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Tungsten-alkynyl and -propargyl compounds for organic syntheses

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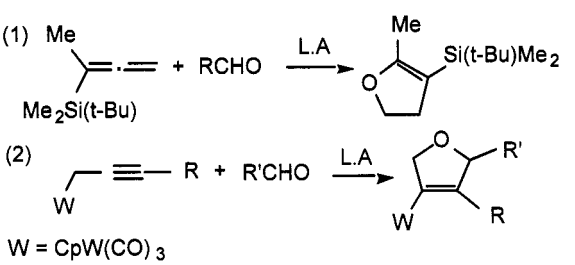
Abstract: This study focuses on synthetic application in the alkoxycarbonylation reaction of tungsten-propargyl complexes as well as the cycloalkenation reaction of tungsten-alkynol complexes; these two reactions were useful for efficient synthesis of furan, pyran and α-methylene butyrolactones.

Metal carbonyls such as $CpFe(CO)_2$, $M(CO)_5$ (M = Mn, Re) and $CpM(CO)_3$ (M = Mo, W) are important functionalities in organometallic chemistry.[1] These carbonyls are also useful reagents for organic syntheses[2] because they resemble trimethylsilyl groups as electron donating groups. The similarity of these two functional groups is best manifested by the same reaction pattern in Lewis-acid promoted alkylation of their allyl, propargyl and allenyl compounds[2] with organic carbonyls; these two types of organometallics can afford both [3+2] cycloaddition and S_E'-addition reaction products under suitable conditions. Scheme 1 (eq 1 and 2) shows the examples of [3+2] cycloaddition of allenylsilane[3] and tungsten-propargyl compounds[4] via condensation with aldehydes, yielding 2,3-dihydrofurans and 2,5-dihydrofurans respectively.

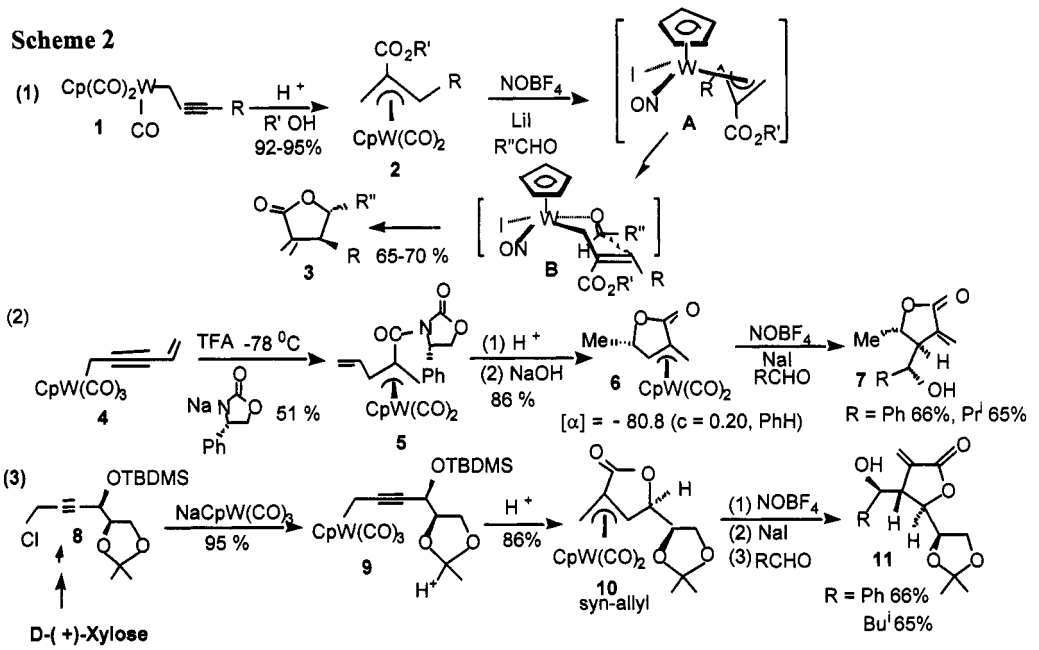
Scheme 1



Synthesis of α-methylene butyrolactones from tungsten-propargyl compounds

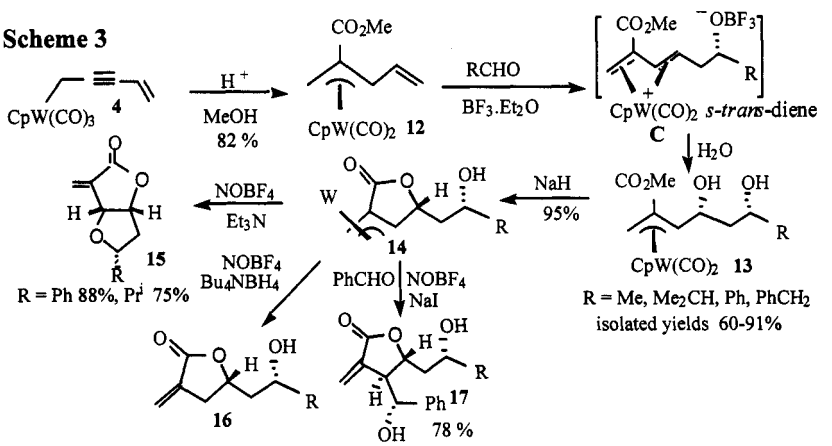
As shown in Scheme 2, the starting tungsten-propargyl complex **2** is readily prepared from propargyl chloride **1** via metalation with $NaCpW(CO)_3$. Two fundamental reactions are involved to convert this propargyl species to the trans-α-methylene butyrolactones **3**[5]: (1) alkoxycarbonylation reaction (2) generation of the allyl anion equivalent **A**. One important feature is that this π-allyl species is prone to π–σ–π dissociation to leave a coordination site for aldehyde to form a chairlike transition-state **B** to yield the *trans* isomer. This phenomenon was first reported by Faller et. al. on the $CpMo(NO)I(\pi\text{-allyl})$.[6] Application of these two reactions on tungsten propargyl species effects efficient syntheses of complex α-methylene butyrolactones. Shown in eq 2 is the enantioselective aminocarbonylation of tungsten-η^1-vinylpropargyl species to provide optically pure tungsten-allyl species **5** in 51 % yield.[7] This π-allyl complex **5** is converted to chiral η^3-anti-γ-lactonyl **6** and further to optically active α-methylene butyrolactone **7** in good yields; the stereochemistry of **7** is elucidated based on a bicyclic transition state structure in analogy to Faller's model.[8] Chiral propargyl chloride **8** was prepared from D-(+)-xylose.[8b] After metalation with $NaCpW(CO)_3$, the resulting tungsten-propargyl complex **9** underwent upon acid catalysis an intramolecular alkoxycarbonylation reaction to yield the *syn*-isomer of the chiral tungsten-allyl complex **10**, which was further converted to **11** according to our synthetic approach described above.

Scheme 2



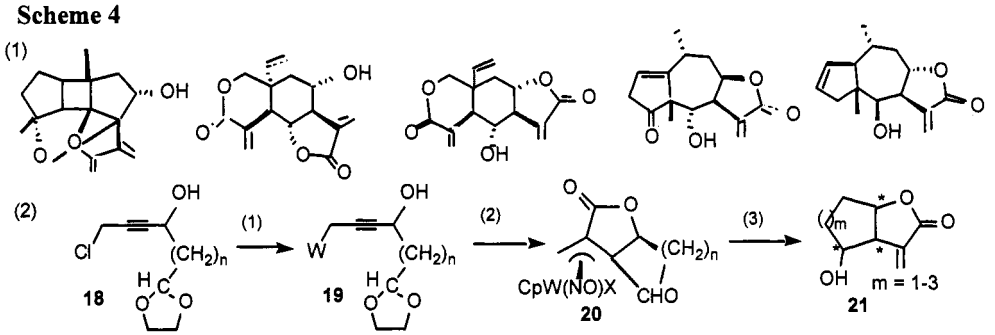
A Prins-type reaction is shown for the tungsten-pentadienyl complex **12** prepared from the alkoxycarbonylation reaction of **4**.[9] This π-allyl complex reacts with aldehydes/$BF_3.Et_2O$ to generate highly reactive s-*trans*-diene cations **C** which after hydrolysis afford tungsten-allyl-1,3-diols **13** with good diastereoselectivity; the yields are 60-90% depending on the R substituent. This reaction allows the generation of *syn*-1,3-diols in a one pot reaction. Further functionalization of the π-allyl compound **13** results in the efficient syntheses of various α-methylene butyrolactones (Scheme 3). Treatment of **14** with $NOBF_4$ generates an allyl cation which in the presence of Et_3N induces intramolecular cyclization reaction to yield bicyclic α-methylene butyrolactone **15** in high yields. Reduction of **14** with Bu_4NBH_4 afforded **16** in good yields, while condensation of the CpW(NO)I derivative of **14** with benzaldehyde via sequential treatment with $NOBF_4$ and NaI gives rise to the complex α-methylene butyrolactone **17** in good yields.

Scheme 3



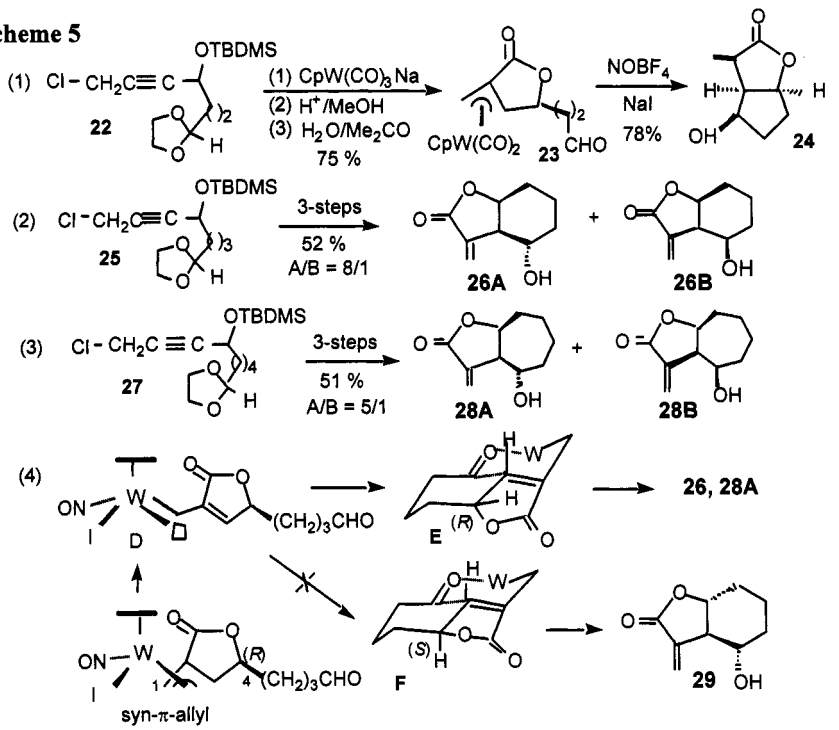
A large number of naturally occurring α-methylene butyrolactones contain not only the α-methylene butyrolactone unit but also possess the functionality of a homoallylic alcohol.[10] Some examples are shown in Scheme 4. Due to rich natural sources, there exists at least one natural product for each specific configuration at the three stereogenic centers. Therefore, stereocontrolled synthesis of the basic unit **121** is an important synthetic challenge in organic chemistry. We developed an efficient synthesis of this type of compound starting from readily available **18**. The three key steps involve (1) metallation (2) intramolecular alkoxycarbonylation and (3) condensation of an aldehyde with the allyl anion **20** (Scheme 4).

Scheme 4



The outcome of this approach is summarized in Scheme 5: the bicyclic [5,5] product **24** derived from **22** is a *cis*-fused and *syn*-homoallylic alcohol (eq 1); and the major products of bicyclic [5,6] and [5,7] rings **26A** and **28A** have *cis*-fused and *anti*-homoallylic alcohol configurations. To account for the stereochemical results, we propose a plausible mechanistic pathway in eq 4. For the π-*syn*-isomer, the π-allyl group *trans* to CO is prone to dissociation to subsequently allow an aldehyde to coordinate; the tricyclic transition state **E** is the prefered one because two stereogenic centers at the tungsten and C4-carbon of **E** is consistent with the starting π-allyl complexes. The tricyclic structure **F** would be sterically less hindered than **E** because the oxygen substituent at the C4-carbon of **F** is placed in the equatorial position. However, the structure of **F** is inconsistent with the starting π-allyl compound as the stereogenic center at the C(4)-carbon of **E** has been inverted; consequently, the resulting product **29** is thus not observed in our reactions.

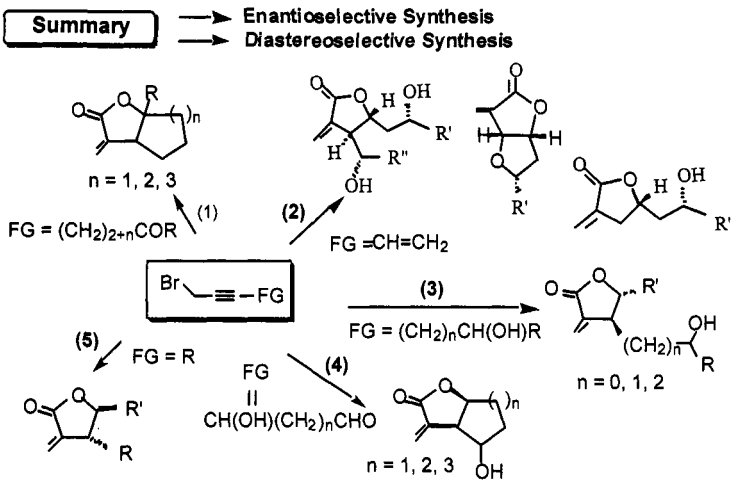
Scheme 5



We have also elaborated other functionalized propargyl halides for the stereoselective syntheses of α-methylene butyrolactones including bicyclic α-methylene bytyrolactones derived from propargyl bromide with tethered aldehydes and ketones;[13] a summary is given in Scheme 6 that also covers the preceding reactions to illustrate the overall scope. Synthesis of the bicyclic α-methylene bytyrolactones in eq 1 can be accomplished with high diastereo-selectivities, the stereochemistry of products depends on the ring sizes and the substituent R; and a bicyclic transition state as discussed

before provides a rationalization for the stereochemical outcome.[13] Shown in eq 3 (Scheme 6) is the elaboration of the intramolecular alkoxycarbonylation for the synthesis of trans-α-methylene butyrolactones having a remote secondary alcohol (n =1, 2).[8] Generation of this remote alcohol can be achieved both with high diastereoselectivity and with good yields. Among the five reactions shown in Scheme 6, reactions 2 and 3 can be carried out enantioselectively.[7,8b]

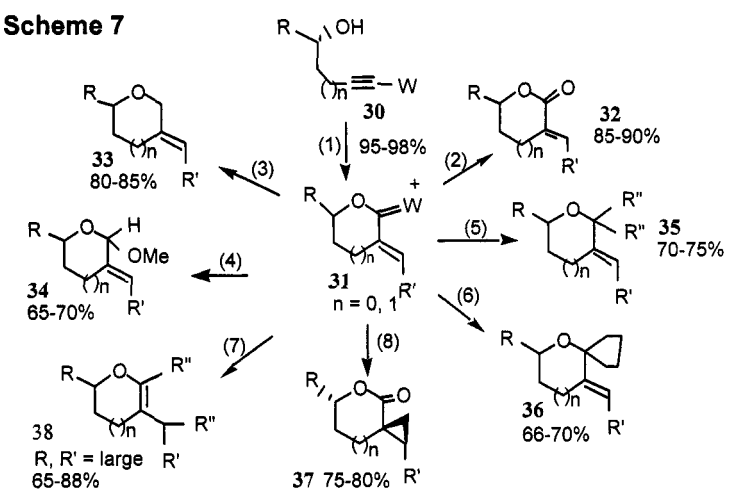
Scheme 6



Synthesis of furans and pyrans from tungsten-alkynols

As shown in Scheme 7, tungsten-alkynols **30** undergo cycloalkenation reactions with R'CHO/BF_3.Et_2O via two intermediates to yield oxacarbenium cmplexes **31** in quantitative yields,[13] which can be isolated and characterized by x-ray diffraction studies. One important feature of these oxacarbenium complexes is the function as a dication synthon to react with two nucleophiles to liberate various furans and pyrans. Treatment of **31** with H_2O under air atmosphere liberates unsaturated γ- and δ-lactones in excellent yields (eq 2). $NaBH_3CN$, $NaBH(OMe)_3$ and Grignard reagent (eq 2-4) can demetalate this oxacarbenium to yield 1,1-addition products **33-35** in good yields. Organocuprates $R_2''CuLi$ can induce the 1,3-dialkylation on **31** to

Scheme 7

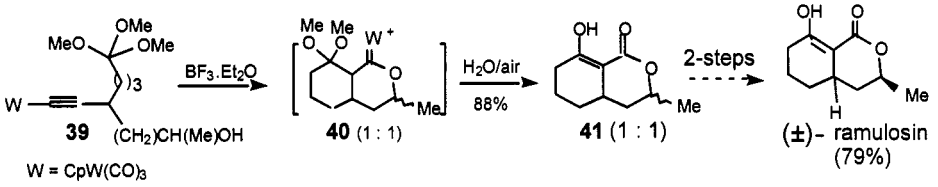


(1) R'CHO/BF_3.Et_2O (2) H_2O/air (3) $NaBH_3CN$ (4) $NaBH(OMe)_3$/MeOH (5) R"MgBr (6) $MgBr(CH_2)_4MgBr$ (7) R''_2CuLi (8) CH_2N_2, H_2O

yield **38** provided that both R' and R" are large phenyl or isopropyl substituents to avoid single addition reactions. The synthesis of the spirofuran and -pyran **36** can be accomplished in reasonable yields by dialkylation of **31** with $BrMg(CH_2)_4MgBr$. Finally, treatment of **31** with dry CH_2N_2 in cold diethyl ether, followed by hydrolysis in air, delivered **37** in good yields. We have rationalized the mechanism for the dicationic nature of **31** as well as its regiochemistry for different nucleophiles; the reaction is proposed to proceed via an enoxonium species.

Intramolecular cycloalkenation has been carried out to yield bicyclic unsaturated esters that are potentially useful for natural product synthesis. For example, the cyclization of the tungsten-alkynol compound **39** was promoted by $BF_3.Et_2O$ to generate the oxacarbenium complex **40** which was subsequently oxidized in air to yield the bicyclic lactone **41** in 88 % yield. Two more steps are required to convert **41** to the target molecule-(±)-ramulosin.

Scheme 8



References

(1) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, chapter 16, 784.

(2) (a) M. E. Welker, *Chem. Rev.* **1992**, *92*, 97. (b) S. Jiang and E. Turos, *Tetrahedron Lett.* **1991**, 4639. (c) P. B. Bell and A. Wojcicki, *Inorg. Chem.* **1981**, *20*, 1585.

(3) R. L. Danheiser; C. A. Kwasigroch. and Y. M. Tsai. *J. Am. Chem. Soc.* **1985**, *107*, 7233.

(4) (a) S. H. Wang, L. H Shiu, Y. L. Liao, S. L.Wang, G. H., Lee, S. M. Peng and R. S. Liu, *J. Am. Chem. Soc.*, **1994**, *116*, 5967. (b) S. K.Shiu, S. H. Wang, L. H Shiu, Y. L. Liao, S. L. Wang, G. H. Lee, S. M. Peng and R. S. Liu, ., *J. Am. Chem. Soc.*,**1996**, *118*, 530

(5) S. H. Lin, W. J. Vong and R. S Liu. *Organometallics,* **1995**, *14*, 1619.

(6) (a) J. W. Faller and D. L. Linebarrier,. *J. Am. Chem. Soc.*, **1989**, *111*, 1937. (b) J. W. Faller, J. A. John and M. R. Mazzieri,. *Tetrahedron Lett.* **1989**, *30*, 1769.

(7) L. H. Shiu, R. S. Liu, unpublished results.

(8) (a) C. H. Chen, J. S. Fan, G. H. Lee, S. M. Peng, S. L. Wang and R. S. Liu, *J. Am. Chem. Soc.* **1995,** *117*, 2933. (b) C. H. Chen, J. S. Fan, G. H. Lee, S. M. Peng, S. L. Wang and R. S. Liu, *J. Am. Chem. Soc.* **1996**, *118*, 9279.

(9) M. H. Cheng, Y. H Ho, S. L. Wang, S. M. Peng and R. S. Liu, *J. Chem. Soc. Chem. Commun.*, **1992**, 45.

(10) (a) H. M. R. Hoffman and J. Rabe, *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 94. (b) Grieco, P. A. *Synthesis,* **1975**, 67. (c) A. R. Sidduri and P. Knochel, *J. Am. Chem. Soc.*, **1992**, *114*, 7579 and references cited therein.

(11) L. H. Shiu and R. S. Liu, unpublished results.

(12) S. J. Shieh, C. C. Chen and R. S Liu, *J. Org. Chem.* **1997,** 62, 1986.

(13) K. W. Liang, W. T. Li, G. H. Lee, S. M. Peng and R. S. Liu, *J. Am. Chem. Soc.* **1997** in press (1997)