additional volume of formic acid–methanol was passed through the column to ensure complete removal of sample from the column. The combined eluent collected from the column was evaporated and products were isolated as described above. The column, after washing with methanol, is then ready for a subsequent sample. Bubbles of carbon dioxide that may adhere to the catalyst can be removed by sharp tapping on the side of the column and do not seem to interfere with the reaction. The same column can be used repeatedly.

Acknowledgment. We thank Pierce Chemical Company for financial support. G.P.R. is a recipient of a Public Health Service Research Career Development Award (5 K GM-00051).

Registry No. Z-Lys, 2212-75-1; Z-Gly-Gly, 2566-19-0; Z-Phe-Phe-OEt, 5276-63-1; Z-Gly-Arg(NO_2), 35146-46-4; Z-Lys(N^{ϵ}-Bzl), 51021-86-4; Boc-Asp(*O*-Bzl), 7536-58-5; Z-Met-Gly-OEt, 27482-82-2; Z-Cys(*S*-Bzl)-Phe-OEt, 71171-87-4; Lys formate, 71171-88-5; Gly-Gly formate, 71171-89-6; Phe-Phe-OEt formate, 71171-90-9; Gly-Arg formate, 71171-91-0; Boc-Asp, 13726-67-5; Met-Gly-OEt formate, 71194-21-3; formic acid, 64-18-6.

Babiker ElAmin, Gattadahalli M. Anantharamaiah
Garfield P. Royer, Gary E. Means*
Department of Biochemistry
The Ohio State University
Columbus, Ohio 43210

Received April 23, 1979

Reactions of Arylsulfonylacetylenes with Organolithium and Grignard Reagents: A New Synthesis of Acetylenes

Summary: α,β-Acetylenic sulfones react with organolithium and Grignard reagents to give a higher acetylene and a sulfinate salt. The process corresponds to nucleophilic substitution by the organometallic for the arylsulfonyl group.

Sir: The reaction of α,β-acetylenic sulfones with nucleophiles in a protic environment[1,2] and with organocopper reagents in an aprotic medium[3] results in products of addition to the triple bond. We wish to report our preliminary results concerning the reaction of α,β-acetylenic sulfones with organolithium and Grignard reagents to give products of substitution rather than addition.[4] Similar results have recently been reported with vinyl sulfones.[5,6]

Alkyl- and aryllithium reagents react rapidly and cleanly with arylsulfonylacetylenes to yield products of substitution (Table I). Alkyl Grignard reagents also give products of substitution in good to excellent yields (Table II).

$$\mathrm{ArSO_2C{\equiv}CR + R'M \rightarrow R'C{\equiv}CR + ArSO_2M} \qquad (1)$$

The reaction of organolithium reagents with α,β-acetylenic sulfones is rapid and complete in less than 1 min, even at −78 °C. Grignard reagents, on the other hand, required 12–24 h at room temperature to react completely. In general, yields are higher and cleaner with organolithium reagents. This reaction sequence represents a new synthesis of acetylenes,[7] including di-*tert*-butylacetylene (Table I, entry 6), from the appropriate α,β-acetylenic sulfone (readily available as by the addition of the sulfonyl iodide to the acetylene and subsequent dehydroiodination).[8]

Table I. Reactions with Organolithium Reagents[a,e]

Ar	R	R′	% yield[b]
C_6H_5	C_6H_5	n-C_4H_9	98
mesityl	C_6H_5	t-C_4H_9	60
mesityl	C_6H_5	C_6H_5	81
mesityl	C_6H_5	p-$CH_3 \cdot C_6H_4$	75
p-$CH_3C_6H_4$	t-C_4H_9	n-C_4H_9	84
p-$CH_3C_6H_4$	t-C_4H_9	t-C_4H_9	95
C_6H_5	H	C_6H_5	61[c,d]

[a] All reactions were carried out in THF as solvent. [b] Yields are actual isolated yields. [c] Yield based on VPC analysis. [d] Two equivalents of organolithium were used. [e] Products were characterized by nuclear, IR, and mass spectroscopic data.

Table II. Reactions with Grignard Reagents[a,d]

Ar	R	R′	% yield[b,c]
mesityl	C_6H_5	n-C_4H_9	75
mesityl	C_6H_5	C_2H_5	87
mesityl	C_6H_5	s-C_3H_7	91
C_6H_5	C_6H_5	C_6H_5	52
C_6H_5	C_6H_5	PhC≡C	24
C_6H_5	C_6H_5	p-$CH_3C_6H_4S$	29

[a] All reactions were carried out in THF as solvent. [b] Yields are actual isolated yields. [c] All products were purified by column chromatography. [d] Products were characterized by nuclear, IR, and mass spectroscopic data.

The reaction is believed to involve initial attachment of the organometallic to the sulfonyl-bearing (α) carbon (presumably facilitated by prior complexation of the organometallic to the sulfonyl oxygens), followed by expulsion of the arylsulfinate leaving group. Additional work on the reaction mechanism and into the scope and limitations[9] of the reaction are continuing in this laboratory. The following procedures are representative.

General Procedure for the Preparation of Alkynes by Treating Arylsulfonylacetylenes with Organolithiums. The reaction was carried out in a 100-mL three-neck flask equipped with a nitrogen inlet tube, rubber stopper, and Teflon magnetic stirring bar. The glassware was assembled cold, flame dried, and allowed to cool in a stream of nitrogen. The sulfone (7–10 mmol) was added to the cooled apparatus. THF (20–30 mL, previously dried over sodium turnings and freshly distilled) was added via syringe and the sulfone was brought into solution by the stirrer. The solution was cooled to −74 °C with a dry ice–acetone bath and an equimolar amount of the organolithium reagent was added via syringe. The rate of addition was usually 1 mL/min, although the rate of addition seems to have no effect on either product outcome or percent yields. Twenty minutes after the last of the organolithium reagent was added, the solution was removed from the dry ice–acetone bath and allowed to warm to room temperature. Upon warming, the solution usually turned from a dark red or dark green to an amber color.

---

(1) W. E. Truce and G. J. W. Tichenor, *J. Org. Chem.*, **37**, 2391 (1972).

(2) W. E. Truce and D. W. Onken, *J. Org. Chem.*, **40**, 3200 (1975).

(3) J. Meijer and P. Vermeer, *Recl. Trav. Chim. Pays-Bas*, **94**, 14 (1975).

(4) Presented at the American Chemical Society–Chemical Society of Japan Chemical Congress, Honolulu, Hawaii, April 1979.

(5) Marc Julia, 8th International Symposium on Organic Sulfur Chemistry, Portoroz, Yugoslavia, June 1978.

(6) Marc Julia, A. Righini, and D. Uguen, *J. Chem. Soc., Perkin Trans 1*, 1646–51 (1978).

(7) Newer approaches to higher acetylenes have been reviewed in "Compendium of Organic Synthetic Methods", Vol. 1–3, Wiley, New York, N.Y., 1971–1977, Chapter 1.

(8) W. E. Truce and G. C. Wolf, *J. Org. Chem.*, **36**, 1727 (1971).

(9) Preliminary indications are that acetylenes bearing at least one propargylic-type hydrogen suffer from complications (possibly isomerizations to the corresponding allenes, etc.) which may limit the general utility of this approach to higher acetylenes.

0022-3263/79/1944-3444$01.00/0

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.

Ronald L. Smorada, William E. Truce*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received May 15, 1979

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%

---

(1) Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178.

(2) Rieke, R. D.; Hudnall, P. M.; Uhm, S. *J. Chem. Soc., Chem. Commun.* **1973**, 269.

(3) Rieke, R. D.; Bales, S. E. *J. Chem. Soc., Chem. Commun.* **1973**, 789.

(4) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

(5) Rieke, R. D.; Chao, L. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 101.

(6) Rieke, R. D.; Ofele, K.; Fischer, E. O. *J. Organomet. Chem.* **1974**, *76*, C19.

(7) Rieke, R. D. *Top. Curr. Chem.* **1975**, *59*, 1.

(8) Rieke, R. D. *Acc. Chem. Res.* **1977**, *10*, 301, and references cited therein.

(9) Rieke, R. D.; Wolf, W. J.; Kujundzic, N.; Kavaliunas, A. V. *J. Chem. Soc.* **1977**, *99*, 4159.

(10) Uhm, S. Ph.D. Thesis, University of North Carolina—Chapel Hill, 1974.

(11) Rieke, R. D.; Kavaliunas, A. V.; Rhyne, L. D.; Frazier, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 246.

(12) Rieke, R. D.; Kavaliunas, A. V. *J. Org. Chem.* in press.

(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).

(15) Jukes, A. E.; Dua, S. S.; Gilman, H. *J. Organomet. Chem.* **1970**, *24*, 791.

(16) Birchall, J. M.; Hazard, R.; Haszeldine, R. N.; Wakalski, W. W. *J. Chem. Soc. C* **1967**, 47.

0022-3263/79/1944-3445$01.00/0