Oxidative Coupling of Acetylenes. II[1]

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Eglinton and Galbraith found that copper(II) acetate in methanol–pyridine was an effective reagent for the oxidative coupling of acetylenes.[2] They found that catalytic quantities of the copper(II) salt, with oxygen, could be used but they preferred to use excess of the reagent because the reaction was slow.

Sondheimer[3] has effectively utilized this system for the preparation of some unusual macrocyclic rings.

We have found that tertiary amine complexes of copper(I) salts function as catalyst for the oxidative polymerization of certain 2,6-disubstituted phenols with oxygen to high molecular weight polyarylene ethers.[4] Copper(II) salts were ineffective as catalysts in this reaction with the exception of the copper(II) carboxylates which functioned as catalysts of much reduced activity (*ca.* an order of magnitude).

Many ethynyl compounds are also oxidatively coupled rapidly, using amine complexes of copper(I) chloride, at room temperature, in almost quantitative yield.[1] Tertiary amines are preferred and by proper choice of the amine the catalyst is soluble even in nonpolar solvents such as benzene. Copper(I) chloride is the most convenient copper salt to use. Most copper(II) salts are inactive as catalysts with the exception of copper(II) carboxylates which gave catalysts of reduced activity.

In most cases the reactions are rapid enough at room temperature to be essentially diffusion controlled even when vigorously stirred. Since they are vigorously exothermic, the reaction mixtures usually must be cooled. However, purely aliphatic ethynyl compounds are oxidized quite slowly utilizing these catalysts. When a bidentate ligand such as *N,N,N′,N′*-tetramethylethylene diamine is used, the reaction is considerably faster. Catalysts formed using ligands of this type are particularly attractive since they are very soluble in many organic solvents. In contrast, a monodentate tertiary amine such as pyridine usually functions satisfactorily only when considerably more than two amines per copper are present, since there is a much greater tendency to form insoluble copper(I) acetylides at low ligand concentrations. Even propargyl alcohol can be satisfactorily coupled when the bidentate amines are ligands; with monodentate amines the copper(I) derivative is quantitatively precipitated from the solution.

A limited amount of quantitative data was obtained to compare the effectiveness of the three types of catalysts in the oxidative coupling of ethynyl compounds: 1) copper(II) acetate–pyridine, 2) copper(I) chloride–pyridine, 3) copper(I) chloride–*N,N,N′,N′* - tetramethylethylenediamine. Three different substrates were chosen to represent the most commonly available ethynyl compounds: 1) phenylacetylene, 2) 1-ethynylcyclohexanol, and 3) hexyne-1.

The reactions followed the expected stoichiometry shown in equation 1.

$$2RC{\equiv}CH + 1/2O_2 \longrightarrow RC{\equiv}C{-}C{\equiv}CR + H_2O \quad (1)$$

This is a summation of the reactions shown in equations 2 and 3.

$$2RC{\equiv}CH + 2Cu(II) \longrightarrow RC{\equiv}C{-}C{\equiv}CR + 2H^+ + 2Cu(I) \quad (2)$$

$$2Cu(I) + 1/2O_2 + H_2O \longrightarrow 2Cu(II) + 2OH^- \quad (3)$$

The course of the reaction was followed by measuring the absorption of oxygen. Using equation 1, the concentration of the acetylene at any given time could be calculated. A plot of $[RC{\equiv}CH]^{-1}$ *vs.* time (min.) gave a straight line, in most cases to above 90% reaction and in all cases to greater than 50% reaction. Thus, the reaction is second order in acetylene and the rate is proportional to $[RC{\equiv}CH]^2$. The relative rates of reactions with different catalysts and different substrates are conveniently compared by using the times of half reaction.

Table I lists the times of half reaction (in minutes) for the three acetylenes using the three different catalyst systems. It is apparent that the copper(I)-diamine catalyst is by far the most effective catalyst known for the oxidative coupling of acetylenes. It offers some definite advantages: 1) The reaction can be run in a wide variety of organic solvents; 2) only a catalytic amount of copper(I) chloride and the diamine are necessary; therefore, the isolation of the product is facilitated; 3) the coupling reaction can be run under essentially neutral conditions, since only enough amine to complex the copper is necessary; and 4) lower temperatures can be used, since the catalyst is more active. If the substrate to be oxidized is sensitive to oxygen, then a stoichiometric amount of "preoxidized" catalyst can be used to effect the coupling reaction.

As can be seen from Table I, phenylacetylene couples faster than 1-ethylnylcyclohexanol, which couples faster than hexyne-1. This is in agreement with previous observations.[2]

The oxidative coupling of aromatic diynes and aliphatic diynes to high molecular weight linear

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(1) A preliminary account of this work appeared in *J. Org. Chem.*, **25**, 1275 (1960). This is paper I.

(2) G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, 889 (1959).

(3) F. Sondheimer, R. Wolovsky, and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 755 (1960) and previous publications.

(4) A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, *ibid.*, **81**, 6335 (1959).

polymers will be the subject of a future publication.

Experimental

Oxidation of 1-Ethynylcyclohexanol. General Procedure.—To a 250-ml. wide-mouthed Erlenmeyer flask in a water bath at 28° was added 135 ml. of acetone, 1 g. (0.01 mole) of copper(I) chloride and 1.2 g. (0.01 mole) of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine. Oxygen was bubbled into the solution which was vigorously stirred by means of a "Vibromixer" stirrer. Over a 15-min. period, 25 g. (0.20 mole) of 1-ethynylcyclohexanol was added in a dropwise manner to the reaction mixture. The temperature rapidly rose to 42°. After the addition was complete, the reaction was continued for 20 min., then the acetone was evaporated and there was added 20 ml. of water containing 1 ml. of concentrated hydrochloric acid. The colorless solid was filtered in a Büchner funnel, washed with a small amount of water, and dried *in vacuo*. There was obtained 22.9 g. (0.093 mole, 93% yield) of 1,1'-butadiynylenedicyclohexanol,[5] m.p. 177° (lit. 173–174°).

The following acetylenes were oxidized in an identical fashion (yield of the coupled product and melting point of the coupled product in brackets): phenylacetylene (97.0%, 87–88°); 3-hydroxy-3-methyl-1-butyne (85.0%, 138°); 3-hydroxy-3-methyl-1-pentyne (82.3%, 93–95°); 1-ethynylcyclopentanol (89.5%, 138–140°).

Determination of Rates.—The quantitative rate experiments were performed in a 100-ml. reactor equipped with an oxygen inlet tube, vibromixer stirrer, and a dropping funnel in a water bath at 30°. Oxygen was supplied to the reactor at atmospheric pressure by means of a 100-ml. gas burette and leveling bulb. The catalyst was preoxidized and when the system reached equilibrium the acetylene was added and the progress of the reaction was followed by the change in volume in the gas burette. Table I outlines the experiments.

TABLE I

[Cu] (M × 10^{-3})	RC≡CH[a]	$t_{1/2}$ (min.) A[b]	B	C
5	Phenylacetylene	270	96	10[c]
15	1-Ethynylcyclohexanol	420	360	13
60	Hexyne-1	550	950	55

[a] The concentration of the acetylene in all cases is 0.4 *M* and all the reactions were run at 30°. [b] In A the catalyst is copper(II) acetate hydrate in pyridine solvent; B is copper(I) chloride in pyridine solvent; C is copper(I) chloride plus an equivalent amount (moles) of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine in isopropyl alcohol solvent. Acetone, which was used in the larger scale preparative examples, could not be used here because of its high vapor pressure at 30°. The half-times were reproducible within ±3%. [c] In this example Methyl Cellosolve was the solvent. When isopropyl alcohol was used, some phenylethynylcopper(I) deposited giving erratic results.

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Systems Containing a Silicon–Oxygen–Vanadium Linkage[1]

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In 1958 Orlov, *et al.*,[3] reported the preparation of tris(triphenylsilyl)vanadate(V) by reaction of tris(*n*-butoxy)vanadate(V) and triphenylsilanol. Cohen and Dessy[4] have reported the preparation of tetrakis(triphenylsiloxy)vanadium(IV) by reaction of sodium triphenysilanolate and vanadium(IV) chloride. As part of our work in the preparation of inorganic macromolecules containing a silicon–oxygen–metal linkage, we have developed new methods for the preparation of tris(triphenylsilyl)vanadate(V) and have modified the reported methods to give high yields of the vanadium(IV) product. Further, we have prepared the previously unreported compound tris(triphenylsilyl)thiovanadate(V) and have developed a quick and accurate method for the quantitative determination of silicon and vanadium in these esters.

Experimental

Preparation of Tetrakis(triphenylsiloxy)vanadium(IV).—Tetrakis(triphenylsiloxy)vanadium(IV) was prepared by the reaction of sodium triphenylsilanolate and vanadium(IV) chloride in anhydrous benzene.

In a typical preparation 10.2 g. (0.037 mole) of triphenylsilanol was dissolved in 100 ml. of anhydrous benzene and an excess of clean metallic sodium added. The reaction mixture was stirred for 5 hr. at room temperature, the unchanged sodium metal separated, and the solution of sodium triphenylsilanolate used immediately.

The vanadium(IV) chloride was prepared by the reaction of ferrovanadium (74% vanadium content) and chlorine gas at 350° in a tube furnace. The crude vanadium(IV) chloride was purified by distillation and the portion boiling 147–148° at 1 atm. pressure used (lit., b.p. 147.5°).

One milliliter (0.094 mole) of the purified vanadium(IV) chloride was dissolved in 75 ml. of anhydrous benzene and added slowly with vigorous stirring to the freshly prepared solution of sodium triphenylsilanolate. The reaction mixture was kept at 15° with an ice bath and protected at all times by a blanket of dry nitrogen or natural gas. A purple precipitate formed immediately.

After addition of the vanadium(IV) chloride solution, the reaction mixture was stirred vigorously for a few minutes and the mixture of tetrakis(triphenylsiloxy)vanadium(IV) and sodium chloride removed by filtration. The filter cake was washed, first with cold water until no trace of chloride ion appeared in the wash water, then with benzene to remove traces of triphenylsilanol and the by-product tris(tri-

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[3] N. F. Orlov, B. N. Dolgov, and M. G. Voronkov, *Dokl. Akad. Nauk SSSR*, **122**, 246 (1958).

[4] H. S. Cohen and R. E. Dessy, Abstracts of Papers, 138th National Meeting, American Chemical Society, New York, 1960, Page 20-N, Division of Inorganic Chemistry.