing our studies of these metals and will report these results in the near future.

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Registry No. Copper, 7440-50-8; cuprous iodide, 7681-65-4; pentafluorophenyl iodide, 827-15-6; pentafluorophenylcopper, 18206-43-4; decafluorobiphenyl, 434-90-2; pentafluorobenzene, 363-72-4; 4-iodonitrobenzene, 636-98-6; 4,4′-dinitrobiphenyl, 1528-74-1; allyl bromide, 106-95-6; (pentafluorophenyl)-2-propene, 1736-60-3; uranium, 7440-61-1; uranium tetrachloride, 10026-10-5; allyl iodide, 556-56-9; 1,5-hexadiene, 592-42-7; benzophenone, 119-61-9; tetraphenylethylene, 632-51-9; uranocene, 11079-26-8; cyclooctatetraene, 629-20-9.

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Oxidations with Solid Potassium Permanganate

Summary: A solid oxidant, $KMnO_4$–$CuSO_4(H_2O)_5$, converts secondary alcohols into ketones under much milder conditions and with less reagent than does the recently reported $KMnO_4$ on molecular sieves. Primary alcohols and alkenes do *not* react effectively with the $KMnO_4$–$CuSO_4(H_2O)_5$ combination.

Sir: Regen and Koteel recently communicated their discovery that molecular sieves impregnated with $KMnO_4$ oxidize alcohols.[1] In a typical run, 0.25 g of cyclododecanol in 20 mL of benzene was stirred for 1.5 h at 70 °C with 15.0 g of sieve/$KMnO_4$ to give cyclododecanone in 90% yield. Control experiments, using powdered $KMnO_4$ instead of $KMnO_4$-coated molecular molecular sieve, gave no product after 50 h at 70 °C. Activation on molecular sieves was offered as an attractive alternative to phase-transfer and triphase catalysis in organic synthesis, but the source of the sieve effect was not explored. We now report results which explain the data of Regen and Koteel and which improve the synthetic potential of the method. Conditions are defined under which powdered $KMnO_4$ can react even *faster* than oxidant adsorbed onto molecular sieves.

We were initially alerted to the complexities of the solid-state oxidation[2] when we attempted to duplicate the above control reaction with powdered $KMnO_4$ and obtained anywhere from 0 to 55% yield of ketone after 4 h. The erratic behavior was eventually associated with the presence of moisture. If the $KMnO_4$ was first carefully dried over P_2O_5 at reduced pressure, then oxidation invariably failed. A similar dependence on water was observed for the sieve/$KMnO_4$ reagent. Thus, oxidant prepared by stripping water from a mixture of aqueous $KMnO_4$ and Linde 4A molecular sieve gave the reported reaction time of 1.5 h for cyclododecanone formation.[1] Drying the reagent over P_2O_5 at 25 °C and 0.2 mm for 3 days, however, reduced the ketone yield to 16% after 8.5 h. Exposing the reagent to the same conditions but without the P_2O_5 did *not* lower the yield. Apparently, a primary function of the molecular sieve support is to supply the necessary trace quantities of water. Since the pore openings of the sieve are too small to accommodate secondary alcohols, oxidation with moist sieve/$KMnO_4$ probably takes place at $KMnO_4$ layers external to the cavities.

In the course of our experiments we found that $CuSO_4(H_2O)_5$ (although by itself inert toward alcohols) activates the oxidizing ability of powdered $KMnO_4$. For example, 2-octanol (0.13 g) in 3 mL of benzene stirred with 1.0 g of $KMnO_4$ and 0.50 g of $CuSO_4(H_2O)_5$ at 25 °C produced 2-octanone in 94% yield. Oxidation with $KMnO_4$–$CuSO_4$ has the same advantage as the molecular sieve approach (i.e., easy workup) but can be run at room temperature and with much smaller quantity of solid oxidant. Our mixed-solid reagent will not react with carbon–carbon bonds (tested with 1-dodecene amd methyl cinnamate), thereby permitting a degree of selectivity not usually associated with permanganate oxidations. Table I lists reaction conditions and yields for several $KMnO_4$–$CuSO_4$ oxidations.

A typical preparative scale alcohol oxidation was carried out as follows. A mixture of 1.0 g of $KMnO_4$ and 0.50 g of $CuSO_4(H_2O)_5$ was ground to a fine powder and added to 0.18 g of cyclododecanol in 3 mL of benzene at room temperature. After 8 h of magnetic stirring,[3] the oxidant was removed by filtration and the benzene was evaporated to give 0.17 g of cyclododecanone (92%) with a satisfactory melting point, TLC, and NMR.

The role of the hydrated $CuSO_4$ is not fully understood at present. Its catalytic activity was the same whether the $KMnO_4$ and $CuSO_4$ were ground together as solids or dissolved in water followed by removal of the water. Perhaps the hydrated $CuSO_4$ participates in the electron transfer process or else it acts, like the molecular sieve, as a source of water. Water is certainly a factor because drying the mixed-solid reagent over P_2O_5 reduced the yield of 2-octanone under standard conditions to 21% after 6 h. The water levels required for a favorable reaction time are small: adding 25–400 μL of water to reaction mixtures of $KMnO_4$–$CuSO_4(H_2O)_5$ and 2-octanol in 3 mL of benzene (Table I) did not further improve the reaction time.[4] In our hands, solid $Cu(MnO_4)_2$ (Mide Chemical Corp., powdered but otherwise used as received) performed nearly as well as the $KMnO_4$–$CuSO_4$ couple.

Table I. Oxidations of Alcohols in Benzene[a] to the Corresponding Carbonyl Compounds by Solid Mixtures of $KMnO_4$ and $CuSO_4(H_2O)_5$

alcohol (wt, mg)	temp, °C	$KMnO_4$, g	$CuSO_4$, g	reaction time, h	yield, %[b]
2-octanol (50)	70	0.25	0.25	4	96
2-hexadecanol (2400)	70	10	10	3	100 (84)[c]
benzhydrol (180)	70	0.50	0.50	4	100
1-cyclohexylethanol (130)	70	0.50	0.50	4	96
3-methylcyclohexanol (120)	25	0.50	0.50	2	97
ethyl lactate (120)	25	1.0	0.50	8	73
cholestanol (190)	25	1.0	0.50	11	91[c]
1-octanol (130)	25	1.0	0.50	20	<20[d]

[a] Reactions were all carried out in 3 mL of benzene except for the second entry which used 50 mL. [b] Yields were determined by GLC using internal standards except where indicated otherwise. [c] Isolated yield. [d] Consisted of roughly equal amounts of aldehyde and acid.

It will be noted from the last entry in Table I that primary alcohols react slowly with $KMnO_4$–$CuSO_4$. Regen and Koteel[1] also observed sluggish oxidation of primary alcohols by their molecular sieves, but they did not comment further on this behavior. In order to devise a synthetically useful method for oxidizing a secondary alcohol in the presence of a primary one, we exposed a mixture of 1-octanol and 2-octanol in benzene to solid $KMnO_2$–$CuSO_4$. To our surprise, we found that *both* alcohols resisted oxidation under the typical conditions. Only 24% total carbonyl product formed in 18 h at 25 °C. Obviously, a component in the reaction mixture was inhibiting oxidant activity. We suspect that this component is octanoic acid (detected in small amounts upon oxidizing 1-octanol) because of the following experiment. 2-Octanol (133 mg) in 5 mL of benzene was stirred with 1.5 g of solid oxidant. After 0.5 h, 60% 2-octanone was present as judged by GLC. Octanoic acid (41 mg) was then added

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(3) Reaction mixtures were invariably stirred, although this did not appear to greatly affect the reaction times or yields. Powdering the oxidant is, however, necessary for a satisfactory yield.

(4) Addition of 25–200 μL of water to reaction mixtures containing dried $KMnO_4$ but no $CuSO_4$ gave erratic yields of ketone and thus is not recommended for synthetic purposes.

and the reaction was allowed to proceed for another 3 h. Analysis of the reaction mixture at this point indicated only 69% ketone. Octanoic acid exerted a comparable inhibition when added to 2-octanol at the outset. Although these results show that a selective oxidation is unfeasible, they also illustrate the intricacies of organic reactions on solid surfaces and the need for future research in the area.

Acknowledgment. This work was supported by the National Science Foundation and the National Institutes of Health.

Registry No. 2-Octanol, 123-96-6; 2-hexadecanol, 14852-31-4; benzhydrol, 91-01-0; 1-cyclohexylethanol, 1193-81-3; 3-methylcyclohexanol, 591-23-1; ethyl lactate, 97-64-3; cholestanol, 80-97-7; 1-octanol, 111-87-5; 2-octanone, 111-13-7; 2-hexadecanone, 18787-63-8; diphenyl ketone, 119-61-9; 1-cyclohexylethanone, 823-76-7; 3-methylcyclohexanone, 591-24-2; ethyl 2-oxopropanoate, 617-35-6; cholestan-3-one, 566-88-1; octanal, 124-13-0; $KMnO_4$, 7722-64-7; $CuSO_4$, 7758-99-8.

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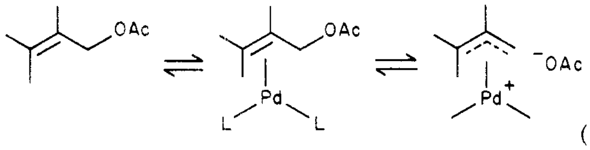
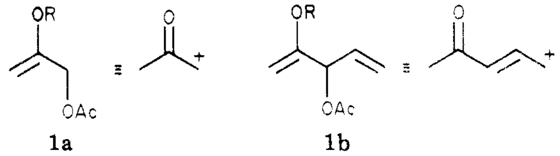
An Approach to Enolonium Equivalents. Application to a Total Synthesis of (±)-Pyrenophorin

Summary: Alkoxy-bearing allylic acetates can serve as substrates for palladium(0) catalysts under special conditions and thus constitute the equivalent of an enolonium and a vinylogous enolonium ion, a feature that has led to a formal synthesis of pyrenophorin and a synthesis of a fragment of zealeranone.

Sir: Allylic alkylations catalyzed by palladium(0) complexes have proven quite versatile for structural elaboration.[1,2] Activation of allylic acetates by a palladium complex involves initial coordination to form an olefin–metal(0) complex followed by ionization of the acetate (eq 1). Allylic acetates that fail to react frequently do so presumably because of the unfavorability of formation of the initial olefin complex. Whereas electron-withdrawing substituents facilitate the formation of such complexes, electron-donating ones greatly hamper it.[3] On the other hand, allylic acetates bearing an electron-donating group like a heteroatom should be particularly useful as carbonyl equivalents; for example, **1a** would be an equivalent of an enolonium ion[4] and **1b** an equivalent of a vinylogous enolonium ion. In this communication, we wish to report that, while the usual procedures for alkylation of allylic acetates like **1** fail, we have uncovered a successful set of conditions for alkylation. Furthermore, use of such systems evolved the equivalent of a reductive acylation, a stereocontrolled enol ether synthesis, and the synthesis of oxygen-bearing dienes. The reductive acylation is applied to the synthesis of the antifungal and cytostatic agent pyrenophorin[5] and a segment of the commercial anabolic agent zealeranone.[6]

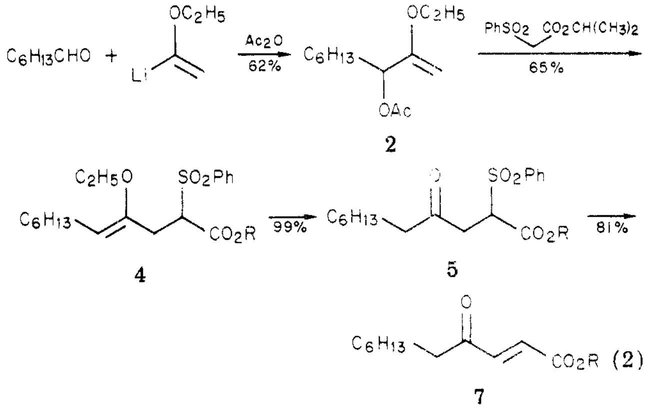


(1)



1a **1b**

The requisite substrates are readily available by the addition of lithiated ethyl vinyl ether[7] to aldehydes (THF, −78 °C) followed by acetylation (C_5H_5N, Ac_2O, room temperature) as in eq 2. For synthetic purposes, our interest focused upon the anions from sulfonylacetates. Treatment of **2** with methyl benzenesulfonylsodioacetate in THF in the presence of tetrakis(triphenylphosphine)palladium (**3**) led to mostly decomposition. On the other hand, reaction with isopropyl benzenesulfonylacetate[8] and DBU in hot toluene in the presence of 10–15 mol % of **3** proceeded smoothly to give a single product, **4**.[9] It is interesting to note that higher regioselectivity is observed here compared to allylic acetates without the heteroatom substituent and that a single stereoisomeric enol ether is formed as shown by chromatography and spectral analysis including ^{13}C NMR spectroscopy. The appearance of the vinyl carbons at δ 115.5 and 148.4 suggest the *Z* configuration,[10] in agreement with reaction via the expected syn palladium complex. Hydrolysis of **4** (0.02 N HCl in THF, room temperature) unmasks the carbonyl group to give **5**.[9] In principle, desulfonylation[11]



(2)

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