Nearly all alkynyl, alkenyl, and aryl halides studied will form stable organocopper compounds at 25 °C or lower as evidenced by the fact that quenching the reactions with water produces the reduced products "R-H" in moderate to excellent yields. Earlier workers in this laboratory isolated and characterized C_6F_5Cu produced from the reaction of C_6F_5I with a much less reactive Cu^0.[16] In addition, quenching C_6F_5Cu and PhCH=CHCu with D_2O produces the expected deuterated product in moderate to good yield. Table II summarizes some of the stable organocopper species produced.

Cross-coupled products can also be formed with the stable organocopper species. Table III summarizes some of the cross-coupling reactions which we have attempted to date. Reaction of the arylcopper compounds with benzoyl chloride produces benzophenones in high yield. Reaction of PhCu with reactive halides such as allyl or benzyl bromide yields the desired product in only low to moderate yield. The major products in these reactions are the homocoupled bibenzyl and 1,5-hexadiene. If two alkyl halides are mixed in equal molar amounts and then allowed to react with copper, a mixture of all three possible products is formed in approxiamately the statistically expected amounts.

In summary, a highly reactive zerovalent copper has been produced. The copper undergoes rapid oxidative addition under very mild conditions into alkyl, aryl, and vinyl halides. Significantly, the organic halides can contain a variety of functional groups. These organocopper species formed undergo several reactions described for traditional organocuperates. Accordingly, we feel this approach will significantly improve the general utility of organocopper intermediates.

Acknowledgment. We gratefully acknowledge support of this work by the Division of Chemical Sciences, Department of Energy (Contract No. De-AC02-80ER10603), and the U.S. Army Research Office.

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[16] Rieke, R. D.; Rhyne, L. D. *J. Org. Chem.* **1979**, *44*, 3445.

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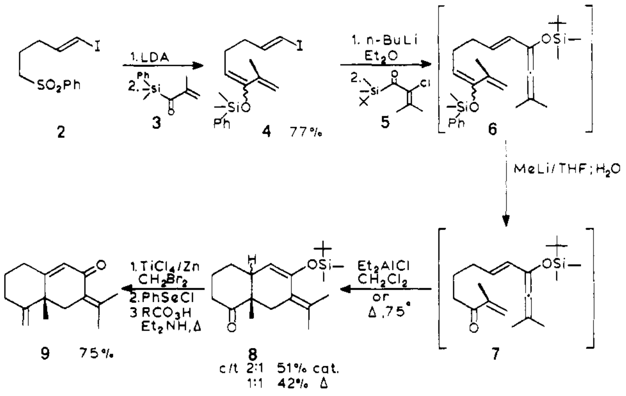
Silyl Ketone Chemistry. Preparation of Eremophilane and Eudesmane Sesquiterpenes by Vinylallene Cycloaddition[1]

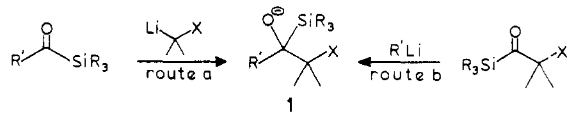
Summary: The Diels-Alder cyclization of enone siloxyvinylallenes leading to dehydrofukinone and selina-4(14),7(11)-dien-8-one are described. Several silyl ketone (acylsilane) reactions were used to prepare key enol silyl ether intermediates.

Sir: A wide range of enol ethers can be prepared from β-X-substituted-α-silylalkoxides 1 by a sequence involving C to O silyl migration with concomitant expulsion of X.[1b,c,2]

Scheme I



The precursor 1 is available by several routes, two of which are shown in eq 1. The mildness of the reaction conditions



(1)

and flexibility of the method make it attractive for the preparation of polyfunctional molecules. We report here several applications of this chemistry to the efficient synthesis of siloxyvinylallene enones, as well as studies of their Diels-Alder cyclization[3] to eremophilane and eudesmane sesquiterpenes.

The key steps of the synthesis are outlined in Scheme I. The α-lithio sulfone prepared by deprotonation of sulfonyl vinyl iodide (LDA, THF, -78 °C, 20 min) 2 reacted smoothly with 2-propenyl phenyldimethylsilyl ketone (3)[4] (eq 1, route a) to give siloxy diene 4 (1:3 *E*/*Z* mixture). This material, which could be purified by short column chromatography, was subjected to metal-halogen exchange (*n*-BuLi, Et_2O, -78 °C, 20 min), and the vinyllithium reagent so formed was treated with α-chloro silyl enone 5,[1c] giving directly the vinylallene 6 (eq 1, route b). Cleavage of the phenyldimethylsilyl enol ether in the presence of TBDMS proceeded smoothly (MeLi, THF, -78 °C to 0 °C) and led after enolate protonation to the key intermediate 7. Cycloaddition was best accomplished by Lewis acid catalysis (Et_2AlCl, 1.1 equiv; CH_2Cl_2, -78 °C to 0 °C) but could also be carried out thermally. Neither 6 nor 7 was purified (although characterized by NMR spectroscopy) so the yields of 8 quoted are over the three steps 4 to 8. The cycloaddition gave mixtures of *cis*- and *trans*-decalin structures, with cis being favored by a 2:1 margin in the Et_2AlCl-catalyzed reaction.[6] The synthesis

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[1] For earlier papers in this series, see: (a) Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423. (b) Reich, H. J.; Rusek, J. J.; Olson, R. E. *J. Am. Chem. Soc.* **1979**, *101*, 2225. (c) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949. Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119.

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[3] Diels-Alder reactions of vinylallenes have not been studied extensively. Intermolecular: Jones, E. R. H.; Lee, H. H.; Whiting, M. C. *J. Chem. Soc.* **1960**, 341. Fedorova, A. V.; Petrov, A. A. *Zh. Obsch. Khim.* **1962**, *32*, 3537. Bertrand, M.; Grimaldi, J.; Waegell, B. *Bull. Soc. Chim. Fr.* **1971**, 962. Heldeweg, R. F.; Hogeveen, H. *J. Org. Chem.* **1978**, *43*, 1916. Intramolecular: Deutsch, E. A.; Snider, B. B. *J. Org. Chem.* **1982**, *47*, 2682. Snider, B. B.; Burbaum, B. W. *J. Org. Chem.* **1983**, *48*, 4370.

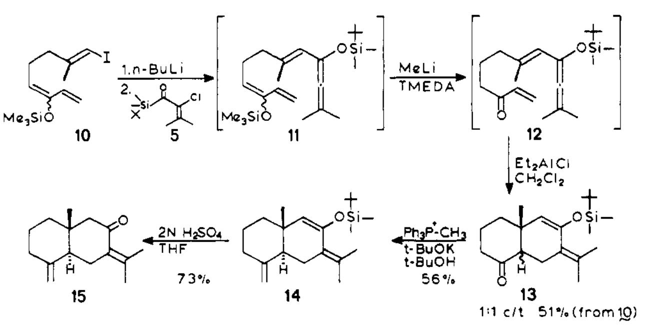
[4] This ketone was prepared by addition of (phenyldimethylsilyl)lithium (Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520) to methacrolein (THF/Et_2O, -78 °C, 71% yield) followed by Swern oxidation[5] (Me_2SO, $(COCl)_2$, NEt_3, -50 °C to 25 °C, 83% yield).

[5] Mancuso, A. J.; Huang, S.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

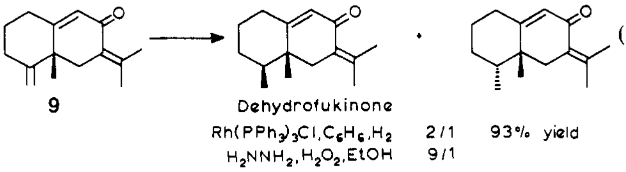
[6] We have been able to locate one nonallenic Diels-Alder cyclization similar to the transformation of 7 to 8 i.e., introduction of an angular methyl group (unpublished result of D. F. Taber and B. P. Gunn cited in E. Ciganek, *Org. React. (N.Y.)* **1984**, *32*, 1 (entry 27, Table 3a)). This system gave a 42/21 ratio of cis/trans ring-fusion products.

0022-3263/84/1949-5282$01.50/0

Scheme II



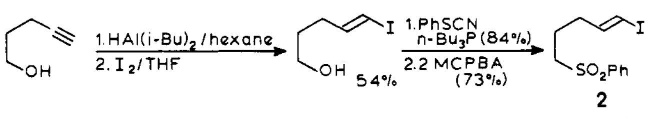
of dehydrofukinone[7] was completed by methylenation using the very effective $TiCl_4/Zn/CH_2Br_2$ procedure of Takai, Hotta, Oshima and Nozaki,[9] conversion of enol ether to enone by selenation and oxidative elimination,[10] and reduction of the exo-methylene function (eq 2).



(2)

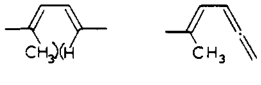
Wilkinson's catalyst gave product in excellent yield, but with only a 2/1 stereoisomer ratio. Diimide reduction (using the $N_2H_4/H_2O_2/CuSO_4$ procedure[11]) gave a 9/1 ratio, but could not be achieved in yields greater than 20%.

The precursor 2 was prepared in a straightforward fashion as shown in eq 3 by hydroalumination–iodination of 4-pentynol,[12] followed by conversion of hydroxy to sulfone. Note that functional groups were directly introduced in protected form so that no protection and only one deprotection step was required during the synthesis.



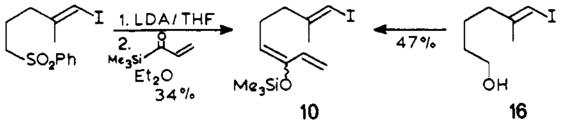
(3)

The success of the Diels–Alder cyclization of 7, as well as that of several other analogues with methyl groups at the vinyl and allenyl positions replaced by hydrogens, encouraged us to attempt synthesis of the eudesmane skeleton using a similar approach. This requires that a cis methyl group be present in the vinylallene "diene" portion (12). Cis substitution normally sharply reduces or eliminates entirely the reactivity of Diels–Alder dienes,[13] but there was reason to hope that the much smaller steric interaction present in a vinylallene compared to a diene would work in our favor. In fact, as shown in Scheme II, the three-step sequence from 10 to 13 can be achieved in identical yield to that for the preparation of 8. Furthermore, the thermal cycloaddition of 12 actually proceeded more rapidly than that of 7, although the yield (23%) from 12 was much poorer. This is probably because 1,5-hydrogen shifts occur with great facility in suitably substituted vinyl allenes, a reaction effectively used by Okamura and co-workers[14] for the preparation of polyenes.



The Diels–Alder cyclization again shows little stereochemical selectivity, giving a 1:1 mixture of ring-fusion isomers.[15] However, conversion to pure *trans*-14 proved simple: under equilibrating Wittig conditions (Ph_3PCH_3Br, *t*-BuOK, *t*-BuOH, THF, 25 °C) the 1:1 mixture 13 was converted in 56% yield to pure *trans*-14, with 33% of 93% pure *cis*-13[16] recovered. The cis isomer enolizes under the reaction conditions and thus cannot give an olefin. Hydrolysis of the enol ether function (0.07 N H_2SO_4, THF, H_2O, room temperature) gives selina-4-(14),7(11)-dien-8-one (15).[17]

Compound 10 could not be prepared in useful yield by a procedure analogous to that in eq 2, since the α-lithio sulfone reacted with vinyl trimethylsilyl ketone to give principally 1,4-addition/polymerization products. Instead, a more lengthy route to 10 was used, which begins with the Negishi carboalumination–iodination[19] of 5-hexyn-1-ol to give 16. This vinyl iodide was then subjected to a standard oxidation,[5] vinyl Grignard addition, oxidation[5] sequence to give enone, followed by TMSCl/$(TMS)_2NH$/LiI silylation.[20]



In summary, the chemistry described above shows that silyl ketones are useful precursors to allenyl and dienyl silyl ethers and that cycloadditions of vinylallenes promise to have broad applicability in synthesis. The exo–endo stereoselectivities have been poor in the two systems illustrated but can become very high as a result of steric interactions between the substituents at the vinyl and allenyl terminus.[21]

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[7] Dehydrofukinone was first reported in 1968.[8a] Several syntheses have been completed.[8] The ^{1}H and ^{13}C NMR spectra of material purified by HPLC were identical with those reported.[8b]

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[15] Several other catalysts tried ($BF_3{\cdot}OEt_2$, $AlCl_3$, $SnCl_4$, $EtAlCl_2$, $ZnBr_2$) gave much poorer yields of 13.

[16] The equilibrium cis/trans mixture of 13 is 85/15 and the diketone prepared by hydrolysis of 13 is 32/68.

[17] Selina-4(14),7(11)-dien-8-one (15) was first reported in 1974.[18a] Several syntheses have been reported.[18b,c] The ^{1}H NMR spectrum of material purified by preparative TLC is identical with that reported.[18b] ^{13}C NMR spectrum (δ $CDCl_3$): 17.3, 22.2, 23.1, 23.3, 29.2, 36.8, 38.0, 41.4, 47.1, 57.6, 106.6, 131.2, 142.0, 148.7, 202.2.

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[21] Reich, H. J.; Eisenhart, E. K.; Kelly, M. J., unpublished results.