parameters are listed in Table V. All data processing were performed on a PDP 11/60 computer using the Enraf-Nonius SDP program library.[49] Neutral atom scattering factors and anomalous dispersion corrections applied to all non-hydrogen atoms were those given by Cromer and Waber.[50]

The structure was solved by a combination of Patterson and difference Fourier techniques and refined by full-matrix least-squares methods—the function $\sum w(|F_o| - |F_c|)^2$, $w^{-1} = \sigma_F^2 = {}^1/_4(\sigma(I)/(I) + (0.06)^2(I))$,[51] being minimized. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the final difference Fourier map and refined isotropically. Fractional atomic coordinates, thermal parameters, and structure factor amplitudes are available.[52]

Acknowledgment. We wish to thank Mr. J. Y. Le Gall for recording the NMR spectra.

Registry No. 1, 12176-06-6; 2, 12128-26-6; 3, 12091-64-4; 4, 12091-65-5; 5, 87101-95-9; 6, 87101-96-0; 7, 87101-97-1; 8, 87101-98-2; 9, 87101-99-3; 10, 87102-00-9; 11, 87102-01-0; 12, 87102-02-1; $(\eta^5\text{-}C_5H_5)(Co)_2PPh_3WH$, 33085-24-4; dicyanoacetylene, 1071-98-3; cyanoacetylene, 1070-71-9.

Supplementary Material Available: Tables of final fractional atomic coordinates, thermal parameters, and structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

(49) Frentz, B. A. "The Enraf-Nonius CAD4-SDP. A real Time for Concurrent X-ray Data Collection and Crystal Structure Determination"; Schenk, M., Olthof-Hazekamp, R., von Koningsveld, M., Bassi, G. C., Eds.; Delft University Press: Delft, 1978.
(50) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975, Vol. IV.
(51) McCaudlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr., Sect. A* **1975**, *A31*, 245.
(52) See supplementary material.

Communications

Regiochemical Control in the Molybdenum-Catalyzed Reactions of Trimethylsilyl- and Ester-Substituted Allylic Acetates

Barry M. Trost* and Mark Lautens

Samuel M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison Wisconsin 53706

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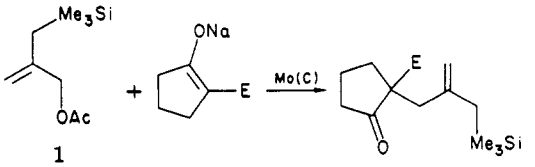
Summary: Molybdenum-catalyzed allylic alkylation performed on allylic acetates also containing allylic or vinylic silanes proceed chemoselectively retaining the silane functionality. For those substrates containing γ-acetoxy α,β-unsaturated esters, both substitution of the allyl acetate and choice of nucleophile allow for complementary regiochemistry.

The transition-metal-catalyzed allylic alkylation offers a new dimension for controlling selectivity in C–C bond formation.[1] Of paramount importance is the question of regiochemical control and the effect of substituents on such a question. The general importance of allyl and vinyl silanes[2,3] and the well-known strong directive effects of electron-withdrawing groups in noncatalyzed reactions led us to examine the trimethylsilyl and carbomethoxy group in molybdenum-catalyzed allylic alkylations.[4] The trimethylsilyl-substituted allyl acetates were of special interest as substrates because of their high propensity to undergo desilylation concomitant with alkylation in palladium-catalyzed reactions.[5]

2-((Trimethylsilyl)methyl)allyl acetate (1), the substrate that efficiently loses the elements of trimethylsilyl acetate in the presence of palladium catalysts,[6] became our first target to test the lability of the Me_3Si group in the presence of molybdenum catalysts. Gratifyingly, alkylation of the



1 2

sodium salt of 2-carbomethoxycyclopentanone gave the simple alkylation product **2** in 60% yield [25% mol% $Mo(CO)_6$, $PhCH_3$, reflux, 72 h] with no trace of a protodesilylated byproduct. The utility of such a product for three carbon intercalation[7] is enhanced due to its easy accessibility from the very stable and easily handled allyl acetate **1** via this molybdenum-catalyzed process. Encouraged by this result, we examined a broader range of trimethylsilyl-substituted allyl acetates with special attention to regioselectivity as summarized in Table I using dimethyl malonate (**3**) and dimethyl methylmalonate (**4**) with 10–20% Mo(c) in refluxing toluene in the presence of *O,N*-bis(trimethylsilyl)acetamide (BSA) as base. The insensitivity of the organosilanes toward desilylation in the Mo-catalyzed reaction in contrast to the Pd-catalyzed reaction is highlighted in entries 2 and 3 in which both an allyl- and vinylsilane survive.

The low regioselectivity in the case of entry 1 is surprising in light of the high regioselectivity for attack at the secondary carbon of crotyl acetate with dimethyl malonate.[8] The increased C–Si bond length compared to a

(1) Trost, B. M. *Science (Washington, D.C.)* **1983**, *219*, 245.
(2) Trost, B. M.; Yoshida, J.-I.; Lautens, M. *J. Am. Chem. Soc.*, accepted for publication. Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 4962. Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223. Negishi, E.; Luo, F. T.; Rand, C. L. *Tetrahedron Lett.* **1982**, *23*, 27. Tzeng, D. J.; Weber, W. P. *J. Org. Chem.* **1981**, *46*, 265.
(3) For reviews see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. Fleming, I. *Comp. Org Chem.* **1979**, *3*, 539. Magnus, P. D. *Ibid.* **1982**, *7*, 515.
(4) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.
(5) Trost, B. M.; Self, C. R. *J. Am. Chem. Soc.*, accepted for publication.
(6) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429; **1983**, *105*, 2315; 2326.
(7) Cf.: Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680.
(8) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1983**, *105*, 3343.
(9) For the preparation of the corresponding alcohols see: Tanikaga, R.; Nozaki, Y.; Tamura, T.; Kaji, A. *Synthesis* **1983**, 134; *Chem. Lett.* **1982**, 1703.

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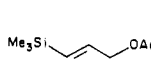
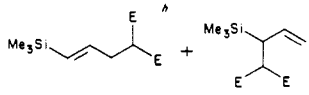
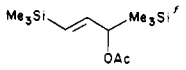
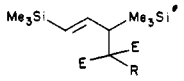
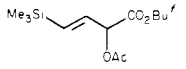
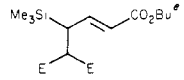
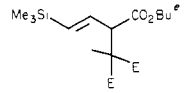
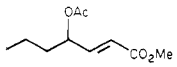
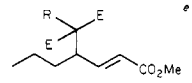
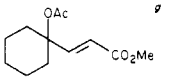
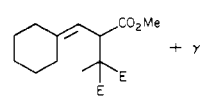
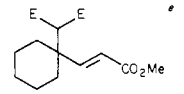
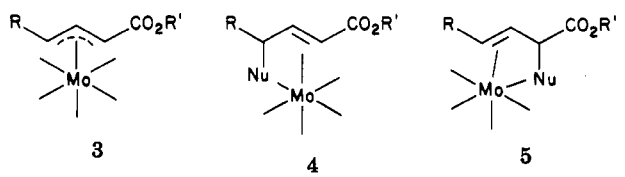
Table I

entry	allylic acetate	nucleophile	time, h	product[a]	% yield[b,c]
1		CH_2E_2	9	 1:1.2	35
2		CH_2E_2	2.5	 R = H or Me	49
3		CH_3CHE_2	2.5		58 (80)[i]
4		CH_2E_2	12		43
5		CH_3CHE_2	7		57
6		CH_2E_2	4	 R = H or Me	33 (66)[d]
7		CH_3CHE_2	2		60
8		CH_3CHE_2	1.5	 6:1	52
9		CH_2E_2	2.5		62

[a] All products have been identified by spectroscopic methods and by high resolution mass spectrometry. [b] Isolated yields of pure products. [c] These represent unoptimized yields. [d] Yield based on recovered starting material, longer reaction times led to destruction of product. [e] Only the trans stereoisomer was detected. [f] See ref 5. [g] See ref 9. [h] See ref 10. [i] See ref 11.

C–C bond may account for this observation. In contrast to this result, very high regioselectivity is observed in entries 4 and 5. We had previously noted that dimethyl malonate tends to form a C–C bond to the more substituted carbon of an allyl unit, whereas dimethyl methylmalonate forms this bond to the less substituted carbon of an allyl unit.[8] These two entries reflect this general trend. The failure of the carbo-*n*-butoxy group to alter this intrinsic bias is most surprising.

This regioselectivity suggests that steric factors are more important than electronic factors. To examine whether any electronic effect exists, the alkylations summarized in entries 6 and 7 were examined. In both cases, γ-alkylation totally dominates. Such a result is expected on the basis of the effect of a strong electron-withdrawing group on (1) the charge distribution in the (π-allyl)molybdenum intermediate **3** and (2) the stability of the initial π-olefin product **4** compared to **5**.



3 **4** **5**

To verify that the complementary regioselectivity of the two nucleophiles in entries 4 and 5 results from steric factors and not an electronic effect of the trimethylsilyl group, the alkylations outlined in entries 8 and 9 were examined. The fact that complementary regioselectivity continues to be observed strongly supports the notion that steric effects dominate.

These results support the proposition that the regioselectivity of molybdenum-catalyzed reactions depends upon (1) steric approach of the nucleophile, (2) the nature of the ligands on the molybdenum, (3) charge distribution in the intermediate (π-allyl)molybdenum complex, and (4) the relative stability of the initial (π-olefin)molybdenum(0) complex. The first and fourth factors would appear to be somewhat more important than the third one. Attempts to explore the effect of ligands by using (2,2′-bipyridyl)-molybdenum tetracarbonyl were thwarted by elimination superceding alkylation. The ability to control such alkylations, especially the ability to selectively attack a position α to a carbonyl group in an enolate with a nucleophile (i.e., an enolonium equivalent), has not been possible in the absence of transition-metal catalysts. The lack of desilylation during alkylation is in stark contrast to the palladium-catalyzed reactions and suggests important differences in bonding characteristic between (π-allyl)palladium and (π-allyl)molybdenum complexes. Synthetically, such a complementary behavior proves most useful. In the present case, the retention of the trimethylsilyl group and the fact that it is easily replaced by

(10) For the reactions of 1-trimethylsilyl acetate with nucleophiles under Pd^0-catalyzed conditions see: Hirao, T.; Enda, J.; Oshiro, Y.; Agawa, T. *Tetrahedron Lett.* **1981**, *22*, 3079.
(11) Brandi, A., unpublished work in these laboratories.

a hydrogen permit this substituent to serve as a regiochemical control element!

Acknowledgment. We wish to thank the National Science Foundation for their generous support of our programs. M. L. thanks the Natural Sciences and Engineering Research Council of Canada for a predoctoral fellowship.

Registry No. 1, 72047-94-0; 2, 86970-30-1; 2-carbomethoxycyclopentanone sodium salt, 86970-29-8; $Me_3SiCH{=}CHCH_2OAc$, 80401-14-5; $Me_3SiCH{=}CHCH(OAc)SiMe_3$, 86970-25-4; $Me_3SiCH{=}CHCH(OAc)CO_2Bu$, 86970-26-5; $CH_3CH_2CH_2CH(OAc)CH{=}CH\ CO_2Me$, 86970-27-6; CH_2E_2, 108-59-8; CH_3CHE_2, 609-02-9; $Me_3SiCH{=}CHCH_2CHE_2$, 86970-31-2; $Me_3SiCH(CHE_2)CH{=}CH_2$, 86970-32-3; (*E*)-$Me_3SiCH{=}CHCH(SiMe_3)CHE_2$, 86422-29-9; (*E*)-$Me_3SiCH{=}CHCH(SiMe_3)CE_2CH_3$, 86970-33-4; (*E*)-$Me_3SiCH(CHE_2)CH{=}CHCO_2Bu$, 86970-34-5; (*E*)-$Me_3SiCH{=}CHCH(CE_2CH_3)CO_2Bu$, 86970-35-6; (*E*)-$CH_3CH_2CH_2CH(CHE_2)CH{=}CHCO_2Me$, 86970-36-7; (*E*)-$CH_3CH_2CH_2CH(CE_2CH_3)CH{=}CHCO_2Me$, 86970-37-8; $Mo(CO)_6$, 13939-06-5; methyl 3-(1-acetyloxycylohexyl)propenoate, 86970-28-7; $C_6H_{10}{=}CHCH(CE_2CH_3)CO_2Me$, 86970-38-9; (*E*)-2-methyl-2-[1-(carbomethoxyethenyl)cyclohexyl]propandioic acid dimethyl ester, 86970-39-0; (*E*)-2-[1-(carbomethoxyethenyl)-cyclohexyl]propanedioic acid dimethyl ester, 86970-40-3.

Addition of Carboxylic Acids to Alkynes Catalyzed by Ruthenium Complexes. Vinyl Ester Formation

Michal Rotem and Youval Shvo*

Department of Chemistry, Tel Aviv University
Tel Aviv 69978, Israel

Received March 22, 1983

Summary: $Ru_3(CO)_{12}$ as well as $[Ru(CO)_2(O_2CCH_3)]_n$ are catalyst precursors for the addition of aliphatic and aromatic carboxylic acids to di- and monosubstituted acetylenes which yields vinyl esters. The kinetic product results from a cis addition to the triple bond; a rearranged product is also formed.

Catalysis involving transition-metal complexes is a rapidly growing field of chemistry.[1] In this communication we present preliminary data concerning a new catalytic system. It is based on $Ru_3(CO)_{12}$ which serves as a catalyst precursor in an addition reaction of carboxylic acids to alkynes. The reaction is exemplified with diphenylacetylene and acetic acid (eq 1); the reaction conditions

$$PhC{\equiv}CPh + AcOH \xrightarrow{Ru_3(CO)_{12}} \underset{1\ (E+Z)}{PhCH{=}C(OAc)Ph} + \underset{2}{Ph_2C{=}C(OAc)H} \quad (1)$$

are described in Table I, footnote *a*. The reaction is conveniently monitored by GLC, and eventually the mixture was separated by chromatography (silica; CH_2Cl_2–petroleum ether). The properties of the isolated substances (MS, IR, NMR) are consistent with structures 1 (*E* and *Z*) and 2, and the melting points are identical with those reported in the literature.[2-4] The product distributions and other experimental data are presented in Table I (entry 1). Other carboxylic acids and also different alkynes exhibit similar behavior (Table I). In most of the cases the products were separated (silica) and purified, and their structures were assigned by comparing the spectral data with that of the known 1 (*E* and *Z*) and 2.[5]

The following additional experiments were performed:

1. Several control experiments, omitting the catalyst, have revealed only traces (<1%) of vinyl esters.

2. GLC monitoring of the reaction (entry 1) has indicated a slow conversion of the $E \rightarrow Z$ isomer. This was also verified in a separate experiment, by subjecting (*E*)-α-(benzoyloxy)stilbene to the original reaction conditions.

3. When subjected to the original reaction conditions, a mixture of (*E*)- and (*Z*)-α-acetoxystilbenes did *not* produce the rearranged product 2. From the experimental data presented we can derive the following conclusions:

a. $Ru_3(CO)_{12}$ is a catalyst precursor for the addition of carboxylic acids to alkynes, generating vinyl esters. The reaction seems to be a general one, in as much as various aliphatic and aromatic carboxylic acids, as well as structurally diverse alkynes, are reactive (Table I). In general, the conversions are good and the stereoselectivity is variable.

b. An interesting isomeric rearranged product, viz., 2, accompanies the *E* and *Z* vinyl ester mixtures. It is a *primary* product that is being formed in parallel with the normal vinyl esters. To the best of our knowledge, such a reaction is without precedent in organic chemistry.

c. Most probably the kinetically controlled product results from a cis addition of the acids to the triple bond.

d. The addition of carboxylic acids to alkynes is known to be catalyzed by strong acids, Lewis acids, and electrophiles.[2,6] Notably, mercury salts, where organomercurials are serving as intermediates, are useful catalysts; in many cases stoichiometric quantities of mercury salts are used.[2,6] We believe that our catalytic system is more complex in as much as $RuCl_3$, which may be considered as a Lewis acid catalyst, is totally inactive in the above addition reaction.

e. The reactions listed in Table I have not been parameterized. It is noteworthy that practically quantitative yields were recorded in entries 8–10 (Table I). Entry 8 represents the only unsymmetrical alkyne that was examined. Although listed as a rearranged product, α-(benzoyloxy)styrene (23%) may have actually resulted from the inverse addition of benzoic acid to phenylacetylene. Neither are we sure that the β-(benzoyloxy)styrenes are not, in fact, rearranged products. Nevertheless, it is noteworthy that the major product of this reaction is β-(benzoyloxy)styrene (77%)—a formally anti-Markovnikov addition product. This observation also supports our previous contention that the addition is not induced by simple acid catalysis.

Since only one product was isolated in entries 9 and 10, it is difficult to characterize them stereochemically.[5] We have assigned the *E* configuration to 4-acetoxy-4-octene (entry 9). Its vinyl proton resonates at 5.13 ppm compared to 5.04 ppm for (*E*)-2-acetoxy-4,4-dimethyl-2-pentene[6] and 4.79 ppm for the *Z* isomer.[6] The assigned configuration is consistent with cis addition of acetic acid to 4-octyne.

Some insight into the reaction under investigation may be gained by examining reaction 2. This type of reaction, with various acids, was studied by several investigators.[7,8]

(1) Parshall, G. W. "Homogenous Catalysis"; Wiley: New York, 1980.
(2) Bach, R. D.; Woodward, R. A.; Anderson, T. J.; Glick, M. D. *J. Org. Chem.* **1982**, *47*, 3707.
(3) Barnes, R. P.; Cooper, S. R.; Tulane, V. J.; Delaney, H. *J. Org. Chem.* **1943**, *8*, 153.
(4) Mičović, V. M.; Rogič, M. M.; Mihailović, M. L. *Tetrahedron* **1957**, *1*, 340.
(5) The vinyl proton resonance is a reliable structural indicator. For (*E*)- and (*Z*)-α-acetoxystilbenes and 1-acetoxy-2,2-diphenylethylene δ-($CDCl_3$) 6.45, 6.70, and 7.63, respectively. Very similar chemical shifts were recorded for all other vinyl esters, thus enabling structural assignments to be made.
(6) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966 and references cited therein.

0276-7333/83/2302-1689$01.50/0