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REGIOCHEMICAL DIVERSITY IN ALLYLIC ALKYLATIONS VIA MOLYBDENUM CATALYSTS**

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Abstract - The use of molybdenum as a template to control regioselectivity in allylic alkylations is explored. The feasibility of performing allylic alkylations with preformed π-allylmolybdenum complexes is established. As in palladium reactions, addition of excess phosphine has a profound effect on the rate of these reactions. A catalytic reaction based upon molybdenum hexacarbonyl is developed. Using malonate anion, excellent regioselectivity for attack at the more substituted end of an allyl system regardless of the positional identity of the initial leaving group exists. With β-ketoesters, substrates which possess a secondary and a primary carbon in the allyl unit lead to preferential attack at the secondary carbon. However, substrates that possess a tertiary and a primary carbon at the termini lead to attack at the primary carbon. Anions derived from substituted malonates and 1,3-diketones lead to substitution at the less substituted position of allyl systems. The presence of strongly electron withdrawing substituents has little effect on these orientational biases. Mechanistic implications of these results are discussed.

The utilization of transition metal catalysts to activate poor leaving groups towards displacement provides the opportunity to utilize chemically more stable alkylating agents that may represent less of a biohazard. In the case of allyl alkylating agents[1], the possibility of modifying the normal behavior of such substrates by manipulation of the template arises. For example, the stereochemical requirement of simple displacements with inversion of configuration translates to a displacement with net retention of configuration in the palladium catalyzed version.[3] Of equal interest is the question of regioselectivity. S_N2 versus S_N2' displacements remain capricious in straight displacements with S_N2 processes normally predominating.[4] In transition metal catalyzed reations, the intermediacy of organometallic complexes may liberate the regioselectivity from being determined by the position of the leaving group in the starting material.

Allylmetal complexes may be either of a σ, eg. 1, or π, eg. 2, nature. If of the former type, the possibility of rapid tautomerization between the two σ-allyl complexes destroys the positional identity of the metal. Thus,

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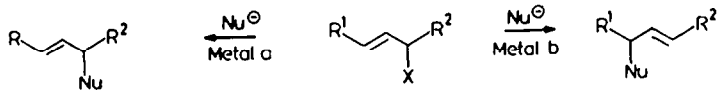
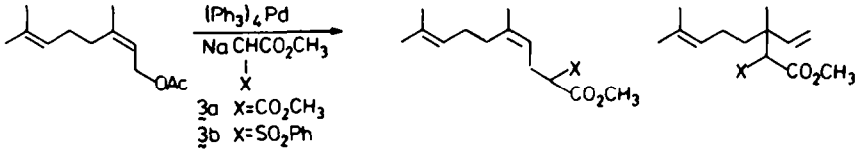
Dedicated in honor of the 65th birthday of Professor Hans Wynberg

1 2

with either type of intermediate, the positional selectivity of subsequent reactions may be determined by factors such as the nature of the substitution pattern on the allyl fragment and of the metal and its ligand field. If the latter could exercise control, from a single substrate, either regioisomeric product may arise simply by manipulating the controlling template according to eq. 1. Our initial work focussed on palladium templates.[5-12] It became evident that in these alkylations, steric and electronic effects may operate in opposing directions. For

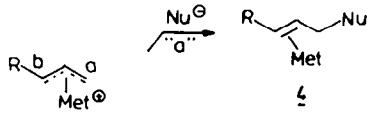


example, neryl acetate reacts with malonate anion 3a to give predominantly attack at the tertiary center but the sulfone stabilized anion 3b results in predominant attack at the primary center.[3,13] Such a selectivity can be understood on the basis of electronic effects dominating in the transition



3a X=CO_2CH_3
3b X=SO_2Ph

state (ts) leading to reactions at the tertiary center but steric effects dominating in the ts leading to reaction at the primary carbon. However, the complicated nature of this process is revealed by the fact that geranyl acetate leads to predominant reaction at the primary center with both nucleophiles although a trend in the direction of greater tertiary attack with 3a still exists. While nucleophile modification permits optimizing attack at the primary carbon under the influence of palladium catalysis, modifications to optimize tertiary attack except in isolated cases failed with palladium templates. It was reasoned that utilizing a more



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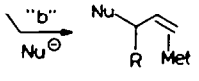

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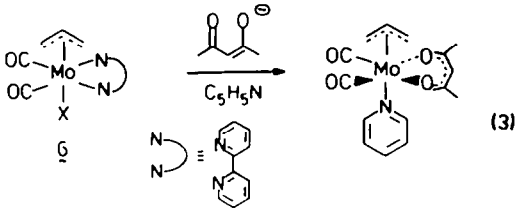
electropositive metal may enhance the importance of electronic versus steric effects. Furthermore, if we examine the kinetic products of attack on a monosubstituted allyl complex, i.e. the olefin metal complexes 4 and 5, steric and electronic factors with respect to olefin-metal(0) complexation should favor formation of 5. Octahedral molybdenum complexes appeared to be a reasonable choice as catalysts to maximize the importance of these factors and, thus, to enhance attack at the more substituted positions.[11]

While π-allylmolybdenum complexes were well known,[14-19] their use in alkylation reactions at the allyl fragment were extremely scarce. In fact, some of the results were quite discouraging. For example, the molybdenum complex 6 is reported to undergo substitution at the metal (eq. 3).[16,20]



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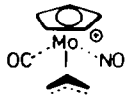
Subsequently, rearrangement of this product to that of C-allylation has been reported.[21] The most encouraging work has been the excellent studies of Faller on the stoichiometric molybdenum cationic compexes 7 which have led to good yields of C-alkylation with nucleophiles like enamines, hydride, dithiocarbamate, and malonate anion.[14,22] In these cases, the cyclopentadienyl ring may be envisioned to shield the molybdenum from nucleophilic attack. Thus, we initiated a study to determine if molybdenum complexes not bearing Cp ligands can undergo attack at the carbon of the allyl fragment and if a catalytic reaction may ensue.



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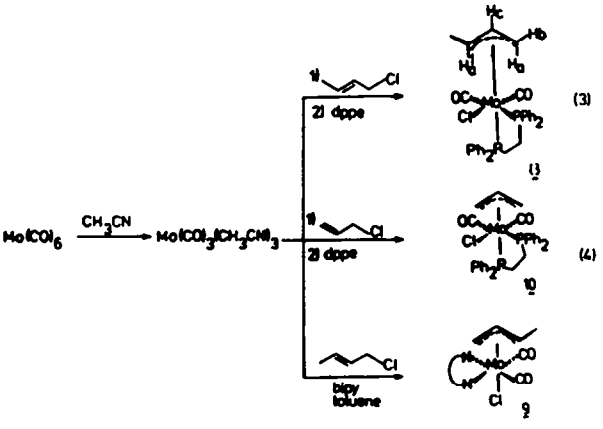
Stoichiometric Reactions

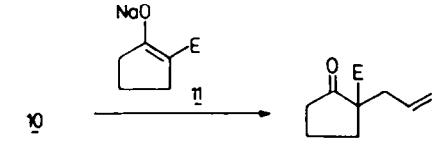
Initial studies were focussed on determining the suitability of pi-allylmolybdenum complexes as electrophilic species in reactions with soft nucleophiles. Two complexes, 8 and 9, as well as the known complex 10 were prepared by modification of existing routes in 67% and 90% yields according to eq. 4[23] and 5[16].

The geometry of the complexes were assumed to be analogous to the products derived from otherwise identical reactions with allyl chloride,



whose structures were determined by X-ray crystallography.[23]

To examine the alkylation in the absence of complicating regiochemical and stereochemical issues, initial studies concentrated on alkylation of the sodium salt of 2-carbomethoxycyclopentanone 11 with complex 10. Alkylation does proceed according to eq. 6 in refluxing THF in 40% yield. The yield improves to 65% upon addition of 1 eq. of dppe.



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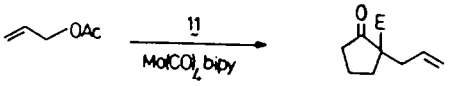
Alkylating the crotyl complex 8 under identical conditions as above with 2 eq. of triphenylphosphine generated two products in a 4:1 ratio. Nmr spectroscopy establishes attack occurred only at the primary carbon [^{1}H, δ 1.63 (major) and 1.61 (minor), two doublets; ^{13}C, δ 126.9 and 124.1 (major), 128.9 and 124.9 (minor)] as shown in eq. 7. Alkylation of the

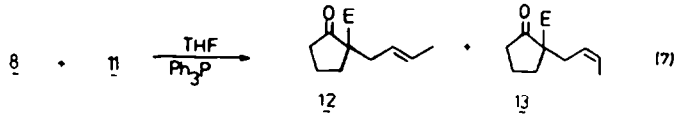
TABLE 1

Effect of Solvent on the Alkylation of Allyl Acetate



Entry	Solvent	Temp.	Time	Yield
1.	DME	65°	24 h	10%
2.	THF	65°	24 h	<10%
3.	diglyme	110°	24 h	10%
4.	toluene	110°	8 h	70%
5.	dioxane	102°	24 h	70%
6.	benzene	80°	24 h	<10%

bi-pyridyl complex 9 under otherwise identical conditions showed, by vpc, that four products were produced in a 2.3:9:6.5:1 ratio. Two of the four compounds were identified as 12 and 13, the products from primary alkylation due to their identical retention times with the alkylation



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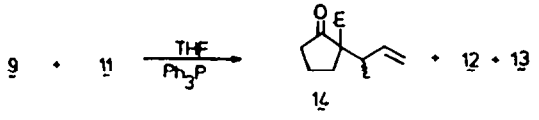
products of complex 8. The other two products, which eluted more rapidly, were determined to be a diastereomeric mixture 14 arising from alkylation at the secondary carbon atom. Signals in the ^{1}H NMR spectrum at δ 0.98 and

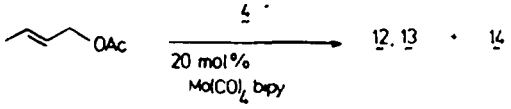


0.93 ppm assigned to the methyl group suggested a mixture of diastereomers whose ratio by vpc was 1:3.9. The ratio of primary to secondary alkylation products was 1.5:1.

Development of a Catalytic Reaction

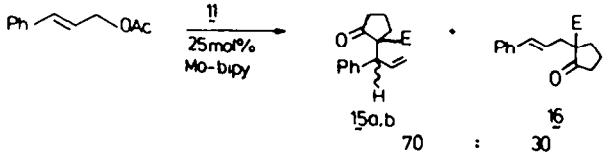
With the establishment of the feasibility of the alkylation step, it became desirable to combine the pi-allyl metal complex formation and alkylation reactions to create a catalytic cycle. It was known that even the much less reactive allyl acetate was a suitable precursor to a pi-allyl molybdenum complex[16] via its reaction with $Mo(CO)_4$bipy.[18] When an equivalent of allyl acetate was heated in an organic solvent with 0.5 eq. of 11 in the presence of 20 mol% of $Mo(CO)_4$bipy, we obtained the desired alkylation product in varying yields (See Table 1). That the catalyst was necessary was easily shown by heating 11 and allyl acetate in toluene at reflux for 24 h and observing that no reaction had occurred. It should be noted from the table that Lewis basic solvents had a deleterious effect on the rate of reaction. Furthermore, the temperature of the reaction played a crucial role in achieving acceptable rates of reaction (entry 4 vs 6).

With these results in hand, we proceeded to examine other allylic acetates to determine the reactivity and regioselectivity of alkylations with this new catalyst. Alkylation of crotyl acetate was studied to allow comparisons with the stoichiometric alkylations of complex 9. The reaction was found to be much slower than the analogous reaction with allyl acetate. Even under the optimum conditions (i.e. refluxing toluene) 30% of unreacted starting material remained after 48h. Nevertheless, we again observed substantial amounts of products derived from alkylation at the secondary carbon atom (vpc ratio 12+13:14 =1:1.3).



The use of a more reactive substrate such as cinnamyl acetate increased the rate of the reaction such that the starting material was consumed after 16 h. Two products were obtained by flash chromatography[24] of the crude reaction. The major component (42%), which eluted more rapidly, was shown to be a mixture of diastereomers, 15 a,b, derived from alkylation at the secondary carbon atom. The minor product, 16, (28%) was a single isomer by ^1H and ^{13}C NMR spectroscopy.

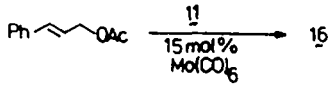
The ratio of diastereomers, determined by integration of signals in the ^1H NMR spectrum at δ 4.39 and 2.27 ppm, was found to be 1.3:1 but these were not further assigned. These signals, along with a doublet of triplets at δ 6.10 ppm (J=18.1 and 8.8 Hz) and two doublets at δ 5.19



ppm (J=8,8 Hz) and 5.14 ppm (J=18.1), confirmed the existence of a terminal vinyl group in these alkylation products.

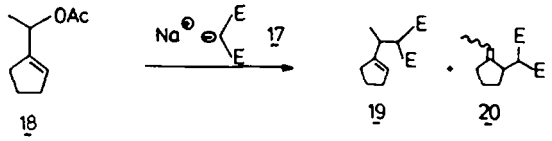
Attempts to extend this methodology to a wider variety of allylic acetates failed. It became apparent that the activity of the catalyst was insufficient. In general, alkyl substitution retarded the rate of the reaction to such an extent that a search began for a more suitable catalyst. $Mo(CO)_4$dppe[18,25] and $Mo(CO)_4$TMEDA were both studied in the alkylation of crotyl acetate with the anion of ketoester 4, but the former was even less reactive and the latter, while approximately as reactive as $Mo(CO)_4$bipy,[26] showed no enhancement in the regioselectivity. Also the use of N-methylmorpholine-N-oxide[27] to oxidize a carbon monoxide ligand to carbon dioxide, which should dissociate more readily, had no effect on the rate of reaction.

Finally, we turned our attention to the starting material for all these catalysts which was simply $Mo(CO)_6$. Initial concerns regarding the reactivity of this substance toward the nucleophiles present in the reaction mixture were unfounded. Alkylation of crotyl acetate with nucleophile 11 in toluene took place in 12h at reflux, providing a 5:1 ratio of 12 and 13 in 75% yield. It should be noted that 14 could not be seen in either the ^{1}H NMR spectrum or by vpc. The reaction of cinnamyl acetate and nucleophile 11 with $Mo(CO)_6$ as catalyst in toluene at reflux for 8h provided 16 as a single regio- and stereoisomer.



Regioselectivity[28]

Reactions with a hindered nucleophile such as 11 had shown that the catalyst had a marked effect on the regioselectivity. Would a less hindered nucleophile such as dimethyl malonate anion 17 show similar behavior? Allylic acetate 18[3] was reacted with 17 in the presence of $Mo(CO)_4$bipy and $Mo(CO)_6$ as catalysts. As expected, $Mo(CO)_4$bipy was a rather



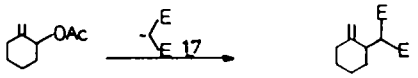
$Mo(CO)_4$bipy	100	:	0
$Mo(CO)_6$	15	:	85
$Pd(PPh_3)_4$	100	:	0

unreactive catalyst, providing 19 in 45% yield after 72h at reflux in toluene. Molybdenum hexacarbonyl was substantially more reactive, giving a mixture of 19 and 20 in 69% yield after 48h in refluxing toluene.

The minor isomer in the $Mo(CO)_6$ catalyzed reaction was identical in all respects to a compound prepared via palladium(0) catalyzed alkylation[3] of

18 with 17. The major product contained two pairs of olefinic signals in the ^{13}C NMR spectrum at 143.1, 117.3 and 142.9, 118.0 along with two doublets at 1.48 and 1.47 in the ^{1}H NMR spectrum which, in conjunction with vpc, allowed the assignment of 20 and the ratio of 19:20.

The unexpected regioselectivity seen in the reaction using $Mo(CO)_6$ as the catalyst prompted us to explore further its reactions with a related acetate 21. This compound reacted smoothly with 17 in the presence of $Mo(CO)_6$ to provide 22 as a single regioisomer in 76% yield. The exocyclic methylene unit was easily identified by ^{1}H NMR spectroscopy (two



21 22

singlets at 4.73 and 4.60 ppm) and ^{13}C NMR spectroscopy (δ148.9 and 107.9 ppm).[30] The reaction of 21 with 11 and methyl 5-methyl-3-oxohexanoate, 23, were examined to determine the effect of substitution (in a beta-ketoester) on regioselectivity. Whereas the product of the latter reaction providing 25 had spectral characteristics similar to 22 (although most peaks were doubled due to the presence of a 1:1 mixture of diastereomers), the reaction of 11 yielded an oil which, by ^{1}H NMR spectroscopy, contained a single olefinic resonance at 5.48 ppm allowing the assignment of its structure as 24.

In the competition between a secondary and a primary carbon atom, unhindered nucleophiles such as 17 and 23 reacted at the more hindered position. Would this also be true for competitions involving tertiary vs primary carbons? Alkylations with geranyl 26 and linalyl acetate 27 permitted the testing of this question, along with the more fundamental issue regarding the intermediacy of a pi-allyl complex. If both isomers gave the same product then a symmetrization must have occurred, which would be fully in accord with a pi-allyl intermediate or at least rapidly equilibrating sigma complexes. When 26 and 27 were allowed to react with 17 in the presence of 20 and 5 mol% of $Mo(CO)_6$ respectively, three products were produced in an 85:12:3 ratio, as measured by vpc and summarized in Table 2. The products were identified by comparison of their ^{1}H NMR spectra and VPC retention times with those of authentic samples previously prepared[3] using palladium(0) catalysis. The major product 28 arose from alkylation at the tertiary carbon. As shown in Table 2, the choice of base had a marked effect on the reactivity of the catalyst and on the ratio of the regioisomers. Dramatically, a coordinating base such as BSA gave very high selectivity for the tertiary product 28 (entry 4). Nevertheless, too strongly coordinating bases such as DBU poisoned the catalyst (entry 7). The counterion also had an effect on regioselectivity (cf, entries 1 and 2

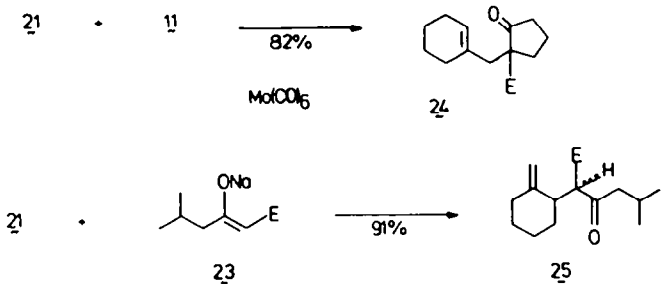
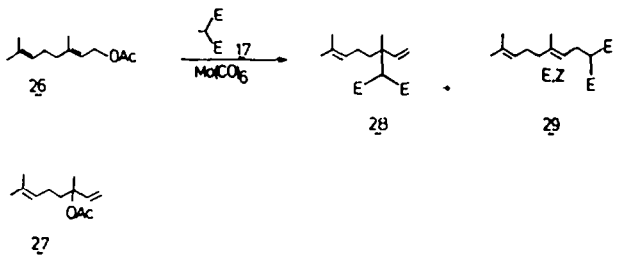


TABLE 2

Molybdenum Catalyzed Alkylations of Geranyl and Linalyl Acetate



Entry	Substrate	Base	Time	Ratio Products 28:29Z:29E	Yield
1.	27	NaH	3h	85:3:12	80%
2.	27	KH	2h	80:3:17	82%
3.	27	KH[a]	5h	80:5:14	82%
4.	27	BSA	1.5h	97:0.5:2.5	82%
5.	26	NaH	48h	85:3:12	65%
6.	27	KF	48h	------	N.R.
7.	27	DBU	48h	------	N.R.
8.	27	BSA[b]	5h	85:3:12	75%

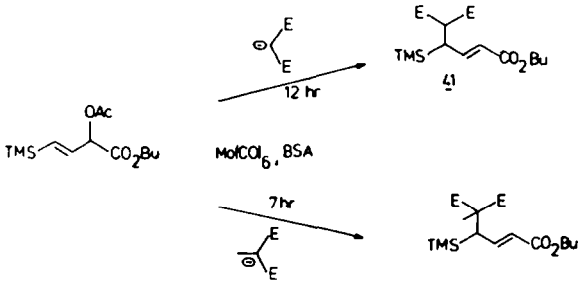
(a) Reacted with 1.1 eq. 2-methyl-2-butanol before addition of dimethyl malonate.

(b) Reaction carried out in decane (110°).

versus 4). While the product distribution from the alkylation of 26 and 27 was identical, the rate of reaction was substantially slower for the isomer with the more substituted olefin. i.e. 26. This factor will be noted several times throughout the studies which follow.

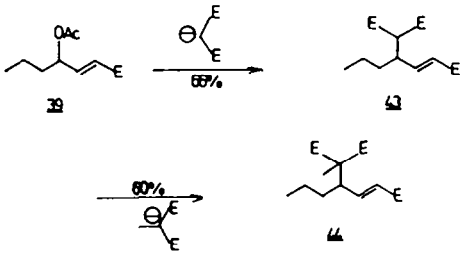
Acetate 30[31] was chosen to examine the regioselectivity of alkylations of substituted malonates and 1,3-diketones in the absence of the complicating issue of olefin stereochemistry which could have arisen from alkylations of 27. Alkylation with 2,4-pentanedione, 3-methyl-2,4-pentanedione, dimethyl methylmalonate and acyclic beta-ketoester 23 in the presence of a catalytic amount (5-10 mol%) of molybdenum hexacarbonyl gave products derived from alkylation at the primary carbon atom, as could be clearly seen by examination of their ^1H NMR spectra, which all contained a single olefinic proton at δ 4.90, 4.81, 4.95, and 5.18 ppm for Ha in 31, 32, 33, and 34 respectively. In contrast to these more bulky nucleophiles, alkylation with malonate anion

Surprisingly, 2-acetoxy-β,γ-unsaturated ketones 36 and 37 failed to react. On the other hand, the silyl derivative 38 reacted with malonate anion 17 without incident to give a single regioisomer 41 in an unoptimized yield of 43%. Although both an ester and silicon destabilize an alpha cationic center, the former group should exert a stronger effect. In addition, the site adjacent to the trimethylsilyl group is the sterically



more congested site. Based on our previous findings, alkylation should be expected at this position on both steric and electronic grounds. Whereas, more hindered nucleophiles have now been shown to react at the less hindered site, in this case, electronic factors oppose this regiochemistry. Nevertheless, dimethyl methylmalonate anion provided the regiocomplementary product as a single isomer in 56% yield. The silicon had acted as a regiochemical control element since desilyation of 41 and 42 would lead to isomeric alkylation products. However, the failure of 36 and 37 to alkylate with either 17 or dimethyl methylmalonate anion showed that the role of silicon was much more than simply a steric one.

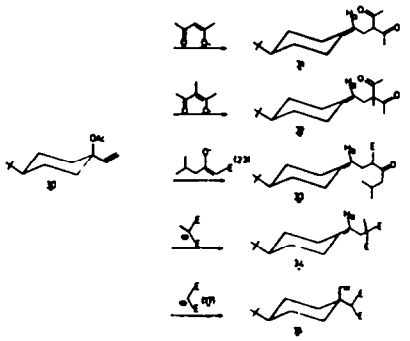
Hypothesizing the role of silicon as an electronic one whereby the olefin becomes a better -acceptor in back-bonding from the metal, stronger electron accepting groups in the olefin as exist in 39 and 40 should lead to higher reactivity than their α-acetoxy-β,γ-unsaturated analogues. This notion proved to be true. Alkylations of 39 with the anion of dimethyl malonate and its methyl analogue proceeded to give 43 and 44 in 66 and 60% yields respectively. In contrast to the silicon case, both nucleophiles led to the same regioisomeric product.



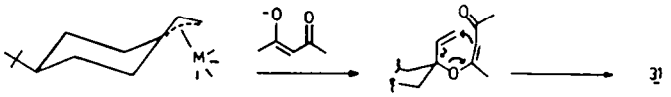
On the other hand, acetate 40 does contain conflicting steric and electronic effects. Once again, we observed the complementary behavior of the two malonate type nucleophiles with the less hindered nucleophile reacting exclusively at the tertiary carbon to give 45 and the more hindered one reacting preferentially at the less hindered position to give predominantly 46 (46:47:48, 6:1:1).

17 gave only the product of attack at the tertiary position, 35.

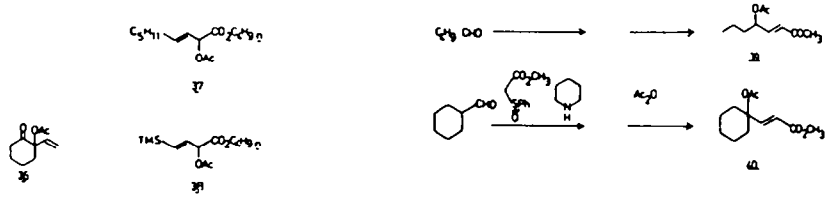
The regioselectivity exhibited by dimethyl methylmalonate is best explained by steric approach control in which the more bulky nucleophile simply reacts at the less hindered carbon of the pi-allyl intermediate. Ketoester 23 shows the sensitivity of these molybdenum catalyzed alkylations toward subtle changes in substrates, i.e. 23 reacts at the less hindered carbon atom in 30, but at the more hindered site in 21. The 1,3-diketones examined reacted at the less hindered carbon atom even though 2,4-pentanedione should be of approximately the same steric bulk as dimethyl malonate. Two explanations can be put forth to rationalize this result. The first is one of reactivity of the nucleophile; the diketone is

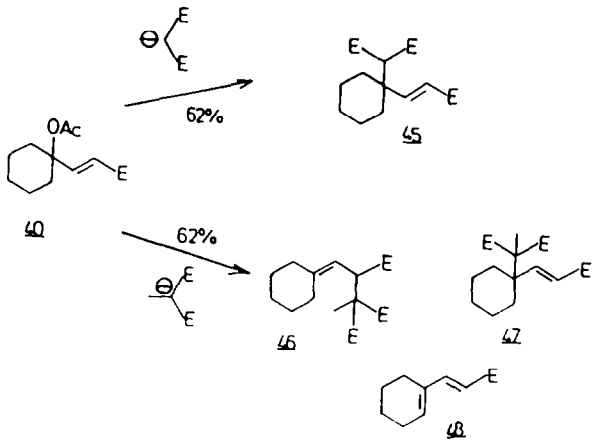


substantially more acidic than the analogous malonate derivative (pk_a=9 vs 13) and should, therefore, be less nucleophilic. As the nucleophilicity decreases, the transition state moves toward the product end of the reaction coordinate resulting in the formation of the thermodynamically more stable adduct.[32] A second explanation derives from considerations of the propensity of the diketones vs malonates to alkylate at oxygen vs carbon. If the diketone was to react at oxygen at C-1 of the allylic complex, a system is created which is capable of undergoing a Claisen rearrangement. This reaction may or may not be catalyzed by the presence of the transition metal, although palladium(0) catalyzed Claisen rearrangements have recently been reported.[33]



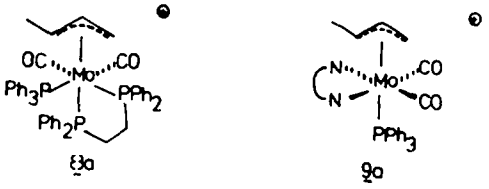
As electronic effects can frequently override the intrinsic steric bias in a system, we synthesized five acetates, 36 - 40, to examine this question in molybdenum catalyzed reactions. The routes to 36, 37, and 38 simply involved subjecting the appropriate ketone or aldehyde to reaction with a vinyl organometallic species and acetylating the resultant alcohol. The methodology reported by Tanikaga[34] provided β-acetoxy -α,β- unsaturated esters 39 and 40.





Discussion

The notion that allylmetal intermediates signify nucleophilic reagents derives from main group chemistry. Transition metals offer the opportunity to invert that "normal" reactivity pattern. Most earlier work has centered on palladium, but this study reveals that molybdenum complexes offer many opportunities. In the stoichiometric reactions, it is interesting to note that the alkylations of 8 and 9 were substantially improved by the addition of triphenyl phosphine. An explanation arises in considering the possible inducement of the chloride to ionize upon adding the phosphine.[14,22,35-37] The resultant cationic complexes 8a and 9a should be much more electrophilic which should result in enhanced ease of alkylation. A similar effect has been noted in the palladium catalyzed reactions. An

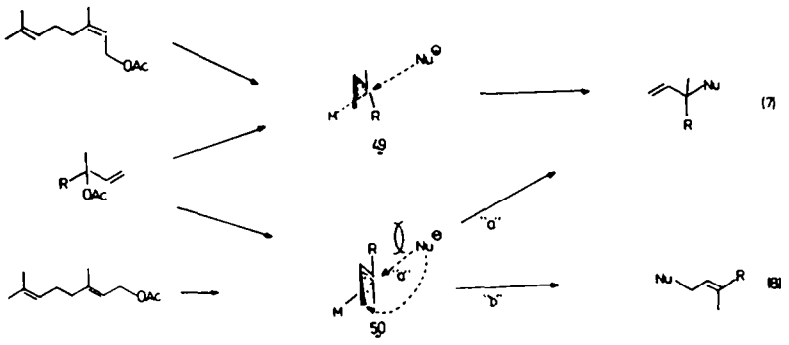


alternative explanation considers the relative stability of olefin-molybdenum complexes which frequently require oxidation of the metal to effect decomplexation.[22] The phosphine might facilitate displacement of an olefin from molybdenum and thereby enhance the rate of olefin-olefin exchange -- a critical aspect of any catalytic cycle.

In considering the regioselectivity exhibited by each of the transition metal complexes toward a variety of nucleophiles, several contributing factors must be weighed. These factors include 1) the steric hindrance of the regioisomeric alkylation sites, 2) the reactivity of the nucleophile, 3) the steric hindrance of the nucleophile, 4) the charge distribution in the intermediate pi-allyl complex and, 5) the relative stability of the two possible metal-olefin complexes.

That very different products arise by simply changing the catalyst implies that the magnitude of each contribution is quite different for molybdenum, palladium[3] and tungsten.[8] Palladium, by far the most thoroughly studied of the catalysts, exhibits highly regioselective C-C bond formation at the less hindered position of the pi-allyl intermediate regardless of the nucleophile in spite of the anticipated charge effect in the intermediate π-allyl cationic complexes favoring attack at the center

bearing the lowest electron density, i.e. the more substituted position. It appears that the steric factors associated with the nucleophile and substrate, i.e. factors 1 and 3, are more important than factors 2, 4 and 5. Two published apparent exceptions to this generalization do follow the course predicted by charge effects. The alkylation of 2-acetoxy-2-methylbut-3-ene[13,38] and neryl acetate[3,13] with dimethyl malonate anion both give large amounts of attack at a teriary carbon atom. Consideration of the trajectory of nucleophilic attack on the intermediate π-allylpalladium cationic complexes as depicted in eq. 7 may account for

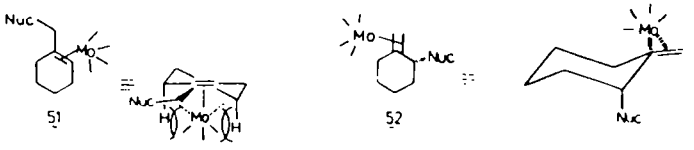


these results. In the complex 49 ($M=^{+}PdL_2$), the three carbons of the allylic fragment and the two substituents are approximately in a single plane so that steric hindrance to attack at the tertiary center is minimized. Thus, charge effects dominate. However, the geranyl derived complex 50 ($M=^{+}PdL_2$) leads to preferential attack at the primary carbon (eq. 8). The fact that the trajectory of the incoming nucleophile brings that attacking species closer to the syn substituent, which is methyl in 49 but is homoisoprenyl in 50, leads to the larger unfavorable non-bonded interactions in the latter case for attack at the tertiary position. Once again, steric factors may dominate in the palladium reaction. An alternative explanation invoking complexation of the remote double bond in the intermediate complex 50 affecting regioselectivity has also been advanced.[3,13]

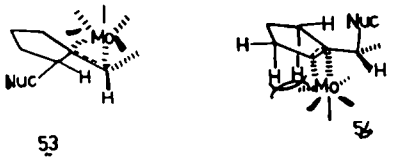
Contrary to normal displacement chemistry, linalyl acetate, which contains a leaving group at a tertiary carbon, reacts more rapidly than geranyl acetate, which possesses a leaving group at a primary carbon. This reactivity pattern resembles what would be expected for a S_N1 type transition state. Although the molybdenum catalyst might be thought to have some Lewis acidity[39] that might promote a S_N1 type reaction, the stereochemistry whereby the metal initiates ionization with inversion of configuration disputes this notion. A more likely explanation lies in the easier ability of low valent metals to coordinate a mono- versus a disubstituted double bond. By initiating a displacement of the leaving group by a non-bonding electron pair in an intramolecular sense, steric hindrance that inhibits displacement at a tertiary center is minimized. Thus, the key feature that controls the rate of ionization is the weaker bond of the leaving group at a tertiary compared to a primary carbon. The same trend is observed in palladium catalyzed reactions.

From the results obtained thus far, it appears that steric factors are somewhat less important in the molybdenum catalyzed reactions. If small,

highly reactive nucleophiles are used, alkylation occurs at the more hindered carbon, whereas less reactive and/or bulky nucleophiles follow the pathway chosen by palladium(0) catalyzed reactions. For example, a large and highly nucleophilic species such as dimethyl methylmalonate leads to attack at the less hindered carbon even when electronic factors may oppose such a regioselectivity as in 38 and 40. On the other hand, a sterically less demanding but approximately equally nucleophilic species such as dimethyl malonate reacts at the more substituted position even though the product presumably is the thermodynamically less stable one. Consider the formation of 22 and 25 which stands in contrast to the palladium catalyzed reactions. In a comparison of relative stability between methylenecyclohexane and 1-methylcyclohexene the latter is found to be more stable by 2.89 kcal,[40] presumably due to $A^{1,3}$ strain[41]. Yet, alkylation of 21 leads only to a methylene-cyclohexane derivative 22 which, not only requires attack at the more hindered center, but also gives the less thermodynamically stable organic product. The product of alkylation is, however, not a free organic compound but an olefin-molybdenum complex. Comparing the two complexes 51 and 52 derived from alkylation reveals that the former is more hindered, both because the olefin fragment is more highly substituted and, because interactions between the axial ring C-H'S and the metal template are more likely than in 52. Furthermore, complexation of an olefin to a metal allows a rehybridization to occur[145] which would serve to relieve the angle strain created in forming an olefin exocyclic to a ring and also to decrease the 1,3 interactions. In addition, back-bonding from the metal to the olefin is more favorable with olefins bearing fewer alkyl substituents as in 52. All of these effects should lower the transition state energy leading to 52 compared to that leading to 51.



Alkylation of 18 to produce 19 and 20 is slightly less selective since the degree of substitution in the product olefins is now identical and also attack at either position results in the formation of a tertiary carbon. Nevertheless, in the presumed initial metal complexes with 19 and 20, a decrease in across-ring interactions and a decrease in apparent $A^{1,3}$ strain upon complexation favors the endocyclic attack of some nucleophiles, eg. 53 is favored over 54.



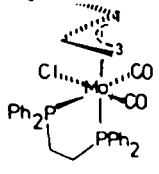
The contrast between the molybdenum and palladium catalyzed reactions of geranyl acetate is quite instructive (eq. 8). Whereas, the increased steric strain in path "a" in 50 may be responsible for redirecting the nucleophile to the less substituted terminus in the palladium reaction, the enhanced importance of the factors associated with the metal in the

molybdenum catalyzed reaction follows our initial predictions. If the distal olefin coordination does play a role in the palladium reaction, the fact that the molybdenum catalyst is now likely coordinatively saturated would also explain the difference between the two catalysts in this case. Nevertheless, the fact that many other substrates also exhibit the same divergence where there is no possibility of this remote binding suggests the latter may not be the dominating factor if it exists at all for molybdenum.

The fact that these trends are unperturbed in the cases of the ester substituted substrates demonstrates the ability of the metal to dominate over substituents that normally are extremely strong directors in their own right. It is interesting to note the difference in reactivity of 36 and 37, both which fail to react, and 38 which reacts easily. The higher reactivity of 38 may stem from the electron acceptor properties of silicon which should lower the energy of the LUMO. The initial coordination of the low valent metal with the olefin depends on the π-acceptor capabilities of the latter. The lower the energy of the LUMO, the better the olefin is as a -acceptor. If, indeed, electron-poor olefins are better substrates due to their enhanced initial complexation, 39, and 40 should be better substrates than their γ,δ-unsaturated counterparts. This notion appears to be true.

A frontier orbital approach may partially rationalize this regioselectivity.[43] In a series of calculations conducted by Curtis, the LUMO coefficients for C(1) and C(3) in 8 of -0.28 and 0.32, respectively, predict a slight bias for alkylation at C(3). Rotation of the allyl group to that shown in 8a to minimize steric interactions changes the coefficients to -0.19 and 0.30 which would result in enhanced selectivity. Examination of 9 reveals that the coefficients are roughly equal and, therefore, an increased tendency for attack at C-1 should result.

Extending this approach to the $Mo(CO)_6$ catalyzed reactions is frustrated by our lack of knowledge of the catalytically active species. Attempts to generate a presumed species such as 55 by reaction of an



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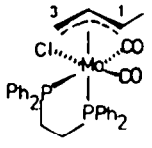
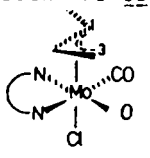
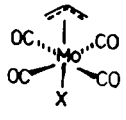


8a



9

allylsilane with tetracarbonylmolybdenum dichloride[44] have led to an oligomeric complex instead.[45] Qualitatively, it appears that σ-donating ligands as in 9 enhance C(1) attack compared to ligands that are better



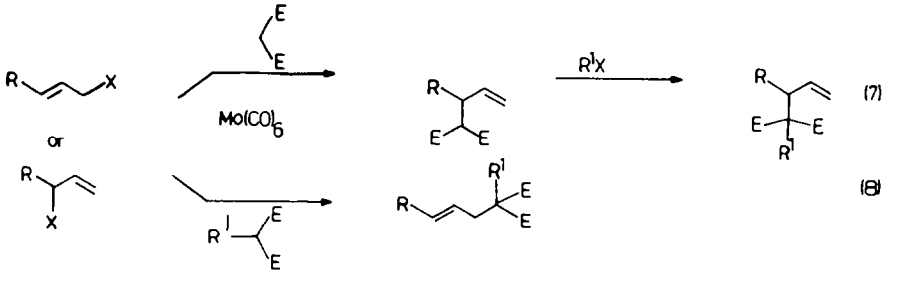
55

π-acceptors as in 8. Since all of the ligands in molybdenum hexacarbonyl are clearly strong π-acceptors, a frontier orbital picture predicts that these should be substituted by σ-donating ligands in the malonate anion reactions to justify the high propensity for C(1) attack. The special effects of BSA as well as malonate anion[46] itself may result from its

serving as a ligand to molybdenum as well as a base. The rate differences between malonate (slower) and methylmalonate (faster) anions also support the notion that attack of the malonate anions but not methylmalonate anion on molybdenum decreases the reactivity of the molybdenum templates. Further discussion must await more definitive evidence for the exact structure of the catalytically active species.

On the other hand, the reactions of hindered nucleophiles such as substituted malonates and beta-ketoesters appear more straightforward. The larger steric interactions simply override the electronic preferences to yield the alkylation product from reaction at the less substituted carbon atom. Non-substituted beta-ketoesters and both substituted and non-substituted 1,3-diketones are saddle points in the reaction and may lead to either regioisomer. In the first place, they have steric bulk intermediate between the above-mentioned cases, but, more importantly, they are of lower reactivity due to the increased stability of their anions. Whereas a product development control argument can be put forth in the reaction of hindered nucleophiles, more subtle factors must be considered with these "intermediate" nucleophiles.

Molybdenum catalysts now permit excellent selectivity for alkylation at a more hindered terminus of an allyl fragment with dimethyl malonate anion independent of the regioisomeric nature of the starting material in a very general sense. As noted above, the molybdenum template can dominate over strong directing substituents in the substrate. Such an ability of external templates to overwhelm normal reactivity patterns of organic



substrates should prove to be a valuable tool in synthesis. Total control in forming substituted malonates is now possible. By using the parent malonate followed by alkylation, regioselection for the more substituted allyl isomeric product exists (eq. 7). Direct alkylation with an alkylmalonate provides selection for the less substituted allylic product (eq. 8). While other nucleophiles may sometimes show this trend as does 23, this regioselectivity cannot be reliably predicted at the moment and must be determined for each case. Other catalysts may provide an opportunity for expanding the scope of this control. Such efforts continue in our laboratories as well as elsewhere.

EXPERIMENTAL

General

Unless otherwise noted all reactions were run under a positive pressure of dry nitrogen in flasks which were flame dried and allowed to cool under a stream of nitrogen. ^1H NMR spectra were recorded in $CDCl_3$ or C_6D_6 which was dried over 4A° molecular sieves. As noted within each procedure they were recorded on a IBM WP200 at 200 MHz or on a Bruker WH270 at 270 MHz

with the chemical shifts reported in δ units, parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designed as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants are reported in hertz, Hz. ^{13}C NMR spectra were recorded in $CDCl_3$ at 50.10 MHz on a JEOLCO-FX-200 spectrometer and are reported in ppm relative to the center line of a triplet at 77.0 ppm which is attributed to the solvent. Infrared spectra were recorded on a Beckmann Acculab 7 or a Perkin Elmer 1420 as neat oils on sodium chloride plates or as deuterochloroform solutions in 0.1 mm path length sodium chloride cells run against deuterochloroform in the reference beam and are reported in cm^{-1}. Mass spectra were recorded on an AEI-MS902 or Kratos MS80 at 30 or 70 eV ionizing current. Melting points were obtained on a Thomas Hoover apparatus in open capillary tubes and are uncorrected. Microanalyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan or Galbraith Microanalytical Laboratories, Knoxville, Tennessee. VPC analyses were performed on a Varian Model 3700 with a flow rate of 30ml/min measured at the initial temperature for those systems studied with a temperature program. Integrations were carried out on a Hewlett Packard 3390A connected to the gas chromatograph.

For reactions requiring solvents, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), ethyl ether, toluene and benzene were distilled from sodium and benzophenone. Pyridine, methylene chloride, acetonitrile, benzene-d_6 (C_6D_6) and dimethylformamide (DMF) were distilled from calcium hydride. Sodium hydride was employed as a 60% dispersion in mineral oil and weights are recorded for the dispersion. All palladium (0) catalysts were transferred to flame dried vials in a glove bag, then dissolved in freshly distilled THF and transferred to the reaction via syringe techniques.

Flash chromatography following the method of Still [98] employed Merck EM silica gel 60 (230-400mesh) with the elution solvent described in the experimental section giving an R_F=0.25 for the fastest eluting compound.

Molybdenum hexacarbonyl (Mo-c) was used as received from Aldrich Co. All other reagents were distilled before use and their purity checked by 100 MHz NMR spectroscopy. Evaporation *in vacuo* refers to removal of solvent with a Buchi Brinkman rotary evaporator using a water aspirator.

Preparation of $Mo(C_4H_7)(Cl)(dppe)(CO)_2$(8)

Following the general procedure of Faller[23] a mixture of molybdenum hexacarbonyl (650 mg, 2.5 mmol) in acetonitrile (5mL) was heated at reflux for 18h. To the cooled solution was added crotyl chloride (226 mg, 2.5 mmol). After heating to reflux for 15 min., the solution was cooled and 1,2-bis(triphenylphosphino)ethane (1.0 gm, 2.5 mmol) added and the mixture stirred for 1h. Filtration of the mixture provided a solid which was recrystallized from hexane-benzene yielding the title compound, 1.06 gm (67%) dec.pt. 198°C, as an orange solid. ^1H NMR (270 MHz, $CDCl_3$) 7.80-7.30 (20H, m), 3.90 (1H, m), 3.58 (1H,m), 3.10-2.00 (5H,m), 1.98 (3H,d,J=7Hz), 1.70 (1H,d,J=10 Hz), IR ($CDCl_3$) 3150, 3060, 1938, 1840, 1600. Anal. Calc. for $C_{32}H_{31}ClMoO_2P_2$: C, 59.97; H, 4.87. Found: C,60.24; H, 4.94.

Preparation of $Mo(C_4H_7)(Cl)(bipy)(CO)_2$ (9)

Following a modified procedure of Brisdon,[16] a flask containing Mo-c (1.32 gm, 3.0 mmol), 2,2'-bipyridyl, toluene (20 mL) and crotyl chloride (4.8 mL, 5.0 mmol) was heated at reflux for 3 h. Upon cooling, a red solid was produced which was filtered and then dried, under vacuum, providing the title compound 1.82g (90%),dec pt. 212°C. This highly insoluble material was characterized by IR and combustion analysis only. IR 3050, 1928, 1847, 1605, 1460, 1443, 1310, Anal. Calc. for $C_{16}H_{15}ClMoN_2O_2$: C, 48.18; H, 3.83. Found: C,47.90, H; 4.13.

Alkylation of (10) with 2-Carbomethoxycyclopentanone

2-Carbomethoxycyclopentanone (56 mg, 0.44 mmol) was added to a slurry of sodium hydride (17 mg, 0.43 mmol) in THF. To the solution produced was added 1,2-bis(diphenylphosphino)ethane (160 mg, 0.4 mmol) and complex 10 (270 mg, 0.4 mmol). The mixture was heated at reflux for 3 h, the solvent was removed under reduced pressure and the resulting oil taken up in ether and washed twice with 10% aqueous potassium hydroxide. The organic phase was dried over magnesium sulfate, the solvent was removed *in vacuo*, and the resulting oil purified by flash chromatography (5:1 hexane:ether) to yield 2-(2-propenyl)-2-carbomethoxycyclopentanone[47] (127 mg, 70%).

Alkylation of (8) with 2-Carbomethoxycyclopentanone

To a solution of 4.0 mmol of the sodium salt of 2-carbomethoxycyclopentanone in 10 mL of THF at room temperature was added the pi-allyl complex 8 (1.29 gm.,2.0 mmol) and triphenylphosphine (1.048 gm. 4.0 mmol). This mixture was heated at reflux for 6h and then the crude reaction mixture diluted with ether. The organic layer was washed with 10% aqueous potassium hydroxide, and aqueous hydrochloric acid and then dried

($MgSO_4$). Flash chromatography (2:1 hexane:ether) followed by bulb-to-bulb distillation (0.5 mm Hg at 110°) provided a clear oil, (275 mg, 70%). ^1H NMR (200 MHz $CDCl_3$): δ 5.55 (1H,m), 5.30(1H,m), 3.70(3H,s), 2.50(4H,m), 1.95(4H,m), 1.63(3H,d, J=7 Hz). ^{13}C NMR ($CDCl_3$): δ213.2, 170.7, 128.9, 126.9, 124.9, 124.1, 59.6, 37.3, 36.1, 31.5, 30.2, 19.0, 18.9, 17.2, 12.2. IR (neat): 1762, 1737, Calc. for $C_{11}H_{16}O_3$: 196.1095. Found: 196.1100.

Alkylation of 9 with 2-carbomethoxycyclopentanone.

To a solution of 1.5 mmol of the sodium salt of 2-carbomethoxycyclopentanone in 10 mL of THF was added complex 9 (200 mg, 0.5 mmol) and triphenylphosphine (264 mg, 0.5 mmol). After heating the mixture at reflux for 20h, work-up consisted of diluting with ether and washing the organic layer with 10% aqueous hydrochloric acid, 10% aqueous potassium hydroxide (3x), followed by drying ($MgSO_4$). Evaporation of solvent followed by flash chromatogaphy (4:2 hexane:ether) yielded 70.0 mg (70%) of a clear oil. VPC (5% SE-30 on Chrom W, 80/100 mesh, 213 cm x 3.2 mm, T=100° 2 min, 15°/min to 180°) revealed 4 peaks in a 2:3.9:6.5:1 ratio [retention times 6.8, 7.5 min (2° alkylation products), 8.2, 8.3 min, (cis, trans 1° alkylation products]. These compounds were identified by comparision to authentic samples.

General Procedures for Molybdenum Catalyzed Alkylations.

(A) Toluene was added to a flask containing sodium hydride (washed two times with hexane) following by dropwise addition of the nucleophile to the rapidly stirred suspension. The thick slurry was heated to 100°C for 10 min., cooled to room temperature, then the allylic acetate added followed by the catalyst (5-20 mol %). The reaction was then heated at reflux until t.l.c. showed disappearance of starting material. Work-up consisted of diluting the mixture with ether and then pouring into a separatory funnel containing ether-10% aqueous sodium hydroxide. The organic layer was extracted three times with 10% aqueous sodium hydroxide and then one time with saturated aqueous sodium hydrogen sulfate. Drying over magnesium sulfate followed by evaporation of the solvent under reduced pressure yielded yellow-brown oils. Purification was performed using bulb-to-bulb distillation when possible or flash chromatography. (B) To a flask containing toluene and the nucleophile was added O,N-bis(trimethylsilyl)acetamide and the mixture heated to reflux for one hour. After cooling the solution to room temperature, addition of the allylic acetate and catalyst (5-20 mol %) was followed by heating the reaction to reflux until t.l.c. indicated disappearance of starting material. Work-up of the reaction involved diluting with ether and washing the organic phase once with saturated aqueous sodium hydrogen sulfate, then three times with 10% aqueous sodium hydroxide. Drying over magnesium sulfate followed by evaporation of the solvent under reduced pressure yielded yellow-brown oils. Purification involved bulb-to-bulb distillation or flash chromatography.

Alkylation of Crotyl Acetate Using $Mo(CO)_4$bipy(Mo-bipy) as catalysts

Following general procedure A, 228 mg. (2.0 mmol) of crotyl acetate, 803 mg (5.5 mmol) of 2-carbomethoxycyclopentanone, 200 mg (5.0 mmol) of sodium hydride and 75 mg (10 mol%) of Mo-bipy in 6 mL of toluene were combined and heated at reflux for 48 h. Work-up followed by flash chromatography yielded 125 mg (40%) of alkylated products. VPC analysis of the crude reaction mixture showed the ratio of 2°:1° to be 1.4:1. From the vpc analysis of the crude reaction a large (30%) amount of starting material remained but this was not isolated. ^1H NMR (2° alkylation products): δ 6.50-6.30(1H,m), 6.00(2H,m,), 3.69(1.5H,s), 3.67(1.5H,s), 3.09 (1H, d, J=7.4 Hz), 2.4-1.80 (8H, m), 0.98(1.5H,d, J=6.8 Hz), 0.90 (1.5H, d, J=6.8 Hz). IR ($CDCl_3$): 1734, 1709, cm^{-1} Anal. Calc. for $C_{11}H_{16}O_3$: 196.1098. Found: 196.1100.

Preparation of Methyl 1-(2'-propen-1'-yl)-2-oxocyclopentane-carboxylate (11)

Alkylation with excess Allyl Acetate.

Following general procedure A, allyl acetate (405 mg, 4.05 mmol), 2-carbomethoxycyclopentanone (394 mg, 2.7 mmol), sodium hydride (100 mg, 2.7 mmol) and Mo-bipy (100 mg, 10 mol%) in dioxane (6mL) were heated at reflux for 24 h. Standard work-up and flash chromatography (3.1 hexane:ether) provided the title compound as a clear oil, 324mg (66% yield). The identical experiment in toluene also provided 324 mg (66% yield) of product.

Alkylation in Toluene with Excess Nucleophile.

Following general procedure A, sodium hydride (300 mg, 8.10 mmol), 2-carbomethoxycyclopentanone (1.36 gm, 10.0 mmol), allyl acetate (540 mg, 10.0 mmol), and Mo-bipy (200 mg, 10 mol%) in toluene (6 mL) gave, after heating 14 h at reflux and work-up, 905 mg (93% yield) of product.

Preparation of 2-(2'-butenyl)-2-carbomethoxycyclopentanone (12,13)

Following general procedure A, crotyl acetate (224mg, 2.0 mmol), sodium hydride (150 mg, 3.75 mmol), 2-carbomethoxycyclopentanone (584 mg, 4.0 mmol) and Mo-c (105 mg, 20 mol%) in toluene (5mL) gave, after heating at reflux for 8 h and standard work-up, 294 mg (75% yield) of the title compound as a clear oil. The spectral data were identical in all respects to the product from the alkylation of the crotyl molybdenum complex with 2-carbomethoxycyclopentanone. VPC analysis (5% SE-30 on Chrom W, 213cm x 3.2cm, T=100°-2 min., 15°/min to 180°) showed 2 peaks in a ratio of 10:1 (T=8.2, 8.3 min) which by comparison to the ^{1}H NMR spectra reported earlier were shown to be the trans and cis isomers of the title compound.

Alkylation of Cinnamyl Acetate using Mo-bipy as catalyst.

Using general procedure A, cinnamyl acetate (500 mg, 3.0 mmol), 2-carbomethoxycyclopentanone (730 mg, 5.0 mmol), sodium hydride (190 mg, 4.8 mmol), toluene (6 mL) and Mo-bipy (273 mg, 25 mol%) gave, after heating at reflux for 16 h and work-up 204 mg (28% yield) of 16 as a clear oil, R_f=0.51, and 320 mg (42% yield) of 15 as a clear oil R_f=0.58 (1:1 hexane:ether). Data is presented below for the major diastereomer. The minor diastereomer exhibited signals at 4.27 ppm (J=8 Hz) and 3.54 ppm (3H,s) assigned to the benzylic hydrogen and methyl ester. The ratio of diastereomers was found to be 1:1.3 by integration of the signals at 4.39 and 4.27 ppm. The data for the minor diastereomer of 15 is shown below since only this compound could be obtained free of other isomers. ^{1}H NMR (200 MHz $CDCl_3$): δ 7.22(5H, m), 6.10(1H, dt, J=18.1,8.8 Hz), 5.19(1H, d, J=8.8 Hz), 5.14(1H, d, J=18.1 Hz), 4.39(1H, d, J=8.8 Hz), 3.70(3H, s), 2.69(1H, m), 2.13(2H, m), 1.57(3H, m). ^{13}C NMR ($CDCl_3$): δ 212.7, 169.5, 138.9, 136.3, 129.7, 128.1, 126.9, 117.4, 65.8, 52.7, 52.6, 38.5, 28.3 19.4. IR(neat): 1762, 1735, 1648, 1609, 1503 cm^{-1} Anal. Calc. for $C_{16}H_{18}O_3$: 258.1251. Found: 258.1255.

Preparation of 2-(3'-phenyl-2'propenyl)-2- carbomethoxycyclopentanone (16)

Following general procedure A, cinnamyl acetate (250 mg, 1.5 mmol), 2-carbomethoxycyclopentanone (438 mg, 3.0 mmol), sodium hydride (100 mg, 2.5 mmol), Mo-c (60 mg, 15 mol%) and toluene (5 mL) gave, after heating at reflux for 8 h and work-up, 250 mg (69% yield) of 16 as a clear oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.25 (5H, m), 6.45 (1H, d, J=15.8 Hz), 6.10(1H, dt, J=7.1, 15.8 Hz), 3.70(3H,s), 2.80(1H, dd, J=15.8,7 Hz), 2.16-1.80 (7H, m). ^{13}C NMR ($CDCl_3$): δ 203.2, 171.1, 136.8, 133.8, 128.2, 127.1, 125.9, 124.3, 59.9, 52.2, 37.7, 36.8, 31.9, 19.2. 16.2. IR(neat): 1760, 1734, 1608, 1507, 1458 cm.$^{-1}$ Anal. Calc. for $C_{16}H_{18}O_3$: 259.1252. Found: 258.1255.

Alkylation of 1-(1-Acetoxy-1'-ethyl)cyclopentene (18) with Dimethyl Malonate

Mo-bipy as Catalyst

Following general procedure A, allylic acetate 18 (60 mg, 0.35 mmol), dimethyl malonate (70 mg, 0.53 mmol), sodium hydride (20 mg. 0.50 mmol), and Mo-bipy (20 mg, 10 mol%) in toluene (2 mL) gave, after heating at reflux for 72h and work-up, 35 mg (45% yield) of product and 6 mg (8%) of recovered starting material. The product has spectral data identical to an authentic sample.[3]

Mo-c as Catalyst:

Following general procedure A, allylic acetate 18 (166 mg, 1.0 mmol), sodium hydride (72 mg. 1.8 mmol), dimethyl malonate (264 mg, 2.0 mmol), and Mo-c (52 mg, 20 mol%) in toluene (3 mL) gave, after heating at reflux for 48 h, 154 mg (69% yield) of a clear oil identified as the alkylated products and 32 mg (21%) of recovered starting material. ^{1}H NMR (200MHz, C_6D_6): δ 5.35(1H,m), 3.69 (0.15 H, d,J=9 Hz), 3.60 (0.85H, d, J=9 Hz), 3.32 (3H, s), 3.30 (3H, s), 2.90-1.40 (7H, m), 1.48 (1.28H, d, J=6.7 Hz), 1.47 (1.27H, d, J=6.6 Hz), 1.11 (9.45H, d, J=7 Hz). ^{13}C NMR ($CDCl_3$): δ 168.6, 168.3, 143.1, 142.9, 118.0, 117.3, 54.9, 53.8, 51.5, 43.6, 39.4, 32.3, 30.1, 29.9, 27.9, 23.9, 22.5, 14.2. IR (neat): 1739cm.$^{-1}$ Calc. for $C_{12}H_{18}O_4$: 226.1200. Found: 226.1206.

Preparation of Dimethyl (1-methylenecyclohexan-2-yl)malonate (22)

Using procedure A, allylic acetate 21 (154 mg, 1.0 mmol), dimethyl malonate (264 mg, 2.0 mmol), sodium hydride (75 mg, 1.8 mmol), and Mo-c(40 mg, 15 mol%) in 3 mL of toluene gave, after heating and work-up, 160 mg (76% yield) of 22 as a clear oil. ^{1}H NMR(200 MHz, CDl_3): δ4.73 (0.5H, s), 4.60 (0.5H, s), 3.79 (3H, s), 3.75 (1H, d, J=6 Hz), 3.70 (3H, s), 2.98 (1H, m), 2.15 (2H ,m), 1.55 (6H, m). ^{13}C NMR ($CDCl_3$): δ168.7, 168.5, 148.9, 107.9, 53.9, 52.0, 43.2, 33.9, 30.8, 28.1, 23.2. IR(neat): 1770, 1745, 1648 cm^{-1} Anal. Calc. for $C_{12}H_{18}O_4$: C, 63.68; H,8.02. Found: C, 63.70; H, 8.21.

Preparation of 2-(1'-Cyclohexenylmethyl)-2-carbomethoxycyclopentanone (24):

Following general procedure A, allyl acetate 21 (154 mg, 1.0 mmol), 2-carbomethoxycyclopentanone (284 mg, 2.0 mmol), sodium hydride (70 mg, 1.75 mmol), and Mo-c (53 mg, 20 mol %) in 3 mL of toluene gave, after heating 6h at reflux, and work-up, and flash chromatography (2:1 hexane: ether) 215 mg (82% yield) of 24 as a clear oil. ^{1}H NMR (200 MHz, $CDCl_3$):δ 5.48 (1H, br s), 3.70 (6H, s), 2.73 (1H, d, J=13 Hz), 2.44 (1H, m), 2.33 (2H, m), 2.21 (1H, d, J=13 Hz), 1.95 (6H, m), 1.78 (2H, m), 1.52 (4H, m). ^{13}C NMR($CDCl_3$): δ 213.6, 170.7, 133.0, 125.7, 59.9, 51.9, 41.6, 37.2, 31.4, 28.8, 25.0, 22.5, 21.7, 18.9. IR(neat): 1759, 1730, cm^{-1} Anal. Calc. for $C_{14}H_{20}O_3$: 236.1407. Found: 236.1412.

Preparation of Methyl 2-(2'-methylenecyclohex-1'-yl)-5-methyl-3-oxohexanoate (25)

Following general procedure A, substrate 21 (154 mg, 1.0 mmol), sodium hydride (72 mg, 1.8 mmol), methyl 2-oxo-5-methylhexanoate (320 mg, 2.0 mmol), and Mo-c(40 mg, 15 mol%) in 4 mL of toluene gave, after heating at reflux for 10 h and bulb-to-bulb distillation (0.01 mm Hg at 140°), 230 mg(91% yield) of 25 as a clear oil. ^{1}H NMR(100 MHz, $CDCl_3$):δ4.71 (1H, s), 4.58 (1H, s), 4.49 (1H, s), 3.89 (0.5H, d, J=5 Hz), 3.83 (0.5H, d, J=5 Hz), 3.72 (1.5H, s), 3.68 (1.5H, s), 3.05 (1H, m), 2.35 (1H, d, J=7 Hz), 2.40 (1H, d, J=7 Hz), 2.15 (2H, m),1.55 (6H, m), 0.90 (3H, d, J=6 Hz,) 0.87 (3H, d, J=6Hz). ^{13}C NMR($CDCl_3$): 203.4, 202.9, 168.9, 168.6, 149.3, 148.7, 108.3, 107.6, 61.8, 61.7, 51.8, 51.6, 50.5, 42.9, 34.1, 34.0, 31.3, 30.7, 28.3, 28.2, 23.9, 23.6, 23.4, 23.2, 22.2. IR(neat): 1750, 1725, 1650, cm^{-1} Anal. Calc. for $C_{15}H_{24}O_3$: C, 71.37; H, 9.59. Found: C, 71.61; H, 9.70.

Preparation of Methyl 3, 7-dimethyl-3-ethenyl(2-carbomethoxy) oct-6-enoate (28)

With Sodium Hydride as Base

Following general procedure A, linalyl acetate 22 (198 mg, 1.0 mmol), dimethyl malonate (264 mg, 2.0 mmol), sodium hydride (72 mg, 1.8 mmol), and Mo-c(50 mg, 20 mol%) in toluene (3 mL) gave, after heating at reflux for 3 h and work-up, 205 mg (80% yield) of a clear oil. VPC analysis (145°, SE 30, 259 cm x 0.32 mm column) showed 3 peaks corresponding to 3°:1°(Z):1°(E) in a ratio of 85:3:12. Identification of the isomers involved comparison to authentic samples.

With BSA as Base

Similarly following general procedure B, linalyl acetate 22 (50 mg, 25 mmol), dimethyl malonate (66 mg. 0.50 mmol), BSA (91 mg, 0.45 mmol), and Mo-c(10 mg, 12 mol%) in toluene gave, after heating at reflux for 1.5 h and work-up, 55 mg (82% yield) of product. VPC analysis as above provided at 97:0.5:2.5 ratio of 3°:1°(Z):1°(E) alkylation products.

Alkylation of Geranyl Acetate with Dimethyl Malonate

Following general procedure A, geranyl acetate 26 (196 mg, 1.0 mmol), dimethyl malonate (264 mg, 2.0 mmol), sodium hydride (70 mg, 1.80 mmol) and Mo-c (50 mg, 20 mol%) in 4 mL of toluene were heated at reflux for 20h. The reaction mixture was cooled to rt and a second portion of catalyst (50 mg, 20mol%) was added and the mixture heated at reflux a further 28h. Standard work-up and flash chromatography as usual provided the alkylation products (100 mg, 40%) and recovered starting material (50 mg, 25%). VPC analysis of the alkylation mixture provided an 85:2:13 ratio of 3°:1°(Z):1°(E).

Alkylation of Allylic Acetate 30

With 2,4- Pentanedione, Preparation of 31:

Following procedure B, allylic acetate 30 (228 mg, 1.0 mmol), 2,4-pentanedione (200 mg, 2 mmol), BSA (335 mg, 1.75 mmol), toluene (3 mL) and Mo-c(40 mg, 15 mol%) in 3 mL of toluene gave, after heating at reflux for 19 h and work-up, 90 mg (34% yield) of 31 as a clear oil. ^{1}H NMR(200 MHz, $CDCl_3$): δ 4.90 (1H, br s), 3.65 (1H, t, J=7 Hz, diketone form), 2.95 (2H, d, J=7 Hz,enol form), 2.2 (6H, s, diketone form), 0.88 (9H, s, diketone form), 0.85 (9H, s, enol form). IR(neat): 1760, 1720, 1700 cm-1.

With 3-Methyl-2,4-pentanedione. Preparation of 32:

Following procedure B, allylic acetate 30 (228 mg, 1.0 mmol), BSA (325 mg, 1.6 mmol), 3-methyl-2,4-pentanedione (205 mg, 1.8 mmol) and Mo-c (30 mg, 11 mol%) in 3 mL of toluene gave, after heating at reflux for 1 h and purification by bulb-to-bulb distillation (0.05 mm Hg at 120°), 283 mg (84% yield) of 32 as a clear oil. ^{1}H NMR(200 MHz, $CDCl_3$): δ 4.81 (1H, t, J=7 Hz), 2.61 (1H, d, J=8 Hz), 2.55 (2H, d, J=7 Hz), 2.10 (3H, s), 2.09(3H, s), 0.90-2.10 (8H,br Vs), 0.85 (9H, s). ^{13}C NMR($CDCl_3$): δ 206.4, 142.9, 114.0, 66.3, 48.0, 36.9, 31.9, 31.8, 28.9, 28.3, 28.0, 27.2, 26.2, 17.7.

IR(neat): 1761, 1700 cm.$^{-1}$ Anal. Calc'd for $C_{18}H_{30}O_2$: 278.2238. Found: 278.2247.

With Methyl 5-methyl-2-oxohexanoate: Preparation of 33:

Following procedure A, allylic acetate 30 (228 mg, 1.0 mmol) sodium hydride (72 mg, 1.8 mmol), toluene (4 mL,) methyl 5-methyl-2-oxohexanoate (320 mg, 2.0 mmol) and Mo-c (20 mg, 7.5 mol%) in 4 mL of toluene gave, after heating at reflux for 3.5 h and work-up, 258 mg (79% yield) of 34 as a clear oil. ^{1}H NMR(200 MHz,$CDCl_3$):δ 4.95 (1H, t, J=7 Hz), 3.70 (3H, s), 3.45 (1H, t, J=6 Hz), 2.70-1.50 (9H, m), 0.90 (6H, d, J=6.5 Hz), 0.80 (9H, s). ^{13}C NMR($CDCl_3$): δ 204.1, 169.8, 142.5, 116.2, 59.5, 59.4, 51.9, 51.0, 48.3, 36.9, 32.3, 29.1, 28.5, 27.5, 26.1, 23.9, 22.4, 22.3. IR(neat): 1750, 1715 cm.$^{-1}$ Anal. Calc'd for $C_{20}H_{34}O_3$: 322.2499. Found: 322.2508.

With Dimethyl Methylmalonate: Preparation of 34:

Using general procedure B, allylic acetate 30 (228 mg, 1.0 mmol), BSA (375 mg, 1.8 mmol), dimethyl methylmalonate (292 mg, 2.0 mmol), and Mo-c (25 mg, 10 mol%) in 3 mL of toluene gave, after heating for 1.5 h and work-up, 245 mg (79% yield) of 34. ^{1}H NMR(200 MHz, C_6D_6): δ 5.18 (1H, t, J=7 Hz), 3.48 (6H, s), 2,88 (2H, d, J=7 Hz), 2.62-1.00 (11H, m). (1.52 (3H, s), 0.80 (9H, s). ^{13}C NMR($CDCl_3$):δ172.3, 143.5, 114.2, 77.2, 53.8, 52,0, 48.3, 37.1, 33.2, 29.1, 28.5, 28.3, 27.4, 19.6. IR (neat): 1739 cm.$^{-1}$ Anal. Calc'd for $C_{18}H_{30}O_4$: 310.2136. Found: 310.2145.

Preparation of Methyl 4-acetoxyhept-2E-enoate (39)

Piperidine (593 mL, 6.0 mmol) was added dropwise to a solution of pentanol (636 mg, 6.0 mmol) and methyl 2-phenylsulfinyl acetate (1.0 gm, 5.1 mmol) in acetonitrile (10 mL) at 0°. After stirring the reaction at r.t for 5 h, the solution was diluted with ether and washed with 10% aqueous hydrochloric acid and twice with water. Drying the organic phase (magnesium sulfate) followed by evaporation of ether in vacuo yielded an oil. Flash chromatography (2:1 hexane:ether to 1:1 hexane:ether) of the oil provided methyl 4-hydroxyhept-2E-enoate (620 mg, 76% yield) whose NMR spectrum was identical to that reported by Tanikaga.[34]

A solution of the alcohol prepared above (750 mg, 4.7mmol), DMAP (100 mg, 0.82 mmol) and pyridine (850 mg, 9.1 mmol) in ether (20 mL) were cooled to 0°. Addition of acetyl chloride (835 mg, 9.0 mmol) over 10 min was followed by warming the reaction to rt and stirring for 17h. The work-up consisted of dilution with ether and washing the organic phase with saturated aqueous copper sulfate (2x), water (1x) and drying (magnesium sulfate). Evaporation of the ether in vacuo and flash chromatography (3:1 hexane:ether) provided 770 mg (82%) of the title compound as a clear oil. ^{1}H NMR (200 MHz,$CDCl_3$): δ 6.85 (1H, dd, J=16,6 Hz), 5.95 (1H, dd, J=16, 2 Hz), 5.42 (1H, q, J=6 Hz), 3.77 (3H, s), 2.10 (3H,s), 1.68 (2H, m), 1.50 (2H,m), 0.95 (3H, t, J=7 Hz). IR(neat): 1732, 1721, 1663, cm.$^{-1}$ Anal. Calc'd for $C_{10}H_{16}O_4$ C, 59.98; H,8.05. Found: C, 59.75; H, 7.94.

Preparation of Methyl 3-(1'-acetoxycyclohex-1'-yl)propenoate (40)

Piperidine (0.119 mL, 1.2 mmol) was added to a solution of cyclohexanecarboxaldehyde (134 mg, 1.2 mmol) and methyl 2-phenylsulfinylacetate (199 mg, 1.0 mmol) in acetonitrile (2 mL) at 0°C. After the addition was complete, the reaction was warmed to rt and stirred for 1h producing a thick white slurry. Heating the reaction to reflux for 4h was followed by cooling, dilution with ether and washing the organic phase with 10% aqueous potassium hydroxide, (1x), water (1x) and drying (magnesium sulfate). Removal of solvent in vacuo and flash chromatography of the oil (1:1 hexane:ether) provided methyl 3-(1'-hydroxycyclohex-1'yl)prop-2E-enoate (106 mg, 58%) whose ^{1}H NMR spectrum was identical to that published by Tanikaga.[34]

A solution of alcohol prepared above (1.1 gm, 5.9 mmol), DMAP (100 mg, 0.8 mmol) and pyridine (5 mL) in methylene chloride was cooled to 0°C and acetic anhydride (1.15 mL, 15 mmol) added dropwise over 10 min. The mixture was warmed to rt and stirred for 17 h. Dilution of the crude reaction with ether was followed by washing with saturated aqueous copper sulfate (3x) and water. Removal of the solvent in vacuo, and flash chromatography (3:1 hexane:ether) of the resultant oil provided 40 as a clear oil, 1.05 gm (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.11 (1H, d, J=16 Hz), 5.85 (1H, d, J=16 Hz), 3.72 (3H, s), 2.20 (2H, m), 2.05 (3H, s), 1.55 (8H, m). IR(neat): 1738, 1660, cm.$^{-1}$ Anal. Calc'd for $C_{12}H_{18}O_4$: 226.1206. Found: 226.1200.

Preparation of Butyl 5,5-bis(carbomethoxy)-4-trimethylsilylpent-2E-enoate (41)

A solution of dimethyl malonate (97 mg, 0.74 mmol) and BSA(142 mg, 0.70 mmol) in toluene (0.750 mL) was heated for 45 min at reflux. The allylic acetate 38 (100 mg, 0.36 mmol) was added followed by Mo-c (19 mg, 20 mol%) and the mixture heated at reflux for 12 h. Work-up consisted of dilution with hexane, washing of the organic layer with water and drying over sodium

sulfate. Evaporation of solvent in vacuo followed by flash chromatography (2:1 hexane:ether) yielded 54 mg (43%) of a clear oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.98 (1H, dd, J=18, 10 Hz), 3.70 (3H, s), 3.68 5.69 (1H, d, J=18 Hz), 4.10 (2H, t, J=8 Hz), (3H, s), 3.60 (1H, d, J=8 Hz), 2.60 (1H, t, J=8 Hz), 1.62 (2H, m), 1.37 (2H, m), 0.90 (3H, t, J=7 Hz), 0.02(9H,s). IR(neat): 1745, 1722, 1645, cm.$^{-1}$ Anal. Calc'd for $C_{16}H_{28}O_6Si$: 344.1647. Found: 344.1654.

Preparation of Butyl 2-(1'1'-bis(carbomethoxy)-1-ethyl-4-trimethylsilylbut-3E-enoate (42)

As above, a solution of dimethyl methylmalonate (108 mg, 0.74 mmol) BSA (142 mg, 0.70 mmol), allylic acetate 38 (100 mg, 0.36 mmol), and Mo-c(19 mg, 20 mol%) in toluene (0.75 mL) gave, after heating at reflux for 7h, work-up, and purification by flash chromatography (4:1 hexane:ether), 73 mg (56%) of the title compound. ^{1}H NMR (200 MHz, $CDCl_3$): 6.98 (1H, dd, J=18, 10 Hz), 5.69 (1H, d, J=18 Hz), 4.10 (2H, t, J=8 Hz), 3.70 (3H, s), 3.68 (3H, s), 3.60 (1H, d, J=8 Hz), 2.50 (1H, t, J=8 Hz), 1.62 (2H, m), 1.37 (2H, m), 0.90 (3H, t, J=7 Hz), 0.02 (9H, s). IR(neat): 1745, 1722, 1645, cm^{-1} Anal. Calc. for $C_{16}H_{28}O_6Si$: 344.1647. Found: 344.1654.

Preparation of Methyl 4-(bis(carbomethoxy)methyl)hept-2E-2E-enoated (43)

Following general procedure B, BSA (304 mg, 1.5 mmol), dimethyl malonate (198 mg, 1.5 mmol), allylic acetate 39 (200 mg, 1.0 mmol) and Mo-c(40 mg, 15mol %) in toluene (1 mL) gave, after heating at reflux for 2 h, work-up and chromatography (2:1 hexane:ether), 100 mg (50% yield) of starting material and 90 mg (33% yield, 66% based on recovered starting material) of a clear oil identified as the product. ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.78 (H, dd, J=16, 9.5 Hz). 5.87 (1H, d, J=16 Hz), 3.75 (3H, s), 3.72 (3H, s), 3.70 (3H, s), 3.45 (1H, d, J=8.5 Hz), 2.97 (1H, m), 1.2 (4H, m), 0.89 (3H, t, J=6.6 Hz). IR(neat): 2962, 2888, 1760, 1740, 1662, cm^{-1}. ^{13}C NMR ($CDCl_3$): 167.9, 167.8, 166.1, 147.7, 122.9, 55.7, 52.2, 52.1, 41.8, 33.8, 20.0, 13.4. Anal. Calc'd for $C_{13}H_{20}O_6$: 272.1254. Found: 272.1260.

Preparation of Methyl 4-(1',1'-bis(carbomethoxy)ethyl)hept-2E-enoate (44).

Following general procedure B, the allylic acetate 39 (200 mg, 1.0 mmol), BSA (365 mg, 1.8 mmol), dimethyl methylmalonate (292 mg, 2.0 mmol), and Mo-c (40 mg, 15 mol%) in toluene (1 mL) gave, after heating at reflux for 2h, work-up, and flash chromatography (3:1 hexane:ether), 172 mg (60% yield) of 44 as a clear oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.75 (1H, dd, J=15, 10 Hz), 5.82 (1H, d, J=15 Hz), 3.75 (6H, s), 3.69 (3H, s), 2.90 (1H, m), 1.45 (4H, m), 0.89 (3H, t, J=7 Hz). IR(neat): 1739, 1661, cm^{-1} ^{13}C NMR($CDCl_3$):δ171.0, 166.1, 147.1, 123.9, 57.4, 52.2, 51.2, 46.9, 31.5, 20.7, 17.3, 13.5. Anal. Calc'd for $C_{14}H_{22}O_6$: 286.1410. Found: 286.1415.

Preparation of Methyl 3(1',1'-bis(carbomethoxy)methylcyclohex-1'-yl)prop-2E-enoate 45

Following general procedure B, dimethyl malonate (132 mg, 1.0 mmol), BSA(203 mg, 1.0 mmol), allylic acetate 40 (100 mg, 0.44 mmol) and Mo-c(10 mg, 8 mol%) in toluene (0.50 mL) gave, after heating at reflux for 2.5 h, work-up, chromatography (3:1 hexane:ether then 1:1 hexane:ether), 5 mg of diene and 81 mg(62% yield) of 45 as a clear oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ7.13 (1H, d, J=16.2 Hz), 5.83 (1H, d, J=16.2 Hz), 3.75 (3H, s), 3.70 (3H, s), 3.56 (1H, s), 1.85 (4H, m), 1.54 (6H, m). IR(neat): 1760, 1738, 1660, cm^{-1}. ^{13}C NMR($CDCl_3$): δ 167.4, 166.7, 152.1, 121.6, 60.1, 51.9, 51.3, 41.8, 33.6, 25.5, 21.9. Anal. Cal'd for $C_{15}H_{22}O_6$:298.1410. Found: 298.1416.

Alkylation of Methyl 3-(1'-acetoxycyclohex-1-yl)prop-2E-enoate with Dimethyl methylmalonate

Following general procedure B, dimethyl methylmalonate (240 mg, 1.65 mmol), allylic acetate 40 (150 mg, 0.66 mmol), BSA (304 mg, 1.50 mmol) and Mo-c(14 mg, 8 mol%) in toluene (0.80 mL) gave, after heating at reflux for 1.5 h, work-up and flash chromatography (4:1 hexane:ether), 105 mg (52% yield) of the alkylated products and 16 mg (10% yield) of methyl 3-(cyclohex-1'-en-1'-yl)prop-2E-enoate.

The alkylation products were a 6:1 ratio of alpha : beta attack as shown by measuring the integration of a doublet at 5:15 vs a doublet at 6.95 ppm which are assigned as the protons beta to the original carbomethoxy group in the allylic acetate. The ^{1}H NMR spectral data which follow corresponds to the 6:1 mixture mentioned above. ^{1}H NMR(200 MHz, $CDCl_3$): δ 6.95 (0.14H, d, J=17 Hz), 5.82 (0.14H, d, J=17 Hz), 5.15 (0.86H, d, J=10 Hz), 4.05 (0.86H, d, J=10 Hz), 3.68-3.74 (9H, several singlets), 2.15 (4H, m), 1.59 (3H, s), 1.54 (6H, m). IR(neat): 1742, cm.$^{-1}$ ^{13}C NMR($CDCl_3$): δ 172.3, 171.3, 171.1, 151.5, 146.2, 113.5, 56.4, 52.5, 51.8, 47.5, 37.3, 29.1, 28.4, 27.5, 26.5, 22.3, 17.9. Anal. Calc. for $C_{16}H_{24}O_6$: 312.1566. Found: 312.1572.

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