One hour after removal from the dry ice–acetone bath the reaction was quenched by addition of 20 mL of water to the reaction flask and permitting the reaction to stir for 5 min. The organic and aqueous layers were separated and the aqueous layer was extracted three times (30 mL each time) with diethyl ether. The etheral extracts were added to the original THF layer followed by drying ($MgSO_4$). The solvent was removed in vacuo to yield the product acetylene, usually in high purity. Solid products were recrystallized from 95% ethanol while liquid products were purified either by column chromatography (silica gel eluted with hexane) or bulb-to-bulb distillation.

General Procedure for the Preparation of Alkynes by Treating Arylsulfonylacetylenes with Grignard Reagents. The same procedure was followed as described with organolithiums with the following modifications. After being removed from the dry ice–acetone bath, the reaction was allowed to stir at room temperature for 24 h. The reaction mixture was then quenched by addition of 20 mL of saturated aqueous ammonium chloride, followed by stirring for 30 min. The organic layer was separated and the aqueous layer was extracted three times with diethyl ether (20 mL each time), and the ethereal extracts were added to the original organic layer. The THF–ether solution was then extracted twice with 0.1 N NaOH (15 mL each time) and then with 20 mL of water. Drying ($MgSO_4$) and solvent removal in vacuo yielded the product acetylene.

Registry No. Phenyl 2-phenylethynyl sulfone, 5324-64-1; mesityl 2-phenylethynyl sulfone, 71138-70-0; *p*-tolyl 2-*tert*-butylethynyl sulfone, 28995-90-6; phenyl ethynyl sulfone, 32501-94-3; butyllithium, 109-72-8; *tert*-butyllithium, 594-19-4; phenyllithium, 591-51-5; *p*-tolyllithium, 2417-95-0; phenylbutylacetylene, 1129-65-3; phenyl-*tert*-butylacetylene, 4250-82-2; diphenylacetylene, 501-65-5; phenyl-*p*-tolylacetylene, 3287-02-3; butyl-*tert*-butylacetylene, 19482-57-6; di-*tert*-butylacetylene, 17530-24-4; phenylacetylene, 536-74-3; ethylphenylacetylene, 622-76-4; phenyl-*sec*-propylacetylene, 1612-03-9; 1,4-diphenyl-1,3-butadiyne, 886-66-8; phenyl-*p*-tolylthioacetylene, 63707-12-0.

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Preparation of Highly Reactive Metal Powders. Activated Copper and Uranium. The Ullmann Coupling and Preparation of Organometallic Species

Summary: Reduction of cuprous iodide with potassium yields highly reactive copper powder; reduction of uranium tetrachloride with sodium–potassium alloy yielded an extremely reactive form of uranium metal.

Sir: In 1972, we reported a general procedure for the preparation of highly reactive metal powders.[1] The basic procedure involved the reduction of a metal salt in a hydrocarbon or ethereal solvent.[1-12] We have noted that the reactivities and in some cases products are highly dependent on the reduction conditions, i.e., anion, reducing agent, solvent, temperature, and presence of added alkali salts, Lewis acids, or Lewis bases.[3-12] Herein is described an extension of that work to the preparation of activated copper and activated uranium.

Activated copper is readily prepared by the reduction of cuprous iodide with a stoichiometric amount of potassium and approximately 10% naphthalene in dimethoxyethane under an argon atmosphere.[13] The reduction requires about 8 h for completion.[14] The activated copper slurry is a gray–black granular solid suspended in a clear colorless solution. This slurry should be used immediately. Extended periods of stirring should be avoided since the activated copper physically sinters to coppery colored beads with a drastic loss of reactivity.

This activated copper has been used for the Ullmann biaryl synthesis under very mild conditions; furthermore, the intermediate organocopper compound can be isolated from the reaction mixture. Utilizing this highly reactive form of copper, important mechanistic data concerning the Ullmann reaction may now be accessible.

This activated copper was permitted to react with pentafluorophenyl iodide (molar ratios of 3.3:1) at room temperature in dimethoxyethane for 30 min. The supernatant solution was then anaerobically transferred to another flask where the solvent and excess aryl iodide were removed under vacuum to leave a tan solid containing pentafluorophenylcopper. This tan solid was difficult to purify; however its chemistry matches that published for pure pentafluorophenyl copper.[15] It yields decafluorobiphenyl upon air oxidation or thermal decomposition and pentafluorobenzene is obtained upon hydrolysis.

If the same reaction is performed for extended times or in refluxing dimethoxyethane (85 °C) the Ullmann coupling reaction occurs to yield decafluorobiphenyl in 83% yield. The only other product is pentafluorobenzene obtained in 17% yield. Previous workers obtained a 72% yield of decafluorobiphenyl from the same reaction at 300 °C for 10 h in a sealed tube with no solvent using normal copper bronze.[16] Thus the use of activated copper has drastically eased the strenuous conditions previously found necessary.

Less reactive aryl iodides give larger amounts of the side product and lesser quantities of the biaryl when the reaction is performed in dimethoxyethane. For example, 4-iodonitrobenzene under the same conditions yields 36%

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[13] An example of a typical reduction for copper is as follows: Into a 50-mL two-neck flask is placed 0.3522 g (9.006 mmol) of potassium, 1.7075 g (8.996 mmol) of cuprous iodide, 0.1204 g (0.9393 mmol) of naphthalene, and 10.0 mL (96 mmol) of dimethoxyethane. This is stirred vigorously until the reduction is complete (~8 h). The activated copper appears as a gray-black slurry which settles out of the clear colorless solution. The cuprous iodide used was purchased from Cerac, Inc., Milwaukee, Wisconsin, and was 99% pure.

[14] The reduction is complete when the solution is clear and colorless. There should be no hint of the green naphthalide radical anion visible in the supernatant solution. This slurry does not flash or show other indications of alkali metal when syringed onto the surface of water. If the reduction is incomplete or after a partial reaction of the activated copper, the above aqueous quench will cause the precipitation of white cuprous iodide (decomposition of the soluble copper complexes occurs).

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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.