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AN ALKYNE PROTECTING GROUP

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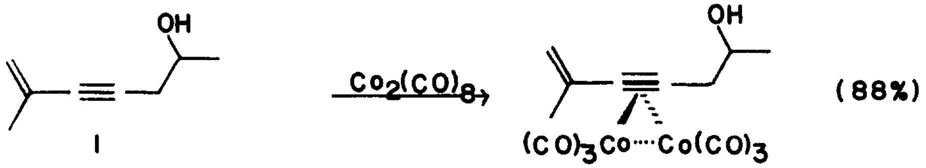
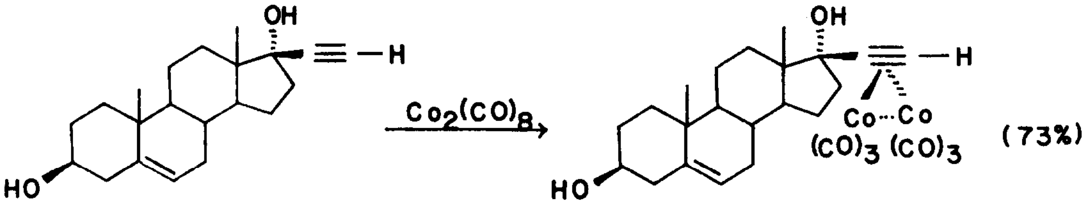
Due to the greater reactivity of triple bonds to several of the more common addition reactions, (i.e. reduction,[1] hydroboration,[2] and acid-catalyzed hydration[3]) it is generally very difficult to selectively induce double bonds to undergo addition in the presence of triple bonds. We report that reaction of an organic molecule containing both a double and triple bond with cobalt carbonyl readily leads to the formation of the corresponding acetylene-dicobalt hexacarbonyl complex; the coordinated triple bond is now inert to addition reactions thus permitting selective transformations of the non-coordinated olefinic bond. The facile formation and removal[4] of the metal moiety in high yield make these complexes useful protecting groups for triple bonds.

The complexes are readily prepared by stirring dicobalt octacarbonyl and the alkyne overnight at room temperature in a hydrocarbon solvent.[5] The complexes may be isolated in 70-90% yield, sufficiently pure for further reaction,[6] by column chromatography over alumina. Some examples relevant to this work are shown below.



I

II

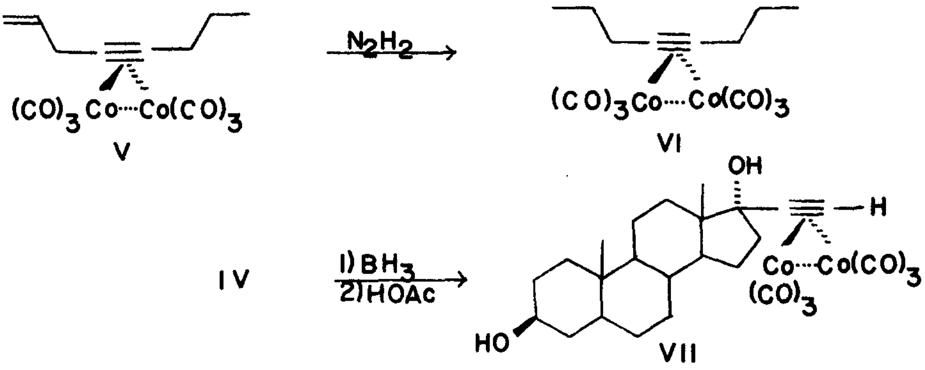


III

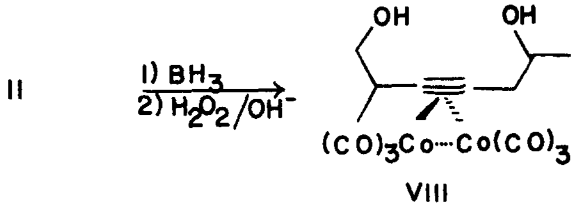
IV

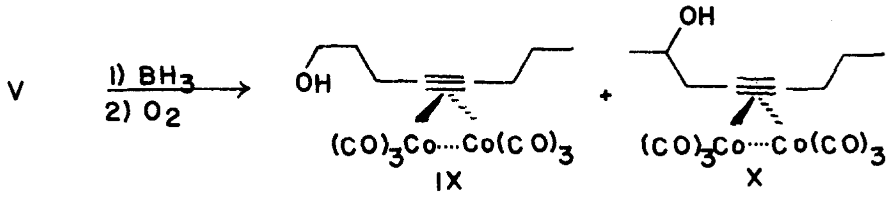
Attempts to catalytically hydrogenate free double bonds in several different complexes were unsuccessful. Thus, treatment of II, IV or V with H_2 in the presence of 5% Pd on carbon or PtO_2 in EtOH or HOAc gave only starting material. Addition of cyclohexene caused no hydrogen uptake indicating that the complexes were catalyst poisons.

Reduction can be achieved, however, by treatment with diimide or BH_3/HOAc. For example, the ene-yne complex V, upon addition of $KO_2C\text{-}N{=}N\text{-}CO_2K$ and acetic acid in methanol, gave the reduced complex VI, in 92% yield.[8] Reaction of the cobalt complex of 17-ethynl-$\Delta^{5,6}$-dehydroisoandrosterone (IV) with BH_3 followed by HOAc gave a 60% yield of 17-ethynlisoandrosterone-$Co_2(CO)_6$[9] (VII).

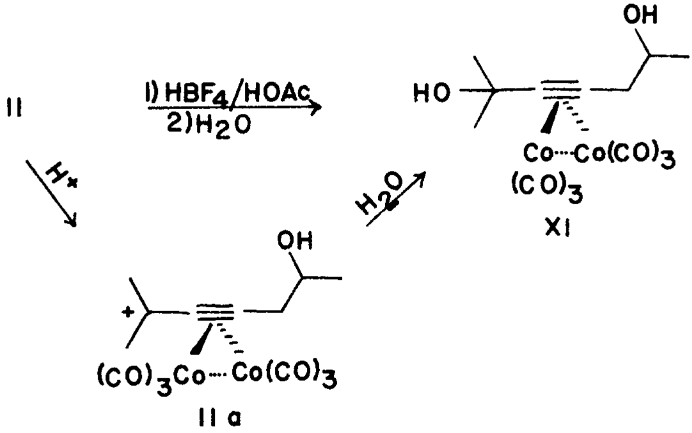


Hydroboration of ene-yne complexes II and V gave exclusively the products of reaction at the double bond. Thus, treatment of II with BH_3 followed by oxidation with H_2O_2/OH^- gave the diol VIII (45%). Complex V was converted to alcohols IX and X in 62% yield in a ratio of 5:1, respectively, by reaction with BH_3 followed by cleavage with oxygen. Cleavage by oxygen[10] is the preferred method since the peroxide-base combination causes partial decomposition of the cobalt complex.

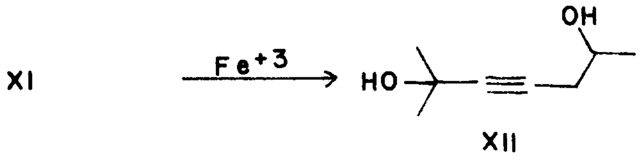


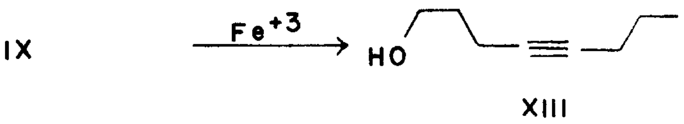


Vinyl acetylenes, when treated with strong acids, generally form the product of hydration of the triple bond.[11] The ene-yne-ol I reacted with a fluoboric-acetic acid mixture at 25° after 24 hours to form an intractable mixture of products. Its complex II, on the other hand, reacted at 0° after 15 minutes to give, upon aqueous workup, a 91% yield of the diol XI. This facile reaction can be attributed to the intermediacy of the metal-stabilized carbonium ion IIa.



Importantly, the ligand may be recovered by oxidative degradation of the complex with $Fe(NO_3)_3 \cdot 9\ H_2O$ in 95% ethanol. Dilution with water and extraction with ether affords the product in excellent yield. Thus the complex XI gives an 81% yield of the diol XII. Similarly, the complex IX afforded the ligand XIII (90%).





Further synthetic applications are being explored.

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2. H. C. Brown, "Hydroboration" (W. A. Benjamin, Inc.) 1962.
3. R. C. Fahey, "Topics in Stereochemistry", vol. 3, pp. 237-342 (Interscience) 1968.
4. Seyferth (*J. Amer. Chem. Soc.*, **92**, 5520, 1970) has reported the Friedel-Crafts reactions of diphenylacetylene-$Co_2(CO)_6$. The organic ligand was retrieved by oxidation with $(NH_4)_2Ce^{IV}(NO_3)_6$ in acetone.
5. H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby and I. Wender, *J. Amer. Chem. Soc.*, **78**, 120 (1956).
6. The complexes were difficult to obtain analytically pure. NMR analysis of the complexes followed by defradation and nmr and mass spectra of the resulting ligands completed the characterization. All alcohols were converted to their trimethylsilyl ethers for mass spectral analysis.
7. Prepared according to H. E. Stavely, *J. Amer. Chem. Soc.*, **61**, 79 (1939).
8. No attempts were made to improve yields.
9. Complex characterized by degradation to the free ligand, m.p.=253-255°; lit.=255-257°, von L. Ruzicka and K. Hofmann, *Helv. Chim. Acta*, **20**, 1280 (1937).
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11. A. W. Johnson, "The Chemistry of the Acetylenic Compounds", vol. 1, p. 56 (Edward Arnold & Co.) 1946.