29, 18, and 15% yields, respectively.

A reaction was run under the same conditions as above but with THF as the solvent. Three products were isolated, III, X, and XI, in 45, 16, and 17% yields, respectively. When the same reaction was run in hexane with a fivefold excess of vinyldimethylchlorosilane, III, X, XII, and XIII were obtained in 11, 3, 10, and 19% yields, respectively. A reaction with a 20% mixture of THF in hexane as the solvent gave only III, X, and XI in yields of 48, 19, and 23%, respectively.

The NMR data for the new products are as follows. Cyclopentadienyldimethylvinylsilane (XII): 0.04 (s, 6 H), 3.11 (m, 1 H), 5.60–6.40 (m, 3 H), 6.64 (m, 4 H). *exo*-2,2-Dimethyl-3-neopentyl-2-silanorborn-5-ene (*exo*-XIII): 0.02 (s, 3 H), 0.17 (s, 3 H), 0.46 (m, 1 H), 0.95 (s, 9 H), 1.05–1.24 (m, 2 H), 1.60 (m, 2 H), 1.96 (m, 1 H), 2.60 (m, 1 H), 5.85 (m, 2 H). *endo*-2,2-Dimethyl-3-neopentyl-2-silanorborn-5-ene (*endo*-XIII): −0.03 (s, 3 H), 0.24 (s, 3 H), 0.80–0.95 (m, 1 H), 0.96 (s, 9 H), 1.18 (m, 2 H), 1.53 (m, 2 H), 2.05 (m, 1 H), 2.83 (m, 1 H), 5.85 (m, 2 H).

**Anthracene as the Trapping Reagent in Benzene Solvent.** To a mixture of 0.05 mol of vinyldimethylchlorosilane with 0.01 mol of anthracene in 250 mL of benzene was added 0.01 mol of *tert*-butyllithium at room temperature. Analysis after the usual hydrolytic workup gave three products, III, X, and XIV, in 20, 12, and 43% yields, respectively. When the reaction was run with sufficient benzene to dissolve all the anthracene, ~600 mL, a 70% yield of XIV was obtained. However, when this reaction was run at 80 °C, only III was obtained in 75% yield.

NMR data for the new compound are as follows. 2,2-Dimethyl-3-neopentyl-5,6,7,8-dibenzo-2-sila-bicyclo[2.2.2]octane (XIV): −0.03 (s, 3 H), 0.07 (s, 3 H), 0.19–0.59 (m, 1 H), 0.99–1.39 (m, 2 H), 1.14 (s, 9 H), 3.87 (s, 1 H), 4.17 (d, 1 H, $J$ = 2.4 Hz), 7.10 (s, 8 H). Analytical data for the new compounds are given in Table I.

**Acknowledgments.** The authors gratefully acknowledge the Robert A. Welch Foundation and the North Texas State Faculty Research Fund for their support of this work.

# Palladium-Assisted Alkylation of Olefins

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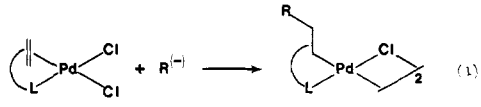
**Abstract:** Stabilized carbanions ($pK_a$ = 10–17) react with olefin–palladium(II) complexes to result in alkylation of the olefin predominantly at the 2 position after a reductive or $\beta$-elimination isolation procedure. Two equivalents of triethylamine is optimum for this alkylation reaction, and the key step is thought to involve external (trans) attack of the complexed olefin. With the addition of HMPA to the above system, anions with $pK_a$s up to ~30 reacted well. With propene exclusive attack at the 2 position was observed, while with 1-hexene attack at the 1 position was almost exclusive. With the addition of HMPA, internal disubstituted olefins as well as terminal olefins reacted in reasonable yield.

## Introduction

The ability to directly alkylate simple olefins with carbanions would be of significant use in organic synthesis. While unactivated olefins are generally inert toward nucleophiles, complexation to appropriate transition metals can promote reaction in some cases. Chelated olefin complexes of palladium(II), such as those of dicyclopentadiene[1] and other diolefins, and of allylic and homoallylic amines[2] and sulfides[2,3] readily undergo reaction with stabilized carbanions of acetylacetone, ethyl acetoacetate, and diethyl malonate to form isolable $\sigma$-alkylpalladium(II) complexes stabilized by chelation (eq 1). (Carbanions with $pK_a$s in excess of




(1)

L = C≡C, $-NR_2^1$, $-SR^1$

15 result in reduction of the metal rather than alkylation of the olefin.) This "carbopalladation" of *N*,*N*-dimethylallylamine was the key step in an elegant synthesis of the prostaglandins.[4]

The alkylation of simple olefins *not* held into coordination with a metal by chelation is a much less general process. Cationic olefin complexes of $\eta^5$-cyclopentadienyliron dicarbonyl undergo facile alkylation of the coordinated olefin by a wide range of carbanions, from malonates through organocuprates, to produce very stable $\sigma$-alkyliron complexes from which removal of the metal is difficult. The regiospecificity of this process with unsymmetrical olefins is low. Grignard and organolithium reagents result in olefin displacement and reduction of the organometallic complex, rather than alkylation.[5] Ethylene and methyl acrylate complexes of iron tetracarbonyl also react with malonate ester anions to give moderate yields of alkene alkylation products after oxidative removal of the iron from the product.[6] Finally, styrene reacts with methyllithium in the presence of palladium(II) acetylacetonate to give *trans*-$\beta$-methylstyrene in 90% yield. In contrast to the above reactions, this is thought to proceed by insertion of the olefin into a "Pd–$CH_3$" complex, rather than by external attack of the carbanion on the palladium-coordinated styrene.[7,8] Recently we reported the palladium(II)-assisted alkylation of olefins by stabilized carbanions ($pK_a$ = 10–17).[9] Herein we report the full details of that study as well as the successful extension of this alkylation reaction to much less stabilized carbanions.

## Results and Discussion

While in principle nucleophilic attack on palladium-complexed olefins is a very general process, in practice competing side reactions, particularly olefin displacement and/or reduction of the metal by the nucleophile, often seriously limit the synthetic utility of this type of reaction. Previous studies directed toward palladium-assisted amination of olefins[9,10] indicated that these side reactions could be suppressed by carrying out the reaction at low temperatures. The observation that 2 equiv of amine *in excess* of the one acting as the nucleophile was required for reasonable yields suggested either that the step involving amination of the

(1) J. K. Stille and D. B. Fox, *J. Am. Chem. Soc.*, **92**, 1274 (1970).
(2) R. A. Holton and R. A. Kjonaas, *J. Am. Chem. Soc.*, **99**, 4177 (1977).
(3) R. A. Holton and R. A. Kjonaas, *J. Organomet. Chem.*, **142**, C15 (1977).
(4) R. A. Holton, *J. Am. Chem. Soc.*, **99**, 8083 (1977).
(5) P. Lennon, A. M. Rosan, and M. Rosenblum, *J. Am. Chem. Soc.*, **99**, 8426 (1977).
(6) B. W. Roberts and J. Wong, *J. Chem. Soc., Chem. Commun.*, 20 (1977).
(7) S-i. Murahashi, M. Yamamura, and N. Mita, *J. Org. Chem.*, **42**, 2870 (1977).
(8) Refluxing styrene with diethyl sodiomalonate and $Pd(acac)_2$ in THF produced diethyl ($\alpha$-methylbenzylidene)malonate (alkylation at the benzylic position) in 18% yield. See ref 7.
(9) T. Hayashi and L. S. Hegedus, *J. Am. Chem. Soc.*, **99**, 7093 (1977).
(10) B. Akermark, J. E. Backvall, L. S. Hegedus, K. Zetterberg, K. Sirrala-Hansen, and K. Sjoberg, *J. Organomet. Chem.*, **72**, 127 (1974).

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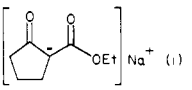
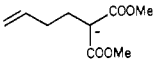
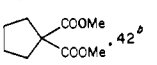
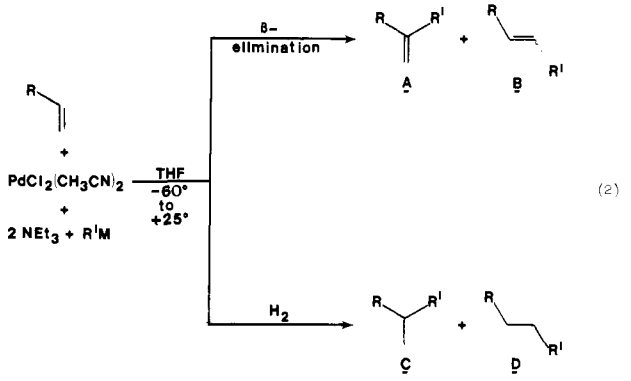
Table I. Palladium-Assisted Alkylation of Olefins by Stabilized Carbanions

| olefin | R'M | isolation | products, % yield[a] (eq 2) $Et_3N$ | products, % yield[a] (eq 2) $HMPA/Et_3N$ |
|---|---|---|---|---|
| ethene | $NaC(Me)(COOEt)_2$ | $H_2$ | C, 95 | |
| ethene | $NaC(Me)(COOEt)_2$ | β-elimination | A, 93; C, 4 | |
| propene | $NaC(Me)(COOEt)_2$ | β-elimination | A, 90; C, 6[b] | |
| 1-butene | $NaC(Me)(COOEt)_2$ | $H_2$ | C, 61; D, 24[b] | |
| 1-hexene | $NaC(Me)(COOEt)_2$ | $H_2$ | C, 55; D, 24 | |
| styrene | $NaC(Me)(COOEt)_2$ | $H_2$ | C, 42 | C, 43 |
| cyclopentene | $NaC(Me)(COOEt)_2$ | β-elimination | A, 37 | A, 37 |
| cyclohexene | $NaC(Me)(COOEt)_2$ | $H_2$ | 0 | 0 |
| *cis*-2-butene | $NaC(Me)(COOEt)_2$ | $H_2$ | D = C, 36 | D = C, 42 |
| *trans*-2-butene | $NaC(Me)(COOEt)_2$ | $H_2$ | D = C, trace | D = C, 30 |
| isobutene | $NaC(Me)(COOEt)_2$ | $H_2$ | C, trace | C, 12 |
| ethene | $NaC(C_6H_{13})(COOMe)_2$ | β-elimination | A, 87[b] | |
| ethene | $NaCH(COOMe)_2$ | β-elimination | A, 53[b,c] | |
| ethene | $NaCH(COOMe)_2$ | $H_2$ | C, 65 | |
| propene | $NaCH(COOMe)_2$ | β-elimination | A, 58[b,c] | |
| propene | $NaCH(COOMe)_2$ | $H_2$ | C, 63; D, 3[b] | |
| *N*-vinylacetamide | $NaCH(COOMe)_2$ | $H_2$ | C, 88 | |
| ethene | $NaCH(COMe)CO_2$-*t*-Bu | $H_2$ | C, 60[b] | |
| ethene | LiCH(Ph)COMe | $H_2$ | C, 72 | |
| propene | LiCH(Ph)COMe | $H_2$ | C, 73 | |
| 1-hexene | LiCH(Ph)COMe | $H_2$ | | C, 52; D, 18 |
| 1-hexene | LiCH(Ph)COOEt | $H_2$ | C, 37; D, 21 | C, 51; D, 21 |
| ethene |  (1) | β-elimination | A, 78 | |
| ethene | i | $H_2$ | C, 71 | |
| propene | $NaCH(Me)(COOEt)COCH_2Li$ | $H_2$ | C, 62[d] | *e* |
| |  | $H_2$ |  42[e] | |

[a] Yields, based on $PdCl_2(CH_3CN)_2$ employed, are for isolated, purified material. [b] Yields were determined by GLC using appropriate internal standards. [c] In these products the double bond has rearranged into conjugation with the esters. [d] Alkylation occurred exclusively at the *more* stabilized carbanion site. [e] See text.

olefin required a palladium–olefin complex containing *two* amine ligands or that 2 equiv of amine was required to ensure a sufficient equilibrium concentration of the reactive species. Accordingly, alkylation of palladium(II)-coordinated olefins in the presence of 2 equiv of triethylamine was attempted, and was successful with a wide range of olefins and stabilized ($pK_a$ = 10–17) carbanions (eq 2, Table I).



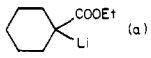
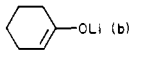
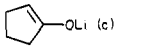
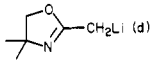
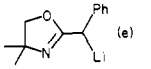

(2)

Several features of this reaction warrant comment. Foremost is the requirement of 2 equiv of triethylamine to ensure good yields. Although somewhat dependent on the specific olefin–carbanion combination studied, in general alkylation attempts in the absence of added amine went in very low yield, the major process being reduction of the palladium(II) as evidenced by formation of a copious black precipitate. Addition of 1 equiv of amine increased the yield substantially, while addition of 2 equiv of amine led to optimal yields. The nature of the amine was also quite important. For the alkylation of propene by diethyl methylmalonate, triethyl-, tri-*n*-propyl-, and diisopropylamine were the most effective, resulting in virtually quantitative yields of alkylation. Trimethylamine (77%) and *N*,*N*-dimethylaniline (65%) were somewhat less effective, while pyridine (28%) and diethylamine (5%) were ineffective, as were the strongly coordinating ligands triphenylphosphine (0%) and tetramethylethylenediamine (TMEDA, 0%). These results indicate that the alkylation step involves a palladium–olefin complex containing 2 equiv of amine or that 2 equiv of amine is required to ensure a sufficient equilibrium concentration of the reactive complex. The basicity of the added amine was of minor importance, since both triethylamine ($pK_a$ = 10.6) and *N*,*N*-dimethylaniline ($pK_a$ = 5.1) were effective, while diethylamine ($pK_a$ = 11) and pyridine ($pK_a$ = 5.3) were not.

A variety of stabilized carbanions reacted in good yield in this system including those of β-diesters, β-keto esters, and benzyl ketones and esters. Within the range of ~10–17 $pK_a$, neither the specific nature nor the steric bulk of the anion affected the yields significantly, with bulky tertiary anions (i.e., dimethyl *n*-hexylmalonate) forming quaternary centers in good yield. However, less stabilized anions, such as the lithium enolate of acetone, reacted very poorly, giving less than 2% alkylation under the reaction conditions of Table I. Consonant with this behavior was the observation that the dianion of ethyl methylacetoacetate reacted *exclusively* at the more stabilized anionic carbon, with *no* product resulting from alkylation at the terminal carbanionic site being observed.

In contrast, the nature of the olefin had a profound effect on the course of the reaction. Terminal monoolefins reacted in highest yields, with ethene and propene reacting in almost quantitative yield. As the alkyl chain increased in length a slight decrease in yield was noted. The electron-rich olefin *N*-vinylacetamide also reacted in excellent yield, while electron-deficient olefins such as methyl acrylate were unreactive since they did not complex effectively to palladium. With propene alkylation occurred exclusively at the 2 position, as expected for external nucleophilic attack of a complexed olefin. With longer chain olefins this regioselectivity decreased. While attack at the 2 position predominated in all cases, significant amounts of terminal alkylation occurred as well. Styrene alkylated in 20–50%, depending on carbanion, exclusively at the benzylic position. Internal olefins were less

Table II. Palladium-Assisted-Alkylation of Olefins by Nonstabilized Carbanions (Equation 2)

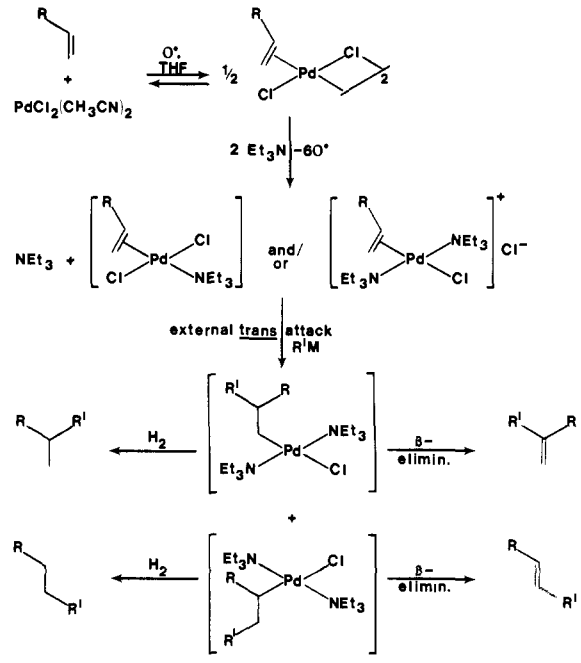
| olefin | R'M | isolation | products, % yield[a] |
|---|---|---|---|
| 1-hexene |  (a) | $H_2$ | D, 79 |
| 1-hexene | a | β-elimination | B, 80[f] |
| propene |  (b) | $H_2$ | C, 40[b] |
| 1-hexene | b | $H_2$ | D, 62 |
| styrene | b | $H_2$ | C, 22; D, 15 |
| *cis*-2-butene | b | $H_2$ | C = D, 13 (15 dialkylation)[c] |
| *trans*-2-butene | b | $H_2$ | C = D, 42 (11 dialkylation)[d] |
| isobutene | b | $H_2$ | C, ~3 |
| propene |  (c) | $H_2$ | C, 19; D, 9[e] |
| 1-hexene | c | $H_2$ | D, 58 |
| 1-hexene | c | β-elimination | B, 47[f] |
| *N*-vinylacetamide | c | $H_2$ | C, 52 |
| styrene | $LiCH_2COCH_3$ | $H_2$ | D, 29; C, 1 |
| 1-hexene | $LiCH_2COCH_3$ | $H_2$ | D, 49 |
| 1-hexene | $LiCH_2COCH_3$ | β-elimination | B, 50[g] |
| propene |  (d) | $H_2$ | D, 50; C, <2 |
| 1-hexene | d | $H_2$ | D, 57; C, 3 |
| propene |  (e) | $H_2$ | C, 82 |
| 1-hexene | e | $H_2$ | C, 49; D, 27 |
| ethene | LiC(CN)-($OMe_3Si$)(Ph) | $H_2$ | $PhCOC_2H_5$, 50[h] |
| 1-hexene | $PhCH_2MgCl$ | $H_2$ | C, 17; D, 6 |

[a] Yield of isolated, purified product, based on $PdCl_2(CH_3CN)_2$. [b] *o*-Isopropylphenol (10%) was also obtained from β-elimination, rearrangement, and disproportionation of the original monounsaturated alkylcyclohexanone. [c] 15% of 2,6-di(*sec*-butyl)cyclohexanone was also obtained. [d] 11% of 2,6-di(*sec*-butyl)cyclohexanone was also obtained. [e] Considerably higher crude yields were obtained, but losses due to volatility during purification occurred. [f] Complex mixture of double-bond isomers. [g] Exclusively *trans*-3-nonen-2-one from rearrangement of the initial γ,δ-unsaturated product. [h] After deprotection and hydrolysis.

efficiently alkylated, with cyclopentene and *cis*-2-butene reacting in ~40% yield, while cyclohexene, *trans*-2-butene, and isobutene were not alkylated under these reaction conditions. This reactivity pattern parallels that observed for other reactions of palladium(II)–olefin complexes with external nucleophiles, particularly amines.[10] In an intramolecular version of this reaction, methyl 2-carbomethoxyhex-5-enoate cyclized to dimethyl cyclopentane-1,1-dicarboxylate in modest yield.

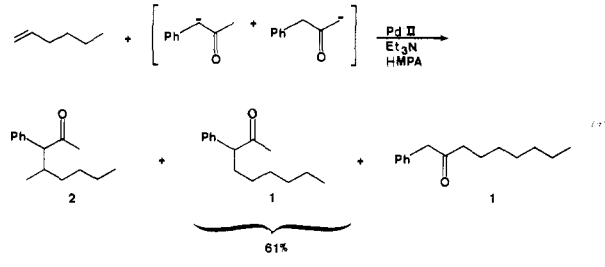
In an effort to broaden the scope of this alkylation reaction, the effects of adding a number of different ligands to the reaction system were studied. While most added ligands either had no effect on the reaction or, in fact, decreased its efficiency, HMPA [$(Me_2N)_3PO$, 10–20 equiv/equiv of Pd(II)] proved to be remarkably useful in two respects. Firstly, with stabilized carbanions as nucleophile, addition of HMPA to the reaction system of Table I resulted in higher yields of akylation and increased regioselectivity for alkylation at the 2 position. This is best illustrated by considering the reaction of ethyl phenylacetate with 1-hexene, for which the best yields (72%) and regioselectivity (7:3) were observed by addition of 20 equiv of HMPA to the olefin–palladium(II) complex prior to addition of amine and carbanion (Table I). With 2 equiv of HMPA and no triethylamine, 20 equiv of HMPA and no triethylamine, or 20 equiv of HMPA and 1 equiv of triethylamine, only 40–50% overall yields were realized, and the product was a 1:1 mixture of regioisomers. Similar effects were noted with the enolate of phenylacetone, and in the reaction of *trans*-2-butene. Remarkably, even isobutene reacted under these

Scheme I




conditions, giving a low (12%) yield of diethyl (*tert*-butyl)(methyl)malonate, from attack at the 2 position. No isopropyl-containing product, from attack at the much less hindered 1 position, was observed. In contrast, cyclohexene, cyclopentene, styrene, and *cis*-2-butene were relatively unaffected by HMPA addition.

A second, and more significant, effect of the use of HMPA as an additive was the extension of this alkylation reaction to considerably less stabilized carbanions (Table II). Under these conditions, ketone and ester enolates, oxazoline anions (carboxylic acid carbanion equivalents), and protected cyanohydrin anions (acyl anion equivalents) alkylated olefins in fair to good yield. Even benzylmagnesium chloride reacted under these conditions, although in rather low yield. These nonstabilized anions were considerably more regioselective in their reactions with olefins than were the stabilized carbanions in Table I. This effect was most apparent in a comparison of the reaction of 1-hexene with the methyl- and benzyloxazolines, respectively. The methyloxazoline reacted almost exclusively (25:1) at the terminal carbon of the olefin (even with propene), while the relatively more stabilized benzyloxazoline reacted predominantly (~2:1) at the 2 carbon. Similarly in the reaction of a mixture of kinetic and thermodynamic enolates of phenylacetone with 1-hexene, the stabilized enolate reacted to give a 2:1 mixture of 2 vs. 1 attack, while the less stabilized enolate reacted exclusively at the terminal carbon (eq 3). Additionally, the reaction of the dianion of ethyl




methylacetoacetate with propene in the presence of HMPA gave mixtures of mono- and dialkylation products, from alkylation at both carbanionic centers.

With nonstabilized carbanions propene reacted almost exclusively at the 2 position with all carbanions except the methyloxazoline, which reacted primarily (25:1) at the terminal position. 1-Hexene reacted exclusively at the 1 position with all anions studied except for the relatively stabilized phenyloxazoline and the highly reactive benzyl Grignard reagent. The regiochemistry

of reactions involving styrene was variable, with acetone enolate reacting exclusively at the $\beta$ position and cyclohexanone enolate reacting at both the $\alpha$ and $\beta$ positions (1.5:1). *N*-Vinylacetamide reacted exclusively at the position $\alpha$ to nitrogen.

Both *cis*- and *trans*-2-butene reacted with cyclohexanone enolate in modest yield. Surprisingly, both olefins also gave substantial amounts of 2,6-dialkylation. Isobutene gave only 3% alkylation product, exclusively 2-*tert*-butylcyclohexanone.

While the $pK_a$ of the carbanion was clearly of major importance in this alkylation reaction, it was not the sole factor involved. Sulfur-containing carbanions such as those of dithiane [$CH_2(SCH_2CH_2CH_2S)$] and the more highly stabilized $MeSCH_2S(O)Me$ reacted in only very low yield under the above reaction conditions. With these anions it is likely that sulfur coordinates strongly and irreversibly to the palladium, displacing the olefin and thereby suppressing the alkylation reaction. Preliminary attempts at alkylation using organolithium reagents also met with no success. In these cases, reduction of Pd(II) to Pd(0) was the major process observed. Studies to extend this alkylation reaction to these very reactive carbanions continue.

**Course of the Reaction.** Scheme I presents a reasonable sequence which accommodates the currently available information and closely approximates the proposed mechanism for the reaction of secondary amines in the same system.[10] Reaction of the olefin with Pd(II) generates the dimeric olefin–palladium(II) complex. The addition of the requisite 2 equiv of triethylamine generates either the mono- or bisamine palladium–olefin complex. (Low temperatures are required for this step since competing displacement of olefin by amine becomes serious at moderate temperatures (−20 °C).) Since nucleophilic attack on the complexed olefin results in a substantial increase of electron density on the metal, the formally cationic bisamine palladium–olefin complex would be expected to be more reactive toward nucleophiles than the neutral monoamine complex.[5] However, the nature of the reactive intermediate has not yet been experimentally demonstrated. External trans attack by uncomplexed nucleophile generates the unstable $\sigma$-alkylpalladium complexes, which either $\beta$-hydride eliminate to give olefinic products or are hydrogenated to give saturated products.[11,12] In reactions involving HMPA, one (or more) of the amines is replaced by this ligand. The role of HMPA was *not* simply to change the polarity of the solvent system, since DMF in varying amounts did not promote this reaction. To be effective HMPA had to be added to the olefin–palladium(II) complex at 25 °C, followed by cooling to −78 °C and addition of the triethylamine. The relatively large amounts of HMPA required for effective reaction imply that the complexation constant of HMPA with the reactive palladium species is low and that a high concentration of HMPA is required to result in significant complexation. However, the nature of the interaction remains obscure. The regiochemistry (1 vs. 2 attack) depends upon the nature of the olefin, the carbanion, and the reaction conditions, with less stabilized anions reacting at the 1 position and stabilized anions at the 2 position.

This difference in regioselectivity may be due to the inherent differences in reactivity between stabilized and nonstabilized carbanions. Alternatively, it has been suggested in related palladium systems[7,13] that nonstabilized carbanions attack the palladium directly forming alkylpalladium complexes. Cis insertion reactions of olefins into preformed alkylpalladium complexes result in alkylation at the less substituted olefin terminus.[14] Thus a change in mechanism upon going from stabilized to nonstabilized carbanions may be responsible for the observed change in regiochemistry. This question is currently under investigation.

## Experimental Section

**General.** Melting points were taken with a Mel-Temp apparatus and are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 267 spectrophotometer and are reported in $cm^{-1}$. Nuclear magnetic resonance (NMR) spectra were measured with either Varian Associates Model T-60 or EM-360 or JEOL MH100 spectrophotometers using $Me_4Si$ as the internal standard and are reported in $\delta$. Analytical preparative vapor phase chromatography was performed on a Bendix Model 2300 gas chromatograph equipped with 10 ft × $^1/_4$ in. columns (A, Carbowax 10% on Chromosorb W NAW 60–80 mesh; B, SE-30 10% on Chromosorb W NAW 60–80 mesh) and a thermal conductivity detector. Peak areas were determined by the cut and weigh method. For reactions having VPC yields, pure material was obtained by preparative VPC under the same conditions. Liquid chromatography was performed using moderate (40–80 psi) pressures with either 15 × 250, 15 × 1000, or 25 × 1000 mm columns (a, b, and c, respectively) packed with Woelm Type 206 silica gel. Column chromatography was performed using Baker reagent grade silica gel (60–200 mesh). Analytical thin layer chromatography was performed using Brinkmann precoated silica gel F-254 plates (0.25 mm). Preparative thin layer chromatography was performed using 20 × 20 cm plates coated with silica gel (2 mm, E. M. Laboratories 60 PF-254). Products were visualized with UV light, iodine vapor, or phosphomolybdic acid–ethanol spray.

**Materials.** All solvents were freshly distilled and stored under an argon atmosphere. Immediately before use they were degassed and saturated with argon. Tetrahydrofuran (THF) (Baker Analyzed reagent grade) was refluxed over lithium aluminum hydride and distilled at atmospheric pressure. Hexamethylphosphoramide (HMPA) (Aldrich) was refluxed over calcium hydride and distilled at reduced pressure. Diisopropylamine was refluxed over calcium hydride and distilled at atmospheric pressure. Liquid olefins (Aldrich) were distilled at atmospheric pressure. Gaseous olefins (Matheson) were used without further purification. Butyllithium, purchased from Alfa as a 2.4 M hexane solution, was titrated using the 2-butanol–1,10-phenanthroline method of Watson and Eastham.[15] Triethylamine (Aldrich) was used without further purification. Palladium chloride was obtained from Engelhard and converted to its bisacetonitrile complex by stirring overnight in acetonitrile and collecting the resulting orange-yellow crystals by filtration.

**General Reaction Procedure for Alkylation without Added HMPA.** The $PdCl_2 \cdot 2CH_3CN$ (0.76 g, 3.0 mmol) was weighed into a 200-mL, two-necked, round-bottomed flask fitted with a magnetic stir bar, stopcock, and rubber serum cap. The flask was alternately evacuated and filled with argon (four cycles). Addition of THF (100 mL) and stirring for 0.2 h at room temperature produced an amber suspension. Addition of the olefin[16] (2–4 equiv based on Pd) followed by stirring for 0.2 h gave a homogeneous solution. The flask was cooled to −78 °C.

Triethylamine (2.0 equiv per Pd) was added dropwise slowly with vigorous stirring over 0.2 h followed by stirring at −78 °C for 0.2 h. The cold bath was allowed to warm to −60 °C (ca. 0.25 h), at which time the anion (1.2–2.0 equiv per Pd) was added as a THF solution (cooled to −78 °C before addition) over 0.2 h via a precooled (dry ice) syringe. The cold bath was maintained at −60 °C for 0.5 h. To obtain saturated (reduced) products the flask was flushed with hydrogen, a hydrogen balloon affixed to the stopcock, and the cold bath removed. The reaction mixture was allowed to warm to room temperature, stirring vigorously, and stirred overnight under a hydrogen atmosphere. The resulting suspension was filtered and the solvent concentrated on a rotary evaporator.

Alternatively, the unsaturated ($\beta$-elimination) products were obtained by simply allowing the reaction flask to warm to room temperature under an argon atmosphere. After 2 h the heterogeneous reaction mixture was filtered and the solvent concentrated on a rotary evaporator. The alkylated products were isolated and purified by standard methods.

**General Reaction Procedure for Alkylation in the Presence of HMPA.** The $PdCl_2 \cdot 2CH_3CN$ (0.76 g, 3.0 mmol) was weighed into a 200-mL, two-necked, round-bottomed flask fitted with a magnetic stir bar, stopcock, and rubber serum cap. The flask was alternately evacuated and filled with argon (four cycles). Addition of THF (100 mL) and stirring for 0.2 h at room temperature produced an amber suspension. Addition of the olefin[16] followed by stirring for 0.2 h gave a homogeneous solution. Addition of HMPA (10–20 equiv per Pd) caused a slight darkening of the amber color. After 0.1 h the flask was cooled to −78 °C. Tri-

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(12) Recently the trans addition of the anion of acetylacetone to ethylene in the cationic complex $[Pd(\eta^5\text{-}C_5H_5)(PPh_3)(CH_2{=}CH_2)]^+$ was directly demonstrated: H. Kurosawa and N. Asaka, *Tetrahedron Lett.*, 255 (1979). However, this is a coordinately saturated olefin complex which has no accessible vacant coordination site to allow prior complexation of the carbanion, as is required for cis addition.

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(16) Gaseous olefins were introduced by opening the stopcock to a balloon containing the appropriate olefin and stirring until homogeneous.

ethylamine (2.0 equiv per Pd) was added dropwise over 0.2 h followed by stirring at −78 °C for 0.2 h. The cold bath was allowed to warm to −60 °C (ca. 0.25 h), at which time the anion was added as a THF solution over 0.2 h via a precooled (dry ice) syringe. The cold bath was maintained at −60 °C for 0.5 h. To obtain saturated (reduced) products the flask was flushed with hydrogen, a hydrogen balloon affixed to the stopcock, and the cold bath removed. The reaction mixture was allowed to warm to room temperature and stirred overnight under an atmosphere of hydrogen. The resulting suspension was filtered and the solvent concentrated on a rotary evaporator. Alternatively, the unsaturated (β-elimination) products were obtained by simply allowing the reaction flask to warm to room temperature under an argon atmosphere. After 2 h the heterogeneous reaction mixture was filtered and the solvent concentrated on a rotary evaporator.

The products were separated from the HMPA by the following procedure. The mixture was taken up in ether (100 mL) and washed with water (3 × 60 mL) and brine (1 × 60 mL). The organic phase was dried over $MgSO_4$ and filtered, and the solvent concentrated on a rotary evaporator. The crude products obtained in this manner were virtually free of HMPA and could be purified by standard methods.

**Preparation of the Carbanions.** Lithium diisopropylamide (LDA) was prepared by dropwise addition of a stoichiometric amount of butyllithium solution to diisopropylamine in THF (2 mL/mmol) at 0 °C under an argon atmosphere. The solution was then cooled to −78 °C. Lithium carbanions were generated by dropwise addition of the appropriate substrate to the LDA solution at −78 °C followed by stirring at −78 °C for 0.5 h. Sodium hydride (50% mineral oil suspension) was washed with distilled, dry petroleum ether under an inert atmosphere. Most of the petroleum ether was removed via syringe. The remaining petroleum ether was removed by carefully evacuating the flask on the vacuum line. The flask was then flushed with argon and the THF (2 mL/mmol) added. The appropriate substrate was added to the sodium hydride suspension at 0 °C at a rate sufficient to promote gentle evolution of hydrogen. If necessary the flask was allowed to warm to room temperature and stir until homogeneous. The resulting pale gray carbanion solution *was cooled to −78 °C before addition to the palladium complex.* Potassium carbanions were prepared from potassium hydride by the same procedure as described for sodium hydride.

**Reaction of Sodium Diethyl Methylmalonate (No HMPA). A. With Ethene ($H_2$).** Isolation by medium-pressure liquid chromatography (15:1 hexane–ether) gave 576 mg (95%) of ethyl 2-methyl-2-carboethoxybutyrate[17] as a colorless liquid: NMR ($CCl_4$) δ 0.90 (t, $J$ = 7 Hz, 3, $CH_3$), 1.35 (t, $J$ = 7 Hz, 6, $CH_3$), 1.40 (s, 3, $CH_3$), 1.95 (q, $J$ = 7 Hz, 2, $CCH_2$), 4.20 (q, $J$ = 7 Hz, 4, $OCH_2$–); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{10}H_{18}O_4$) C, H.

**B. With Ethene (β-Elimination).** Purification by medium-pressure liquid chromatography (20:1 hexane–ethyl acetate) gave 560 mg (93%) of a colorless liquid, ethyl 2-methyl-2-carboethoxybut-3-enoate: NMR ($CCl_4$) δ 1.25 (t, $J$ = 7 Hz, 6, $CH_3$), 1.48 (s, 3, $CH_3$), 4.12 (q, $J$ = 7 Hz, 4, $OCH_2$), 5.10 (m, 2, $=CH_2$), 6.25 (m, 1, C=CH); IR ($CCl_4$) 3080 (=CH), 1740 (C=O), 1634 (C=C) cm$^{-1}$. Anal. ($C_{10}H_{16}O_4$) C, H. In addition, 3% reduced material, ethyl 2-methyl-2-carboethoxybutyrate, was obtained.

**C. With Propene (β-Elimination).** Quantitative VPC analysis (column A, 130 °C, 4.5 min, *n*-tetradecane internal standard) showed two products. The major product was ethyl 2,3-dimethyl-2-carboethoxybut-3-enoate[18] (90%): NMR ($CCl_4$) δ 1.29 (t, $J$ = 7 Hz, 6, $CH_3$), 1.61 (s, 3, $CH_3$), 1.89 (br s, 3, $CH_3C$=), 4.20 (q, $J$ = 7 Hz, 4, $-CH_2O$), 4.95 (m, 2, $C=CH_2$); IR ($CCl_4$) 3082 (C=CH), 1740 (C=O), 1630 (C=C) cm$^{-1}$. Anal. ($C_{11}H_{18}O_4$) C, H. The minor product (6%) was reduced material, ethyl 2,3-dimethyl-2-carboethoxybutyrate: NMR ($CCl_4$) δ 0.96 (d, $J$ = 7 Hz, 6, $HC(CH_3)_2$), 1.28 (t, $J$ = 7 Hz, 6, $CH_3$), 1.36 (s, 3, $CH_3$), 2.52 (septet, $J$ = 7 Hz, 1, $HC(CH_3)_2$), 4.21 (q, 4, $J$ = 7 Hz, $-OCH_2$); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{11}H_{20}O_4$) C, H.

**D. With 1-Butene ($H_2$).** Quantitative VPC analysis as in C showed that the major product (61%) was ethyl 2,3-dimethyl-2-carboethoxypentanoate:[19] NMR ($CCl_4$) δ 0.93 (d, $J$ = 7 Hz, 3, $CHCH_3$), 1.27 (t, $J$ = 7 Hz, 6, $-OCH_2CH_3$), 1.35 (s, 3, $CCH_3$), 0.8–1.9 (m, 5, $CHCH_2CH_3$), 1.9–2.5 (m, 1, CH), 4.19 (q, $J$ = 7 Hz, 4, $OCH_2$); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{12}H_{22}O_4$) C, H. The minor product (24%) was ethyl 2-methyl-2-carboethoxyhexanoate:[20] NMR ($CCl_4$) δ 0.7–2.5 (m, 9, *n*-$C_4H_9$), 1.27 (t, $J$ = 7 Hz, 6, $OCH_2CH_3$), 1.42 (s, 3, $CH_3$), 4.18 (q, $J$ = 7 Hz, 4, $OCH_2$–); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{12}H_{22}O_4$) C, H.

**E. With 1-Hexene ($H_2$).** After purification by medium-pressure liquid chromatography (20:1 hexane–ethyl acetate), two products were isolated. The major product (55%) was ethyl 2,3-dimethyl-2-carboethoxyheptanoate:[21] NMR ($CCl_4$) δ 0.93 (d, $J$ = 7 Hz, 3, $CHCH_3$), 1.27 (t, $J$ = 7 Hz, 6, $OCH_2CH_3$), 1.35 (s, 3, $CCH_3$), 0.7–1.9 (m, 9, *n*-$C_4H_9$), 2.0–2.6 (m, 1, CH), 4.18 (q, $J$ = 7 Hz, 4, $OCH_2$); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{14}H_{26}O_4$) C, H. The minor product (24%) was ethyl 2-methyl-2-carboethoxyoctanoate:[22] NMR ($CCl_4$) δ 0.7–2.4 (m, 11, *n*-$C_4H_{11}$), 1.27 (t, $J$ = 7 Hz, 6, $OCH_2CH_3$), 1.4 (s, 3, $CH_3$), 4.18 (q, $J$ = 7 Hz, 4, $OCH_2$–); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{14}H_{26}O_4$) C, H.

**F. With Cyclopentene (β-Elimination).** Quantitative VPC analysis (column A, 170 °C, 4 min) as in C gave ethyl 2-carboethoxy-2-cyclopentenylpropionate as an unseparated mixture of olefin isomers in 31% yield: NMR ($CDCl_3$) δ 1.28 (t, $J$ = 7 Hz, 5, $-CH_2CH_3$), 1.31 (s, 0.5, $CH_3$, minor isomer), 1.40 (s, 2.5, $CH_3$, major isomer), 1.6–2.0 (m, 2, ring $CH_2$), 2.50 (m, 3.5, C=CC*H*), 4.2 (q, $J$ = 7 Hz, 4, $OCH_2$), 5.2 (s, 1.5, C=CH); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$.

**G. With *cis*-2-Butene ($H_2$).** Isolation by preparative layer chromatography (benzene, $R_f$ 0.35) gave 41.5 mg (36%) of ethyl 2,3-dimethyl-2-carboethoxypentanoate, identical in all respects with that prepared in part D above.

**H. With Styrene ($H_2$).** Purification by preparative layer chromatography (10:1 hexane–ether, $R_f$ 0.4) gave 54 mg (42%) of ethyl 2-methyl-2-carboethoxy-3-phenylbutyrate,[23] a colorless liquid: NMR ($CCl_4$) δ 1.14 (t, $J$ = 7 Hz, 3, $OCH_2CH_3$), 1.20 (d, $J$ = 7 Hz, 1, $CHCH_3$), 1.31 (t, $J$ = 7 Hz, 3, $OCH_2CH_3$), 1.35 (s, 3, $CH_3$), 3.60 (q, $J$ = 7 Hz, 1, $CHCH_3$), 4.05 (q, $J$ = 7 Hz, 2, $OCH_2$), 4.20 (q, $J$ = 7 Hz, 2, $OCH_2$), 7.25 (s, 5, $C_6H_5$); IR (neat) 1730 (C=O) cm$^{-1}$. Anal. ($C_{16}H_{22}O_4$) C, H.

**Reaction of Sodium Dimethyl *n*-Hexylmalonate with Ethene (β-Elimination).** Quantitative VPC analysis (column A, 160 °C, *n*-tetradecane internal standard, 6.2 min) indicated an 87% yield of methyl 2-vinyl-2-carbomethoxyoctanoate: NMR ($CDCl_3$) δ 0.7–1.7 (m, 11, $C_5H_{11}$), 1.8–2.2 (m, 2, β-$CH_2$), 3.71 (s, 6, $OCH_3$), 4.96–5.35 (m, 2, $CH=CH_2$), 6.29 (d of d, $J$ = 12, 17 Hz, 1, $CH=CH_2$); IR ($CCl_4$) 1740 (C=O) cm$^{-1}$. Anal. ($C_{13}H_{22}O_4$) C, H.

**Reaction of Sodium Dimethyl Malonate. A. With Ethene (β-Elimination).** Quantitative VPC analysis (column A, 130 °C, 7.1 min) showed a 53% yield of methyl 2-carbomethoxybut-2-enoate:[24] NMR ($CDCl_3$) δ 1.98 (d, $J$ = 7.5 Hz, 3, $C=CHCH_3$), 3.77 (s, 3, $OCH_3$), 3.83 (s, 3, $OCH_3$), 7.09 (q, $J$ = 7.5 Hz, 1, $CH_3CH=C$); IR (neat) 1710 (C=O), 1630 (C=C) cm$^{-1}$. Anal. ($C_7H_{10}O_4$) C, H.

**B. With Ethene ($H_2$).** The reaction was run as in A to give 65% of dimethyl ethylmalonate, identical in all respects with authentic material.

**C. With Propene (β-Elimination).** The reaction was run as in A and analyzed (column A, 120 °C, 10.7 min) to give 58% methyl 2-carbomethoxy-3-methylbut-2-enoate:[25] NMR ($CDCl_3$) δ 2.09 (s, 6, $=C(CH_3)_2$), 3.77 (s, 6, $OCH_3$); IR (neat) 1720–1710 (C=O), 1655, 1647 (C=C) cm$^{-1}$. Anal. ($C_8H_{12}O_4$) C, H.

**D. With Propene ($H_2$).** The reaction was run and analyzed as in A (140 °C, 2.0 min), giving 63% methyl 2-carbomethoxy-3-methylbutyrate:[26] NMR ($CDCl_3$) δ 1.02 (d, $J$ = 8 Hz, 6, $CH(CH_3)_2$), 2.41 (octet, $J$ = 8 Hz, 1, CH), 3.18 (d, $J$ = 8 Hz, 1, $HC(COOMe)_2$), 3.74 (s, 6, $OCH_3$); IR (neat) 1740 (C=O) cm$^{-1}$. Anal. ($C_8H_{14}O_4$) C, H.

**E. With *N*-Vinylacetamide ($H_2$).** Purification by silica gel chromatography (EtOAc) gave 95 mg (88%) of methyl 2-carbomethoxy-3-acetamidobutanoate, a colorless oil: NMR ($CDCl_3$) δ 1.30 (d, $J$ = 7 Hz, 3, $CH_2CH_3$), 1.98 (s, 3, $COCH_3$), 3.65 (d, $J$ = 5 Hz, 1, $CH(COOMe)_2$), 3.73 (s, 3, $OCH_3$), 3.78 (s, 3, $OCH_3$), 4.5–5.0 (m, 1, $CHCH_3$), 6.3–6.8 (broad, 1, NH); IR (neat) 1770–1740 (COOMe), 1660 (–CONHMe) cm$^{-1}$. Anal. ($C_9H_{15}NO_5$) C, H, N.

**Reaction of Sodium *tert*-Butyl Acetoacetate with Ethene ($H_2$).** Quantitative VPC analysis (column A, 130 °C, 2.5 min) indicated a 60% yield of *tert*-butyl 2-acetylbutyrate:[27] NMR ($CDCl_3$) δ 0.95 (t, $J$ = 7 Hz, 3, $CH_2CH_3$), 1.50 (s, 9, $C(CH_3)_2$), 1.80 (quintet, $J$ = 7 Hz, 2, $CH_2$), 2.23 (s, 3, $COCH_3$), 3.25 (t, $J$ = 7 Hz, 1, CH); IR ($CHCl_3$) 1730 (COOR), 1704, (C=O) cm$^{-1}$. Anal. ($C_{10}H_{18}O_3$) C, H.

**Reaction of Lithium Phenylacetonate (Benzyl Enolate). A. With Ethene ($H_2$).** Purification by preparative layer chromatography (silica

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gel, benzene, $R_f$ 0.35) gave 58 mg (72%) of 3-phenylpentan-2-one:[28] NMR ($CDCl_3$) $\delta$ 0.85 (t, $J$ = 7 Hz, 3, $CH_2CH_3$), 1.5–2.0 (m, 2, $CH_2$), 2.06 (s, 3, $COCH_3$), 3.53 (t, $J$ = 7 Hz, 1, CH), 7.24 (s, 5, ArH); IR (neat) 1700 (C=O), 1620 (Ph) $cm^{-1}$. Anal. ($C_{11}H_{14}O$) C, H.

**B. With Propene ($H_2$).** The reaction was run as in A, and the product purified in the usual manner. The product was 3-phenyl-4-methylpentan-2-one[29] (63 mg, 73%): NMR ($CDCl_3$) $\delta$ 0.69 (d, $J$ = 7 Hz, 3, $-CHCH_3$), 1.01 (d, $J$ = 7 Hz, 3, $CHCH_3$), 2.09 (s, 3, $COCH_3$), 2.1–2.8 (m, 1, $CH(CH_3)_2$), 3.31 (d, $J$ = 9 Hz, 1, ArCH), 7.21 (s, 5, ArH); IR ($CCl_4$) 1710 (C=O), 1620 (Ph) $cm^{-1}$. Anal. ($C_{12}H_{16}O$) C, H.

**Reaction of Lithium Ethyl Phenylacetate with Hexene ($H_2$).** Purification by medium-pressure liquid chromatography (20:1 hexane–ether) gave 0.43 g (58%) of a colorless liquid, which was a mixture of regioisomers. Analysis and separation by preparative VPC (column A, 130 °C) gave a 37% yield of ethyl 2-phenyl-3-methylheptanoate[30] as a 1:1 mixture of diastereoisomers (6.5 min retention time): NMR ($CCl_4$) $\delta$ 0.60, 0.95 (two d, $J$ = 7 Hz, 3, $CH_3CH_2$), 0.7–1.4 (br, 9, $n$-$C_4H_9$), 1.80 (t, $J$ = 7 Hz, 3, $CH_3$), 2.10 (m, 1, CH), 3.10 (d, d, $J$ = 10 Hz, $\Delta\delta$ = 2.5 Hz, 1, ArCH), 4.0 (two q, $J$ = 7 Hz, $\Delta\delta$ = 2.5 Hz, 2, $OCH_2$), 7.2 (s, 5, ArH); IR ($CCl_4$) 1710 (C=O), 1592 $cm^{-1}$. Anal. ($C_{16}H_{24}O_2$) C, H. When run in the presence of added HMPA (20 equiv/equiv of Pd), 51% of ethyl 2-phenyl-3-methylheptanoate and 21% of ethyl 2-phenyloctanoate were obtained.

**Reaction of Sodium 2-Carboethoxycyclopentanone. A. With Ethene ($\beta$-Elimination).** Purification by medium-pressure liquid chromatography (10:1 hexane–ether) gave 0.42 g (78%) of 2-vinyl-2-carboethoxycyclopentanone:[31] NMR ($CCl_4$) $\delta$ 1.28 (t, $J$ = 7 Hz, 3, $CH_3CH_2O$), 1.5–2.5 (m, 6, $(CH_3)_2$), 4.10 (q, $J$ = 7 Hz, 2, $OCH_2CH_3$), ABX system ($\delta_a$ = 5.02, $\delta_b$ = 5.20, $\delta_c$ = 6.00, $J_{AB}$ = 1, $J_{AX}$ = 10, $J_{BX}$ = 17 Hz, 3, $CH_2$=$CH$–); IR ($CCl_4$) 1750 (C=O), 1720 (COOEt), 1635 (C=C) $cm^{-1}$. Anal. ($C_{10}H_{14}O_3$) C, H.

**B. With Ethene ($H_2$).** The reaction was run and product purified as in A, to give 0.39 g (71%) of 2-carboethoxy-2-ethylcyclopentanone:[32] NMR ($CCl_4$) $\delta$ 0.85 (t, $J$ = 7 Hz, 3, $CH_3CH_2$), 1.25 (t, $J$ = 7 Hz, 3, $CH_3CH_2O$), 1.5–2.5 (m, 8, $(CH_2)_4$), 4.10 (q, $J$ = 7 Hz, 2, $OCH_2CH_3$); IR ($CCl_4$) 1750 (C=O), 1720 (COOEt) $cm^{-1}$. Anal. ($C_{10}H_{16}O_3$) C, H.

**Reaction of the Sodium Lithium Dianion of Ethyl Methylacetoacetate[33] with Propene ($H_2$).** Isolation by preparative layer chromatography (benzene, $R_f$ 0.3) gave 57 mg (62%) of ethyl (methyl)isopropylacetoacetate:[34] NMR ($CCl_4$) $\delta$ 0.85 (d, $J$ = 8 Hz, 3, $CHCH_3$), 0.95 (d, $J$ = 7 Hz, 3, $CHCH_3$), 1.28 (s, 3, $CCH_3$), 1.29 (t, $J$ = 7 Hz, 3, $OCH_2CH_3$), 2.17 (s, 3, $COCH_3$), 2.56 (septet, $J$ = 7 Hz, 1, $CH(CH_3)_2$), 4.21 (q, $J$ = 7 Hz, 2, $OCH_2CH_3$); IR ($CHCl_3$) 1275 (COOR), 1700 (C=O) $cm^{-1}$. Anal. ($C_{10}H_{18}O_3$) C, H.

**Cyclization of Methyl 2-Carbomethoxyhex-5-enoate ($H_2$).** $PdCl_2(CH_3CN)_2$ (130 mg, 0.50 mmol) and the unsaturated diester (93 $\mu$L, 0.50 mmol) were stirred in 15 mL of THF for 0.5 h at 0 °C. The temperature was lowered to −60 °C and triethylamine (0.70 mmol) was added followed by LDA (0.50 mmol in 3 mL of THF). The mixture was stirred at −60 °C for 1 h, then exposed to an atmosphere of $H_2$ and allowed to warm to 25 °C. The resulting mixture was filtered, solvent removed under vacuum, and the product quantitatively analyzed by VPC (column A, 160 °C, tetradecane standard, retention time 8 min). The cyclized material, dimethyl cyclopentane-1,1-dicarboxylate,[35] was obtained in 42% yield: NMR ($CDCl_3$) $\delta$ 1.55–1.90 (m, 4 H, $-(CH_2)_2-$), 2.05–2.4 (m, 4 H, $CH_2CH_2C$), 3.71 (s, 6 H, $OCH_3$); IR ($CCl_4$) 1740 (C=O) $cm^{-1}$. Anal. ($C_9H_{14}O_4$) C, H.

**Reaction of Diethyl Methylmalonate with Isobutene (HMPA, $H_2$).** Purification by preparative layer chromatography (10:1 hexane–ether, $R_f$ 0.30) gave 12 mg (12%) of diethyl (methyl-*tert*-butyl)malonate:[36] NMR ($CCl_4$) $\delta$ 1.02 (s, 9, *t*-Bu), 1.20 (t, $J$ = 7 Hz, 6, $CH_3CH_2O$), 1.35 (s, 3, $CH_3$), 4.10 (q, $J$ = 7 Hz, 4, $OCH_2CH_3$); IR ($CCl_4$) 1730 (C=O) $cm^{-1}$. Anal. ($C_{12}H_{22}O_4$) C, H.

**Reaction of Lithium Phenylacetonate (Benzyl Carbanion) with 1-Hexene (HMPA, $H_2$).** A solution of lithium phenylacetone (prepared by dropwise addition of an LDA solution to phenylacetone at 0 °C) (6.0 mmol in 10 mL of THF) was allowed to react with hexene (1.0 g, 12.0 mmol) in the presence of HMPA (6.0 g, 35 mmol), triethylamine (0.61 g, 6.0 mmol), and $PdCl_2{\cdot}2CH_3CN$ (0.76 g, 3.0 mmol) in 100 mL of THF following the general reaction procedure. The reaction mixture was allowed to warm to room temperature under a hydrogen atmosphere. The products were separated by medium-pressure liquid chromatography (30:1 hexane–ether) into three fractions. The fractions in order of elution were 208 mg (32%) of 3-phenyl-4-methyl-2-octanone, one pure diastereomer [NMR ($CCl_4$) $\delta$ 0.6 (d, $J$ = 7 Hz, 3, $CH_3$), 0.9 (m, 3, $CH_3$), 1.3 (m, 6, $CH_2$), 1.9–2.4 (m, 1, CH), 2.0 (s, 3, $COCH_3$), 3.25 (d, $J$ = 10 Hz, 1, ArCHCO), 7.2 (br s, 5, ArH); IR ($CCl_4$) 1720 (C=O) $cm^{-1}$]; 121 mg (20%) of the other pure diastereomer [NMR ($CCl_4$) $\delta$ 0.88 (d, $J$ = 7 Hz, 3, $CH_3$), 0.7–1.45 (m, 9, $CH_2$ and $CH_3$), 1.9–2.4 (m, 1, CH), 1.98 (s, 3, $COCH_3$), 3.25 (d, $J$ = 10 Hz, 1, ArCHCO), 7.2 (broad s, 5, ArH)]; 101 mg (17%) of 3-phenyl-2-nonanone[37] [NMR ($CCl_4$) $\delta$ 0.9 (m, 3, $CH_3$), 1.3 (broad s, 10, $CH_2$), 1.95 (s, 3, $COCH_3$), 3.45 (t, $J$ = 7 Hz, 1, ArCH–), 7.2 (broad s, 5, ArH); IR ($CCl_4$) 1720 (C=O) $cm^{-1}$. Anal. ($C_{15}H_{22}O$) C, H].

**Reaction of Lithium Phenylacetone (Kinetic Mixture of Enolates) with 1-Hexene.** A solution of lithium phenylacetone (prepared by dropwise addition of phenylacetone to LDA at 0 °C) (5.9 mmol in 12 mL of THF) was allowed to react with 1-hexene (1.0 g, 12.0 mmol) in the presence of HMPA (6.0 g, 35 mmol), triethylamine (0.61 g, 6.0 mmol), and $PdCl_2{\cdot}2CH_3CN$ (0.76 g, 3.0 mmol) in 100 mL of THF following the general reaction procedure. The reaction mixture was allowed to warm to room temperature under a hydrogen atmosphere. The products were separated by moderate-pressure column chromatography (30:1 hexane–ether). The alkylation products in order of elution were 3-phenyl-4-methyloctan-2-one, 187 mg (31%) (mixture of diastereomers), 3-phenyl-2-nonanone, 115 mg (17%), and 1-phenyl-2-nonanone,[38] 100 mg (15%): NMR ($CCl_4$) $\delta$ 0.9 (m, 3, $CH_3$), 1.25 (broad s, 10, $CH_2$), 2.32 (t, $J$ = 7 Hz, 2, $COCH_2$), 3.5 (s, 2, $ArCH_2CO$), 7.15 (broad s, 5, ArH); IR ($CCl_4$) 1720 (C=O) $cm^{-1}$. Total yield of alkylated products was 402 mg (61%). The products were compared to those obtained from the reaction of the thermodynamic enolate mixture by NMR and VPC analysis. VPC (column A, 160 °C): $t_R$ = 3.7, 5.95, 11.4 min, respectively.

**Reactions of Olefins with Nonstabilized Carbanions.** All of the following reactions were run following the procedure described for alkylation in the presence of HMPA. The scale was $PdCl_2(CH_3CN)_2$ (0.78 g, 3.0 mmol), olefin (excess when gaseous, 4–6 mmol when liquid), carbanions (3–4 mmol), triethylamine (0.8 mL, 6 mmol), and HMPA (6 mL, 33 mmol).

**Reactions of Lithium Methyl Cyclohexanecarboxylate. A. With 1-Hexene ($H_2$).** Purification by medium-pressure liquid chromatography (30:1 hexane–ether) gave 0.54 g (79%) of methyl 2,2-pentamethyleneoctanoate:[39] NMR ($CCl_4$) $\delta$ 0.7–2.35 (broad m, 23, $CH_2$), 3.65 (s, 3, $OCH_3$); IR ($CCl_4$) 1722 (C=O) $cm^{-1}$. Anal. ($C_{14}H_{26}O_2$) C, H.

**B. With 1-Hexene ($\beta$-Elimination).** Purification as in A gave 0.54 g (80%) of methyl 2,2-pentamethyleneoctenoate: NMR ($CCl_4$) $\delta$ 0.7–2.3 (br m, 19, $CH_2$ and $CH_3$), 3.58 and 3.60 (s, 3, $OCH_3$), 5.15–5.50 (m, 2, $-HC$=$CH$); IR ($CCl_4$) 1720 (C=O) $cm^{-1}$. VPC analysis (column A, 205 °C) showed four components, retention times 1.27, 1.86, 2.24, and 2.67 min, due to different double-bond isomers (positional and cis and trans). Reduction of this mixture ($H_2$, Pd/C) gave methyl 2,2-pentamethyleneoctanoate, identical in all respects with authentic material.

**Reactions of the Lithium Enolate of Cyclohexanone. A. With Propene ($H_2$).** Purification by flash chromatography[40] (7 in. × 20 mm, silica gel, 20:1 hexane–ethyl acetate) gave 168 mg (40%) of 2-isopropylcyclohexanone:[41] NMR ($CCl_4$) $\delta$ 0.90 (d, $J$ = 7 Hz, 6, $CH(CH_3)_2$), 1.2–2.4 (br m, 10, $CH_2$, CH); IR ($CCl_4$) 1700 (C=O) $cm^{-1}$. Anal. ($C_9H_{16}O$) C, H. In addition, 2-isopropylphenol (10%, identical with authentic material) from aromatization of the alkylation product was obtained.

**B. With 1-Hexene ($H_2$).** Purification by medium-pressure liquid chromatography (30:1 hexane–ether) gave 330 mg (62%) of 2-(*n*-hexyl)cyclohexanone:[42] NMR ($CCl_4$) $\delta$ 0.90 (t, $J$ = 7 Hz, 3, $CH_3$), 1.2 (br, 10, $CH_2$ acyclic), 1.2–2.6 (m, 9, $CH_2$ ring); IR ($CCl_4$) 1700 (C=O) $cm^{-1}$. Anal. ($C_{12}H_{22}O$) C, H.

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C. **With Styrene ($H_2$).** Purification by flash chromatography[40] (6 in. × 20 mm, 20:1 hexane–ethyl acetate) gave 225 mg (37% yield) of alkylated products. VPC analysis (column A, 200 °C) showed the product to be a mixture of two compounds: 2-(α-phenethyl)cyclohexanone, retention time 6.0 min, 22% [NMR ($CCl_4$) δ 1.18 (d, $J$ = 6 Hz, 3, $CHCH_3$), 1.2–2.5 (br m, 9, $CH_2$), 3.1 (m, 1, PhCH), 7.15 (br s, 5, ArH); IR ($CCl_4$) 1710 (C=O) $cm^{-1}$. Anal. ($C_{14}H_{18}O$) C, H], and 2-(β-phenethyl)cyclohexanone,[43] retention time 9.9 min, 15% [NMR ($CCl_4$) δ 1.0–2.7 (br m, 13, $(CH_2)_2$ and cyclic $CH_2$), 7.1 (s, 5, ArH); IR ($CCl_4$) 1712 (C=O) $cm^{-1}$. Anal. ($C_{14}H_{18}O$) C, H].

D. **With *trans*-2-Butene ($H_2$).** Purification by flash chromatography[40] (6 in. × 30 mm, 20:1 hexane–ethyl acetate) gave 197 mg (42%) of 2-(*sec*-butyl)cyclohexanone:[44] NMR ($CCl_4$) δ 0.9 (m, 6, $CH_3$'s), 1.0–2.4 (br m, 12, CH's, $CH_2$'s); IR ($CCl_4$) 1700 (C=O) $cm^{-1}$. Anal. ($C_{10}H_{18}O$) C, H. In addition, 54 mg (11%) of a mixture of dialkylated products was obtained.

E. **With *cis*-2-Butene ($H_2$).** Reaction, isolation, and identification as in D gave 13% 2-(*sec*-butyl)cyclohexanone and 15% dialkylation products.

F. **With Isobutene ($H_2$).** Purification by flash chromatography[40] (6 in. × 20 mm, 20:1 hexane–ethyl acetate) gave 12 mg (~3%) of 2-(*tert*-butyl)cyclohexanone:[45] NMR ($CCl_4$) δ 0.92 (s, 9, *t*-Bu), 0.7–2.0 (m, 9, ring $CH_2$); IR ($CCl_4$) 1715 (C=O) $cm^{-1}$.

**Reactions of the Lithium Enolate of Cyclopentanone. A. With Propene ($H_2$).** Purification by flash chromatography[40] (7 in. × 20 mm, 20:1 hexane–ethyl acetate) gave 2-(isopropyl)cyclopentanone[46] (75 mg, 19%) as the major product: NMR ($CCl_4$) δ 0.8 and 1.0 (d, d, $J$ = 7 Hz, 6, diastereotopic $CH(CH_3)_2$), 1.8–2.4 (br m, 8, $CH_2$, CH); IR ($CCl_4$) 1740 (C=O) $cm^{-1}$. In addition, 34 mg (9%) of 2-(*n*-propyl)cyclopentanone was isolated: NMR ($CCl_4$) δ 0.9 (t, $J$ = 7 Hz, 3, $CH_3$), 1.30 (br s, 4, $CH_2$), 1.3–2.4 (br m, 7, ring $CH_2$ and CH); IR ($CCl_4$) 1740 (C=O) $cm^{-1}$.

B. **With *n*-Hexane ($H_2$).** Isolation by medium-pressure liquid chromatography (30:1 hexane–ether) gave 0.294 g (58%) of 2-(*n*-hexyl)-cyclopentanone:[47] NMR ($CCl_4$) δ 0.9 (m, 3, $CH_3$), 1.3 (br, 10, $CH_2$), 1.3–2.4 (br m, 7, ring CH's); $^{13}C$ NMR ($CCl_4$) 216.20 (s, C=O), 48.28 (d, CHCO), 37.19 (t, $CH_2C$=O), 14.01 (q, $CH_3$); unassigned 31.53, 29.48 (2 C's), 29.13, 27.32, 22.48, 20.61; IR ($CCl_4$) 1740 (C=O) $cm^{-1}$. Anal. ($C_{11}H_{20}O$) C, H.

C. **With 1-Hexene (β-Elimination).** Purification by medium-pressure liquid chromatography (50:1 hexane–acetone) gave 0.24 g (47%) of a mixture of 2-(*n*-hexenyl)cyclopentanone and 2-(*n*-hexyl)cyclopent-2-en-1-one (minor amount). Reduction ($H_2$/Pd–C) gave material identical with that obtained in B.

D. **With *N*-Vinylacetamide ($H_2$).** Purification by preparative layer chromatography (silica gel, ethyl acetate, thrice, $R_f$ 0.30) gave 0.264 g (52%) of 2-(2-*N*-acetylaminoethyl)cyclopentanone: NMR ($CCl_4$) δ 1.1, 1.2 (two d, $J$ = 7 Hz, 3, diastereotopic $CHCH_3$), 2.00 (s, 3, $CH_3CO$), 1.6–2.2 (m, 7, ring CH's), 4.2 (m, 1, CHNAc), 6.8 (br, 1, NH); IR ($CCl_4$) 3430 (NH), 1725 (C=O), 1655 (NC=O) $cm^{-1}$. Anal. ($C_9H_{15}NO_2$) C, H, N.

**Reaction of the Lithium Enolate of Acetone. A. With Styrene ($H_2$).** Purification by flash chromatography[40] (6 in. × 20 mm, 20:1 hexane–ethyl acetate) gave 0.14 g (29%) of 5-phenyl-2-pentanone:[48] NMR ($CCl_4$) δ 1.82 (t, $J$ = 7 Hz, 2, $CH_2CO$), 2.00 (s, 3, $COCH_3$), 2.50 (m, 4, $CH_2CH_2$), 7.10 (s, 5, ArH); IR ($CCl_4$) 1710 (C=O), 1605 (aromatic) $cm^{-1}$. Anal. ($C_{11}H_{14}O$) C, H. In addition, a very minor (<1%) amount of 4-phenyl-2-pentanone was isolated.

B. **With 1-Hexene ($H_2$).** Purification by evaporative distillation (100 °C, 2 Torr) gave 0.21 g (49%) of 2-nonanone, identical in all respects with authentic material: NMR, Sadtler no. 48; IR, Sadtler no. 43.

C. **With 1-Hexene (β-Elimination).** Purification by preparative layer chromatography (silica gel, two elutions, 4:1 hexane–ether, then 2:1 hexane–ether, $R_f$ 0.50) gave 0.21 g (50%) of *trans*-non-3-en-2-one:[49] NMR ($CCl_4$) δ 0.9 (m, 3, $CH_3$), 1.25–1.80 (m, 8, $CH_2$), 2.16 (s, 3, $CH_3CO$), 5.85 (d, $J$ = 16 Hz, 1, α CH=), 6.60 (m, 1, β C=CH); IR ($CCl_4$) 1678 (conjugated C=O), 1628 (C=C) $cm^{-1}$. Anal. ($C_9H_{16}O$) C, H.

**Reaction of the Lithium Salt of 2,4,4-Trimethyl-2-oxazoline. A. With Propene ($H_2$).** Purification by evaporative distillation (85 °C, ~3 Torr) gave 0.24 g (50%) of 2-(*n*-butyl)-4,4-dimethyl-2-oxazoline: NMR ($CCl_4$) δ 0.9 (m, 3, $CH_3$), 1.20 (s, 6, ring $CH_3$'s), 1.40 (m, 4, $CH_2CH_2$), 2.15 (m, 2, C(=N)(O)$CH_2$–), 3.75 (s, 2, $OCH_2N$). This product was identical with material prepared by a different procedure.[50] In addition trace amounts (~2%) of the isobutyloxazoline were detected by VPC (column B, 145 °C, retention time 1.83 min).

B. **With 1-Hexene ($H_2$).** Purification by evaporative distillation gave 0.36 g (60% yield) of an alkylated oxazoline. VPC analysis (column B, 145 °C, retention time 0.9 min) showed this to be >95% 2-(*n*-hexyl)-4,4-dimethyl-2-oxazoline: NMR ($CCl_4$) δ 0.90 (m, 3, $CH_3$), 1.20 (s, 6, ring $CH_3$'s), 1.4 (br s, 10, $CH_2$), 2.15 (m, 2, C(=N)(O)$CH_2$), 3.75 (s, 2, $OCH_2N$); mass spectrum $m/e$ 197 (parent), 182, 168, 154, 140, 126, 113 (base peak). This was identical with authentic material.[50] The minor product (<3%) was that which resulted from attack at the 2 position of the olefin.

**Reaction of the Lithium Salt of 2-Benzyl-4,4-dimethyl-2-oxazoline. A. With Propene ($H_2$).** Purification by medium-pressure liquid chromatography (15:1 hexane–acetone) gave 0.57 g (82%) of 2-[1-phenyl-2-methyl-1-propyl]-4,4-dimethyl-2-oxazoline: NMR ($CCl_4$) δ 0.70 and 1.05 (d's, $J$ = 6 Hz, 6, diastereomeric $CH(CH_3)_2$), 1.18 (s, 6, ring $CH_3$'s), 2.1 (m, 1, $CH(CH_3)_2$), 3.05 (d, $J$ = 10 Hz, 1, PhC*H*), 3.70 (s, 2, $CH_2O$), 7.25 (s, 5, ArH); IR ($CCl_4$) 1650 (C=N), 1600 (aromatic) $cm^{-1}$. Anal. ($C_{15}H_{21}NO$) C, H, N.

B. **With 1-Hexene ($H_2$).** Purification by medium-pressure liquid chromatography (10:1 hexane–ether) gave 0.40 g (49%) of 2-[1-phenyl-2-methyl-1-hexyl]-4,4-dimethyl-2-oxazoline as a mixture of diastereoisomers: NMR ($CCl_4$) δ 0.6 and 0.9 (d's, $J$ = 6.5 Hz, 3, diastereomeric $CH_3CH$), 0.9 (m, 3, $CH_3(CH_2)_3$), 1.20 (s, 6, ring $CH_3$'s), 1.4 (br m, 7, $CH_2$'s), 3.15 and 3.26 (d's, $J$ = 9.5 Hz, diastereomeric CHPh), 3.80 (s, 2, $OCH_2$), 7.20 (s, 5, ArH); IR ($CCl_4$) 1650 (C=N), 1600 (aromatic) $cm^{-1}$. Anal. ($C_{18}H_{27}NO$) C, H, N. In addition 0.23 g (27%) of the straight-chain compound, 2-(1-phenyl-1-heptyl)-4,4-dimethyl-2-oxazoline, was obtained. This material was identical in all respects with material prepared by an alternate procedure.[50]

**Reaction of the Lithium Salt of the $Me_3Si$ Derivative of Benzaldehyde Cyanohydrin[51] with Ethene ($H_2$).** The crude material from the alkylation reaction was stirred for 2 h with 2 N HCl. The aqueous mixture was extracted with ether (2 × 40 mL), and the organic extracts were combined, washed with water (3 × 40 mL), 2 N HCl (2 × 25 mL), and water (1 × 30 mL), and then vigorously shaken with dilute NaOH (1 × 40 mL) for 10 min. The aqueous layer was removed and the organic layer washed with water (1 × 30 mL), brine (1 × 40 mL), and dried over $Na_2SO_4$. The solution was filtered and the solvent concentrated on a rotary evaporator. The crude product was separated by moderate-pressure column chromatography (30:1 hexane–ether). Propiophenone was isolated as a clear, colorless oil (200 mg, 50%). The product was identical with authentic material: NMR, Sadtler no. 34; IR, Sadtler no. 272.

**Reaction of Benzylmagnesium Chloride with 1-Hexene ($H_2$).** Purification by flash chromatography[40] (20 mm × 7 in., 50:1 hexane–ethyl acetate) gave 0.12 g (23%) of a colorless liquid. VPC analysis (column A, 150 °C) showed two peaks (retention times 5.0 and 7.5 min) in a ratio of 73:27. Collection from preparative VPC gave pure compounds: 1-phenyl-2-methylhexane[52] (17%) [NMR ($CCl_4$) δ 0.8 (d, $J$ = 6.5 Hz, 3, $CHCH_3$), 0.90 (m, 3, $CH_2CH_3$), 1.2–1.9 (br m, 7, CH and $CH_2$'s), 2.50 (m, 2, $PhCH_2$–), 7.15 (s, 5, ArH). Anal. ($C_{13}H_{20}$) C, H] and 1-phenylheptane (6%) identical with authentic material. NMR: Aldrich Library of NMR Spectra, IV 2D.

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