Communications to the Editor

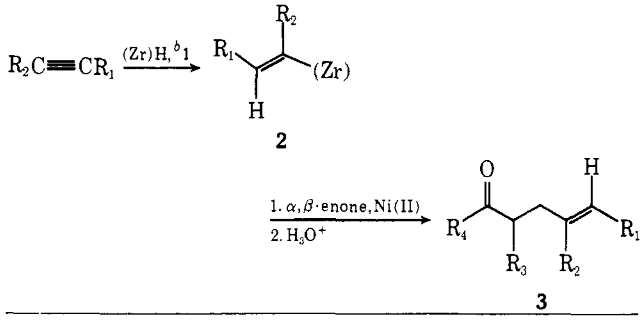
Nickel-Catalyzed Conjugate Addition of Zirconium Alkenyls to α,β-Unsaturated Ketones

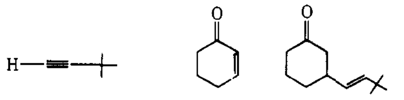
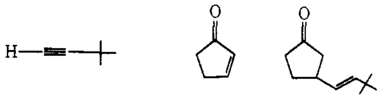
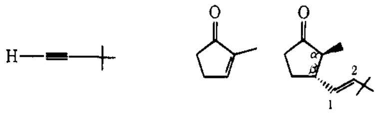
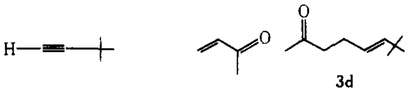
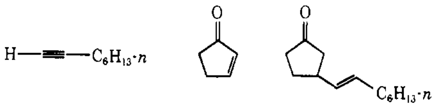
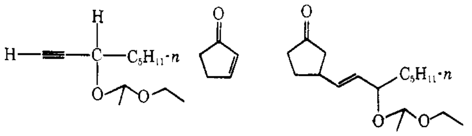
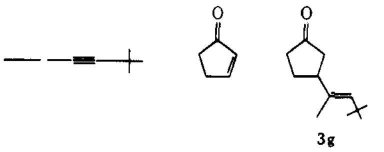
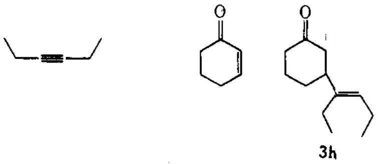
Sir:

Over the past few years conjugate addition of organocuprates has become accepted as an extremely versatile procedure in organic synthesis.[1] Noteworthy in this context is the introduction of vinylic functionality with a high degree of specificity by conjugate addition of alkenylcopper(I) species as employed in synthesis of many natural products. Its utility notwithstanding, this route is limited by the availability of precursors of the alkenylcopper(I) complex, usually lithium or Grignard reagents. Even when such copper(I) compounds are available by this or other routes,[2] it is necessary to make compromises concerning reactivity and efficient use of complexes derived from often-precious vinylic groups: The use of highly reactive divinylcuprates requires the sacrifice of one vinylic unit, while "mixed cuprates" are expedient but of reduced reactivity.[3] The inherent low thermal stability of alkenylcopper(I) complexes is also a disadvantageous feature of these reagents, and 1,3-dienes formed by decomposition of these copper species are often major by-products of their reactions. Clearly the development of reagents which maintain the selectivity of cuprate conjugate additions would be of immediate utility in organic synthesis if these procedures avoided the drawbacks associated with the use of cuprates. If such reagent systems were, as well, more effectively employed than are parallel cuprate-based systems (in terms of the number and yield of steps necessary to perform the overall transformation and the lack of substantial formation of by-products), they would add to the repertory of the synthetic organic chemist significantly. We have recently discovered a mixed Zr-Ni (catalyst) reagent system which enables the conversion of acetylenes to reactive vinylic organometallic complexes and thence to conjugate alkenyl adducts of α,β-unsaturated ketones in a selective high-yield procedure requiring minimal manipulation. This new *catalytic* route is synthetically superior to the reported[2a] Zr-Cu (*stoichiometric*) one in terms of high yield of desired product, low yield of by-products, and ease of implementation. This procedure is, as well, mechanistically different from the known[4,5] Ni-catalyzed conjugate addition of trimethylaluminum to α,β-enones. We wish to report our results concerning this system herein.

Vinylic zirconium complexes are readily prepared stereospecifically from acetylenes and $Cp_2Zr(H)Cl$ (**1**);[6] these complexes do not react with α,β-unsaturated ketones. However, in the presence of a catalytic amount of $Ni(AcAc)_2$ (AcAc = 2,4-pentanedionato), rapid conjugate addition of the terminal vinylic units occurs to give, on hydrolysis, 1,4-enones in high yield.[7] A sample procedure is illustrated as follows. Treating 3,3-dimethyl-1-butyne with **1** in benzene at 25 °C under Ar gives $Cp_2Zr(Cl)[(E)\text{-3,3-dimethyl-1-butenyl}]$ (**2a**) as pale yellow crystals on evaporation of volatiles.[6] Addition of 2-cyclohexenone (620 mg, 6.46 mmol) and anhydrous $Ni(AcAc)_2$[8] (151 mg, 0.59 mmol) to a solution of **2a** (1.92 g, 5.67 mmol in 30 mL of THF) at −78 °C, which is then warmed to 0 °C, rapidly gives rise to a deep red solution. The reaction mixture is stirred 6 h at 0 °C and is then quenched with saturated aqueous NH_4Cl to give, on extraction with pentane, drying ($MgSO_4$), and removal of volatiles, 3-[(*E*)-3,3-dimethyl-1-butenyl]cyclohexanone (**3a**) in high yield (77% by VPC; 73% isolated yield after chromatography on silica gel).[9] Results for procedures involving other acetylenes and ketones are shown in Scheme I. It is interesting to note that a propargylic ether can be converted to an allylic ethereal product (**3f**)

Scheme I[a]



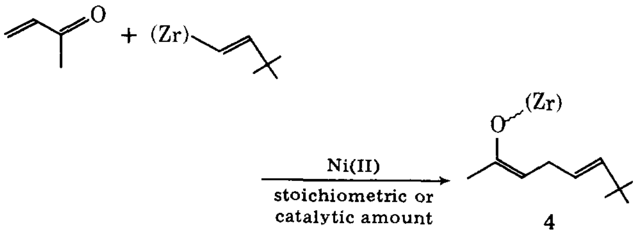
Acetylene	α,β-Enone	Product	Yield, %[c,d]
		3a	77 (73), 59 (57)[e]
		3b	78
		3c	*f*
		3d	>95
		3e	(49), (46)[e]
		3f	(59)
		3g	Low (6–10)
		3h	Low (6–10)

[a] All reactions were performed using **2** as the limiting reagent unless otherwise noted. [b] (Zr) = $(\eta^5\text{-}C_5H_5)_2Zr(Cl)$–. [c] VPC yield. [d] Isolated yield (chromatographed on silica gel). [e] **2** used in excess. [f] Yield not determined quantitatively.

with no discernible reductive cleavage of the ethereal unit. This result, of special importance for the preparation of prostaglandin analogues,[10] stands in marked contrast to reports concerning the preparation using organoaluminum hydrides of precursors of vinylic copper(I) species employed in copper(I)-based syntheses of similar compounds.[10]

It has been noted that $Ni(AcAc)_2$ will catalyze the conjugate addition of $(CH_3)_3Al$ to several unsaturated ketones with varying degrees of success.[4,5] This reported system is believed to proceed through a nickel(0) catalyst. The structure of the active catalyst in the Zr–Ni route described herein is not yet known. It is apparent, though, that in this latter system nickel(II) and *not* nickel(0) partakes. Conversion of nickel(II) to nickel(0) would be accomplished with concomitant oxidative coupling of vinylic units to dienes, and, although in all cases investigated a small amount of such dimer is observed, we note that the use of $Ni(AcAc)_2$ as a *stoichiometric* reagent, under the same conditions noted above, gives rise to essentially the same high yields of conjugate addition products as were observed in Ni-*catalyzed* procedures. Were nickel(0) the active catalytic form, these stoichiometric procedures should lead, contrary to observation, to high yields of dimers (dienes) and to essentially no conjugate addition product. It is interesting to note here that the reaction of dialkylvinylalanes, $Ni(AcAc)_2$, and α,β-unsaturated ketones does give rise to some product of conjugate addition of the vinylic group; however, this product is formed in low yield and then only as one component of a complex mixture of by-products resulting from either 1,2 or 1,4 addition of either the alkenyl or alkyl group of the mixed alane.[11,12]

The initial product of conjugate addition involving either catalytic or stoichiometric amounts of $Ni(AcAc)_2$, prior to hydrolysis, is the zirconium *O*-enolate (as evidenced, for example, clearly by the NMR spectrum of **4**).[13] Hydrolysis yields the observed ketone. For 2-methylcyclopent-2-enone, trans stereochemistry of groups on the C_5 ring is assigned based on analogy to cuprate chemistry in which workup under the conditions described herein also gives the thermodynamically preferred product.[14]



$(Zr) = (\eta^5\text{-}C_5H_5)_2Zr(Cl)-$

The scope of $Ni(AcAc)_2$-catalyzed conjugate addition of alkenyl zirconium compounds is now being explored with regard to types of substrates amenable to this procedure. The nature of the catalytically active species in this sequence is also being examined.[12]

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References and Notes

(1) G. H. Posner, *Org. React.*, **19,** 1 (1972).
(2) (a) M. Yoshifuji, M. J. Loots, and J. Schwartz, *Tetrahedron Lett.*, 1303, (1977); (b) G. Zweifel and R. L. Miller, *J. Am. Chem. Soc.*, **92,** 6678 (1970); (c) J. F. Normant, *J. Organomet. Chem. Libr.*, **1,** 219 (1976); (d) K. Uchida, K. Utimoto, and H. Nozaki, *J. Org. Chem.*, **41,** 2941 (1976).
(3) W. H. Mandeville and G. M. Whitesides, *J. Org. Chem.*, **39,** 400 (1974).
(4) L. Bagnell, E. A. Jeffery, A. Meisters, and T. Mole, *Aust. J. Chem.*, **28,** 801 (1975).
(5) E. C. Ashby and G. Heinsohn, *J. Org. Chem.*, **39,** 3297 (1974).
(6) D. W. Hart, T. F. Blackburn, and J. Schwartz, *J. Am. Chem. Soc.*, **97,** 679, (1975).
(7) Preliminary results indicate that this reaction proceeds when internal acetylenes are used, but in substantially lower yield.
(8) $Ni(AcAc)_2$, dried by heating to 98 °C in vacuo for 24 h, is soluble in THF.
(9) In no case were products of 1,2 addition observed; a small amount of the product of reductive coupling (diene) is always noted (in this example, 3% (by mmole) by VPC). A direct comparison of the Ni and Cu transmetalation routes can be obtained from the following data: for conjugate addition of the (3,3-dimethyl-1-butenyl) group to methyl vinyl ketone vs. dimerization of that group to (*E,E*)-2,2,7,7-tetramethyl-3,5-octadiene, the $Ni(AcAc)_2$-catalyzed route gave >95% ketone and <1% diene (by mmole), whereas the stoichiometric CuOTf procedure[2a] afforded 73% ketone and 11% diene (by mmole) (determined by VPC). For cyclic enones, these yield differences are even more dramatic.
(10) C. J. Sih, R. G. Salomon, P. Price, R. Sood, and G. Peruzzotti, *J. Am. Chem. Soc.*, **97,** 857 (1975).
(11) D. B. Carr, unpublished results.
(12) Negishi has reported (E. Negishi and D. E. Van Horn, *J. Am. Chem. Soc.*, **99,** 3168 (1977)) that vinylic zirconium complexes will couple with aryl halides in the presence of $Ni(PPh_3)_4$ as a catalyst. This nickel(0) complex was found by us to be inactive (as was the nickel(II) species $(PEt_3)_2NiCl_2$) to accomplish the transformation described herein. However, the Ni species formed by treatment of $Ni(AcAc)_2$ with *i*-Bu_2AlH (1 molar equiv based on Ni) at 0 °C effectively catalyzes conjugate addition of (alkenyl)zirconium complexes to α,β-enones at 0 °C.[11]
(13) NMR for **4** prepared by nickel catalysis (in C_6D_6; δ, multiplicity, H): 6.0 (s, 10), 5.2–5.5 (m, 2), 4.1 (t, 1, $J = 7$ Hz), 2.7 (m, 2), 1.6 (s, 3), 0.9 (s, 9). All spectral lines are significantly broadened in the presence of a stoichiometric amount of nickel(II).
(14) We thank W. Krol and P. Demou (Yale University) for obtaining a 270-MHz NMR spectrum of this compound ($J_{H_\alpha,H_\beta} = 11.2$ Hz, $J_{H_1,H_2} = 17$ Hz, $J_{H_1,H_\beta} = 7$ Hz).
(15) Alfred P. Sloan fellow, 1976–.

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Mercury-Sensitized Photodissociation of the Silicon–Silicon Bond. Synthesis of Methylfluorodisilanes via a Disilane "Metathesis" Reaction

Sir:

Photochemically induced reactions of silicon compounds in which a silicon atom is a distinct component of a chromophore remain rather few in number. Many Si–X bonds exhibit characteristic ultraviolet absorption maxima at wavelengths shorter than 2200 Å[1] and are thus inaccessible as chromophores with more commonly employed sources of ultraviolet radiation. Important exceptions are for X = Hg,[2,3] and Si for *poly*silanes.[4] Kumada[5,6] and Sakurai[7] have established that linear and cyclic polyalkylated polysilanes undergo effective elision of a silylene under the influence of UV radiation;[8] however, simple alkyl-, fluoro-, or chlorodisilanes are impervious to direct photolysis under comparable conditions. The difference in behavior between disilanes and polysilanes on direct photolysis is comprehendible on the basis of the well-documented bathochromic shift of absorption maxima in linear permethylated polysilanes on increasing chain length.[9]

An alternative to direct photolysis which has proven very useful for Si–H bond dissociation is mercury-sensitized photolysis at 2537 Å.[10,11] We wish to report here the facile homolytic dissociation of silicon–silicon bonds in simple methyl- and fluorodisilanes under conditions of mercury-sensitized photolysis and specific, high yield synthetic routes to the (largely unknown) representatives of the class of disilanes $Si_2Me_xF_{6-x}$, $1 \leq x \leq 5$.

Our initial interest lay in the cophotolysis of hydrogen-bearing monosilanes with disilanes in the hope that S_H2 reactions at the Si–Si bond would provide synthetic pathways to new mixed disilanes. Indeed, such reactions proved to be